

## REMOVAL OF HEAVY METALS FROM AQUEOUS MEDIUM BY METAL ORGANIC FRAMEWORKS : A REVIEW

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### Abstract

Due to the negative consequences that environmental contamination of heavy metals is having on people all over the world, it is becoming a bigger issue. Because of inappropriate waste management, pesticides, fertilizers, and fast expanding agriculture and metal industries, inorganic contaminants are ending up in our rivers, soils, and environment. Environmental and biological concerns have made the effective disposal of hazardous items from the environment crucial. One of the most appealing cleaning technology strategies is the adsorptive removal of harmful substances from fuel, wastewater, or air. Because of their special properties, porous metal organic framework (MOF) materials have shown great promise recently in the adsorption and separation of different liquids and gases. The most recent research on the adsorptive removal of several hazardous compounds, mostly from fuel, water, and air, using modified MOF materials is compiled in this article. In order to comprehend the adsorption mechanism, potential interactions between the adsorbate and the active adsorption sites of the MOFs will also be covered. The majority of the results that are seen can be described by the following mechanisms: adsorption onto a site that is coordinatively unsaturated, adsorption through acid-base interaction, adsorption through complex formation, and adsorption through hydrogen bonding, adsorption by electrostatic adsorption predicated on certain MOFs.

### INTRODUCTION

The surroundings in which people, animals, plants, and microorganisms live or function are referred to as the environment. It is made up of the ocean, the land, and the atmosphere of Earth. The four spheres that comprise the Earth's system are the hydrosphere (water), lithosphere (land), atmosphere (air), and biosphere (living beings), all of which coexist peacefully. Pollutants and environmental contaminants are substances that are more prevalent than in any other area of the environment [1-3].

Because of their high density or large atomic weight, they are classified as heavy metals. These days, metallic chemical elements and metalloids that are hazardous to both humans and the environment are referred to as "heavy metals." Certain metalloids and lighter metals like aluminium, arsenic, and selenium are hazardous. They have been referred to as heavy metals, albeit some of them—like the element gold—are usually not hazardous [4-7].

**Table 1.** Chromium uses and properties [8-12].

<p>Characteristics</p> <ul style="list-style-type: none"> <li>▪ Density: 7.15 g/cm<sup>3</sup></li> <li>▪ It is twenty first abundant element</li> <li>▪ Isolated as a chromite ore</li> <li>▪ Hard</li> <li>▪ Shiny, Steel-greyish</li> <li>▪ This metal is quite active and reacts with most acids.</li> <li>▪ Creates a coating of chromium (III) oxide, which lessens the metal's corrosiveness.</li> </ul>	
<p>Applications</p> <ul style="list-style-type: none"> <li>▪ Alloys</li> <li>▪ Metal ceramics</li> <li>▪ Electroplating</li> <li>▪ Leather tanning</li> <li>▪ Manufacturing of synthetic rubies,</li> <li>▪ Dye paints</li> <li>▪ Chromium salts are used to colour glass green</li> </ul>	
<p>Effects</p> <p>Oral intake of chromium (VI) usually causes acute poisoning and various humans symptoms including:</p> <ul style="list-style-type: none"> <li>▪ Gastro intestinal ulceration</li> <li>▪ Nausea and vomiting</li> <li>▪ Fever</li> <li>▪ Diarrhea</li> <li>▪ Vertigo</li> <li>▪ Toxic nephritis</li> <li>▪ Liver damage</li> <li>▪ Coma</li> <li>▪ death(usually at 1-3g)</li> <li>▪ Inhalation of chromium(VI) or having repeated skin contact will cause chronic poisoning. Chromium (VI) can cause:</li> <li>▪ Allergic contact dermatitis and eczema,</li> <li>▪ gingivitis</li> <li>▪ irritation of mucous membranes</li> <li>▪ bronchitis</li> <li>▪ liver and kidney disease</li> <li>▪ sinusitis</li> <li>▪ pneumonia</li> <li>▪ lung cancer</li> </ul>	



**Table 2.** Arsenic uses and properties [13-14].

<p>Characteristics</p>	<ul style="list-style-type: none"> <li>▪ Density: 5.75g/cm<sup>3</sup>,</li> <li>▪ 55<sup>th</sup> most common metal,</li> <li>▪ It has three allotropic forms</li> <li>▪ The minerals that were discovered are:</li> <li>▪ arsenopyrite, which is composed of iron and arsenic sulphide;</li> </ul>
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	<ul style="list-style-type: none"> <li>▪ realgar, which is composed of arsenic sulphide and is referred to as "ruby of arsenic"</li> <li>▪ Dark silvery grey Appearance</li> <li>▪ Brittle</li> </ul>
Uses	<ul style="list-style-type: none"> <li>▪ Protection of wood</li> <li>▪ Preparation of glass</li> <li>▪ Insecticides originations</li> <li>▪ Doping material in semiconductors,</li> <li>▪ Pyrotechnics,</li> <li>▪ Bronze making</li> </ul>
Effects on humans	<ul style="list-style-type: none"> <li>▪ Poisonousness causes:</li> <li>▪ Gastro-intestinal system irascibility,</li> <li>▪ Lung irritation</li> <li>▪ Skin fluctuations</li> <li>▪ Reduced manufacture of both red blood cells and white blood cells,</li> <li>▪ Enlarged probabilities of cancer have been proposed.</li> <li>▪ Sterility and miscarriages,</li> <li>▪ Heart difficulties</li> <li>▪ Brain destruction</li> <li>▪ Deoxyribonucleic acid (DNA) destruction</li> <li>▪ Organic arsenic may cause:</li> <li>▪ Stomach set backs</li> <li>▪ Nerve destruction</li> </ul>

**Table 3.** Lead uses and properties [15-18].

Characteristics	<ul style="list-style-type: none"> <li>▪ Density:11.3g/cm<sup>3</sup></li> <li>▪ 37<sup>th</sup> most common metal</li> <li>▪ Found as ore known as galena</li> <li>▪ Silver-grey metal</li> <li>▪ Soft</li> </ul>
Uses	<ul style="list-style-type: none"> <li>▪ Hair dyes</li> <li>▪ Insecticides</li> <li>▪ Lead-acid batteries</li> <li>▪ Lead crystal glass</li> <li>▪ Cable cover</li> <li>▪ Sports kit</li> <li>▪ Canister for toxic fluids</li> <li>▪ In buildings for roofing</li> <li>▪ Lead pipes</li> </ul>
Effects on Human	<ul style="list-style-type: none"> <li>▪ Hypertension</li> <li>▪ Miscarriages</li> <li>▪ Premature and low births,</li> <li>▪ Still births</li> </ul>

	<ul style="list-style-type: none"> <li>▪ Renal damage</li> <li>▪ Brain harm</li> <li>▪ Abdominal soreness</li> <li>▪ Peripheral nerve destruction</li> <li>▪ Sperm destruction</li> <li>▪ Encephalopathic symbols</li> <li>▪ Iron shortage due to trouble of haemoglobin production,</li> <li>▪ Cognitive impairment,</li> <li>▪ In children:</li> <li>▪ Brain and central nervous system growth changed</li> <li>▪ Compact cleverness,</li> <li>▪ A decline in educational attainment,</li> <li>▪ A decrease in the devotion span,</li> <li>▪ Rise in anti-social behaviour</li> </ul>
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**Table 4.** Mercury uses and properties [19].

Characteristics	<ul style="list-style-type: none"> <li>▪ Density: 13.5336 g/cm<sup>3</sup></li> <li>▪ 66<sup>th</sup> the most abundant metal</li> <li>▪ It is found in the ore cinnabar made from mercury sulphide</li> <li>▪ At room temperature, it is a silvery liquid metal,</li> <li>▪ Rare to find in a natural state</li> </ul>
Uses	<ul style="list-style-type: none"> <li>▪ Barometers</li> <li>▪ Thermometers</li> <li>▪ Manufacturing chlorine</li> <li>▪ Gold recovery</li> <li>▪ Tooth fillings</li> <li>▪ Compact fluorescent light bulbs</li> <li>▪ Photochemistry</li> <li>▪ Calomel electrodes</li> <li>▪ Insecticide</li> <li>▪ Rat poison</li> <li>▪ Mercuric Sulphide used as a pigment in paint, bright red</li> <li>▪ Catalyst</li> <li>▪ Rectifiers,</li> <li>▪ Electrical switches</li> </ul>
Effects on Human	<ul style="list-style-type: none"> <li>▪ Inhalation caused:</li> <li>▪ Lung irritation</li> <li>▪ Eye irritation</li> <li>▪ Rashes</li> <li>▪ Vomiting and diarrhoea</li> <li>▪ Genotoxic</li> <li>▪ It damages the DNA and chromosomes,</li> <li>▪ Mongolism, also known as Down's syndrome,</li> <li>▪ Affects the reproductive system, which can lead to:</li> <li>▪ Miscarriages,</li> <li>▪ Congenital disabilities,</li> <li>▪ Sperm damage in men,</li> <li>▪ Neurological disorders,</li> </ul>

	<ul style="list-style-type: none"> <li>▪ Minamata disease or Chisso-Minamata disease:</li> <li>▪ Learning disabilities,</li> <li>▪ Speech defects,</li> <li>▪ Memory loss,</li> <li>▪ Tremors and muscle incoordination,</li> <li>▪ Deafness,</li> <li>▪ Vision complications,</li> <li>▪ Personality changes,</li> <li>▪ Insanity,</li> <li>▪ Paralysis,</li> <li>▪ Coma and death,</li> </ul>
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**Table 5.** Cadmium uses and properties [20-21].

Characteristics	<ul style="list-style-type: none"> <li>▪ Density: 8.69 g/cm<sup>3</sup></li> <li>▪ 64<sup>th</sup> most common metal</li> <li>▪ Found in combination with zinc</li> <li>▪ Silvery bluish tint metal</li> </ul>
Uses	<ul style="list-style-type: none"> <li>▪ Phosphate fertilizer</li> <li>▪ Pesticides</li> <li>▪ Nickel-Cadmium batteries</li> <li>▪ Glassware pigmentation,</li> <li>▪ Corrosion-resistant plating,</li> <li>▪ Stabilizer in plastic production,</li> <li>▪ Nuclear reactors</li> </ul>
Effects on Human	<ul style="list-style-type: none"> <li>▪ It is produce nephrotoxicity</li> <li>▪ Infertility produced by a reproductive system failure,</li> <li>▪ Calcium metabolism changes</li> <li>▪ Bone breakage</li> <li>▪ DNA weakening,</li> <li>▪ Cancer</li> <li>▪ Reported to be genotoxic and ecotoxic in animals</li> <li>▪ Psychological syndromes,</li> <li>▪ Gastrointestinal illnesses,</li> <li>▪ Central nervous system problems,</li> <li>▪ Immune system deficiencies,</li> </ul>

**Table 6.** Copper uses and properties [22-23].

Characteristics	<ul style="list-style-type: none"> <li>▪ Density: 8.96 g/cm<sup>3</sup></li> <li>▪ 26<sup>th</sup> most Common metal</li> <li>▪ Golden Red appearance</li> <li>▪ Found in minerals such as chalcopyrite, bornite (peacock ore)</li> <li>▪ Good conductor of heat and electricity</li> </ul>
Uses	<ul style="list-style-type: none"> <li>▪ Copper alloys</li> <li>▪ Copper wires</li> </ul>

	<ul style="list-style-type: none"> <li>▪ Electroplating</li> <li>▪ Coins</li> <li>▪ Piping</li> <li>▪ Chemical tests for sugar detection in Fehling's solution</li> <li>▪ Copper sulphate to cure mildew in agriculture</li> <li>▪ Protection of wood</li> <li>▪ Protection of fabric</li> <li>▪ Fence cream</li> </ul>
<p>Effects on Human</p>	<ul style="list-style-type: none"> <li>▪ Metal fever giving it self with:</li> <li>▪ flu-like indications</li> <li>▪ diarrhoea</li> <li>▪ vomiting</li> <li>▪ irritation of the eyes</li> <li>▪ dizziness</li> <li>▪ irritation caused in the mouth cavity</li> <li>▪ An acute dose of copper salts causes acute gastroenteritis due to necrosis</li> <li>▪ In excess:</li> <li>▪ Hepatocellular degeneration</li> <li>▪ Necrosis</li> <li>▪ Cytotoxic to erythrocytes leading to haemolysis</li> <li>▪ Wilson's disease (copper accumulated in organs instead of being excreted by bile):</li> <li>▪ Lack of appetite</li> <li>▪ Fatigue</li> <li>▪ Jaundice</li> <li>▪ Kayser-Fleisher rings</li> <li>▪ Speech impairment</li> <li>▪ Difficulty in swallowing</li> <li>▪ Uncontrolled poisoning</li> <li>▪ Brain damage</li> <li>▪ Demyelination</li> <li>▪ Hepatic cirrhosis</li> <li>▪ Oral intake will cause hepatic and kidney disease,</li> <li>▪ Insomnia</li> <li>▪ Anxiety</li> <li>▪ Agitation</li> <li>▪ Restlessness</li> </ul>

**Table 7.** Nickel uses and properties [24-26].

Characteristics	<ul style="list-style-type: none"> <li>▪ Density: 8.9 g/cm<sup>3</sup></li> <li>▪ 22<sup>nd</sup> most common metal</li> <li>▪ Minerals found are pentlandite, sulphide; garnierite</li> <li>▪ Silvery Appearance</li> <li>▪ Repels corrosion at high temperatures</li> <li>▪ Large quantity of Ni came from meteorites</li> </ul>
Uses	<ul style="list-style-type: none"> <li>▪ Jewelry</li> <li>▪ Coins</li> <li>▪ Oat propeller shafts,</li> <li>▪ Rocket engines</li> <li>▪ Nichrome alloy used in appliances that use heat while remaining non-corrosive</li> <li>▪ Electroplating</li> <li>▪ Alloy</li> <li>▪ Welding</li> <li>▪ Armour plating</li> </ul>
Effects on Human	<ul style="list-style-type: none"> <li>▪ Lung embolisms</li> <li>▪ Asthma</li> <li>▪ Allergic reactions (jewellery)</li> <li>▪ Respiratory failure</li> <li>▪ Heart disorders</li> <li>▪ Dizziness (following gas exposure)</li> <li>▪ Increased possibilities of cancer</li> <li>▪ Nickel sulphide, nickel oxide and soluble nickel compounds are all carcinogenic. Workers in the nickel industry who are exposed to inhalation of the metal are at a greater risk of acquiring lung and nasal cancer</li> </ul>

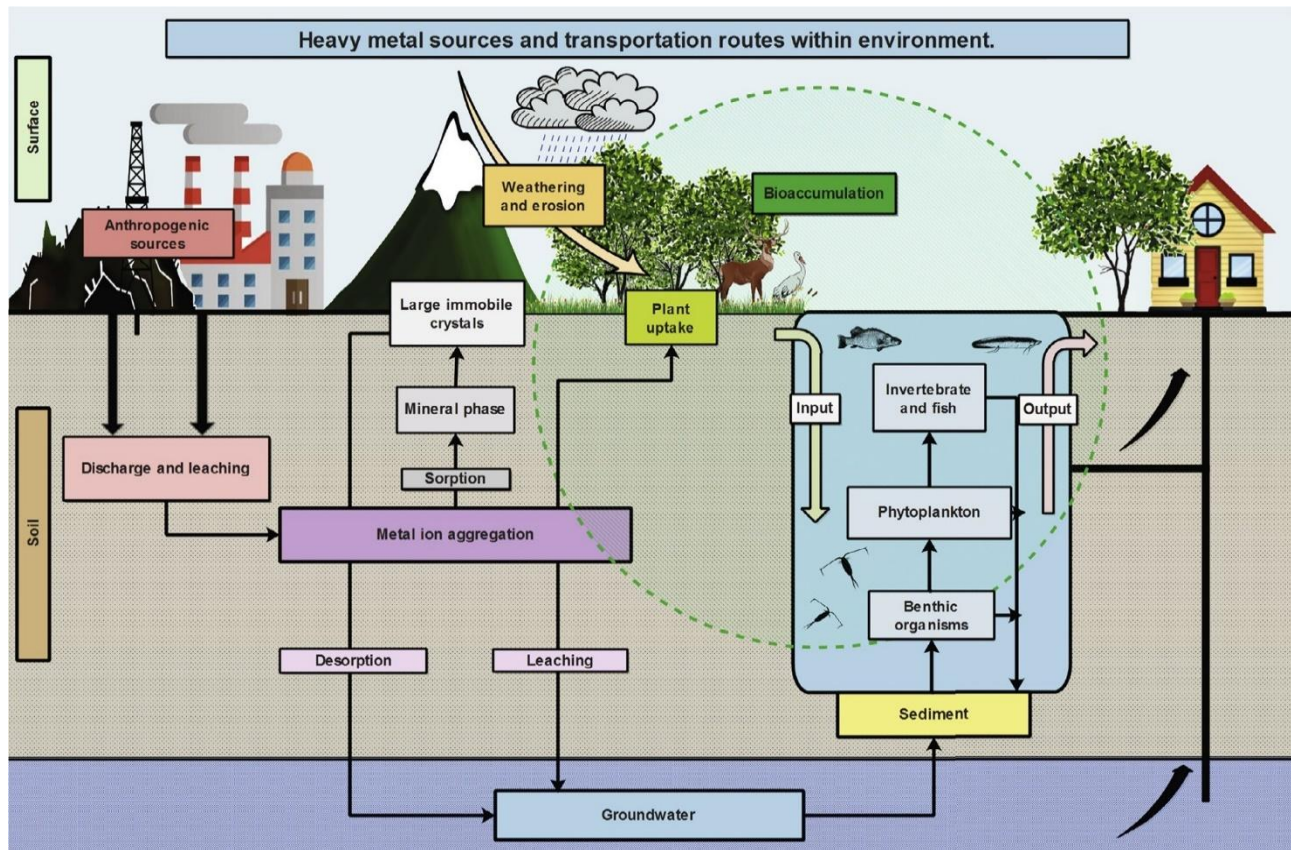
**Anthropogenic sources**

The primary source of drinking water and a vital resource for humanity, ground water reservoirs are mostly affected by anthropogenic organic and inorganic pollution. This pollution eventually poses a concern to human health and may cause poisoning in both aquatic and terrestrial animals. It is crucial to keep an eye on and manage any sources of pollution. This include sources such runoff from metropolitan areas, railroads, highways, mines, dredged sediments, landfills, sewage systems, and agricultural and industrial locations [27].Heavy metals can also be redistributed throughout the ecosystem as a result of ground water pollution, either by sorption/complexation (to particulate organic

matter) or plant absorption. Figure 1, provides a broad summary of how heavy metals are transported via ground water systems. In general, a lot of human activities that cause heavy metal pollution may be linked to the processes involved in the manufacture, use, and disposal of goods in a variety of contexts, including industry, agriculture, and transportation. The elements released by these processes might originate from point sources or diffuse sources, and they are discharged into the environment as gases or particles in solid or watery forms. Pollutants from agriculture might come from fertilizers and other products used for crop management. For instance, phosphoric fertilizers have different amounts of zinc and cadmium depending on the kind of rock

they are made of. Increased Cd concentration in sedimentary derivatives and decreased Cd content in derivatives of igneous rock [28]. Heavy metals are no longer included in pesticides; none the less, the use of metal-rich chemicals in the past caused arsenic, lead, and mercury to accumulate in soil and ground water. Because sewage effluents contain a lot of nutrients, they have been widely employed for soil enrichment over the past 100 years. Sewage effluents have benefits, but they can also include boron,

cadmium, copper, lead, nickel, and zinc, which can be harmful to plants. Another significant cause of the environmental contamination caused by heavy metals is industrial activity. This is especially concerning for regions of the world that do not yet have contemporary legislation pertaining to this issue. The primary industrial causes of pollution are coal combustion, mining, waste water treatment, and product waste disposal. Large amounts of waste rock are produced by mining,



**Fig 1.** A flow chart showing how soil, fresh-and ground water systems redistribute heavy metal so anthropogenic origin

rock (As, Cu, Cd, Pb, and Hg) still contains small amounts of heavy metals. These trace metals are deposited in mine tailings and are subject to weathering and oxidizing conditions that cause acid drainage. The heavy metals are subsequently released, seeping into the nearby rock, soils, and even drinking water supplies. Fossil fuel combustion is another industrial form of pollution that mostly

contributes to atmospheric heavy metal pollution (As, Cd, Mo, Zn, and Pb from petrol additives). Solid waste produced during industrial operations.

**Adsorptive removal of Toxic Substances**

Due to its relatively low cost, broad variety of applications, ease of design and operation, low



production of toxic secondary products, and simple adsorbent renewal, adsorption has been deemed preferable to alternative decontamination techniques. The basis of adsorptive removal is a porous adsorbent's capacity to specifically adsorb certain molecules from the environment or refinery streams. Since the chemicals have easy access to the solid soil's pores, they can be removed via adsorption if they are of an appropriate size and form. An adsorbate and a porous sorbent can interact in different ways, leading to the classification of adsorption as either chemical or physical [29]. Adsorptive adsorption is the common term for physical adsorption, while reactive adsorption is the term used for chemical adsorption.

Adsorbates are often confined inside the pores of solid adsorbents by weak (van der Waals) pressures in the case of adsorptive removal. As a result, simple solvent exchange or other physical processes like sonication and calcination can readily replenish the adsorbent. Conversely, genuine chemical bonds between the adsorbate and the adsorbent are formed during reactive adsorption. Chemical treatments are often used to regenerate the wasted adsorbent. The key factors influencing the effectiveness of adsorptive removal are the adsorbents' adsorption capacity, their durability, regenerability, and selectivity for certain chemicals. Hazardous chemical

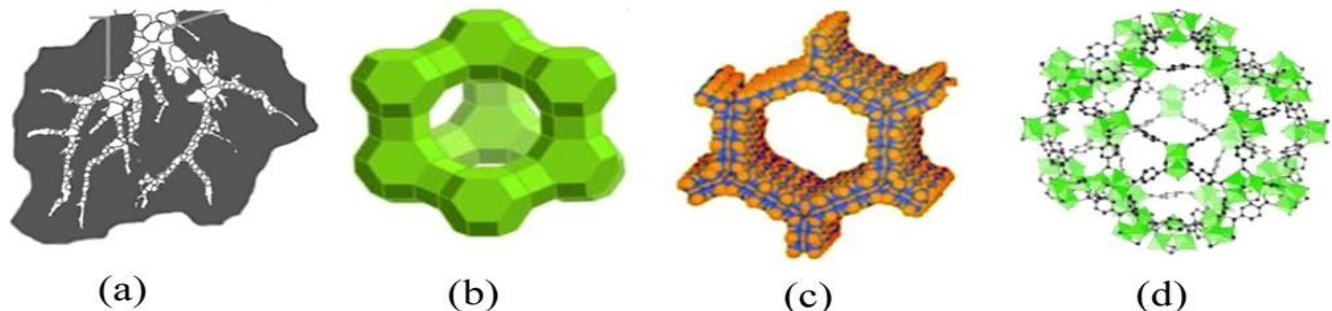


Fig 2. Widely used porous sorbents: (a) activated carbon, (b) HY (FAU) zeolite, (c) MCM-41 and (d) MIL-101 (Cr).

adsorptive removal has been explored for a variety of porous adsorbents Fig. 2, including zeolites [30-32], activated carbons [33-36], mesoporous materials [37-

40], and MOFs [41-43]. Porosity, pore shape, and specific adsorption sites are necessary for effective adsorptive removal.



Fig 3. Techniques used for the removal of heavy metals from aqueous solutions

However, the metabolism of the human body only needs a little amount of metals as trace elements. They pose a serious risk to life if their amount rises. Figure 3 illustrates the many techniques now in use for removing heavy metal ions, including adsorption, chemical procedures, resin-mediated ion exchange, and fluctuation.

### Metal Organic Frameworks

A metal ion or cluster of metal ions and an organic molecule known as a linker make up the two main parts of MOFs. Di-, tri-, or tetradentate ligands are the most common

organic units [44- 45]. Fig. 4 displays a few common MOFs. Since the inorganic component of porous hybrid frameworks comprised either a solitary polyhedral or tiny clusters similar to those seen in coordination chemistry, they were previously referred to as coordination polymers. But it wasn't long before it was discovered that bigger dimensions inorganic components within porous hybrid solids might result in the formation of chains (1D), layers (2D), and even three-dimensional frameworks known as MOFs[46].

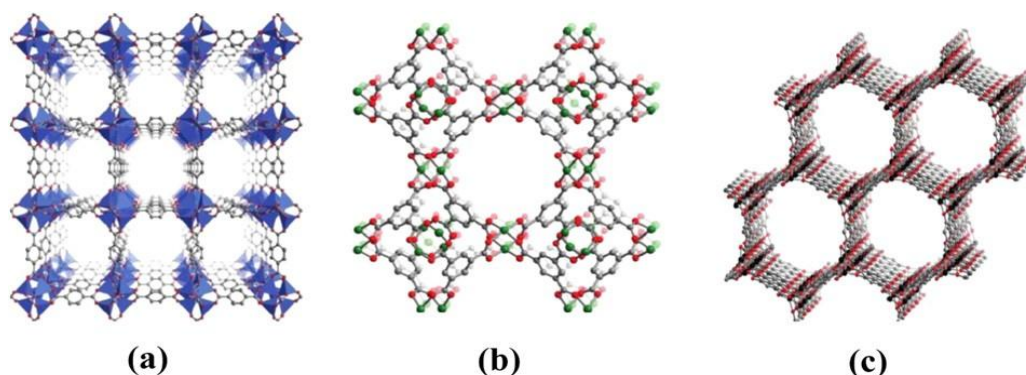


Fig 4. Structures of typical metal-organic frameworks. (a) MOF-5, (b) Cu-BTC and (c) CPO-27.

When compared to materials of the zeolite type, MOF materials provide several benefits. For zeolite-related inorganic hybrid materials to develop, an organic or inorganic template is required; however, the primary templating molecule in MOFs is a solvent. In contrast to inorganic materials, which rely on a few number of cations like Si, Al, and P, the majority of metal cations may take part in the production of MOFs, which is another significant characteristic. By only altering the ligand lengths of the same metal species, MOFs have made tremendous progress towards the construction of a series known as isorecticular MOFs, in which the pore size of the matching frameworks is dependent upon the ligand length. Additionally, a number of similar MOFs may be created using the same ligands and other metallic components [47-48]. The enormous

porosity and ease with which the pore size and shape of MOF-type materials can be tuned from microporous to mesoporous scale by varying the nature of the organic linkers and the connectivity of the inorganic moiety, as well as the materials' capacity for hydrogen storage, vapour adsorption, chemical separation, drug delivery/biomedicine, polymerization, magnetism, catalysis, luminescence, and other processes. Because MOFs have potential applications in a wide range of industries, there has been a significant growth in both the number of publications (per year) and research on MOFs. Due to their simple pore surface modification, which allows for the selective adsorption of certain guest molecules with certain functional groups, MOFs are interesting materials for adsorption-related applications[49-59].



Fig 5. Application of MOFs in the environment cleanup

Because of their enormous porosity and pore geometry, MOF-type materials have recently been extensively studied for the adsorptive removal of numerous hazardous chemicals from the environment [60-62]. Furthermore, MOFs are superior to other porous adsorbents for the effective adsorptive removal of hazardous compounds because of the central metals [63-66], cooperatively unsaturated sites (CUS or open metal sites) [67-69],

functionalized linkers [70-72], and loaded active species [73]. These interactions have been used successfully for a number of additional interactions between the adsorbates and MOF materials. Preferred adsorption is influenced by a variety of host-guest interactions, including acid-base [74],  $\pi$ -complexation [75], H-bonding [76], and coordination with open metal sites [77-79].

Table 8. Overview of pure MOFs as adsorbents for metals in aqueous systems. This table is organized for metals, concentration, the MOF adsorbents and their maximum uptake.

Metal	The concentration of MCL causes health effects (mg /L)	MOF adsorbent	Maximum MOF Adsorption capacity (mg / g)	References
Antimony(V)	0.006	NU-1000	287.88	80
Antimony(III)		NU-1000	136.97	80
Arsenic(V)	0.01	Zn-MOF-74	325	81
		UiO-66	303	82
		ABUM-1	103	83
		MIL-100-Fe	110	84
		H-ZIF-8-14	90.9	85
		ZIF-8	76.5	85
		H-ZIF-8-12	74.0	85
		H-ZIF-8-11	72.6	85
		ZIF-8-MeOH	72.33	85
Arsenic(III)	0.01	Fe-Co-MOF-74	292	86
		Zn-MOF-74	211	87
		UiO-66	202	82
		UiO-66-(SH)2	40	87

Metal	The concentration of MCL causes health effects (mg /L)	MOF adsorbent	Maximum MOF Adsorption capacity (mg / g)	References
Barium(II)	0.02	Zr-bdc-NH <sub>2</sub> -SO <sub>4</sub>	181.8	88
		MOF-808-SO <sub>4</sub>	131.1	89
		MIL-101-Cr-SO <sub>3</sub> H	70.5	89
Cadmium(II)	0.005	MOF-808-EDTA	528	90
		FJI-H9	225	91
		NH <sub>2</sub> -Zr-MOF	177.35	92
		Cu <sub>3</sub> (BTC) <sub>2</sub> -SO <sub>3</sub> H	88.7	93
		UiO-66-NHC(S)NHMe	49	94
		TMU-4	48	95
		TMU-5	43	95
Chromium(VI)	0.1	TMU-6	41	95
		1DFe-gallic acid	179.2	96
		ZJU-101	245	96
		SCNU-Z1-Cl	241	97
		FIR-54	103	98-99
		Zn-Co-SLUG-35	68.5	100
		1-ClO <sub>4</sub>	63	101
SLUG-21	62.8	102		
		FJI-H9	71.8	103

Metal	The concentration of MCL causes health effects (mg /L)	MOF adsorbent	Maximum MOF Adsorption capacity (mg / g)	References
		Cu-BTC	48	104
		1-NO <sub>3</sub>	37	95
Chromium	(III)	TMU-4	127	95
		TMU-5	123	95
		TMU-6	118	95
Cobalt(II)	0.04	UiO-66-Schiff	256	95
		MOF-808-EDTA	150	90
		TMU-5	63	95
		TMU-6	59	95
		TMU-4	55	95
Copper(II)	0.13	ZIF-67	617.51	105
		ZIF-8	454.72	105
		MOF-808-EDTA	155	90
		TMU-4	62	95
		TMU-6	60	95
		TMU-5	57	95
Iron(III)	0.200	MOF-808-EDTA	150	90
Lead(II)	0.015	ZIF-67	134	105
		ZIF-8119	67	105
		MOF-808-EDTA	313	105

Metal	The concentration of MCL causes health effects (mg /L)	MOF adsorbent	Maximum MOF Adsorption capacity (mg / g)	References
		TMU-5	251	
		TMU-4	237	
		UiO-66-NHC(S)NHMe	232	
		TMU-6	224	
		NH <sub>2</sub> -Zr-MOF	92.18	
		MIL-101(Cr)	15.78	
Lithium(I)	0.20	Zn-MOF5-12c4	12.3	106-107
		LMOF-321	12.18	
		MIL-121-a	3.89	109
		MOF-808-EDTA	63	90
Manganese(VII)	0.05	SCNU-21	292	99
Mercury(II)	0.002	CaCu <sub>6</sub> [(S,S)-methox] <sub>3</sub> (OH) <sub>2</sub> (H <sub>2</sub> O)	900	110
		JUC-62	836.7	67
		UiO-66-NHC(S)NHMe	769	52
		MOF-808-EDTA	592	48
		FJI-H12	439.8	68
		LMOF-263	380	69
		PCN-100	364.7	70

Metal	The concentration of MCL causes health effects (mg /L)	MOF adsorbent	Maximum MOF Adsorption capacity (mg / g)	References
		UiO-66-(SH) <sub>2</sub>	236.4	71
		MIL-101-NH <sub>2</sub>	30.67	72
		ZIF-90-SH	22.45	73
Nickel(II)	0.1	MOF-808-EDTA	155	90
Selenium(VI)	0.05	NU-1000	62	91
		UiO-66-(NH) <sub>2</sub>	38.5	111-112
		UiO-66-HCl	86	113
		FJI-H9	187	114
Selenium(IV)	0.001	NU-1000	102	115
		UiO-66-(NH) <sub>2</sub>	45	116
Silver(I)	0.000001	MIL-53(Al)	183	116
Thallium(IV)	0.002	UiO-66-(COOH) <sub>2</sub>	350	117
		dMn-MOF	46.35	118
Uranium(VI)	0.000002	HKUST-1	787.4	119
		MIL-101-DETA	350	98
		MOF-76	298	116
		MOF-2	217	96
		MOF-3	109	119



### Mechanism of Adsorption

Depending on the nature of the interaction between the heavy metals (adsorbates) and MOFs (adsorbents), MOFs can remove heavy metals from water by chemical or physical adsorption. Adsorptive adsorption is another name for physical adsorption; reactive adsorption is the general term for chemical adsorption. The adsorptive capacity of MOFs is influenced by the strength of chemical and physical adsorption.

### Chemisorptions

The sorption of heavy metals on MOFs is mostly attributed to chemisorption processes. Coordination bonding, acid-base interaction, and chemical bonding are all included. Heavy metal sorption on MOFs typically results in the observation of a chemical bonding mechanism. The bond may be recognised by FTIR by exhibiting extra bands in the spectrum. An extra band for the Zr-O-As group is seen during the sorption of As(V) on UiO-66 from water as a result of the bonding of the adsorbate (As) with adsorbent (Ui-66). The sorption of heavy metals on three different ZIF morphologies—leaf-shaped ZIFs, dodecahedral ZIFs, and cubic ZIFs—has been reported. This is because the isotherms for these morphologies are better explained by the Langmuir model than by the Freundlich model, indicating that chemical bonding was a predominant mechanism [131].

### Chemical Bonding

Heavy metal ions and adsorbate (modified MOFs) containing reactive groups like carboxyl, thiol (-SH), (-COOH), and amine (-NH<sub>2</sub>) typically exhibit coordination bonding. Create an amine-functionalized version of MIL-101(Cr) by coordinating ethylenediamine with the unsaturated centres of Cr metal. A number of hydrogen ions in the water joined the -NH<sub>2</sub> of MIL-101(Cr) when the pH of the solution was acidic, forming MOF(NH<sub>2</sub>)<sub>3</sub><sup>3+</sup>, which was then coupled with heavy metal ions. This time, however, it was not true since the typical surface area predicted the adsorption capacity of the adsorbate. Modified UiO-66 and virgin have a bigger surface area than MIL-68 and MIL-53-NH<sub>2</sub>, however

the former have a lower sorption capacity than the latter [132].

### Acid Base Interaction

According to some research, the hard-soft acid-base (HSAB) theory is necessary for the acid-base interactions in order for heavy metal ions to sorb onto metal oxide filaments (MOFs). This hypothesis states that although other features are comparable, hard acid responds firmly with hard base and soft acid reacts with soft base. Further more, absorbing or donating electron pairs provides the basis for the Lewis acid-base theory-explained process of heavy metal sorption on MOFs. The possessing donor atoms O or N plays a significant impact in the Cr(III) sorption process on TMU-5 [133-135].

### Physisorption

#### Van Der Waals forces

The van der Waals sorption process often kicks in when the MOFs' surface area and porosity play a significant role. Because MOFs have a unique greater surface area, heavy metals are removed from the water in a selective manner. It is investigated how pore size, pore surface, and pore volume influenced MIL-100(Fe) sorption capacity, which increased as pore volume increased. Together, chemisorption and physisorption boost the sorption capacity, albeit neither process is very significant on its own [136-137].

### Electrostatic Interaction

Electrostatic interaction is the term used to describe the sort of interaction that MOFs can have with heavy metal ions that have opposing charges. Electrostatic contact occurs during the sorption process, which determines whether the MOFs' surface had a negative charge. In addition to altering the pH of the solution, the charge on the MOFs' surface also introduces a unique group that is associated with protonation and deprotonation. The ability of the MOFs surface and the presence of heavy metal ions both influence the sorption process of heavy metals on MOFs. The pH of the solution affects the divalent heavy metals, such as Hg (II), Pb (II), and Cd (II). Common species are M<sup>2+</sup>, M(OH)<sup>+</sup>,

(MOH)<sup>o</sup>, and M(OH)<sub>3</sub>. Greater amounts of hydrated ions H<sub>3</sub>O<sup>+</sup> competed with heavy metal ion sorption on the MOFs at lower pH values. Since the heavy metals and MOFs are both positively charged, there was no electrostatic contact between them. However, the solution has a negative charge at high pH levels, and heavy metals have a positive charge, therefore there is an electrostatic contact between them. the ability of MOF-5 to carry

a negative charge between pH values of 2 and 7, and the capacity of HS-mSi@MOF-5 to carry a negative charge above pH value of 3. The greatest adsorption for Pb(II) and Cd(II) is attained at pH 7, and the capacities of raw MOF-5 and HS-mSi@MOF-5 increased as the pH of the solution increased. As a result, electrostatic interaction dominated the sorption process for both metals [140].

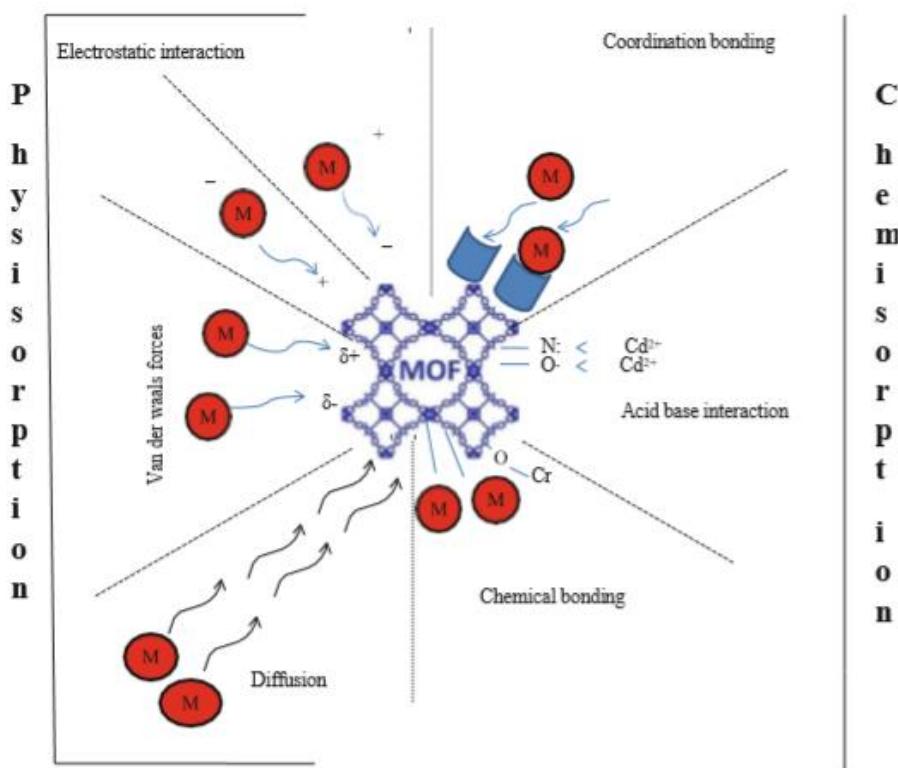


Fig. 6. Mechanistic representation of removal of heavy metals on MOFs

**Conclusion**

Because of its remarkable porosity, large surface area, and chemically adjustable characteristics, Metal-Organic Frameworks (MOFs) have become very successful materials for purifying water. They are better than conventional adsorbents because of their capacity to specifically collect and eliminate impurities such as organic pollutants, heavy metals, and radioactive materials. Their powerful attraction to metal ions, which enables them to efficiently remove harmful compounds from water, is one of the main reasons underlying their effectiveness. They

are a viable option for large-scale water treatment because of their structural adaptability, which also allows for adjustments to improve selectivity and reusability. Even if there are still issues with increasing its stability and scalability, further development and research in MOFs technology has the potential to completely transform water purification, resulting in cleaner water sources and a more sustainable environment.

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