Extraction of Metal Ions with Metal–Organic Frameworks

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Contributor: Natalia Manousi , Dimitrios A. Giannakoudakis , Erwin Rosenberg

Metal–organic frameworks (MOFs) are crystalline porous materials composed of metal ions or clusters coordinated with organic linkers. Due to their extraordinary properties such as high porosity with homogeneous and tunable in size pores/cages, as well as high thermal and chemical stability, MOFs have gained attention in diverse analytical applications.



1. Introduction

The terminology of metal–organic frameworks (MOFs) was initially introduced in 1995, when Yaghi and Li reported the synthesis of a new "zeolite-like" crystalline structure upon the polymeric coordination of Cu ions with 4,4′- bipyridine and nitrate ions, resulting to large rectangular channels ^[1]. MOFs are known to have superior characteristics, such as high surface area (theoretically up to 14.600 m²g⁻¹) ^[2], porosity of uniform in structure and topology nanoscaled cavities, and satisfactory thermal and mechanical stability. Therefore, metal–organic frameworks were established as successful candidates for various applications like environmental remediation, detoxification media of toxic vapors, heterogeneous catalysis, gas storage, imaging and drug delivery, fuel cells, supercapacitors, and sensors ^{[2][3][4][5][6][7][8][9][10][11][12][13]}.

In the field of analytical chemistry, MOFs have been employed in various analytical sample preparation methods including solid-phase extraction (SPE), dispersive solid-phase extraction (d-SPE), magnetic solid-phase extraction (MSPE), stir bar sorptive extraction (SBSE), and pipette tip solid-phase extraction (PT-SPE) ^{[14][15][16][17][18]}. Metal– organic frameworks have been also tested as stationary phases for high-performance liquid chromatography (HPLC), capillary electrochromatography (CEC), and gas chromatography (GC) with many advantages. Moreover, with the use of chiral MOFs, separation of chiral compounds has been also reported ^{[19][20][21][22]}.

Metal–organic frameworks have been synthesized and successfully applied for the preconcentration of heavy metals from environmental samples prior to their detection/analysis with a spectroscopic technique. The most common metal ions used in MOFs are Zn(II), Cu(II), Fe(III), and Zr(IV), while terephthalic acid, trimesic acid, or 2-methylimidazole have been excessively used as organic linkers ^[23]. Many efforts have been made in order to overcome the low water stability of MOFs toward the preparation of suitable sorbents for the extraction of metal

ions ^[24]. Compared with other sorbent materials, MOFs have a significant advantage of stable and homogeneous pores of specific sizes ^[25].

The effect of trace heavy metals on human health has attracted worldwide attention. Their increasing industrial, domestic, agricultural, and technological utilization has resulted in wide distribution in the environment. Metals such as cadmium, lead, mercury, chromium, and arsenic are considered as systemic toxicants and it, therefore, is essential to determine their levels in environmental samples ^[26]. Among the different analytical techniques that are widely used for the determination of metal ions are flame atomic absorption spectroscopy (FAAS), electrothermal atomic absorption spectroscopy (ETAAS), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) ^{[27][28][29]}.

Due to the low concentrations of metals and the presence of various interfering ions in complex matrices, the direct determination of such ions at trace levels is still challenging. Various novel materials including graphene oxide, activated carbon, carbon nanotubes, porous oxides, and metal–organic frameworks have been successfully employed for this purpose [30][31][32][33].

2. Stability of MOFs in Aquatic Environment

The stability of the framework in aqueous solutions depends on the strength of the metal–ligand coordination bonds ^[34]. The collapse of MOFs in the presence of water is linked to the competitive coordination of water and the organic linkers with the metal ions/nodes. The stability of the structure is also associated with other factors like the geometry of the coordination between metal-ligand, the surface hydrophobicity, the crystallinity, and the presence of defective sites ^[35]. The use of additives like graphite oxide, graphitic carbon nitride, nanoparticles, or the deposition on substrates such as carbon, fibers, or textiles, can have a positive effect on the framework stability ^[36] ^[37][38][39][40][41][42]. In order to evaluate the stability and as a result the properness of utilizing a MOF for adsorption application, the pH and the temperature under which the preconcentration of the metal will take place, must be considered.

The strength of the coordination between the organic moieties and the metal ions can be described in general according to the HSAB (hard/soft acid/base) principles ^{[9][42]}. Zr⁴⁺, Fe³⁺, Cr³⁺, and Al³⁺ are regarded as hard acidic metal ions, while Cu²⁺, Zn²⁺, Ni²⁺, Mn²⁺, and Ag⁺ as soft ones ^[34]. On the other hand, carboxylate-based linkers act as hard bases, while azolate ligands (such as pyrazolates, triazolates, or imidazolates) as soft bases. For that reason, most of the Zr-based UiO (University of Oslo) and MIL-53(Fe) (Material Institut Lavoisier) series possess remarkable water stability, while for instance one of the most known and studied MOF, HKUST-1 (Hong Kong University of Science and Technology) does not. On representative paradigm of Zn-based water-stable structure is the zeolitic imidazolate framework (ZIF), formed from imidazolate ligands and Zn²⁺.

When used in analytical chemistry, MOFs must be stable both under adsorption and under desorption conditions. Usually, adsorption of metal ions takes place under weakly acidic conditions (pH = 5-6), while desorption is performed predominately with the addition of a strong acid. However, even though many MOFs are stable under

adsorption conditions, they are decomposed with the addition of strong acids like nitric, hydrochloric, and sulfuric acid ^{[24][28]}. Other reagents that have been employed for the elution of metal ions without decomposing the MOF material are ethylenediaminetetraacetic acid (EDTA), sodium chloride (NaCl), or sodium hydroxide (NaOH) solution in EDTA or in thiourea.

3. Mechanisms of Metal Ions Extraction with Metal–Organic Frameworks

MOFs, as well as their composites, have been successfully applied as adsorbents for various heavy metal/metalloid species. The adsorption of the latter from aquatic environments is still among the ultimate research targets, and there are plenty of reports in which adsorption/removal of heavy metals was a success story ^{[43][44][45]}. Although, not all MOFs are water-stable as discussed above. The most widely reported interactions/mechanisms are collected in **Figure 1** ^[46]. In many cases, more than one mechanism is responsible for the high adsorptive capability of MOFs. The binding/interaction sites can be either the metal or the clusters as well as the linkers. In order to enhance the adsorptive capability and/or selectivity, the functionalization of the linkers, with groups as hydroxyl, thiol, or amide, is a well-explored and successive strategy.



Figure 1. A schematic illustration of the interactions/mechanisms involved in the adsorption of metals by metal– organic frameworks (MOFs).

Lewis acid–base interactions are the most common adsorption mechanism of metal ions by metal–organic frameworks ^[47]. The presence of O-, S-, and N-containing groups that act as Lewis bases is very important for the preconcentration of the various ionic species from aqueous solution since metal ions act as Lewis acids. The donor atoms of the MOFs are present in the molecules of the organic linkers. Pre- or post-synthesis functionalization of the frameworks can increase the number of O-, S-, or N-containing groups in order to enhance the adsorption

selectivity and efficiency of the target metal ions. Since Lewis acid–base interactions are critical for metal adsorption onto the donor atoms of the MOFs, it is obvious that the pH of the solution plays the most critical role, influencing the adsorption process and kinetics. In low pH value, those atoms are protonated, and adsorption cannot take place due to the repulsive forces of the cationic form of metal with the positively charged adsorption sites ^[48]. However, by increasing the pH of the aqueous samples that contain the metal ions, the donor atoms of the adsorbent are deprotonated and they become favorable for complex formation and sorption of the target analytes. In basic solutions, the addition of hydroxide may lead to complex formation and precipitation of many metals, therefore, after a certain pH value, any further increase can lead to a decrease of the sorption efficiency ^[49].

Adsorption by coordination is another adsorption mechanism in which the functionalization plays a key role. For instance, Liu et al. showed that the post-synthetic modification of Cr-MIL-101 with incorporation of -SH functionalities led to an improvement of Hg(II) removal, even at ultra-low concentrations ^[51]. This improvement was linked to the coordination between Hg(II) with the -SH groups. The incorporation of thiol-containing benzene-1,4-dicarboxylic acid (BDC) linkers in the case of UiO-66 MOF resulted in a material capable of simultaneously adsorbing As(III) and As(V) oxyanions. The adsorption of the former occurred via coordination to the -SH groups, while of the latter by the binding of the oxyanions to the $Zr_6O_4(OH)_4$ cluster via hydroxyl exchange ^[52]. The hydroxyl exchange mechanism was also proposed as the predominant capturing pathway in the study of Howard and co-workers ^[53], in which they studied the adsorption of Se(IV) and Se(VI) in water by seven Zr-based MOFs (UiO-66, UiO-66-NH₂, UiO-66-(OH₂), UiO-67, NU-1000, and NU-1000BA).

Additionally, the adsorption mechanism with metal–organic frameworks can be enhanced via the chelation mechanism, after functionalization of MOFs with compounds that can form chelating complexes with the metal ions ^[54]. For example, functionalization of metal–organic frameworks with dithizone can enhance Pb extraction by forming penta-heterocycle chelating complex compounds. In this case, the binding sites of the chelating molecules are also protonated in low pH values and adsorption cannot take place. Adsorption capacity increases with increasing pH until a certain point, normally at a pH value of 5 to 6. Further increase in pH value can lead to precipitation of the target analytes, due to hydrolysis ^[55].

In the case of the physical-based adsorption, various interactions can be responsible for the elevated adsorptive capability of MOFs as mentioned above. The net charge of the framework and the presence of specific functional groups have a positive impact on the extent of the physical interactions ^[56]. The manipulation of the above can be achieved by grafting of particular species/groups into the framework or by tuning the net charge as a result of the solution pH in which the adsorption takes place.

The electrostatic interactions between the negatively charged adsorption sites of MOFs with the oppositely charged adsorbates are the most widely reported pathway ^[57]. The diffusion of the metal ions toward the active sites prior to the blockage of the outer entrances of the channels is also an important aspect and so, the volume, geometry, and size of the pores are of paramount importance ^[58].

4. Sample Preparation Techniques for the Extraction of Metal Ions

Solid-phase extraction (SPE) is a well-established analytical technique that has been widely used for the extraction, preconcentration, clean-up, and class fractionation of various pollutants from environmental, biological, and food samples. Different sorbents have been evaluated for the SPE procedure usually placed into cartridges ^[59]. MOFs have been employed as sorbents for the solid-phase extraction. In a typical SPE application, the sorbent is conditioned to increase the effective surface area and to minimize potential interferences, prior to the loading of the sample solution onto a solid-phase ^{[60][61][62]}. The analytes are retained onto the active sites of the sorbent and the undesired components are washed out. Finally, elution of the analytes with the desired solvent is carried out ^[49].

SPE and other conventional sample preparation techniques like protein precipitation and liquid–liquid extraction (LLE) have fundamental drawbacks such as time-consuming complex steps, difficulty in automation, and need for large amounts of sample and organic solvents. Novel extraction techniques, including MSPE, d-SPE, SBSE, and PT-SPE, have been developed in order to overcome these problems. **Figure 2** shows the typical steps of MSPE and d-SPE. Recently, MOFs have been used as sorbents for these extraction techniques [63].



Figure 2. Typical magnetic solid-phase extraction (MSPE) and dispersive solid-phase extraction (d-SPE) procedures for the enrichment and analysis of trace metal ions.

Dispersive solid-phase extraction is performed by direct addition of the sorbent into the solution that contains the target analytes. Various MOF materials have been employed for the d-SPE of metal ions from complex sample matrices. After a certain time, the sorbent is retrieved from the solution with centrifugation or filtration and the solution is discarded. Elution with an appropriate solvent is performed and the liquid phase is isolated for instrumental analysis. The dispersion is often enhanced by stirring, vortex mixing, or ultrasound irradiation, in order to enable an efficient transfer of the target analytes to the active sites of the sorbent. Therefore, several devices

including shakers, vortex mixers, and ultrasonic probes and baths have been implemented for sorbent dispersion. Until today, the ultrasound-assisted dispersive solid-phase microextraction is the most common d-SPE approach [24][64].

MSPE is based on the use of sorbents with magnetic properties. There are several different procedures to fabricate magnetic MOFs that have been employed to prepare sorbents for MSPE. The most common approaches are the direct post-synthesis of magnetic MOF materials with magnetic nanoparticles and the second one, in situ growth of magnetic nanoparticles during the synthesis of the framework. In the first case, the desired MOF and the magnetic nanoparticles (Fe₃O₄) are synthesized separately and mixed under sonication. For the in situ approach, the MOF is added to a solution containing the reagents for the synthesis of Fe₃O₄ in order to give a magnetic material. Moreover, single-step MOF coating can take place by adding the Fe₃O₄ nanoparticles into a mixture of inorganic and organic precursors for MOF synthesis. Carbonization of some MOFs can shape magnetic nanoparticles due to a goregation of the metallic component of the MOF. At the same time, the organic linker is converted to a porous carbon. Finally, the layer-by-layer approach is based on the sequential immobilization of the different components of the MOFs into a functionalized support.

For the typical MSPE procedure, a magnetic sorbent is added to the sample for sufficient time in order to ensure a quantitative extraction. After this period of time, an external magnet is employed to retrieve the sorbent and the sample is discarded. The sorbent is washed and an appropriate solvent is added in order to desorb the analytes. After magnetic separation, the eluent can be directly analyzed or it can be evaporated and reconstitute in an appropriate solvent prior to the analysis ^{[65][66]}.

Other extraction techniques that can be coupled with MOFs in order to extract different analytes from complex matrices are stir bar sorptive extraction (SBSE) and pipette tip solid-phase extraction (PT-SPE). SBSE is an equilibrium technique, initially introduced by Baltussen et al. In this technique, extraction of the analytes takes place onto the surface of a coated stir bar ^{[67][68][69]}. PT-SPE is a miniaturized form of SPE in which ordinary pipette tips act as the extracting column and small amount of sorbent is packed inside the tip ^{[70][71]}. Only a small range of SBSE and PT-SPE sorbents are commercially available, which limits the possible applications of those techniques. MOF materials have been successfully used as coatings for stir bars and as packed sorbents in pipette tips ^{[67][68]}

Although MOFs pose several benefits as extraction sorbents for SPE, MSPE d-SPE, SBSE, and PT-SPE, their water stability and selectivity have to be enhanced with appropriate functional groups or pore functionalization. Therefore, the type of metal–organic framework and the possible functionalization should be carefully chosen. Other parameters that should be thoroughly investigated are the pH value of the sample solution, the extraction and desorption time, the desorption solvent, etc.

As mentioned before, the pH of the sample solution is one of the most critical parameters for the extraction of heavy metals from aqueous samples. Therefore, the pH value has to be optimized carefully in order to allow the

Lewis acid-base interactions between the sorbent and the target analytes and to prevent precipitation due to hydrolysis.

The mass of the MOF material, as well as the extraction time, are other parameters that can influence the extraction step and require optimization. First of all, an optimum adsorbent amount is necessary in order to maximize the extraction efficiency. Certain extraction time is also required to facilitate the interaction between the analytes and adsorption sites of the MOF material. Finally, the sample volume and the volume of the eluent has to be optimized in order to provide a higher enrichment factor that is possible.

Regarding the desorption step, among the parameters that should be thoroughly investigated are the type, the volume, and the concentration of the eluent. In most cases, elution can be achieved with acidic solutions of nitric or hydrochloric acid. The presence of H⁺ ions weakens the interaction between the analyte and the MOF, as it competes for binding with the active sites of the adsorbent. However, decomposition of most MOFs has been observed in acidic conditions. Other reagents that have been used for the elution of metal ions without decomposing the MOF material are EDTA, NaCl, NaOH in EDTA, NaOH in thiourea, etc. Furthermore, enough desorption time should be provided in order to enable the quantitative elution of the adsorbed analytes.

Other parameters that can be investigated are the stirring speed, salt addition, the use of ultrasonic radiation, etc., depending on the extraction procedure ^{[69][70][71][72][73]}. The optimization of the experimental parameters can be performed by evaluating one-factor-at-a-time or by performing Design of Experiments (DoE), such as Box–Behnken experimental design ^[74].

Finally, the effect of potentially interfering ions that naturally occur in the various sample matrices, the adsorption capacity of the MOF material, as well as the reusability of the sorbent should be also evaluated [69][70][71][72][73].

5. Applications of Metal–Organic Frameworks for the Extraction of Metal Ions

The applications of MOFs for the extraction of metal ions from environmental, biological, and food samples, as well as the obtained recoveries and limits of detection (LODs), are summarized in **Table 1**.

Analyte	Organic Linker of MOF	Metal of MOF	Modification	Matrix	Sample Preparation Technique	Detection Technique	Recovery (%)	LOD (ng mL ⁻¹)	Reusability Ref.
Pd(II)	Trimesic acid	Cu	Fe ₃ O ₄ @Py	Fish, sediment, soil, water,	MSPE	FAAS	96.8– 102.5	0.37	_ [<u>75</u>]

Table 1. Applications of metal–organic frameworks for the extraction of metal ions.

Arrelite		Metal		Matuita	Sample	Detection Technique	Recovery	LOD	Daviashilita	- Def
Analyte	Organic Linker of MOF	of MOF	Modification	Matrix	Technique		(%)	(ng mL ⁻¹)	Reusability	Ref.
	Malonic acid	Ag	-	Water	SPE	FAAS	>95	0.5	Up to 5 times	[<u>60</u>]
	Trimesic Acid	Cu	DHz, Fe ₃ O ₄	Water	MSPE	ETAAS	97–102	0.0046	At least 80 times	[<u>76</u>]
Pb(II)	Trimesic Acid	Cu	Fe ₃ O ₄ @SH	Rice, pig liver, tea, water	MSPE	FAAS	>95	0.29–0.97	-	[72]
	meso-tetra(4- carboxyphenyl) porphyrin	Zr	-	Cereal, beverage, water	d-SPE	FAAS	90–107	1.78	Up to 42 times	[77]
	Trimesic acid	Cu	Fe ₃ O ₄ @4-(5)-imidazole- dithiocarboxylic acid	Fish, canned tune	MSPE	CVAAS	95–102	10	At least 12 times	[<u>78</u>]
Hg(II)	Trimesic acid	Cu	Thiol-modified silica	Fish, sediment, water	d-SPE	CV-AAS	91–102	0.02	-	[73]
	3'5,5'- azobenzenetetracarboxylic acid	Cu	-	Tea, mushrooms	d-SPE	AFS	Average 93.3	>0.58 mg kg ⁻¹	Up to 3 times	[<u>79</u>]
	Benzoic acid and meso- tetrakis(4- Carboxyphenyl)porphyrin	Zr	-	Fish	PT-SPE	CVAAS	74.3– 98.7	20 × 10 ⁻³	At least 15 times	[<u>71</u>]

Analyte	Organic Linker of MOF	Metal of MOE	Modification	Matrix	Sample Preparation	Detection Technique	Recovery (%)	LOD	Reusability	Ref.
					rechnique			(19112)		
Cu (II)	Aminoterephthalic acid	Zn	Fe ₃ O ₄	Water	MSPE	ETAAS	98–102	0.073		[<u>28</u>]
Cd(II)	Terephthalic acid	Fe	Fe ₃ O ₄ @MAA, AMSA	Water	MSPE	FAAS	>96	0.04	Up to 10 times	[<u>80</u>]
Th(IV)	2 –hydroxyterephthalic acid	Zr	-	Water	d-SPE	Spectrophotometry	>90	0.35	At least 25 times	[<u>81</u>]
	[1,1'-biphenyl]-4-carboxylic acid	Eu	-	Water	Probe	UV	N.A.	24.2	N.A.	[<u>82</u>]
U(VI)	4,4',4"-(1,3,5-triazine- 2,4,6-triyltriimino)tris- benzoic acid	Те	-	Water	d-SPE	ICP-MS	94.2– 98.0	0.9	At least 3 times	[<u>83</u>]
Se(IV), Se(VI)	Terephthalic acid	Cr	Fe ₃ O ₄ @dithiocarbamate	Water, agricultural samples	MSPE	ETAAS	>92	0.01	Up to 12 times	[<u>84</u>]
Cd(II), Pb(II)	Trimesic acid	Cu	Fe₃O₄@Py	Fish, sediment water	MSPE	FAAS	92.0– 103.3	0.2–1.1	-	[<u>85</u>]
Cd(II) Pb(II) Ni(II)	Trimesic acid	Cu	Fe ₃ O ₄ @TAR	Sea food, agricultural samples	MSPE	FAAS	83–112	0.15–0.8	-	[<u>86</u>]

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Analyte	Organic Linker of MOF	Metal of MOF	Modification	Matrix	Sample Preparation Technique	Detection Technique	Recovery (%)	LOD (ng mL ⁻¹)	Reusability F	Metal-
Cd(II), Pb(II),	Trimesic acid	Cu	Fe ₃ O ₄ -benzoyl isothiocyanate	Vegetables	MSPE	FAAS	80–114	0.12-0.7	- [nic
Zn(II) Cr(III)	Terephthalic acid	Fe	Fe ₃ O ₄ -ethylenediamine	Agricultural samples	MSPE	FAAS	87.3– 110	0.15–0.8	- 1	iron- hem.
Cd(II), Pb(II), Ni(II), Zn(II)	Trimesic Acid	Cu	Fe ₃ O ₄ @DHz	Fish, sediment, soil, water	MSPE	FAAS	88–104	0.12–1.2	- 1	or
Pb(II), Cu(II)	Trimesic acid	Dy	-	Water	d-SPE	FAAS	95–105	0.26–0.40	At least 5 times	^{50]} L1,
Cd(II), Co(II), Cr(III), Cu(II), Pb(II)	4-bpmb	Zn	-	Water	d-SPE	ICP-OES	90–110	0.01-1	_ [24) S for
0 (11)										al
Cu(II), Cu(II), Pb(II), Cd(II), Ni(II), Cr(III),	4,4'-oxybisbenzoic acid	Cd	Fe ₃ O ₄	Water	MSPE	ICP-OES	>90	0.3–1	- 1	pringe
1 Mn(II)										nts for
Hg(II), Cr(VI)	Terephthalic acid	Cu	Dithioglycol	Tea	d-SPE	AFS, AAS	95–99	Not mentioned	Up to 3	ia.
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1	Analyte	Organic Linker of MOF	Metal of MOF	Modification	Matrix	Sample Preparation Detection Technique Technique	Recovery (%)	LOD (ng mL ⁻¹)	Reusability Ref.	s violet
	Pb(II)									. A
	Cd(II)									

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