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Effects of functional groups in metal-organic frameworks of isoreticular UiO-66 topology in heavy metal removal: A Review

R.M.H.Y. Rajapaksha[a], T.M.M. Marso[b,e], N.P. Liyanage[c], N.P.W. Rathuwadu[a] and S.B. Alahakoon[d*]
[a]Institute for Combinatorial Advanced Research and Education (KDU-CARE), General Sri John Kotelawala Defence University, Ratmalana 10390, Sri Lanka.
[b] Department of Chemical Sciences, Faculty of Applied Sciences, Southeastern University, Sammanthurei, Sri Lanka.
[c] Department of Science and Technology, Faculty of Applied Sciences, Uva Wellassa University, Badulla, Sri Lanka.
[d]Department of Chemistry, Faculty of Sciences, University of Peradeniya, Peradeniya, Sri Lanka.
[e] Postgraduate Institute of Science, University of Peradeniya, Peradeniya, Sri Lanka

*** Corresponding author email address**: sampath.alahakoon@sci.pdn.ac.lk

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Abstract:

Wastewater treatment is a critical process for maintaining environmental sustainability and human health. Heavy metal pollution in wastewater poses a significant challenge due to its toxicity and persistence in the environment. Consequently, there is a growing endeavour to create efficient and reliable technologies for the elimination of heavy metals and, researchers have been driven to investigate emerging areas of material science due to their desire to create cost-effective, streamlined approaches. Metal-organic frameworks (MOFs) have emerged as promising materials for the removal of heavy metals from wastewater mainly due to high stability at aqueous medium, high surface area, tuneable pore sizes, and exceptional adsorption capacities. Suitable synthesis or post-synthesis functionalization strategies can be employed to attain the desired characteristics in MOFs. Among the various MOFs, UiO-66 topology-based frameworks have demonstrated excellent performance in heavy metal removal, owing to their tailorable surface chemistry, selectivity, and regenerability. This review article aims to explore the effects of functional groups in heavy metal adsorption processes in MOFs of isoreticular UiO-66 topology in wastewater treatment. It provides an overview of the synthesis methods, structural properties, and surface modifications of UiO-66 MOFs. Furthermore, the article highlights the role of functional groups in enhancing the adsorption efficiency and selectivity of UiO-66 MOFs in heavy metal sorption and the stability of the MOFs in aqueous conditions.

Keywords: Heavy metals, Metal-organic frameworks (MOFs), Adsorption.

1. Introduction

Water is crucial for all forms of life and is a fundamental feature of our planet. While most of the water is found in oceans (97.5%), only a small portion (1%) is available for extraction and utilization for drinking purposes/ direct consumption. Over recent years, there has been growing apprehension about water pollution caused by new and hazardous pollutants resulting from human activities. Advanced economies have taken steps to enhance the quality of discharged water from public wastewater treatment plants (WWTPs) and other specific sources since the early 1970s[1]. Up until now, the primary sources of water pollution encompass industrial waste, resource mining, oil spills, leaks of nuclear waste, application of pesticides, etc. These activities result in a variety of harmful residues that contaminate water and pose significant risks to the environment and human health. The primary contaminants found in wastewater typically consist of heavy metal ions (or oxyanions/cations/metal complexes), radioactive materials, polyaromatic hydrocarbons, pesticides, pharmaceuticals, and dyes[2]. In contrast to organic pollutants, metal ions are non-degradable, non-volatile, and tend to accumulate in living organisms over time. Heavy metals are metallic elements or metalloids with atomic weights between 63.5 and 200.6 g/mol and specific gravities above 5.0 and found naturally in the environment, but their concentration is rapidly increasing due to industrial wastewater[3]. The common heavy metal ions found in wastewater comprise As, Cu, Cr, Pb, Hg, Ni, and Zn ions[4].

Therefore, it is crucial to remove them at the early stages of anthropogenic activities. To address these concerns, numerous strategies and techniques have been suggested for treating and purifying wastewater, including coagulation, filtration, chemical precipitation, adsorption, and similar methods. In terms of energy and economic considerations, employing adsorption or utilizing photocatalytic reactions with sunlight to eliminate water pollutants is a more favourable and promising approach. Adsorption is a simple, cost-effective, and widely used method for eliminating heavy metals from waste solutions in wastewater treatment facilities[5]. Adsorption process using metal organic frameworks (MOFs) have recently been studied for the removal of heavy metals in water, among various other methods.

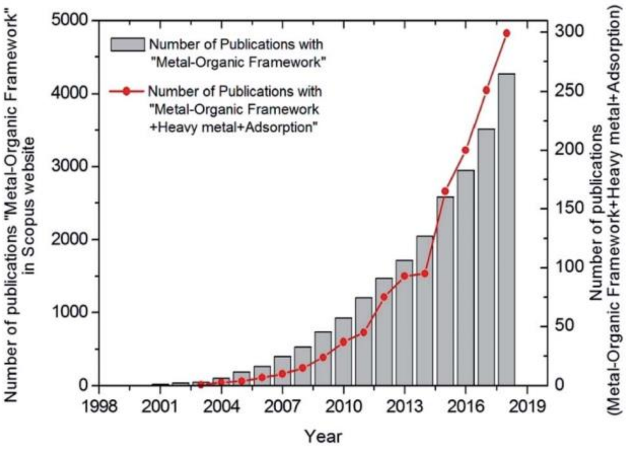

Fig.1. Number of publications on MOFs and metal adsorption based on data in the Scopus database[6].

Metal organic frameworks were initially reported in the 1950s, and the word "MOF" gained popularity in the 1990s[5]. MOFs are crystalline porous coordination polymers made up of metal ions connected by organic bridging ligands[7]. A wide range of MOFs with various topologies and physicochemical properties have been synthesized over the past decades. Among them the most often utilized MOFs are HKUST-1[8], MIL-88B[9], MIL-53[10], the ZIF family[11], MIL-101[12], PCN-221[13] and UiO-66[14]. MOF-based materials have shown promise in gas storage and separation, sensors, catalysis, solar cells, medication delivery, and environmental cleanup applications[15]. The UiO-66 MOF exhibits remarkable features in the heavy metal adsorption process due to several reasons: high surface area, tuneable pore size, exceptional stability, Lewis acidity, and regenerability. By incorporating functional groups into porous MOFs, these groups can be effectively disseminated and utilized. Furthermore, the number of functional groups in MOFs, particularly UiO-66-type MOFs, may be easily and precisely adjusted, which is useful for systematically understanding the effect of functional groups on heavy metal adsorption[16].

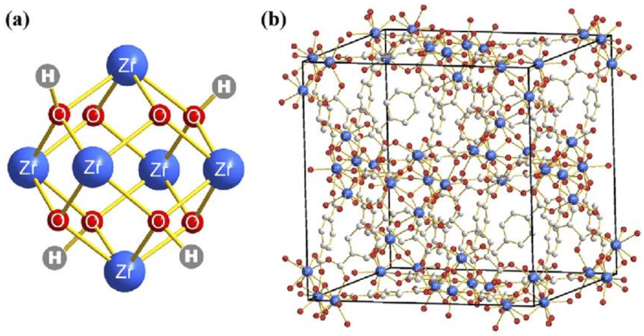

Fig. 2. A color-coded illustration of the octahedral zirconium cluster and 3D unit cell of UiO-66 framework MOF[7].Blue, red and grey represent Zr, oxygen and H atoms, respectively

This review investigates the effects of functional groups in heavy metal adsorption processes in Metal-Organic Frameworks with isoreticular UiO-66 topology in wastewater treatment. UiO-66 is made up of a cubic framework of cationic $Zr_6O_4(OH)_4$ nodes (produced in situ through ZrCl4 hydrolysis) and 1,4-benzenedicarboxylate linkers (BDC) (Figure 1.). It presents an overview of UiO-66 MOF synthesis methods, structural characteristics, and surface modifications. Furthermore, the research emphasizes the importance of functional groups in improving the adsorption efficiency and selectivity of UiO-66 MOFs towards heavy metal ions, as well as their stability in aqueous conditions.

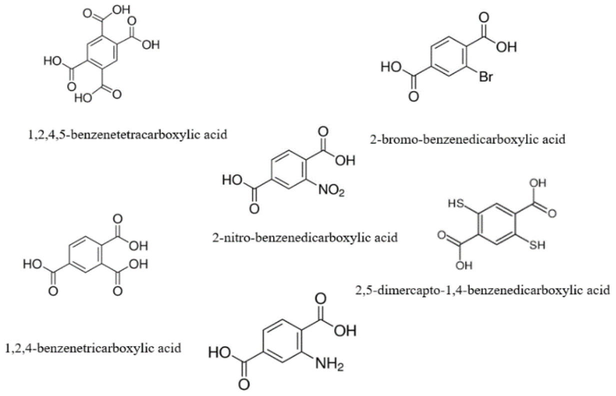

Fig. 3. Organic linkers used for the synthesis of functionalized UiO-66 MOF derivatives.

2. UiO-66 MOF and derivatives

UiO-66 and its derivatives are currently regarded as shining beacons in the realm of crystalline materials due to their exceptional properties compared to other literature MOFs.

These material's remarkable porosity, tunability, and unmatched versatility, make them invaluable for a myriad of applications. The most prevalent technique for heavy metal remediation is to anchor organic functions (Figure 2) on easily accessible MOF sites to improve affinity and selectivity toward the target metal ion. Leus et al. at the University of Oslo, produced UiO-66, a Zr-based MOF, in 2008[17]. It consists of a highly stable inorganic brick of inner $Zr_6O_4(OH)_4$ cores coupled to 12 carboxylate groups arising from the 1,4-benzenedicarboxylic acid struts to form $Zr_6O_4(OH)_4(CO_2)_{12}$ clusters. The stable Zr—O bonds generated between the inorganic brick and the carboxylate groups account for unusually high heat stability (up to 540 ℃). Its cubic 3D structure is made up of an octahedral cage that is linked to eight corner tetrahedral cages[18]. The functionalization of benzene 1,4-dicarboxylic acid (BDC) adds to the modification of the chemical and physical properties of UiO-66 on its own. There have been numerous reports on the systematic creation of a succession of frameworks with structures based on the skeleton of UiO-66, where the pore functioning and size have been varied without affecting the original topology[19]. In numerous research efforts, extended structures of the Zr-based MOF UiO-66 were assembled with various commercially available ligands such as 2- aminobenzene- dicarboxylic acid(H_2N-H_2BDC)[20],2,5-dimercapto-1,4-benzenedicarbo -xylic acid (H_2DMBD)[21], 2 nitrobenzene- dicarboxylic acid (O_2N-H_2BDC)[19], and 2-bromobenzene- dicarboxylic acid(Br-H_2BDC),5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin (H_2TCPP)[13],(UiO-66-$(COOH)_n$, n = 0,1,2,4) [16] etc.

Table 1. Extended structures of the Zr-based MOF UiO-66 assembled with various commercially available ligands.

MOF Type	Modification-Linker	Ref.
PCN-221	5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin (H_2TCPP)	[13]
UiO -66(Z r)-N H_2	H_2BDC- NH_2	[22]
UiO-66-COOH and UiO-66-$(COOH)_2$	Trimellitic (1,2,4-BTC acid) 1,2,4,5-benzenetetracarboxylic acid (H_4BTEC)	[14]
MOF-801	Fumaric acid	[23]
Zr-DMBD	2,5-dimercapto-1,4-benzenedicarboxylic acid (H_2DMBD)	[24]
UiO-66-NO_2	2-nitroterephthalic acid (H_2BDC-NO_2)	[25]
UiO-66- Br	H_2BDC-Br	[26]

3. Synthesis methods

MOFs have appealing physicochemical features, making them appropriate for a wide range of applications, including water purification. MOFs can be created using a variety of synthetic methods. They are divided into two types: conventional and non-conventional approaches. Hydrothermal and solvothermal processes are examples of conventional methods. Non-conventional techniques include microwave-assisted, electrochemical, ionothermal, and mechanochemical procedures. The most typical technique for heavy metal remediation is to anchor organic functions on easily accessible MOF sites to improve affinity and selectivity toward the target metal ion. These adjustments could be made during the MOF fabrication process (in -situ) or after the MOF synthesis process (post-synthesis)[5]. The UiO-66 MOF derivatives are depicted in Figure 3 together with scanning electron microscopy (SEM) pictures of the produced MOFs in particle form. Some of the most recent approaches for UiO-66 MOF derivatives functionalization using organic ligands are briefly reviewed in the subsections.

3.1 N- based functionalities

Nitrogen-based functionality (N-donors) is tough to borderline bases in the Hard Acid Soft Base (HASB) concept and could interact successfully with heavy metals and actinides. These N-based organic functionalities have been studied for decades and integrating them into MOFs improves their affinity for metal ions.

Chavan *et.al* used solvothermal synthesis to create a series of amine-functionalized mixed-linker metal organic frameworks (MOFs) of the UiO-66 framework topology, with the idealized structural formula $Zr_6O_4(OH)_4(BDC)_6X(ABDC)_6X$ (where BDC = benzene-1,4-dicarboxylic acid, ABDC = 2-aminobenzene-1,4-dicarboxylic acid)[20]. The adsorptive removal of Pb^{2+} and Cu^{2+} from wastewater solutions was investigated using the Zr-based MOFs UiO-66 and UiO-66-NH_2, by Lei et al. In that study, loading metal-organic frameworks (UiO-66 and UiO-66-NH_2) on flexible cellulose aerogels as metal-organic frameworks-cellulose aerogels composite materials and utilizing situ growing process at room temperature. The pre-synthetic cellulose aerogels are soaked in the metal ion precursor, and then the organic ligand is introduced to allow the MOFs to develop on the Cellulose aerogels[27]. Microwave heating was utilized to synthesize UiO-66-NH_2 MOF, which was then integrated into polyacrylonitrile/chitosan nanofibers for the removal of Pb(II), Cd(II), and Cr(VI) ions studied by Jamshidifard et al.[28]. A simple solvothermal method was used in another study to successfully create the zirconium metal-organic frameworks (UiO-66 and UiO-66-NH_2), which were then used to adsorb As(III) from contaminated water[29]. The synthesis of the functionalized MOF UiO-66-NO_2 was initiated by Kandiah et al., using O_2N-H_2BDC, $ZrCl_4$, and DMF as the starting materials and producing MOFs with the same topology of the parent UiO-66[18].

3.2 S-based functionalities

The usage of S-containing MOFs is a frequent technique, especially for removing soft metal ions such as Hg(I), Cd (II), and Hg(II). Adsorption by MOF adsorbents is facilitated by the strong interaction between S-donor soft bases and soft acids.

The Zr-DMBD frameworks are formed by solvothermal conditions reacting $ZrCl_4$ with 2,5-dimercapto-1,4-benzenedicarboxylic acid (H_2DMBD) to form the hard carboxyl and soft thiol functionalities. Syntheses of the Zr-DMBD framework were carried out with varying amounts of acetic acid added as modulators to promote crystallization [21](Ding et al., 2018a).

3.3 O-based functionalities

Zhao et.al, developed a sequence of UiO-66-(COOH)$_n$ (n = 0, 1, 2, 4) MOFs successfully in an intriguing work, using conventional solvothermal methods. Comparable topological shapes but varied carboxyl group distributions in the produced materials. In order to confirm the function of -COOH and the potentials of these UiO66-type MOFs in Pb^{2+} adsorption, a systematic analysis of adsorption performances was conducted[16]. Katz et al. designed a UiO-66-(OH) and UiO-66-(OH)$_2$ structures with the use of hydroxyl functional groups[18].

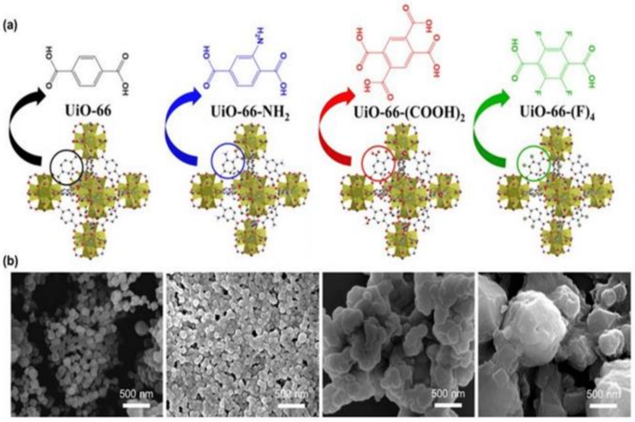

Fig. 4. The structures of the UiO-66-based MOFs with different functional groups, including UiO-66, UiO-66-NH$_2$, UiO-66-(COOH)$_2$, and UiO-66-(F)$_4$ and (b) the corresponding SEM images of these synthesized MOFs[31].

3.4 Other functionalities

Kandiah et al., synthesis the functionalized MOF, UiO-66-Br by determining the reaction conditions necessary to produce MOFs with the same topology of the parent UiO-66. [19]. In here, to develop the MOF, Br-H_2BDC, $ZrCl_4$ and DMF utilized as starting materials.

4. Physical properties of UiO-66 MOFs derivatives

MOF-based adsorbents have gained a lot of attention due to their high surface area and porosity structure. A MOF's surface area is largely influenced by the metal ion and organic linker and, to a lesser extent, by the synthesis method, solvent, etc. When MOFs are modified with organic functions, these functionalities are grafted into the MOF pores, reducing the surface area and pore diameter[19]. In a nutshell, the MOF's surface has many active sites, which contribute to the adsorption process, and metal ions diffuse via the framework's pores. The abundance of active sites for the binding of metal ions on the surface more than makes up for the decrease in surface area. Due to their crystalline structure and pore size distribution, MOFs have highly organized pores. To ensure high sorption capacities, pore size and ionic radius, the compatibility of the adsorbate is a further crucial factor.

Water stability is a crucial requirement for an adsorbent to be used in wastewater treatment. Industrial wastewaters differ widely in pH, which is mostly dependent on the contents. Acidic high-level waste solutions are produced by nuclear energy installations. Due to their great structural stability in basic/acidic conditions, Zr-MOFs are one of the most frequently utilized materials for heavy metal decontamination[32]. Selective host-guest interactions result from the creation of recognition sites on the MOF surface by the presence of certain moieties. According to Pearson HSAB theory, the ligands with O, N, and S as the donors might be categorized as hard, hard to borderline, and soft bases, respectively.

In this brief description, it is intended to how the binding of carboxyl, thiol, and amine groups enhances the physical properties of UiO-66 derivatives. These functional groups improve the adsorption capacity, stabilize the framework structure, provide additional coordination sites, and enhance absorptivity. Table 2. shows the physical and structural features of variously functionalized MOFs.

4.1 Effect of carboxyl group

The introduction of carboxyl groups onto UiO-66 MOF alters its physical properties, including surface charge, hydrophilicity, and adsorption capacity. Zhao et al. study on the synergetic effect of pore structure and amount of carboxyl site for effective removal of Pb^{2+} in Metal-Organic Frameworks. The FTIR spectra of UiO-66-COOH, UiO-66-(COOH)$_2$, and UiO-66-(COOH)$_4$ show extra peaks at 1720 cm^{-1}, indicating the presence of uncoordinated COOH groups in the three MOFs. Additionally, because of the three MOFs' practical COOH group contents, the band in the spectra of UiO-66-COOH is weaker than those of UiO-66-(COOH)$_2$ and UiO-66-(COOH)$_4$. Obviously, the BET specific surface areas and pore volumes of the MOFs gradually reduced as the number of carboxyl groups increased[16].

Zhang et al. created UiO-66 and its carboxyl derivatives (UiO-66-COOH and UiO-66-(COOH)$_2$) and tested them for their ability to extract Th (IV) from a weak acidic solution. While the average particle size of carboxylated UiO-66s (UiO-66-COOH and UiO-66-(COOH)$_2$) remains unchanged, the carboxyl groups' insertion has resulted in the coarsening of the particle surface at the interfaces[14].

Table 2. Summary of the physical properties and adsorption behaviour of functionalized UiO-66 MOF derivatives on heavy metals in aqueous solutions under various experimental circumstances (Co-Initial concentration of the metal ion solution and Q_m- maximum adsorption capacity of the adsorbent toward heavy metals).

	Physical Properties			**Experimental conditions**							
MOF	**S_{BET} ($m^2 g^{-1}$)**	**Pore Volume ($cm^3 g^{-1}$)**	**Geometry**	**Metal ion**	**C_o (ppm)**	**pH**	**Time/h**	**T/K**	**Q_m (mg g^{-1})**	**Removal %**	**Ref.**
UiO-66-COOH	645	0.43	Octahedron	Pb(II)	0−1000	4.8	12	303	140.0	33.31	[16]
UiO-66-$(COOH)_2$	443	0.22	Octahedron	Pb(II)	0−1000	4.8	12	303	420.2	99.99	[16]
UiO-66-$(COOH)_4$	135	0.23	Octahedron	Pb(II)	0−1000	4.8	12	303	253.2	60.25	[16]
UiO-66-NH_2	113.4	0.332	Octahedron	As(III), As(V)	-	1.0–13.5	24	298	200 71.13	73.47 75.51	[29]
Zr-DMBD	262.81	0.33	Octahedron tetrahedral	Hg(II), Pb(II), Cd(II), Cu(II)	500	6	6	298	171.5 97.0 43.8 40.2	99.64 56.36 25.45 23.36	[33]

4.2 Effect of thiol group

The combination of carboxyl and thiol thus illustrates the broader applicability of the hard-and-soft approach for functional frameworks. A potentially effective molecular design technique for coordination networks is the combining of carboxylic and sulfur functionalities (such as thioether or thiol). Strong, porous coordination networks have free-standing, reachable thiol functionalities (SH) implemented for a variety of solid state reactivities and characteristics. The thiol groups decorate the pores and the carboxyl group is linked to the rigid Zr(IV) core. The surfaces of thiol-modified Zr-DMBD samples are rougher than that of UiO-66. Incorporating the highly reactive thiol group has clear benefits such as, 1) The stronger-binding thiol groups would allow the uptake of various metal ions into MOF pores—for example, for efficient removal of heavy metal ions, 2) The adaptable organic transformations by thiols also allow for convenient post-crystallization (post-synthetic) modifications, for example, covalent cross-linking inside the pores[24].

In this study, Zr-DMBD's free energy of adsorption (E) values are greater than 8 kJ/mol, indicating that chemical adsorption effects predominate in the adsorption process.

4.3 Effect of amine group

The introduction of amine groups onto UiO-66 MOF leads to changes in its physical properties, including altered surface charge, modified pore structure, and enhanced reactivity towards acidic species. UiO-66-NH_2, the fully amino functionalized isostructural analogue, is thermally less stable than unmodified UiO-66, which is consistent with findings on other framework types. Additionally, due to the steric barrier provided by the high density of pendant NH_2 groups pointing into the cavities, post-synthetic alteration of UiO-66-NH_2 can be difficult. The fully functionalized amino MOF is less porous than the parent UiO-66. Since the NH_2 group will block a portion of the vacant area, this is to be expected. Additionally, it is seen that the surface area and pore volume consistently decrease as the ABDC content of the framework rises[20]. One interesting study shows the Polyacrylonitrile/chitosan /UiO-66-NH_2 nanofibrous adsorbent has a larger potential for metal ions sorption than other investigated adsorbents due to the large specific area and functional groups of MOF, such as carboxylic, amine, hydroxyl, and oxygen for chelating with metal ions. The flux and Pb(II) ion rejection by MOF-loaded nanofibers were 452 $Lm^2 h^{-1}$ and 94%, respectively[28].

5. Adsorption process of UiO-66 MOF derivatives toward heavy metals

The adsorption process is the adhesion of an adsorbate, i.e., atoms, ions, or molecules, from a gas, liquid, or dissolved solid to a solid surface creating a film on the adsorbent surface. Since it is a phenomenon that occurs on the surface, adsorbents with a higher surface area will favour the adsorption process. In this sense, UiO-66 MOF-based derivative adsorbents have gained a lot of attention due to their great stability and high adsorption capacities relative to other MOFs[18]. The adsorption process of heavy metals on

UiO-66 derivatives is influenced by various factors that play a crucial role in determining the adsorption capacity and efficiency. Understanding these factors is essential for optimizing the design and application of UiO-66 derivatives in heavy metal removal processes. Factors such as the structural properties of UiO-66 derivatives, including pore size, surface area, and crystallinity, significantly affect the adsorption process by providing suitable sites for heavy metal ion binding. The presence of functional groups, such as carboxylic, amine, or nitrite groups, on the surface of UiO-66 derivatives also plays a vital role in facilitating interactions with heavy metal ions.

Thus, modified MOF containing either N or S-donors can more effectively adsorb soft and borderline metal ions such as Hg(II), Hg(I), Pb(II), Pd(II), Cd(II), Ag(I), and Au(III). Similarly, hard metal ions like Cr(III), As(III), Ln(III), Th(IV), and U(VI) have a greater binding affinity for MOFs having O-donor functions. The focus is now on creating highly selective metal-binding ligands and their anchoring mechanisms thanks to the most recent strategy of employing macrocyclic groups or chelating ligands with numerous donor sites[5]. Additionally, parameters like pH, temperature, contact time, initial concentration of heavy metals, and competing ions in the solution can influence the adsorption process by altering the electrochemical properties and surface chemistry of UiO-66 derivatives. By comprehending the intricate interplay of these factors, researchers can optimize the adsorption process and develop efficient strategies for heavy metal removal using UiO-66 derivatives.

The subsequent text elucidates the impact of various functional groups on the capacity of adsorption.

In the presence of attached carboxylic groups in UiO-66 derivatives exerts a significant influence on the adsorption capacity due to their ability to enhance intermolecular interactions, providing additional binding sites and promoting stronger adsorbate-sorbent interactions. The theory of hard and soft acid-base reactions has been used to generate stable MOFs using high-valence Zr (IV) cations with rigid carboxylate-type ligands.

UiO-66-$(COOH)_2$ has a greater adsorption capability than UiO-66, UiO-66-COOH, and UiO-66-$(COOH)_4$ (removal percentage, >99.99%). It should be observed that UiO-66-$(COOH)_4$ has a lower adsorption capacity than UiO-66-$(COOH)_2$ despite having more COOH groups. Moreover, the measurement of SEM-EDS mapping (scanning electron microscope -energy dispersive X-ray system) was used to directly verify the UiO-66 type MOFs' distinct adsorption behaviour. The carboxyl-grafted UiO-66s exhibit Pb^{2+} adsorption and the most pronounced Pb^{2+} mapping occurs to UiO-66-$(COOH)_2$.

Zhao et al. performed the two common isothermal modes, the Freundlich and Langmuir isothermal models, to match the adsorption data. According to the fitting results, the four MOFs' adsorption behaviours match better with the Langmuir isotherm model, indicating that Pb^{2+} was adsorbed as a monolayer in these UiO-66-type MOFs. From the fitting results, it can be seen that Pb^{2+} adsorption on UiO-66-COOH, UiO-66-$(COOH)_2$, and UiO-66-$(COOH)_4$ can fit better with the pseudo second-order model, indicating a chemisorption process may be the rate-limiting step in the adsorption process of these MOFs.

The computed value of ΔH at 303-323 K, 6.836 kJ mol^{-1}, suggests that the adsorption process was an endothermic one. The increase in randomness during the adsorption process was indicated by the positive ΔS value, while the spontaneous adsorption of Pb^{2+} in UiO-66-$(COOH)_2$ was indicated by the negative ΔG value [16].

Thiol groups can effectively grab metal ions as independent and accessible groups, and the chemically hard carboxyl group binds the hard Zr(IV) core for the development of a framework.

Ding et al., explained the adsorption behaviour of thiol functionalized UiO-66 derivatives and, in the isotherm studies, better explained the Langmuir model than the Freundlich model, which suggested that the adsorption process of heavy metals with UiO-66-SH MOFs, showing homogeneous adsorption process[33].

The incorporation of attached amine groups in UiO-66 derivatives exerts a remarkable influence on the adsorption capacity owing to their capability to facilitate interactions through hydrogen bonding, electrostatic attractions, and coordination with adsorbates, thereby enhancing the overall adsorption performance. UiO-66@CA(CA- cellulose aerogels) and UiO-66-NH_2@CA modified MOF's Adsorption capacity was determined to be Lei et al. and he explained the adsorption of Pb^{2+} and Cu^{2+} metal ions on this two types of MOFs, was time-dependent, and a pseudo-second-order kinetic model with the rate constant k_2 provided a good fit to the data[27].

The presence of attached nitrite groups in UiO-66 derivatives exerts a profound impact on the adsorption capacity due to their unique electronic properties and ability to undergo redox reactions. These nitrite groups serve as electron acceptors or donors, facilitating electron transfer processes during adsorption, and thereby significantly enhancing the adsorption performance and capacity of UiO-66 derivatives.

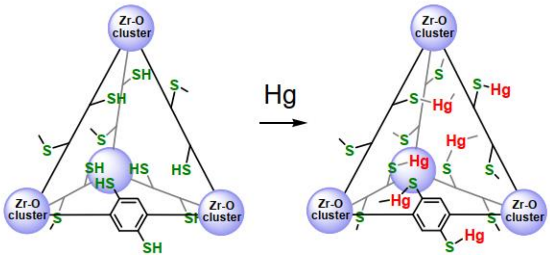

Fig.5. Adsorption of Hg(II) on the Zr-DMBD network[21].

Yang et al. studies the gelatine/UiO-66-NO_2 film composite hydrogels' adsorption rate with heavy metals and the adsorption process is best explained by the pseudo-second-order kinetic model. By exchanging or sharing electrons with the gelatine/UiO-66-NO_2 film composite hydrogels, Pb (II), it is suggested that the adsorption is a chemisorption that involves valence forces. The adsorption behaviour of Pb(II) gelatine/UiO-66-NO_2 film composite hydrogels is better described by isotherm fitted curves and the Langmuir model, indicating that Pb(II) is taken up by monolayer adsorption in both the gelatine hydrogel and the gelatine/UiO-66-NO_2 film composite hydrogels[25].

6. Adsorption mechanisms of UiO-66 derivatives for heavy metal adsorption

The adsorption mechanisms of UiO-66 derivatives with heavy metals involve a complex interplay of various factors, which contribute to their exceptional adsorption performance. Understanding these mechanisms is crucial for optimizing the design and application of UiO-66 derivatives in heavy metal removal processes. Several key factors, including the structural properties of UiO-66 derivatives, the presence of functional groups, and the nature of the heavy metal ions, greatly influence the adsorption capacity and efficiency. By comprehending the intricate interplay between these factors, researchers can unravel the underlying mechanisms and devise tailored strategies for efficient heavy metal removal using UiO-66 derivatives.

Acidic functional groups like COOH can be useful for the capture of heavy metal ions due to the better electron-accepting ability of heavy metal ions than that of H^+. Acidic groups can be effectively disseminated and utilized further by adding them to porous MOFs. Additionally, the number of functional groups in MOFs may be easily and accurately altered, particularly for the UiO-66-type, which is helpful in thoroughly comprehending the impact of functional groups on metal adsorption. Zhao et al. carried out, DFT calculations (density functional theory) and XPS measurements to elucidate the coordination mode between Pb^{2+} and carboxyl groups, particularly in UiO-66-$(COOH)_2$ to illustrate how Pb^{2+} and UiO-66-$(COOH)_2$ interact strongly. Overall, the Pb-O bond was created during the adsorption process, and Pb^{2+} can interact strongly with the free COOH groups in the MOF. According to mechanism analysis, carboxyl groups are crucial to the Pb^{2+} adsorption process and create the Pb–O bond.[16]. In the Th^{4+} adsorption process on UiO-66-COOH MOF, the exchange with organic solvent contribute to the Th^{4+} uptake, Th^{4+} sorption in the carboxylated UiO-66s happened through the coordination of carboxyl anions with Th^{4+} ions.[14]

In the heavy metal adsorption on thiol functionalized MOFs, the softer thioether group (and even the thiol group) could persist as free-standing, secondary donor groups, but the harder, ionic carboxyl tends to attract metal ions for network formation.

The thioether function has been intensively explored in this context, leading to the creation of a number of porous networks containing free-standing thioether groups that have shown beneficial for metal uptake and other applications[24].

The presence of -SH groups in Zr-DMBD, along with its wide surface area and easily accessible cages, contribute to its improved ability to capture heavy metal ions.

Ding et. al well explained the mechanism of adsorption of heavy metals on thiol functionalized UiO-66 derivatives. Due to the strong chelation between the -SH groups and Hg (II) ions, the Hg(II) ions are quickly adsorbed onto the surface of Zr-DMBD. Thereafter, a proton exchange reaction causes the hydrogen atoms of the -SH groups to be replaced and released as H^+ ions in the reaction system. The reaction equation of thiol groups on Zr-DMBD is:[33]

$$-SH + Hg^{2+} + 2NO_3^{-} \rightarrow -S-Hg^{+} + H^{+} + 2NO_3^{-}$$

With the exception of As(V), the UiO-66-$(SH)_2$ showed greater absorption of all the metal ions. According to its unique adsorption process, which involves the ions being adsorbed by the zirconium clusters through Zr-O-As coordination bonds, which are more readily accessible without the steric hindrance of the thiol groups, the anomaly for As(V) absorption can be explained[34].

Adsorption of heavy metals on nitrite functionalized UiO-66 MOF, was interestingly explained by Yang et al. An adsorbent of the UiO-66-NO_2 film was chemically deposited on gelatine hydrogel and developed for Pb (II) removal both in water and apple juice. These findings imply that during the adsorption phase, Pb(II) interacted with the functional groups containing N. The gelatine/UiO-66-NO_2 film composite hydrogels successfully adsorb Pb (II), which suggests that the main adsorption mechanisms involved Pb(II) interaction with carboxyl and functional groups containing N on the surface of the hydrogels, hydrogels made of gelatine and UiO-66-NO_2[25]. He et al., explained the adsorption properties of UiO-66 and UiO-66(NH_2), indicating a similar adsorption mechanism. According to the determination of Gibbs free energy and the D-R isotherm model, the As adsorption processes were recognized as chemisorption and exothermic reaction. XPS and FTIR analysis revealed that the Zr-O bonds were important in As elimination. The major production of bidentate mononuclear complexes for As(V) and bidentate binuclear complexes for As (III) on the hexanuclear Zr cluster of UiO-66 was revealed by EXAFS spectra (Extended X-ray absorption fine structure)[29].

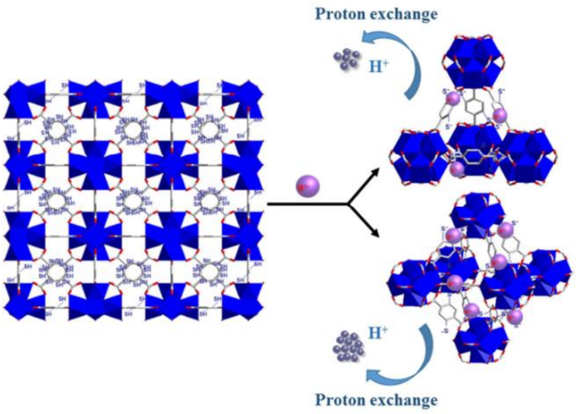

Fig.6. Hg(II) coordinated with S of thiol groups on Zr-DMBD through a proton exchange reaction mechanism[30].

7. Regeneration capability of UiO-66 derivatives

The regeneration ability of UiO-66 derivatives after the adsorption process of heavy metals is a critical aspect to consider in their practical application for environmental remediation. While the efficient removal of heavy metal ions from contaminated water or soil is essential, the ability to regenerate and reuse the adsorbent material enhances its sustainability and economic viability. Understanding the regeneration mechanisms and factors influencing the restoration of the adsorption capacity of UiO-66 derivatives is vital for developing effective regeneration strategies. By exploring innovative techniques and optimizing parameters such as pH, temperature, and desorbing agents, researchers can unlock the full potential of UiO-66 derivatives in long-term, sustainable heavy metal removal applications.

From various research studies, several methods have been identified for the regeneration of UiO-66 MOF derivatives after the adsorption of heavy metals. Widely applicable methods are available such as thermal regeneration, chemical regeneration, and solvent extraction to restore the adsorption capacity of UiO-66 derivatives. Here briefly mention a few techniques for further knowledge.

For the purpose of removing Pb^{2+} from Pb^{2+}@MOF, hydrochloric acid was chosen as the eluent in research studies. In order to prepare the eluent, hydrochloric acid was added to a solution of dimethylformamide and water. After Pb^{2+} adsorption, the sample was agitated in the eluent at 303 K for 12 hours during the regeneration process. The solid was then collected by centrifugation, rinsed with pure water, and then dried at 403 K overnight[16].

The ability of Zr-DMBD-Hg to regenerate, examined by Ding et al., using EDTA-2Na; Zr-DMBD-Hg complexes exposed to EDTA solution three times and stirred at 298 K for two hours each time. The Zr-DMBD-Hg was recycled in six successive adsorption and desorption cycles[33]. Yang et al. tested the reusability of produced gelatine/UiO-66-NO_2 film composite hydrogels-Pb (II) by immersing them in 0.1 M HCl for 7 hours, followed by a Pb(II) adsorption experiment on the eluted gelatine/UiO-66-NO_2 film composite hydrogels. After 8 times of reuse, the removal efficiency only shows a slight drop, indicating that the as-synthesized gelatine/UiO-66-NO_2 film composite hydrogels have considerable promise in the practical application of Pb(II) uptake[25]. Hua et al. effectively regenerated PAN/UiO-66-$(COOH)_2$-60 nanofibrous membranes with adsorbed Ln^{3+} ions using 0.25 M HCl aqueous solution as eluent[35].

8. Conclusion

In conclusion, this review has highlighted the effects of functional groups and heavy metal adsorption processes on metal-organic frameworks (MOFs) of isoreticular UiO-66 topology in the context of heavy metal removal. The study focused on UiO-66 MOFs and their derivatives due to their exceptional adsorption properties and tunability through functionalization.

Various synthesis methods were explored, providing researchers with a wide range of options to tailor the properties of UiO-66 MOF derivatives, such as pore size, surface area, and functional group incorporation. These methods play a crucial role in optimizing the performance of UiO-66 derivatives for heavy metal adsorption.

The physical properties of UiO-66 MOF derivatives, including their crystallinity, thermal stability, and surface morphology, were found to greatly influence their adsorption capacity. The presence of functional groups, such as carboxylic, amine, or nitrite groups, introduced additional binding sites and promoted stronger adsorbate-sorbent interactions, enhancing the overall adsorption performance.

The adsorption mechanisms of UiO-66 derivatives for heavy metal adsorption involve a complex interplay of electrostatic interactions and coordination reactions. Exploring these mechanisms provides valuable insights into the fundamental processes occurring during adsorption and aids in developing tailored strategies for efficient heavy metal removal.

Additionally, the regeneration capability of UiO-66 derivatives was highlighted as a crucial aspect for their practical application in heavy metal removal. Understanding regeneration mechanisms and developing efficient techniques for restoring the adsorption capacity of UiO-66 derivatives enhances their sustainability and economic viability.

Overall, this review emphasizes the significance of the synergistic effects between functional groups and heavy metal adsorption processes on UiO-66 MOFs and their derivatives for efficient heavy metal removal. Further research is needed to optimize synthesis methods, understand adsorption mechanisms, and explore regeneration and reusability techniques to fully harness the potential of UiO-66 derivatives in this field. The findings presented here provide a foundation for future studies aimed at advancing the use of functionalized UiO-66 MOFs in heavy metal removal applications.

9. The challenges and future perspectives of functionalized UiO-66 MOFs for wastewater treatment

Functionalized UiO-66 MOFs holds immense potential for wastewater treatment due to their unique adsorption properties. However, several challenges and future perspectives need to be addressed to maximize their effectiveness in this application. Firstly, optimizing the synthesis methods of functionalized UiO-66 MOFs is crucial to enhance their structural stability, surface area, and porosity, thereby improving their adsorption capacity for various pollutants. Additionally, gaining a deeper understanding of the adsorption mechanisms involved in wastewater treatment is essential to develop tailored strategies for specific contaminants. This includes investigating the effects of pH, temperature, and competing ions on adsorption efficiency.

Another critical aspect is the regeneration and reusability of UiO-66 MOFs. Exploring effective regeneration techniques is necessary to restore their adsorption capacity and ensure their long-term viability and cost-effectiveness. Research should focus on developing environmentally friendly and energy-efficient methods for regeneration, such as using mild desorbing agents or applying advanced technologies like photocatalysis or electrochemical regeneration.

Furthermore, future studies should aim to assess the performance of functionalized UiO-66 MOFs under realistic wastewater conditions, including complex mixtures of contaminants. Understanding the selectivity and kinetics of adsorption in such scenarios will enable the design of more efficient and targeted treatment processes.

Overall, optimizing synthesis methods, investigating adsorption mechanisms, exploring regeneration techniques, and assessing real-world wastewater treatment scenarios are key areas that require further research. Addressing these challenges will unlock the full potential of functionalized UiO-66 MOFs for effective and sustainable wastewater treatment.

Conflicts of Interest

There are no conflicts to declare.

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