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Recent progress in high-performance environmental impacts of the removal of radionuclides from wastewater based on metal–organic frameworks: a review

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The nuclear industry is rapidly developing and the effective management of nuclear waste and monitoring the nuclear fuel cycle are crucial. The presence of various radionuclides such as uranium (U), europium (Eu), technetium (Tc), iodine (I), thorium (Th), cesium (Cs), and strontium (Sr) in the environment is a major concern, and the development of materials with high adsorption capacity and selectivity is essential for their effective removal. Metal–organic frameworks (MOFs) have recently emerged as promising materials for removing radioactive elements from water resources due to their unique properties such as tunable pore size, high surface area, and chemical structure. This review provides an extensive analysis of the potential of MOFs as adsorbents for purifying various radionuclides rather than using different techniques such as precipitation, filtration, ion exchange, electrolysis, solvent extraction, and flotation. This review discusses various MOF fabrication methods, focusing on minimizing environmental impacts when using organic solvents and solvent-free methods, and covers the mechanism of MOF adsorption towards radionuclides, including macroscopic and microscopic views. It also examines the effectiveness of MOFs in removing radionuclides from wastewater, their behavior on exposure to high radiation, and their renewability and reusability. We conclude by emphasizing the need for further research to optimize the performance of MOFs and expand their use in real-world applications. Overall, this review provides valuable insights into the potential of MOFs as efficient and durable materials for removing radioactive elements from water resources, addressing a critical issue in the nuclear industry.

Introduction

Recently, with the lack of renewable energy sources, nuclear energy has become one of the world's vital sources of electrical power.[1–4] The waste from these nuclear processes contains a high level of liquid, which contains many radioactive ions.[5,6] The field of nuclear research, in addition to nuclear power plants, non-peaceful uses of nuclear energy as lethal weapons, and nuclear accidents, besides mining, is the most dangerous source of radioactive elements.[7,8] Some of these radioactive elements exist naturally in the minerals of monazite and thorite.[9,10]

Radioactive waste is matter contaminated by some radioactive elements.[11,12] Nuclear waste is divided into three groups as follows. (a) High-level waste (HLW) is comprised of radionuclides from fuel rods, moderators, and any radiation target in the reactor. (b) Transuranic waste (TRU) includes radionuclides in the cleaning waste, which emit alpha-particles (except for plutonium 238 and 241, which undergo fission). (c) Low-level waste (LLW) is waste that is contaminated by small amounts of radionuclides and is generated mainly by hospitals, research organizations, nuclear energy operations and nuclear reactors.[13,14] Radionuclides such as strontium, cesium,[15–19] rare earth elements, thorium, and uranium[20,21] that result in waste are summarized in Table 1. All of these radioactive elements lead to nuclear waste and cause numerous health problems, such as kidney damage, cancer, and lung and liver cancers due to exposure to radiation from these radioactive elements.[22,23] Due to their severity and toxicity, these radioactive elements must be separated from wastewater;[15,24] therefore, it is important to remove these unpleasant dangerous sources and develop an easy treatment method.

Metal–organic frameworks are coordination polymers composed of organic ligands (linker) and inorganic metal or

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Table 1 Common radionuclides

Nuclide	T-half (year)	Analog	Forms
^{3}H	12.3	H	H_2O, H^+, OH^-, H_2 (g)
^{14}C	5×10^3	C	HCO_3^-, H_2CO_3, CO_3^{2-}, CO_2, CH_4
^{36}CI	3.1×10^5	CI	Cl^-, HCI (g)
^{63}Ni	100	Ni	Ni^{2+}, $NiOH^+$, $NiCl_2$, $NiCO_3$, $Ni(OH)_2$
^{90}Sr	29.0	Sr, Ca	Sr^{2+}, $SrCO_3$
^{93}Zr	1.5×10^6	Zr	$Zr(OH)_2^{2+}$, $Zr(OH)_5^-$, $ZrSiO_4$
^{94}Nb	2×10^4	Nb	$Nb(OH)_5$
^{107}Pd	7×10^6	Pd, Pt	Pd^{2+}, $Pd(OH)_2$, $PdCl_4^{2-}$
^{129}I	2×10^7	I, CI, Br	I^-, 10_3^-
^{135}Cs	3×10^6	Cs, Rb	Cs^+
^{137}Cs	30.0	Cs, Rb	Cs^+
^{154}Eu	8.2	Eu, REE	Eu^{3+}, $Eu(OH)_2^+$, $EuSO_4^+$, $Eu(OH)_3$
^{79}Se	6.5×10^4	Se, S	Se^{2-}, HSe^-, Se(s), SeO_4^{2-} SeO_3^{2-}
^{93}Mo	3.5×10^3	Mo	Mo^{4+}, MoO_4^{2-}, MoS_2
^{99}Tc	$2 \times l0^5$	Re, Mn	TcO_4^-, Tc^{4+}, TCO_2 TCS_2, $Tc(OH)_4$
^{106}Ru	1.0	Ru, Mo	RuO_4^{2-}, RUO_2, RUS_2
^{126}Sn	$1 \times l0^5$	Sn	SnH, $Sn(OH)^+$, SnS, SnO_2
^{147}Sm	1.3×10^{11}	Sm, Nd	Sm^{3+}, $Sm(OH)_2^+$, $Sm(OH)_3$
^{151}Sm	90.0	Sm, Nd	Sm^{3+}, $Sm(OH)_2^+$, $Sm(OH)_3$
^{210}Pb	22.0	Pb	Pb^{2+}, $Pb(OH)^+$, PbS, $PbCl^+$
^{226}Ra	1.6×10^3	Ra, Ba, Sr, Ca	Ra^{2+}
^{227}Ac	22.0	REE	Ac^{3+}, $Ac(OH)_2^+$, $Ac(OH)_3$
^{230}Th	8×10^4	Th	Th^{4+}, $Th(OH)_3^+$, ThO_2, $Th(OH)_2$
^{232}Th	1.4×10^{10}	Th	Th^{4+}, $Th(OH)_3^+$, ThO_2, $Th(OH)_4$
^{231} Pa	3×10^4	Pa	$Pa(OH)_5$
^{234}U	2.5×10^5	U	U complexes
^{235}U	7×10^8	U	U complexes
^{238}U	4.5×10^9	U	U complexes
^{237}Np	2×10^6	Np, U	NpO_2^+, NpO_2
^{238}Pu	88.0	Pu, Th	Pu^{3+}, PuO_2^+, PuO_2
^{239}Pu	2.4×10^4	Pu, Th	Pu^{3+}, PuO_2^+, PuO_2
^{241}Am	432.0	Nd	$Am(OH)^{3+}$, AmO_2
^{243}Am	7×10^3	Nd	$Am(OH)^{3+}$, AmO_2
^{243}Cm	28.0	Nd	$Cm(OH)_3$, Cm complexes

cluster-metal oxide as a metal node (Fig. 1a). The coordination complex that forms between the metal node and the ligand donor atom is called a secondary building unit (SBU). The connection between the ligand and the metal may form a dote structure or a chain structure arranged in one dimension, as well as a layer shape arranged in two dimensions and three dimensions, leading to a network structure[25–27] (Fig. 1b).

The shape of MOFs is affected by the molar ratio between the metal cluster or ion and the organic linker, for example, in general, a 1 : 2 molar ratio between the linker and the metal node leads to a two-dimensional structure such as in the case of the synthesis of cobalt MOFs in the presence of *N*-(3-pyridyl) nicotinamide ligand when four molecules of the linker are coordinated with the metal node. MOFs have potential voids and pores over their frameworks, and varying the organic linker and/or the metal node causes tuning of the pores. Also as the organic chain of the linker increases the pore size will increase.[28,29] Based on the nature and the pore size of the MOFs, various potential uses have been applied such as gas separation, sensors, bio-medical applications, ion exchanger, adsorption, gas purification, and gas storage.[30–35] One application of MOFs is as adsorbents due to their low density, chemical and thermal stability, and large pore size. Their insolubility in water and other aqueous media and extended surface areas, from 10^3 to 10^4 m^2 g^{-1}, enhance their applicability in the removal and separation of radionuclides and toxic metals.[35,36] Consequently, these properties have allowed MOFs to surpass the traditional materials that are used for the same purpose, such as porous organic frameworks (POFs), zeolites, and carbons.

The impact of using organic solvents and solventless methods in the fabrication of MOFs on the environment, the mechanism of MOFs toward radionuclides, regeneration and reusability of MOFs toward radionuclides, behaviors against strong radiation conditions, applications such as catalysis and adsorption, and the separation of MOFs have been discussed in many reviews.[37–40] Hot topics such as removing pollution, including dyes,[41,42] emerging contaminants,[43] and the removal of organic compounds,[42,44] have also been overviewed. MOFs and their compounds have recently been shown to be remarkable solid porous materials that trap toxic and radioactive metal ions.[45–48] This review aims to provide an overview of the most recent advances in the applications of MOFs as absorbents for water purification. To do this, we critically provide some focused examples and comparisons to evaluate the removal properties, conditions and mechanisms starting from precipitation methods and ending with MOFs including different synthetic methods, kinetic and thermodynamic stabilities, MOFs mechanism for removal of radionuclides, and metal ions,

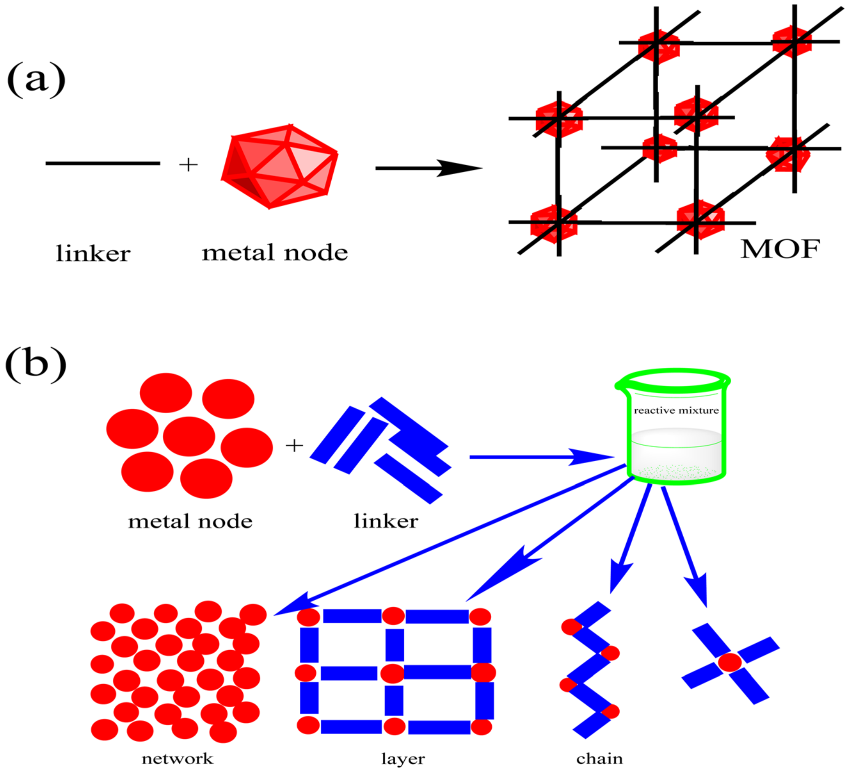


Fig. 1 (a) A model of MOF fabrication. (b) Different MOF structures.

and the evaluation of the different MOF materials for the removal of various radionuclides.

Radioactive water decontamination removal techniques

The preconcentration of waste elements before the separation process is essential; these metal ion concentrations are deficient. Therefore, it is crucial to preconcentrate these ions to allow measurement and detection with high accuracy, a low detection limit, and sensitivity. Various separation methods are used for this target[49] (Fig. 2), such as membrane filtration, electrolysis, ion exchange, co-precipitation, flotation, and some other methods[50,51] that will be discussed in detail in the following sections.

Precipitation

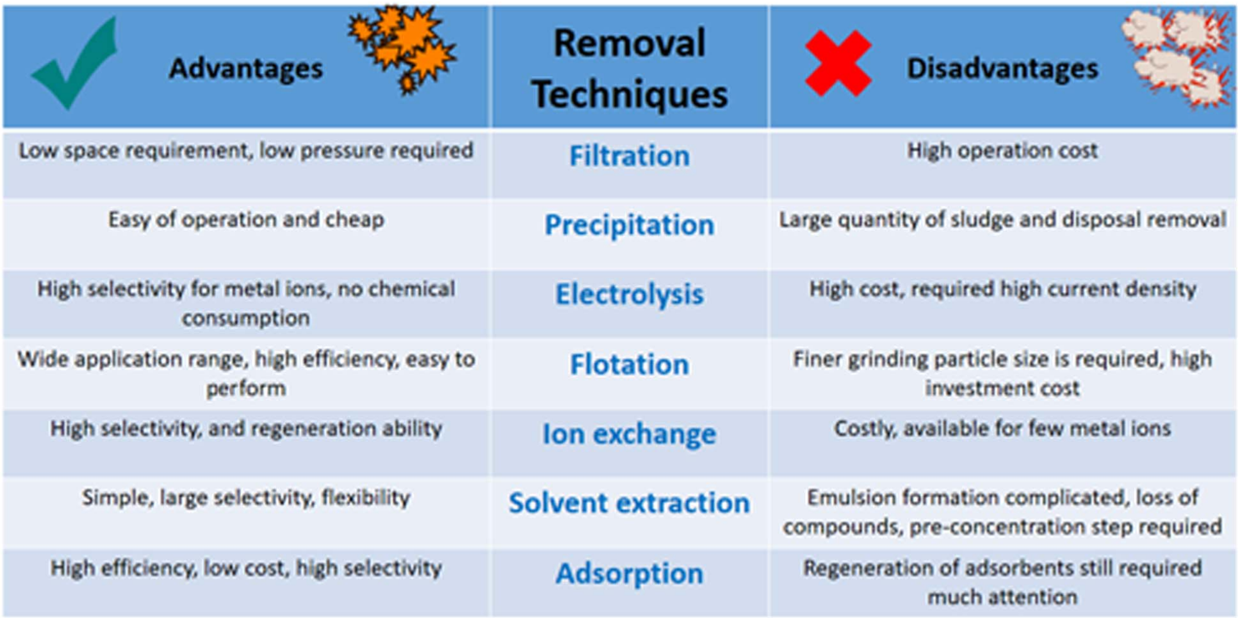
Precipitation is the process of separating a specific ion from a solution based on the ionic equilibrium changes of the target ions in that solution; the soluble ion is converted into an insoluble form by nucleation and crystal growth and separated by separation techniques such as filtration. Precipitation usually separates heavy metal ions and hardness from water.[52–54]

Filtration

Wastewater treatment relies heavily on filtration to eliminate physical impurities from the water. This process involves passing the water through a bed of granular media, which removes suspended solids such as microorganisms, turbidity, particulates, and color. These impurities can be present in the water or produced during pre-treatment. The ultimate goal of filtration is to produce a clear and clean effluent that meets the necessary quality standards for safe discharge or reuse. Effective filtration is crucial to ensure the success of wastewater treatment and protect the environment from harmful contaminants.[55] Several filtration techniques are commonly employed in wastewater treatment, including gravity filtration, vacuum filtration, centrifugal filtration, hot filtration, cold filtration, granular media filtration, and mechanical filtration. Each technique relies on different mechanisms to remove suspended solids from the water and produce a clear effluent. The choice of filtration technique depends on various factors, such as the nature of the wastewater, the required level of treatment, and the available resources. Understanding the advantages and limitations of each filtration technique is essential to select the most appropriate method for a particular application.[56–60] Among these techniques, a filter membrane is used to remove soluble ions or molecules from solutions, based on the passing of these ions or molecules through a semipermeable membrane under applied pressure. The filter membrane has a wide range of separation methods, such as reverse osmosis (RO), filtration, and ultra-filtration processes. It is used for the separation of some organic materials,[61,62] and some heavy metals.[63,64]

Ion exchange

Ion exchange is a separation technique that can be used to separate anions and cations from solution using an anion



✓ Advantages	Removal Techniques	✗ Disadvantages
Low space requirement, low pressure required	Filtration	High operation cost
Easy of operation and cheap	Precipitation	Large quantity of sludge and disposal removal
High selectivity for metal ions, no chemical consumption	Electrolysis	High cost, required high current density
Wide application range, high efficiency, easy to perform	Flotation	Finer grinding particle size is required, high investment cost
High selectivity, and regeneration ability	Ion exchange	Costly, available for few metal ions
Simple, large selectivity, flexibility	Solvent extraction	Emulsion formation complicated, loss of compounds, pre-concentration step required
High efficiency, low cost, high selectivity	Adsorption	Regeneration of adsorbents still required much attention

Fig. 2 Techniques for the removal of toxic and radioactive elements.

exchanger with large porosity to allow the diffusion of ions to replace the exchanger ions, and these replaced ions will diffuse into the solution and be used for the removal of some organic molecules[62] and some heavy metals.[65–68]

Electrolysis

The electrolysis separation technique depends on an applied electrical current to separate elements and components from each other and is considered highly efficient. It is used for the separation of gases from wastewater and isolating metals from their ores.[69,70]

Solvent extraction

Solvent extraction is considered the ideal separation technique for separating lower-concentration contaminants by distribution between two immiscible layers; it is a simple and fast separation technique. The substance is distributed from one layer to another in liquid–liquid extraction. Solvent extraction is utilized to separate radioactive materials, as well as liquid–solid extraction and other special techniques.[71–73]

Adsorption

In 1881, Kayser was the first to introduce the term adsorption to describe gas condensation on surfaces.[74,75] Adsorption occurs on surfaces *via* the accumulation of substances called adsorbates on the surface of another substance called the adsorbent. This leads to an increased concentration of a specific substance at one interface as compared to another. The adsorption phenomenon is classified as either physical adsorption, called physisorption, or a chemical process called chemisorption. Chemisorption is a chemical interaction between the adsorbate on the surface of the adsorbent by electron sharing or exchanging. As a result, a new strong chemical bond is formed between the adsorbate and the adsorbent. Thus, chemisorption is a slow and irreversible adsorption phenomenon.[76] Physisorption is a physical interaction between the adsorbate and adsorbent that involves a variety of interactions such as dipole–dipole forces, van der Waals forces, hydrogen bonds, and polarity. Physisorption is a fast and reversible adsorption phenomenon so the bonds are easily formed and broken.[77]

Flotation

Flotation is the process of separating and concentrating one type of particle from another through selective etching on liquid–liquid interfaces. Electrolytic flotation and dissolved air flotation are the best examples for water treatment.[78] The flotation process has many advantages, such as removing heavy metals since it removes cadmium, copper, zinc, and chromium from wastewater using the ion flotation method. Ion flotation has many advantages such as low energy consumption, fast operation, availability for low concentrations, small space requirement, and low operating costs.[79]

Decontamination of radioactive elements from water resources using different adsorbents

Many types of adsorbents have been used for the removal of contaminants from waste, such as coal, wood-activated carbon, bone chars, resins, zeolites, and clays.[80–89] Adsorption takes place when the adsorbate (solid) has a significant affinity for the adsorbent surface as compared to its solution. The chemical properties of the adsorbent and its compositional properties are essential in determining the nature of the interaction between the adsorbate and the adsorbent surface. Meanwhile, the presence of pores on the adsorbent surface causes the enhancement of the adsorption process.[90,91]

Organic adsorbents

Organic adsorbents are used for various applications such as purification, drying, separation, catalysis, and controlling pollutants. These organic sorbents, such as activated carbon, chitosan, and other organic adsorbents, consist of aromatic sheets condensed over each other, forming a hydrophobic character. Thus, when a nonpolar-organic material is exposed to its surface, it causes an interaction *via* van der Waals forces. In contrast, it is not suitable for an inorganic material except in the presence of some functional groups. Inorganic functional groups such as carbonyl, carboxyl, and hydroxyl enhance their interaction with the inorganic materials, which may be polar or charged materials like metal ions.[91,92]

Activated carbon

Activated carbon is a commonly used adsorbent in wastewater treatment.[89,93–95] The popular common sources for obtaining activated carbons are coal, wood, and coke, in addition to nutshells.[96,97] The activation of these materials is divided into two types: physical and chemical activation.[86] The chemical activation process involves soaking the inactivated carbonized material in a strong dehydrating agent, usually phosphoric acid, then heating it at a high temperature of about 700–900 °C. After activation, the surface of the activated carbon requires some modifications to increase the chances for adsorption and the activated carbon adsorption properties;[98–102] the modification processes increase the hydrophilic characteristics. The modification process may be a gas phase or liquid phase oxidation modification. In the case of gas modification, the surface of the activated carbon is exposed to hot oxygen gas at about 425 °C, which causes the formation of non-organic functional groups such as carbonyl and hydroxyl groups.[98,99] In the case of liquid modification, it involves the oxidation of the activated carbon surface using inorganic acids like nitric and phosphoric acids at high temperatures so that carboxylic groups are formed.[98–100] These modifications improve the hydrophobic characteristics, increasing the adsorption ability. Granular activated carbon, fibrous activated carbon, powdered activated carbon, and clothed activated carbon are the four types of activated carbon that vary in size and shape,[103] such as mercury,[104] copper,[105] lead,[106] chromium,[103,107–111] cadmium,[112,113] zinc,[114] lithium,[115] and uranium.[116–118]

Chitosan

Chitosan is an organic adsorbent produced from the *N*-deacetylation of chitin. Chitin exists in the exoskeleton of crustaceans and shellfish. It is a polysaccharide and the most naturally abundant biopolymer after cellulose.[119] Chitosan contains a higher nitrogen content, so it is a suitable metal adsorbent and was used for the removal of cadmium,[120] mercury,[121] chromium,[122] copper,[123] vanadium,[124] and platinum.[103] Moreover, it is used for agricultural applications such as plant defense, increasing the yield of crops, and other different applications.[125]

Polyurethane foam

Polyurethane is an organic polymer composed of urethane monomers; it is widely used for producing soft car seats, mats, and toys and, additionally, in medicine for manufacturing prostheses. In 1970, polyurethane was first used for the removal of metal ions[126,127] and then for the removal of organic materials.[128,129] Polyurethane foam has two types; loaded and unloaded. Unloaded polyurethane foam has a low adsorption capacity for anions.[127,130] It is used for the removal of metal ions; the adsorption of metal ions on unloaded polyurethane foam is carried out after the formation of a complex with organic or inorganic ligands, such as the thiocyanate ligand. Unloaded polyurethane is used for the removal of many metal ions such as zinc and molybdenum,[131] cadmium,[132] cobalt,[133] iron,[132] tungsten and technetium,[134] osmium,[135] lead,[136] platinum,[137] ruthenium,[138] zirconium,[139] and hafnium,[139] in the presence of thiocyanate ligands. Whereas, the loaded polyurethane foam can contain and collect a large amount of organic and inorganic compounds-reagents, which causes modification and enhances the adsorption process. This can be achieved by using oxygenated or nitrogen-containing organic chelating reagents.[126] These reagents and compounds are fixed on polyurethane foam by physical or chemical methods. During the synthesis of polyurethane foams, some compounds can be loaded; this is called chemical loading. The chemical immobilization of compounds on polyurethane foam is exhaustive so physical immobilization is most commonly used.[126] Loaded polyurethane foam has a wider field of application than unloaded polyurethane foam. It is used for the removal of many heavy metals such as cadmium, copper, nickel, cobalt, zinc, manganese, lead,[131] thorium,[140] and uranium.[141]

Coal

Activated carbon, produced from coal, is a highly versatile material with several beneficial properties. It has a high specific surface area, a well-developed internal pore structure, and numerous functional groups on its surface. Additionally, activated carbon has a low density, good mechanical strength, and excellent chemical and thermal stability. These properties, along with its potential for large-scale production and the ability to change its properties using specific solvents, make activated carbon a desirable choice for a wide range of applications. Recently, activated carbon has garnered significant attention in water supply and sewage systems due to its favourable adsorption properties, economic efficiency, regenerative capacity, large quantity, and environmentally sustainable nature.[142] Coal is well-known for its advantageous physical and chemical properties, which make it an effective adsorbent for removing dyes and heavy metals from polluted solutions; for example, it can effectively remove cadmium[143] and mercury[144] from such solutions.

Inorganic adsorbents

Inorganic adsorbents such as zeolites, metal oxides, activated alumina, bentonite, and silica gel have attracted great interest in separation methods due to their properties such as thermal stability, radiation stability, and difficulty to be reduced or oxidized. Among these inorganic adsorbents is activated alumina. Activated alumina is produced from the dehydroxylation of aluminum hydroxide, which produces high porosity and a large surface area, making it available to be utilized as a catalyst, desiccant, filter, and adsorbent.[145] Thus, activated alumina is used for the removal of some heavy metals such as chromium,[145] arsenic,[146] antimony,[147] copper,[148] cadmium, and lead.[149]

Another example is bentonite, which is an adsorbent consisting of montmorillonite-aluminum phyllosilicate clay and some other components such as calcium aluminosilicate and sodium aluminosilicate, which are called calcium and sodium feldspar.[150] Bentonite can be divided into two types based on the exchangeable cations Ca and Na, which are known as sodium or calcium bentonite.[151] The main structure of bentonite consists of three sheets: two of them are tetrahedral silica, and the other is alumina, which is octahedral and lies in the centre between the two silica tetrahedral sheets.[152] Sodium bentonite has considerable swelling ability as compared to calcium bentonite, which has no capacity for swelling and is dispersed in water, forming colloidal solutions.[150] Bentonite layers are attached through electrochemical forces and the surface acquires a negative charge, making its face an anion that is balanced by cations. The dominant cations are calcium and sodium, called calcium and sodium bentonite, where not only Ca and Na but also other alkaline earth metal cations can balance the negative charge of the surface.[150] Bentonite has great commercial value due to its applicability in various industrial applications such as paper making, drilling fluid, paints, pharmaceutical products, dyes, water treatment,[150] and the separation of different heavy metals such as lead, nickel, chrome, and copper.[153]

Organic and non-organic hybrid adsorbents

Metal–organic frameworks (MOFs) are hybrid materials combining organic linkers with metal ions or clusters. This results in materials that possess the advantageous properties of both inorganic and organic components, resulting in unique and desirable properties.[154,155] MOFs, also called porous coordination polymers (PCPs),[156–158] are a class of microporous crystalline materials.[159–161] They are also new regulable and modifiable porous materials, combining coordination chemistry and material science.[162,163] These properties allow MOFs to be promising materials for removing toxic and radioactive metal ions in nuclear waste.[164–166] Recently, MOFs have been reported for the removal of toxic and radioactive elements from the environment to manage pollution.[167–170]

MOFs: an overview and fabrication methods

MOFs, part of the crystal porous materials family, are made up of metal assemblies – such as metal ions or groups – and linkers linked together by coordination bonds.[167,168] It is well known that MOFs are among the most extensively researched materials in the twenty-first century due to their structure tailorability, high crystallinity and controlled porosity.[26,169,170] Metal ions that are widely used to fabricate MOF include Fe^{3+}, Cu^{2+}, Ca^{2+}, Al^{3+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Zr^{2+}, Ln^{3+} and Ti^{3+}, which can have different coordination geometries such as diagonal, pyramidal, square, tetrahedral and octahedral.[171–182] Metal ions such as Co^{2+} and Cd^{2+} or Eu^{3+} and Ag^{+} are known to be toxic or expensive but are still crucial for studying their participation in MOF fabrication and applications.[183–187] Linkers such as melamine, carboxylates, 4,4′-biphenyldicarboxylic acids, 1,4-naphthalene dicarboxylic acids, and aliphatic polycarboxylates are regarded as the main components to synthesize MOFs.[188–193] The reversibility of coordination bonds between metal nodes and organic linkers is critical for forming well-organized MOF structures. Because the metal nodes can easily adjust their coordination connections, highly ordered MOF architectures can be created.[194,195] One of the commonly used techniques for the fabrication of MOF is the bottom-up method,[196] which allows direct reaction between metal ions and organic linkers under specific reaction conditions to provide the targeted MOF.[197] In general, MOFs can be synthesized using a variety of methods, including non-aqueous or aqueous direct synthesis and mixed non-aqueous or aqueous synthesis. Solvothermal growth, hydrothermal synthesis, chemical–mechanical synthesis, layer-by-layer assembly, ultrasonic synthesis, electrochemical synthesis, microwave-assisted synthesis, and high throughput synthesis are all standard synthesis techniques. The reversible nature of coordination bonds between metal nodes and organic linkers is critical in the formation of well-ordered MOF structures.[194,197] A more detailed description of the linkers, metals, modulators and synthesis of MOFs is given below. Greater permanent porosity than any other class of porous materials is a beneficial property of MOFs with their ordered porous structures. This renders MOFs promising sorbent materials with remarkably high absorption efficiency for toxic and radioactive elements.[187,198–206]

Numerous organic linkers are used in MOFs, such as the following. (i) Melamine: Adekoya *et al.* synthesized a graphitic carbon nitride modified by copper and titanium nitrate, g-C_3N_4 through the calcination of melamine at 550 °C for 3 h, then copper and titanium were impregnated by wet impregnation. Cu–Ti-gC_3N_4 was used for the reduction of carbon dioxide into methanol and formic acid.[188] Yang *et al.* constructed a melamine-based MOF called MIL-125/Ag/g-C_3N_4 (Fig. 3a), which was used as a photocatalyst for the oxidation of alcohols and the reduction of nitro compounds.[207] Yu *et al.* prepared AgCl–Ag/g-C_3N_4 (Fig. 3b), which was used for the photo-degradation of methyl orange.[208] Yao *et al.* synthesized Ag Pb-graphitic carbon nitride, which was used as a photocatalyst for the degradation of formic acid (Fig. 3c). Here, melamine was calcined at 823 K for 4 h and silver and lead were supported on the calcined carbon nitride *via* stirring for 24 h.[209] Li *et al.* synthesized four new coordination polymers based on melamine as a linker and four lanthanide salts, Sm, Gd, Er, and Nd nitrates, using the hydrothermal method.[210] Baraka *et al.* synthesized a silver melamine-based MOF in the presence of acetic acid *via* the hydrothermal method (Fig. 3d). The MOF synthesized by Baraka was used for the selective removal of methyl orange dye.[211]

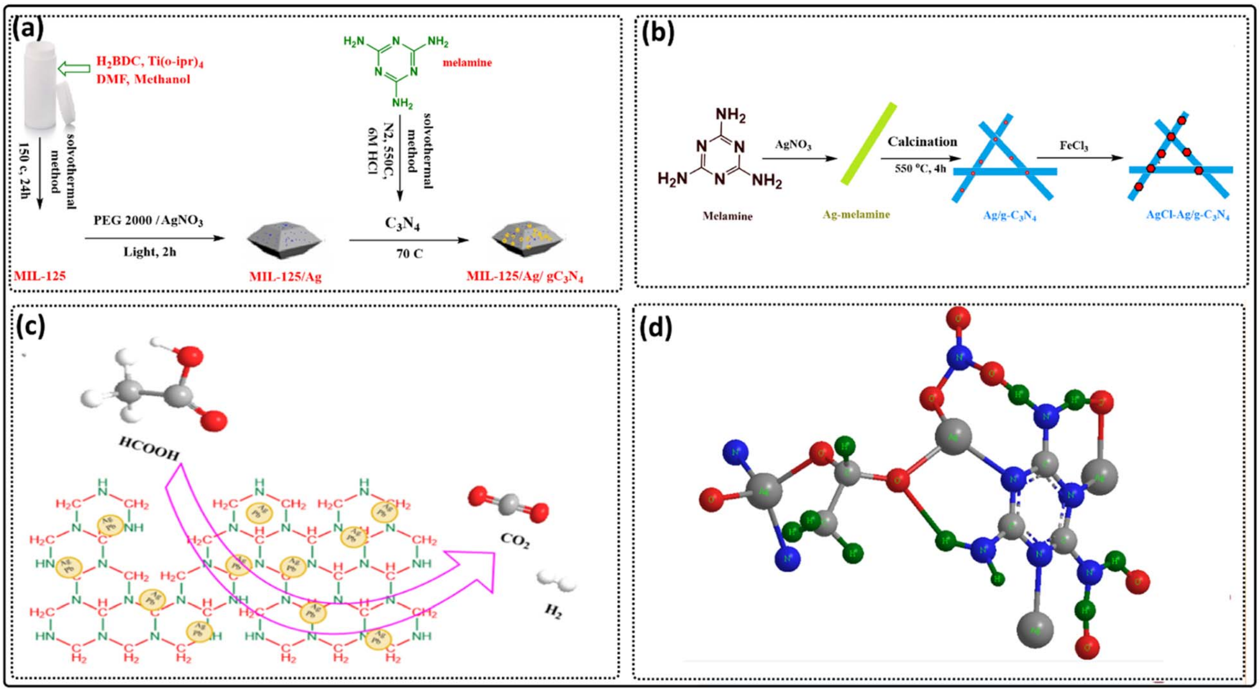


Fig. 3 (a) An illustration of the preparation of MIL-125/Ag/g-C_3N_4 [adapted from ref. 207 with permission from Elsevier B.V., copyright 2016]. (b) Schematic illustration of the synthesis of AgCl–Ag/g-C_3N_4 [adapted from ref. 208 with permission from Elsevier B.V., copyright 2019]. (c) High efficient release of hydrogen from formic acid using AgPd/g-C_3N_4 [adapted from ref. 209 with permission from Elsevier B.V., copyright 2017]. (d) Silver melamine-based MOF structure in the presence of acetic acid [adapted from ref. 211 with permission from Elsevier Inc., copyright 2019].

(ii) Terephthalic acid: Li *et al.* synthesized two coordination silver-based polymers using terephthalic acid as a linker and 1,6-(2-methylbenzimidazolyl)hexane *via* sonication and a hydrothermal method. The constructed compounds were used for the degradation of methylene blue with high efficiency.[189] Ehrenmann *et al.* fabricated the MIL-101 MOF based on terephthalic acid as a linker, and used it for heat transformation applications due to its high stability.[212] Scholz *et al.* prepared a strontium terephthalate MOF (Fig. 4a) using terephthalic acid by milling the powdered reactants for an hour.[213] (iii) 4,4′-Biphenyldicarboxylic acid: Wang *et al.* synthesized NiCo-MOF using 4,4′-biphenyldicarboxylic acid as a ligand, *via* the solvothermal method, which was then used as an electrode material (Fig. 4b).[190] (iv) 1,4-Naphthalenedicarboxylic acid: Yang *et al.* synthesized Zn-MOFs based on 1,4-naphthalenedicarboxylic acid *via* the hydrothermal method (Fig. 4c). These MOFs were used for the detection of dichromate ions and glyoxal.[191] (v) Aliphatic polycarboxylates such as oxalic acid:[192,193] Carballo *et al.* synthesized four MOFs (Fig. 4d) using oxalic acid as a linker using the hydrothermal method,[214] with succinic acid[215] and adipic acid (Fig. 5a)[216,217] as ligands.

To create MOFs, metal cations, including transition metals,[218] rare earths,[219,220] representative elements,[221,222] and actinide metals[223] can be utilized. Organic linkers can combine with metal cations, including alkaline earth metals such as Mg, Ca, Sr, and Ba, to form MOFs. Although MOFs based on these alkaline earth metals have been synthesized, they have not been as extensively studied as MOFs based on transition metals or lanthanides. MOFs containing alkaline earth metals, such as those prepared by Platero-Prats *et al.* who used Mg, Sr, Ba, and Ca as metal components (Fig. 5b)[225] with anthraquinone-2,6-disulfonate ligands, showed thermal stability at high temperatures up to 500 °C.[224–226] The unique properties of alkaline earth MOFs, such as their low toxicity, lightweight nature, air stability, and low cost, make them an appealing research subject.[227] The presence of alkaline earth metals in MOFs can cause the formation of empty positions in the coordination sphere, resulting in the formation of Lewis acid sites.[228]

Moreover, modulating agents are usually added to the MOF reaction mixture and are required for controlling the properties of materials (*e.g.*, morphological and porous features), such as HCl, acetic acid, and formic acid. Katz *et al.* synthesized UiO-67 (Fig. 5c) and UiO-66 MOFs (Fig. 5d) using hydrochloric acid as a modulator to condition the solvent used in synthesis (DMF), neutralizing the basic character of the solvent and/or enhancing the formation of the cluster structure of the required MOFs.[229–231] HF was also used for modulating the crystal size and morphology of the prepared MOFs. Yang *et al.* used hydrofluoric acid as a modulator to study its effect on the crystallinity and morphology of the zirconium metal–organic framework UiO-66. They found a strong effect on the crystallinity and the crystal size of UiO-66 MOFs.[232] Atzori *et al.* studied the effects of benzoic acid as a monocarboxylic organic acid modulator on the synthesis of UiO-66. They proved that benzoic acid used for modulation enhanced the reactivity of the MOFs toward their required application (adsorption, photocatalyst, and sensor). Meanwhile, it increased the MOFs' surface porosity because it allowed defects in the MOFs cluster structure.[233]

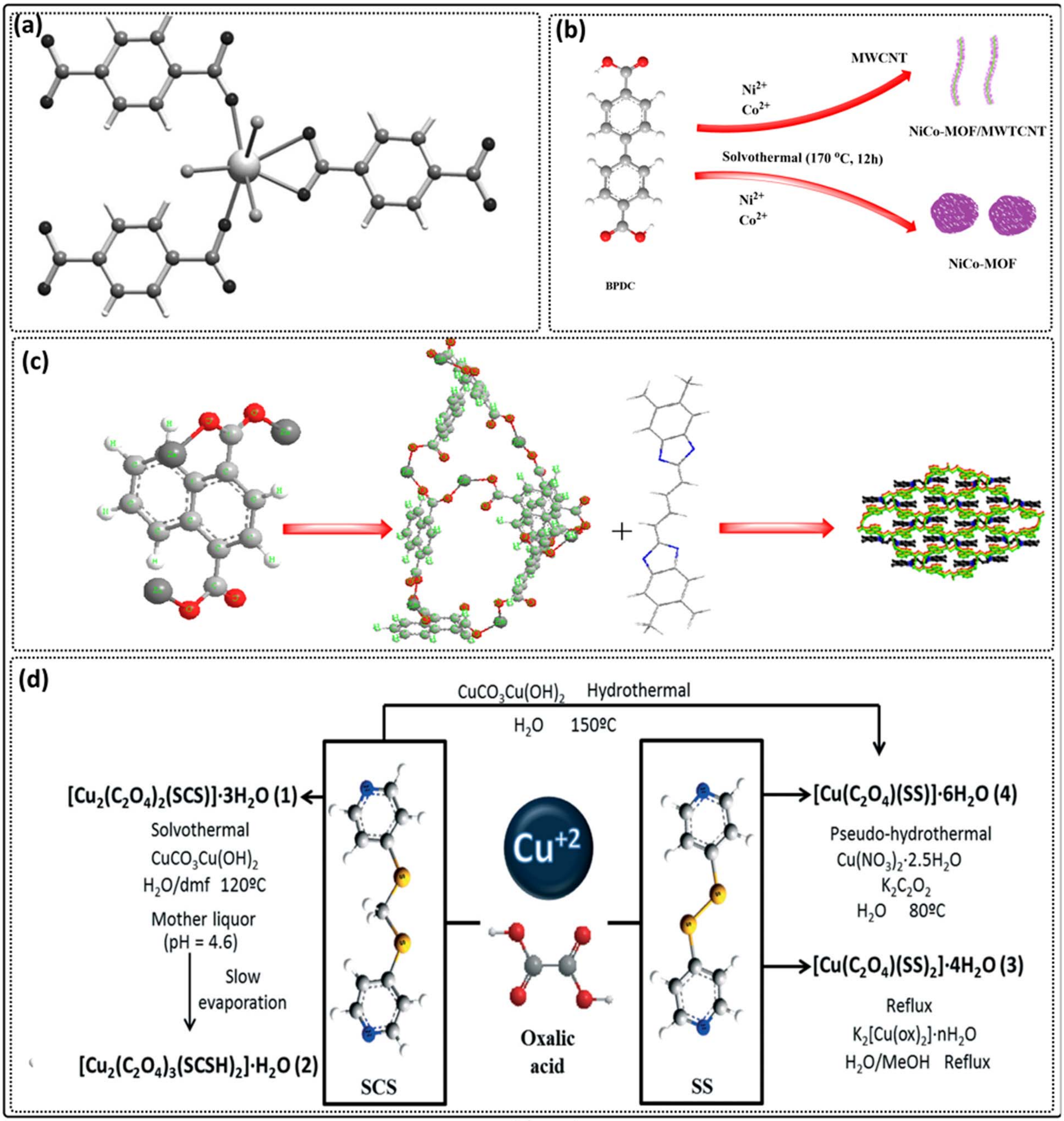


Fig. 4 (a) A strontium terephthalate MOF structure [adapted from ref. 213 with permission from WILEY-VCH Verlag, copyright 2013]. (b) NiCo-MOF using 4,4′-biphenyldicarboxylic acid [adapted from ref. 190 with permission from Elsevier Inc, copyright 2019]. (c) Zn-MOFs based on 1,4-naphthalenedicarboxylic acid [adapted from ref. 191 with permission from Elsevier Inc, copyright 2019]. (d) Four MOFs using oxalic acid as a linker [adapted from ref. 214 with permission from Royal Society of Chemistry, copyright 2013].

Schaate *et al.* used acetic and benzoic acids as modulators for increasing the crystal size and crystallinity of UiO-MOFs.[234] The presence of modulators during fabrication causes decreases in the reaction rate, leading to proper crystal growth, which improves the crystalline property and repairs the lattice defects. On the other hand, adding an excess amount of modulator causes lattice defects due to the replacement of ligands by modulators in the lattice structure[235] Bai *et al.* found that replacing terephthalates in UiO-66 by trifluoroacetate caused lattice defects and, therefore, the high catalytic activity of MOF.[235]

The methods used to create long afterglow materials significantly impact the microstructure features and defect distribution within the material.[236] For the synthesis of MOFs, two directions can be taken related to solvent: one of these is solvent-based synthesis, and the second is a solvent-free synthesis, which is the conventional method.[237] To achieve the desired compositions for long-lasting glow materials, high sintering temperatures are frequently used. However, this can

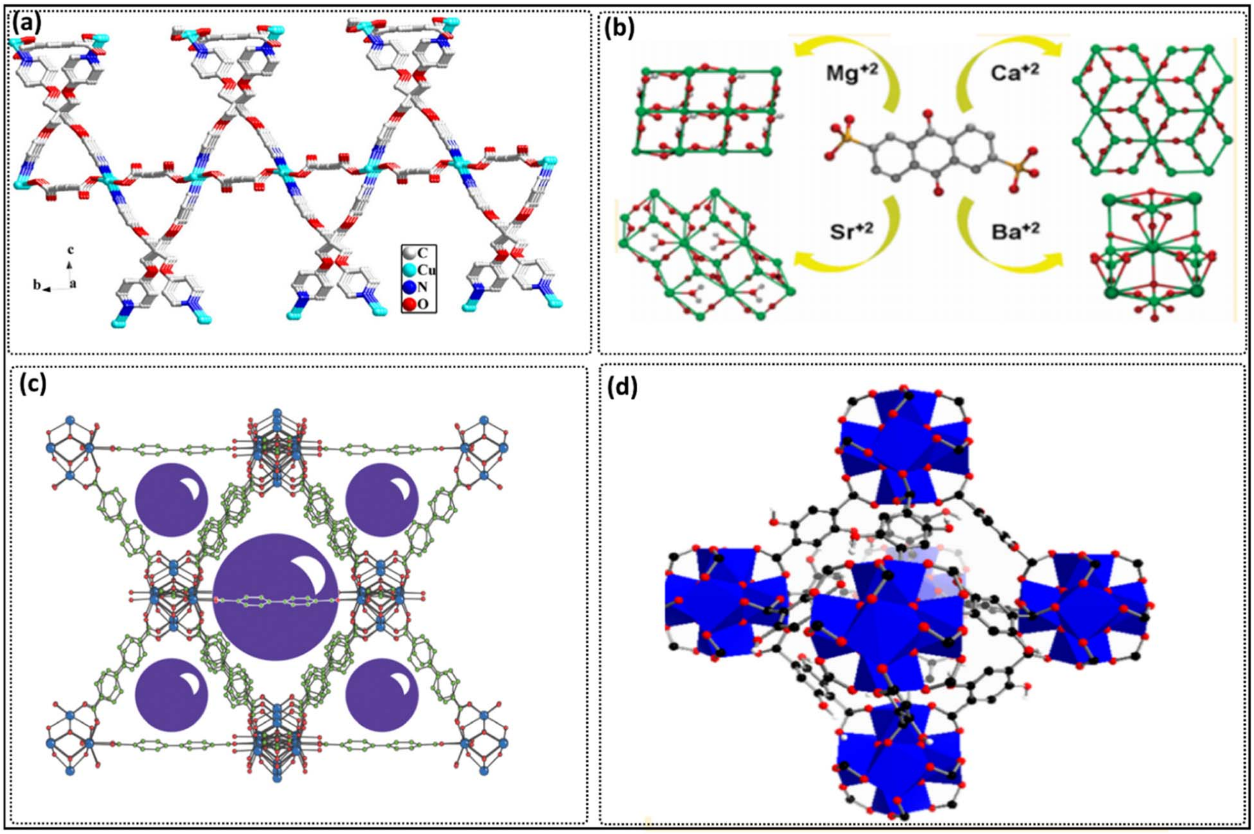


Fig. 5 (a) Adipic acid-Cu MOF [adapted from ref. 216 with permission from Elsevier B.V., copyright 2012], (b) Ca, Sr, Mg and Ba ions MOFs with anthraquinone-2,6-disulfonate [adapted from ref. 225 with permission from American Chemical Society, copyright 2011], (c) structure of UiO-67 showing a single octahedral cage [adapted from ref. 229 with permission from The Royal Society of Chemistry, copyright 2013], (d) structure of UiO-66 [adapted from ref. 231 with permission from American Chemical Society, copyright 2017].

result in agglomerated, irregularly shaped products. Chemical synthesis methods, such as the sol–gel method, which involves liquid phase reactions, can be used to overcome this challenge.[238] On the other hand, solvothermal,[239] hydrothermal,[240] coprecipitation,[241] combustion,[242] sintering,[243] solid phase,[244] sonochemical,[245,246] mechanochemical,[247,248] microfluidic,[249] and electrochemical methods,[250] can lead to the formation of different morphologies and structures of MOFs.

Solvothermal and hydrothermal methods

These two synthesis methods involve dissolving specific amounts of metal salts and ligands in water or an organic solvent, and then the precursor is transferred to a stainless-steel Teflon reactor and heated at a specific temperature for a certain time. These two methods lasted from a few hours to days with a temperature range of 297–473 K. Within this time, high temperature and pressure in the reactor are generated and result in the formation and enhancement of MOFs with good morphology.[251] Varying the synthesis time, temperature, molar concentration ratios of metal salts and ligands, and solvent volume help to control and/or modify the morphology and growth of the prepared MOF.

The solvothermal method is based on dissolving the ligand and salts in an organic solvent such as amines, alcohols, or basic organic solvents.[252] Yaghi *et al.* fabricated ZIF-MOFs using (DMF) *N*,*N*-dimethylformamide and (DEF) *N*,*N*-diethylformamide.[253] Alcohols are the alternative solvents for amides, and they are extensively used in MOFs synthesis due to their volatility and low price. Liu *et al.* synthesized Zn-MOF using methanol to dissolve the metal salt, $Zn(NO_3)_2 \cdot 6H_2O$, with 2-methylimidazole.[254] Due to the high cost of treatment of organic solvents for pollution reduction, recent methods of synthesis using pure aqueous and mixed solutions have been reported. Pan *et al.* fabricated Zn-MOFs in a water and 2-methyl imidazole mixture.[255] Also, the hydrothermal method is shorter than the solvothermal method in terms of fabrication time.[256]

Sonochemical method

The sonochemical method yields uniform nucleation and crystallization in a short time so it is more efficient and economical. The sonochemical method reduces the fabrication time from days to a few hours.[257] In addition, smaller and more uniform particle sizes of MOFs are produced from sonochemical methods than from other traditional methods as reported by Seoane *et al.*[258]

Mechanochemical synthesis

The mechanochemical method is regarded as a green chemistry synthesis method, which shows quantitative output and large-scale production without using solvents and high temperatures. Adams *et al.*[259] mechanochemically fabricated a Zn-imidazole-MOF using imidazole and $ZnCl_2$ through two steps using KOH. The synthesis of ZIFs-MOFs at room temperature using NH_4^+ was also reported.[260] Tanaka *et al.* synthesized Zn-imidazole-MOFs without using solvents or any reactants other than ZnO and 2-methylimidazole.[261]

Other fabrication methods

Microfluidic synthesis is synthesis using the microchannels of a micromixer for mixing reactants. It is favorable for controlling reaction parameters such as time, temperature, and pressure and avoiding variations between prepared batches.[262] Faustini *et al.* fabricated ZIF-8 MOFs using the microfluidic method *via* a tubular reactor.[262] Also, ZIF-8 was fabricated by Yamamoto *et al.* using a t-type micromixer.[263] Dry-gel methods attract significant attention in MOFs synthesis.[264] Lee *et al.* found that MOFs prepared by dry-gel produced an excellent MOF yield and smaller particle size than those produced by solvothermal, microwave, mechanochemical and microfluidic methods.[265] Microwave heating has several advantages over traditional synthesis methods, including rapid heating, uniform heating, high efficiency, and ease of control,[266] resulting in the most stable MOF.

The impact of using organic solvent and solventless fabrication of MOFs on the environment

MOF chemistry has several limitations that need to be addressed further, including issues with stability, toxicity, efficacy, safety, high energy consumption, and biodegradability.[267,268] To address these challenges, incorporating the twelve principles of green chemistry recommended by Paul Anastas and John Warner, as outlined by the Environmental Protection Agency, can be an effective strategy for MOF synthesis.[269] The focus on developing green MOFs gained traction in the latter part of the decade, and researchers such as Kumar *et al.* investigated their potential for creating sustainable materials with minimal environmental impact. To achieve this goal, various factors in the design of MOFs must be considered, such as the use of green solvents, energy-efficient processes, eco-friendly linkers, low-toxicity metal salts, less hazardous byproducts, biodegradable products, and green applications. These strategies are critical for the green chemistry of MOF design.[269] To create a safer coordination framework, it is critical to carefully select raw materials that are compatible with biomass, use safer solvents, and employ energy-efficient processes that preserve the material's unique properties, structure, and crystallinity. Significant progress has been made in developing low-impact MOF synthesis, emphasizing the importance of continued progress in this field.[270]

Solvent-based synthesis

The solvents used in MOF synthesis are necessary because they influence the creation of controlled environments. Solvents can act as structural guides or metal ion coordinators, and thus play a vital role in the formation of MOFs.[271] The MOF's final crystal lattice template is heavily influenced by the solvent used.[271] Conventional studies on MOF manufacturing methods tend to adopt *N*,*N*-dimethylformamide (DEF), and dimethylformamide (DMF).[272,273] These solvents are attractive for increasing acidity. The acidic and basic properties of the molecules of organic solvents have a profound effect on the interpretation of solute–solvent reactions.[274] The slow evaporation rate and high boiling points of these solvents provide an extended period of reaction media availability. Nonetheless, the utilization of such solvents during heating or burning can produce a considerable quantity of hazardous amines.[275]

The toxicity of MOFs is attributed mainly to the use of solvents.[276] To ensure process safety and minimize environmental impact, finding alternatives to traditional solvents is crucial. The use of green solvents can help to create a safer environment for chemicals, but the economic feasibility of such solvents must also be taken into account. The environmental impact of solvents can be evaluated based on factors such as their effect on human health, impact on natural resources, ecosystems, and potential for renewable resources. Disposing of solvents that can be recycled or reused can help reduce the risk and toxicity associated with their use.[277,278]

Alternatives such as methyl lactate or ethyl, dimethyl sulfoxide (DMSO), ionic liquids, and water can be used to avoid environmental and harmful solvent impacts.[279,280] Glycerol products (such as triacetin),[281] and lactone-based solvents, including *c*-butyrolactone and valerolactone, are additional alternatives to conventional solvents.[282] We have summarized the most common solvents used for the fabrication of metal–organic frameworks in Table 2.

Water

Out of all the solvents, water is the most advantageous due to its abundance, affordability, and ability to facilitate the purification and recycling of artificial substances.[270] Water is particularly well-suited for the development of scalable, sustainable, and water-based alternatives to MOFs.[283,300] Organic solvents are not ideal for industrial-scale use as they require processing in a controlled and non-flammable environment. In contrast, water-based synthesis is a safer, more affordable, and more straightforward method of processing synthetic materials.[284] Recent research on MOF synthesis, particularly for MILs and zeolite imidazolate (ZIF) frameworks, has emphasized the use of water at ambient temperatures and atmospheric pressure.[301]

The use of aqueous media for MOF synthesis has some limitations, including reduced final product stability, loss of crystallinity, and potential phase transitions. These limitations are often attributed to the interfacial interactions between water molecules and the hydrophilic parts of the MOF.[302,303] Conveniently, the high specific heat and latent heat of the water will cause a high cost of evaporating energy. Due to their insolubility, the synthesis of coordination compounds in water is also difficult.[304] Most organic salts and seals overcome these limitations and will require the following.

Table 2 Examples of the most common solvents used for the fabrication of metal–organic frameworks

No.	MOF	Solvent	Temp.	Time	Application	Ref.
Water	ZIF-93	H_2O	RT	18 h	CO_2 adsorption	283
	MOF-74 (Ni)	H_2O	160 °C	1 h	—	284
	MOF-303 (Al)	H_2O	100 °C	24 h	Production of water from desert air	285
	Al-MIL-53	HTW	250 °C	10 min	—	286
	MIL160(Al)	H_2O	60 °C	24 h	Energy-reallocation systems	287
	Co-MOF	H_2O	160 °C	72 h	Biodiesel	288
Supercritical carbon dioxide	Pt@MIL-101(Cr)	$scCO_2$	220 °C	10 h	Catalyst	289
	Cu-MOF (1D)	$scCO_2$	60 °C	24 h	—	290
	ZIF-8	CO_2	35 °C	10 h	CO_2 adsorption	291
	ZIF-8	$scCO_2$	65 °C	2 h	—	292
	$Cu_3(BTC)_2$	$scCO_2$	60 °C	24 h	Catalyst	293
	HKUST-1	$scCO_2$	40 °C	1 h	—	294
Ionic liquid	UiO-66 (Zr-MOF)	1-Octyl-3-methylimidazolium chloride	RT	1 h	—	295
	HKUST-1	Cholinium ionic liquid	RT	30 min	Adsorption kinetics	296
	Zn-MOF IL-1-propyl-3-methylimidazolium bromide	Zn-MOF IL-1-propyl-3-methylimidazolium bromide	160 °C	120 h	—	297
	Polyoxometalate MOF (Cu and Zn)	([bmim]Br)	170 °C	120 h	—	297
	La-MOFs	1-Butyl-3-methylimidazolium hexafluorophosphate	RT	24 h	—	298
	Zn, Cu and Fe MOF	([emim]BF_4)	65 °C	10 h	—	299

- The use of hydrophobic organic moieties (such as alkoxy acids and silicone polymers) and modifiers (such as polyvinylpyrrolidone (PVP) and formic acid).
- Understanding the detailed binding properties of MOFs, such as those associated with fluorination, N bonding, and chiral ligands, as well as the use of specific metal salts (*e.g.* oxides and sulfates), can aid in the synthesis of MOFs with desired properties.[305–308]

Water as a solvent has resulted in the development of novel MOF structural archetypes.[309] Numerous novel MOFs have been manufactured since then, including MOF-74 (Zn) (Zn),[304] CAU-22 (Zr),[310] and MIL-91 (Ti).[311] Water use is also perfect especially when making water-sensitive MOFs containing carboxylic acids, such as Cu_3 $(BTC)_2$ and Mg-MOF-74 (ref. 312). Due to the stability issue of MOFs in aqueous media, these MOFs can reduce crystallinity, phase transition, and structural decomposition.[303] However, UiO66 (carboxylate containing MOF) has excellent water stability, which can be attributed to many chemical and steric factors.[312] The small pore size of UiO-66 confirms that metal carboxylate sites can be used for a single water molecule. Preliminary research on MOF synthesis is based on a binary water/ethanol solvent to reduce the harmful effects of water.[313] In these binary solvent systems, a wide range of reaction conditions lead to the formation of toxic by-products. Comprehensive research work focusing on sustainability focuses on limiting the formation of harmful pollutants. For example, it has been proven that the reagent Cu $(OH)_2$ is completely converted to Cu_3 $(BTC)_2$ in an aqueous solution of ethanol at room temperature.[314] Using a non-wasteful manufacturing method, it is possible to improve the performance of materials and prepare various other subcategories of zeolitic imidazolate frameworks (ZIFs). One example is the production of stable ZIF-93, which can be synthesized in ammonia based on the water route.[283] ZIF-93 has been deemed an attractive alternative to various ecologically sound programmes, such as eliminating carbon dioxide from the environment. Jian *et al.*[315] have reported a series of fine syntheses of ZIF-8 in water based on salts of metals (*e.g.*, Zn $(OAc)_2$ or $ZnSO_4$) without the addition of regulators. Several parameters (such as water content, metal salt, and its ratio to ligand) were found to significantly impact the morphology of ZIF-8 in their study. Environmentally friendly X-MIL-53 (Al) materials have also been synthesized.[304] MIL-53 has little or no unreacted connection salt in the pores, which can provide high-quality products. Zirconium-based frames (UiO type) are being reported for their new characteristics (such as stability and versatility). However, more sustainable synthetic methods are needed to increase the production of materials effectively. Chen *et al.*[316] reported that the successful crystallization of Zr-based metal–organic frameworks (MOFs) such as UiO-66 and NU-901 was achieved at room temperature through the hydration process, facilitated by the addition of modulating agents such as trifluoroacetic acid and acetic acid.

This promising type of MOF has caught the attention of researchers as a potential replacement for high-quality hazardous solvents. The industry welcomes the use of solvents with less environmental impact. Additionally, eco-friendly MOFs could open up opportunities for effectively adsorbing toxic chemicals in both aqueous and gaseous systems. The hydrothermal synthesis of coordination scaffolds is expected to facilitate a transition to commercial production at high rates while simultaneously reducing the environmental impact and production costs.

Supercritical liquids

Supercritical liquids are another interesting option for environmental interaction media. Supercritical carbon ($scCO_2$) provides high-potential carbon dioxide and green water solvents for MOF synthesis. Various MOFs can be produced by green synthesis technologies using supercritical liquids.[317] Green solvents with adjustable properties, such as polarity, viscosity, surface tension, and phase, can be synthesized by controlling the conditions of the synthesis process. These adjustable properties make these solvents suitable for recycling, eliminating the need for distillation and reducing energy consumption.[318,319] When the temperature and pressure exceed a critical point, water's polarity and hydrogen bonding properties undergo significant changes. High-temperature water (HTW) exhibits similar relative dielectric constant, ionization constant, and density as nonpolar solvents, which makes it capable of dissolving organic compounds (such as linkers) under normal conditions. However, the operating conditions required to achieve these properties are extremely high.

While it is true that the dissolution of compounds can be enhanced by increasing temperature and pressure, high-temperature water (HTW) and supercritical water solvents may not always be feasible in MOF synthesis due to certain limitations. To address these issues, researchers have studied the viability of water at 300 °C as a green solvent for the synthesis of de-solvated microporous Zn(II)-carboxylate MOFs.[320] HTW may enhance MOF manufacturing for industrial uses by allowing reuse without cleaning, whereas organic solvents tend to degrade at high temperatures. Carbon dioxide is a non-flammable, low-impact, and virtually inexhaustible gas due to its low critical temperature (31.1 °C) and moderate pressure (73.83 bar). Liquid $scCO_2$ and CO_2 expanded liquid (CXL) are receiving much attention as solvents. Changing the operating temperature and pressure can change the consistency, density, and phase of $scCO_2$. The various chemical properties of $scCO_2$ aid in the simple dissolution of water-insoluble organic compounds.[321,322] The above findings indicate that $scCO_2$ holds excellent promise as a solvent for a wide range of applications, such as extraction, polymerization, biomedicine, catalytic reactions, and synthetic methods.[323]

Supercritical fluid was primarily used to clean pores after entrapped solvent synthesis. However, its utility in developing innovative and sustainable processes for extremely porous MOFs has recently been demonstrated.[289] Reactive crystallization with $scCO_2$ solvents has enabled the fabrication of more intricate one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) coordination structures. Utilizing $scCO_2$ and two bipyridyl ligands, a copper coordination complex with a 1D structure was successfully developed.[290] Portolés-Gil *et al.* reported the successful development of a copper coordination complex with a 1D structure using $scCO_2$ and two bipyridyl ligands, and this green synthesis approach has been extended to construct a 2D MOF based on either Cu(II) or Zn(II), with the addition of a small amount of *tert*-butyl pyridine to improve the solubility of $scCO_2$. Furthermore, $scCO_2$ was employed for the active crystallization of a bio-MOF (Zn [curcumin]) composed entirely of bimolecular building blocks.[324,325] The use of $scCO_2$ in the one-pot synthesis of Zn(2-methylimidazole) (ZIF-8) has been shown to provide several advantageous properties for MOF structures, which include a highly active surface, and a reduced risk of pore collapse.[291] Marret *et al.*[292] investigated the ability of $scCO_2$ solvents to convert the ionic precursor ZnO into ZIF-8 under mild conditions in the presence of imidazole-based linkers. This approach emphasizes gram scale availability for commercial scalability.

Ionic liquids

Ionic liquids (ILs) provide a new way to replace toxic solvents. These liquids are made up of organic or inorganic anions and cations and can withstand temperatures up to 100 °C. The IL's positively charged side chains can be ammonium/tetra phosphonium, pyridinium, or imidazolium, even though the anionic side chain could be tetrachloroaluminate, tertiary or hexafluorophosphate, or halogen.[291,326] Compounds with a melting point below the boiling point of water can be classified as ionic liquid (IL) compounds, providing a promising option for sustainable and eco-friendly solvents. However, certain ILs, such as 1-butyl-3-methylimidazolium, perfluoroanions, and imidazole, are considered unsafe.[327,328] Under ambient conditions, pure salts in liquid form can be held together solely by strong electrostatic discharge interactions, which can have a significant impact on the properties of ionic liquids (ILs) when used in the dissolution of charged solutes. Traditional solvents, on the other hand, are typically neutral. Because of their low vapor pressure, volatility, and flammability, ILs have recently received increased attention as green solvents.[329] A vital factor to consider is the vast array of ionic combinations that can be achieved by modifying the ions, which provides a high degree of tunability. This feature makes ILs an ideal choice as "designer solvents" that can be utilized as modulators for porous structures and coordinating agents for MOF precursors.[330]

Many MOF structures have been synthesized and explored using ILs, such as polyoxometalate-based MOFs, and 3D ferroelectric MOFs.[331] To date, in either room-temperature or isothermal conditions, MOF synthesis using IL-based compounds could be carried out. A mix between $scCO_2$ and ILs has been submitted for the quick fabrication of MOFs at room temperature. In this combination, $scCO_2$ can alter the viscosity of ionic liquids to be lower to enhance mass transfer at minimum temperatures and with shorter intervals.[299] There have been limited studies on the use of IL/$scCO_2$ combinations to fabricate MOFs. However, some recent research has explored the synthesis of microporous and mesoporous Co-MOFs using an IL/$scCO_2$-based dual-functional system.[332] Additionally, scCO2/imidazolium IL solvent mixtures have been utilized to synthesize various metal-based MOFs, such as those containing Zn, Cu, and Fe nodes.[299]

Bioderived solvents

Using biomass as a sustainable, renewable raw material for catalytic conversion into biochemicals and useable energy has gained significant attention. Biomass possesses several interesting properties, including its diversified nature, chirality, and oxygenation pattern, making it a highly favorable raw material for the production of high-value chemicals.[333] Many downstream protocols have been scaled up from laboratory research to large-scale commercialization.[334] In synthetic chemistry, it is currently not feasible to replace aprotic solvents like DMF and *N*-methyl-2-pyrrolidone (NMP) with alternative solvents.[335]

The use of bio-derived solvents as a potential alternative to aprotic solvents is discussed in this article, with a focus on 6,8-dioxabicyclo[3.2.1]octan-2-one (also known as Cyrene), an aprotic dipolar green solvent that can be obtained from various biomass sources such as larch trunks, bagasse, and poplar wood. The most productive biomass source for synthesizing levoglucosenone (OCT)/Cyrene (2H-OCT) is cellulose. The production of 2H-OCT involves two steps: first, the solid biomass is converted to LGO, and then LGO is reduced to 2H-LGO through a hydrogenation protocol. It is worth noting that the conversion of solid biomass into neutral energy only releases water into the environment.[336,337] Pyrolysis is a common method for converting cellulose into LGO and then to Cyrene. However, a novel continuous approach to transforming cellulosic biomass directly into 2H-LGO without pretreatment has been developed.[335] The conversion process involves using a Pd/Al_2O_3 catalyst and an IL on porous char, which yields 8.1% under a hydrogen gas atmosphere. Furthermore, in addition to its high potential in terms of reactivity profile when in the presence of acids, bases, nucleophiles, and peroxides, Cyrene has also been studied for its effectiveness as a solvent.[338]

In MOF synthesis, Cyrene is used to achieve crystallinity and a high surface area for MOF production, *e.g.*, HKUST-1, $Zn_2(BDC)_2$ (DABCO), UiO-66, MOF-74, and ZIF-8.[339] Glycerol and its byproducts are polar compounds with a high boiling point, low toxicity, and low vapor pressure. Furthermore, glycerol can dissolve a wide range of inorganic/organic salts, including metal ion complexes. Glycerol production from organic waste is regarded as an economically viable product in the biodiesel industry. This approach to glycerol production is both robust and environmentally friendly.[340] Several further solvents that possess comparable features, such as ethyl-lactate (ethyl 2-hydroxypropanoate), methyl lactate, *c*-butyrolactone, and 2-methyltetrahydrofuran (2-MeTHF), were also studied.[340] In particular, 2-MeTHF, an aprotic renewable lignocellulosic biomass-derived ether solvent, possesses favorable base and acid stability, limited miscibility with water, and is commercially available.[341] Those solvents generate less waste. In this account, 2-MeTHF has been applied to a variety of chemical processes, including the high-scale manufacturing of di-aryl and aryl ketones *via* Suzuki–Miyaura cross-coupling reactions,[342,343] furan-functionalized polyesters,[344] and quinazolinone synthesis.[345] The exceptional sustainability of 2-MeTHF as a solvent has revolutionized synthetic chemistry as it can be easily used and scaled up. Additionally, the prospects for 2-MeTHF can be extended to the development of eco-friendly MOFs, further enhancing their potential as a green solvent.

Solventless fabrication methods

Although using a solvent enhances the synthesis kinetics of MOFs with a suitable crystalline nature, researchers have exerted tremendous effort to demonstrate a superior eco-friendly method *via* solventless fabrication. The free solvent fabrication of MOFs dissolves the difficulty in the selection of a suitable solvent that changes the method from environmental to green based on mechanochemical methods.[346,347] Mechano-methods achieve a high production yield in a shorter time when compared to solvent-based methods.[348]

The adsorption mechanism of MOFs toward radionuclides

It is important to investigate the mechanism for the removal of radionuclides using MOFs. The mechanism was investigated through experimental studies and their corresponding observations, spectroscopic analysis techniques, and theoretical calculations. The performance of MOFs toward radionuclide removal is affected by intermolecular interactions between the radionuclides and MOF, as well as the intrinsic properties of MOF (*e.g.*, pore size, surface charge, crystallinity, shape, electronic state, surface-to-mass ratio, and the surface functional groups),[349] therefore numerous mechanisms may control the removal of radionuclides. The exact mechanisms for radionuclide removal could be investigated through macroscopic experiments and microscopic analysis.

The removal mechanism from the macroscopic experimental view

The removal mechanism could be investigated based on the reaction conditions, such as time, power of hydrogen (pH), and temperature. The reaction between MOFs and radionuclides was mainly affected by the solution pH.[350,351] This is because the adsorbates may have more than one species and/or change the charge over the adsorbent and the functional groups.[352,353] For example, U has more than one species. Thus, the removal is affected by the solution power of hydrogen.[352] At a pH lower than three, uranium ions exist as UO_2^{2+} and at a pH higher than three, they exist as $UO_2(OH)^+$, $(UO_2)(OH)_2^{2+}$, and $(UO_2)_3(OH)^{5+}$, while they precipitate at pH above eight.[354] In addition, the charge over the framework depends on the solution pH, and as a result, the pH could control the adsorption capability of radionuclides based on the point of zero charge of MOF. When the MOF surface is protonated, it becomes cationic and is available for the removal of anionic radionuclides. The reverse is correct when the surface is deprotonated and the point of zero charges becomes lower than the solution pH; MOFs in this situation become ready for cationic radionuclides.[355]

Factors that affect adsorption time and speed, the adsorption control step, and the diffusion mechanism of radionuclides can be investigated *via* adsorption kinetics.[349,353] For kinetic studies, some models must be applied and taken into consideration. The pseudo-first and second order models, the intraparticle diffusion model, and the Elovich model are commonly used for kinetic demonstration.[354] Generally, the correlation coefficient, R^2 is the value used for checking the best model[352,356] but in general, the adsorption rate of radionuclide removal depends on intraparticle diffusion. Thus, the intraparticle diffusion model is suitable for explaining the diffusion mechanism over the framework.[357] Also, the rate-controlling step is preferred for understanding the mechanism of radionuclide removal over MOFs. Related to the theory of Brownian movement, due to the variation in the Brownian motion, the removal of radionuclides by MOF is affected by temperature change.[358,359]

The removal mechanism from the microscopic analysis view

Numerous characterization techniques are used for the estimation of the surface properties of MOFs, the mechanism of removal, and the reaction pathway of MOFs with radionuclides through elementary analysis and functional group identification before and after the removal process.[360–362] Microscopic analysis is the next important step, besides macroscopic analysis, for understanding the removal mechanism of radionuclides. XPS analysis estimates the type and composition of the MOF surface and the valence of the surface elements.[360,362] FTIR analysis was used to estimate the functional groups over MOFs before and after radionuclide removal, which is clear evidence for the existence of the bonding between the MOF active sites and groups with the interested radionuclides.[354] Other superior analysis techniques have become available and are more favorable for understanding the removal mechanism, such as Raman, XRD, and UV-visible analysis.[363]

MOFs usability for the decontamination of wastewater from radionuclides

Cesium

Very few MOFs are reported for the separation of Cs^{137} such $UO_2(NO_3)_2\cdot 6H_2O$ with 3,5-di(4-carboxyl phenyl) benzoic acid, which showed a large capacity toward cesium.[206] Noeimie *et al.* fabricated a novel ferric-benzene tricarboxylic acid MOF by the hydrothermal method. They modified it by impregnation with potassium nickel hexacyanoferrate and applied it in the removal of Cs ions from aqueous solutions with an adsorption capacity of 153 mg g^{-1}. It showed high selectivity for sodium and potassium ions, and equilibrium was achieved after about 45 min.[364] On the other hand, $[(CH_3)_2NH_2][UO_2(L_2)]$ $0.5DMF\cdot 15H_2O$ was reported for the removal of Cs with a large uptake percent of 94.51% after 20 minutes under acidic conditions (pH 3).[365]

Barium

Ba^{133} is one of the most toxic radionuclides, resulting in radioactive waste, so its removal from waste is a point of interest to protect humans and animals from a long-term threat. Zhong *et al.* reported that MOF-808-SO_4 and MIL-101-SO_3H were suitable materials with good removal performance toward barium due to the strong interactions between barium and sulfate ions. Both functionalized MOFs are suitable for the removal of barium with 90% uptake percent after five minutes and reached 99% after equilibrium. MOF-808-SO_4 showed a removal capacity of 131.3 mg g^{-1} and 70.5 mg g^{-1} for MIL-101-SO_3H.[366] Also, Zr-BDC-NH_2–SO_4 was used by the same group for the removal of Ba at room temperature, showing a large removal capacity of about 181.8 mg g^{-1}.[367]

Uranium

More than twenty MOFs have been reported for the removal of uranium, which exists in the form UO_2^{2+}. Lin *et al.* fabricated the first MOF materials (UiO-68) that were applied in the removal of uranium ions from solutions, which showed excellent sorption capacity for uranium ions, about 217 mg g^{-1}[368] Wu *et al.* fabricated a ferric oxide-ZIF-8 composite (Fig. 6a) and used it for the removal of uranium(VI). The results showed a high uptake capacity (539 mg g^{-1}) with a contact equilibrium time of 30 minutes.[369] Also, MIL-101(Cr) has been reported for the removal of UO_2^{2+} from aqueous solutions with a high selective recovery and capacity of about 5.32 mg g^{-1} at pH 3 and 27.99 mg g^{-1} after an equilibrium contact time of 6.25 hours.[370] The modifications of MIL-101 with amine, ethanediamine, and diethylenetriamine have been reported to show excellent and superior removal capacity: MIL-101-NH_2, MIL-101-ED, and MIL-101-DETA showed 90, 200, and 350 mg g^{-1}, respectively.[371] Moreover, MIL-101 functionalized by the carboxyl group showed the suitable removal of uranium with a capacity of 314 mg g^{-1} after an equilibrium time of 2 h in a neutral pH medium.[372] UiO-66-AO is the first amidoxime-based MOF fabricated by the post-modification method (Fig. 6b). It has been reported for the removal of uranium ions from seawater with high efficiency and a very fast removal time, and removed about 500 ppm of uranium ions in less than 10 minutes. UiO-66-AO showed an adsorption capacity equal to 2.68 mg g^{-1}.[373] Zhang *et al.* reported that Zn-MOF-74 modified with coumarin enhanced the opening of the pore sites of the MOFs and showed a high adsorption capacity for uranium ions of about 360 mg g^{-1}.[374] Another strategy for improving the adsorption capacity for the removal of uranium ions rather than modification is the addition of a ligand in the body of the MOFs framework, as reported by Zhang *et al.*[374] $Zn(HBTC)(L)\ (H_2O)_2$ showed excellent ability for great performance in the removal of uranium ions with a capacity of 115 mg g^{-1} at lower pH. Meanwhile, MOF-76 (Fig. 6c) has been reported for the removal of uranium ions with an adsorption capacity of 298 mg g^{-1}.[375] On the other hand, MOF-5 was reported for the removal of uranium with a large removal capacity of 237 mg g^{-1} after a very short time (5 minutes) at pH 5.[376]

Thorium

Thorium exists in nuclear waste in the oxidation state (IV). The first MOF applied in thorium removal was UiO-66, which showed a maximum sorption capacity of 47.5 mg g^{-1}. Modification with carboxyl groups to give UiO-66-(COOH) resulted in

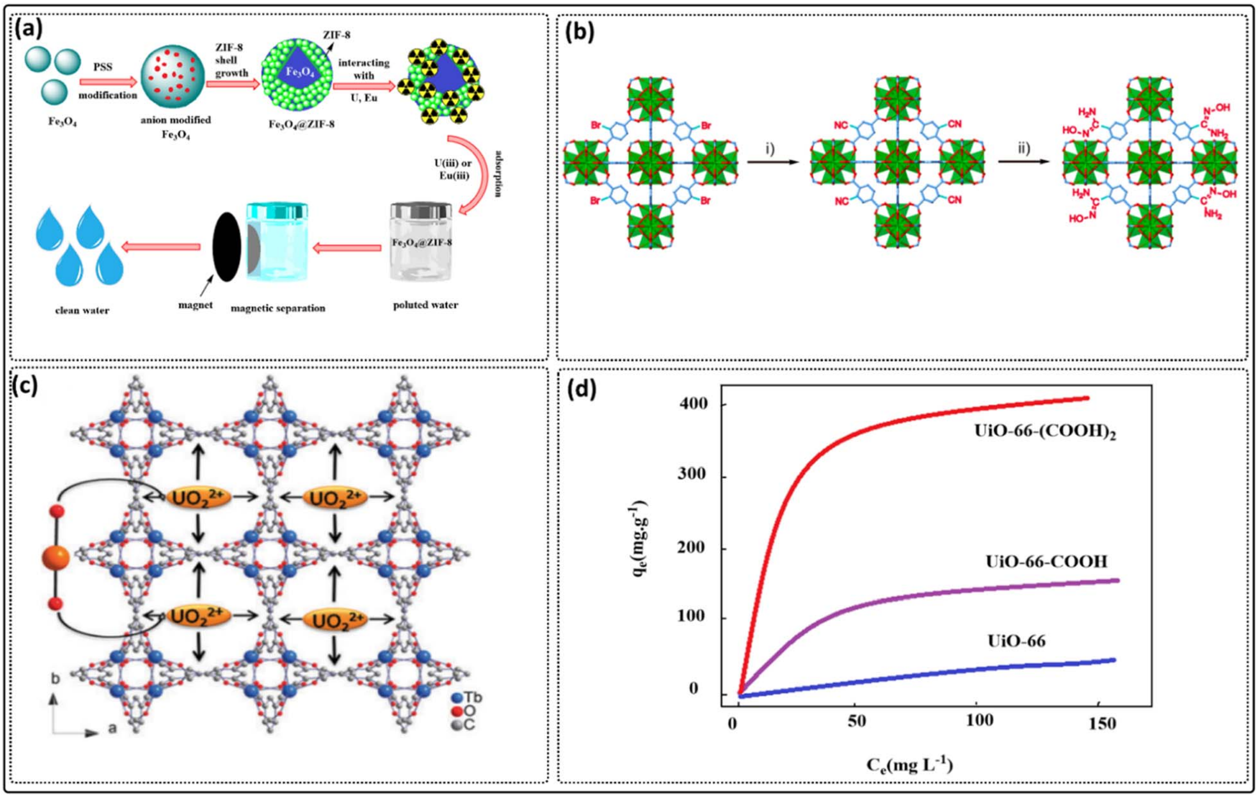


Fig. 6 (a) Ferric oxide ZIF-8 composite synthesis and removal mechanism [adapted from ref. 369 with permission from Elsevier B.V., copyright 2019]. (b) The synthetic route for UiO-66-AO: (i) CuCN, *N*-methyl pyrrolidone, microwaved at 170 °C for 20 min; (ii) $NH_2OH \cdot HCl$, CH_3CH_2OH, refluxing for 24 h [adapted from ref. 373 with permission from American Chemical Society, copyright 2017]. (c) Schematic of the capture of UO_2^{2+} ions in the one-dimensional channels of MOF-76 [adapted from ref. 375 with permission from The Royal Society of Chemistry, copyright 2013]. (d) Schematic sorption properties of UiO-66, UiO-66-COOH, and UiO-66-(COOH)$_2$ [adapted from ref. 368 with permission from Elsevier Inc, copyright 2019].

maximum capacity (150 mg g^{-1}). This is due to the uptake of thorium occurring as a result of the coordination bond between Th(IV) and carboxyl groups –COOH, while further modification gave UiO-66-(COOH)$_2$, which showed adsorption capacity (350 mg g^{-1}). Also, UiO-66-(COOH)$_2$ showed a large uptake of thorium when compared with UiO-66-(COOH) and UiO-66 (Fig. 6d).[368] Xiao *et al.* fabricated MnSO-MOF, which showed suitable removal ability toward thorium ions from rare earth elements with an adsorption capacity of 46.3 mg g^{-1}, by making coordination bonds with N and O atoms present on the framework.[368]

Iodine

The I^{129} isotope is radioactive and harmful and should be removed from nuclear waste due to its long lifetime.[377] Zeng *et al.* synthesized a Zn-lactate-pyridyl benzoate MOF that showed good adsorption toward iodine (Fig. 7a), where one gram of $Zn_3(DL\text{-}lac)_2(pybz)_2$ is available for the removal of one gram of iodine.[378] ZIF-8 has been reported by Sava *et al.* for iodine capture with high capacity[379] (Fig. 7b).

Strontium

Strontium ions were removed using SZ-4 MOF through an ion exchange mechanism *via* two steps, which achieved an adsorption capacity of 121 mg g^{-1} at pH 2 within 20 minutes (Fig. 7c).[380] MOF-808-C_2O_4 and MOF-808-SO_4 have also been synthesized and used for Sr ions removal with high selectivity and the adsorption capacity of 167.56 mg g^{-1} for MOF-808-SO_4 and 206.34 mg g^{-1} for MOF-808-C_2O_4.

Europium

Europium is a representative element for trivalent lanthanides, and its radioisotopes are listed among the hazardous species found in radioactive waste solutions. A little work has been done employing MOFs as sorbents for removing Eu(III) ions from aqueous solutions. Hua *et al.*[381] fabricated a nanofibrous membrane MOF for the removal of Eu(III) ions, and its sorption capacity was about 191.9 mg g^{-1}. Lin *et al.* fabricated a novel MIT-101-DGA MOF to remove Eu(III) with a maximum sorption capacity of 33 mg g^{-1} at pH 3.5.[382] Hamouda *et al.* fabricated a novel bi-ligand strontium-based MOF (MTSr-MOF), which showed a lower removal percentage of approximately 13.59% for $^{152+154}$Eu radionuclides. To enhance its performance, MTSr-MOF was modified using various modifiers. The results showed that the MTSr-MOF modified with oxalic acid demonstrated a significantly higher removal efficiency for $^{152+154}$Eu radionuclides as compared to other modified MOFs, with a removal efficiency of approximately 96.42%. This finding suggests that

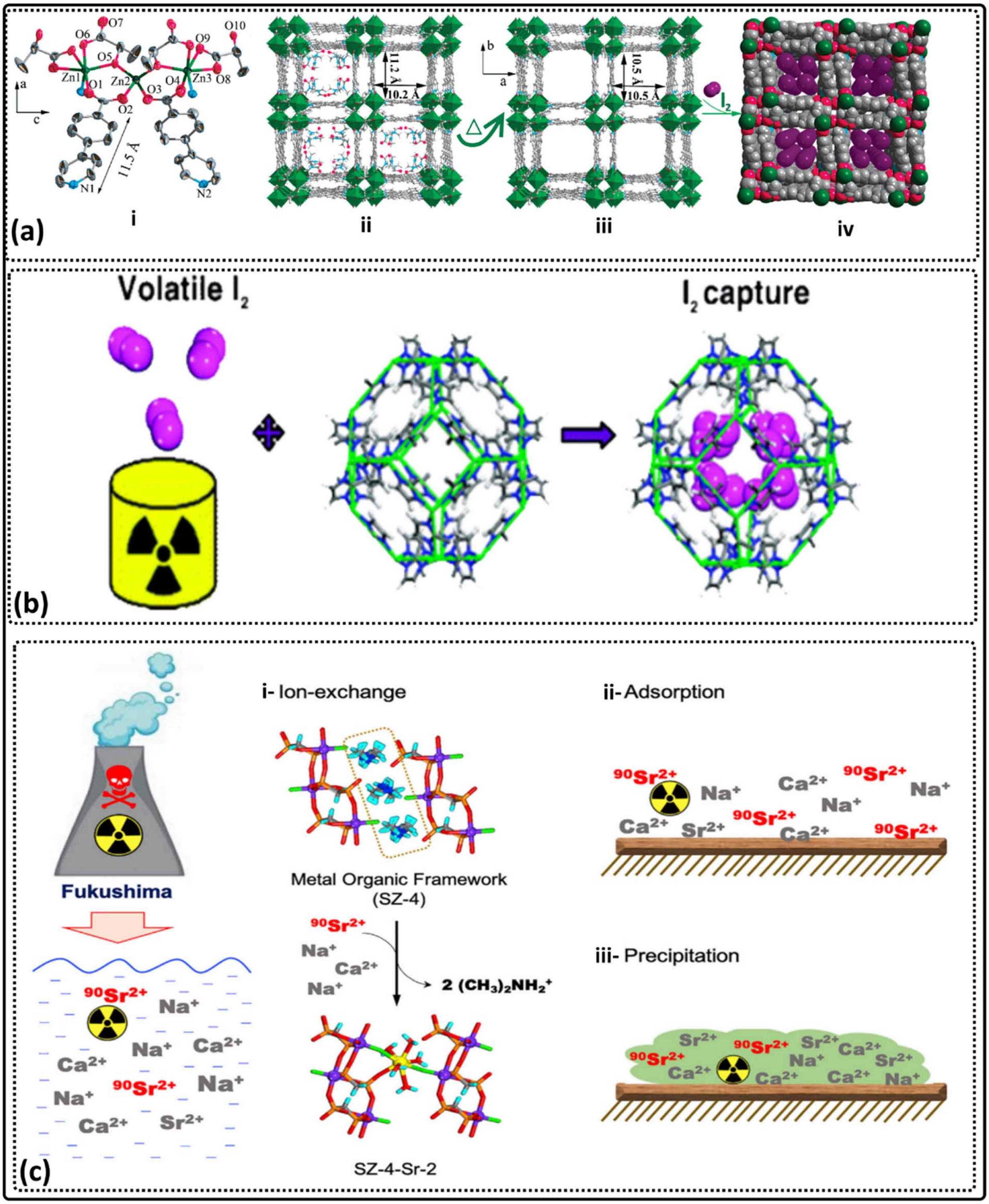


Fig. 7 (a) Single-crystal to single-crystal, the controlled uptake and release of iodine, and electrical conductivity [adapted from ref. 378 with permission from American Chemical Society, copyright 2010]. (b) Zeolitic imidazolate framework-8 structure and its captured molecular iodine (I_2) [adapted from ref. 379 with permission from the American Chemical Society, copyright 2011]. (c) The selective uptake of radioactive strontium-90 ions [adapted from ref. 380 with permission from Elsevier Inc, copyright 2019].

MTSr-MOF modified with oxalic acid has the potential to be a promising candidate for the removal of $^{152+154}$Eu radionuclides from radioactive waste in the future, based on using bi-ligand MOFs.[383]

Organic frameworks-based materials behaviors against strong radiation conditions

For industrial applications, MOFs should possess high thermal and hydrothermal stabilities, while for radionuclide applications, they should acquire higher radioactive stability. The radioactive stability of MOFs could be tested *via* the study of the structure and crystallinity before and after radiation penetration, and also through the study of the surface area and the capacity of the investigated MOF toward a radioactive substrate of interest.

MOF stability has been examined for a few MOFs, such as a thorium-based MOF that showed superior radiation stability for up to 200 KGy of radiation.[384] On the other hand, UiO-66, HKUST-1, and MIL-100 have been fabricated based on a transition metal node. They showed higher radiation stability; among them, MIL-101 was the most stable MOF, which retained its stability under high radiation levels equivalent to 2 MGy.[385–387]

The higher stability against radiation increased in ligands with extended π-systems due to the higher delocalization energy. Thus, the fabrication of promising radiation-stable MOFs required suitable ligand poses that extended π-systems.[388] Gilson *et al.* fabricated a Th-based MOF using extended π-system ligands and showed higher stability to γ-rays with 4 MGy.[388]

Regeneration and reusability of MOFs toward radionuclides

The removal of radionuclides from the MOF's framework is an economic issue. MOFs can be regenerated after a series of removals of radionuclides or for another application. The most common and applicable method for the reusability of MOF is the elution of the adsorbed radionuclide substrate using a suitable eluting agent, which could be acid, salt, base, water, and others. The most common acids used are HCl and HNO_3.[371,389–395] Generally, NaOH is a suitable base used for regeneration.[396,397] Salts such as sodium and potassium carbonates could also be used.[206,375,398,399] Other eluting agents such as EDTA are used,[400,401] and ion exchangers containing $SO_4{}^{2-}$, $NO_3{}^{1-}$, and Br^{1-} (ref. 402–404) could also be used. The reusability of MOFs for radionuclide removal can be affected by several factors, including the stability and selectivity of the MOF, the concentration, and types of radionuclides in the sample, and the presence of competing ions or other contaminants. The stability of MOFs in the presence of radiation is a critical factor that can limit their reusability. MOFs can degrade or become structurally unstable when exposed to ionizing radiation, which can decrease their effectiveness and limit their reuse. To enhance the reusability of MOFs, several strategies have been proposed, including the modification of the MOF structure to increase its stability and selectivity, the use of multiple MOFs in combination to increase the range of target radionuclides, and the use of pre-treatment processes to remove interfering contaminants from the sample matrix before adsorption by the MOF.

Assessing MOFs *versus* conventional methods for radioactive waste cleanup

Effective methods for separating radionuclides from environmental samples are crucial for the safe and efficient removal of radioactive waste. Various conventional techniques, such as precipitation, membrane separation, ion exchange, extraction chromatography, solid-phase extraction, and liquid–liquid extraction (LLE), are available for this purpose, each with its pros and cons that must be considered when selecting the most suitable method for a particular application. While precipitation and coprecipitation are common methods that offer high recovery and repeatability, they are time-consuming and laborious. Membrane separation can achieve high decontamination factors but membrane fouling and structural instability are issues. Ion-exchange techniques offer high specificity and decontamination but are also time-consuming. Extraction chromatography combines the ease of use of ion exchange chromatography with the selectivity of LLE, making it useful for the separation of actinides and lanthanides. Solid-phase extraction techniques have several benefits, including the removal of non-target elements from the sample matrix, minimal waste production, and the ability to selectively separate target elements, among others. LLE is widely used due to its high selectivity, efficiency, scalability, and ability to selectively separate target radionuclides from other components in the waste stream, resulting in a significantly reduced waste volume for disposal. However, LLE has some drawbacks, including complex chemical reactions, the generation of secondary waste streams, and the handling of hazardous chemicals and radioactive materials.[405] Compared to other techniques, MOFs have several advantages, such as high selectivity, capacity, and ease of synthesis. MOFs can be tailored to selectively capture specific radionuclides while ignoring interfering ions in the sample matrix, and they have high adsorption capacities due to their high surface area and porous nature. The synthesis of MOFs is relatively simple and can be easily scaled up for industrial applications. However, MOFs have some drawbacks, such as their stability in the presence of radiation, sensitivity to changes in pH and temperature, and large particle sizes.[154–166] Overall, the effectiveness and practicality of MOFs as compared to conventional methods for removing radioactive waste require further research. While each method has its strengths and weaknesses, MOFs offer a promising new approach due to their high selectivity, capacity, and ease of synthesis. However, their stability in the presence of radiation must be addressed, and further studies are necessary to identify the most suitable method for practical applications in the field of radioactive waste removal.

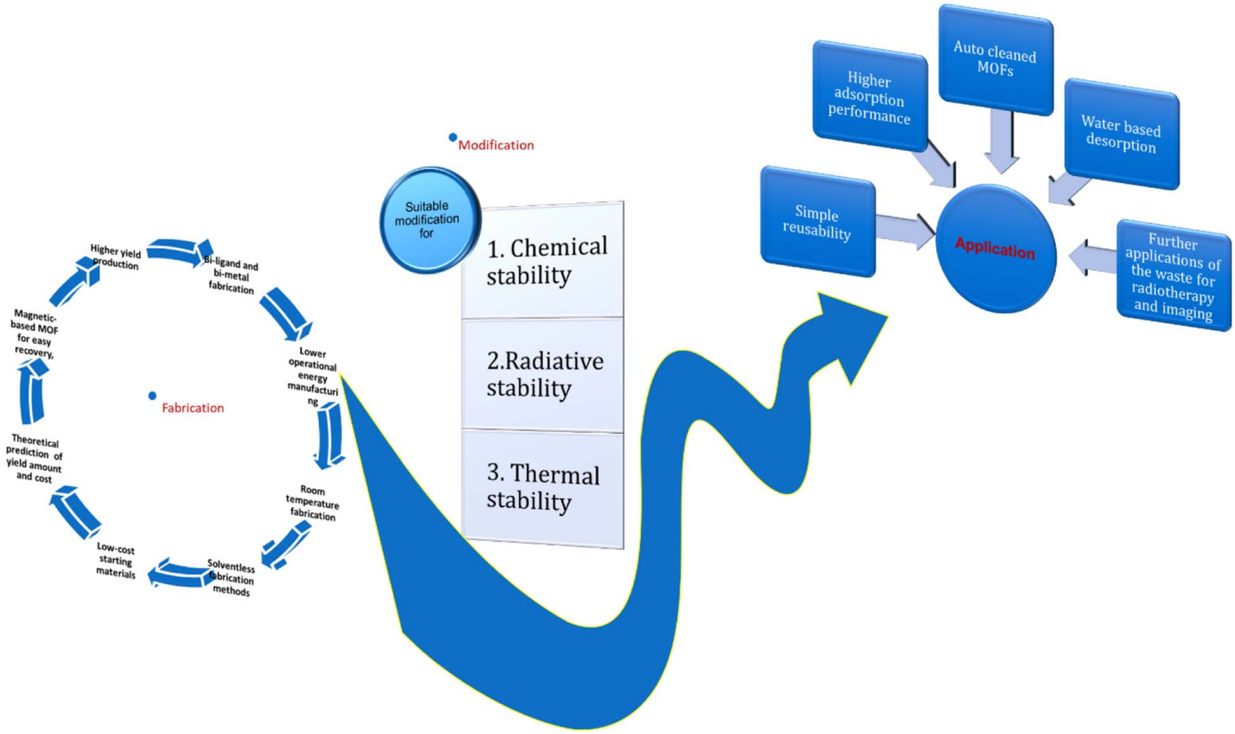


Fig. 8 A roadmap figure from the authors' viewpoint of the future of MOFs materials for the adsorption, removal, and separation of radionuclides and toxic metals from contaminated water sources.

Cost-effectiveness of MOF synthesis and application

It is crucial to consider the cost of preparing and using adsorbents when evaluating their suitability for wastewater treatment, especially given the availability of alternative technologies. There are several methods for determining the adsorbent cost, including the cost of raw materials, discounted cash flow, cost indices, and cost per gram of adsorbate removed. To evaluate the impact of process efficiency on process cost, a quantitative metric for comparing adsorbent costs known as "adsorbent cost performance" is used. This metric is represented in dollars per mole and shows the cost of producing and using 1.0 g of an adsorbent to remove 1 mole of a chemical species at the theoretical maximum uptake. Adsorbents with a cost performance of less than $1 per mol are considered inexpensive, while those above $200 per mol are considered expensive, with most adsorbents falling between these ranges.[406] The cost of MOFs is evaluated over a range of annual production rates, ranging from 50 000 kg MOF per year to 2.5 million kg per year. The projected cost of MOFs is associated with a production facility that is optimized for the specific level of production.[407] The cost of synthesizing MOFs is primarily determined by the cost of starting materials, the energy required for the process, and purification steps. To reduce the cost of starting materials, low-cost and readily available sources can be utilized. The energy requirements for MOF synthesis can be minimized by developing energy-efficient synthesis methods such as microwave-assisted or sonochemical synthesis. Furthermore, reducing the reactor volume and operation times can also lead to a reduction in the cost of MOF manufacturing, resulting in a lower overall manufacturing cost.[406,407] The purification steps, which involve the removal of unwanted by-products or solvents, can also be optimized to reduce the cost of MOF synthesis.

The cost of MOF production per unit weight is influenced by the scale of production. Large-scale production can result in economies of scale, leading to a reduction in the cost per unit weight of the MOF. However, scaling up MOF production can also pose challenges in maintaining the consistent quality and reproducibility of the MOF. In addition, the reusability of MOFs is a critical factor to consider when evaluating their economic feasibility in various applications. The ability to reuse MOFs can significantly reduce the overall cost of MOF-based processes, eliminating the need for frequent replacement and disposal of the MOFs. This makes MOFs a cost-effective alternative to traditional materials.[408,409]

There have been limited studies that have investigated the cost analysis of synthesizing MOFs and their application in absorbing heavy metals and radioactive ions. Most studies have focused on the synthesis of MOFs and their application. Further research is, therefore, needed to optimize the synthesis process and evaluate the economic feasibility of using MOFs for the adsorption of heavy metals and radioactive ions.

Conclusion and perspectives

Metal–organic frameworks (MOFs) have emerged as promising new materials for removing and separating radionuclides and toxic metals from contaminated water sources. Herein, we have summarised the research progress of MOFs for the removal of radionuclides from wastewater. The properties of MOFs, such as low density, chemical and thermal stability, large pore size, and extended surface area, make them ideal candidates for this application. The choice of metal ions and organic linkers and the use of modulators during fabrication can impact the properties and morphology of the resulting MOF. The synthesis of MOFs using sustainable and eco-friendly alternatives such as water as a solvent has been explored, including the cost analysis of MOFs synthesis and application, which is dependent on various factors and requires a case-by-case analysis to determine the economic feasibility of MOFs. Researchers are working to overcome the limitations associated with this approach. MOFs have shown promising potential for the selective removal of radionuclides such as cesium, barium, uranium, thorium, iodine, and strontium from wastewater. MOFs are also stable under strong radiation conditions and can be regenerated and reused, making them a cost-effective solution for the removal of radionuclides from wastewater. However, further research is needed to investigate the use of MOFs for radionuclide removal and develop more efficient and eco-friendly methods for the synthesis and application of MOFs for this purpose.

MOFs are booming in the field of radionuclide removal, but several main challenges are still being overcome to achieve the highest selective adsorption in practical applications, which include the following.

(1) From a structural perspective, stability is an important consideration for MOFs, particularly in terms of their chemical stability under strong acid and radiation conditions. The stability of MOFs can limit their potential practical applications. However, more information can be obtained by conducting the synthesis of bi-metal, bi-ligand MOFs, as fewer MOFs with stable structures have been developed and are effective for removing ions from radioactive wastewater.

(2) To assess the performance of MOFs, it is necessary to analyze their adsorption behavior for radioactive ions. Additionally, more information can be obtained by studying various factors, such as biological contamination, high salinity, pH, competing ions, and long-term use.

(3) From an application perspective, the majority of MOFs utilized in wastewater treatment are in the form of powder, which can be challenging to manage and recover. This can result in possible secondary pollution, which restricts their practical use. To address this issue, certain improvements can be made to retain their exceptional adsorption capacity. For instance, modifying the shape of MOFs, combining them with magnetic materials, creating devices or films, or combining them in three-dimensional structures.

(4) Considering the economic aspects, the practical application of porous materials in wastewater treatment is hindered by obstacles, such as the synthetic processes of MOFs, a limited range of organic linkages, and low yields. Researchers have focused on using cost-effective organic monomers to reduce synthesis costs to overcome these limitations. Also, microwave-assisted or radiation-assisted synthesis is widely used in materials synthesis. Widespread and inexpensive methods are constantly being discovered.

(5) Future research should focus on developing more accurate and reliable models for predicting the cost of adsorbent synthesis and usage, taking into account factors such as energy requirements, scaling up production, regeneration, and the impact of different operating conditions on adsorption efficiency. A roadmap figure from the authors' viewpoint of the future of these materials is presented in (Fig. 8).

(6) The experimental study (synthesis and application) could be merged with a computational study to reduce the efforts used in that work and allow it to be a large-scale study to get more important results in industrial applications.

MOFs have shown tremendous promise as adsorbents for efficient radioactive removal in wastewater treatment. Even though their use in aquatic systems is still being developed, more investigation into their characteristics and mechanisms is needed. We anticipate that they will play a substantial role in eliminating radionuclides from wastewater in complicated systems due to their potential for further development.

Conflicts of interest

There are no conflicts to declare.

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