Metal Organic Framework-Based Sensor For Detecting Mercury In Freshwater

[1]**Vanshika Mishra**, [2]**Simran Kaur,**

[1]Amity University (Amity institute of Biotechnology), Lucknow,Uttar Pradesh, India.

[2]Christ (Deemed-to-be) university Department of life Sciences Bengaluru 560029 Karnataka India.

Abstract

Metal Organic Frameworks (MOFs) are noted as exceptional candidates towards the detection and removal of specific analytes. MOFs were reported in particular for the detection/removal of environmental contaminants, such as heavy metal ions, toxic anions, hazardous gases, explosives, etc. Among heavy metal ions, mercury has been noted as a global hazard because of its high toxicity in the elemental (Hg^0), divalent cationic (Hg^{2+}), and methyl mercury (CH_3Hg^+) forms. To secure the environment and living organisms, many countries have imposed stringent regulations to monitor mercury at all costs. Regarding the detection/removal requirements of mercury, researchers have proposed and reported all kinds of MOFs-based luminescent/non-luminescent probes towards mercury. This review provides valuable information about the MOFs which have been engaged in detection and removal of elemental mercury and Hg^{2+} ions. Moreover, the involved mechanisms or adsorption isotherms related to sensors or removal studies are clarified for the readers. Finally, advantages and limitations of MOFs in mercury detection/removal are described together with future scopes.

Keywords: Hg^{2+}; CH_3Hg^+; elemental mercury; luminescent detection; adsorption isotherms; MOFs; real analysis; non-luminescent probes; organic linkers; metal nodes

1. Introduction

Due to the harmful and hazardous effects on ecosystem, detection/removal of mercury in different states, such as elemental, ionic, and organometallic (like methyl mercury), is in high demand and has attracted intense research interest. Accumulated mercury in environmental water often sedimented and converted as toxic methylmercury, which entered the food cycle and caused serious diseases in living beings as stated next etc [1].Therefore, U.S. Environmental Protection Agency (EPA) regulated an allowable maximum with the development of innovative tactics towards detection and removal of mercury are still the main focus of many research groups [2]. In this light, luminescent approaches comprising of nanoprobes, small molecules, supramolecular assemblies, aggregation induced emission, and covalent or metal organic frameworks (COFs/MOFs) are seemingly impressive with respect to their applicability, such as in vitro/vivo imaging studies.[3]Existence of porosity to adsorb specific analyte, improved aqueous solubility, exceptional photophysical and chemical properties. In fact, the majority of the MOFs are composed of organic ligand and metal nodes with certain porosity and tend to form different micro/nano-structures, such as particles, cubes, rods, spheres, etc [4]. Moreover, they also find their applications in multiple opto-electronics, photovoltaics, electronics, solar cells, light emitting devices (LEDs), field effect transistors (FETs), DNA detection, bio-analysis, real time detection/removal of specific analytes, etc. In sensory studies, they can behave as single, dual, and non-emissive materials, which tend to provide diverse responses upon interaction with guest analytes [5]. Moreover, the MOFs may display luminescent responses when interact with guest analytes via one-dimension (1D) (wavelength change and intensity alteration) or two-dimension (2D) (radiometric variation

combined with 1D responses) signals. However, by tuning the functional organic units mediated responses, [6]. Similarly, by modulating the functional units in MOFs, capture and removal of specific analytes can be achieved and become an effective approach for toxic analyte removal. In this track, studies on detection and removal of highly toxic mercury and its analogous can find inspiring and exceptional applicability towards the environmental and health safety. So far, diverse MOFs have been demonstrated for exceptional detection and removal elemental mercury and Hg2+. In fact, detection of Hg2+ can be attained by assorted mechanisms, such as bands overlapping, ligand interaction, cation exchange, and framework collapse, etc. On the contrary, removal of elemental mercury and Hg2+ ions are mostly achieved by tuning structural functionalities with organic ligands [7]. In addition, metal-organic coordination polymers and MOFs composited materials were demonstrated for mercury determination and removal [8]. So far, reviews on MOFs-based mercury detection and removal are deficient in valuable information, which encourages us to deliver a compact review to summarize the recent studies on this subject. In this review, we described the sensory detection and removal utilities of simple and polymeric MOFs and composited MOFs towards elemental mercury and Hg2+ as noted in **Figure 1**. Moreover, mechanism, electron transport, and structural benefits for mercury quantification were outlined for readers clarifications. Finally, a brief note on the synthesis of MOFs involved in discrimination and removal of mercury and its analogous was provided in this paper.

Figure 1: Schematic illustration of three possible MOFs-based mercury detection and removal mechanisms by (**A**) cavity trapping, (**B**) metal node displacement, and (**C**) interactive organic linkers (Reproduced with the permission from Ref).

2. MOFs in Optical Detection of Hg2+

Like nanomaterials-based sensors, micro/nano-structures of MOFs can be utilized for efficient detection of Hg2+. The zirconium (Zr) metal-incorporated MOFs were used to measure the amount of Hg2+ ions by luminescent and colorimetric methods[5] . Yang and his colleagues created a porous phorpyrinic luminous metal-organic framework (LMOF; PCN-224) using meso-tetra(4-carboxyphenyl) porphyrin (TCPP) ligands and Zr metal nodes through a modified solvothermal process [9]. They then used this framework to detect Hg2+ ions, achieving the desired sensing capability. Upon detecting Hg2+, the probe exhibited a rapid and noticeable decrease in fluorescence, shifting from a bright red to a dark red color. Additionally, it revealed a color change from purple to light green within a time frame of 2 minutes. The sensor response of PCN-224 remained unaffected by the presence of any competing ions and demonstrated reversibility in the presence of KI solution for up to seven cycles, as shown in Figure 2. The PCN-224 exhibited a direct and proportional reaction to Hg2+ in the concentration range of 0.1 to 10 micromole (μM), with a detection limit (LOD) of 6 nanomole (nM). In addition, probe PCN-224 shown greater efficacy in detecting Hg2+ in actual samples, including tap and river water.
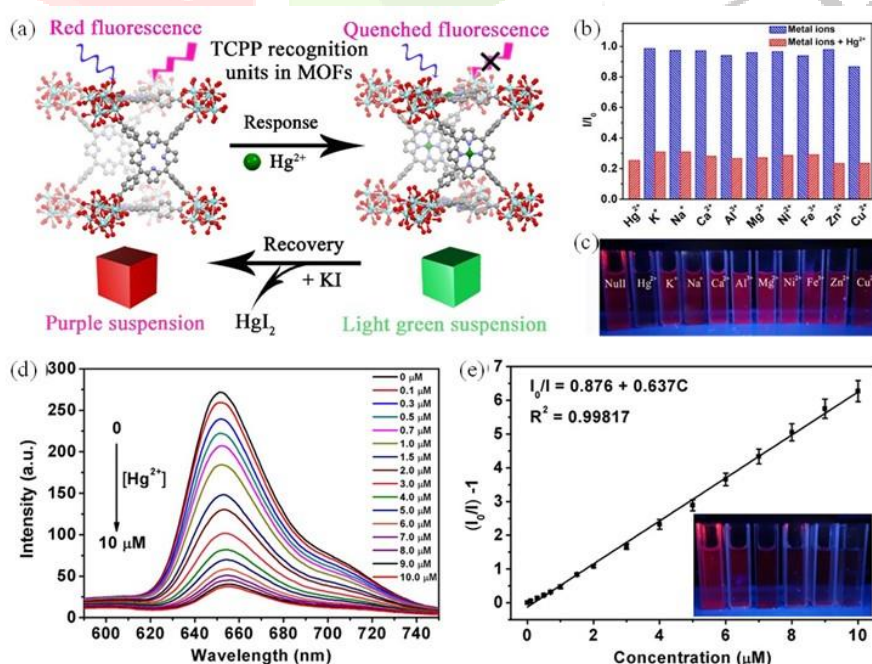

Figure 1: a) The design of this sensor hinges on a specific TCPP linker. This linker serves a dual purpose: it acts as the recognition site for Hg²⁺ ions and also reports the presence of the ion through a signal. When a solution is introduced to the PCN-224-Hg²⁺ complex, the Hg²⁺ ions are displaced, causing the fluorescence of PCN-224 to return and a visible color change from light green to purple

b) This picture portrays the sequential procedure for assembling a sensor. The TCPP linker, a crucial element, has a dual role: it can detect Hg²⁺ ions and indicate their existence by causing a quantifiable alteration. The introduction of a KI solution causes a disruption in the binding of Hg²⁺ ions in the PCN-224-Hg²⁺ complex

c) The photos below show vials containing a suspension of PCN-224 along with other metallic cations (at a concentration of 5 micromolar) and mercury (II) cations (Hg²⁺, also at 5 micromolar). The ultraviolet (UV) lamp emits light with a wavelength of 365 nanometers, illuminating all the vials.

d) The fluorescence spectra of a PCN-224 suspension (50 mg L-1) in a HEPES buffer solution (pH = 7, 60 mM) were seen as different amounts of Hg2+ were added. The excitation wavelength used was 430 nm.

e) The graph illustrates a Stern-Volmer plot that shows the correlation between the reduced fluorescence intensity of a PCN-224 suspension and the rising concentration of Hg²⁺ ions. The inset displays digital photos of the PCN-224 suspension in a quartz cuvette, which is being irradiated by a UV lamp with an excitation wavelength of 365 nm (λex = 365 nm). The inset illustrates the impact of adding Hg²⁺ to the solution, with concentrations varying from 0 to 10 µM (from left to right).

The UIO-66, a well-known metal-organic framework (MOF), was discovered to be highly efficient in detecting Hg2+. The substance consists of metal nodes made out of a zirconium oxide complex, which are connected by terephthalic acid (1,4-benzenedicarboxylic acid) ligands [10]. Enhancements in the detection of Hg2+ in water can be achieved by adjusting the structural characteristics of UIO-66 by modifications to the terephthalic acid bridging unit or through a post-doping process (PSM). Zhang et al. synthesized the fluorescent metal-organic framework (MOF) named UIO-66-PSM by combining UIO-66-N3 with phenylacetylene [11]. This MOF was designed for the purpose of detecting Hg2+ in water-based solutions. The details of this study may be found in reference. The synthesis of UIO-66-N3 involved the utilization of terephthalic acid containing an azide group. This compound exhibited reactivity towards phenylacetylene. The Brunauer–Emmett–Teller (BET) surface area of UIO-66-PSM was determined to be 606 m2 g1 when exposed to N2 gas at a temperature of 77K. The study found that UIO-66-PSM exhibited high selectivity towards Hg2+ by effectively reducing fluorescence in a linear manner within the concentration range of 0 to 78.1 µM. The estimated limit of detection (LOD) for Hg2+ was determined to be 5.88 µM

. Furthermore, the UIO-66-PSM was able to detect Hg2+ in tap and lake water samples [12]. Nevertheless, further investigation is required to determine the adsorption capacity of UIO-66-PSM for Hg2+ in the presence of other ions. Similarly, Samanta and her colleagues detailed the process of creating UIO-66@Butyne by combining ZrCl4 with 2,5-bis(but-3-yn-1-yloxy) terephthalic acid. They then utilized this compound to measure the concentration of Hg2+ in a water-based solution. The UIO-66@Butyne exhibited a reduction in fluorescence due to the presence of Hg2+ through the reaction-based chemodosimeter method. The acetylene unit, which is bonded with three bonds, reacted with Hg2+ on the surface, resulting in the suppression of green fluorescence with a limit of detection (LOD) of 10.9 nM. Furthermore, it exhibited greater selectivity towards Hg2+ in comparison to other ions. The BET surface area of UIO-66@Butyne was determined to be 74 square meters per gramme for Hg2+ at a temperature of 77 Kelvin. Xiaoxiong et al. suggested a method of post-doping Eu3+ onto the surface of a UIO-66 type metal-organic framework (Eu3+@UIO-66 (DPA)) synthesised by reacting ZrCl4 and isophthalic acid with 2,6-pyridinedicarboxylic acid (DPA). This modification was proposed for use in sensor research. The introduction of Eu3+ doping resulted in the MOF exhibiting a pronounced red fluorescence, which was achieved through the coordination of Eu3+ with the pyridine "nitrogen" and acid group. When metal ions were added to the MOF system mentioned above, only Fe3+ and Hg2+ ions exhibited fluorescence quenching at a wavelength of 615 nm in water. This quenching occurred due to the displacement of Eu3+ atoms.

By introducing hydrogen peroxide (H2O2) as a masking agent for Fe3+, the issue of Fe3+ interfering with Hg2+ selectivity was resolved. This resulted in a linear response range of 10 nM to 2.5 µM, with a limit of detection (LOD) of 8.26 nM, which is lower than the permissible limit. This work is commendable in terms of its strategy and level of detail (LOD). However, the paper lacks real-time application examples. Wang and colleagues developed a new Zr-based metal-organic framework (MOF) called RuUIO-67. This MOF was combined with a ruthenium (Ru) complex to create a colorimetric sensor for detecting Hg2+ ions. The sensor's

response to Hg2+ ions could be reversed by using a solution of potassium iodide (KI). The UIO-67 consists of Zr6O4(OH)4 nodes connected by linear 4,4′-biphenyldicarboxylic acid (H2bpdc) bridging ligands. The RuUIO-67 MOF is produced by doping it with the ruthenium complex Ru(H2bpydc) (bpy)(NCS)2. This is obtained by reacting [RuCl2(p-cymene)]2, 2,2′-bipyridine (bpy), 2,2′-bipyridine-5,5′-dicarboxy (H2bpydc), and ammonium thiocyanate (NH4NCS). When Hg2+ is added to RuUIO-67 in a mixture of methanol and water (8:2) with HEPES buffer at pH 7.4, the original absorption band at 540 nm slowly disappears. Instead, a new band at 435 nm becomes visible, which is caused by the strong adsorption of the Sulphur "S" atom in the NCS group.

The Metal-Organic Framework (MOF) exhibited a direct and proportional reaction within the concentration range of 0–13 µM. The Limit of Detection (LOD) for this reaction was determined to be 0.5 µM (equivalent to 0.1 parts per million), and it was also possible to visually detect concentrations as low as 7.2 µM without the need for any additional instruments [13]. Furthermore, the sensory system was able to undergo up to six cycles of reversibility when I- (KI solution) was introduced. Nevertheless, it is imperative to prioritize competing interrogations. Li et al. reported on the modified UIO-68 (Zr6O4(OH)4 clusters connected with 4,4′-terphenyldicarboxylate (TPDC)) MOFs UIO-68-NCS, UIO-68-R6G, and UIO-68-R6Gl using a post-synthetic modification technique for the purpose of colorimetric and fluorescent detection of Hg2+[14]. The UIO-68-NH2 compound reacted with thio-phosgene and triethylamine to produce UIO-68-NCS. This UIO-68-NCS was then reacted with N-(rhodamine-6G) lactam-ethylenediamine (R6G-EDA) and Hg (NO3)2 hydrate to give UIO-68-R6G and UIO-68-R6Gl, respectively. When Hg2+ is present, UIO-68-R6G exhibits a red color and shows an increased "turn-on" red emission. This is accompanied by changes in particle sizes, as depicted in Figure 3. The BET surface area of UIO-68-NH2, UIO-68-NCS, UIO-68-R6G, and UIO-68-R6Gl were determined to be 674 cm3 g−1, 620 cm3 g−1, 405 cm3 g−1, and 326.83 cm3 g−1, respectively, based on the N2 uptake at 77K. The reduction in BET surface area was ascribed to the inclusion of a greater rhodamine-thiocarbamide component, which diminished the porosity. The UIO-68-R6G exhibited a proportional reaction to Hg2+ in the range of 10−8 to 10−1 M when dissolved in Tris-HCl buffer solution. The limit of detection (LOD) was determined to be 0.1 nM. Furthermore, the UIO-68-R6G confirmed its suitability for bio-imaging experiments conducted in vitro and in vivo. Kim and his colleagues introduced the MOF-SALI-MAA-3eq by adding three equivalents of mercaptoacetic acid to NU-1000. NU-1000 is made up of Zr6(µ3-O)4(µ3-OH)4(H2O)4(OH)4 nodes and tetratopic 1,3,6, 8-(p-benzoate) pyrene linkers. This was done to detect the presence of Hg2+. The BET surface area of NU-1000 and SALI-MAA-3eq were determined to be 2253 m2 g−1 and 1906 m2 g−1, respectively, based on the N2 adsorption-desorption isotherms at 77K [15]. The reduction in surface area was attributed to the inclusion of mercaptoacetic acid.

The SALI-MAA-3eq exhibited a linear relationship in water within the concentration range of 0.1 to 10 mM. However, the limit of detection (LOD) was not specified. Additional research is needed to explore competition and assess the suitability of this work. The boric acid (BA)-functionalized lanthanide metal-organic framework (BA-Eu-MOF) was created by combining 5-boronobezene-1, 3-dicarboxylic acid with Eu3+ ions [16]. This framework was then used to detect Hg2+ and CH3Hg+ species in an aqueous media, as reported in reference. The BA-Eu-MOF exhibited a morphology characterized by mesoporous nanoparticles, which displayed a consistent size distribution of approximately 400 nm. Additionally, it exhibited red emission, excellent dispersibility, and solubility in water. At first, the negative effect caused by the "antenna" was neutralized by boric acid (BA), resulting in mild red emission from the BA-Eu-MOF. When detecting the Hg2+ and CH3Hg+ species using a chemodosimeter reaction between BA and the analytes, the phenomenon known as the "antenna" effect was observed. This resulted in a significant increase in red fluorescence when exposed to a UV-lamp with a wavelength of 365 nm. The BET surface area of BA-Eu-MOF was determined to be 39.7 m2 g1 using N2 gas at a temperature of 77K. The introduction of Hg2+ and CH3Hg+ resulted in a proportional increase in photoluminescence (PL) response at 620 nm within the concentration ranges of 1–60 µM and 1–80 µM. The limit of detection (LOD) for Hg2+ was determined to be 220 nM, while the LOD for CH3Hg+ was found to be 440 nM. Furthermore, BA-Eu-MOF exhibited superior selectivity compared to other mono- and di-valent cations in real-time river water applications.
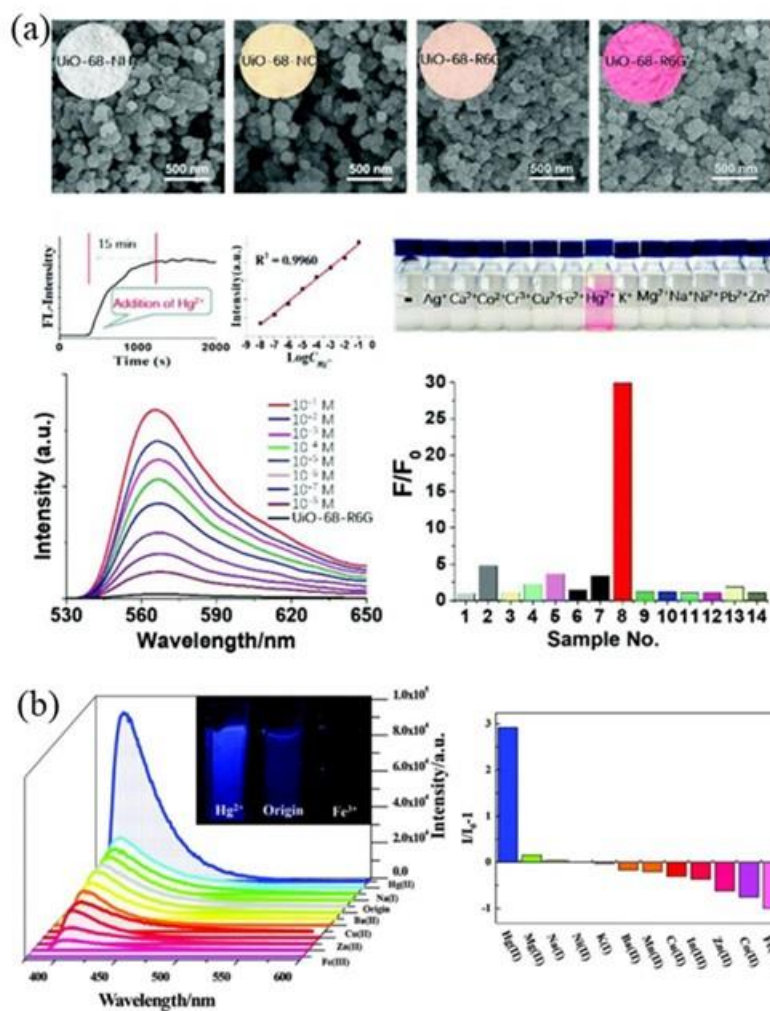
: a) **This study investigates the use of UIO-68-R6G, a specific type of metal-organic framework (MOF), for the purpose of detecting Hg²⁺. Scanning electron microscopy (SEM) images (a) provide a visual representation of the structure and shape of different metal-organic frameworks (MOFs) in their original form after synthesis. Part (b) examines the fluorescence quenching of UIO-68-R6G by Hg²⁺ in a Tris-HCl buffer solution. The quenching is quantified using the Stern-Volmer constant (Ksv = 4.1 × 10⁹ L mol⁻¹). The inset plots presumably illustrate the correlation between the concentration of Hg²⁺ and the strength of emission, together with the emission response that changes over time. Section (c) assesses the selectivity of UIO-68-R6G for Hg²⁺ by evaluating its emission response to different metal ions (10⁻⁴ M) in an aqueous solution. If included, inset images can visually demonstrate potential colour changes that may occur when interacting with certain metal ions.**

b) **Exposing suspensions of [Ag(2,4′-Hpdc)(4,4′-bpy)]n to radiation at a wavelength of 300 nm causes the molecules to get excited, resulting in the emission of photoluminescence at a wavelength of 401 nm. The enclosed image illustrates the substance under 365 nm ultraviolet (UV) radiation.**

MOFs containing different lanthanide metal nodes have also been used to discriminate Hg2+ ions. The Ln (TATAB) (DMF)4(H2O) (MeOH)0.5 MOFs were synthesized in high yields by reacting the organic ligand "4,4′,4″-s-triazine-1,3,5-triyltri-p-amino-benzoic acid (H3TATAB)" with lanthanide metals (Ln = Eu, Tb, Sm, Dy and Gd) [17]. These MOFs were then investigated for their ability to detect metal ions. Only the TbTATAB in water exhibited specific sensitivity to Hg2+ and did not respond to the other lanthanide ions (Eu, Sm, Dy, and Gd) found in MOFs.   While detecting Hg2+, the luminescence of TbTATAB at wavelengths of 494, 544, 587, and 622 nm (with a quantum yield of 77.48%) decreased in a linear manner from 0 to 50 μM, with a limit of detection (LOD) of 4.4 nM.

This study also showcased the ability to detect Hg2+ in actual water samples, including river water, drinking water, and tap water. However, details on the nanostructure and BET surface area were not provided. Li et al. recently created two Metal-Organic Frameworks (MOFs) called [Tb2(bpda)3(H2O)3] H2O and [Dy2(bpda)3(H2O)3] H2O. They made these MOFs by reacting 2,2′-bipyridine-4,4′-dicarboxylic acid (H2bpda) with LnCl3.6H2O (Ln = Tb and Dy) [18]. The researchers then used these MOFs for sensory

investigations. The compound [Dy2(bpda)3(H2O)3] H2O exhibited a reduction in fluorescence when exposed to Hg2+ ions at wavelengths of 489, 543, 582, and 620 nm, with an excitation wavelength of 310 nm. The Stern-Volmer constant (KSV) for this interaction was determined to be 20,406 M−1, and the limit of detection (LOD) was found to be 7.2 nM. Further research is needed to explore the BET surface area and investigate potential interferences.

Additionally, studies on the detection of Hg2+ utilizing metal-organic frameworks (MOFs) containing zinc were also discussed. Morsali's research group proposed a method called double solvent sensing (DSSM) to accurately detect Hg2+ using a zinc-based metal-organic framework (MOF) called TMU-34(-2H), which consists of 4,4′-oxybis (benzoic acid) (OBA), 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine (DPT), and N, N-dimethylformamide (DMF). The BET specific surface area of TMU-34(-2H) to N2 gas at 77K was 667 m2 g1 and its N2 gas adsorption capacity was 201 cm3 g1 [19]. When exposed to Hg2+, the TMU-34(-2H) exhibited 1D-transduction signals with a 243% enhancement in photoluminescence (PL) at a wavelength of 648 nm (excitation wavelength of 504 nm) in water. In acetonitrile, the TMU-34(-2H) showed a 90% decrease in PL at a wavelength of 618 nm (excitation wavelength of 458 nm). The estimated limits of detection (LODs) for Hg2+ were determined to be 1.8 µM in water and 6.9 µM in acetonitrile, respectively. These results were obtained within a time frame of 15 seconds. Nevertheless, both solvents had disruptive effects caused by other ions. Thus, the DSSM strategy was suggested to enhance the sensitivity to Hg2+ by merging water and acetonitrile.

The sensing factor of Hg2+ was determined to be 41 by constructing a 2D sensing curve. This value was found to be greater than the sensing factors of all other metal ions, which ranged between 0 and 2. Therefore, the disruptive influences were eradicated. Nevertheless, the suitability of its application remains uncertain due to the absence of mechanistic elements. Subsequently, a negatively charged metal-organic framework (MOF) called Zn-TPTC (TPTC stands for [2,2′:6′,2″-Terpyridine]-4,4′,4″-tricarboxylic acid) was introduced as a means of detecting Hg2+ using luminescence. When Hg2+ was added, the Zn-TPTC showed a decrease in the intensity of its photoluminescence (PL) at a wavelength of 492 nm. This decrease occurred within a concentration range of 1 to 100 µM, and the limit of detection (LOD) was calculated to be 3.7 nM. The nitrogen (N) atoms of the metal-organic framework (MOF) can form strong interactions with Hg2+ ions because to their higher affinity [20]. There is a lack of data regarding the BET surface area, as well as the studies on competition and application. Later, Pankajakshan and colleagues reported the capability of [Zn(4,4l-AP) (5-AIA)] to detect Hg2+ ions.

The compound (DMF)0.5n, which consists of 4,4′-azopyridine, deprotonated 5-amino isophthalic acid (5-AIA), and N, N′-dimethylformamide (DMF), undergoes photoluminescence (PL) quenching at 405 nm in an aqueous solution. The MOF probe has a quantum yield (QY) of 11% and a Brunauer-Emmett-Teller (BET) surface area of 173 m2 g−1. The substance remained stable over a pH range of 4 to 11 and showed a consistent decrease in photoluminescence (PL) in response to the presence of Hg2+ ions. This response was observed within a concentration range of 9.99 µM to 20 mM [21]. In addition, the MOF exhibited a strong preference for Hg2+ compared to other cationic species with different valences, such as mono-, di-, and tri-valent ions. The limit of detection (LOD) was as low as 10−11 M, and the estimated KSV value was 1.011×10^9 M−1 s−1 [22]. The sensitivity was ascribed to a particular interaction between Hg2+ and the unattached -N=N- group of 4,4′-azopyridine. Undoubtedly, this study may be deemed exceptional due to its outstanding effectiveness in detecting Hg2+ in real-time, across various water sources such as sea water, river water, tap water, and drinking water, as well as on single crystals of MOF on an aluminum foil. Khatun and her colleagues then created the luminous MOF-Zn2(NDC)2(DPTTZ) with an NDC antenna and DPTTZ pillars [23]. This MOF exhibited the ability to detect Hg2+ by red-shifts in its photoluminescence emission, as reported in reference.

Furthermore, a MOF-Zn2(1,4-BDC)2(DPTTZ)2 compound was synthesized for the purpose of comparison. Here, the abbreviation 1,4-BDC stands for 1,4-benzenedicarboxylic acid. The BET surface area and pore volumes of MOFs-Zn2(NDC)2(DPTTZ) and Zn2(1,4-BDC)2(DPTTZ)2 for CO2 were determined to be 106.8 m2 g−1 and 113.4 m2 g−1, and 6.6 10−2 cm3 g−1 and 7.8 10−2 cm3 g−1, respectively. [24] Despite the absence of empirical proof, it was hypothesized that the shift in photoluminescence (PL) could be ascribed to the interaction between Hg2+ and the DPTTZ group. This task necessitates additional focus on the level of detail (LOD), conflicting research papers, and real-time implementations. A recent study showcased the use of Zn-based MOF-ZnAPA with 5-aminoisophthalic acid (H2APA) organic linkers for detecting Hg2+ in water through fluorescence quenching. The photoluminescence (PL) emission of the metal-organic framework (MOF) at a wavelength of 405 nm was consistently reduced in a linear manner when exposed to concentrations of Hg2+ ranging from 0 to 100 µM. The limit of detection (LOD) for Hg2+ was determined to be 0.12 µM.

This could be attributed to the strong binding affinity between Hg2+ and the nitrogen atom of the amino group. This study demonstrated a high level of selectivity compared to other mono- and di-valent cationic species. However, further emphasis should be placed on investigating the BET surface area and practical applications. The Cd-based MOFs were also involved in distinguishing Hg2+ ions, similar to Zn-based MOFs [25]. As an illustration, Wu and his colleagues created a compound called Cd containing a three-dimensional MOF-[Cd1.5(C$_{18}$H$_{10}$O$_{10}$)] (H$_3$O) (H$_2$O)3n-Cd-EDDA. This compound has the ability to emit two different types of light and was used to detect Hg2+ in pure water using a ratiometric method. The Cd-EDDA compound was synthesized with an 80% yield by reacting 5,5′-[ethane-1,2-diylbis(oxy)] diisophthalic acid (H4EDDA) with Cd (ClO$_4$)2 6H$_2$O using a hydrothermal method. When Hg2+ was added to Cd-EDDA, the intensity of PL emission at 350 nm reduced dramatically (KSV = 4.3 103 M−1). This decline was accompanied by the appearance of a new PL peak at 410 nm. The response was linear within 15 seconds for concentrations ranging from 4 to 25 µM.

The computed limit of detection (LOD) was 2 nM, which was below the allowed threshold. It is important to mention that Cd-EDDA exhibited high selectivity towards various metal ions by causing the breakdown of crystallinity, and this selectivity was not reversible with Na2S. Thus, the probe functions as a chemodosimeter. Further investigations are needed to gather information on the BET surface area and its real-time applicability. A yellow crystal MOF, [(Me2NH$_2$) Cd3(OH)(H$_2$O)3(TATAB)2] (DMA)6], was synthesized by solvothermal reaction of Cd (NO$_3$)2 6H$_2$O and 4,4′,4”-s-triazin-1,3,5-triyltri-p-aminobenzoic acid (H3TATAB) in DMA (N, N-dimethylacetamide), methanol, and HCl at 95 ◦C for 3 days [26]. This MOF was then used for detecting luminescent Hg2+ in water.

The inclusion of Hg2+ resulted in the quenching of PL emission at 365 nm due to the interaction between the 'N' atoms of amino and triazine groups. However, the selectivity was greatly influenced by the presence of Fe3+. Furthermore, there was a lack of information regarding the BET surface area and its relevance. A recent study utilized microwave synthesis to create the Cd2+-containing MOF-NH2-Cd-BDC by reacting Cd (ClO4)2.6H2O with 2-aminoterephthalic acid (NH2-H2BDC). This MOF was then employed for the detection of Hg2+ through the suppression of photoluminescence at a wavelength of 427 nm [27]. The amino group (-NH2) of NH2-Cd-BDC underwent a reaction with Hg2+ resulting in a decrease in emission intensity in a concentration range of 1 to 20 µM. The Stern-Volmer constant (KSV) for this reaction was determined to be 28.0 x 10^3 M−1, and the limit of detection (LOD) was found to be 0.58 µM [28]. While the work appears to be rather satisfactory compared to previous publications, it still lacks data on the BET surface area, real-time application, and comparative research. The Fe (II)-MOF-NPs, which are nanoparticles composed of ferrous (Fe2+) ions, were created using a solvothermal reaction between FeSO4.7H2O and nano linkers. These nano linkers were synthesized by refluxing 1, 2-phenylenediamine and 5-aminoisophthalic acid. The Fe (II)-MOF-NPs were then used for colorimetric and PL detection of Hg2+.The nanoparticles have dimensions ranging from 100 to 250 nm and also contain magnetic characteristics. Upon the introduction of Hg2+ ions, the photoluminescence (PL) emission exhibited a 'turn-on' behavior and experienced a red shift from 416 nm to 422 nm.

The absorption peak at 427 nm was both intensified and pushed towards longer wavelengths to 456 nm, resulting in a change in color from yellow to colorless. The absorption and photoluminescence (PL) both exhibited a linear response within a concentration range of 1 nM to 1 µM. The limit of detection (LOD) for absorption was 1.17 nM and for PL was 1.14 nM. The limit of quantification (LOQ) for absorption was 1.59 nM and for PL was 1.48 nM [29]. Furthermore, the Fe (II)-MOF-NPs dissolved in DMSO shown efficacy in distinguishing Hg2+ in both competitive and authentic settings, including tap water, mineral water, river water, sea water, and wastewater. According to the data mentioned above, the Fe (II)-MOF-NPs have great potential for distinguishing Hg2+ [30]. However, in order to proceed with studies on removing Hg2+, it is necessary to conduct mechanistic investigations and BET adsorption experiments. In order to detect Hg2+ ions, Li and his colleagues introduced a hydrostable bromine-functionalized Mn-based MOF called [Mn2(Bript)2(4,4l-bpy).5(DMF)] (H2O) . In this context, H2Bript, 4,4′-bpy, and DMF refer to 4-Bromoisophthalic acid, 4,4′-bipyridine, and dimethylformamide, respectively [5]. The MOF's BET surface area was determined to be 210 m2 g−1 and decreased to 33 m2 g−1 after Hg2+ was loaded. The PL emission at 468 nm was linearly quenched from 0 to 0.03 M due to the strong binding affinity between the Br atom and Hg2+ ion. The quenching constant (KSv) was determined to be 1390.5 M−1. The estimated limit of detection (LOD) was 48 µM.

The MOF exhibited a high degree of selectivity towards Hg2+ ions in water, even in the presence of various other competing species. Nevertheless, additional emphasis should be placed on conducting studies regarding the practicality and limits of real-time application and levels of detection (LODs) before progressing any

further [31]. In their study, Song et al. demonstrated the exceptional specificity of Ag coordinated MOF in detecting Hg2+ ions. They synthesised three metal-organic frameworks (MOFs) containing Ag+/Cu2+ ions using a hydrothermal method [32]. The MOFs were named [Ag(2,4l-Hpdc) (4,4l-bpy)] n, [Ag(2,2l-Hpdc) (4,4l-bpy)0.5] n, and [Cu(2,2l-Hpdc)2(1,4-bib)] n. In these names, 2,4′-Hpdc, 2,2′-Hpdc, 4,4′-bpy, and 1,4-bib represent 2,4′-biphenyldicarboxylic acid, 2,2′-biphenyldicarboxylic acid, 4,4′-bipyridine, and 1,4-bis(1-imidazolyl) benzene, respectively. Out of all the compounds tested, only the [Ag(2,4l-Hpdc) (4,4l-bpy)] n in water demonstrated selectivity towards Hg2+ by exhibiting a 'turn-on' response with photoluminescence emission at 401 nm. It is important to observe that the Fe3+ exhibited photoluminescence (PL) quenching in the selectivity investigations, as depicted in Figure 4. The PL emission of the MOF (in water) was increased in a linear manner between Hg2+ concentrations ranging from 0 to 100 μM due to the strong attraction between 2,4′-Hpdc and Hg2+.

 The limit of detection (LOD) for Hg2+ was determined to be 9.63 nM [33]. Nevertheless, further optimisation is necessary to enhance the BET surface area, conduct competitive analysis, and apply the method to real samples. Additionally, other MOFs were utilized for the detection of various analytes apart from Hg2+, as described below. For instance, a ligand called 4,4′-(benzothiadiazole-4,7-diyl) dibenzoic acid has been used in the synthesis of metal-organic frameworks (MOFs) such as [Mn4(C20H10N2O4S)2-(HCOO)4(DEF)2] and [Pb(C20H10N2O4S) (DMF)]. These MOFs were created using solvothermal synthesis, with DEF representing N, N′-diethylformamide and DMF representing N, N′-dimethylformamide [34]. These MOFs have been found to be effective in sensing the presence of Hg2+ and Tl3+ metal cations, as well as chromate, dichromate, and permanganate anions.

 The detection of metal ions was linked to the interaction between the 'S' atom and metal cations. Furthermore, the photoluminescence (PL) emission at a wavelength of 500 nm was promptly suppressed with limits of detection (LODs) as low as parts per billion/parts per million (ppb/ppm) in the presence of these substances being analyzed. It should be emphasized that both MOFs can be utilized for the detection of Hg2+ in samples that do not contain Tl3+ [35]. Therefore, these Metal-Organic Frameworks (MOFs) can be classified as sensors for detecting Hg2+ ions. Nevertheless, they lack selectivity. A ratiometric Hg2+ sensor was proposed using a solvent called MOF-[Zn(tpbpc)2], which was prepared using a solvothermal technique. The organic linker Htpbpc (4′- [4,2′;6′,4″]-terpyridin-4′-yl-biphenyl-4-carboxylic acid) and DMF solvent were used along with Zn metal nodes. This Zn-MOF was also able to detect CrO42− and Cr2O72− species in water by observing the quenching of PL (photoluminescence) at 414 nm.

The interaction between the pyridine 'N' atoms and Hg2+ ions, as well as the inhibition of energy transfer processes by CrO42− and Cr2O72− ions, may explain the observed sensory results. The PL emission peak at 414 nm was linearly quenched as Hg2+ ions were added in concentrations ranging from 0 to 1200 μM, with a limit of detection (LOD) of 0.32 μM. Additionally, a new peak at 500 nm (green emission under UV lamp λex = 365 nm) appeared during this process. However, the selectivity may be compromised when conducting investigations in the presence of Cr (VI) ions (CrO42− and Cr2O72). Therefore, additional inquiries are necessary because of the insufficient data regarding the selectivity, BET surface area, and practical uses. The stable dye-incorporated MOF-[(CH3)2NH2] [In (TNB)4/3] was developed by Ma's research group [36]. The MOF-DSM system was synthesized using a solvothermal technique, in which H3TNB (4,4′,4″-nitrilotribenzoicacid) served as the organic linker and was combined with a dye 4-[p-(dimethylamino)styryl]-1- ethylpyridinium (DSM) . The MOF-DSM system exhibited sensing capability for Hg2+, Cr2O72-, and a diverse range of nitro-compounds. The calculated BET surface area of the MOF and MOF-DSM systems were 491 m2 g−1 and 236 m2 g−1, respectively. When discriminating Hg2+ ions, the photoluminescence (PL) emission peaks of MOF-DSM in water were observed to decrease in a linear manner at wavelengths of 478 and 630 nm. This quenching effect occurred within a concentration range of 1-10 μM. The limit of detection (LOD) for Hg2+ ions was assessed to be 1.75 parts per billion (ppb), and the Stern-Volmer constant (KSV) value was determined to be 1.48×10^5 M−1. The energy transfer efficiency of the π-π* transitions decreased as a result of the strong interaction between Hg2+ and the 'N' atoms of DSM [37]. The MOF-DSM shown superior efficacy in detecting Cr2O72- in aqueous solutions and detecting nitro-compounds in both vapour and aqueous environments. Li et al. used the solvothermal method to create the Co-based MOF-[Co (NPDC)(bpee)] DMF 2H2O, where NPDC represents 2-nitro phenylenedicarboxylate and bpee represents 1,2-bis(4-bipyridyl) ethylene.

They found that this MOF has the ability to detect Hg2+ and MnO4- ions. This metal-organic framework (MOF) exhibited a decrease in photoluminescence (PL) when exposed to MnO4- ions in water, and an increase in PL at a wavelength of 471 nm in the presence of Hg2+ ions. The MOF demonstrated a linear response to

Hg^{2+} ions in the concentration range of 1–120 µM, with a limit of detection (LOD) of 4.1 µM. Nevertheless, this work still exhibits mechanistic deficiencies with suboptimal limits of detection (LODs) and lacks information regarding its applicability. In this study, Yang and his colleagues synthesized two Cd-based MOFs, specifically Cd(L)(atpa)]n and [Cd(L)(tbta)(H2O)]n, using a hydrothermal method. The compounds were then used as dual luminescent sensors in water. [Cd(L)(atpa)] n was able to detect Cu^{2+} and $Cr_2O_7^{2-}$, while [Cd(L)(tbta) (H2O)] n was able to detect Hg^{2+} and $Cr_2O_7^{2-}$. The chemical names H2atpa, H2tbta, and L represent 2-aminoterephthalic acid, tetrabromoterephthalic acid, and 1,4-bis(benz-imidazol-1-yl)-2-butene, respectively. The photoluminescence (PL) intensity of [Cd(L)(tbta) (H2O)] n at a wavelength of 294 nm was progressively reduced in a linear manner upon the addition of Hg^{2+} ions, ranging from 0 to 0.25 mM. The limit of detection (LOD) for this quenching process was determined to be 0.043 µM, and the Stern-Volmer constant (KSV) was found to be 1.72×10^5 M^{-1}.

In addition, the fluorescence of [Cd(L)(tbta) (H2O)] n in water at 294 nm was also suppressed in the presence of $Cr_2O_7^{2-}$. This study lacked information regarding the BET surface area, differentiation between Hg^{2+} and $Cr_2O_7^{2-}$ (Cr6+), and practical applications. Afterwards, the compounds 2,6-naphthalenedicarboxylic acid (NP) and 1,5 dihydroxy-2,6-naphthalen edicarboxylic (DNP) were combined with lanthanide cations (La3+ and Ce3+) to create luminous MOFs. These MOFs are specifically named AUBM-2 (Ce) and AUBM-2(La) when using the NP ligand, and AUBM-3(Ce) and AUBM-3(La) when using the DNP ligand. They were involved in the examination of sensory phenomena. Upon being stimulated at wavelengths of 300 and 370 nm, the AUBM-2 (Ce) and AUBM-3 (Ce) exhibited sensory reactions to Hg^{2+}, Cr3+, Pb2+, Cd2+, and As3+ through either increasing or decreasing fluorescence [2]. Additional refinement is needed for the detection of Hg^{2+} in this investigation. Ren et al. suggested using amino-MIL-53(Al) nanosheets, which are made by combining $AlCl_3.6H_2O$ with 2-amino-terephthalic acid through a hydrothermal synthesis process, for the purpose of detecting Hg^{2+} and glutathione (GSH) using luminescence. The emission of amino-MIL-53(Al) nanosheets at a wavelength of 435 nm in an aqueous solution was consistently reduced in proportion to the concentration of Hg^{2+} ions, ranging from 1.96 nM to 38.27 µM [38].

The minimum concentration of Hg^{2+} ions that could be detected was determined to be 0.23 nM. In addition, the decrease in luminescence was partially reversed by the addition of GSH. The linear range of detection was from 210 nM to 15.25 µM, with a limit of detection of 8.11 nM. Nevertheless, this work is still deficient in terms of providing information regarding the BET surface area. Cadmium-based metal-organic frameworks (MOFs) were synthesized using solvothermal methods. The first MOF, [(Cd (II)BPDC)0.5(L1) (NO3)] 3.4DMF, consists of 4,4′-biphenyldicarboxylic acid (BPDC), 1-(3,5-di(1H-imidazol-1-yl) phenyl)-1H-imidazole (L1), and Dimethylformamide (DMF). The second MOF, ((Cd2(4-tp-3-lad) (1,4-BDC)2)2MeCN) n, consists of 2,3,5,6-tetra(pyridin-4-yl)-bicyclo [2.2.0] hexane (4-tp-3-lad), deprotonated 1,4-benzenedicarboxylic acid (4-BDC), and acetonitrile (MeCN). These MOFs were proposed for the detection of Hg^{2+} and nitro-explosives through fluorescence quenching. Nevertheless, the lack of adequate data on the BET surface area, conflicting research, and feasibility issues renders these results unimpressive. Later, Su et al. reported that the Co-based MOF [Co2(L)(hfpd) (H2O)] 1.75H2On (where H4hfpd and L denote 4,4′-(hexa-fluoroisopropylidene) diphthalic acid and 4,4′-bis (imidazol-1- yl)-biphenyl) has the ability to sense Hg^{2+} and acetylacetone by luminous quenching responses. The MOF, which was synthesized by hydrothermal methods, exhibited a decrease in luminescence when exposed to Hg^{2+} concentrations ranging from 0 to 200 µM [39]. The Stern-Volmer constant (KSV) for this quenching effect was determined to be 6497 M^{-1}, and the limit of detection (LOD) was found to be 4 µM. However, this work necessitates additional investigations into the BET surface area, nano/micro-structure, competing studies, and applicability [40].
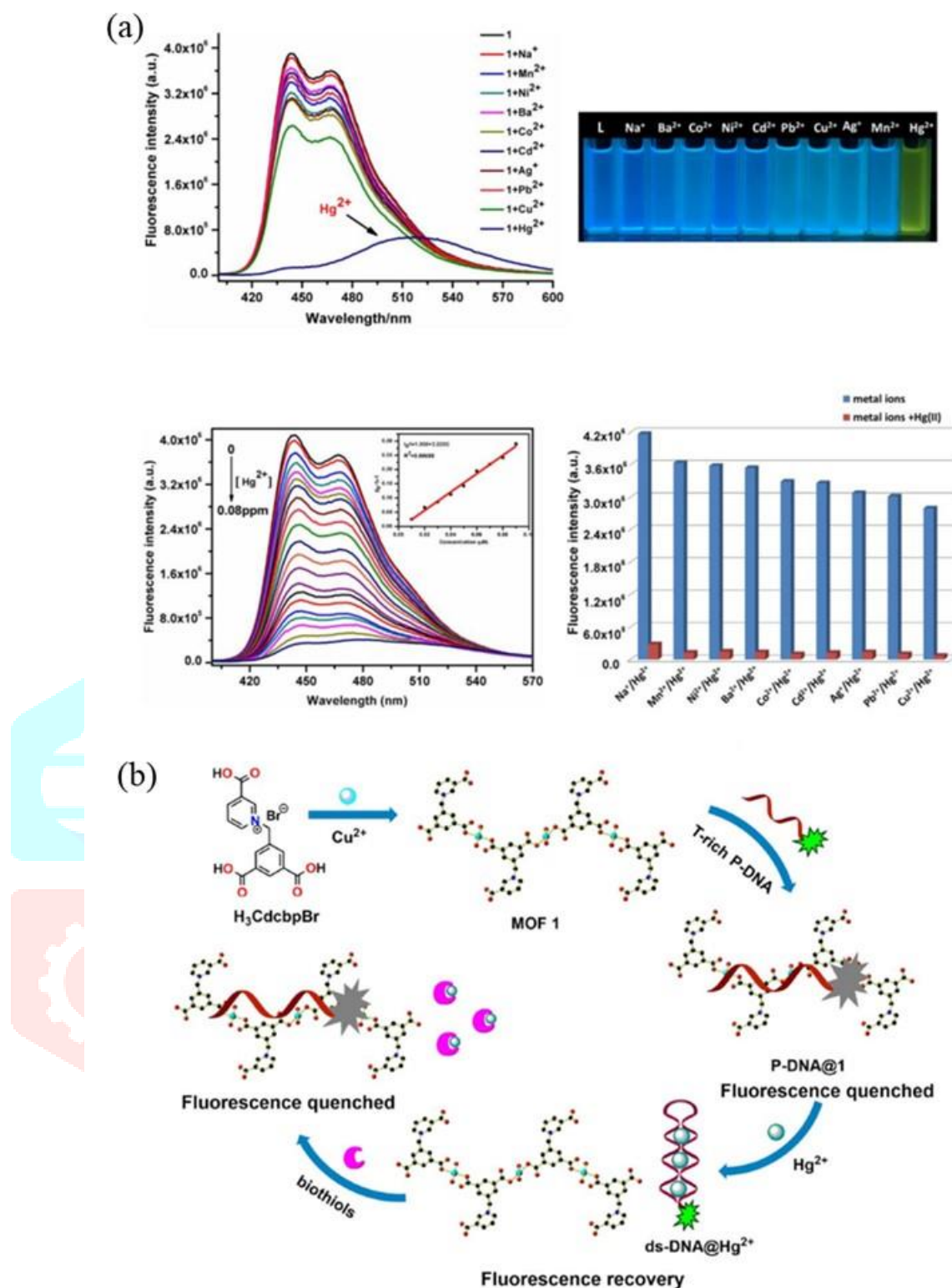
A) **This study examined the luminescent characteristics of a metal-organic framework (MOF) called Zn-MOF in solutions of N,N-dimethylformamide (DMF). The objective was to comprehend the impact of various metal ions on the emission behaviour of Zn-MOF. Panel (a) investigated the impact of Mn^{2+} ions on the emission spectra of Zn-MOF dispersed in DMF. Panel (b) recorded the alterations in colour noticed when Zn-MOF suspensions with different metal ions were exposed to UV radiation. Panel (c) assessed the impact of escalating Hg^{2+} concentration (ranging from 0 to 0.08 ppm) on the emission spectrum of Zn-MOF in DMF. The inset in this panel demonstrated the direct correlation between quenching efficiency and Hg^{2+} concentration at lower levels (0-0.018 ppm), indicating the possibility of quenching by Hg^{2+} ions. Panel (d) ultimately assessed the fluorescence intensity of Zn-MOF when exposed to DMF solutions containing individual metal ions (excited at 389 nm). This intensity was then compared to the intensity recorded when mixes comprising both Hg^{2+} and the same metal ions were present. This thorough examination offers useful insights into the impact of metal ions on the luminous characteristics of Zn-MOF, with Hg^{2+} potentially serving as a suppressor.**

B) **The following article outlines a detection method for mercury ions (Hg²⁺) and biological thiols (biothiols) using a hybrid material known as P-DNA@1.**

Metal-coordinated polymers utilized as luminescent sensors for detecting Hg2+ ions.

Furthermore, metal-containing coordination polymers were suggested as a means of detecting Hg2+ by luminescence sensing. As an example, the research group led by Sun created coordination polymers using zinc (Zn) and cadmium (Cd) called [Zn (TPDC-2CH3) (H2O)2]. The compounds mentioned are H2O and [Cd (TPDC- 2CH3) (H2O)4]. H2O is produced by reacting 2′,5′-dimethyl-[1,1′:4′,1″-terphenyl]-4,4″-dicarboxylic acid (H2TPDC-2CH3) with Zn^2+ and Cd^2+ ions using solvothermal methods. The resulting compounds are then used for sensory analysis of metal ions. The release of the [Zn (TPDC-2CH3) (H2O)2] compound. The concentration of H2O metal polymer in water was reduced in a linear manner between 1–10 femtomole (fM) at a wavelength of 380 nm [41]. The limit of detection (LOD) for this process was determined to be 3.6 fM.

The CHEQ effect, which involves the quenching of fluorescence, is caused by the coordination between the carboxyl group and Hg2+. Nevertheless, this research failed to include any data on the BET surface area and the feasibility of the subject matter. Subsequently, the Eu/IPA CPNPs were synthesized using the solvothermal method by combining Eu3+ coordination polymer nanoparticles (CPNPs) with isophthalic acid (IPA) bridging ligands. These CPNPs were then utilized for the detection of Hg^2+. The absorbance band of Eu/IPA CPNPs in Tris-HCl buffer (25 mM, pH 7.0) initially overlapped with imidazole-4,5-dicarboxylic acid (Im), resulting in a decrease in emission intensity at 615 nm due to the inner filter effect (IFE). Upon the addition of Hg^2+, the intensity of the initial fluorescence emission (IFE) was diminished, and subsequent restoration of emission at a wavelength of 615 nm was detected. The linear correlation of Hg2+ varied from 2 nanomolar (nM) to 2 micromolar (µM), with a limit of detection (LOD) of 2 nM. The probe's effectiveness was further demonstrated by its applicability in biological fluid samples. However, it is important to assess the application of information related to BET surface area due to its outstanding usefulness.

In their study on the development of Hg2+ sensors, Li et al. discussed a 3D coordination polymer called [Zn2(1,4-bpyvna) (1,3,5-BTC) (OH)] H2on, which was synthesized using solvothermal methods. In this polymer, 1,4-bpyvna and 1,3,5-H3BTC refer to 1,4-bis(2-(pyridin-4-yl) vinyl) naphthalene and 1,3,5-benzene-tricarboxylic acid, respectively. The researchers identified this polymer as a potential Hg^2+ sensor. The compound [Zn2(1,4-bpyvna) (1,3,5-BTC) (OH)] H2O in DMF exhibited fluorescence quenching at wavelengths of 444 and 472 nm due to the interaction impact of 1,4-bpyvna with Hg^2+, as shown in Figure 5.

The polymer exhibited a linear response within the concentration range of 0 to 0.018 ppm, with a limit of detection (LOD) of 0.057 ppm [42]. Additionally, a transition in hue from blue to yellow was noted, which exhibited fluorescence. However, additional investigations are still need to determine the BET surface area and explore real-time applications. Zhang and colleagues later demonstrated the ability of a fluorescent coordination polymer, [Zn(H3TTA) (H2O)2] 2H2O (where H_3TTA denotes [2,2′:6′,2″-terpyridine]-4,4′,4″-tricarboxylic acid), to sense Hg^2+ in an aqueous solution. The polymer was synthesized hydrothermally. The emission band at a wavelength of 500 nm was suppressed in the presence of Hg^2+ ions, with a KSV value of 4695 M−1. This work remains unfinished as a result of insufficient data regarding the BET surface area, limits of detection (LODs), and feasibility. Several research groups have documented the use of luminous coordination polymers based on Zn and Cd for the quantification of Hg^2+ and Cr2O72-. Due to the well-established reputation of Cr2O72- as a source of Cr^6+ ions, distinguishing between them is not possible in those studies. Consequently, such research cannot be regarded as exceptional investigations into Hg^2+ sensors. In a study conducted by Lin et al., they showed that a coordination polymer called [Ln2(PBA)3(H2O)3] DMF 3H2O, which contains Eu^3+, has the ability to sense Pb^2+ and Hg^2+ ions [43]. This sensing ability was observed in both DMF and aqueous media. In this context, PBA, DMF, and H2O refer to deprotonated 5-(4-pyridin-3-yl-benzoylamino)-isophthalic acid, Dimethyl-formamide, and water molecules, respectively. The polymer can be utilized for the detection of Hg^2+ in samples that do not contain Pb^2+ [44]. Therefore, these MOFs can be classified as Hg^2+ sensors. Nevertheless, they lack selectivity. Rachuri and co-workers have described a luminous coordination polymer, [Zn(µ2-1H-ade)(µ2-

SO4)], which was synthesized using a solvothermal reaction between adenine (HAde) and Zn(SO4) 7H2O. This is detailed more in reference. The research shows that the fluorescence intensity of [Zn(μ2-1H-ade) (μ2-SO$_4$)] at a wavelength of 395 nm in water was reduced in a linear manner when the concentration of Hg2+ was between 0-1 mM. The limit of detection (LOD) was determined to be 70 nM, and the Stern-Volmer constant (KSV) value was found to be 7.7 x 10^3 M−1 [45]. Furthermore, this polymer exhibits the added benefit of selectively detecting 2,4,6-trinitrophenol (TNP) in a water-based solution. The detection of Hg2+ is mostly due to its interaction with the basic sites (N atoms) of adenine and TNP through resonance energy transfer (RET). It is important to mention that this study also discussed the detection of Hg^2+ in paper strips. Therefore, it has the potential to be applied for efficient removal of Hg^2+ in actual samples using directed BET surface area analysis. Later, Zhu et al. showed that two luminescent coordination polymers, [Cd(L)(NTA)] n and [Ni(L)(NPTA) H2O] n, can be used to detect Hg^2+ ions. These polymers were synthesized using the solvothermal method and the compounds L, H2NTA, and H2NPTA represent 1,6-bis(benzimidazol-1-yl) hexane, 2-nitroterephthalic acid, and 3-nitrophthalic acid, respectively. The emission peaks at 292 nm and 295 nm of the polymers [Cd(L)(NTA)] n and [Ni(L)(NPTA) H2O] n (in water), respectively, were reduced in a linear manner by the presence of Hg^2+ in a concentration range of 1–200 μM. The corresponding limits of detection (LODs) were determined to be 3.05 μM and 2.29 μM, and the KSv values were found to be 3565 M–1 for 1 and 7432 M–1. Furthermore, both polymers exhibited exclusivity solely towards acetylacetone in comparison to all other solvents. Nevertheless, this task necessitates data regarding the BET surface area, rival research studies, mechanistic inquiries, and feasibility [46].

3. MOFs containing composites for the optical detection of Hg2+ ions.

In order to improve the detection capabilities of MOFs for Hg^2+, researchers have suggested synthesizing MOFs that consist of composites, as explained below. The researchers developed a metal polydopamine framework (MPDA) by using a sonochemical reaction of Co (NO$_3$)2 and 2-methylimidazole to create ZIF-67 primarily [47]. This framework was found to act as a fluorescent quencher for detecting Hg2+ and Ag+ ions. The detection sensitivity was enhanced by using exonuclease III signal amplification, resulting in very low limits of detection (1.3 pM for Hg^2+ and 34 pM for Ag+) [48]. This study was documented in reference. When Hg^2+ is added to the system containing MPDA-T-rich ssDNA (where T-rich ssDNA refers to single stranded Deoxyribonucleic acid with a high concentration of thymine), there is a noticeable increase in the emission of light at a wavelength of 520 nm. This increase in light emission follows a linear pattern, ranging from 0 to 2 nM, and the limit of detection (LOD) is determined to be 1.3 pM. The extinguished luminescence of MPDA, which was conjugated with single-stranded DNA rich in thymine bases, was restored by the formation of a complex between thymine bases and mercury ions upon the addition of Hg^2+ [49]. This approach was also effectively showcased in tap and river water applications. In this study, Huang and colleagues described the use of Cu-based MOFs as a hybrid sensory system. They utilized C-rich or T-rich DNA probes to detect Ag+, Hg^2+, and thiol-containing species at nanomolar concentrations by T-Hg^2+-T complexation. Huang et al. created a Metal-Organic Framework (MOF) called [Cu4(Dcbb)4(Dps)2(H$_2$O)2] n by combining H$_2$DcbbBr (1-(3,5-dicarboxybenzyl)-4,4′-bipyridinium bromide) and Dps (4,4′-dipyridyl sulphide) with Cu (NO$_3$)2·3H$_2$O [50]. This MOF was designed to detect Ag+, Hg^2+, and biothiols with a limit of detection in the nanomolar range. Similarly, the MOF, known as [Cu (Cdcbp) (H$_2$O)2·2H$_2$O] n (created by combining H3CdcbpBr (3- carboxyl-(3,5-dicarboxybenzyl)-pyridinium bromide) with CuSO$_4$ 5H$_2$O), was used to detect Hg^2+ and biothiols with low detection limits in the nanomolar range. Both scenarios involved the formation of a hybrid system between the MOF and thymine-rich DNA (referred to as P-DNA) loaded with a fluorescent dye [51].

This resulted in the suppression of fluorescence. The substance was subsequently retrieved by introducing metal ions, specifically Hg^2+, through T-Hg^2+-T complexation. The detection of Hg^2+ and biothiols using the hybrid MOFs-DNA system is depicted in Figure 6, along with the associated mechanism. Similarly, Zr- and Ce-based metal-organic frameworks (MOFs) called UIO-66-NH2 and Ce/TBC were shown to effectively differentiate Hg2+ ions with very low detection limits in the nanomolar range. The Ce/TBC, also known as mixed-valence state cerium-based metal-organic framework (MVC-MOF), was used in combination with thymine-rich ssDNA to create colorimetric peroxidase-like sensors [52]. These sensors were able to detect Hg^2+ using the oxidase substrate 3,3′,5,5′-tetramethylbenzidine. The Hg^2+ detection results exhibited a linear response throughout a concentration range of 0.05 to 6 μM, with a limit of detection (LOD) of 10.5 nM [53]. These findings were further corroborated by the analysis of ambient

water. Several MOF-DNA hybrid systems have been documented for the purpose of detecting metal ions, amino acids, and nucleic acids. This approach is highly accurate.

Recently, researchers demonstrated the use of gold nanoclusters combined with metal-organic frameworks (MOFs) to discriminate Hg^2+ ions. Specifically, two types of composites were used: AuNCs/MIL-68(In)-NH2/Cys and AuNCs@UIO-66. The AuNCs/MIL-68(In)-NH$_2$/Cys was created by initially synthesizing MIL-68(In)-NH$_2$ using a solvothermal reaction between in $(NO_3)3$ xH_2O and 2-Aminoterephthalic acid (H$_2$ATA), and subsequently equally distributing the AuNCs on its surface. The AuNCs displayed emission peaks at 438 nm and 668 nm, with an excitation wavelength of 370 nm.

The introduction of cysteine into the aforementioned mixture resulted in the production of AuNCs/MIL-68(In)-NH2/Cys, which exhibited improved emission. When Hg^2+ was added to the AuNCs/MIL-68(In)-NH$_2$/Cys at pH 7.4 (in a phosphate buffer), the emission at 638 nm was suppressed but the peak at 438 nm remained unaffected. The PL quenching displayed two linear responses, due to the strong binding affinity between Hg^2+ and the thiol (-SH) group of cysteine. These responses covered a concentration range of 20 pM to 0.2 μM and from 0.2 μM to 60 μM, with a limit of detection (LOD) of 6.7 pM. The accuracy of these findings was confirmed through examination of real water samples and using a microfluidic paper device. The UIO-66 compound was synthesized using a solvothermal reaction between zirconium chloride and 1,4-benzenedicarboxylic acid (H$_2$BDC). AuNCs@UIO-66 was created by combining synthesized UIO-66 with AuNCs, resulting in a quantum yield of 11%. The photoluminescence (PL) emission of the AuNCs@UIO-66 was detected at a wavelength of 650 nm at a pH of 7.2. The emission was consistently reduced by Hg^2+ in a linear manner, with concentrations ranging from 800 nM to 10 μM. The limit of detection (LOD) for Hg^2+ was determined to be 77 pM. The emission quenching was ascribed to the amalgamation of Au-Hg through the interacting amino groups of bovine serum albumin (BSA) that are present on the surface of AuNCs. The sensory study was successfully proved to be applicable to tap and river water, making it a suitable option for discriminating Hg^2+.

In this study, Marieeswaran and colleagues demonstrated the ability of a composite material consisting of a magnetic nanoscale metal-organic framework (MNMOF) linked with fluorescein amidite (FAM)-labeled single-stranded DNA (ssDNA) to sense Hg2+ ions. The MN-MOF was synthesized by a one-pot reaction including Fe3O4 nano-spheres (prepared via hydrothermal synthesis), FeCl$_3$.6H$_2$O, and 2-aminoterephthalic acid. The emission intensity at a wavelength of 495 nm, in a Tris-HCl buffer, was reduced by 62% due to the adsorption of FAM-labeled single-stranded DNA on the MNMOF. The presence of Hg^2+ resulted in a further decrease in the emission quenching at 495 nm, reaching a level of 52%, due to the formation of a T-Hg^2+-T complex.

The linear regression analysis for the detection of Hg^2+ ranged from 2 to 20 nM, with a limit of detection (LOD) of 8 nM. This work was also seen in environmental water samples. Nevertheless, the data regarding the BET surface area and other related research findings require updating. Hu and his colleagues discovered that the [Cu (Dcbb)(Bpe)] Cl compound (where H2DcbbBr and Bpe represent 1-(3,5-dicarboxybenzyl)-4,4′-bipyridinium bromide and trans-1,2-bis(4-pyridyl) ethylene, respectively) can be used to sequentially measure the amounts of Hg^2+ and I- ions. This is achieved through the T Hg2+ T motif and a fluorescence response that switches "off-on-off". The presence of Hg^2+ and I- was confirmed by circular dichroism (CD), and the underlying process was elucidated through fluorescence anisotropy, determination of binding constant, and simulation studies. The limits of detection (LODs) for Hg2+ and I- sensors were determined to be 3.2 and 3.3 nM, respectively . While the sensor demonstrated a high level of selectivity, it can be regarded as supplemental due to its use of a similar T Hg2+ T motif method.

The AuNP@MOF composite nanoparticles were utilized in a colorimetric Hg2+ assay by using their gold amalgam-triggered reductase mimic activity in an aqueous environment. The AuNP@MOF composite was created by attaching gold nanoparticles to the porous surface of an iron-5,10,15,20-tetrakis (4-carboxyl)-21H,23H-porphyrin-based metal-organic framework (Fe-TCPP-MOF). This composite was then used for colorimetric detection of Hg^2+. In this experiment, the presence of Hg2+ initiated the catalytic reduction of methylene blue mediated by Au, resulting in a change from blue to colorless. This change was accompanied by a decrease in the absorbance peak of methylene blue at 665 nm, as depicted in Figure 7. In addition, the absorption at a wavelength of 665 nm was consistently reduced in a linear manner within a time frame of 2 seconds by the presence of Hg2+ ions at concentrations ranging from 200 to 400 picomolar (pM), with a limit of detection (LOD) of 103 pM. In addition to the absence of BET surface area

data, the conflicting studies on tap and river water investigations have confirmed the effectiveness of AuNP@MOF in detecting Hg2+. the highest adsorption capacity of 824 mg g−1. The distribution coefficient (Kd) of ZrSulf to Hg2+ was estimated as 4.98 105 mL g−1 at pH 6.8 Moreover, it was reusable for more than five cycles after washing with HCl and thio-urea. The high selectivity of Hg2+ was attributed to the covalent bond formation with sulfur-based functionality. From kinetic studies, it was established that the adsorption followed the pseudo-second order model and, at the same time, controlled by the film diffusion and pore diffusion [54]. This material can be considered as a good candidate for Hg2+ removal in terms of its adsorption capacity and practicality.

Subsequently, Leus and co-workers solvothermally synthesized the thiolated Zr- based MOF-UIO-66-(SH)2 (by reacting $ZrOCl_2.8H_2O$ and 2,5-dimercaptoterephthalic acid- (H_2BDC-2,5SH)) and applied it for selective removal of Hg species. The Langmuir surface area of UIO-66-(SH)2 was estimated as 499 m2 g−1 [55]. The UIO-66-(SH)2 showed a maximum Hg^{2}+ adsorption capacity of 236.4 mg g−1 between pH 3.0–5.0. Due to the presence of -SH group, adsorption of Hg2+ showed the best fit with Langmuir isotherm and followed the pseudo-second order kinetics. Moreover, adsorption and desorption of Hg^{2}+ can be extended up to three cycles by using 1 M HCl and 0.66 M thiourea. This work was also applied in waste water-based Hg2+ removal. The use of thiolated UIO-66-SH (an archetypal thiolated Zr-based MOF-Zr6(OH)4O4(BDC)6, where BDC represents benzene- 1,4-dicarboxylate) towards Hg species removal applications was also demonstrated by Li and co-workers. However, the presence of Zn2+ and Pb2+ may reduce the adsorption of Hg2+ by UIO-66-SH.
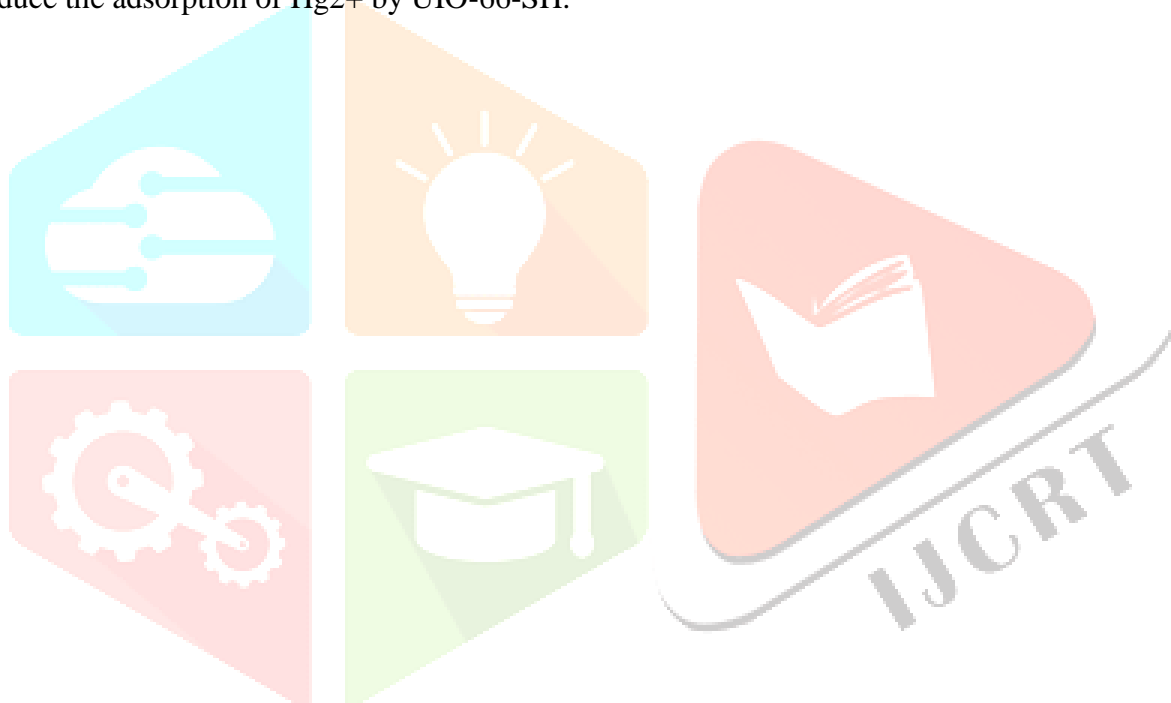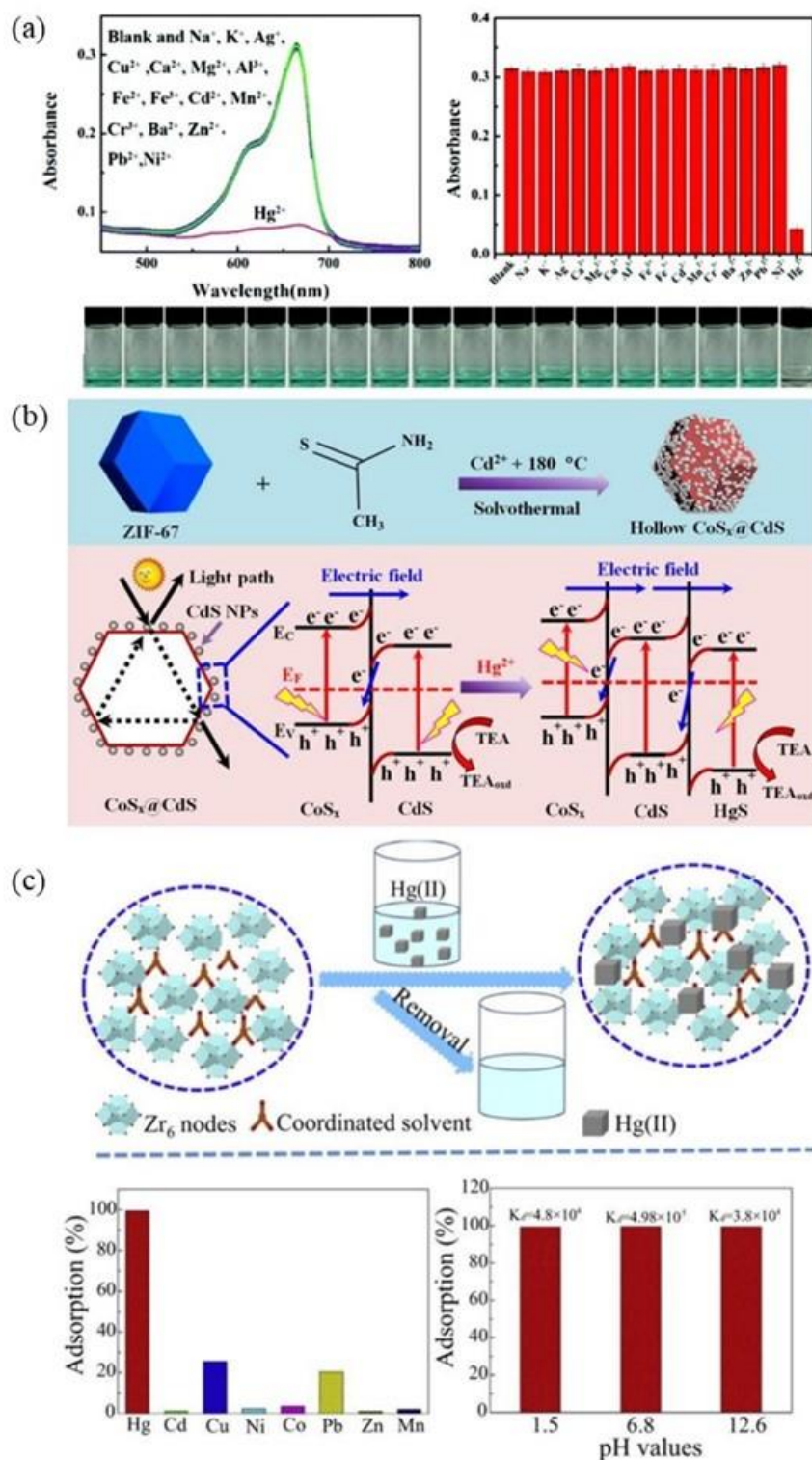
: a) **The specificity of the AuNP@MOF sensor for Hg²⁺ ions was evaluated by comparing its response to different metal ions (Na⁺, K⁺, Ag⁺, etc.) at regulated concentrations (1 nM for all except Hg²⁺, which varied from 1 nM to 10 nM). Three methodologies were utilised to assess the sensor's reaction: The UV-visible spectra were used to observe alterations in light absorption when exposed to various metal ions. The reaction for each metal ion was assessed by measuring the UV absorbance at 665 nm. (C) Photographs captured visual alterations resulting from the introduction of different metal ions. The objective of this experiment was to ascertain the sensor's unique response to Hg²⁺ in the presence of other metal ions.**

b) **This section outlines the process of creating hollow polyhedrons made of cobalt sulphide (CoSₓ) and their combination with cadmium sulphide (CdS). Furthermore, it investigates the underlying mechanism responsible for the observed photocurrent response in these CoSₓ@CdS composites. The picture, which is not included here but mentioned, demonstrates the band structures of CoSₓ@CdS/mercury sulphide (HgS) composites and highlights the phenomenon of charge separation when exposed to visible light.**

Next, Fu et al. employed the post-functionalized UIO-66-NH2 (Zr-based MOF) with 2,5-Dimercapto-1,3,4-thiadiazole to produce the UIO-66-DMTD for effective removal of Hg2+ in water. Due to the Hg2+ adsorption over the MOF surface, the calculated BET surface area of UIO-66-DMTD-Hg decreased from 651 m2 g−1 to 42 m2 g−1, thereby confirming the adsorbing ability of the proposed MOFs. The maximum adsorption of Hg2+ was 670.5 mg g−1 at pH 3. The adsorption kinetic followed the pseudo-second-order and was linearly fitted with Langmuir isotherm [56]. Moreover, selectivity to Hg2+ by the UIO-66-DMTD and its analogous (UIO-66-NH2 and UIO-66-SO3H) was higher than that of other species as seen in Figure 10.

At a fixed Hg^{2}+ removal time of 120 min, recyclable usage of the UIO-66-DMTD was found to be effective up to 10 times. The Hg^{2}+ removal is highly fascinated and can be effective in the lab wastewater-based extraction due to the high affinity of thiol (-SH) group to Hg^{2}+. In a study by Ding and colleagues, a Zr-based metal-organic framework (MOF-Zr-DMBD) was presented as a potential material for removing Hg2+ ions. This MOF was synthesized by reacting 2,5-Dimercapto-1,4-benzenedicarboxylic acid (H2DMBD) with ZrCl4. This proposal was made in reference to a similar MOF called MOF-UIO-66-(SH)2. However, because this work bears a significant resemblance to the research conducted on UIO-66-(SH)2, it will not be elaborated on any more. In reference, Li et al. discussed the use of Zr-based MOFs, specifically ZrOMTP, which contains dense thiol arrays formed by reacting 4,4′,4″,4‴-(pyrene-1,3,6,8-tetrayl)tetrakis(2,6-dimercaptobenzoic acid) (H4OMTP) with ZrCl4, for the effective removal of Hg2+ species [57]. The BET surface area of ZrOMTP to N2 gas was determined to be 1290 m2 g1, while the distribution coefficient (Kd) for Hg2+ was calculated to be 1.60 108 mL g1. This value is significantly higher than that of other MOFs that include thiol. This can be ascribed to the compact thiol arrays found in the ZrOMTP framework. The adsorption of Hg2+ adhered to the first-order kinetic model and was most accurately represented by the Langmuir isotherms [58]. In addition, these MOFs effectively reduced Hg-based pollutants from parts per million (ppm) down below the permissible drinking water level of 2 parts per billion (ppb).

A highly concentrated alkyl thiol compound, consisting of MOF-Zr-MSA, was synthesised using a hydrothermal reaction between ZrCl4 and mercaptosuccinic acid (HOOC-CHSH-CH2-COOH, MSA) in an aqueous solution. This compound was then used for the elimination of Hg^{2}+ ions. The Zr-MSA exhibited a 99.99% adsorption efficiency for Hg^{2}+ in a pH range of 0-7 pH over a 5-minute timeframe. Additionally, it was capable of being reused for up to five cycles using 6 M HCl. In addition, the Zr-MSA exhibited a maximum adsorption capacity of 734 mg g−1 and a Kd value of 1.82 108 mL g−1, which demonstrated the strongest correlation with the Langmuir isotherm. As a result of the stronger attraction between -SH and Hg2+, this study successfully decreased the Hg concentration from 10,000 ppb to 0.11 ppb, which was significantly lower than the permissible limit for drinking water [59]. The Zr-MOFs-SH(O) was synthesized by a one-pot reaction involving ZrCl4, meso-tetra(4-carboxyphenyl)porphine (H2TCPP), and thiol-containing MOFs.

The modulators used for Hg2+ adsorption were mercaptoacetic acid (MAA) or alpha lipoic acid (ALA). The Zr-MOFs-SH(P) was synthesized by modifying the Zr-MOFs-SH(O) using a post-synthetic process. It was then used for adsorption investigations. The Zr-MOFs-SH(O) exhibited a greater adsorption capacity (843.6 mg g−1) for Hg2+ compared to the Zr-MOFs-SH(P) (138.5 mg g−1) due to its higher -SH content. The adsorption of Hg2+ by Zr-MOFs-SH(O) followed the pseudo-second-order kinetic model and was most accurately described by the Langmuir isotherm. Furthermore, this investigation demonstrated favorable selectivity, reusability, and chemical durability. The NH2-UIO-66 was functionalized with L-cysteine to obtain Cys-UIO-66, which was then utilized for the elimination of Hg2+ from a solution. The Cys-UIO-66 exhibited a peak adsorption capacity of 350.14 mg g−1 (after 180 minutes) for Hg2+ adsorption at pH 5.0 [60]. The adsorption process followed the pseudo-second-order model and was accurately described by the Langmuir isotherm. The reusability of Hg2+ adsorption/desorption was enhanced up to five cycles by the strong attraction of -SH (from cysteine) to Hg^{2+} [61]. This was achieved using a 0.1 M HNO3 and 1% thiourea solution. This study may require further enhancements in terms of its capacity and time consumption. Liu and his colleagues introduced a similar method to develop cysteamine functionalized MOFs-MIL-101-SH (Cr) and UIO-66-SH (Zr) for the purpose of removing Hg2+. The MOFs exhibited adsorption capacities of 10 and 250 mg g−1 at a pH of 5, respectively, while also demonstrating a degree of reusability.

Four Zr-based metal-organic frameworks (MOFs), named Zr-L1, Zr-L2, Zr-L3, and Zr-L4, were created using four different types of organic ligands that have bulky Sulphur side chains. These frameworks, which consist of Zr (IV)-carboxylate structures, were designed specifically for the purpose of selectively removing Hg2+

ions [62]. The ligands used in the frameworks are carboxylic acid linker molecules that have been deprotonated and equipped with thioether groups. The dissociation constants (Kds) of

The estimated values for Zr-L1, Zr-L2, Zr-L3, and Zr-L4 were 1.95 x 10^3 mL g^-1, 1.47 x 10^4 mL g^-1,

The values are 4.47 x 10^3 mL g^-1 and 2.40 x 10^4 mL g^-1, respectively. In addition, the adsorption of Hg by Zr-L1, Zr-L2, Zr-L3, and Zr-L4 followed the Langmuir isotherm. The capacities for Hg adsorption were 193 mg g−1, 275 mg g−1, 245 mg g−1, and 322 mg g−1 respectively, at a pH of 6.8. Nevertheless, additional research is required to explore interference studies and real-time applications in this study. The Zr-based MOF-DUT-67 (Zr), which was synthesized using a solvothermal reaction between zirconium chloride and 2,5-thiophene-dicarboxylic acid, exhibited removal efficiencies ranging from 69% to 90% for Hg2+ and from 30% to 77% for CH3Hg+. At a pH of 6, the DUT-67 (Zr) exhibited. The effectiveness of adsorption for Hg2+ and CH3Hg+ is high, with adsorption capacities of 0.0451 mg g−1 and 0.0374 mg g−1, respectively [63].

The process of adsorption adhered to the pseudo-second-order kinetic model. This work was also exhibited in samples of river and lake water; however, additional investigations are needed to explore the mechanism and interference. The ZrO2-based (MOF)-808, synthesized using a sol-gel approach, underwent a wet-chemistry process to graft amidoxime (AO) onto it, resulting in the formation of MOF-808/AO. This material was utilized for the removal of Hg2+ and demonstrated remarkable effectiveness, as reported in reference [64]. Specifically, the MOF-808/AO exhibited superior adsorption effectiveness across all pH levels. The BET surface area of MOF-808 was determined to be 2152 m2 g−1, while the BET surface area of MOF-808/AO was found to be 1899 m2 g−1. In addition, the adsorption capabilities of MOF-808 and MOF-808/AO for Hg2+ were determined to be 383.8 mg g−1 and 343.6 mg g−1 (at 70 min), respectively. The adsorption of Hg2+ in both MOFs conformed to the pseudo-second-order kinetic model and was accurately described by Langmuir isotherms. This task necessitates increased exertion to get supplementary data regarding the process, interference effect, and real-time analysis [65]. The Zr-based metal-organic frameworks (MOFs) and zinc-metal nodes that make up the MOFs were also utilized for the removal of Hg2+, as explained in the next section. The compound MOF-74-Zn, also known as Zn2(DHBDC)(DMF)2 (H2O)2, was created by reacting ZnNO3 with 2,5-dihydroxy-1,4-benzenedicarboxylic acid (DHBDC) using solvothermal synthesis [66]. This compound was then used for the purpose of removing Hg2+ ions. The MOF-74-Zn exhibited a maximum adsorption capacity of 63 mg g−1 (for Hg2+ ions at a pH of 6 within a duration of 90 minutes). The adsorption of Hg2+ followed the pseudo-second-order kinetic model, and it was most accurately described by the Langmuir isotherm rather than the Freundlich isotherm.

The -OH group played a direct role in the adsorption of Hg^2+ [67]. Nevertheless, this study demonstrated a limited ability to adsorb and did not provide any data on the impact of interference. Wang and colleagues introduced a Zn-based MOF called NTOU-4. This MOF was synthesized by a hydro(solvo)thermal process by reacting ZnNO3 with 1H-1,2,4-triazole-3,5-diamine and 1,4-benzenedicarboxylate organic linkers. The purpose of NTOU-4 is to remove Hg2+ in various applications. The NTOU-4 exhibited an adsorption capacity of 163 mg g−1 after 30 minutes and was effective throughout a pH range of 3 to 11 [68]. However, additional explanation is needed for the underlying mechanism, kinetic model, and isotherm research. In their study, Esrafili et al. investigated the use of a dual functionalized Zn-based MOF called TMU-32S for the purpose of adsorbing and removing Hg2+ ions. TMU-32S was synthesized by incorporating varying amounts of N1, N3-di(pyridine-4-yl) malonamide into TMU-32, which is a Zn-containing MOF with urea linkers. The TMU-32S exhibited a significant adsorption capacity of 1428 mg g−1 within a short period of 17 minutes, thanks to the powerful binding forces generated by the urea and malonamide functional groups. Furthermore, its efficiency was enhanced at a pH of 4.4.

The system adhered to the linear pseudo-second-order model and was linearly adjusted to fit the Langmuir isotherm. In addition, the material exhibited adsorption and desorption (using 0.2 M of EDTA) for up to three cycles with an efficiency of 65%. This task Further research is needed to investigate the interference effect of various metal analytes [69].

Afterwards, the Cu-based MOFs were approved as effective adsorbents for the removal of Hg2+ as explained in the next section. Wu et al. created a porous MOF called JUC-62, which contains copper and 3,30,5,50-azobenzenetetracarboxylic acid. This MOF was specifically designed for removing Hg2+ from tea and mushroom samples. The details of this development may be found in reference. The JUC-62's ability to adsorb Hg2+ was determined.

The concentration reached 836.7 milligrams per gramme at a pH of 4.6 within a 15-minute timeframe in a liquid solution. This study utilized the pseudo-second-order model and was fitted with the Langmuir adsorption isotherm [70]. Furthermore, it could be reused with EDTA for up to four cycles. However, additional inquiries are necessary regarding the interference studies. Mon and colleagues utilized a copper-based metal-organic framework (MOF), specifically Cu4II [(S, S)-methox]2.5H2O (where methox represents bis[(S)-methionine] oxalyl diamide), for their research on removing HgCl2. The microporous MOF was modified with thioalkyl chains, allowing it to effectively adsorb HgCl2 and form the HgCl2S2 adduct.

The MOF exhibited a remarkable adsorption capacity of 99.95% for HgCl2 in just 15 minutes, effectively reducing the concentration of Hg2+ in drinking water from 10 ppm to below 2 ppb. Nevertheless, this work was deficient in providing details regarding the potential for reuse, conducting kinetic tests, and demonstrating practical applications. The study discussed the use of polysulfides functionalized benzene-1,3,5-tricarboxylic acid and Cu-containing Sx-MOF (where MOF represents Cu-BTC synthesized using solvothermal technique and Sx2−, X = 3, 4, 6) for effective adsorption of Hg2+. Out of all the materials tested, the S4-MOF showed excellent selectivity for Hg2+ ions. It had a limit of detection (LOD) of 0.13 µg L−1 and a linear response range of 30–200 µg L−1 at pH 6 over a 30-minute timeframe [71].

The metal-organic framework (MOF) exhibited varying adsorption capabilities for different metal ions, with the highest capacity seen for Hg (II), followed by Pb (II), Zn (II), Ni (II), and Co (II). The use of Hg^{2}+-S bonding allowed for efficient and practical adsorption in sea, tap, and wastewater. Nevertheless, there is currently a lack of knowledge concerning kinetic investigations. A compound consisting of a copper metallacycle, namely Cu2(PDMA)2(DMF), was shown to effectively remove Hg^{2}+ ions. The complex is composed of 3,3′-((1E,1′E) -(pyrimidine-4,6-diylbis(2-methylhydrazin-2-yl-1-ylidene)) bis (methanylylidene)dibenzoic acid (H2PDMA)). This discovery was reported in reference. Because of the many binding sites, the MOF exhibited a 61.4% efficiency in adsorbing Hg^{2}+ ions (compared to Hg^{2}+, Mn^{2}+, Cd^{2}+, and Pb^{2}+ ions), with an adsorption capacity of 300 mg g^{-1}. Furthermore, this Metal-Organic Framework (MOF) exhibited reusability when combined with Ethylenediaminetetraacetic acid (EDTA) [72]. The adsorption of Hg^{2}+ followed a kinetic model known as pseudo-second-order. Xu and his colleagues suggested using the SH@Cu-MOF for the adsorption of Hg^{2}+ and Hg (0) species by attaching dithioglycol to the Cu-MOF modified with 5-aminoisophthalic acid. While the material appears outstanding in comparison to other reports, its adsorption capacity (173 mg g−1 in 6 h) did not meet the criteria. Nevertheless, this study indicates a novel path for the future advancement of Cu-based MOFs.

Liang and colleagues reported the use of a sulfur-functionalized Co-based MOF called FJI-H12, which consists of NCS-, Co (II), and 2,4,6-tri(1-imidazolyl)-1,3,5-triazine (Timt), for the purpose of removing Hg2+ from water. The FJI-H12 exhibited a Kd value of 1.85 x 10^6 mL g−1, along with an adsorption capacity of 439.8 mg g−1 at pH 7. The adsorption process was highly effective due to the strong affinity between Hg2+ and S (of SCN-), making it suitable for continuous removal purposes. In addition, this study adhered to the pseudo-second-order kinetic model. The work is commendable due to its reusability. Jiang et al. developed a durable metal-organic framework (MOF) called [Co3(µ3-OH) (DMTDC)3(INT)3]-[Co2(OH) (H2O)2] (NO3)19-(H2O)7(DMA)11, which contains stable Sulphur and cobalt components [73].

The specific compound being referred to is NENU-401, with DMTDC, INT, DMF, and DMA representing the chemical components 3,4-dimethylthieno [2,3-

The compounds used for Hg2+ removal in this study were thiophene-2,5-dicarboxylic acid, isonicotinate, N, N-dimethylformamide, and N, N-dimethylacetamide. To do this, an INT group was introduced into NENU-400-[Co3(µ3-OH) (H2O)3(DMTDC)3] (NO3)10-(H2O)6(DMF)6. The researchers were able to successfully remove Hg2+ using this compound. In contrast to the NENU-400, which exhibited a tendency to collapse when exposed to Hg2+ adsorption, the NENU-401 maintained its structural integrity, making it extremely suitable for extracting Hg2+. The Kd value of NENU-401 at 25 ◦C was determined to be 8.3 106 mL g−1, indicating a high adsorption capability.

The concentration reached 596.57 milligrams per gramme in a time period of 10 minutes. The NENU-401 exhibited superior performance compared to numerous MOFs containing thiol groups. Furthermore, the NENU-401 was able to extract up to 90% of Hg2+ and this extraction could be recovered using a thioglycol solution. The NENU-401 was also reusable for more than four cycles due to the efficient coordination between Hg2+ and the '-S' atom. The NENU-401-based extraction of Hg2+ adhered to the pseudo-second-order kinetic model and was accurately represented by the Langmuir isotherm [58]. This study showcased a remarkable methodology to enhance the structural integrity of MOFs. In addition, it exhibited a degree of preference for

Pb^{2+} ions (about 70%), although additional refinement was still necessary. Sun's research group recently suggested using sulfur-rich two-dimensional (2D) Co-based MOF nanosheets, specifically 2D-NCS ([Co(NCS)2(pyz)2]; where pyz denotes pyrazine), for highly effective removal of $HgCl_2$. The BET surface area of the 2D-NCS material when exposed to N2 gas at a temperature of 77K was determined to be 365 square meters per gram [74]. The highest amount of N2 gas that can be adsorbed by this material in 15 minutes is 1698 milligrams per gramme. The Kd value, which represents the equilibrium constant for the adsorption process, is measured to be 2.26 x 106 milliliters per gramme.

The MOF nanosheets rapidly decreased Hg2+ concentrations from 10 parts per million (ppm) to 1 part per billion (ppb) in just 15 minutes. Furthermore, they exhibited efficacy in environmental samples with pH levels ranging from 4 to 9. The study employed the pseudo-second-order model and was fitted with the Langmuir isotherm. As a result of the robust Hg-S interactions, the extraction process was highly effective for up to five cycles using a thioglycol solution [75]. This method might be further adjusted to create three-dimensional materials that could be used in future environmental remediation efforts. Another cobalt-based metal-organic framework (MOF), FJI-H30, was used for Hg2+ adsorption. FJI-H30 was synthesised by solvothermally refluxing TPMA (tris(pyridin-4-ylmethyl) amine) and Co (SCN)2, similar to the FJI-H12 MOF. The remarkable interaction between SCN− groups and Hg2+ resulted in a maximal adsorption capacity of 705 mg g−1, with minimal interference. The BET surface area of FJI-H30 in contact with CO2 gas at a temperature of 195K was measured to be 221 square meters per gramme. The material exhibited a Kd value.

The efficiency of the system was 1.84×105 mL g−1 and it functioned optimally within a pH range of 4–9. The system could be regenerated using KSCN [76].

The solution achieves a success rate of over 90% within three cycles. The study employed the pseudo-second-order model and was fitted with the Langmuir isotherm. It may be utilized in treating industrial wastewater, making it a commendable endeavor [77].

Halder et al. utilized the thiocyanato ligand (SCN-) in a three-dimensional nickel-based compound.

The Metal-Organic Framework (MOF) [Ni(3-bpd)2(NCS)2] n, where 3bpd represents 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene, is highly efficient in removing Hg^{2+} from water-based solutions. Due to the strong bonding between the uncoordinated S atom of SCN− and Hg^{2+}, the formation of the mercuric thiocyanate adducts resulted in a significant adsorption capacity of 713 mg g−1. However, this study still needs additional refinement to address the interference effect, adsorption kinetics, and practicality [78]. A method involving post-synthetic modification was suggested to create a thiol (-SH) functionalized In-based MOF called SH-MIL-68(In). This MOF was primarily derived from NH2-MIL-68(In), which was obtained by reacting 2-amino-benzene-1, 4-dicarboxylic acid (NH2-H2BDC) with in (NO3) through solvothermal means, followed by post-synthetic modification. The purpose of this modification was to enhance the MOF's ability to extract Hg^{2+} ions. The SH-MIL-68(In) exhibited a maximum Hg2+ adsorption capacity of 450 mg g−1 and a rapid adsorption rate (rate constant k2 = 1.25 g mg−1 min−1). Figure 11 demonstrates that the adsorption process occurred within a time frame of 2 minutes at a pH of 4, which can be attributed to the existence of unbound -SH groups.

The material demonstrated reusability for up to five cycles in the presence of 0.01 M HCl and 0.1% thiourea. The study utilized the pseudo-second-order model and was subjected to linear fitting using the Langmuir isotherm. The work is remarkable given its brief processing time and few interferences. Nevertheless, the practicality of real-time implementation still requires validation. Using diffusion and solvothermal methods, Li et al. synthesized three thioether-based MOFs, specifically [(ZnCl2)3(L1)2·χ(solvent)] n-(1), [(Cu2I3O2)4(CH4N0.5)4(L1)4(DMA)4·3(H2O) ·χ(solvent)] n-(2).

The compound is [(CuBr2)2(L2)2 CH3CN χ(solvent)] n-(3), where L1 and L2 are 1,3,5-tris ((pyridin-4- ylthio) methyl) benzene and 2,4,6-trimethoxy-1,3,5-tris((pyridin-4-ylthio) methyl) benzene respectively. The solvent used is DMA. Dimethylacetamide (DMA) can be employed for efficient elimination of Hg^{2+} from water. At pH levels 4 and 5, MOFs achieved a 90% removal of Hg^{2+} during a 5-minute timeframe. The highest adsorption capacities of MOFs (1), (2), and (3) were determined to be 362.3 mg g−1, 227.4 mg g−1, and the values are 341.7 milligrams per gramme and 1 gramme per gramme, respectively. The greater efficiencies obtained for Hg^{2+} were ascribed to the strong interaction between Hg and S. They could be reused for up to five cycles, using Na2S. This study employed the pseudo-second-order model and demonstrated a linear correlation with the Langmuir model.

An isotherm is a line on a graph that represents a constant temperature. This study is regarded as commendable due to the little interference effect, however, additional optimization is necessary to enhance the adsorption capacity. The bi-metallic MOFs were also used for the removal and extraction of Hg^2+, as previously mentioned. Proceeding. Han and his colleagues fabricated the heterometallic metal organic framework (HMOF):

The compound $[(CH_3)2NH_2]$ $InCu_4L4$ xS, also known as BUT-52, was designed to effectively remove Hg^2+ ions. This compound has in $(COO)4$ and $Cu6S6$ clusters that were intentionally included. The BET surface area of BUT-52 when exposed to N_2 gas at a temperature of 77K was measured to be 126.2 cm3 g1. The results indicated a mercury elimination effectiveness of 92% in ethanol. This work necessitates additional optimization in the areas of anti-interference, pH, time, and real-time application studies [79]. Mon et al. reported the use of a porous bimetallic MOF (metal-organic framework) called CaIICuII6[(S, S)-method]3(OH)2(H2O) 16H2O (where methox represents bis[(S)-methionine]oxalyl diamide) for the elimination of Hg2+ and CH3Hg+ in water. The BioMOF effectively decreased the concentrations of Hg2+ and CH3Hg+ from 10 ppm to 5 and 27 ppb, respectively. This reduction was achieved by Hg–S interactions, resulting in an adsorbing ability of 99.95% and 99.0% for dissolved $HgCl_2$ and CH_3HgCl salts, respectively. Nevertheless, optimization is necessary in order to examine the adsorption kinetics and practical implementations. Concurrently with the use of MOFs for extracting and removing Hg^2+, some MOFs have also been found to be effective in removing several heavy metal ions, including Hg^2+. While the results showed successful elimination of Hg^2+, they were also influenced by the presence of other ions, which caused interference [80]. In order to mitigate the disruptive impacts, a complex masking method is necessary. Hence, those reports will not be deliberated upon in this review.
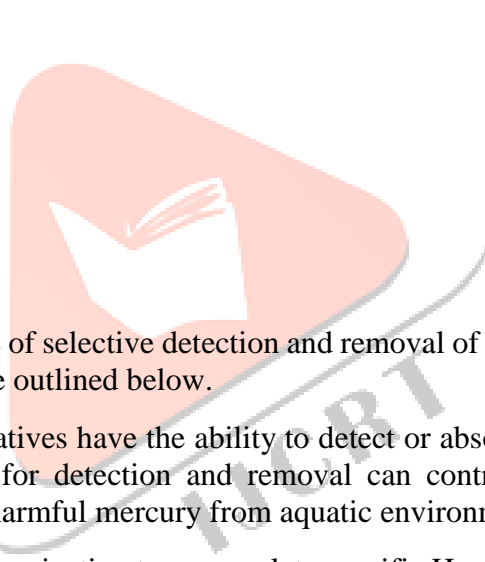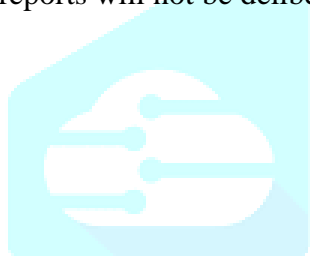
Advantage

The utilization of MOFs and their analogues for the purpose of selective detection and removal of Hg2+ offers numerous benefits, along with certain limitations, which are outlined below.

1. Most metal-organic frameworks (MOFs) and their derivatives have the ability to detect or absorb mercury species in water. Therefore, investigations using MOFs for detection and removal can contribute to an environmentally beneficial procedure by decontaminating harmful mercury from aquatic environments.

2. The porous nano/micro structure of MOFs allows for customization to encapsulate specific Hg species. This customization can be further improved through post-synthetic alteration or loading of specific groups, such as thiols (-SH).

MOFs and their analogues have the benefit of being able to detect numerous analytes, such as Hg^2+, by adjusting the detection conditions, using masking agents, and varying the analyte concentrations.

MOFs can serve as probes for the detection and elimination of Hg species using several strategies, including optical, electrochemical, and photoelectrochemical methods. Therefore, they are recognized as materials with unique benefits [81].

By fine-tuning the compositions to modify the specific porous surface, several composites consisting of MOFs possess distinctive benefits in collecting Hg species even when other interfering analytes are present [82].

The approach of detecting and removing Hg using MOFs can also be expanded to identify specific bio-analytes, including glutathione, cysteine, and thiol-containing species.

Disadvantage

1. The synthesis of specific MOFs and their similar structures is still regarded as a challenging undertaking because to several constraints, including the potential production of co-adducts, appropriate strategies, reaction conditions, and solvents [83].

2. While MOFs exhibit great sensitivity through fluorescence quenching or amplification, a significant number of them include hazardous metals, such as Al, Cr, Zr, Lanthanides, and so on. As a result, the use of these MOFs for bioimaging or biological tests of Hg2+ is limited [84].

3.MOFs that contain organic linkers with free thiol (-SH) groups also exhibit selectivity towards Pb2+, Cd2+, and Ag+ ions. However, this selectivity limits their ability to selectively detect Hg species due to certain interfering effects.

4.The majority of investigations on the adsorption or removal of Hg2+ using MOFs were constrained by various criteria, including the concentration of MOFs, their structural stability, porosity, pH, duration, operating temperature, and the choice of an appropriate eluent. Those variables necessitate additional scrutiny.

5. The design and development of some composites made of MOFs are constrained by complex methods, which not only raise the cost of the processes but also hinder the commercialization of materials.

6. In order to fully understand and describe the Hg assay and removal processes, it is necessary to utilize expensive instruments such as scanning electron microscopy (SEM), powder-X-ray diffraction analyzer (PXRD), elemental analyzer, and thermogravimetric analyzer (TGA). This limitation hinders future research on the development of materials based on MOFs for the purpose of mercury remediation [85].

7. The adsorption capabilities of certain MOFs were seen to be influenced by the combined interference effects and the physical/chemical stability of MOFs during the Hg assays conducted on actual samples. Therefore, there is a high expectation for significant attention to be directed towards resolving this issue [86].

Summary and Outlook

This review offers significant insights into the applications of MOFs and their effectiveness in detecting and removing mercury species, including Hg0, Hg2+, and CH3Hg+. By modifying the organic linkers and metal nodes, the physical and chemical characteristics of MOFs can be tailored to specifically target certain forms of Hg [87]. The majority of the metal-organic frameworks (MOFs) exhibited specific sensing reactions to Hg2+ ions by reducing their luminescence, which has the potential to be utilized in future adsorption research. Under ideal circumstances, the use of MOFs for adsorbing Hg^2+ or Hg_0 can be highly effective, thus opening up possibilities for real-time applications. MOFs with free thiol (-SH) or Sulphur groups exhibit excellent adsorption and removal capabilities for Hg species through Hg–S bonding, making them extremely suitable for such applications [85]. By adjusting the ratios of MOFs in composites, the pore size and specific surface area can be modified to efficiently capture Hg species. In addition to the aforementioned assertions, the following things must be considered in order to enhance the effectiveness of mercury detection and removal using MOFs [88].

1. A proposal is needed for a standardized, cost-efficient method to synthesize and purify MOFs for the purpose of detecting and removing mercury, in order to ensure effective environmental cleanup. It is necessary to create luminescent MOFs with minimal toxicity by utilizing less toxic metal nodes and organic linkers in order to detect the presence of Hg2+ ions in biological samples. There is a limited number of papers on the use of MOFs for detecting Hg2+ through fluorescence enhancement. Therefore, these designs need to be given more attention in the future [89]. The precise principles underlying the electrochemical detection of Hg2+ using MOFs are not fully understood, necessitating further experimentation and inquiry.

Many MOF-DNA hybrid systems have successfully stabilized the T-Hg2+-T coordination-based Hg2+ detection. It has the potential to be expanded to include removal studies, which are now unfinished [90].

There is insufficient evidence to strongly support the claimed mechanisms in many investigations that focus on detecting and removing mercury using MOFs. This may necessitate further focus.

Various parameters, including the concentrations of MOFs, pH, time, eluent solvent, and temperature, need to be thoroughly analyzed and regulated in order to effectively remove mercury. These parameters add complexity to the separation processes. Hence, it is crucial to design MOFs that can efficiently adsorb Hg even in suboptimal settings [91].

There is currently limited reporting on the development of MOFs for the detection and removal of CH3Hg+ and Hg0, therefore it requires more attention.

Several Metal-Organic Frameworks (MOFs) that contain free thiol (-SH) groups have been documented for the purpose of removing Hg2+. Therefore, it is necessary to design a cutting-edge approach using specific well-established MOFs (such as UIO-66) in order to achieve commercialization [92].

The efficacy of post-synthetically modified metal-organic frameworks (MOFs) compared to unmodified MOFs for the removal of mercury is currently a topic of discussion. Therefore, additional evidence is required to substantiate the effectiveness of the post-synthetic modification (PSM) technique [93].

When mercury (Hg) reacts with selenium (Se), it forms a compound called HgSe, which is not soluble in water and remains stable. This compound acts as an adduct, enhancing the ability to recycle the MOF probe. Therefore, this design should be research that focuses on the future [94].

Some MOFs also exhibited modest adsorption of ions other than efficient mercury removal. This issue must be resolved in order to achieve efficient separation of Hg in actual samples.

There is a scarcity of research that provide information on both the detection and removal of Hg2+ ions. These kinds of studies have the potential to significantly contribute to environmental restoration and deserve increased attention. While recent studies on mercury detection and removal using MOFs do not fully meet the aforementioned criteria, they are nevertheless regarded as excellent materials that may be used in water-based environments and demonstrate higher effectiveness compared to other existing methods [95]. Currently, many researchers are dedicated to developing Metal-Organic Frameworks (MOFs) for the purpose of recognizing and separating mercury. This research is important for environmental remediation and healthcare applications. The ultimate goal is to overcome existing challenges and make MOFs commercially viable as mercury absorbers in the near future [96].

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