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Review

Metal-Organic-Frames (MOFs) Based Electrochemical Sensors for Sensing Heavy Metal Contaminated Liquid Effluents: A Review

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Abstract: Toxic heavy metal ions may have adverse health effects on human health. Sensing and effective removal is an important issue. Metal-organic frameworks (MOFs) are a novel group of crystalline porous materials. Because of their extremely high surface areas, optimized pore volumes and pore size distributions for specific detection, electrochemical sensors based on MOF's are gaining popularity. They are reliable, easy to use and have good sensitivity. This review gives an insight into the selection of MOF's as heavy metal sensing devices and the mechanism behind the detection of specific metal ions also be explained. Challenges and prospects for practical applications of MOFs in heavy metal ion detection are also discussed.

***Keywords*:** metal-organic frameworks (MOFs), electrochemical sensors, heavy metals detection

1. Introduction

1.1 *Heavy metal pollution*

In general, metals or metalloids having a density of 5 times or more than that of water are collectively called heavy metals. Heavy metals are everywhere in the environment and are non-biodegradable in nature [1]. Rapid mining, manufacturing sector growth, excessive use of underground water causes depletion of groundwater level, and uncontrolled industrial wastes discharge has lead heavy metal ion polluted environment which further affects water bodies [2]. Various routes of discharge of heavy metals into the environment and major health effects on the human body are pictorially represented in Figure 1.

Heavy metals intake in very low concentration is required for human health as they are cofactors of various enzymes. However, metal intake above certain a prescribed value leads to many life-threatening diseases [3, 4].

Among various heavy metals, some metal ions cause a severe impact on the total environment [5]. Exposure of heavy anaemia, kidney failure, neurological damage, loss of memory, etc. Chromium (Cr), mercury (Hg), uranium (U), cadmium (Cd), lead (Pb) and arsenic (As), etc., even at low exposure concentration are toxic for human health and can lead to various problems on the environment and human health. Exposure to them leads to cardiovascular diseases, cancer mortality, neurological disorders, etc. [6]. Table 1 explains the harmful health effects of various heavy metals.

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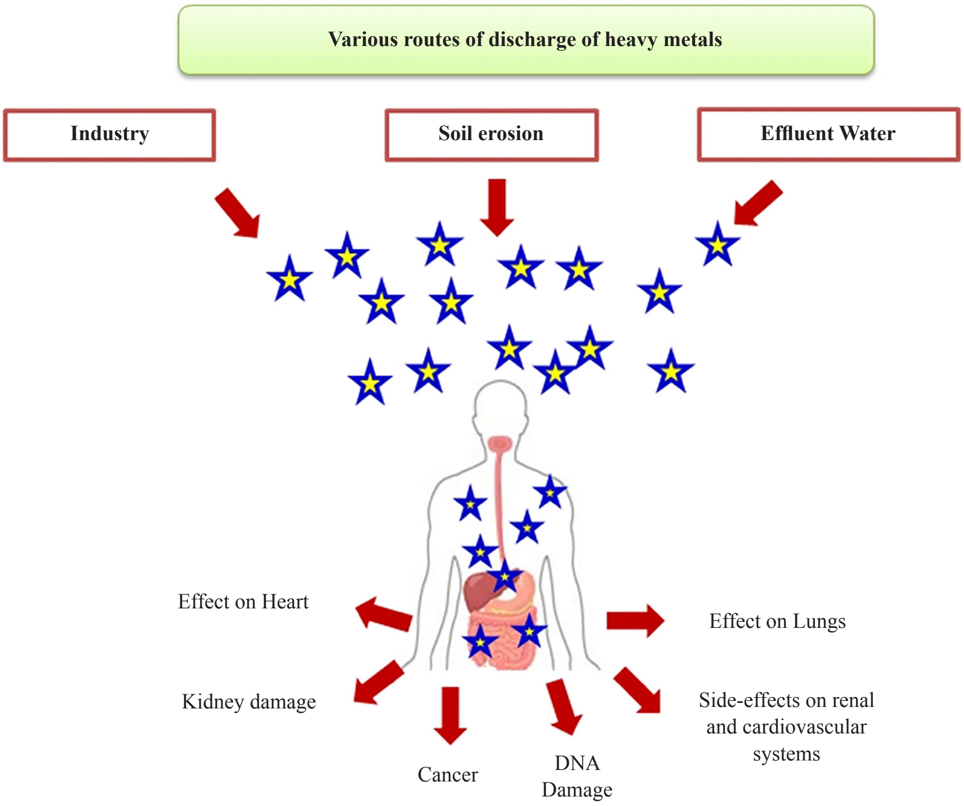

Figure 1. Schematic presentations of various routs of discharge of heavy metals and their effects on human health

Table 1. Harmful effects of various heavy metals on human health

Heavy metal	Exposure sources	Harmful health effects	Reference
Mercury	Fish, amalgam-based dental fillings, burning of coal and mining of gold	High blood pressure or heart rate, damage of the brain, damage of developing fetuses, skin rashes and eye irritation, lungs and kidneys, vomiting and diarrhea, etc.,	[7]
Cadmium	Smelters, burning fossil fuels, incineration of municipal waste such as plastics and nickel-cadmium batteries	Development of cancers of various organs like kidney, prostate, lung, and stomach, damages of renal, skeletal, respiratory and cardiovascular systems.	[8]
Lead	Paint, dust, soil, drinking water, air, folk medicines, ayurvedics, and cosmetics	Damages brain, skeleton, liver, heart, kidneys, and nervous system, disturbance in hemoglobin synthesis which further causes anemia	[9]
Chromium	Metallurgy, and in the manufacturing of paints, preservatives, pigments, pulp and papers, electroplating, metallurgy, etc.	Slow healing ulcers, DNA damage	[10]

Permissible limits for heavy metals as described by Indian Standards are mentioned in Table 2. Therefore, sensing and removal/remediation of metal ions at low concentration is extremely important for environmental protection and for the better health of human.

Table 2. Permissible limits of various heavy metals as per IS standards

Heavy metal	Permissible limit (mg/L, Max)	Permissible limit in absence of other sources	Reference
Cadmium (Cd)	0.003	No relaxation	IS 3025 (Part 41)
Lead (Pb)	0.01	No relaxation	IS 3025 (Part 47)
Mercury (Hg)	0.001	No relaxation	IS 3025 (Part 48)
Total arsenic (As)	0.01	0.05	IS 3025 (Part 37)
Total chromium (Cr)	0.05	No relaxation	IS 3025 (Part 52)

1.2 *Heavy metal sensing and detection using conventional methods and their limitations*

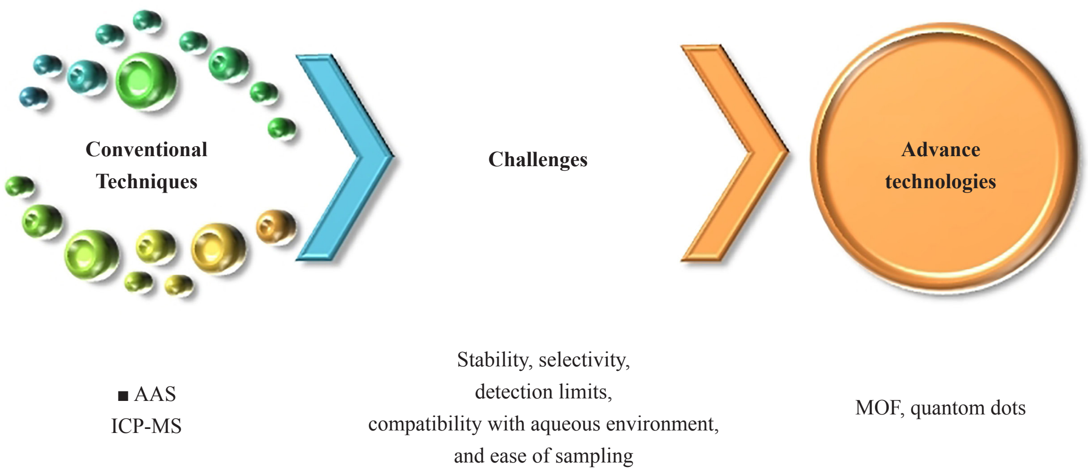

Figure 2. Progressive development in heavy metal sensing & detection from conventional methods to advance techniques

In past sincere efforts have been given by various researchers for development the of heavy metal sensing and detection systems. Conventional procedures for sensing mainly rely on chromatography and spectrometry techniques. Atomic absorption spectroscopy (AAS), X-ray Fluorescence Spectrometry (XRF), inductively coupled plasma mass spectroscopy (ICP-MS), UV/Vis spectroscopy, Neutron activation analysis (NAA) and inductively coupled plasma-optical emission spectrometry, (ICP-OES) are employed for detection of heavy metals in complex matrices. Various other conventional methods have been applied for the detection of heavy metals at low levels using different techniques like liquid chromatography, capillary electrophoresis (CE), microprobes (MP), fluorometry, colorimetry, enzymatic biosensors. Above mentioned techniques are versatile and useful because using this simultaneous determination of heavy metal ions for various elements is possible. These techniques are highly sensitive and selective and offer very low detection limits, but the major drawback is that they are time-consuming and require tedious sample preparation, cleanup, difficult procedures, skilled operators, and sophisticated instruments. Also, these techniques are only suitable for quantitative analysis and need to be coupled with other chromatographic techniques for performing metal ion speciation [11]. Optical techniques like spectrophotometric measurements are also applied for the detection and monitoring of heavy metals. Optical methods involve costly and complex equipment like lasers, photo detectors, etc., which require high precision and high-power operations and are most likely not suited for in-field applications. Therefore, the development of accurate, simple, time-saving, inexpensive, and reliable techniques suitable for in-situ and on-time measurements of heavy metals is urgently required. Electrochemical detection may be counted as a facile, inexpensive, and time-saving detection method [12]. High stability, selectivity, low detection limits, compatibility with an aqueous environment, and ease of sample handling are major challenges and to address this advanced electrochemistry could be a possible solution. Figure 2, pictorially represents the progress in sensing and detection.

1.3 *Various types of electrochemical sensors*

An electrochemical sensing device converts an electrochemical signal into a significant analytical signal, which can further be utilized for the quantitative measurement of sensing data. They offer cost-effective sensing compared to other sensing devices. Various compounds/metal ions can be detected by electrochemical sensors, and at the same time, multiple analytes sensing is also possible. The electrochemical sensor can be classified into the following five types on the basis of their functioning (Figure 3).

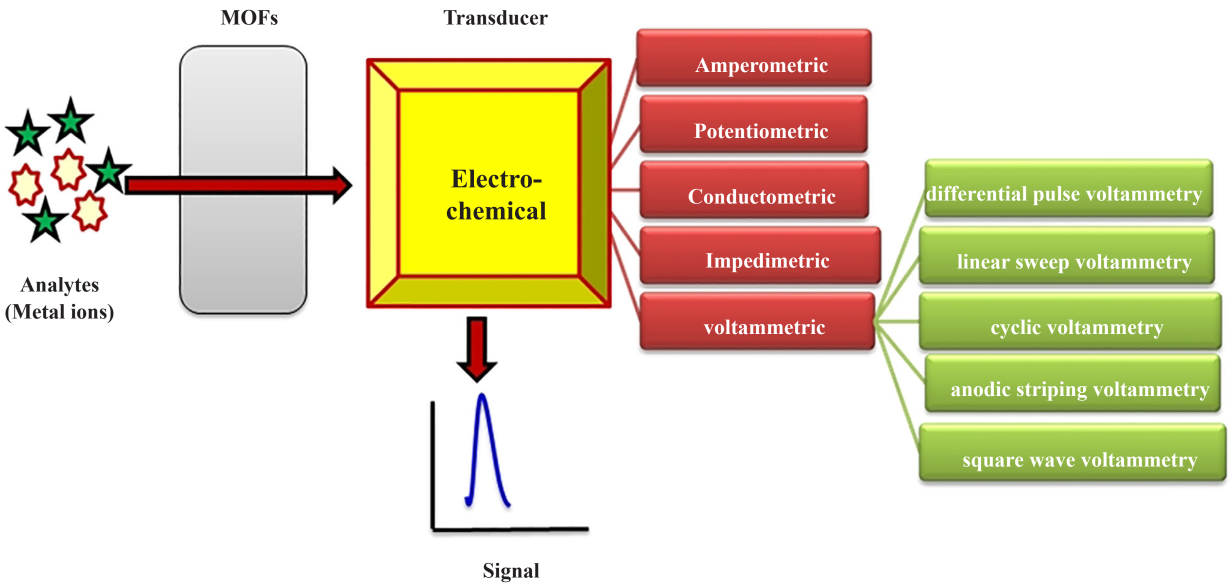

Figure 3. Basic principle of MOFs based electrochemical sensors and its classification

1) Amperometric- In amperometric electrochemical sensors detection of heavy metal ions in a solution is measured by changes in electric current resulting from oxidation or reduction of metalion.

2) Potentiometric- In this type of sensor potential is measured when no current is passed and thus the analytical concentration of ions in an analyte is obtained.

3) Conductometric- Conductometry is widely applied to analyze ionic species and to monitor the chemical reaction by studying the electrolytic conductivity of the reacting species.

4) Impedimetric- Impedimetric sensors measure the changes in charge conductance and capacitance at the sensor surface as the selective binding of the target.

5) Voltammetric- In voltammetricvoltameteric electrochemical sensors, change in the potential of the working electrode is measured with reference to the working electrode. Various subdivisions of voltammetric techniques are available such as; cyclic voltammetry (CV), linear sweep voltammetry (LSV), differential pulse voltammetry (DPV), anodic stripping voltammetry (ASV), and square wave voltammetry (SWV).

Various factors such as surface passivation loss, background noise, over potential requirements, surface heterogeneity, non-repeatability of surface conduct, and slow kinetics of electrochemical reactions onto the surface of the electrode affect the sensitivity and selectivity of the electrochemical sensor. To improve the selectivity and sensitivity of a particular sensor surface modification may be performed. In particular, polymer films, surfactants, inorganic/organic, metal and semi-metallic nanoparticles (NPs), metal-organic electroactive materials, biomaterials, and nanocomposites are utilized to improve the surface of electrodes. The characteristic of the materials applied for the functionalization of the electrode is an important parameter which helps to develop reliable and high-performance electrochemical sensors [13].

2. Metal-organic frameworks for sensing applications

Metal-organic frameworks are crystalline highly porous molecular materials having very high surface area and pore volume, which makes them more advantageous over other competitive materials. They are built by attaching metal ion-containing units to organic ligands through coordinate bonds. Long organic linkers are the reason for unprecedently large and permanent inner porosity, large storage space and high pore volume and potential to functionalize and it leads to numerous applications [14]. Major applications of MOFs are given in Figure 4. They have shown their potential as adsorbent and catalyst in the removal of hazards from water as well as air. Work [15] shows that MOFs-based membranes were more effective in comparison to conventional members for heavy metal removal from water.

Framework functionalization and design architecture make them extremely versatile with promising applicability in fields such as catalysis, separation, gas storage, biomedical imaging, drug delivery, adsorption and electrolytic reduction. The potential of MOS's has also been tested for chemical sensing by various researchers and the results are promising. MOF Structures are superior to convectional sensor materials because of their exceptional chemical properties and high structural tunability. Pore size tunability is important for the size-selective detection of analytes [16]. Additional functionalities may be added to tune a MOF for specific sensors application, for example, metal doping or nano particle entrapping within the framework and then the change in MOF properties can be measured as a sensing signal [17].

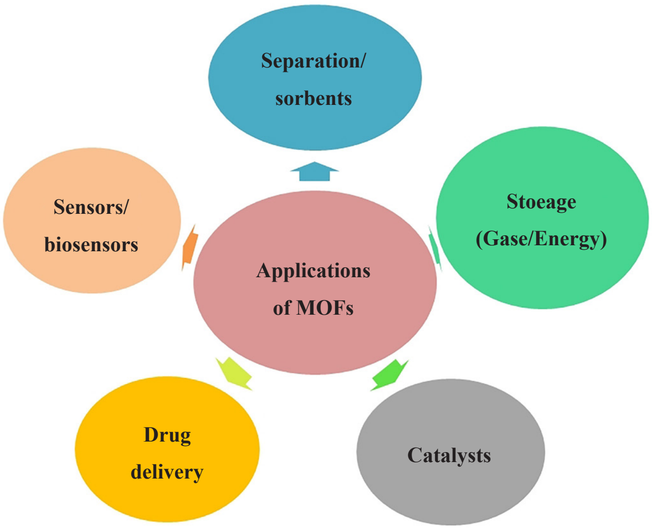

Figure 4. Application of MOFs in various sectors

On the basis of signal transduction, MOFs-based sensors are divided into four categories as mentioned in Figure 5. In the presence of luminescent atomic subunits, MOF may be used as optical sensors. For electrochemical sensing applications conducting MOFs can be developed by hybridizing with nanomaterials based on carbon and metals. Electrochemical devices are very reliable, attractive, highly sensitive, versatile and easy-to-use tools and the use of MOFs as sensor material may add to these qualities. Recently published work [18] explains the fabrication and working of MOF coated electrodes and performance in energy storage.

It can be seen that MOF-based electrochemical systems have great potential for future sensing devices, but the topic has received less attention compared to other MOF applications. Out of numerous research papers available on MOF's, there are hardly a few hundred papers available on electrochemical applications of MOF's [19, 20]. Much more efforts need to be given to quality research on the electrochemical sensing quality of MOF's. For maintaining good sensing quality, MOF-based sensors should have high selectivity, high sensitivity and reliability.

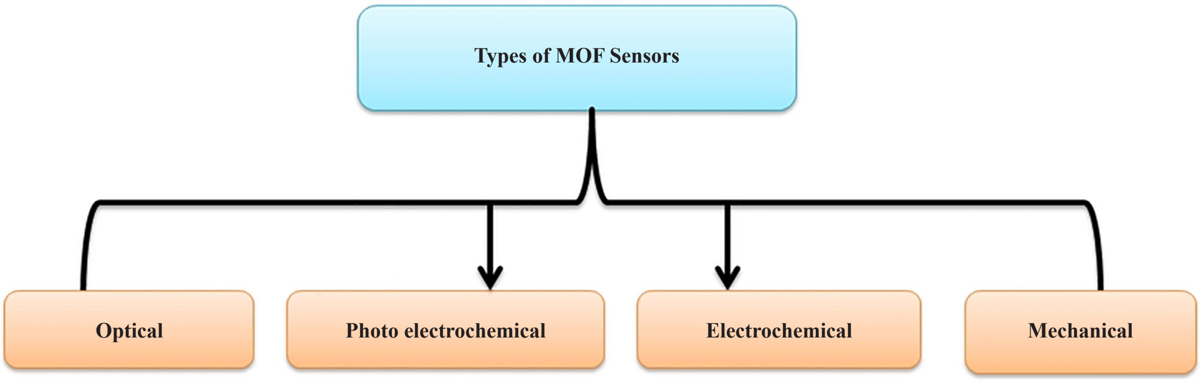

Figure 5. Various types of MOFs based sensors based on the signal transduction

Recent research papers published on MOFs show its popularity and create demand for review articles. A recent work [21] has reviewed the application of MOF-based electrochemical sensors for the detection of neurotransmitters that control various functions of our central nervous system. They have focused on synergistic and complimentary effects of MOFs with various materials as electrochemical sensors and explained how MOF electrode modifiers and various MOF composites could be of great importance in the detection of neurotransmitters and disease diagnosis. Another review work [22] discusses the recent developments and challenges in MOF-based materials for electrochemical sensing applications. Review work [23] reviews the MOF-based electrodes for detection of various analytes such as uric acid, Hydroquinone and Dopamine, etc. There are limited review articles available that have used MOF-based electrochemical sensors for heavy metal sensing or extraction [24, 25]. This work specifically focuses on heavy metal sensing using MOFs and other materials and also discusses the parameters responsible for improved sensing and detection.

3. MOFs based electrochemical sensors, design challenges for improved sensing

MOFs are used for various Electrochemical applications such as Electrochemical energy storage, electro catalysis and Electrochemical sensing.

Following are various effective parameters that make MOFs very useful for heavy metal sensing:

1) large porosity- The pore size of MOFs is sufficient to grab heavy metal and also the pore size can be tailored as per the requirement which is very helpful in the adsorption of heavy metals.

2) High permeability and adsorbability- Permeability and adsorbability both are very good for MOFs which eases heavy metal adsorption.

3) high specific surface area- Specific surface area is generally very high for MOFs which facilitates the adsorption.

4) Rich active sites- Rich active sites of MOFs adsorbs heavy metal ions and in turn provide good sensing and detection properties.

5) Tunable chemical functionalization- Functional groups specific to a particular heavy metal on MOFs can be added to improve the detection and adsorption of the specific heavy metal ion.

6) Diverse structure- There is so much diversity in structures of MOFs that makes direct electron transfer easy and hence useful for heavy metal Electrochemical sensing. Structural rearrangement flexibility is also responsible for enhanced performance as compared to other porous materials with rigid structures because this allows interaction with molecules in the pores in the presence of guest metal [26]. Transition metal-based MOFs are of low cost and have excellent electrocatalytic activity for practical implementation [27]. As a consequence, the Electrochemical performance enhanced as electron transfer and ionic diffusion both can be facilitated in these structures [23]. The structural modification also helps in improving conductivity and stability and the auxiliary ligand helped in improving stability and conductivity of Zn-MOF by chelating the Zn^{2+} nodes and which in turn helped in eliminating post procedures for use as electrode modifier [22]. Remarkable improvement in electrical conductivity and surface area has been reported by structural modification in MOF-derived electrodes [23].

7) Synthesis parameters- Synthesis parameters also play an important role in the improved performances of MOFs. [23] reports 4.5 times increase in surface area of Cu- based MOF when calcinated in the presence of nitrogen compared to air during synthesis. Electrical conductivity in MOFs can be improved drastically by making a composite with electrically conductive non-MOF materials. Various materials such as CNT, graphene and porous carbons can be used as conducting non-MOF materials MOF-based composites integrate the advantages of the highly porous MOFs with high-density active sites and the electrically conductive non-MOF materials. The addition of various nano particles, silver, gold and platinum facilitates charge transport in MOFs [25]. Functional groups having multi-binding sites can be incorporated into the pore structure of MOFs using various synthesis methods without major loss of porosity, as mentioned earlier [25].

Because of the diverse and tailored structure, ultra-high specific areas, adjustable porosity and MOFs are ideal matrices to accept guest molecules. There are reported MOFs having very high surface areas compared to other porous materials such as 7000 and 10 000 $m^2 \cdot g^{-1}$ too [23, 25]. Because of the availability of pores on MOF structure, functional materials can easily get integrated into the MOF surface and this in turn helps in providing stability to MOF structure and improving the conductivity of the sensor. MOFs have outstanding electrocatalytic activity. Table 3 shows the comparison of BET surface areas and other performance features responsible for the higher extraction of MOFs.

Table 3. Comparison of specific properties of MOFs with other materials

Material	BET [$m^2 \cdot g^{-1}$]	Total pore vol. [$cm^3 \cdot g^{-1}$]	Pore width [Å]	Reference
ZIF-67	1980	0.69		28
Basolite F300	1070	0.49	18-22	28
ZIF-8	1820	0.8	-	28
Z-1000	1902	2.5	-	23
NOTT-102	2942	1.138	8.3	29
NOTT-103	2929	1.142	8.0	29
CMK-3-100	1260	1.1	3.0	30
CMK-3-130	1250	1.30	4.3	30
Zeolite Y	930	0.33	7.4	28

The basic science behind all chemical applications involves the process of charge transport. Electrons move from molecular orbitals and are counterbalanced through the movement of ions. For using the MOFs as advanced electrode materials and matrices, they must have some specific qualities [31]. Target hosts having different sizes, shapes, polarities, and conformation are trapped in MOF matrix pores radially as well as in volume [32]. Various factors are responsible for the selection of specific hosts such as Lewis acidic or basic sites in ligands, hydrophobic interactions, open metal sites, and aromatic π groups in MOFs. The introduction of catalytic or redox-active sites and conductivity improvement are major design challenges. This can be encountered by the introduction of active ligands or metal ions, and active complexes as building blocks. Electrochemical activity in MOFs is promoted by capturing active guest molecules, enzymes, bacteria, nanoparticles, etc. [33]. Catalytic sites are substrate effective which improves the selectivity of the sensor material. The Electrochemical activity of MOFs-based Electrochemical sensor may be improved by adding catalytic or redox-active sites. Target selectivity is achieved by improved Electrochemical activity. Mass and energy conversion is falicited by the Electrochemical activity of MOFs. The Electrochemical activity of a MOFs sensor is noticed mainly by fast extension of ionic permeability, phase change through Electrochemical mechanism and restructuring of MOFs structure.

In order to improve MOFs conductivity, metal nodes and conductive ligands are common choices to form long-range delocalized electrons for charge mobility. However, mixing with electrical conductors/integrating guest molecules is the alternative method. The MOFs film, which is attached to the substrate surface facilitates direct electron transfer and further in device building. For enhancement of electrocatalytic affinity, the range between active sites and the substrate shall be short and there should be possibility of direct interaction between them. The highly ordered and crystalline nature also increases precision in the identification and characterization of MOFs sensors. MOFs-based sensors are very promising for Electrochemical applications if selectivity, sensitivity and electron affinity and many other Electrochemical properties are improved. The incorporation of diverse new properties and multifunctional capabilities can further enhance the sensing performance of MOFs-based sensors [34]. Because of tunable porosity and periodic network structure MOFs are effective coating materials with superior catalytic capacity. Characteristic properties of MOFs like high porosity and large surface area are very useful to address the limitations of mass transfer of the analytes. This further helps to amplify the signal response effectively to enhance sensitivity and detection limit. MOFs-based supports exhibit excellent selectivity for a particular analyte because of its characteristic features like availability of channels and cavities.

4. Insight to synthesis, fabrication and characterization of MOFs based sensing devises

For MOFs synthesis, various approaches such as hydro/solvothermal, microwave, electrochemical, mechanochemical, ultrasonic, layer-by-layer, and high-throughput syntheses are reported in various research papers [35]. MOFs-based sensors having extremely high surface area, specifically designed pore size has been fabricated by various researchers [36-38]. To ensure spontaneous growth of crystal structure with complex super molecular structure, self-assembly synthesis is preferred [39]. With chemicals functionalization-controlled growth of crystal lattice is obtained [40]. Pore position in MOFs crystals is controlled by patterning and delocalization. MOFs-carbon composite materials are prepared to obtain high porosity, conductivity, surface area, mechanical strength, and corrosion resistance [41, 42]. MOFs carbon composite electrode materials reveal favorable electroanalytical performance. Additional additives can be added for preparing more complex sensors and biosensors. As can be seen in recent work [43] Elaborate designs and functionalization help in improving the efficiency of MOFs. Another work [44] has summarized the recent experimental and computational studies on sensing. They have also explored MOFs for liquid phase applications, including water treatment and chemicals.

Few shortcomings such as High cost of production, synthesis difficulty, lower hydrothermal and chemical stability, regeneration and recycling issues are to be resolved with proper chemical and structural tuning while using MOF-based Electrochemical sensing devices [45].

For characterization of MOFs, various characterization techniques such as XRD analysis, BET analysis, SEM analysis, FT-IR analysis, XPS analysis, etc. are used. XRD pattern of MOFs before and after adsorption gives a clear picture of lattice structure and also an explanation of why the surface area is high or low. Surface areas of different MOFs can be quantitatively compared by the BET surface area analyzer. Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM) are helpful in knowing surface morphology and particle sizes. Before and after adsorption change in surface morphology to know how fast and slow restructuring is. Elemental and structural information of the particles are studied by and energy-dispersive X-ray spectroscopy (EDX elemental mapping, X-ray diffraction analysis and attenuated total reflectance FT-IR spectra. FT-IR analysis is important for knowing the various functional groups on MOF surface and will also be helpful in knowing the mechanism behind selective adsorption. Dynamic light scattering (DLS) for knowing surface charge and hydrodynamic diameter [46].

5. Heavy metal ion sensing using MOFs based electrochemical sensors

Concern for heavy metal ions pollution specially lead (II), copper (II), cadmium (II), and mercury (II) have recently increased due to the expansion of industry and agriculture [47]. Demand for detection techniques for heavy metal ion has also increased in recent years. Conventional spectroscopic or scattering-based detection techniques use cumbersome and complicated instruments and are hence not suitable for in situ applications [48]. Electrochemical techniques offer many advantages over these methods because of highly sensitive, fast simple and economical detection. Electrochemistry-based devices are portable and can also be used for inline trace detection [49]. Metal-organic frameworks (MOFs) are a fascinating class of highly ordered crystalline coordination polymers formed by the coordination of metal ions/clusters and organic bridging linkers/ligands. MOF modified electrochemical sensor to analyze heavy metal ions have also been reported. These sensors offer extremely extra-highly ordered, porous, well-characterized structures with modifiable chemical functionality [50].

For any electrochemical detection study, one needs an electrode and an electrolyte wherein potential is measured at the interface of electrode and electrolyte solution. For heavy metal ion detection metal ion solution acts as an electrolyte. Electrode potential is measured in reference to an electrode named reference electrode and MOF-based detector will be the working electrode.

An excitation signal is passed through an external power supply and the response function is measured in the metal ion solution while other system variables are kept constant. This has been pictorially represented in Figure 6. The presence of different heavy metal ions causes changes in sensing properties like current, electrochemical impedance, voltage, charge and electroluminescence, which are measured as response functions. Electrochemical techniques are classified as per the electrical signal, viz: voltammetric, impedance measurement, potentiometric, amperometric, coulometric and electrochemiluminescent techniques. In amperometric techniques, the current is measured while in voltammetric techniques, the voltage change is measured. In case of potentiometric techniques, no signal is provided and potential across the electrode is measured to determine the type of heavy metal. For impedance measurement, changes in double layer capacitance are measured. In Electrochemiluminescence techniques, heavy metal ion concentration is measured in response to the luminescence effect. A detailed description of various electrochemical techniques for selective determination of heavy metal ions while maintaining low detection limits and high sensitivity is available in previous work [51].

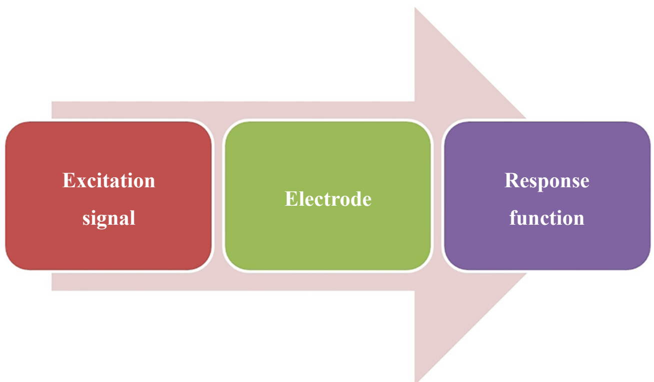

Figure 6. Working principal of electrochemical detection using MOF-based sensor

The health hazards of various heavy metals have already been discussed in this work. MOFs can be employed for the exclusion of heavy metal ions because of their excellent binding ability. Tolerable limits for Hg^{2+}, Pb^{2+}, As^{3+} & Cd^{2+} are 11 μg d^{-1}, 255 μg d^{-1}, 3.5 μg d^{-1}, 65 μg d^{-1} respectively [52]. A good sensor should be able to detect in low detection limits. In previous studies, MOFs-based electrochemical sensors have been tested for sensing heavy metals. Few examples of MOFs-based electrochemical sensors for various heavy metals have been given in Table 4.

Table 4. List of electrochemical sensors for heavy metal ions and their detection limits

MOFs based Sensor	Heavy metal ion	Limit of detection	Reference
Zr-DMBD MOFs based electrode	Hg^{2+}	0.05 μM	[52]
Cu-MOFs	Pb^{2+}	4.8 fM	[53]
Manganese dioxide formed in situ (MOF)	Pb^{2+}	917 mg/g	[54]
$Zn_4O(BDC)_3$	Pb^{2+}	4.9 nM	[55]
Ni-MOF	As^{3+}	0.5 μM	[56]
Fe-MOF	As^{3+}	0.034 nM	[57]
Fe (III)-based MOF	As^{3+}	6.73 pM	[58]
Cr-MOF	Cd^{2+}	3 μM	[59]
Zr-MOF	Cd^{2+}	0.3 μM	[60]
TMU-16-NH_2 ($[Zn_2(NH_2\text{-}BDC)_2(4\text{-bpdh})]_3DMF$)	Cd^{2+}	0.2 g L^{-1}	[61]
$[[Cd_{1.5}(TPO)(bipy)_{1.5}]_3H_2O]_{2n}$	Co^{2+}	0.31 μM	[62]
Me_2NH_2@MOF-	Cu^{2+}	1 pM	[63]

6. Mechanism behind electrochemical sensing of various heavy metal ions

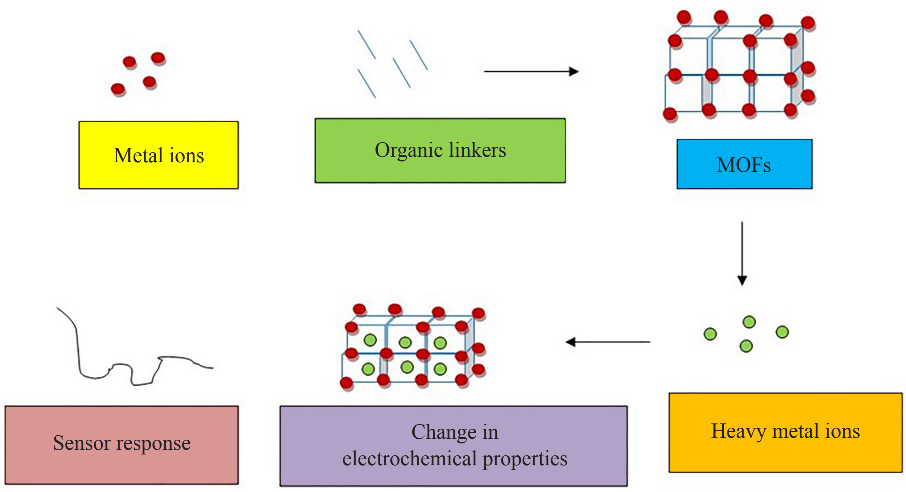

Figure 7. Mechanism of metal ion detection using MOFs based electrochemical sensor

The mechanism of MOF-based electrochemical sensors is mainly attributed to the absorption of metal ions by the functional material that causes electron and hole transfer, or the metal ions react on the surface of the functional material, resulting in changes in any specific electrochemical property of sensing material which in turn is measured as analytical signal (Figure 7).

Metal ion may get absorbed into the MOFs surface by adsorption or by chemical reaction. Various reported mechanisms of metal ion adsorption over the surface of MOF are as follows.

6.1 *Chelation between the metal ion and MOFs*

Various functional groups and active sites available on MOFs surface form chelate with the heavy metal and thus ease the adsorption and detection of the heavy metal ion. In a recent work [60], an electrochemical sensor UiO-66-NH_2@PANI was successfully developed by polymerizing the conductive polyaniline (PANI) polymer using the metal-organic framework UiO-66-NH_2 and applied for the detection of cadmium ions (Cd^{2+}). Cadmium ions form a chilate with the amine group which in turn changes electrochemical properties and the response is recorded as an analytical signal. Linear detection of 0.5-600 μg L^{-1} concentration range under optimized conditions was repeatable with a 0.3 μg L^{-1} lowest level detection limit. Cadmium accumulation on UiO-66-NH_2@PANI/GCE surface increases accumulation time increase and hence oxidation peak current greatly increases. However, for an accumulation time of more than 120 seconds, the oxidation peak current almost remains constant because the amount of cadmium at the UiO-66-NH_2@PANI electrode surface tends to saturate so 120 seconds is considered as the optimum accumulation time [60].

6.2 *Adsorption of metal ion over MOFs surface*

There are cases where adsorption of metal ion takes place on MOFs surface because surfaces are conductive and have active sites which adsorb metal ion. In a recent work [64], hexagonal lanthanide MOF, ZJU-27 modified glassy carbon electrode of an electrochemical sensor was used for detection of Cadmium (Cd^{2+}) and lead (Pb^{2+}) ion traces respectively and simultaneously with a detection limit of 0.228 ppb for Pb^{2+} under optimized conditions. The sensor showed an excellent selectivity, sensitivity and anti-interface ability for Cd^{2+} and Pb^{2+} in an aqueous solution. Heavy metal ions were adsorbed over the surface of ZJU-27/GCE and the signal produced from electrochemical property change was sensed using the square wave anodic stripping voltammetry method (SWASV). The sensor also showed excellent repeatability and high stability [64].

6.3 *Adsorption followed by complex formation of metal ion over MOF surface*

Advantages of high permeability and absorbability are achieved because of abundant porosity and tunable structure. Adsorption becomes more prominent when a complex formation takes place with the target metal ion over the surface of MOFs. In work [65], UiO-MOFs was fabricated and its various composites were explored as sorbent for binding and removal of heavy metal ions. Adsorption characteristics and mechanisms of UiO-MOFs of various metals were studied. Results showed that this follows Langmuir isotherms, Freundlich isotherm, and pseudo-second-order kinetics. Thermodynamic studies also showed that the adsorption process of metal ions is spontaneous [65].

7. Conclusion & future outlook

Heavy metal pollution in water bodies and its remediation is an important issue that requires immediate attention thus there is an urgent need to discuss about the materials having exceptional detection properties towards heavy metal ions. MOFs-based materials show exceptional sensing and detection properties due to its characteristic features like enhanced chemical and physical properties such as outstanding surface area, structural diversity, conductivity, electrochemical activity, etc. The selectivity of MOFs reveals their promising electrochemical applications. MOFs at the molecular level give the precision for selective adsorption and electrochemical response to the targets. This work shows that the MOFs are multi-functional materials to develop efficient electrochemical sensors for the easy and cost-effective detection of heavy metal ions. MOFs have excellent chemical and physical properties. The synthesis of various

MOFs, and their electrode fabrication is also briefly explained. The development of MOF-based electrochemical sensing of toxic metal ions such as mercury, lead, arsenic and cadmium in water samples during the past decade has been discussed. Various MOF-derived materials have strong interactions and the selective binding of target species for the toxic metal detection ions is also discussed in detail. The possible reaction mechanism for the binding of heavy metal ions has also been explained MOFs based materials and its applications in the electrochemical sensing field are gaining a lot of interest and there is a need to work on this aspect. MOFs-based electrochemical sensors have applications in the rapidly developing field acquired with fruitful achievements. Various ways to improve the detection and sense properties of MOFs have been discussed in this work.

MOFs-based sensor are still under limited laboratory use due to various reasons. The water stability and conductivity of many MOFs is relatively poor because of clavation of metal-ligand coordination bonds by water molecules. Also, MOFs have recyclability and reusability issues that need to be catered. Thus, there is a need to develop easy to handle, low-cost, environment friendly electrochemical sensors using MOFs for large scale applications in near future.

It can be summarized that MOFs have exceptional potential for heavy metal pollution remediation. More efforts are required for designing MOF-based materials and smart handy sensors for heavy metal sensing with long life and reusability. Innovative research in the field of MOFs-based sensor will improve its practical applications and industrial uses.

Conflict of interest

The authors declare no competing financial interest.

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