Metal-Organic Frameworks for the Removal of Heavy Metals from Water

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Abstract:
Water pollution is a foremost problem across the world that endangers the survival and development of man and society. As a result of this menace, the effective and efficient removal of heavy metal ions from water has become a serious concern. Metal–organic frameworks (MOFs) have gained attention as promising materials for liquid-phase adsorptive removal of heavy metal ions. Properties such as large surface area, high adsorption capacity, tunable porosity, hierarchical structure and recyclability give MOFs an edge over conventional adsorbents. In this article, recent advances in the removal of toxic heavy metal ions from water by MOFs are highlighted.

Keywords: Metal-organic frameworks (MOFs); Heavy metal removal; Adsorption technology

1. Introduction

Water is the most important substance on earth. It is very essential to survive all man, animal and plants. There would be no life on earth if there was no water. However, with the escalation of human activities and the fast progress of modern industry, water pollution is one of the most serious worldwide problems that endangers the survival and development of human society. Rapidly growing water contamination by heavy metal ions (Hg^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, etc.) has turned into a major threat worldwide. The main source of heavy metal ions are industries like electroplating, battery manufacturing, metallurgical, tannery, and metal finishing.[1,2] Water pollution due to heavy metal ions has become a severe threat to environment and public health.[3] Even at low concentrations heavy metal ions are very much toxic to living organisms. Unlike organic contaminants, heavy metal ions are non-biodegradable in nature and they tend to gather in the environment which causes the negative effect on the environment and ecosystem.[4,5] Heavy metals in water can cause acute and chronic toxicity which leads to learning disabilities, cancer, and even death. Therefore, the exclusion of these pollutants has attracted a great attention to the researchers.

Over the years, several techniques have been applied for the removal of heavy metals from water namely adsorption, ion exchange, precipitation, membrane separation, electro dialysis, and photocatalysis.[6] Among them, the metal-organic frameworks (MOFs) were used as adsorbent for the removal of heavy metal ions from aqueous medium. Bakhtiari[2] and Rivera *et al*.,[7] established that MOF-5 is a effective adsorbent for the removal of heavy metal ions like lead and copper from aqueous solution.

Metal-organic frameworks (MOFs) are a new type of porous materials, composed of metals ions or clusters and organic ligands have been developed as an active field in coordination chemistry over the past decades.[8,9] Pores in MOFs are highly ordered, their size and shape can be adjusted by variation in linkers and metal ion.[10] High surface area, porosity, unique structure, variable functional groups made MOFs valuable in various applications as storage, catalysis, sensing, bio-imaging.[11] High specific surface area and porous nature of MOFs permits these groups of materials to be used as an excellent adsorbent to capture the contaminants from water.[12] This article is focused on advance in applications of MOFs to remove toxic heavy metal ions through adsorption from the water.

2. Removal of Heavy Metal ions using Adsorption Technology

2.1. Adsorption Technology

To remove the hazardous materials from water adsorption technology have been applied. Compared with other methods, this technique has several unique advantages like low cost, easy operation, simple design and recyclability of the adsorbents. The adsorptions are classified into two ways- i) physical adsorption and ii) chemical adsorption based on the interactions between adsorbents and adsorbates.[13,14] In case of physical adsorption, the adsorbates are usually coordinated by van der Waals forces and adsorbed into the pore structures of the adsorbents. On the other hand, the adsorbates are combined with the adsorbent via chemical bonds during chemical adsorption, leading to a much stronger interaction than physical adsorption. Due to the high specific surface area, a variety of functional groups and controllable pore structure, MOFs have been utilized as superior adsorbents to eliminate hazardous substances such as organic compounds, heavy metals and toxic gases through various interactions including acid-base interaction, hydrogen bonding, π−π interaction and π-complexation.[15,16,17,18,19,20,21,22,23]

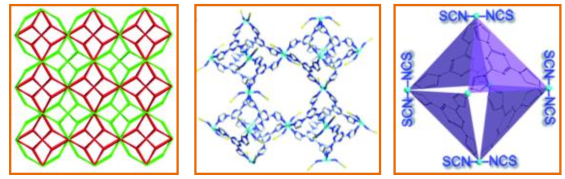
2.2. Removal of Heavy Metal ions

Water pollution because of the contamination of heavy metal ions is a significant environmental concern directly connected to the health of human beings and other life forms along with the food chain. Industrial wastewater have various heavy metals e.g, mercury, lead, chromium, zinc, uranium, cadmium, selenium, arsenic, silver, nickel and gold. Among them, mercury, cadmium, lead and arsenic exposure are major threats to individual health according to World Health Organization (WHO). They may damage central nervous function, lungs, kidneys, liver, and bones which may increase the risk of some cancers.[24] Various techniques have been applied to remove the heavy metal ions from wastewater. Some of them are well established methods.[25,26,27,28] Among them adsorption technology has attracted considerable attention due to its simplicity and low cost. A few examples of MOFs applied for the removal of various heavy metal ions are illustrated here. Ke and his coworkers[29] synthesized a thiol-functionalized 3D Cu-based MOF, i.e. $[Cu_3(BTC)_2(H_2O)_3]_n$ (HKUST-1, BTC = benzene-1,3,5-tricarboxylate), by a facile coordination based post synthetic strategy, and demonstrate their application for removal of heavy metal ion from water. They also examined that the thiol-functionalized $[Cu_3(BTC)_2]_n$ shows high Hg^{2+} adsorption capacity of 714.29 mg g^{-1} from water, whilst the unfunctionalized compound shows no adsorption of Hg^{2+} under the same condition. Liang et. al.[30] reported a novel sulfur-functionalized MOF FJI-H12 produced by octahedral cages (M_6L_4) and free NCS-lignds. This MOF is able to remove Hg^{2+} ions entirely and specifically from water with much adsorption capacity of 439.8 mg g^{-1} among other MOFs materials. Moreover, a nonstop and speedy removal of Hg^{2+} ions from water has also been occurred through by means of a column loaded with FJI-H12 microcrystalline. Yu and his coworkers[31] developed a porous Zn(II)-based MOF decorated with O^- groups for the removal of Pb^{2+} ions. The MOF exhibits exceptionally high Pb^{2+} adsorption capacity of 616.64 mg g^{-1}, compared to the other estblished MOF adsorbents. In addition, it is capable of adsorption of Pb^{2+} ions predominantly with a large amount of efficiency (>99.27%) amid other ions. Besides, it exhibits very high adsorption capacity (>99.21%) ignoring the presence of other competitive ions, like Ca^{2+} or Mg^{2+}, in a short period. A water-stable triazine-based MOF (CAU-7-TATB) was effectively synthesized and used for removal of Pb(II) from water and almost 80.6% removal of Pb(II) was achieved, demonstrating adsorption capacity of 63 mg/g within 20 min in presence of interfering ions Cr(III), Co(II), Ni(II), Mn(II), Zn(II), Mg(II) and Ca(II).[32] However, almost two hours duration was required by activated carbon to remove about 90% of Pb(II) from aqueous solution.[33] Several other articles reported the adsorption of heavy metals by MOFs which are listed in table 1.

Table 1 Heavy metal adsorption by MOFs

MOF	Pollutant	Adsorption capacities (mg/g)	Ref.
Fe-Co MOF	As(V)	292.29	34
Al-MOF-GO	As(III)	65	35
Zr-MOF	As(III)	205.0	36
UiO-66	As(V)	303.4	37
Zn-MOF	U(VI)	129.36	38
La-PDA	U(VI)	247.6	39
MIL-101-DETA	U(VI)	350	40
Fe_3O_4@ZIF-8	U(VI)	523.5	41
HKUST	U(VI)	787.4	42
3D bioMOF	Hg(II)	900	43
Tb-MOF	Pb(II)	547	44
FJI-H9	Cd(II)	286	45
$Cu_3(BTC)_2$-SO_3H	Cd(II)	88.7	46

Crystal Structures of some selected MOFs



(a) (b) (c)

Figure1. (a) The topological structure of **FJI-H12** ($[Co_3(Timt)_4(SCN)_6(H_2O)_{14}(EtOH)]_n$) with a two-fold penetration. (b) Stick model of one-fold network composed of M_6L_4 cages (C=grey, N=light blue, S=yellow, Co=cyan). (c) Schematic representation of one M_6L_4 cage with free-standing NCS- groups. [30]

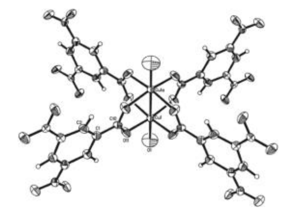


Figure 2. 3D structure of $[Cu_3(BTC)_2(H_2O)_3]_n$ (HKUST-1)[29]

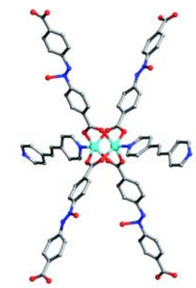


Figure 3. Coordination environment of the Zn centers in $\{[Zn_3L_3(BPE)_{1.5}]\cdot 4.5DMF\}_n$ [31] (Zn=Cyan, O=Red, N=Blue,C=Gray)

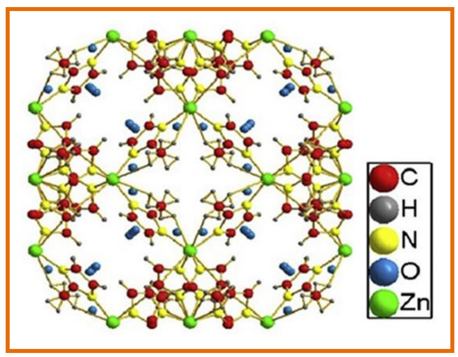


Figure 4. Crystal structure of ZIF-8 [36]

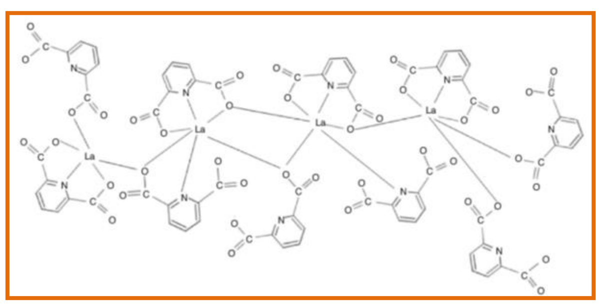


Figure 5. Crystal structure of $\{[La_4(PDA)_{10}(H_2O)_8]\cdot 2H_2O\}_n$ (La-PDA) [39]

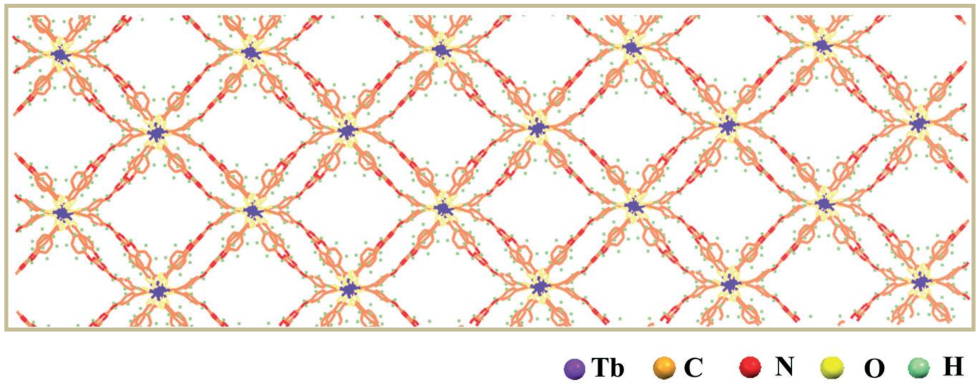


Figure 6. Crystal structure of Tb-MOF [44]

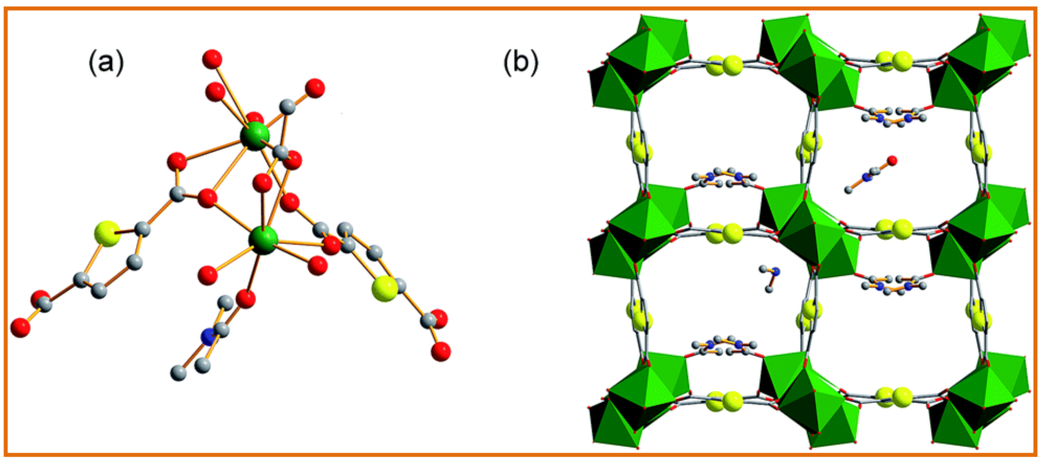


Figure 7. (a) The coordination environment of **FJI-H9**, (C = grey, N = blue, O = red, S = yellow, Ca = green); (b) the 3D structure of **FJI-H9** [45]

3. Conclusion

Due to the fast enhancement of industrial and mining activities, water pollution by heavy metal ions has become a severe threat to environment as well as public health. The toxic heavy metal ions are responsible for the water pollution. So the removal of these metal ions from water is very urgent. Numerous techniques have been developed to efficiently remove these toxic metal ions. The remediation of water and environmental protection are chief concerns globally. Adsorption is the most important application of MOFs for removal of emerging pollutants from water. High surface area and tunable porosity of MOFs enhances the ability to capture the heavy metal ions from aqueous media. Phytoremediation is more eco-friendly process among the other methods for removal of heavy metals.

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