

Recent Progress on Adsorptive Removal of Cd(II), Hg(II), and Pb(II) Ions by Post-synthetically Modified Metal-organic Frameworks and Chemically Modified Activated Carbons

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Abstract

Fast-paced industrial and agricultural development generates large quantities of hazardous heavy metals (HMs), which are extremely damaging to individuals and the environment. Research in both academia and industry has been spurred by the need for HMs to be removed from water bodies. Advanced materials are being developed to replace existing water purification technologies or to introduce cutting-edge solutions that solve challenges such as cost efficacy, easy production, diverse metal removal, and regenerability. Water treatment industries are increasingly interested in activated carbon because of its high adsorption capacity for HMs adsorption. Furthermore, because of its huge surface area, abundant functional groups on surface, and optimal pore diameter, the modified activated carbon has the potential to be used as an efficient adsorbent. Metal-organic frameworks (MOFs), a novel organic-inorganic hybrid porous materials, sparked an interest in the elimination of HMs via adsorption. This is due to their highly porous nature, large surface area, abundance of exposed adsorptive sites, and post-synthetic modification (PSM) ability. This review introduces PSM methods for MOFs, chemical modification of activated carbons (ACs), and current advancements in the elimination of Pb²⁺, Hg²⁺, and Cd²⁺ ions from water using modified MOFs and ACs via adsorption.

Keywords: *Heavy metals (HMs), Environmental pollution, Activated carbon, Metal-organic frameworks (MOFs), Chemical modification, Post-synthetic modification*

1. Introduction

Water contamination is a global issue, as it endangers both economic and ecological systems. The problem of industrial wastewater containing excessive levels of heavy metals (HMs) is becoming more serious. [1]. Copper (Cu), Lead (Pb), Mercury (Hg), Cadmium (Cd), Arsenic (As), Chromium (Cr), Zinc (Zn), Nickel (Ni), Iron (Fe), and Cobalt (Co) are some of the most common HMs found in soil and water[2]. Given their high water solubility, many heavy metal compounds can swiftly enter into the food chains of living organisms and accumulate in the surrounding environment. HMs are associated with substantial health hazards in humans because of their non-degradable nature and cumulative accumulation[3-5]. These HMs are obtained from natural as well as anthropogenic (man-made) origins. Natural origins are volcanic eruptions, weathering, and attrition of the earth's surface, whereas anthropogenic origins are industrial effluents, fertilizers, and sewage waste[6]. Lead has been utilized for centuries in building materials, ce-

ramic glazes, and water pipes. Submarine cable sheathing, radiation barriers in sheeting, solid blocks, protective aprons, crystal glass, and ammunition are examples of current applications. Lead is known to induce acute and chronic poisoning, affecting practically all body organs, but most notably the central nervous system (CNS)[7, 8]. Cadmium is a hazardous metal that accumulates in the kidneys and liver. Prolonged cadmium consumption causes cell damage and death in biological systems. It is used as a stabilizer in plastics, plating, coating, and nickel-cadmium batteries. Since cadmium is harmful to both humans and animals, it is critical to treat industrial effluents before releasing them into receiving water bodies[9]. Mercury is the sixteenth rarest element found in the Earth's crust. Mercury levels in the environment are rising as a result of pollution from the mining, cement, and nonferrous metal manufacturing industries. High amounts of mercury are also caused by urban and medicinal waste incineration, as well as emissions from coal-fired power plants. Mercury is non-biodegradable in nature and affects the central nervous system, kidneys, liver, and immune system. It can cause hearing loss, paralysis, insomnia, and emotional instability. Thus, mercury elimination from waste water effluents is imperative. Industrial effluent streams must be decontaminated before discharge into rivers or ponds to mitigate potentially serious environmental and health effects[10]. The maximum permitted levels of the most hazardous HMs as per the regulations of world health organization (WHO)

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Table 1. The Maximum Permissible Concentration of Heavy Metals in Drinking Water and Their Adverse Health impacts

Heavy metal	Maximum permissible concentration (mg/l)	Health impact
Cu	2.0	Kidney disorder, allergies, and anemia
Zn	3.0	Neuronal and respiratory disorders, prostate cancer
Pb	0.005	Neuro degenerative diseases, Alzheimer's disease, senile dementia, kidney damage, and cancers
Hg	0.001	Effects on digestive system, impaired neurologic development, and hypertension
Cd	0.003	Acute toxicity with headaches, osteomalasia, skin ulcers, dermatitis nausea, diarrhea, and cancers
As	0.01	Instigates bronchitis, hypokeratosis, cancer, ulcer, dermatitis, liver-cirrhosis, and mental disturbance

was given in Table 1[11].

Elimination of HMs from industrial or domestic effluents has so far employed diverse unit operations such as precipitation, ion exchange, biological, electrochemical and membrane separation[12, 13]. Adsorption technology for contaminant removal from wastewater is advantageous due to its simple utilization, high efficacy, and low cost[14]. Adsorption takes place on the surface of a substance. The surface chemistry of an adsorbent has a significant impact on its ability to remove pollutants. Adsorption performance is dependent on the surface of the adsorbent, which serves as its interface with the external environment. Consequently, enhancing the adsorbent's surface features is essential. Physical and chemical methods can be used to alter the surface of a material. Since chemical surface modification directly modifies the surface chemistry, it is preferred over other surface modification procedures for adsorbents. Using this approach, low-cost precursor materials can be transformed into high-value products with outstanding adsorption properties. For example, chemical surface modification adds additional surface characteristics to an adsorbent that are not present in the bulk adsorbent. When an adsorbent is chemically modified, its skeleton and surface characteristics are significantly affected[15]. Several adsorbents such as activated carbon (AC), metal-organic frameworks (MOFs), zeolites, and clay were explored for the elimination of HMs[16 - 19]. The purpose of this study was to discuss the chemical modification methods of ACs, post-synthetic modification (PSM) methods of MOFs, and current developments in the elimination of Pb^{2+} , Hg^{2+} , and Cd^{2+} ions from water using modified MOFs and ACs by means of adsorption.

2. MOFs and their post-synthetic modification (PSM) methods

MOFs are inorganic-organic hybrid porous materials that are highly crystalline in nature and can be fabricated through diverse metal ions and organic linkers. Metal ions and linkers choice for the MOF synthesis can alter the entire framework topology, shape, and size of pores as well as its chemical functionality. The key distinction between MOFs and other porous inorganic materials (e.g., zeolites and AC) is that MOFs are composed of organic and inorganic components that are highly tunable in terms of their pore structures[20]. Since MOFs contain organic components, it is feasible to customize these organic linkers with additional functional groups that would improve the overall performance of these materials, and this unique property makes them

promising candidate materials for applications like gas storage, gas separation, catalysis, and drug delivery[21-26]. Without modification, MOFs can be employed directly as adsorbents. Zhang *et al.* reported the removal of Pb^{2+} and Cd^{2+} ions from aqueous solutions using iron and trimesic acid (H_3BTC)-based MOFs in 2 min of equilibration time [27]. In a study by Hasnkola *et al.*, a zirconium and 5,10,15,20-tetrakis (4-carboxyphenyl)porphyrin (H_2TCPP) based MOF was prepared under solvothermal conditions and this MOF attained 233 mg/g of maximum adsorption capacity (Q_{max}) of Hg^{2+} ions within 30 min[28].

Functionalizing the pore walls of MOFs gained much interest in recent years as a result of its ability to modify both physical and chemical properties. In the past, a pre-functionalization modification in which altering an organic linker with specified functional groups containing moieties and then employing the modified linker during the solvothermal or hydrothermal synthesis of the required MOF was the only way to include functionality into an MOF. This pre-functionalization method resulted in MOFs with $-OH$, $-Br$, $-NH_2$, and other comparatively simple functional groups on the MOF pore channel walls. The isoreticular metal-organic framework (IRMOFs), zeolitic imidazolate frameworks (ZIFs), and material institute Lavoisier (MIL) class of MOF materials contain these types of groups[29-31]. Wang *et al.* reported a zirconium based MOF with amino groups (NH_2 -Zr-MOF), synthesized from $ZrCl_4$ and amino-terephthalic acid (NH_2 -TPA) in DMF under rapid microwave conditions[32]. Nearly all of the Pb^{2+} and Cd^{2+} ions were removed at 10 ppm solution. At optimum conditions (40 ppm of initial concentration, pH 6, 303.15 K temperature, and 120 min equilibration time), 177.35 and 166.4 mg/g of Q_{max} values were obtained for Cd^{2+} and Pb^{2+} ions, respectively. The results of X-ray photoelectron spectroscopy (XPS) data suggested the complexation of Pb^{2+} and Cd^{2+} ions with $-NH_2$ groups was key for the elimination of HMs. Zhang *et al.* investigated complexation of Hg^{2+} ions with $-NH_2$ groups on a series of luminescent MOFs using ligand-to-metal charge transfer (LMCT) effect[33]. In a 60 minutes of contact time, NH_2 -MIL-53(Al) showed quick reaction with mercury ions. The Q_{max} obtained for mercury ions was 153.85 mg/g. The authors reported that this MOF was stable up to four sorption cycles. Although direct solvothermal synthesis has yielded functionally varied MOFs, the range of functional groups has remained relatively limited due to high temperatures and pressures generated under solvothermal conditions. Due to their instability, these conditions are not suitable for all functional groups[34].

Another way to obtain functionalized MOFs is to modify them after

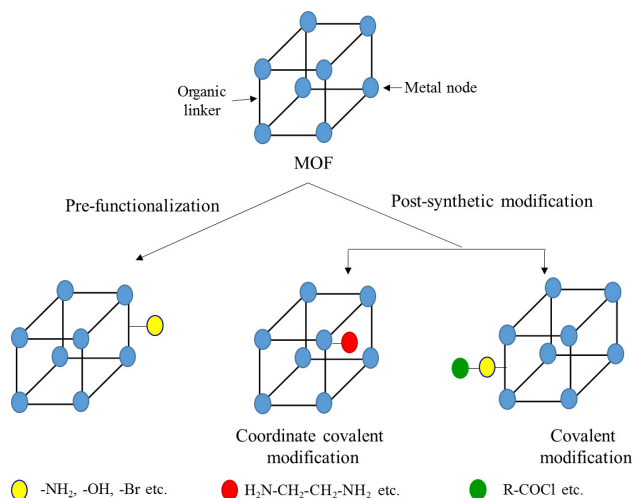


Figure 1. Schematic representation of MOF modification methods.

they have been synthesized. This process is called post-synthetic modification (PSM). An MOF can be made and then changed heterogeneously after the solid lattice has been formed. The functionalization of MOFs using PSM has proven to be a generic and useful technique. Pre-functionalization, on the other hand, does not allow for as much control over the MOF structure with respect to functional groups. It is possible to functionalize both the metal and organic components of a framework using the PSM technique without compromising its overall stability. Topologically equivalent but functionally distinct frameworks can be created using the PSM technique[35-37].

Covalent and coordinate covalent modifications are two of the most common PSM techniques for functionalizing MOFs[35]. The modification of an organic linker in an MOF with additional functional groups is known as covalent modification. Altering the amino groups of IRMOF-3 with acetic anhydride was the first report on PSM by Wang *et al.*[38]. In this study, they modified the amino groups of IRMOF-3 with acetic anhydride to generate a MOF that contained methyl amide substituents. Fu *et al.* reported covalent modification by altering the amino groups of a Zr-based MOF (UiO-66-NH₂) with resorcylic aldehyde (2,4-Dihydroxybenzaldehyde) at 343.15 K in anhydrous ethanol, and the resultant MOF was named UiO-66-RSA[39]. In the case of Pb²⁺ ions removal, the Q_{max} (189.8 mg/g) obtained for modified UiO-66-RSA was greater than the Q_{max} (46.9 mg/g) of unmodified UiO-66-NH₂. In accordance with the XPS results, the adsorption process was identified as a chelation reaction between lead and -OH/N-containing compounds.

The coordinate covalent modification involves the anchoring organic linkers to the metal clusters in the MOF. The initial findings of this PSM method was the replacement of coordinated water molecules which are attached to the open copper metal sites by pyridine molecules in Cu-based MOF[40] and anchoring of ethylene diamine to the coordinately unsaturated chromium metal sites in a Cr-based MOF[41]. This PSM approach alters the coordination environment of metal clusters or secondary building units (SBUs) without changing the overall MOF structure[42]. Ke *et al.* prepared a thiol-modified Cu-based MOF {Cu-BTC or [Cu₃(BTC)₂(H₂O)₃]_n,

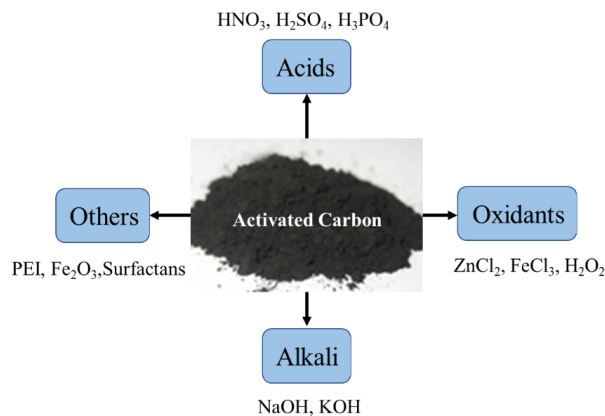


Figure 2. Schematic representation of chemical modification methods of activated carbons.

where BTC denotes benzene-1,3,5-tricarboxylate} at room temperature using dithioglycol (HSCH₂CH₂SH)[43]. The introduction of -SH groups led to a very high Hg²⁺ ion adsorption from water. Cu-BTC comprises a three-dimensional square-shaped channel system. Each formula unit holds up to ten extra water molecules. These coordinated water molecules can be easily removed under vacuum at 423.15 K, resulting in coordinatively unsaturated Cu(II) metal centers, which are accessible sites for coordinate covalent modification. When the dehydrated Cu-BTC was treated with dithioglycol in anhydrous toluene, thiol-modified Cu-BTC was prepared through the coordinate covalent bonding of unsaturated Cu(II) centers with thiol groups in dithioglycol. The experimental results of modified MOF showed a Q_{max} of 714.29 mg/g for Hg²⁺ ions, whereas no adsorption was observed for the unmodified Cu-BTC. A schematic representation of the pre-functionalization and post-synthetic modification of the MOFs is shown in Figure 1.

3. Activated carbon and their chemical modification methods

Activated carbon (AC) is a potential adsorbent in HMs removal due to a huge surface area and pore volume. The morphology as well as surface chemical functionalities of the AC may be altered[44]. In the absence of oxygen, pyrolysis of organic compounds at elevated temperatures yields AC. The Adsorption efficiency of AC is influenced by the raw materials, production techniques, and environmental variables[45].

An essential factor in the adsorption of AC is the chemical composition of the AC and the species and quantity of active functional groups on the surface, and it is critical to tailor the AC to each specific adsorbate. Mostly, surface chemical modification of AC is used to alter its acidity and basicity, introduce or remove specific surface functional groups, and therefore enhance its adsorption capacities. Numerous strategies have been developed to increase the adsorption efficiency of ACs towards HMs[15]. Chemical reagents such as acids, bases, polymers, and other reagents were generally utilized for altering the surface functionality of AC, as depicted in Figure 2.

A common example of acid modification is the wet oxidation

process. HNO_3 , H_2SO_4 , H_3PO_4 , and HCl are examples of acids that can be employed to modulate the surface properties of ACs[46-49]. Organic acids, such as citric acid, are rarely used owing to their low strength and weak effect[50]. Acidification increases the acidity and hydrophilicity of AC by lowering the amount of minerals on its surface. As a result of acid alteration, the surface of activated carbon is enriched with oxygen-containing groups (O-containing groups) such as carboxyl, carboxylic anhydride, hydroxyl, quinone, lactone, nitro, and carbonyl groups. These groups are significant in defining the surface chemical properties of AC. After acid treatment, metal ion adsorption can be improved because anionic acid groups can form metal complexes with positively charged metal ions[51]. Huang *et al.* treated lignite, which is a type of low-rank coal containing both inorganic (iron dolomite) and organic (aliphatic and aromatic hydrocarbons) components, with nitric acid[52]. Acid modification enhanced the pore size and reduced the surface area of the adsorbent. The polarity of adsorbent was improved, because of formation of O-containing groups, and nitric acid modified lignite shows an improved Q_{\max} (30.68 mg/g) compared to pristine lignite (14.45 mg/g) for Pb^{2+} ions. Girgis *et al.* reported phosphoric acid as a modifying agent to derive AC from peach stone shells[53]. Five different ACs were produced by the pyrolysis of phosphoric acid impregnated peach stone shells under different gas flow conditions, i.e., in the absence of any gas flow (PS55), under a flow of N_2 (PS55N), CO_2 (PS55C), air (PS55A), and steam (PS55S) at 773.15 K. The derived AC had a high surface area in the range of 1053~1404 m^2/g , high microporosity, and low mesoporosity. Carbon porosity is reduced by running external gases, except for air and steam, which generate more mesoporous carbon at the expense of microporous carbon. The addition of H_3PO_4 to the pyrolysis process resulted in the formation of O-containing groups on AC surface. Pyrolysis under air flow significantly increased Q_{\max} value of Pb^{2+} ions, reaching 204 mg/g compared to the 65~115 mg/g found in other carbons and increasing the adsorbed species area by 21%. It was observed that the high lead ion uptake might be because of numerous acidic O-containing groups developed on AC surface that participate in the cation exchange process. These acidic functions dissolve in water, releasing H^+ ions and providing negatively charged sites for metal ions. Furthermore, it is expected that metal adsorption will involve both inorganic and organic phosphate groups. Ge *et al.* reported a polyacrylic acid (PAA) modification of activated carbon, and the resultant modified adsorbent (PAA-Ac) possessed an ear-like shape[54]. The introduction of -COOH groups in the PAA-Ac resulted in a marked increase in Cd^{2+} ion adsorption. At a contact time of 15 minutes, Q_{\max} of 473.2 mg/g was obtained for Cd^{2+} ions. The authors reported that the novel fabrication method of PAA modification, which develops -COOH groups on the carbon surface, is quick and provides a good adsorption capability for Cd^{2+} ion removal. Chen *et al.* modified commercially available AC with citric acid (CA) to enhance Cu^{2+} ion adsorption from aqueous solutions[55]. After CA modification, a 34% reduction in specific surface area and a 0.5-unit reduction in point of zero charge (pzc) were reported. CA immobilization on the AC surface introduced more active sites, primarily -COOH groups, and equilibrium

adsorption experimental results indicated that CA modification resulted in a 140% higher Cu^{2+} ion adsorption capacity than unmodified carbon.

In alkaline modification, reducing agents, such as NaOH , KOH , LiOH , Na_2SiO_3 , and Na_2CO_3 , can reduce and modify the surface functional groups of AC at the optimal temperature, which improves the content of alkaline groups and thereby enhances the non-polar nature of the carbon surface. Because of this reduction process, the surface structure of AC can be changed. Chemical activation with strong bases takes less time and requires less energy than physical modification[56]. Liu *et al.* synthesized AC from rice husks by treating them with KOH . As per the characterization results, rice husk-AC was porous and had O-containing groups[57]. Langmuir model was the best fit to predict the isotherm of Hg^{2+} ion adsorption on rice husk-AC, and the obtained Q_{\max} for Hg^{2+} ions was 55.87 mg/g. Shahrokhi-Shahraki *et al.* carbonized crushed discarded tires and treated with KOH [58]. Single and diverse metal ion batch adsorption tests were carried out on the resultant tire-derived activated carbon (TAC) for the elimination of Pb^{2+} , Cu^{2+} and Zn^{2+} ions from water. Similar adsorption tests were carried out on commercial activated carbon (CAC) for reference. TAC showed a higher tendency to eliminate HMs than CAC. Higher Q_{\max} values were obtained for Pb^{2+} , Cu^{2+} and Zn^{2+} ions for TAC (322.5, 185.2, and 71.9 mg/g, respectively) than CAC (42.5, 15.0, and 14.0 mg/g respectively). According to the results of competitive adsorption tests, the TAC and CAC exhibited a similar order of adsorption capacity ($\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$), which was in good agreement with the results obtained under single adsorption conditions. However, lesser adsorption capabilities (12.7%, 14.6%, and 38.9%, respectively for Pb^{2+} , Cu^{2+} , and Zn^{2+} ions) were noticed in diverse ion adsorption tests than single-ion adsorption tests. In contrast, 14.3%, 24.8%, and 49.9% reduction rates were observed for CAC in the diverse ion adsorption tests. Physical and chemical adsorption mechanisms inferred from isotherm and kinetic data could account for the HMs adsorption on TAC and CAC. The authors stated that, based on FT-IR, XPS and zeta potential data, electrostatic interactions as well as surface complexation reactions were more significant on TAC. A high cation exchange capacity value for CAC suggests that ion exchange is the major route for HMs removal. Norouzi *et al.* reported the adsorption of Cr^{6+} ions on NaOH -treated AC derived from Date Press Cake[59]. This chemically modified AC had Q_{\max} values of 282.8 mg/g and 198.0 mg/g at pH values of 2 and 5, respectively. Zhang *et al.* reported the oxidation of rigid carbon foam via KOH activation followed by HNO_3 hydrothermal oxidation[60]. The resultant material was named as ORCF and exhibited a fluffy and hierarchical porous structure with a high proportion of O-containing groups. The ORCF exhibited a Q_{\max} of 157.80 mg/g for Pb^{2+} ions. The authors stated that the zeta potential value became negative at an elevated pH value, which indicated the stronger pronation capacity of adsorbent's surface. Electrostatic interactions as well as O-containing groups were crucial in elimination of Pb^{2+} ions.

In addition to acidic and alkali methods, chemical modification can be performed with chemical reagents such as oxidizing agents (KMnO_4 and H_2O_2) and neutral agents (ZnCl_2 and NaCl)[61-64]. Nayak *et al.* reported the preparation of chemically AC from sawdust using ZnCl_2

Table 2. Modified Activated Carbons and Their Adsorption Parameters

Adsorbent	Type of Modification	Activating/ Modifying agent	HMI	Isotherm Model	Kinetic Model	Q _{max} (mg/g)	Ref.
PS55A	Acid	H ₃ PO ₄ followed Air	Pb ²⁺	NA	NA	204	[53]
PS55S		H ₃ PO ₄ followed Steam				115	
PAA-Ac	Acid	Polyacrylic acid	Cd ²⁺	Langmuir	PSO	473.2	[54]
TAC	Alkaline	KOH	Pb ²⁺	Langmuir & D-R	PSO	322.5	[58]
ORCF	Acid & Alkaline	KOH followed by HNO ₃	Pb ²⁺	Langmuir	PSO	157.80	[60]
CASD-KOH	Alkaline	KOH	Cd ²⁺	Langmuir & D-R	PFO	119.14	[65]
CASD-ZnCl ₂	Neutral reagent	ZnCl ₂				25.85	
BAC@SiO ₂ -EDTA	N-containing reagent	EDTA	Pb ²⁺	Langmuir	PSO	123.45	[71]
AC-HI.5	Acid	H ₃ PO ₄	Hg ²⁺	Langmuir & R-P	PSO	107.0	[77]
AC-S	S-containing reagent	Sulfur				129.0	
ACS	S-containing reagent	3-MPTS	Hg ²⁺	Langmuir	PSO	235.7	[78]
Product-K ₂ S	S- containing reagent	K ₂ S	Pb ²⁺	Langmuir		111.9	[79]
AT-MAC	N- and S- containing reagent	2-Aminothiozole	Hg ²⁺	Langmuir	PSO	252.5	[81]
			Pb ²⁺			310.9	
Fe ₃ O ₄ @AC	Metal oxides &	Fe ₃ O ₄ nanoparticles & 1,4-butane sultone	Cd ²⁺	Langmuir	PSO	115.13	[86]
Fe ₃ O ₄ @AC@SO ₃ H	S- containing reagent		Pb ²⁺			151.51	
NiFe ₂ O ₄ -PAC-SH	S- containing reagent	Thioglycolic acid	Hg ²⁺	Langmuir	PSO	366.3	[87]

HMI: heavy metal ion; Q_{max}: maximum adsorption capacity; PFO: pseudo-first-order model; PSO: pseudo-second-order model; D-R: Dubinin-Radushkevich model; R-P: Redlich-Peterson model; NA: not applicable.

Table 3. Post-synthetically Modified Metal-organic Frameworks and Their Adsorption Characteristics

Adsorbent	Type of Modification	Modifying agent	HMI	Isotherm Model	Kinetic Model	Q _{max} (mg/g)	Ref.
NH ₂ -Zr-MOF	¹ PFNC	NA	Cd ²⁺	NA	PSO	177.35	[32]
NH ₂ -MIL-53(Al)	PFNC	NA	Hg ²⁺	Langmuir	PSO	153.85	[33]
TMU-16-NH ₂	PFNC	NA	Cd ²⁺	Freundlich	PSO	126.6	[73]
Zn(hip)(L)·(DMF)(H ₂ O)	PFNC	NA	Hg ²⁺	Langmuir	PSO	333	[74]
TMU-32S-65%	PFNC	NA	Hg ²⁺	Langmuir	PSO	1428	[75]
UiO-66-DMTD	² CNSC	2,5-Dimercapto-1,3,4-thiadiazole	Hg ²⁺	Langmuir & D-R	PSO	670.5	[83]
Melamine-Zr MOF	³ CCNC	Melamine	Pb ²⁺	NA	PSO	205.0	[76]
FJI-HI2	CCNC	thiocyanate	Hg ²⁺	NA	PSO	439.8	[80]
FJI-H9	CCNC	dimethylamine	Cd ²⁺	Langmuir	NA	225.0	[82]
NH ₂ -MIL-53(Al)@IOMN	Metal oxide	Fe ₃ O ₄ nps	Pb ²⁺	Freundlich	NA	492.4	[88]
MIL-125/Chitosan Beads	Chitosan	Chitosan	Pb ²⁺	Langmuir	PSO	407.5	[94]

¹ Pre-functionalization with N-containing reagent ² Covalent with N- and S- containing reagent ³ Coordinate covalent with N-containing reagent

and KOH as activating agents[65]. Under activation conditions of 873.15 K, 1 h, and 1:0.5 ratio, AC activated with ZnCl₂ (CASD-ZnCl₂) had microporosity, but AC activated with KOH (CASD-KOH) exhibited mesoporosity. For Cd²⁺ ions, CASD-KOH had a higher Q_{max} (119.14 mg/g) than CASD-ZnCl₂ (25.85 mg/g) despite similar pH, tem-

perature, and adsorbate concentrations.

The following sections describe the recent progress in the chemical modification of ACs and post-synthetic modifications of MOFs for Cd²⁺, Hg²⁺, and Pb²⁺ ion removal. The parameters are summarized in Tables 2 and 3 for the ACs and MOFs, respectively.

4. Loading of nitrogen and sulphur-containing groups on ACs and MOFs

The use of nitrogen- and sulfur-rich organic reagents to modify ACs and MOFs is gaining popularity because nitrogen- and sulfur-containing functional groups can enhance binding HMs compared to their pristine materials[66, 67].

4.1. Modification with nitrogen group containing organic reagents

Polyethyleneimine (PEI) is a common polyamine with a strong metal-ion adsorption capacity and selectivity. However, because PEI has a high loss rate when used as an adsorbent in water remediation, grafting PEI onto any other porous material is preferable to avoid PEI leaching from the pores and enhance the stability of the composite material. Xie *et al.* reported PEI-modified AC for Cd²⁺ ion adsorption[68]. At pH 6–7, the modified adsorbent exhibited a Q_{max} of 45 mg/g. The enhancement in Cd²⁺ ion adsorption by modified AC was justified by the loading of PEI on the surface of the AC. Saleh *et al.* produced PEI-modified AC using a hydrothermal technique to remove Hg²⁺ ions[69]. The modified AC was regenerable and had good adsorption performance. Polydopamine is another type of polyamine that contains both amine and catechol functional groups that are capable of HMs adsorption. Sun *et al.* reported the polymerization of dopamine into polydopamine in the pores of Fe-BTC MOF[70]. The Fe³⁺ sites in the MOF catalyzes the polymerization reaction. The resulting composite was water-stable and rapidly removed Pb²⁺ and Hg²⁺ ions. This composite material exhibited Q_{max} values of 1634 and 394 mg/g for Hg²⁺ and Pb²⁺ ions, respectively. These Q_{max} values were almost 10 and 2.6 times higher than that of unmodified Fe-BTC, respectively. The authors also reported that, when a 1 ppm solution was treated this adsorbent, almost all of the HMs were eliminated (over 98.8%) in seconds. Ethylenediaminetetraacetic acid (EDTA) is an aminopolycarboxylic acid that contains four carboxyl and two tertiary amino groups and employed as a chelating agent for HMs and it forms strong metal complexes. However, the higher water solubility of the EDTA-metal complexes limits its direct usage in HMs adsorption applications and its anchoring to an adsorbent's surface is an alternative to inhibit this problem. Lv *et al.* reported an EDTA-anchored bamboo activated carbon (BAC) named BAC@SiO₂-EDTA[71]. It was prepared by grafting EDTA onto BAC with a cross-linking agent, tetraethyl orthosilicate. BAC@SiO₂-EDTA exhibited higher Q_{max} values for Pb²⁺ and Cu²⁺ ions when compared to unmodified BAC, with Q_{max} values increasing from 45.45 to 123.45 mg/g and 6.85 to 42.19 mg/g for Pb²⁺ and Cu²⁺ ions, respectively. HMs removal was pH dependent and optimum values were reported as pH 5–6. Chelation and electrostatic interactions were the key factors in the elimination of HMs. Peng *et al.* reported the development of a broad-spectrum HMs removal by grafting EDTA on Zr-BTC (MOF-808), and the resulting composite material (MOF-808-EDTA) showed over 99% removal efficiency for 22 metal ions (covering hard, soft, and borderline Lewis metal ions) in single-component adsorption experiments, and efficacy remains consistent when diverse HMs were treated concurrently[72]. Breakthrough adsorption experiments revealed that the

effluent concentration of diverse metal ions solution, which contains 19 kinds of metal ions, was reduced from 5 ppm to 0.01–1.9 ppb, much below the permissible limits in drinking water regulations. Roushani *et al.* reported the synthesis of a mixed-MOF material and applied it to the removal of Cd²⁺ ions from aqueous solutions[73]. The MOF was synthesized using a mixture of two organic linkers (bipyridyl-type ligand (4-bpdh) and 2-amino-1,4-benzenedicarboxylic acid) and zinc nitrate in DMF and was named TMU-16-NH₂ (TMU = Tarbiat Modares University). The Q_{max} of Cd²⁺ ions was determined to be 126.6 mg/g. 98.91% of maximum removal percentage was found at pH 6.0 and in a 30-min contact time. Coordinative interactions of –NH₂ groups with Cd²⁺ ions were critical in the elimination of Cd²⁺ ions. Luo *et al.* reported mercury removal at an initial concentrations of 1–20 ppb on a Zn(hip)(L)·(DMF)(H₂O) MOF where H₂hip=5-hydroxyisophthalic acid and L=N₄,N₄'-di(pyridine-4-yl)biphenyl-4,4'-dicarboxamide[74]. This MOF pore wall was modified with both hydroxyl and acylamide groups and showed great affinity and substantial Q_{max} (278 mg/g) for Hg²⁺ ions. This MOF removes 66.5% of Hg²⁺ ions from a 2 ppb solution, which indicates that it can effectively remove Hg²⁺ ions from ultra-low-concentration solutions. Esrafilo *et al.* reported a urea- and malonamide-functionalized Zn-MOF was synthesized from Zn(NO₃)₂·6H₂O, 4,4-oxydibenzoic acid, 1,3-di(pyridine-4-yl)urea, and N₁,N₃-di(pyridine-4-yl)malonamide) in DMF[75]. This mixed ligand MOF, TMU-32S 65% (65% malonamide-based linker and 35% urea-based linker) showed a high Q_{max} of 1428 mg/g for Hg²⁺ ions. The higher adsorption capacity might be due to host-guest interactions of active adsorption sites generated inside the pore wall by the malonamide (–HNCO-CH₂-CO-NH–) and urea (–HN-CO-NH–) groups, which produce electrostatic interactions between Hg²⁺ ions and the MOF pore walls. A melamine (1,3,5-Triazine-2,4,6-triamine) functionalized Zr-MOF, melamine-Zr-MOF, was synthesized from ZrCl₄ and 1,4-naphthalenedicarboxylic acid (1,4-H₂NDC) in DMF[76]. The melamine-Zr-MOF showed a higher Q_{max} (122.0 mg/g) for Pb²⁺ ion than that of the unmodified Zr-MOF (72.1 mg/g) at 120 min, 313.15 K, and pH 5. The Q_{max} obtained at pH 6 was approximately 205 mg/g. XPS analysis confirmed the coordination interactions between the –NH₂ groups in melamine and the Pb²⁺ ions. Nitrogen atoms of amino groups act as Lewis bases and can contribute their lone pair of electrons to Pb²⁺ ions, forming a metal complex through a coordinate covalent bond.

4.2. Modification with sulphur-containing reagents

A thiol or thiol derivative is an organosulfur compound that has the formula R-SH, where R is an alkyl or any other organic group. According to the hard and soft acids–bases (HSAB) theory, thiol is a soft base and can easily combine with soft acids, such as Hg²⁺ ions, to form a strong complex. The reaction process also has a high complexation rate. Kazemi *et al.* reported that thiol-incorporated AC was produced from fir wood sawdust by chemical treatment with phosphoric acid impregnation[77]. The Q_{max} of the Hg²⁺ ions of thiol-incorporated AC (129.26 mg/g) was greater than that of the phosphoric acid-activated sample (107 mg/g). Xia *et al.* reported mercury removal on thiol-modified biochar (BC), AC, and graphene oxide (GO)[78].

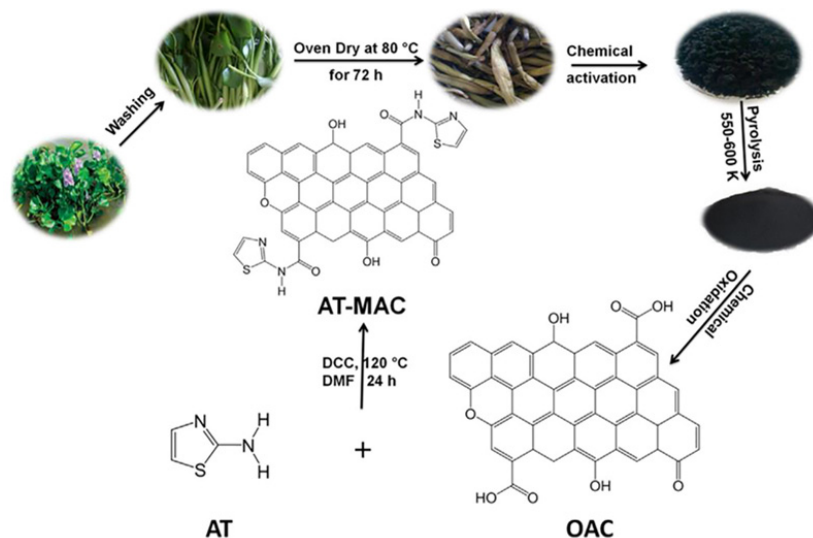


Figure 3. Schematic representation for the preparation of AT-MAC by the chemical modification of activated carbon with 2-Aminothiazole (Adopted from reference number 81).

Thiol modified BCS, ACS, and GOS were produced by the reaction of hydrolyzed 3-mercaptopropyltrimethoxysilane (3-MPTS) with the surface O-containing groups of carbon surface. GOS had the highest concentration of -SH groups with the highest Q_{\max} for Hg^{2+} and CH_3Hg^+ ions (449.6 and 127.5 mg/g), followed by ACS (235.7 and 86.7 mg/g) and BCS (175.6 and 30.3 mg/g), which were much higher than pristine GO (96.7 and 4.9 mg/g), AC (81.1 and 24.6 mg/g), and BC (95.6 and 9.4 mg/g), respectively. GOS and ACS exhibited strong mercury adsorption properties over a wide pH range (2–9). Hg^{2+} ions may be removed by ligand exchange, chelation, and electrostatic interactions. Wajima *et al.* reported the preparation of a sulfur-impregnated carbonaceous adsorbent from heavy oil ash using K_2S treatment[79]. Initially, raw ash was dipped into the K_2S solution, and subsequent pyrolysis of K_2S -adsorbed ash at 573.15 K produced a carbonaceous adsorbent (Product- K_2S) with a high sulfur content. Product- K_2S showed 111.9 mg/g of lead adsorption from an aqueous solution, and the competitive adsorption experiments conducted using a ternary Pb^{2+} - Cu^{2+} - Zn^{2+} ion solution suggested that there was highly selective removal of Pb^{2+} ions over Cu^{2+} and Zn^{2+} ions. It was found that the adsorption was strongly pH-dependent and increasing the pH of the solution resulted in greater removal of Pb^{2+} and Cu^{2+} ions, whereas Zn^{2+} ions could not be removed. According to authors, there are two possible explanations for this pH-dependent behavior. (i) At high pH levels, there is an increase in negatively charged active sites and a reduction in positively charged active sites. This enhances the possibility of electrostatic bonding between metallic ions and product- K_2S . (ii) When the pH is low, the competitive interaction of metal ions and protons with active sites becomes more intense, leading to a decreased metal ion adsorption capacity. Liang *et al.* reported a sulfur-functionalized Co-MOF, FJI-H12, which was synthesized by layering an ethanol solution of 2,4,6-tri(1-imidazolyl)-1,3,5-triazine (Timt) onto an aqueous solution of $\text{K}_2\text{Co}(\text{NCS})_4$ at room temperature for three days[80]. The

resulting FJI-H12 was formulated as $[\text{Co}_3(\text{Timt})_4(\text{SCN})_6(\text{H}_2\text{O})_{14}(\text{EtOH})_n]$ and contained free NCS-groups. Sulfur-containing NCS groups can be introduced into the MOF framework during MOF synthesis by coordinating chemically hard nitrogen atoms with cobalt metal ions, whereas chemically soft sulfur atoms can be available freely for the capture of soft metal ions, such as Hg^{2+} ions. FJI-H12 showed a Q_{\max} of 439.8 mg/g for Hg^{2+} ion removal capacity.

4.3. Modification with reagents containing nitrogen and sulphur groups

Walay *et al.* reported the modification of AC with an organic reagent containing both nitrogen and sulfur functionalities[81]. The composite material (AT-MAC) was prepared by the functionalization of AC with the chelating ligand 2-aminothiazole (AT) via an amidation reaction between the carboxylic groups of AC and the 2-AT ligand in the presence of DCC as a cross-coupling agent (Figure 3). At pH 5.5 and 60 min of contact time, the AT-MAC adsorbent was able to remove 252.5 mg/g & 310.9 mg/g of Hg^{2+} and Pb^{2+} ions, respectively. Xue *et al.* reported that the synthesis of a Ca-MOF named FJI-H9 was synthesized by reacting CaCl_2 with 2,5-thiophenedicarboxylate in a dimethylamine (DMA) solvent[82]. It exhibits the rapid recognition of Cd^{2+} ions at low concentrations, as low as 10 ppm. This MOF exhibits preferential adsorption of Cd^{2+} ions over a series of diverse metal ions (including Ca^{2+} , Mg^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Zn^{2+} , Fe^{2+} , Pb^{2+} , and Cd^{2+} ions). The Q_{\max} of Cd^{2+} ions was found to be 225 mg/g. Instead of thiophenyl, the authors propose that coordinated DMA molecules act as active adsorption sites, and $\text{Cd}(\text{H}_2\text{O})_4^{2+}$ ions were bound by the DMA molecules via hydrogen bonds. The square cavity of FJI-H9 may have a size that is especially appropriate for sealing a pack of Cd^{2+} ions, and this cavity may also be the most important in metal ion adsorption. The FJI-H9 powder (10 mg) was reconstructed into fresh FJI-H9 crystals using 50 mL of HNO_3 . Fu *et al.* reported 2,5-Dimercapto-1,3,4-

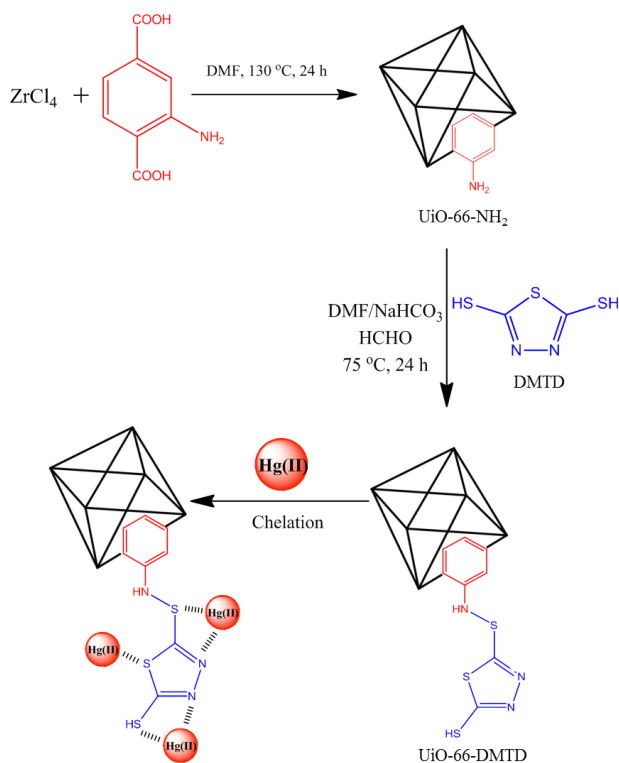


Figure 4. Schematic representation for the preparation of UiO-66-DMTD and the inferred mechanism of Hg^{2+} ions on to UiO-66-DMTD (Reproduced from reference number 83).

thiadiazole (DMTD)-modified Zr-MOF (UiO-66- NH_2) for the selective removal of Hg^{2+} ions from water[83]. A schematic representation of the preparation of UiO-66-DMTD and the inferred mechanism of Hg^{2+} ions on UiO-66-DMTD is depicted in Figure 4. The Q_{max} of Hg^{2+} ions was 670.5 mg/g at the optimum pH of 3. The kinetic and isotherm models matched well with the pseudo-second-order and Langmuir/Dubinin-Radushkevich models, respectively. According to the FTIR and XPS data, the adsorption mechanism appeared to be based on chelation between Hg^{2+} ions and -SH/N-containing groups. Furthermore, when compared to other competitive metal ions, such as Zn^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Mg^{2+} , Fe^{2+} , Ca^{2+} , and Cu^{2+} ions, UiO-66-DMTD showed a selective adsorption for Hg^{2+} ions.

5. Modification with magnetic metal oxides

The adsorption of HMs by metal oxides is considerable and selective. The huge surface area of ACs and MOFs is also useful for impregnating metal oxides, and the modified adsorbent has the advantages of stability and promising regeneration capacity[84]. Recently, magnetic metal compounds have been frequently utilized to support ACs and MOFs because they are convenient for successful separation from treatment-finished solutions. For example, Jain *et al.* reported the fabrication of iron oxide/activated carbon ($\text{Fe}_3\text{O}_4/\text{AC}$) and used it to remove Cu^{2+} , Cr^{6+} , and Cd^{2+} ions from aqueous solutions[85]. The authors evaluated optimal adsorption conditions for every individual met-

al ion. The adsorption process was endothermic and regenerable for up to four adsorption-desorption cycles. Nejadshafiea *et al.* reported a magnetic bio-adsorbent that was produced by the immobilization of Fe_3O_4 nanoparticles (NPs) and 1,4-butane sultone on the surface of AC; 1,4-butane sultone is a novel reagent that contains (- SO_3H) functionality and acts as a strong chelating agent for the separation of HMs[86]. The adsorption capacities of Pb^{2+} , As^{3+} , and Cd^{2+} ions were found to be 147.05 mg/g, 151.51 mg/g, and 119.04 mg/g, respectively. Chen *et al.* reported a thiol-modified magnetic powdered activated carbon (PAC) adsorbent, $\text{NiFe}_2\text{O}_4\text{-PAC-SH}$, via a hydrothermal methanol[87]. The grafting of thiol groups was accomplished using a direct esterification reaction between thioglycolic acid and PAC in the presence of concentrated H_2SO_4 (catalyst), and acetic anhydride (dehydrating agent). The introduction of magnetism was accomplished through a co-precipitation process that involved the charging of acid-resistant magnetic NiFe_2O_4 particles onto the surface of PAC. At 298.8 K and pH 7, $\text{NiFe}_2\text{O}_4\text{-PAC-SH}$ efficiently adsorbs Hg^{2+} ions from aqueous solutions, with a Q_{max} of 366.3 mg/g. An iron oxide magnetic nanoparticle (IOMN) modified, amino-functionalized MOF, was synthesized from $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{NH}_2\text{-TPA}$ in DMF and IOMNs[88]. Density functional theory studies demonstrated that Pb atoms could interact more strongly with the resultant $\text{NH}_2\text{-MIL-53}(\text{Al})\text{-IOMN}$. The composite material showed a 492.4 mg/g for Pb^{2+} ion removal capacity. Under mechanical agitation at room temperature, Wang *et al.* synthesized a composite material from magnetic cellulose nanocrystals (MCNC) and an MOF, based on zinc acetate and benzene-1,3,5-tricarboxylic acid (H_3BTC), which was further named as MCNC@Zn-BTC [89]. The composite material showed a Q_{max} of 558.66 mg/g for Pb^{2+} ions at room temperature. As evidenced by the FT-IR spectra, the Zn-BTC MOF was anchored to the MCNC surface. It has been demonstrated that the -COOH groups on the surfaces of Fe_3O_4 and CNC are abundant, and that Zn-BTC also has a substantial number of -COOH groups. Carboxylic and hydroxyl groups include oxygen atoms that have free pairs of electrons, allowing them to engage with the vacant orbitals of Pb^{2+} ions and form complexes via coordinative bonds. Ke *et al.* reported a magnetic, thiol-functionalized MOF for the selective adsorption of HMs[90]. Initially, the Cu-BTC framework was developed on Fe_3O_4 particles by immersing these magnetic particles in ethanol solutions of copper acetate and H_3BTC . The $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{BTC})_2$ was then treated with dithioglycol in anhydrous toluene to get thiol-functionalized $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{BTC})_2\text{-SH}$. At room temperature, the adsorption capacities of the thiol-functionalized magnetic adsorbent for lead and mercury ions were determined to be 215.05 mg/g and 348.43 mg/g, respectively. In comparison to Ni^{2+} , Na^+ , Ca^{2+} , Zn^{2+} , and Cd^{2+} ions, $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{BTC})_2\text{-SH}$ shows preferential adsorption for Hg^{2+} ions with greater affinity. In contrast, the unfunctionalized $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{BTC})_2$ failed to bind any Hg^{2+} or Pb^{2+} ions. This study further demonstrates the role of thiol groups in improving HMs adsorption.

6. Modification with Chitosan

Chitosan (CS) is a partially deacetylated copolymer of N-acetylglu-

cosamine and glucosamine derived from chitin. Chitosan is structurally similar to cellulose, but instead of hydroxyl groups at carbon-2, it has acetamido, or amino groups. The abundant availability of amino and hydroxyl functional groups on the CS surface can adsorb metal ions through chelation and electrostatic interactions. However, because of its hydrophobicity and low mechanical and thermal stability, CS isn't widely used in wastewater treatment. Therefore, it is necessary to modify other porous materials to form composites or hybrids[91]. Hydari *et al.* prepared a chitosan/activated carbon composite (CH/AC) from commercial CAC and chitosan biosorbent (CH), and the adsorptive removal of Cd²⁺ ions from dilute aqueous solutions was investigated[92]. Cadmium was completely removed by CAC, CH, and CH/AC after two hours, with Q_{max} values of 10.3 mg/g, 10 mg/g, and 52.63 mg/g, respectively. This indicates that chitosan modification of AC enhances the Cd²⁺ ion adsorption capacity. UiO-66-NH₂ MOF was introduced into polyacrylonitrile (PAN)/chitosan nanofibers as described by Jamshidifard *et al.*[93]. An electrospinning method was used to produce this composite material, which can be used to absorb and filter metal ions from aqueous solutions. When tested under ideal conditions (MOF content: 10% wt.%, 1 h equilibration time, 25 °C, pH 6), the PAN/chitosan/UiO-66-NH₂ nanofibrous adsorbent had a Q_{max} of 415.6 mg/g for Cd²⁺ ions. A MIL-125-CS composite material was developed by Liang *et al.* using integrating the titanium-based MIL-125 MOF with chitosan, utilizing a template-free solvothermal method[94]. The composite material showed a Q_{max} of 407.5 mg/g for Pb²⁺ ions in 180 min under ambient conditions. The authors stated that MIL-125 beads were shown to be more stable in water when coated with chitosan. Compared to chitosan beads (60.97 mg/g) and MIL-125 (94.72 mg/g), the experimental adsorption capacity of MIL-125-CS (100.03 mg/g) was higher. The authors stated that there was clear evidence from FT-IR analysis that interactions of Pb with -OH and -COOH groups are critical in Pb adsorption on MIL-125-CS.

7. Conclusions and future perspectives

This review refers to the metal-organic framework modification and chemical modification of ACs, as well as current advancements in the adsorptive removal of Pb²⁺, Hg²⁺, and Cd²⁺ ions using modified MOFs and ACs. The conclusions and future perspectives of modified MOFs and ACs are as follows.

- The modification of ACs and MOFs with nitrogen- and sulfur-containing reagents resulted in better HMs adsorption than traditional modification procedures, such as acid and alkali modification.
- MOFs, compared to AC, appear to be more promising adsorbents owing to their ordered and adjustable structures. MOFs possess a higher accessible volume than ACs, and PSM methods allow for a higher dispersion of functional groups and more stable composite materials than ACs. This is because of the lack of metallic cores or orderly placed organic linkers.
- Most MOFs are known to exhibit poor water stability. MOF degradation creates secondary contamination in the adsorbate sol-

utions and decreases the adsorption capacity of HMs. Because HMs adsorption is often carried out in aqueous medium, water stability is the most important issue to consider.

- Separating magnetic adsorbents from aqueous solutions using an external magnetic field is desirable, but transforming them into shaped bodies, such as extrudates, is required to avoid clogging of the adsorbent bed owing to the smallest particles.
- The majority of adsorbents can only remove a single or a few HMs. Thus, the development of adsorbents that can remove diverse metal ions simultaneously in a more comprehensive manner is required.

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