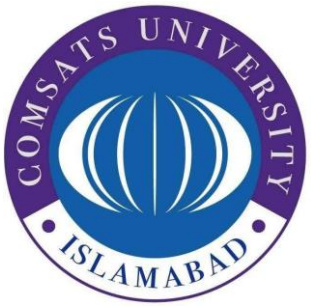
Molybdenum Disulfide-Metal Organic Framework as Electrode Material for Heavy Metal Ions Detection in Aqueous Media



MS Thesis

by

Fatima Amjad

CIIT/SP24-R06-006/LHR

COMSATS University Islamabad
Pakistan

Fall 2025

Molybdenum Disulfide -Metal Organic Framework as Electrode Material for Heavy Metal Ions Detection in Aqueous Media

A thesis submitted to
COMSATS University Islamabad

In partial fulfillment
of the requirement for the degree of

Master of Science
in
Chemistry
by

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COMSATS University Islamabad
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It is certified that Fatima Amjad, CIIT/SP24- R06-006/LHR has carried out all the work related to this thesis under my supervision at the Department of Chemistry, COMSATS University Islamabad, Lahore Campus and the work fulfill the requirement for award of MS degree.

Date:_____

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Dedication

With heartfelt dedication to the Most Merciful,

Allah Almighty

who supported me with unwavering encouragement and wisdom throughout this journey.

To the most beloved

Hazrat Muhammad (SAW),

To my parents, your unwavering love and support have been my rock.

To my dear siblings, your companionship and encouragement enriched every moment.

Together, you have been my steadfast pillars of strength, and for this, I am deeply thankful.

Acknowledgements

Praise to be ALLAH, the Cherisher and Lord
of the World, most gracious and Most Merciful

With utmost reverence, I begin by praising **Allah**, the Almighty and Ever Merciful. Alhamdulillah, His blessings have illuminated my path throughout this research. I bowed in Sajdah of Shukar for His infinite grace. All salutations to the beloved Holy Prophet Muhammad (SAW), a beacon of guidance and enlightenment.

My deepest gratitude goes to my dedicated supervisor, **Dr. Sara Riaz**, who's unwavering guidance, continuous support, and valuable insights have been pivotal in bringing this research to fruition.

I am profoundly thankful to my **parents**, whose unconditional love, encouragement, and unwavering support has been my bedrock. Their belief in me has driven me to pursue and achieve my goals.

A heartfelt thank you to my **fellow students** and **lab members**, whose support and companionship made the journey through the laboratory both productive and enjoyable and I would like to express gratitude to the academic resources, institutions, and libraries that provided the necessary infrastructure and materials for the completion of this thesis.

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Abstract

Molybdenum Disulfide -Metal Organic Framework as Electrode Material for Heavy Metal Ions Detection in Aqueous Media

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Heavy metal ions (HMIs) are highly hazardous environmental pollutants that pose major threats to aquatic ecosystems and human health due to their non-biodegradable nature and strong tendency to accumulate in living organisms. Therefore, it is essential to develop efficient electrode materials for their electrochemical detection in water. For heavy metal ions detection, a hybrid electrode material based on molybdenum disulfide (MoS_2) and an ytterbium-based metal–organic framework (Yb-MOF) was synthesized and characterized. MoS_2@Yb-MOF composite was developed by synthesizing MoS_2 nanosheets and combining them with Yb-MOF to synergistically integrate the active edge sites of MoS_2 with high surface area and abundant coordination sites of porous framework of the Yb-MOF. A flexible and conductive electrode was fabricated by directly integrating the composite onto a carbon cloth surface. The successful formation of composite material was confirmed through structural and morphological characterization using X-ray diffraction, Fourier transform infrared spectroscopy, and scanning electron microscopy. Electrochemical studies conducted using cyclic voltammetry and electrochemical impedance spectroscopy confirmed improved charge transfer behavior and enhanced electrochemical activity of the composite electrode relative to the individual components. These results suggested that the MoS_2@Yb-MOF composite is a promising electrode material for electrochemical detection of heavy metal ions in aqueous media.

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List of Abbreviations

HMIs	Heavy metal ions
PM	Particulate matter
AAS	Atomic absorption spectroscopy
CV	Cyclic voltammetry
EIS	Electrochemical impedance spectroscopy
DPV	Differential pulse voltammetry
SWV	Square wave voltammetry
RE	Reference electrode
WE	Working electrode
CE	Counter electrode
MOF	Metal- organic framework
TMDCs	Transition metal dichalcogenides
MoS_2	Molybdenum disulfide
Yb	Ytterbium
LOD	Limit of detection
XRD	X-ray diffraction
FTIR	Fourier-transform infrared spectroscopy
FE-SEM	Field- Emission Scanning Electron Microscopy
DI	Deionized water
H_3BTC	1,3,5-benzenetricarboxylic acid
DMF	N, N-dimethylformamide
CNTs	Carbon nanotubes

Chapter 1
Introduction

The environment includes all the things that surround us. Environment basically refers to the world where living things(biosphere), air(atmosphere), water(hydrosphere), and soil(lithosphere)-all these environmental components that also shown in Figure 1.1, interrelate to support life on Earth. The rapid growth of industrialization over the last 100 years has led to increased utilization of natural resources. Thus this consequence has been worsening environmental pollution worldwide [1]. Environmental pollution is defined as the undesirable changes that have negative effects on ecosystem. Pollution is mainly caused by a substance referred to as pollutant. A substance is considered as pollutant when it exceeds its permissible concentration limits due to human activities or natural processes [2]. For this substance to cause pollution, it must exceed a certain limit or threshold in the environment, which is considered acceptable or tolerable. Thus, pollution of the environment occurs when a pollutant is present in the surrounding medium of air, water, or soil. These could also be harmful and hazardous and threaten the biota within the degraded ecosystem [3]. Although water is a common substance, it is very significant and widely applicable. Water constitutes nearly two-thirds of the human body, and it plays an important role in their survival. Water scarcity leads to food shortages, while its surplus contributes to disease and death. In addition, there have been numerous studies on water, rendering it one of the most studied substances on Earth. As the major constituent of all living things, liquid water performs a range of functions and is not just a passive solvent [4]. The Earth's surface has an estimated volume of approximately (1.4 billion) cubic km of water. More than (97%) of this total amount of water exists as seawater in our oceans with the remainder (less than 3%) also existing as available freshwater in polar ice caps, glaciers, and groundwater supplies. Due to the large increases in the global population, the demand for freshwater for daily living has increased, which leads to global water shortages [5]. As a result of an increasing global population, there is a global issue regarding water resources and their management due to an increased demand for fresh water for our daily living. The shortage of fresh water and the deterioration of the quality of available fresh water will significantly impact agricultural production, the economy, and the ability to provide basic health and sanitation assistance to millions of people living in developing countries if present trends continue with respect to pollution. The freshwater supplies in developing countries continue to face increasing threats due to outdated treatment technologies for wastewater and increasing levels

of waste generated by urban areas and industrial facilities [6]. Different types of contaminants have been reported in recent studies in contaminated water sources, including heavy metals, household cleaners, medications, pesticides, pigments/dyes, leaking petroleum products and many other organics or aromatic products [7]. Human activities introduce many different toxic chemicals into our ecosystem called environmental pollutants. Environmental pollutants are the substances or particles that enter the environment causing pollution. Environmental pollutants harm wildlife and humans; the effects of environmental pollutants on both species are well known. Pollutants enter the environment through a variety of means (natural as well as through human activity) [8].

1.1. Types of pollutants

Human activities introduce many different toxic chemicals into our ecosystem called environmental pollutants. Environmental pollutants are the substances or particles that enter the environment causing pollution. Environmental pollutants harm wildlife and humans; the effects of environmental pollutants on both species are well known. Pollutants enter the environment through a variety of means (natural as well as through human activity) [8]. Figure 1.1 illustrated various classes of pollutants whereas, their sources and impacts on human beings are discussed in Table 1 below:

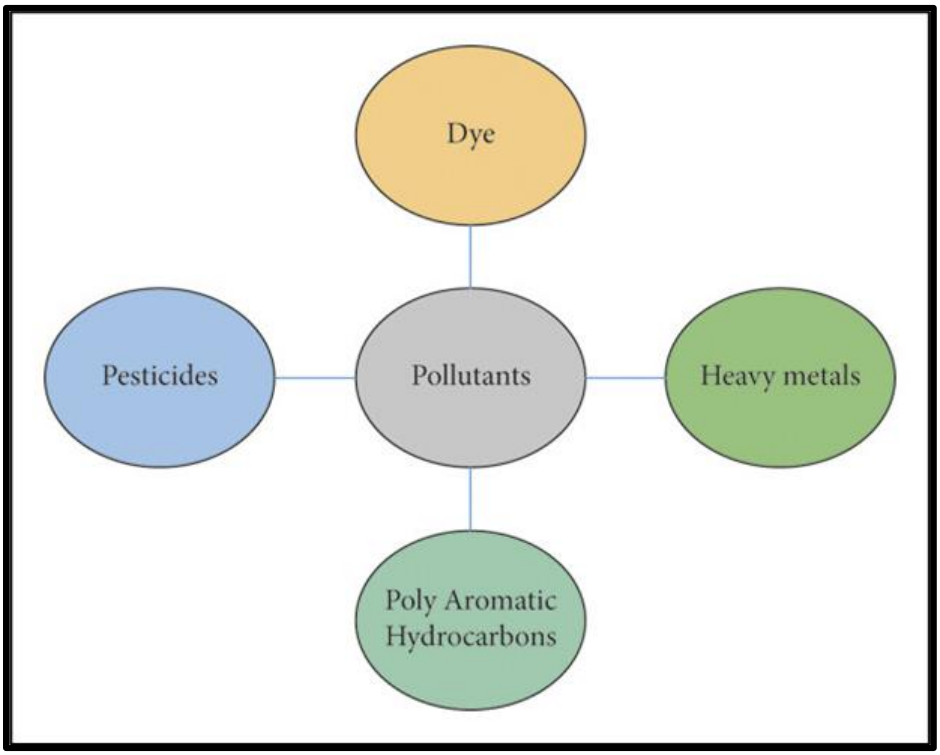

Figure 1.1: Types of Pollutants

Table 1: Classification of pollutants and their impacts on Human health

Pollutants	Sources	Impact on Human Health	Reference
Heavy Metals	Paints, thermal Power plants, fossil fuel combustion, vehicular emission, wood preservatives, tobacco smoke, open fire etc.	Hypertension, cardiovascular diseases, damage to kidney, liver and brain, respiratory disorders, genetic toxicity etc.	**[9-13]**
Particulate Matter	Agriculture waste, fossil fuel combustion, vehicular emission, wood burning etc.	Cardiovascular or respiratory disorders	**[14]**
Dyes	Textile industry, tannery and kraft mill sugar, pulp and paper industry	Bladder cancer, hypertension, renal damage, eutrophication bioaccumulation	**[15]**
Pesticides	Dicofol, sprays, pet shampoos, diazinon	Reproductive effects, immunotoxicity, cardiovascular diseases etc.	**[16]**
Poly Aromatic Hydrocarbons	Cement manufacturing, gasoline-powered engines, wood burning, garbage	Eye irritation, cancer, liver damage, kidney damage, asthma-like symptoms etc.	**[17]**

	burning		
Plastics	Plastic containers, pipes, squeeze bottles, container wraps	Mild dermatitis, hormone disruption, asthma	[18]

1.2. Environmental Pollution by Heavy Metal Ions

Heavy metal pollution is becoming an increasing concern around the world. This environmental issue is growing rapidly due to the detrimental impact on our environment due to this pollution as well as the increasing demand for these products through the agricultural industry, manufacturing of metals, overuse of fertilizers and pesticides, and inappropriate wastewater release [1]. Water pollution caused by toxic heavy metal ions (as shown in the Figure1.2), has become a serious environmental problem. These harmful heavy metal ions in trace amounts have contaminated pure drinking water and water resources, and also bioaccumulate in human bodies via food chain to cause multiple disorder [19].

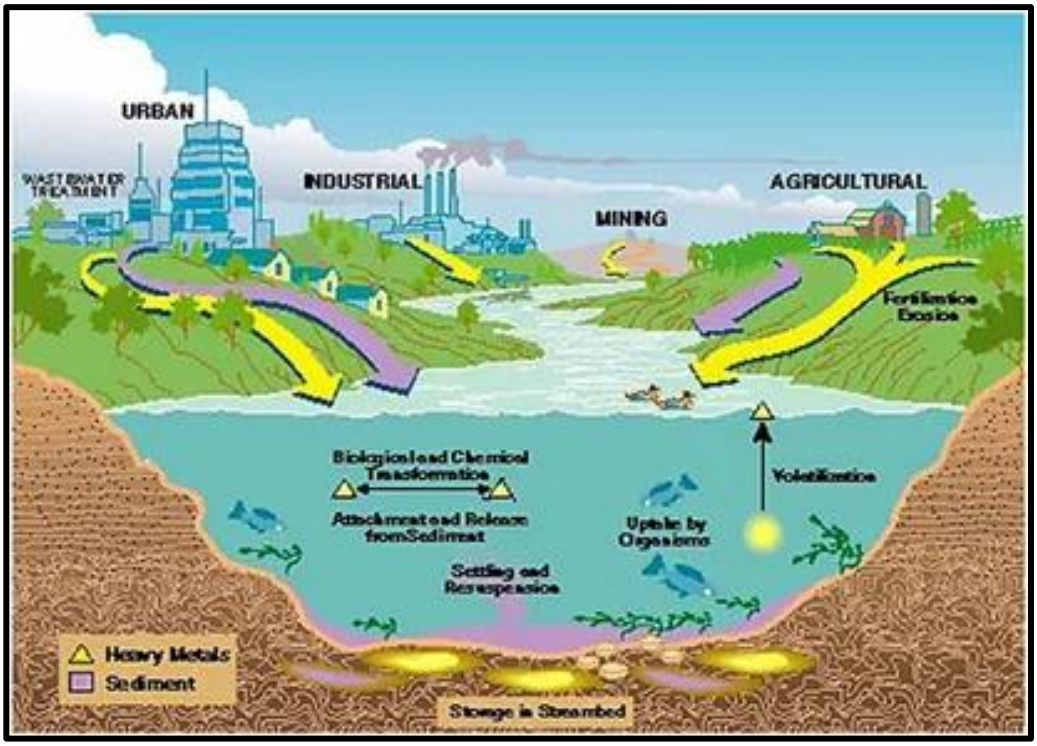

Figure 1.2: Water pollution by Heavy Metal Ions [20].

1.3. Heavy Metals Ions

Metallic elements with high densities and toxicity at trace amounts are referred to as heavy metal ions. The term "heavy metal" is a collective term for all metals or metalloids that have an atomic density exceeding 4g/cm^3 and possess an atomic weight at least 5 times that of water [21]. Many of these metals come from natural processes in the Earth's crust and soil, rock, sediment, water, and microorganisms (the organisms that make up the Earth's biosphere), while anthropogenic activities (i.e., industrial or man-made) can introduce metals into the environment at a higher concentration than would be expected to occur naturally. As heavy metal ions are non- degradable, and therefore remain in the ecosystem forever, they pose persistent health hazards. Prolonged exposure to lead damages nervous system and persistent presence of cadmium cause severe kidney diseases, COPD and lung cancer [22].

1.4. Sources of Heavy Metal Ions

The environment contain different sources of heavy metal ions which can be natural and anthropogenic (human activity) [23] as shown in the Figure 1.3. The primary source of heavy metal pollution is human activity or 'anthropogenic'. They are released into the ecosystem by mining, smelting, foundries, metal-based industries and released through leaching from various places. These places include landfills, waste dumps, excreta, manure from poultry and livestock, runoffs, automobiles, and road works. Agriculture also has a large role to play due to the use of pesticides, insecticides, herbicides, etc. Volcanoes, corrosion of iron and steel, evaporation of metals from the earth's crust, and erosion of soils will create more heavy metal contaminants in our environment than all of the above put together [1].

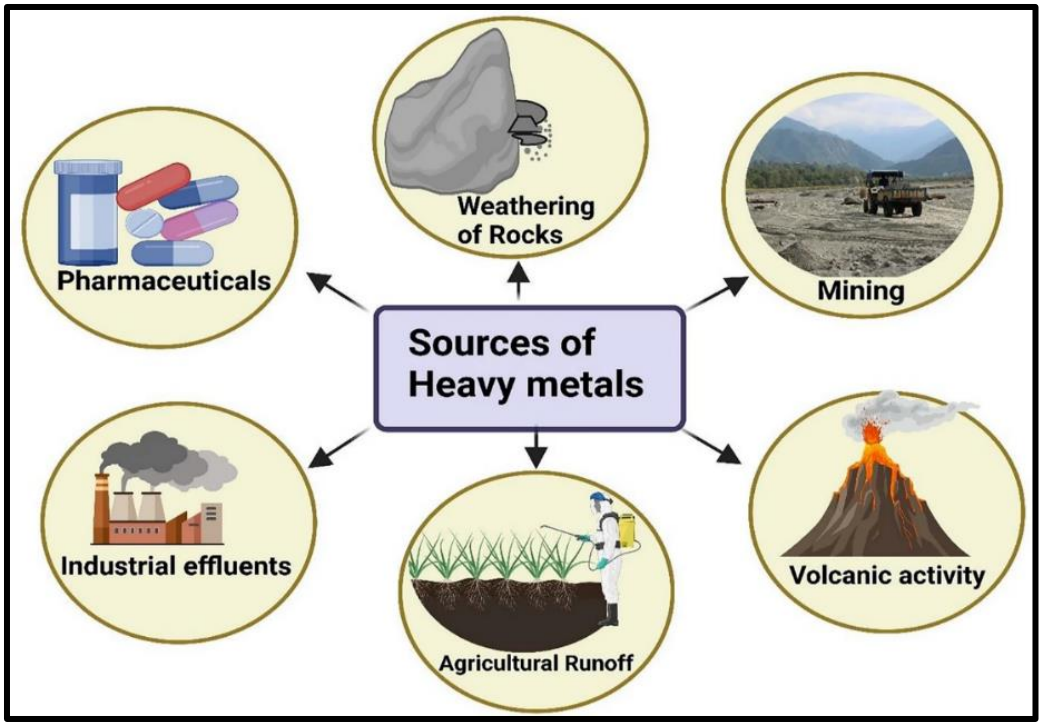

Figure1.3: Sources of Heavy Metal Ions [24]

1.4.1. Natural Sources

Various studies have identified different natural sources of heavy metal ions, and they are released under different environmental conditions such as volcanic eruptions, forest fires, weathering of rocks, biogenic emissions and air-borne soil particles. Heavy metal ions can seep into soil and water from their geological reservoirs. These metal ions can exist in types of hydroxides, oxides, sulphides, sulphates, phosphates, silicates and organic compounds. The most prevalent heavy metal ions are lead, nickel, chromium, cadmium, arsenic, mercury, zinc and copper. Even at low concentration they can still pose serious health issues to humans [25].

1.4.1.1. Weathering

Weathering refers to the deterioration of rocks, soil, and minerals at the same location due to interaction with the atmosphere, water, or living organisms. Weathering involves mechanisms such as physical, chemical, or biological processes.

- Physical weathering is the breakup of minerals due to the action of heat, water, ice, or pressure, resulting in both the reduction in size of particles and the development of surfaces where chemical reaction can take place.

- Chemical weathering entails a reaction between minerals and chemical constituents in the atmosphere or in water, releases heavy metal ions. These weathering processes can take place simultaneously.
- Biological weathering occurs due to plant roots or microorganisms that decompose substances in the rock for nutrients. This makes them prone to other reactions.

Weathering turns minerals into smaller molecules or secondary minerals, some of which are toxic and composed of heavy elements. Despite their natural occurrence in low concentrations within the Earth's crust, weathering, leaching, and geochemical cycles might raise the bioavailability and mobility of both elements mentioned above and many others within those ecosystems [26].

1.4.1.2. Leaching

Leaching involves the release of heavy metal ions from sediments or rock substrates when they encounter leaching substances like water, bases, acids, or organic compounds. Rainfall or fractured rocks that allow metals to dissolve into aqueous media are common causes of natural leaching. Factors like pH, buffering capacity, mineral solubility, redox conditions, organic matter, and microbial activity all affect how much leaching occurs. Leaching is a common industrial technique used in chemical processing and metallurgy, especially for the extraction of metals from ore using acids or other solvents. Because water is a universal solvent, most materials that come into contact with it can leach, depending on their chemical reactivity and porosity [27].

1.5.1.3. Volcanic Eruption

The most widely dispersed byproduct of explosive volcanic eruptions is volcanic ash-like material, which can fall many kilometers from an erupting volcano. Ash can disrupt the water supply system even in tiny amounts [28]. Volcanic ash damages drinking water by raising its pH, acidifying it, and adding turbidity. Due to the presence of droplets in the plume that are made up of the potent acidifying minerals H_2SO_4, HCl, and HF, freshly generated volcanic ash has very acidic layers on its surface. As a result, water that has recently experienced an eruption may have a pH drop that is hazardous to aquatic ecosystem [29]. The atmospheric concentration of heavy metal ions has increased due to global industrialization and population growth [30].

1.5.2 Anthropogenic Sources

Emissions of heavy metals in this environment are currently growing with population and socio-economic activities. Mining, processing of ores, agriculture, electricity generation, as well as other activities in homes such as detergent use, which result in increased concentration of sewage and wastewater heavy metal ions, are among the main sources [31].

Mining represents the greatest, most enduring source of pollution among these, and the impact lingers even after the closure of the mining operation [22]**.** Overall, anthropogenic sources are divided into agricultural and industrial activities [32].

1.5.2.1. Agriculture Activities

The agricultural sector has increased to cater to the growing need for food, but the misuse of herbicides, pesticides, fertilizers, drugs, and water bodies has caused severe contamination of the environment. The agricultural contaminants, which include agricultural chemicals, agricultural wastes, salinized agricultural wastes, and the residues of veterinary drugs, find their path to the rivers, lakes, and the sea [33, 34]. Overuse of nutrients leads to eutrophication of the water body, contributing to biodiversity loss as well as adverse impacts on fishing activities. In addition to that, agricultural chemicals such as herbicides and fungicides can get into the water body and introduce carcinogenic materials that increase pollutants in the food chain [35].

1.5.2.2. Industrial Activities

The direct dumping of domestic waste, industrial trash, and municipal garbage into the body of the water system is one of the main contributions to pollution. The dumping of residual waste causes water pollution. The direct dumping of industrial emissions into water resources is a major contributor to water pollution in both surface and groundwater. Water pollution can come about because of substances like acid, toxic metals, pesticides from agriculture, pigments, and other forms of untreated industrial waste discharged by industries. The discharged substances, which often cause pollution, may reduce habitat diversity in the ocean and pose a danger to people who may fall ill from diseases such as cholera, diarrhea, and so forth [36].

1.5.2.3. Mining

The extraction of rocks, minerals, and other geographical components from the layers of earth is referred to as mining. The mining industry is involved in the extraction of metallic materials that are required by our society for the provision of services such as construction, sound,

telecommunications companies, food, housing, health care, and others for space exploration. Water pollution is another issue that arises from the mining activity [37]. During mining, significant amounts of water is generated from extraction processes, mine cooling, and drainage which can lead to surface and ground water pollution by these materials. The main causes of surface water degradation are mining water discharge, waste material erosion, and accidental releases of dangerous chemicals [38].

15.2.4. Domestic Practices

There are various materials at home that could possibly contribute to environmental issues if not disposed of properly (e.g., paints, batteries, electronic devices). If these types of materials are discarded incorrectly, they may contain heavy metals and thus accumulate in the food chain via polluted soil and water. Most pollutants in waterways created by homes come from the disposal practices associated with household activities (particularly wastewater management). These pollutants can impact both surface water and groundwater sources. Pollutants originating from households typically involve sewage/wastewater; these compositions usually contain human feces, soaps/detergents, oils, and other pollutants. All these materials can potentially contain harmful microorganisms and organic compounds that could potentially enter a water source. Specifically, blackwater has high concentrations of nutrients and bacteria/other pathogens (as opposed to greywater) [39].

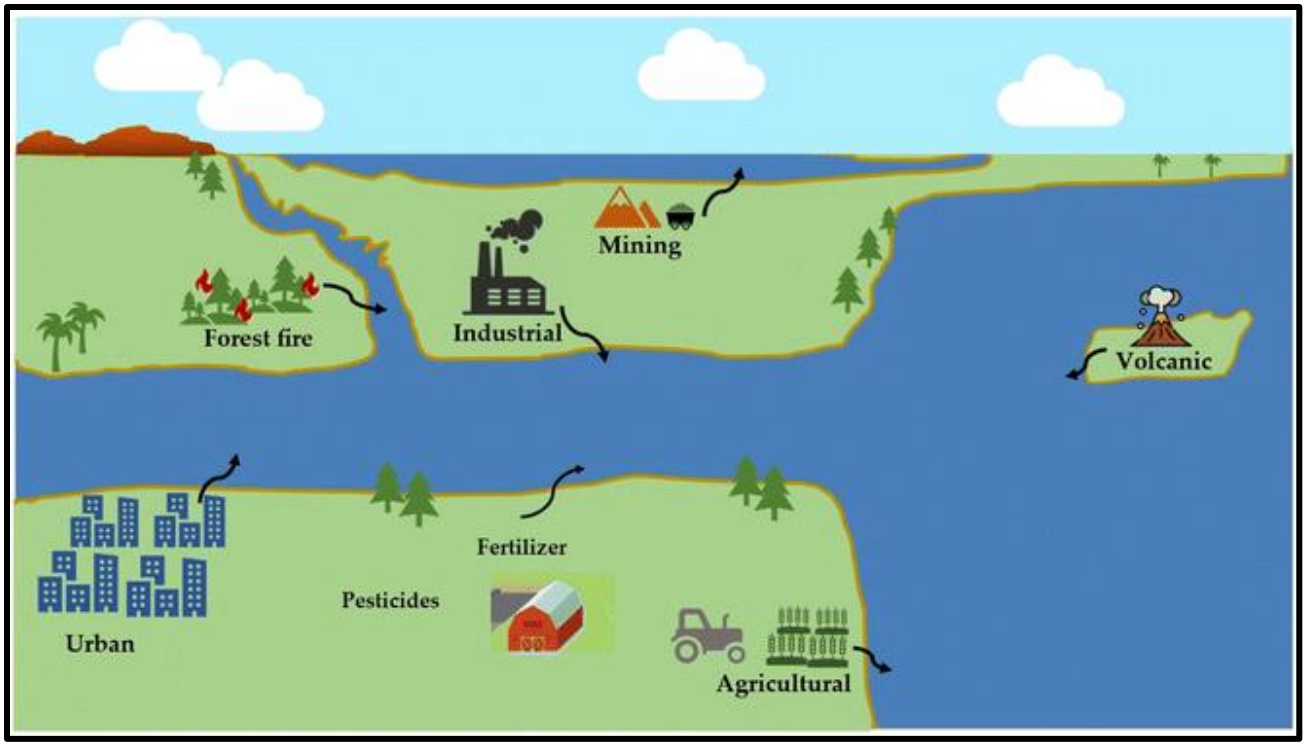

Figure 1.4**:** Sources of HMIs [40].

1.5. Different Heavy Metal Ions

Heavy metal ions pollution is regarded as one of the most severe types of pollution globally, as these are non-biodegradable, and because they are not readily taken up by living things, heavy metal pollution is expected to last for long periods (possibly thousands of years) before environmental systems reset themselves [41]. Some of the most common examples of heavy metals are lead, cadmium, zinc, mercury, arsenic, silver, chromium, copper, iron, platinum [42]. Heavy metals can contaminate surface and near-surface waters (e.g., oceans or seas) and, through bio-accumulation in food chains, threaten not only aquatic ecosystems but also human health by causing bio-accumulation of heavy metals through the food chain [43]. Table 2 summarizes the comprehensive overview of major heavy metal ions along with their permissible limits as defined by WHO guidelines, their predominant environmental sources, and their influence on human health and ecological systems.

Table 2: Major Types of Heavy Metal Ions

Metals	WHO limits (mgL^{-1})	Common Sources	Effect on Humans	Reference
Arsenic (As)	0.05	Pesticides, smelting, mining, rock sediment effluent, wooden electric poles etc.	Lung irritation, Heart problems, brain damage, infertility, skin lesions etc.	[24], [44], [45]
Lead (Pb)	0.015	Electronic waste, manufacturing of batteries, industrial processes etc.	Neurological impairment, behavioral changes, learning difficulties etc.	[24], [46], [47], [48]
Cadmium (Cd)	0.005	Volcanic emissions, paints and pigments, electroplated parts, synthetic rubber etc.	Chronic kidney diseases, hypertension, weight loss, lymphocytosis etc.	[48], [49], [50]
Chromium (Cr)	0.1	Coal combustion, electroplating, paints, petroleum, tannery etc.	Skin blisters, renal impairment, liver dysfunction, hemolysis etc.	[24], [51].
Mercury (Hg)	0.001	Weathering, volcanic emissions,	Lung cancer, digestive issues, neurological	[24], [52], [53]

		metallurgical, solid waste etc.	damage, skin irritation etc.	

1.6. Effect of Heavy Metal Ions

Heavy metals are a growing issue throughout the planet due to the increase in demand and activity associated with heavy metals to accommodate the same growing population. Heavy metal pollution affects land, air, and water, three of the four most common environmental compartments (i.e., natural systems). The majority of industrial activity, mining, waste disposal, leads, fertilizers, pesticides, sewage sludge, irrigation with wastewater, fossil fuel combustion, and petrochemical leakages are the main environmental contributors to heavy metal contamination in soil [54].

1.6.1. Effect on Soil

Soil is the primary sink that stores these ions, that persist for an extended period of time in an ecosystem because they are non-degradable [55].

The deposition of heavy metal ions endangers the future availability of food, to environmental ecosystems, and to the natural biodegradation process of organic contaminants, therefore increasing the chances of pollution in the environment. When ingested directly or indirectly by humans, animals, plants or by means of soil physical or chemical effects, heavy metals affect the health and quality of these life forms and natural soil ecosystems [56]. The effects of these metals on soil is illustrated in the figure 1.5.

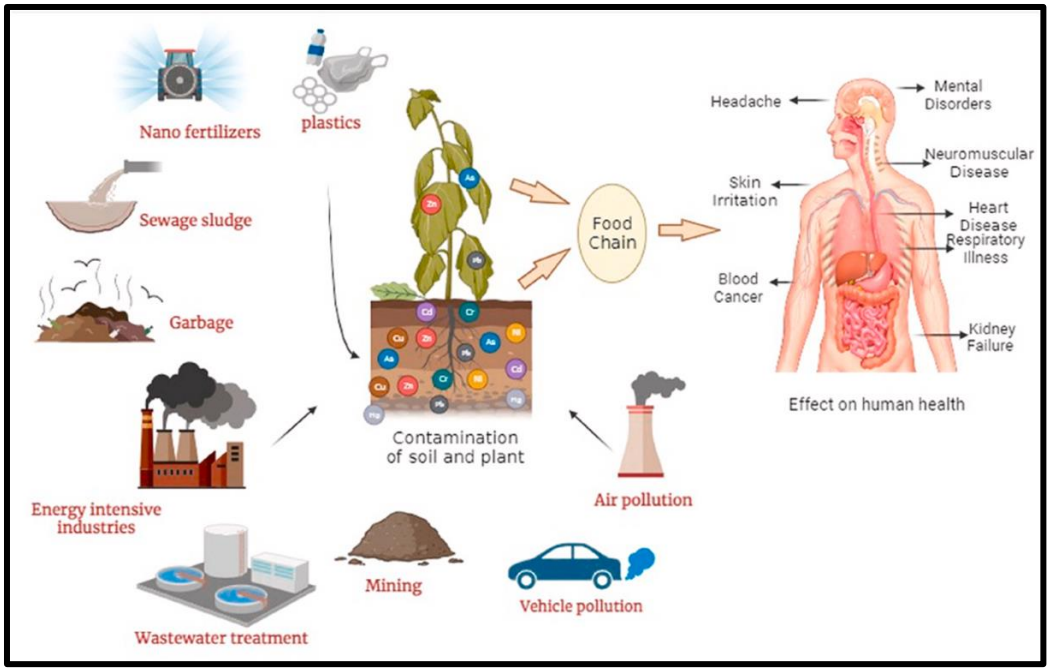

Figure 1.5: Effect of HMIs on Soil[57]

1.6.2. Effect on Water

Industrialization as well as urbanization are both primary reasons for the presence of heavy metal ions in the rivers and lakes in many places throughout the world. Heavy metals from industries, municipalities and urban areas flow into our water systems via runoff, which then builds up in our soils and aquatic sediments. Because even low quantities of these metal ions in our water supply can be quite harmful, the risks from exposure depend on the type of heavy metal, its biological function, the duration of the exposure, and the species being affected (see Figure 1.6). When heavy metals aggregate at the lower levels of the food chain, the food chain is disrupted, and bioaccumulation occurs over time, leading to increase in quantity of heavy metal ions at higher trophic level, especially in people. Humans, as the apex consumers in the food chain, are therefore at the highest risk for serious adverse health effects [58].

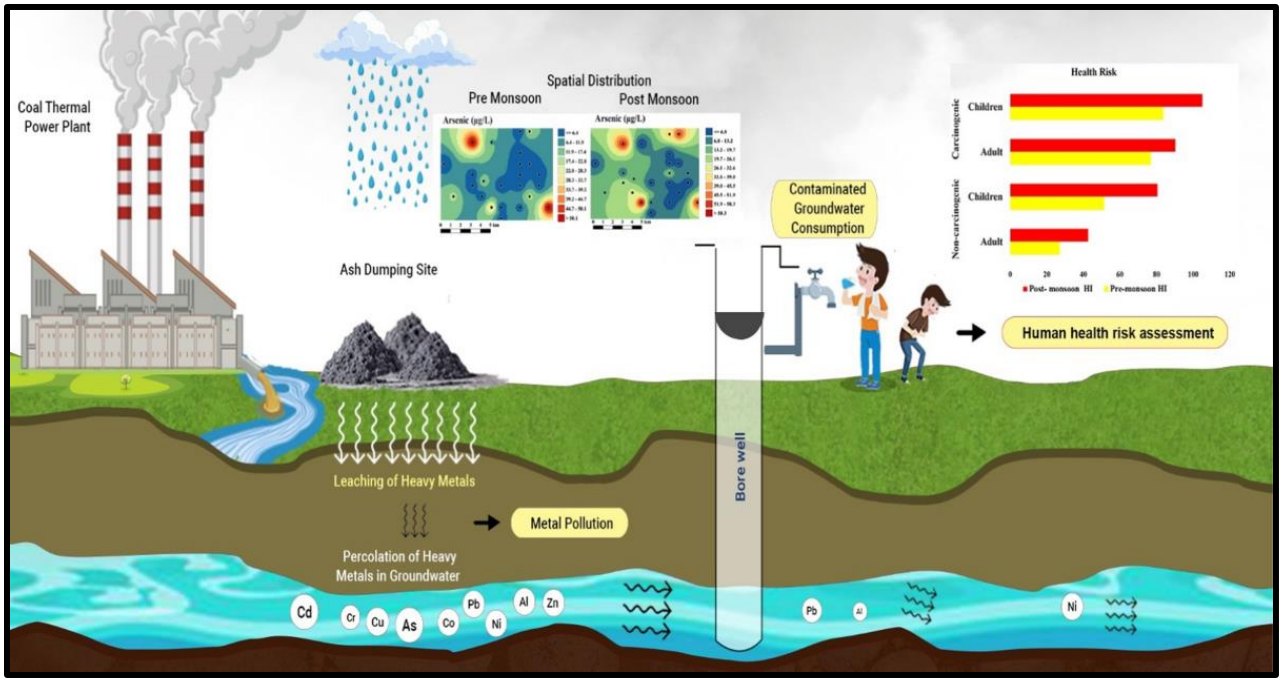

Figure 1.6:Effect of HMIs on water[59]

1.6.3. Effect on Air

Air pollution is becoming an increasingly significant environmental problem. Fine particulate matter ($PM_{2.5}$ or PM_{10}) are the major contributors to worldwide air pollution, originating from both natural and man-made sources. The most serious risks that PM pose are respiratory diseases, cardiovascular diseases, irritation to eyes and skin, and premature death. It also contributes to acid rain, eutrophication, and haze formation, and corrosion of infrastructure [9]. Heavy metals such as Cu, Cd, Pb (group 1), Cr, Mn, Ni, V, Zn (group 2), and Na, K, Ca, Ti, Al, Mg, Fe (group 3) are commonly associated with emissions from industry, traffic, and natural sources [60, 61]. Effect of heavy metal ions on air also clearly shown in Figure1.7 below:

Figure 1.7: Effect of HMIs on Air

1.7. Toxicity of HMIs

Heavy metal ions are poisonous to human beings (also shown in Figure 1.8) when they get accumulated in human body through food, water and air. Their toxicity comes from the fact that they interact with body's important biological compounds i.e. leading to enzyme inhibition, proteins dysfunction and damage to multiple organs. The toxicity of metal ions depends on its metal type, exposure level, chemical form and how much it is exposed [62]. Heavy metal ions enter the human body through many routes. As they are absorbed faster than they are excreted they tend to accumulate in kidney and liver. This will happen when animals tissues that are infected get into the food chain, which exposes human beings to it [63]. Toxicity by heavy metal ions is well documented and poses numerous health risks. These metals disrupt the proper functioning of human body. In some cases, metals act as similar element in the body and interfere with metabolism [64, 65]. According to Agency for Toxic Substances and Disease Registry; lead, cadmium, mercury and arsenic are among the most toxic substances [65].

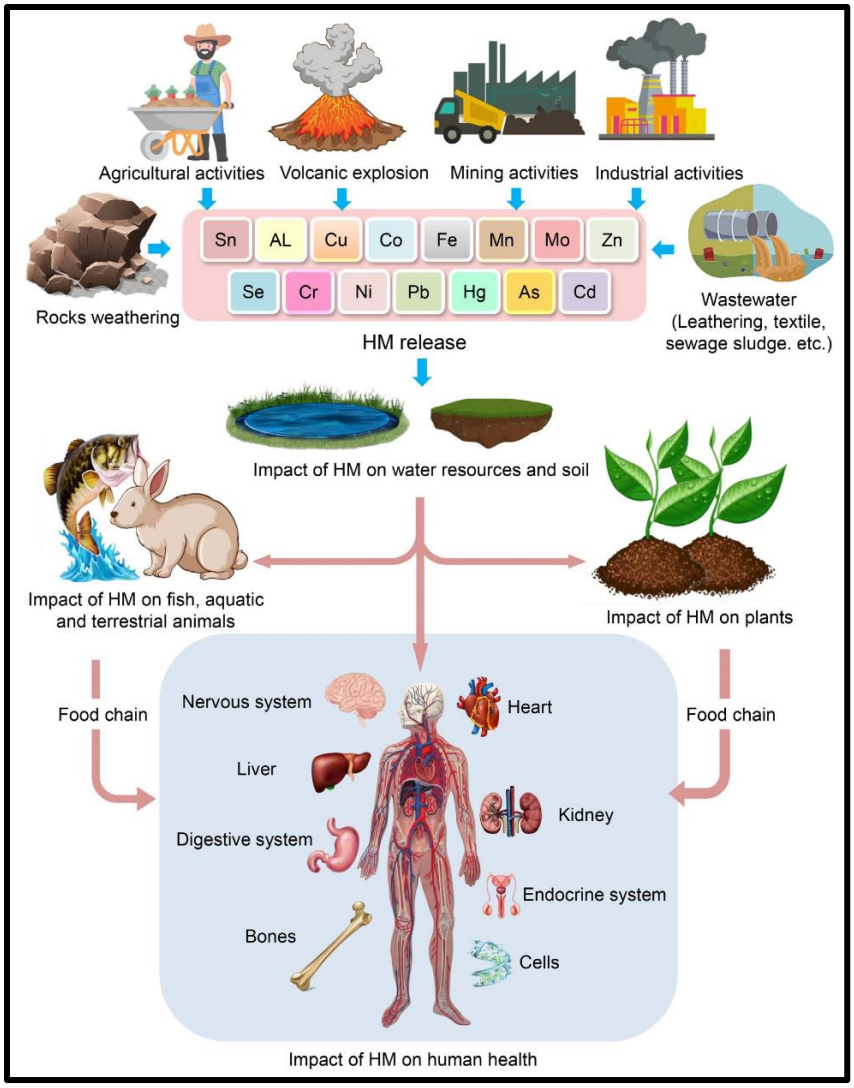

Figure 1.8: Toxicity of Heavy Metal Ions[66]

1.7.1. Effect of Arsenic

Arsenic is considered as one of the most significant heavy metal to worry about for both environment and people's health [67]. It is known to be carcinogenic as it cause serious health problems to human beings [66]. Arsenic is the 20th most common element and is mostly present in the entire environment [68]. Toxicity in the arsenic element is largely determined depending on the chemical form it takes. Inorganic arsenic is mostly known to take the form of As^{3+} or As^{5+}. These compounds happen to be more toxic. Arsenic and the inorganic forms of the element happen to be poisonous to humans. Arsenic, being inorganic, may be easily absorbed by the body through the gastrointestinal tract, accumulating in muscles, while organic arsenic gets easily eliminated

from the body. Arsenic can enter the body by ingestion, inhalation, or cutaneous/mucous membrane contact [67]. Acting like a protoplasmic poison, arsenic damages the sulfhydryl groups of protoplasm, thereby disrupting the process of cellular respiration, enzyme functions, and cell division. Its toxic manifestations, occurring after short exposure, include abdominal pain, diarrhea, vomiting, muscle weakness, and hot flashes, whereas, after prolonged exposure, skin disorders, cancers, etc., can occur [69] also shown in figure 1.9.

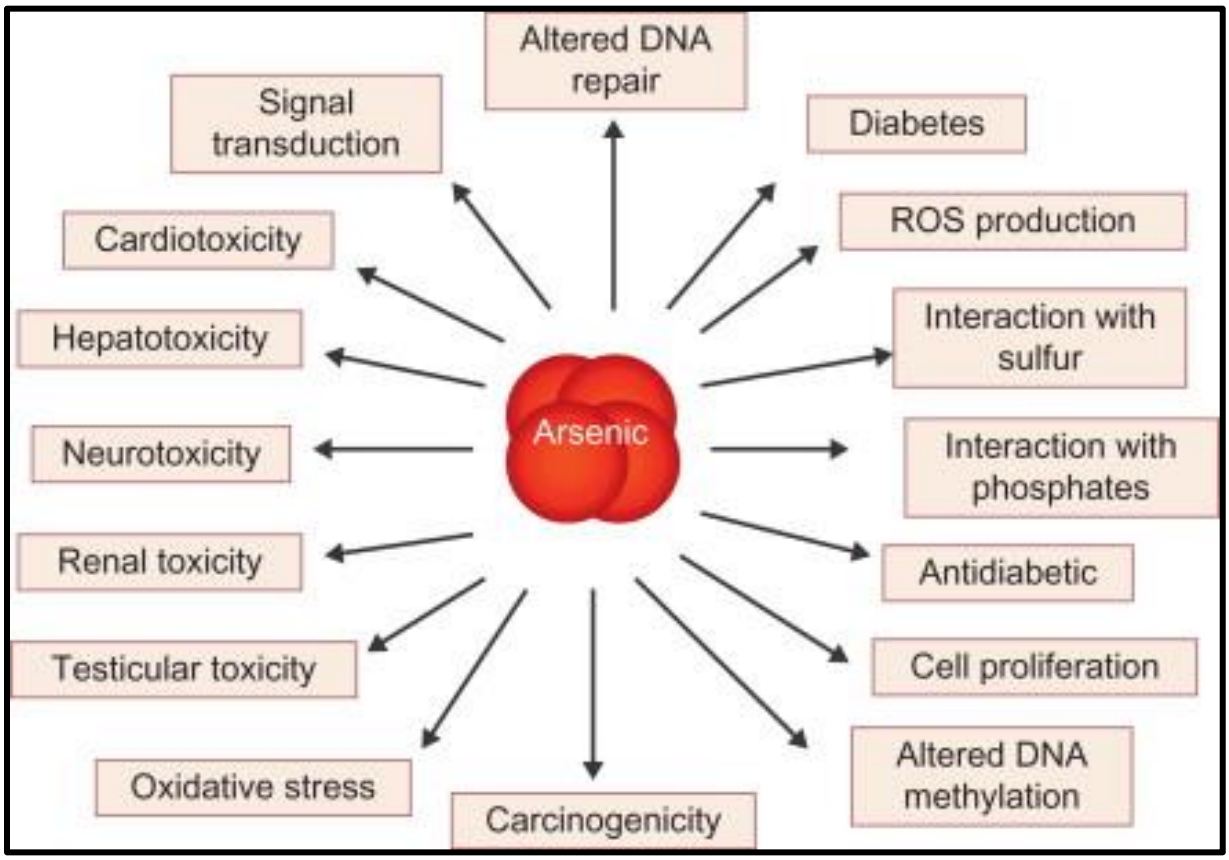

Figure 1.9: Toxic Effect of Arsenic [70]

1.7.2. Effect of Lead

Lead is a very toxic heavy metal that has been employed in large quantities and has affected the environment and the health of many people. Pure lead is a bright and silvery metal which appears bluish in color when in dry form. However, as soon as it is exposed to air, it tarnishes rapidly and forms a complex combination of compounds related to the environment [67]. As a heavy metal, lead is particularly toxic and interferes with many physiological processes in plants. Unlike other essential metals such as zinc, copper, or manganese, lead has no physiological role in a plant.

Large amounts of lead in plants will increase the formation of ROS in the plant [70]. In the case of humans, the presence of lead (Pb) has been associated with various neurological disorders; these range from Alzheimer's disease and Parkinson's disease to amyotrophic lateral sclerosis and attention deficit/hyperactivity disorder (ADHD) [71]. However, aside from the neurological disorder aspect, the exposure of cells of the body to lead can lead to various complications; these range from issues in the liver and the kidney to changes in the white blood cell counts and serum levels of urea, creatinine, aspartate transaminase, and alanine transaminase, hemoglobin, and hematocrit. It is important to note that the presence of these complications is more [72].
Figure 1.10, elaborates different toxic effects of lead on human beings

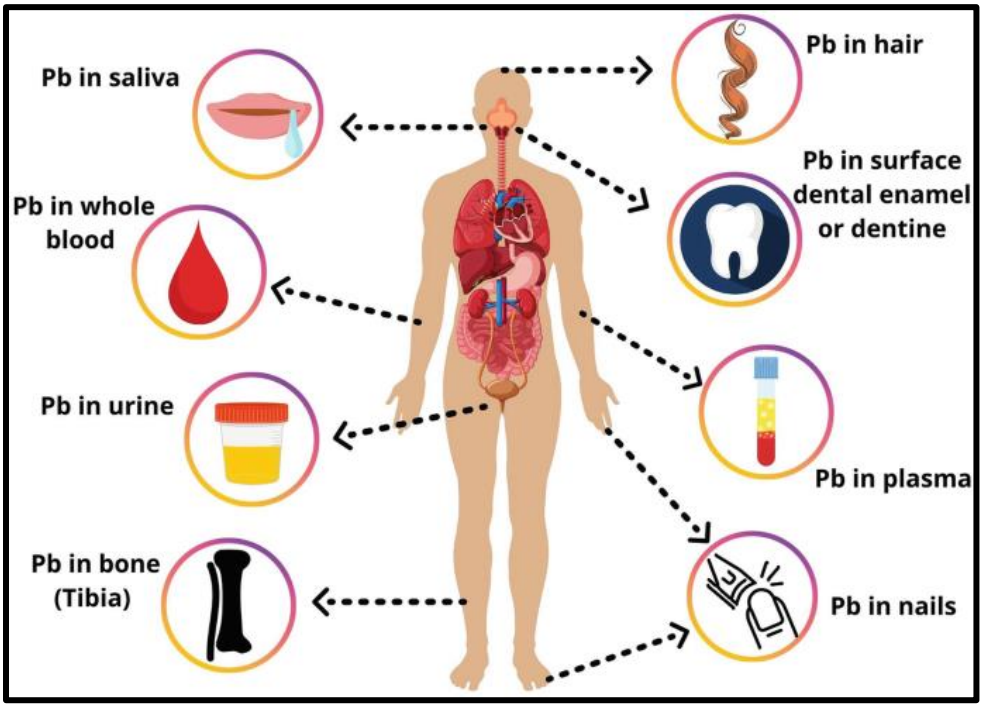

Figure 1.10: Toxic Effect of Lead[73]

1.7.3. Effect of Mercury

One common source of mercury in fish and seafood is its frequency in these products. Currently, the increasing rate of mercury contamination has risen to about ten times its former rate before the industrial era [74]. Methylated mercury leads to the production of methylmercury (MeHg), which has high toxicity and prefers being retained by organisms and then transferred along the

food chain [75]. Mercury mainly targets the brain but can also impact other organs, including the nervous system, kidneys, and muscles. Mercury disturbs the cell membrane, disrupts the balance of calcium within the cell, and prefers to bind to the free thiol groups because the resulting bond is quite stable. Inhalation of the vapor of mercury can trigger respiratory issues, such as bronchitis, asthma, or episodes of breathing problems.

At the cellular level, mercury alters the tertiary and quaternary structures of proteins, causing imbalance in cellular processes. Additionally, it damages selenhydryl and sulfhydryl groups, which react with methylmercury. Finally, it inhibits transcription, translation, ribosome, ER, and natural killer cell function. Mercury exposure induces the generation of free radicals, which can compromise cellular integrity.

The rationale behind heavy metal chelation therapy is based on the concept that, although the mercury-sulfhydryl bonds are quite stable, it is possible for the mercury ions to migrate from one sulfhydryl ligand to another. This leads to the formation of fresh sulfhydryl groups, thereby enhancing the metal's mobility [67]. Figure 1.11 clearly shows how mercury effect human beings.

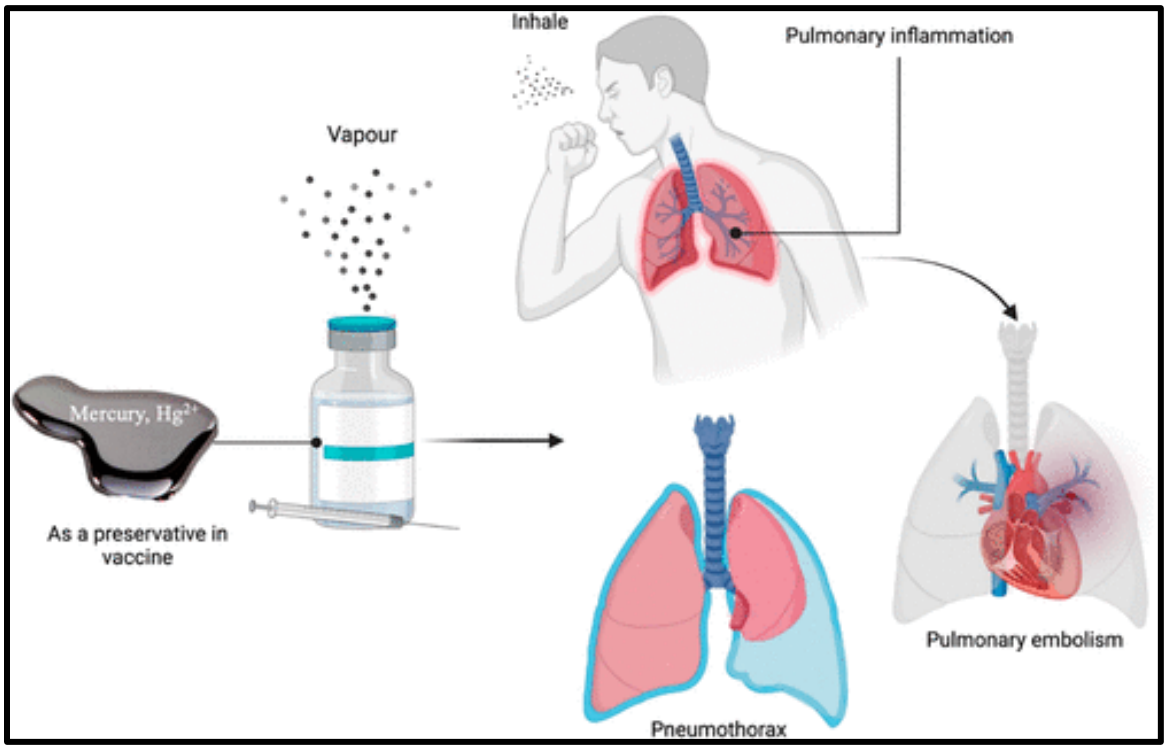

Figure 1.11: Toxicity of Mercury[76]

1.7.4. Effect of Aluminum

The most prevalent naturally occurring metal-based substance in the uppermost layer of the Earth is aluminum (Al). It concentrates on lakes and rivers after being discharged into the atmosphere by actions by humans and biological mechanisms. Because aluminum is neurologically hazardous and builds up in freshwater animals' neural networks, it might be the cause of oxidative damage. Moreover, it alters the function of a variety of cerebral chromosomes, neural cell factors, ACETYL CH activity, and brain chemical concentration. It also activates and inhibits antioxidant enzymes. It additionally results in memory loss, behavioral abnormalities in species, and histological alterations in neurons. Unfortunately, little is known about how being exposed to aluminum affects the growth of water species during its infancy [78]. Toxicity of arsenic shown in Figure 1.13.

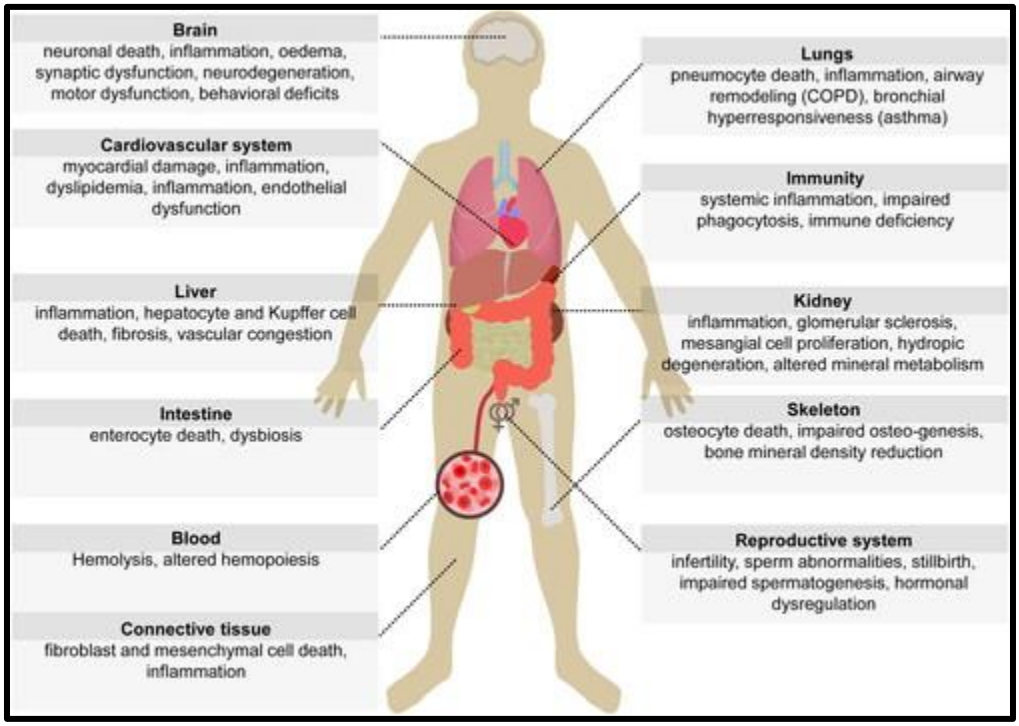

Figure 1.12: Toxicity of Aluminum[79]

1.7.5. Effect of Copper

Copper is a part of jewelry, along with various compounds utilized to produce imitated jewelry. It is applied as a primary metal in defense weaponry, construction, transportation, and industry. Dental surgeries also involve copper (Cu). As your liver is the first organ to access copper accumulation when it enters the bloodstream, chronic copper poisoning primarily affects it. In the first few days of copper poisoning, there is colonic rupture of the mucosal lining of the digestive

tract, hepatocyte necrosis of the cells in the liver, and acute tubular interstitial necrosis of the tubular system in the kidney. There can also be susceptibility, weakness, and hunger [80]**.** Figure 1.14 depicts the effect of copper on human body.

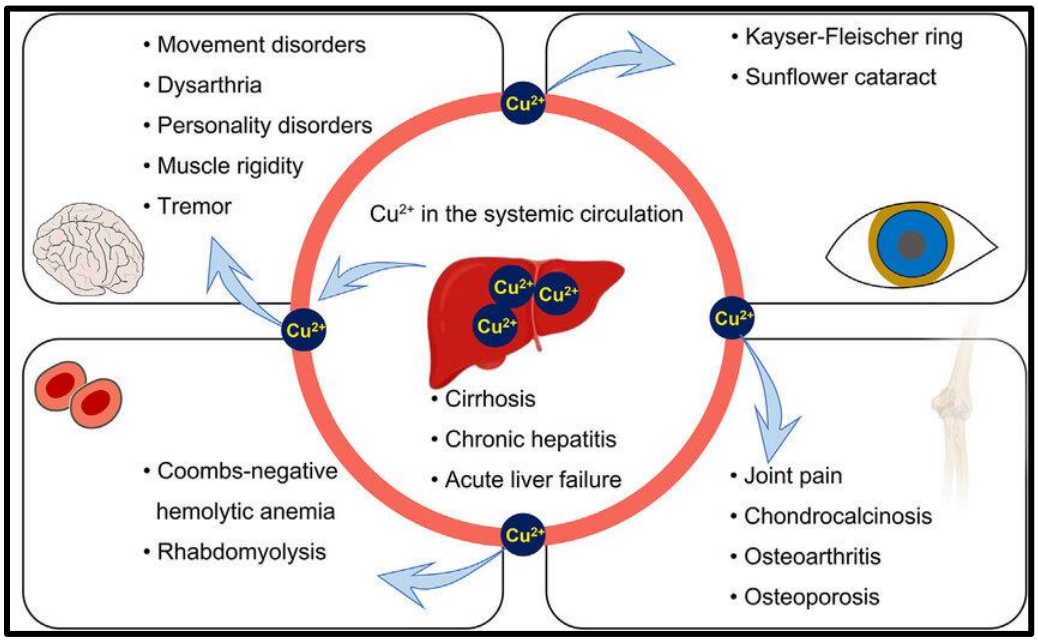

Figure 1.13: Toxicity of Copper[81]

1.7.6. Effect of Silver

Among the most important metals of value, Ag is extensively used in the domains of chemical engineering, solar power generation, and telecommunications. Nevertheless, annually, over 2500 tons of Ag^{+} are discharged into the ecosystem because of inadequate manufacturing runoff disposal. Freshwater organisms' essential enzymes as well as proteins include thiol groups that Ag^{+} interact with to cause permanent cell suicide and upset the water's biological equilibrium. In addition to attacking the helpful microbes in the ground arbitrarily, Ag^{+} contamination in water also results in pH imbalances, nutritional deficiencies, and fertility loss [82]. Effects of silver on human body are clearly shown in Figure 1.15.

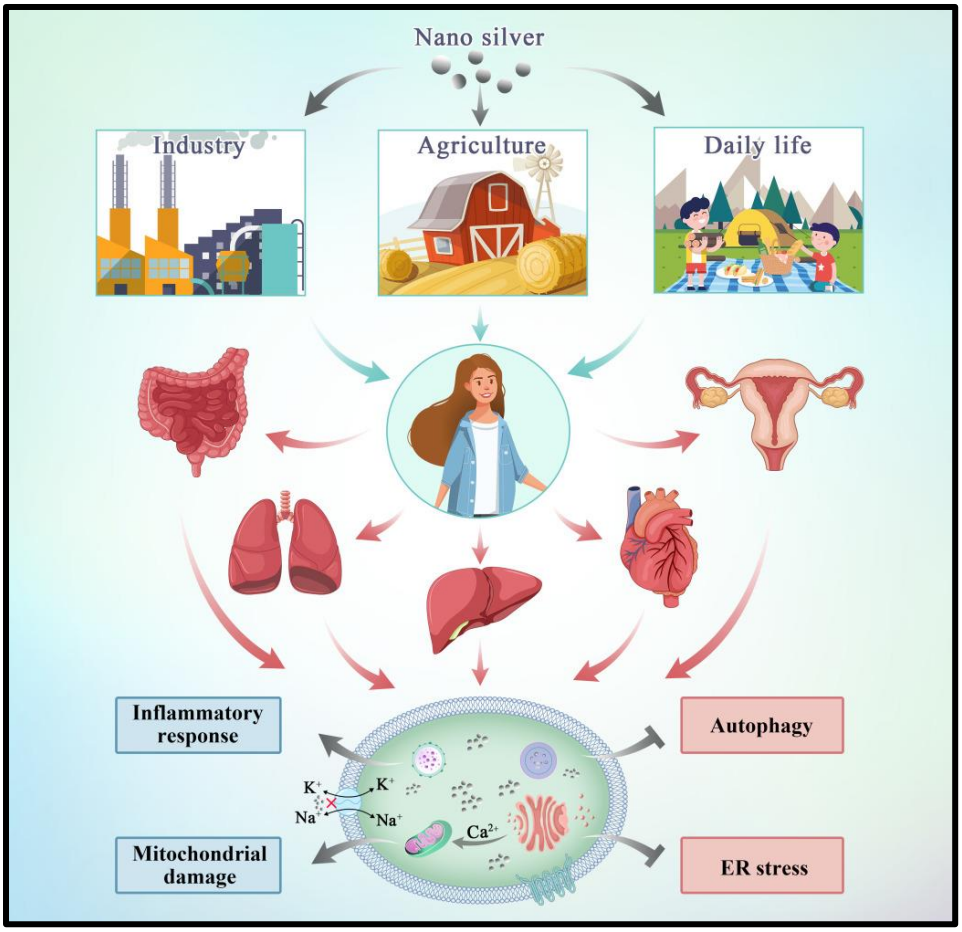

Figure 1.14: Toxicity of Silver

1.8. Techniques for HMIs detection

So, due to toxic effects of these ions it is therefore necessary to detect and quantify any type of heavy metal ions present above the permissible limit and remove it using an appropriate method. A metal ion detector is essentially a device for detecting metal ions in a locality or a region and sometimes estimating the quantity of metal ions present. The development of metal ion–free water systems is vital for protecting water life. Prior to using techniques for eliminating toxic metal ions in water samples, there is a need for analysis instruments or methods capable of detecting metal ions as well as estimating the degree of contamination of the water. This is crucial in determining mechanisms for clearing the water.

Thus, the detection technologies should be rapid, inexpensive, and eco-friendly. Moreover, they should be highly sensitive and accurate to identify trace levels of metal ions. Although several technologies are employed in the detection of heavy metal ions, there is no common technology applicable to all metal ions. These detection methods are [84]

- Spectroscopic Technique
- Optical Technique
- Electrochemical Technique

1.8.1. Spectroscopic Techniques

They are highly versatile for determining the concentration of metal ions [85]. They include highly sensitive techniques that are quite expensive or may be required trained personnel to work on such complex equipment [86]. Some of the most important spectroscopic detection techniques are discussed below:

1.8.1.2. Atomic Adsorption Spectroscopy (AAS)

In Atomic Absorption Spectroscopy, a specific wavelength of light energy is employed to excite isolated atoms from the ground state to the excited state. Light energy absorbed by the atoms in this process can be directly related to the quantity of the sample. Figure 1.17 below illustrates a block diagram of the Atomic Absorption Spectrometer.

The system consists of a main light source, an atomizer for gas-phase atoms or ions preparation for analysis, a monochromator for selection of a precise analytical wavelength, a detector, and an electronic read-out system.

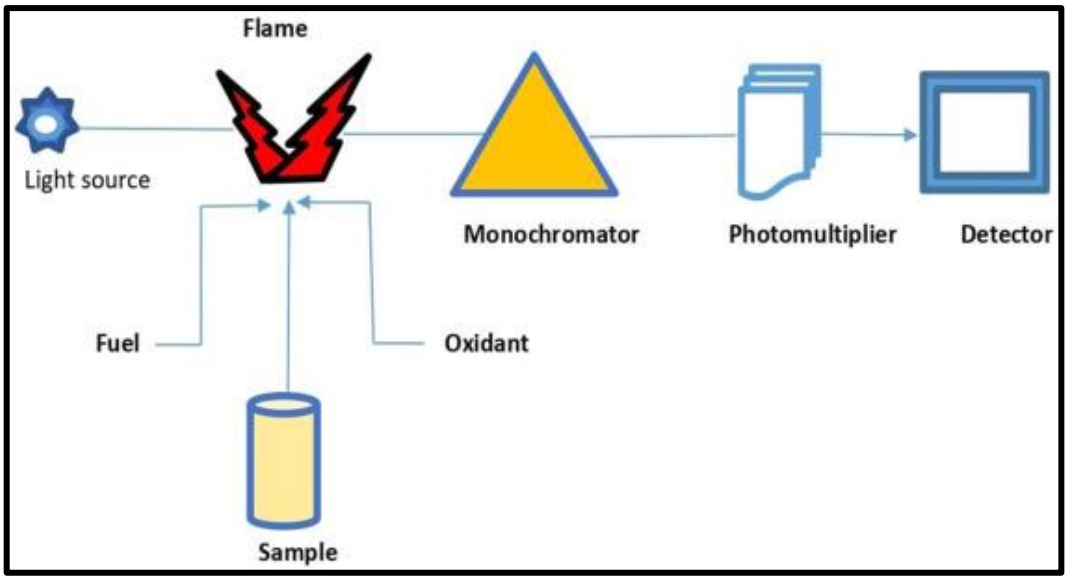

Figure 1.15: Working Principle of AAS [87]

AAS requires gas-phase atoms or ions; thus, the sample must be volatilized so its constituents are well separated in a gas phase. The most common methods for creating gas-phase atoms or ions are plasmas, flames, or electrothermal atomizers. The process by which the analyte is converted to gas-phase atoms and ions is called atomization. Once the atoms or ions are in the gas phase, a light source selectively excites the element of interest. In most cases the excitation is provided by a hollow cathode lamp or an electrodeless discharge lamp whose energy spectrum matches the target element. The are multielement lamps available that allow us to determine several elements without interchanging lamps. The detection typically is done by solid-state detectors or photomultiplier tubes in the AAS instrument. In cases where mercury is the analyte of interest, there is a different method called flow-injection mercury systems [84].

1.8.1.3. Atomic Fluorescence Spectroscopy

Compared to AAS, it operates by a different principle. Like AAS, the sample is first atomized to convert the material into its atomic form. However, in AFS, the atomized species are excited by irradiation from an external light source. As they come back to ground state, they emit characteristic element-specific radiation, which is monitored by the detector as atomic fluorescence. One of its notable applications is the freezing of Prest vapor atomic fluorescence spectroscopy (CV-AFS), which is common for detecting mercury. In this method, the free mercury atoms are carried into the detection cell, where they are excited by a collimated ultraviolet light source. The atoms are then re-emitting the energy they absorbed as fluorescence, which is then detected by a UV photodiode detector or a photomultiplier tube [84].

1.8.1.4. Graphite Furnace Atomic Adsorption Spectroscopy

Graphitic tube is the basic or most important part of graphite furnace with openings on both ends and a central inlet for sample introduction. After the preliminary heating to evaporate the solvent and other volatile materials, the analyte is injected into the graphite tube in preparation for atomization. The analyte will now be in an atomic form ready for measurement by the same atomic detection principle as in FAAS. The main difference between FAAS and GFAAS is the atomization process. While in FAAS, the atomization takes place inside an open flame, in GFAAS, the atomization takes place in a controlled temperature setting. The main disadvantages of GFAAS are it takes longer to process a sample compared to FAAS in flame sampling, and it is capable of detecting fewer elements simultaneously [84]. This technique obviously

It illustrates the increased sensitivity and specificity that GFAAS provides, which enables accurate heavy metal ions with trace sensitivity even at relatively low concentrations [88].

1.8.2. Optical Techniques for the detection of HMIs

Techniques such as absorption, reflection, or luminescence spectroscopy are commonly employed to assess the optical properties of materials. Although, optical methods are frequently applied for the detection of heavy metal ions (HMIs), But restricted by multiple limitations [89] .

1.8.2.2. Indicator dye-based sensors

It is often based on the interaction between metal cations and colorant dyes, which alters the absorbance or fluorescence properties of the binding reagents. In such detectors, the indicator functions as a transducer for HMIs, since direct visual analysis is not feasible [90]. However, many dyes are unsuitable for practical sensing applications due to limitations such as poor analytical wavelength range, low stability, dependence on ancillary reagents, or the unavailability of dyes in sufficiently pure form. Furthermore, several indicators form complexes only under extreme or irreversible pH conditions, which restricts their applicability. These challenges are common to indicator dye-based systems. However, a major benefit of applying optical sensors is their ability to work with different wavelengths. However, this also imposes difficulties, as there are specific requirements for different dyes. There could also exist optimization, making the process of detection more complex [91].

1.8.2.3. Ionophore- based sensors

The ionophores as shown in Figure 1.18 below are also coming into the limelight in the case of heavy metal ions using optical sensing, as the conventional marker molecules and metal-ion complexing agents/organics have their limitations. The ionophores act as carriers, complex agents, and binders in the process of metal ion detection, which qualifies them for the detection of heavy metal ions. The ionophores can be modified to act as metal ion sensors (M^+) through several methods, which include adding fluorogenic/chromogenic moieties as well as binding them with the desired dyes. One effective way is through the employment of the ionophores to trap the ions in the membranes [92, 93], which improves the sensitivity and selectivity. The optical sensor involves a theodoron-selective chromo-ionophore that produces a visible light signal, while heavy metal ions selectively bind to the ionophores, making them suitable for accurate detection [94].

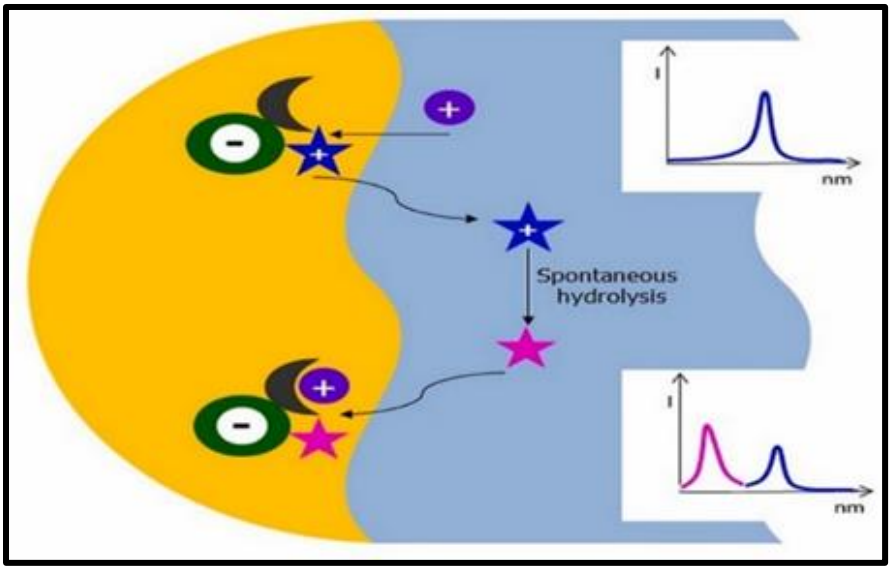

Figure 1.16: Ionophore-based Sensors [95].

1.8.3. Electrochemical Techniques for the Detection of HMIs

Compared to the spectroscopic and other optical approaches, electrochemical methods have several advantages: they are less expensive, easier to operate, and more adaptable to on-site measurements. Among the numerous reported electrochemical techniques, the following ones are the most common for heavy metal ions detection [96, 97].

1.8.3.2. Potentiometry

Potentiometry is a technique that employs two electrodes, namely a measuring electrode and a reference electrode, to measure the voltage of a certain solution. It generally finds application in the quantitative measurement of ion concentration. Potentiometric analysis deals with the measurement of potential difference between electrodes under controlled conditions, and thus, it is a method that accurately determines the HMI concentrations in different samples [98].

Potentiometry utilizes ion-selective electrodes, or ISEs, which are typically pre-calibrated with standard solutions to detect certain HMIs. A sample containing HMIs is introduced into the measurement system and the potential difference between the electrodes is recorded. The concentration of the target ions is determined directly from the calibration curve since the potential difference increases with the increase in ion concentration. However, this may be affected by interfering ions or other substances, which end accuracy. To reduce such interferences, some strategies involve either the use of masking agents or the design of ISEs with high selectivity.

Potentiometry presents several advantages, such as ease of use, wide applicability, and high sensitivity [99, 100].

1.8.3.3. Amperometry

It is an electrochemical technique that uses a steady voltage to analyze the presence of certain electroactive substances like heavy metals as the technique involves the determination of electric current flowing between the electrodes when measured under constant voltages [99]. In the design, the working electrode, reference electrode, and counter electrode are commonly used. Calibration is carried out using heavy metal ions in known concentrations as standard solutions. The current detected in the working electrode for each of the reference solutions is determined. After that, the electrochemical cell is set up, and the sample containing the heavy metal ions is introduced to the setup, and the current is monitored over time as the voltage is held constant [100]. The ion concentration is found where the measured current intersects the calibration curve. Such a method is very effective in identifying heavy metal ions due to its high sensitivity, fast response time, and trace level capability. It works really well for species that take part in redox reactions, since the current you measure is directly proportional to how much electroactive species is present [101].

1.8.3.4. Voltametery

Voltammetry is the electrochemical method applied in the analysis of electro active substances like toxic ions of heavy metals, relying on the study of the resulting electrolytic current in relation to applied voltage. Common methods applied in the identification of toxic metals include stripping voltammetry, differential pulse voltammetry, and square wave voltammetry [102]. Voltametric analysis usually consists of three electrodes: an analytical or working electrode (such as glassy carbon, mercury, or screen-printed electrodes), a reference electrode (usually an Ag/AgCl electrode), and a counter electrode. The analytical sensitivity can be improved by working electrode modification [103]. In analysis, potential is scanned over a fixed potential range where redox reactions of heavy metal ions take place at a fixed potential. By studying peaks of the voltammogram, the presence of particular heavy metal ions can be determined [104]. The concentration of every HMI is proportional to the peak intensity of the current, which makes it possible to quantitatively determine it. Voltammetry is extensively used in the determination of heavy metal ions in industrial processes, environment, and water analysis due to its high

sensitivity, speed of analysis, and ability to analyze complex samples [105].

1.8.3.5. Cyclic Voltametery (CV)

Cyclic Voltammetry (CV) helps to detect the behavior of analytes undergoing redox reactions by monitoring current responding to the change in electrode potential. CV analysis is a popular technique for studying and determining electroactive compounds, such as heavy metal ions. During a CV analysis, the change in potential is linear with time for both cycles of the scan in the positive and negative directions [106] , making it feasible to monitor an analyte undergoing an oxidation or a reduction reaction. CV analysis is an extremely useful technique for detecting a broad analyte spectrum, including industrial and environmental samples [107].

1.8.3.6. Differential Pulse Voltametery (DPV)

A technique called Differential Pulse Voltammetry (DPV) involves applying pulses of potential with a linear background to identify substances with electrochemical activity. Sensitivity in the measurement of heavy metal ions is increased using DPV, which measures the current at the end of the pulse [108].

At the working electrode, metal ions can experience oxidation or reduction reactions, which result in the generation of electron transfer signals. The background current in the linear sweep can be minimized, and the resulting current from the pulses will give a cleaner signal. The signal-to-noise ratio can also be improved as current responses from several pulses are accumulated. This will have a sensitization effect on the heavy metal ions. Based on this, a calibration curve is developed by correlating the peak current with concentration, which helps in estimating the concentration of unknown metal ions by matching them against the standard concentration [109].

1.8.3.7. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is a technique used to establish a system's impedance to alternating currents at a very wide range of frequencies. EIS has become a preferred means to investigate the electric properties of surfaces or materials and understand electrochemical reactions in reality [110]. This way, the resistance level and other interface parameters can be accurately determined and thus very sensitive to the material used or the structure's arrangement. For an electrochemical cell to produce efficient results, there must be compatible electrodes, such as a reference, counter, and working electrode. Heavy metal ions are

primarily involved in the working electrode, where the respective impedance response will be recorded over various frequencies. In practice, you fill the cell with the sample that contains the HMIs and collect the impedance spectra over specific frequencies [111]. The changes in the values of the impedances related to specific frequencies can indicate the presence and amount of the HMIs being targeted. The resulting spectra can then be used to calculate the level of heavy metal ions in the solution [112]. The advantage of using EIS is its ability to distinguish the electrical, electrochemical, and physical processes taking place in a real system. However, it is quite challenging to distinguish these processes since each of them has its own time constant, and in most cases, their time constants change slowly [113] .

1.9. Construction and Principle of Electrochemical Sensors

Electrochemical sensors are composed of a receptor component serving as the recognition element and a transducer or an amplifier for transforming the reaction into a detectable signal. Some recognition to selectively bind or to react with target compounds, thereby affecting their physicochemical properties [114]. To make it possible to detect both qualitatively and quantitatively, the sensor converts such changes into electric or optical signals like current or optical changes. Therefore, a chemical sensor is designed to react selectively to the analyte of interest with the goal of its evaluation [115].

Electrochemical sensors are highly sought after due to simplicity, low cost, and high sensitivity. The three-electrode electrochemical cell as shown in Figure 1.19 requires the use of a potentiostat to regulate the process [116]. In redox reactions, the chemical energy gets converted into electrical energy at the working electrode, WE. The reference electrode, RE, ensures constant potential with respect to time, thereby providing precise control of the applied voltage to the working electrode. The counter electrode, CE, finishes the circuit by providing a redox reaction that complements the previous redox reaction. Hence, the electrolyte solution improves the ionic conductivity in the electrochemical cell, ensuring efficient charge transfer [117]. The function of the working electrode is critical for the accuracy of the test results. Enhancements on the surface of the electrode can significantly increase sensitivity or selectivity by facilitating the flow of electrons. Such enhancements can include adding other substances, which makes the electrodes detect smaller quantities, enhancing the capability of the sensor for detection [119].

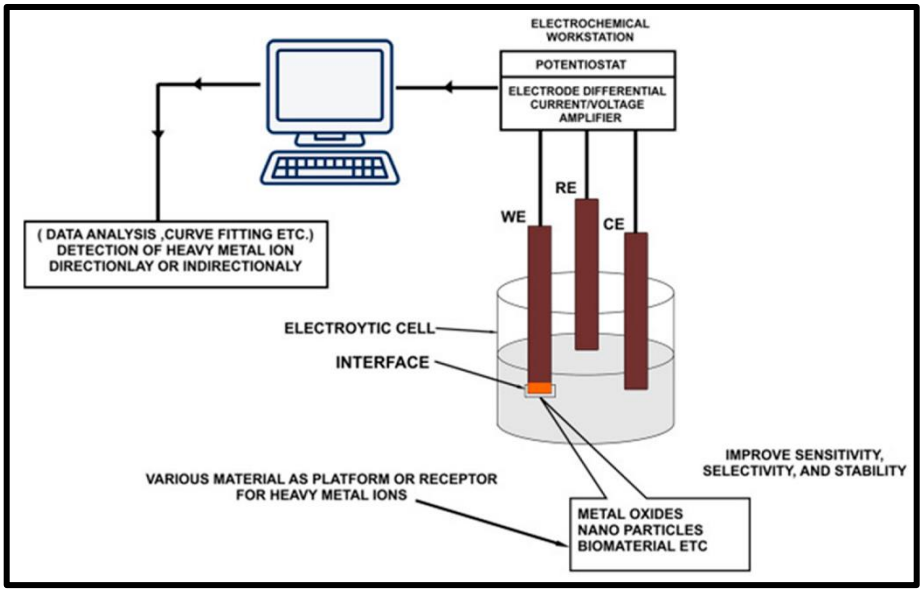

Figure 1.17: Working of Electrochemical Sensors [120]

1.10. Electrode Material for HMIs Detection

Electrodes are the cornerstones in the construction of electrochemical sensing devices for heavy metal ions. Many documented devices involve hybrid electrodes that combine various materials, each of which has a particular advantage. These range from materials that are highly conductive for enhancing electron transfer rates, materials that are porous providing a large surface area for metal ion absorption or catalyst attachment, and materials that possess functional groups that can significantly improve selectivity towards the target metal ions and enhance metal ion coordination. It is worth noting that, instead of focusing on single-component electrodes, the current discussion decomposes electrodes into their various constituent components that each serve a particular purpose [121].

1.10.1. Carbon-Based Nanomaterials

One of the reasons carbon-based nanomaterials are preferred is because of the outstanding electrical and optical properties they possess, which make them of great use in the development of sensors. There has been interest in the use of some of these carbon-based nanomaterials, such as the use of graphitic derivatives, carbon nanotubes, fullerenes, carbon nanofibers, CNT fibers, graphene, and activated carbon as sensors for detecting heavy [122].

1.10.2. Carbon Nanotubes (CNTs)

They are cylindrical carbon nanostructures, exhibiting unique physicochemical characteristics, such as a high surface area, great electrical conductivity, and remarkable mechanical strength. These characteristics make CNTs highly promising for applications in electronics, nanotechnology, and materials science [121]. Owing to these properties, CNTs are regarded as valuable materials for monitoring both inorganic and organic pollutants. Numerous studies have demonstrated that functionalization of CNTs significantly enhances their sensitivity and selectivity toward heavy metal (HM) detection [123].

Generally, carbon nanotubes (CNTs) with a limited presence of polar functional groups, such as carboxylic acid (–COOH), carbonyl (–C=O), and hydroxyl (–OH), demonstrate hydrophobic characteristics and are insoluble in water. Consequently, unaltered CNTs exhibit little ability to bind metal ions in aqueous environments and in result, they are not regarded as efficient electrode modifiers for the Anodic Stripping Voltammetry (ASV) technique [124]. Notwithstanding the individual merits of rGOs and CNTs, the efficacy of hybrid nanocomposites formed from their amalgamation as electrode materials is significantly enhanced [125]. A three-dimensional graphene–multi-walled carbon nanotube (3D G-MWCNT) nanocomposite was synthesized and subsequently employed to modify a glassy carbon electrode (GCE) for the detection of Pb^{2+} and Cd^{2+} ions [109]. The nanocomposite was obtained through the electrochemical reduction of 3D GO-MWCNTs, which were derived from the assembly of two-dimensional GO nanosheets and one-dimensional MWCNTs. The 3D G-MWCNTs had exemplary electric conductivity and facilitated highly sensitive concomitant detection of Pb^{3+} and Cd^{3+} ions at detection limits of 0.1 and 0.2 μg L^{-3}, respectively, via DPASV. Due to the presence of hydrophilic groups in GO, the 3D G-MWCNTs dispersed remarkably in water. MWCNTs can then be made soluble due to π-π interactions with water-soluble GO. Consequently, the G-MWCNTs with hydrophilic properties efficiently chelate and adsorb heavy metals from aqueous solutions [126].

1.10.3. MXenes-Based Nanoparticle

MXenes, as nanocomposites, have been found promising for use as heavy metal ion sensors owing to their ability for high surface modification, high electrical conductivity, and high surface area. Usually, with the combination of MXenes, which stand for two-dimensional transition metal carbides, nitrides, or carbonitrides, with metals, metal oxides, metal sulfides, or carbon materials,

these offer enhanced sensitivity, selectivity, and stability. MXene sensors have been demonstrated for use in biological applications [132].

One of the critical drawbacks of MXenes is their stability. Due to high surface areas, MXenes can easily oxidize in air or water, and the presence of impurities in the MXenes can further adversely affect their properties. Various methods have been employed to overcome such problems: doping MXenes with boron or nitrogen, encapsulating MXenes in matrices of materials like graphene or polymers or modifying the surface of MXenes with hydrophilic or hydrophobic groups. These modifications can significantly enhance the stability and electrochemical properties of MXenes, thus paving the way for the preparation of efficient nanocomposites for the detection of HMI [131].

1.10.4. Metal-Organic Framework MOF- Based Nanomaterial

Metal-organic frameworks, abbreviated as MOFs, are composed of metal ions bonded to organic linkers. These compounds form highly porous and accessible materials with high surface area properties, thus making them ideal for use in selectively adsorbing heavy metal ions. Various heavy metal ions can be detected using metal-organic frameworks due to their selectivity in adsorbing metal ions and their ability to withstand high temperatures without decomposing, thus making them ideal compounds for use in metal ion detection. Therefore, metal-organic frameworks not only can detect heavy metals. When MOFs are blended with other matrices, such as polymers or carbon nanotubes, the sensitivity and selectivity of detection increase. MOFs can be synthesized in various ways, including chemical vapor deposition, sol-gel technique, and electro spun methods[133]. Figure 1.20 illustrates the construction of MOFs from organic linkers and metal ions.

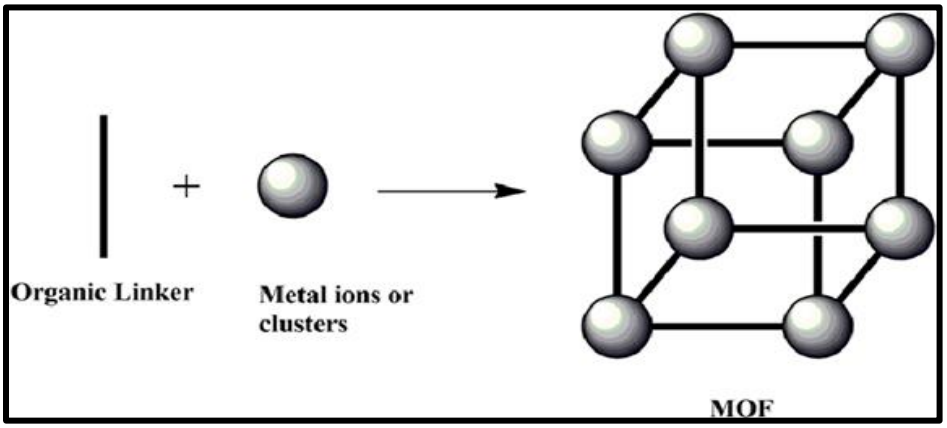

Figure 1.18: Metal Organic Framework MOF [134]

MOFs are structurally distinct from other porous materials due to their tunable porosity, atomic-scale structural uniformity, and the ability to precisely control size, shape, topology, and chemical functionality. These features allow scientists to effectively tailor the framework's structure, porosity, and functional properties. MOFs are unique in comprising both organic and inorganic components linked together in a rigid crystalline porous network [135].

1.10.4.2. Properties of Metal-Organic Framework MOFs

MOF based sensors are increasingly favored for the analysis of HMIs due to their superior properties. MOFs have the potential to be electrochemical sensors for the reasons listed below.

- MOFs have unusual structural features such as wide surface area, adjustable porosity, crystalline shape, and unsaturated metal coordination. Their network architecture is also uniform. Because of their many characteristics, MOFs have great catalytic potential, and they are useful in a material coating of electrocatalytic electrodes for sensing of HMIs [136, 137].
- The extensive surface area and porous architecture of MOFs facilitate the analytes, the analytes detection efficiency and mass transfer enhances, resulting in increased sensitivity and intensity of electric signal responses.
- The practical shape and size of the permeable channels, lops, and freely accessible sites can be used to increase the affinity of MOFs for certain studies through size exclusion effects [138, 139].

1.11. Rare-Earth Metal-Organic Frameworks (RE-MOFs)

Although considerable progress has been achieved in the development of Metal–Organic Framework (MOF)-based materials with diverse applications, the application of MOF materials in the development of electrochemical sensors, especially the detection of heavy metal ions, has some challenges yet to be overcome. This is mainly because of some challenges associated with the MOF sensors that significantly hamper their applications in practice. These challenges include the high sensitivity and specificity of the sensors required for the detection of some heavy metal ions. Moreover, in practical water bodies, the presence of some heavy metal ions such as Pb^{2+}, Cd^{2+}, Hg^{2+}, and Zn^{2+} is common, and it would not be possible for the MOF sensors to distinguish between them independently. Moreover, the nature of MOF, which is highly porous and could be fragile, can affect the stability of the sensors when in contact with harsh chemicals like strong acids or

bases, or in multiple sensing cycles.

All these challenges can hinder the long-term stability and reproducibility of metal-organic framework sensors in heavy metal ion detection. However, rare earth element doping in metal-organic frameworks with Tb, Yb, Er, and Eu has presented an opportunity to improve challenges surrounding these metal-organic framework sensors, especially in terms of their electrochemical sensing properties [140].

Rare earth elements, commonly referred to as the "vitamins of modern industry" because of their very distinctive 4f electron configurations and many oxidation states, remain important due to the extensive applications of REEs in catalysis, optics, magnetic applications, and conversion processes because of the rising need for renewable energy sources and environmental and medical reasons. MOFs possess a remarkable combination of properties—large surface area, porous structure, and multiple functional groups. This renders them highly effective in capturing and separating impurities from water. When REOs produce rare-earth MOFs, they can easily capture heavy metal ions in water using physical adsorption, chemical adsorption, or a combination of ion exchange and electrostatic forces. This ensures the capture of metal ions by the MOFs, thus hindering their transport in water. Consequently, the concentration and mobilization of heavy metals decrease in aquatic ecosystems, leading to a reduction in their ecologic toxicity and associated health hazards to individuals exposed to such water [141] .

Ytterbium metal-organic frameworks (MOFs) have proven very promising for use in the electrochemical sensing of heavy metal ions such as Cd^{2+} and Pb^{2+}. The porous structure provides a high surface area that better interfaces with the analyte, thus increasing sensitivity. The size selection property of the framework also enhances selectivity for the ions of concern. Additionally, the use of Yb^{3+} ions, which have large ionic sizes, aids in the creation of microporosity that facilitates the enrichment of small heavy metal ions on the electrode surface. The combination of these properties makes Yb-MOFs an efficient choice for the electrochemical sensing of heavy metals[142]. Structure of Ytterbium shown in Figure 1.21.

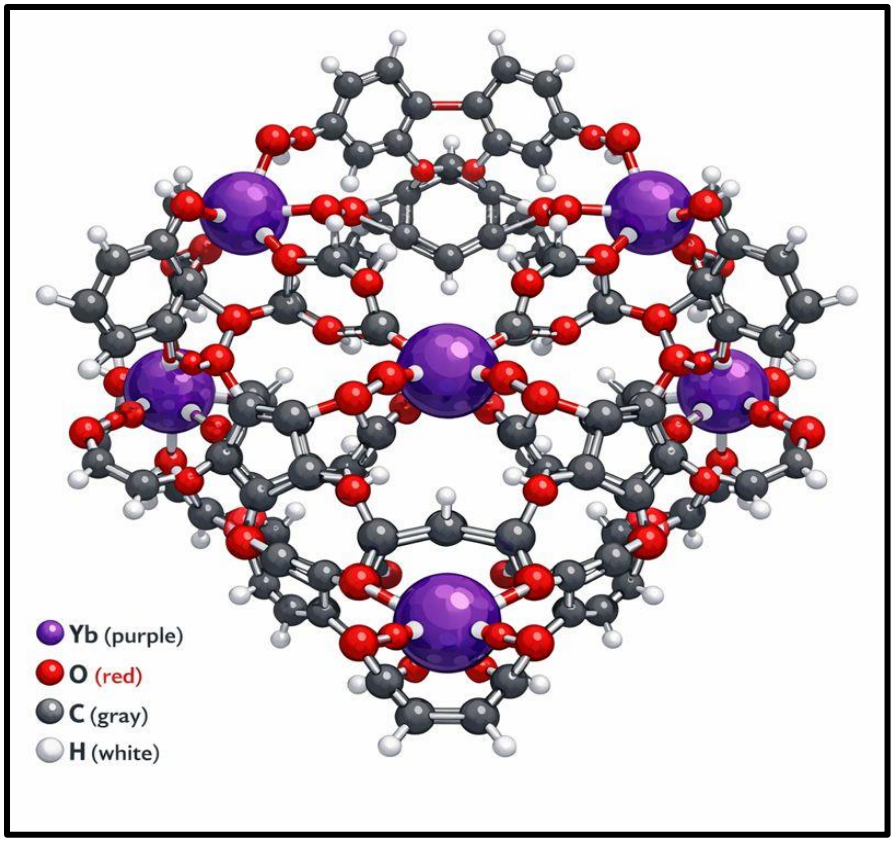

Figure 1.19: Structure of Yb-MOF

Despite the great promise, widespread deployment of RE-MOFs still encounters a host of hurdles. The crucial problems involve enhancing cycling stability, concern about migration and environmental safety of rare-earth ions, and the fact of high synthesis costs with complex fabrication. In this regard, topological tuning, defect engineering, and cross-material composites have been pursued in efforts to wring out higher performance and bridge the gap from lab studies to real-world use [141].

1.12. Transition metal dichalcogenides (TMDs)-based MOF

A large class of advanced materials includes transition metal dichalcogenides like MoS_2 and WS_2 (and CdS and $MoSe_2$), Metal-Organic Frameworks (MOFs), and transition metal oxides like TiO_2, ZnO, MoO_3, and SnO_2. To this list, one can add graphene, boron nitride (BN), and carbon nitrides (g-C_3N_4). These materials and their combinations offer immense potential in diverse areas, including catalysis, energy, and biomedicine [143].

MoS2 is also gaining interest owing to its peculiar electric, optical, and chemical properties. Its two-dimensional layered structure is highly rigid and photo-corrosion-resistant, making it

extremely attractive, apart from having high charge carrier mobility, high active edge positions, and viable band structures, thereby qualifying it as an optimal photocatalytic and electrocatalytic material. Its wide absorption in the visible region also foretells it to be an optimal source of energy. MoS_2 also exists in three crystal forms, namely 1T, 2H, and 3R, offering promising properties. The electrocatalytic properties offered by MoS_2 nanoparticles can prove to be better than those offered by platinum in numerous aspects, thereby qualifying it as the elite class of electrocatalysts. MoS_2 also exhibits potential properties in terms of applications in biological, filtration, conversion, and storage classes [144]. Two-dimensional metal-organic frameworks, or MOFs, are recognized for their high porosity and immense surface area. Metal-organic frameworks get formed because of the bonding of transition metals with organic compounds [145].

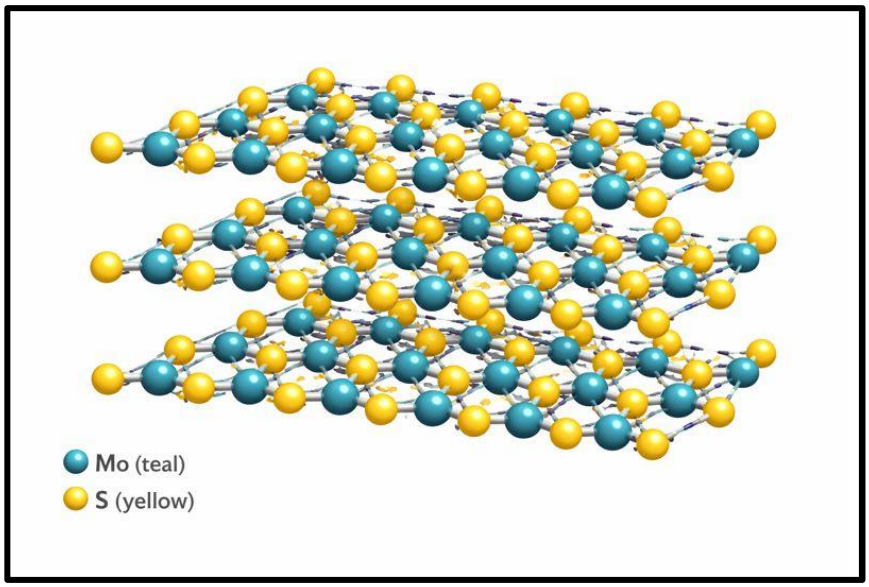

Figure 1.20: Structure of MoS_2

Chapter 2
Literature Review

Mei et al. investigated how to fabricate three-dimensionally flower-like Ni-MOFs. They successfully anchored these onto multi-terminal lamellar MXenes (Ti_3C_2Tx) using the solvothermal method. This work focused on using the resulting composites as flame-retardant fillers in thermoplastic polyurethane. In comparison to pure TPU, TG-IR analysis showed that there was a significant decrease in the release of CO_2, VOCs, hydrocarbons, aromatic compounds, ethers, and other carbonyl-bearing species during combustion in the case of TPU/NiMOF@Ti_3C_2Tx composites [146].

Zhang et al. researched the application of hierarchical electrochemical sensors for the analysis of trace metal ions in the environment. The group synthesized a metal-organic framework termed Yb-MOF-1, which consists of flower-shaped ytterbium coordinated with the organic ligand benzene-1,3,5-tricarboxylate. The metal-organic framework was prepared using the one-step solvothermal process and was assembled into a glass carbon electrode. The structure of Yb-MOF-2 was rod-shaped and was prepared at a pH of 4.26. By contrast, Yb-MOF-1 had an ultrathin nanosheet morphology, which increased the surface area to 462.356 m^2/g, and this facilitated the sensing of Cd^{2+}, Pb^{2+}, and Cu^{2+}. The sensing limits of Cd^{2+}, Pb^{2+}, and Cu^{2+} ions were found to be 9.22 nM, 1.69 nM, and 15.15 nM, respectively. The above results reveal highly selectivity, stability, and reproducibility. Recovery percentages of water samples between 95.8% and 103.5% revealed the efficacy of the electrochemical sensing methods in accurately discriminating heavy metal ions [147].

Wang et al. explored an efficient electrochemical sensor for detecting Pb^{2+} and Cd^{2+}. The sensor exhibits AuNPs grown directly on the L-cysteine-functionalised metalorganic frameworks combined with graphene oxide nanocomposites, shortly named as L-Au-MOFs-GO. Herein, through a one-step hydrothermal method, L-MOFs are grown on GO. The introduction of Lcysteine as reductant to form AuNPs enhances the conductivity and metal ions adsorption on the surface. Characterization was done using TEM, SEM, XPS, FT-IR, and XRD techniques. Electrochemical tests showed its performance compared with GO or MOFs-GO composites. The

Sensor exhibited good sensitivity and selectivity towards Cd^{2+} and Pb^{2+} ions in buffered solution, and Consequently, it showed an excellent performance in real water samples like river water and watermelon leaching solutions This nanomaterial for detecting toxic metals in various samples proved to be a valuable approach [148].

Jiang et.al. assessed heavy metal toxicity by creating a mobile phone-based electrochemical cell for HepG2 cells, which covered lead, cadmium, and mercury, among others. The cell construction involved reduced graphene oxide (RGO) on molybdenum disulfide (MoS_2) composites to make the cells biologically firmer and to give an output of enhanced electrochemical signals. The detection of the signals resulting from the metal ion's toxicity was done using differential pulse voltammetry (DPV). It was thus inferred that the heavy metals primarily affected HepG2 cells, and this was in a dose-dependent manner. The model produced IC50 values of 49.83 μM for cadmium, 36.94 μM for mercury, and 733.90 μM for lead. The first pair Cadmium with lead and mercury with lead evidenced the background effect, whereas an entirely different case was represented by cadmium and mercury showing opposite effect. This combination worked against the effect at lower doses but at higher concentration, the addictive effect was noticed. For the assurance of electrochemical data, flow cytometry, SEM, TEM imaging, and MTT assays were the techniques used. Therefore, these novel electrochemical sensor cells provided a more reliable, sensitive, and flexible approach for the detection of toxicities than cytotoxicity testing techniques [149].

Wang et.al. investigated the efficacy of two-dimensional MoS_2 nanosheets in removing heavy metals from water, applying the two different methods, dispersed suspensions and restacked thin-film membranes. The studies indicated a novel removal process wherein heavy metal ions get oxidized and reduced along with MoS_2. Silver ions (Ag^+) acted as a model for this purpose, and the nanosheets used were synthesized through the chemical splitting of MoS_2. The suspended nanosheets gave an astonishingly high removal capacity of about 4000 mg/g, and only less than 20% of this removal was due to adsorption, thus indicating that reduction of Ag^+ to metallic silver is the chief mechanism. MoS_2 membranes, like the suspended ones, displayed high removal capacity, which was explained by their conductive, permeable multilayer structure that allowed

for electron transfer: electrons transfer from molybdenum disulfide site in the membrane, which is anode to the cathode surface, reducing metal ions into their metallic form. Metal recovery at the membrane surface and in the continuous process continues because the initial products of metal oxidation, soluble and non-toxic compounds of molybdate and sulfur, accumulate at the surface and prevent the formation of an insulating layer. These results imply that MoS_2 membranes are quite excellent in not only the removal but also the recovery of precious heavy metals from wastewaters [150].

Neethipathi et.al. identified Cu^{2+} and other heavy metal ions (HMIs) as the major contributors to the environmental and human health risks. Glassy carbon electrode (GCE)-based electrochemical sensors made on rigid substrates are still the standard method for the detection of these ions. But the sensor applications continue to evolve, and they require sensors even to be flexible or/and to be disposable. The present work conveys a flexible electrochemical sensor built on a screen-printed carbon electrode (SPCE), which has been processed with molybdenum disulphide (MoS_2), for the detection of copper in aqueous media like water. Sensor's performance across the concentration range of 5 μM to 5 mM for Cu^{2+} has a limit of detection (LOD) of 5.43 μM. Studies that are comparative and based on electrochemical impedance spectroscopy (EIS) using MoS_2 modified conventional GCE show that the SPCE-based sensor gives superior linearity ($R^2 \sim 0.99$) and reliable detection of copper ions. The interference tests prove that the sensor does not lose its selectivity in the presence of other HMIs, thus marking its practicality of use for Cu^{2+} detection in water [151].

Dai et.al. developed the analytical methods that were so sensitive, selective, accurate and stable, and with the ultralow detection limits, that the extensive research interest was stimulated. Among such methods electrochemical approach was suitable for Hg^{2+} sensing through metallic 1T-MoS_2 nanosheets, which were produced by a combination of phase engineering and exfoliation. The 1T-MoS_2 nanosheets had much lower charge transfer resistance than the semiconducting 2H-MoS_2 nanoflakes, which led to much enhanced sensitivity and lower limits of detection (LODs). Eventually, the calibration curves were obtained after the modifying and optimization of the electrodes for both types of materials. The LOD for 1T-MoS_2 GCEs was found to be an incredibly

low value of 1.54×10^{-19} M, which is six orders of magnitude lower compared to 2H-MoS_2 LOD of 1.46×10^{-13} M. The 1T-MoS_2-based sensor displayed excellent selectivity against ten other ions due to the strong affinity between Hg and sulfur. It also demonstrated excellent stability and reproducibility, with recovery rates of the spiked real water samples at 99.8% to 101.2% marking its exceptional sensitivity. Such outstanding results establish that metallic 1T-MoS_2 nanosheets are a very promising material for the electrochemical detection of mercury ions [152].

Gan et.al. shown that surface functionalization can be a very efficient method for tuning the 2D material surface that are electronically active to enhance their practical applications. In their research, few-layer MoS_2 nanosheets were surface-functionalized via liquid phase exfoliation with DMF, 1-methyl-2-pyrrolidinone, and formamide, relying on the high coordination ability of these transition metal centers with nitrogen atoms. MoS_2 nanosheets treated with DMF were used for the construction of an electrochemical sensor on a glassy carbon electrode. The sensor showed high sensitivity and selectivity in the measurement of Cd^{2+}, and it had low cytotoxicity against MCF-7 cells and high anti-common ion interference. Theoretical and spectral studies showed that there was Mo–N covalent bonds due to orbital hybridization. The highly selective mechanism was based on the metal ion and DMF oxygen donor atoms interaction on the MoS_2 surface. Under optimal conditions, it had a detection range from 2 nM to 20 μM with a sensitivity of 0.2 nM. [153].

Chen et.al. investigated two-dimensional materials because of their considerable merits in sensor preparation, such as their high surface area, electrochemically active sites, and other distinctive features. In this work, rGO/MoS_2 composites were synthesized by combining the annealed rGO and MoS_2 by using ultrasonic method. Sensing performance was tested for non-contact human body detection and aqueous heavy metal ion sensing. In this study, the rGO/MoS_2 composite ink was cast onto the flexible PET substrate to make the sensor, which demonstrated considerable sensing abilities with up to 1500% for exhaled gas and 5400% for non-contact finger detection under 52% humidity. Moreover, for aqueous heavy metal ion sensing, the sensing ability reached a detection limit of mere 1 nM for Hg^{2+} ions. Overall, it has become clear from this study that the rGO/MoS_2 composites have immense potential as flexible sensors for the determination of human

presence and aqueous heavy metals [154].

Xu et.al. investigated the enhancement of valence-state modulation of transition-metal ions for boosting electrochemical detection of HMIs. They employed an interfacial engineering method to create a MoS_2/NiS_2 complex using DFT calculations, which demonstrated that the atomic-scale junction between MoS_2 and NiS_2 builds an internal electric field that enhances conductivity and promotes valence changes in nickel. At the heterojunction, electron transfer accelerates the Ni^{2+}/Ni^{3+} redox cycle, with electrons flowing from active Mo^{4+} in MoS_2 to Ni^{3+} in NiS_2. This greatly enhances the electrochemical performance of the MoS_2/NiS_2 complex, which displays a high sensitivity of 459.13 $\mu A\ \mu M^{-1}\ cm^{-2}$ toward the detection of Me^{2+}, outperforming most reported materials [155].

Qiao et.al. investigated due to the reduction of fossil fuel resources worldwide and the growing concerns about the negative effects of fossil fuel combustion on the environment, there is an increasing interest in using alternative fuel such as hydrogen gas. However, for the photocatalytic hydrogen generation method, an innovative and advanced photocatalytic material must be developed to increase the rate of hydrogen production. In this work, for MoS_2 material synthesis optimization, several characterizations were conducted to find that 190°C high temperature and 1wt% incorporation of PEG surfactant addition is most suitable. For the synthesis of MOF material, the optimal conditions were found to be the use of copper nitrate as a copper source, 30% ultrasonic amplitude, and 240°C calcination temperature. The addition of 1wt% of MOF to MoS_2 resulted in a flower-like MoS_2@MOF composite material with small and homogeneously distributed particles and macropores. The particles' shape and structure were found to be units of a rough and porous octahedron. The MoS_2@MOF composite material have 0.187 cm^3g^{-1} surface area. Notably, 1MOF/MoS_2 composite had the most -0.135V conduction band edge, with lowest charge transfer resistance (Rct of 1.78 Ω), highest photocurrent (11.1 mA cm^{-2}), lowest PL spectral intensity, and high photocatalytic durability [156].

Yi et.al. have revealed that food containing pathogenic bacteria is a major hazard to human health. They have chosen Salmonella as the test organism in their experiment, which led to the creation of polydopamine/CoFe-MOFs@Nafion nanocomposite an electrochemical immunosensor to

identify Salmonella in milk. In this case, CoFe-MOFs offer great stability, extensive surface area, and excellent porosity, but their drawback is the tendency to come off the electrode surface after modification. A solution to this problem is the Nafion addition that worked well. Subsequently, by means of cyclic voltammetry (CV) PDA film employed on the composite surface and then by polymerization mechanism it was explored. PDA is rich in quinone functional groups, Via the Michael addition reaction or the Schiff base reaction, the covalent bonds connect with the amino or sulfhydryl group, firmly immobilizing the anti-Salmonella antibodies to the electrodes. During optimized conditions, this sensor gave a linear response to Salmonella concentrations from 1.38×10^2 to 1.38×10^8 CFU/mL with LOD of 1.38×10^2 CFU/mL. In addition, it was found that immunosensor have remarkable specificity, stability, and reproducibility, thus offering a fast and reliable way of detecting foodborne pathogens as the main application [157].

Ye et.al. developed an innovative electrochemical sensor that incorporated a MOF-modified glassy carbon electrode for the ultrasensitive detection of Cd^{2+} and Pb^{2+} ions. The sensor is composed of a hexagonal lanthanide metal-organic framework, namely ZJU-27, synthesized through a solvothermal method from $Yb(NO_3)_3 \cdot 5H_2O$ and 1,3,5-benzenetrisbenzoic acid (H_3BTB) in the presence of 2-FBA. The synthesized metal-organic framework was further utilized for surface modification of a glassy carbon electrode. The sensor exhibited pronounced repeatability along with robustness. Moreover, the sensor worked effectively on actual samples. It is worth noting that a detection limit of 0.228 ppb was possible for Pb^{2+}, which indicated high sensitivity of the sensor for the detection of heavy metal ions in the environment [137].

Zhang et.al. successfully developed novel core-shell nanocomposite, Fe-MOF@mFe_3O_4@mC, which is a combination of mesoporous Fe_3O_4@C nanocapsules and an Fe (III)-based MOF, and used it as a promising electrode for HMIs sensing in water. The nanocapsules were synthesized by thermal treatment of hollow Fe_3O_4@C, which was initially prepared by using SiO_2 as a nanoparticle framework, leading to the formation of Fe-MOF. The resulting Fe-MOF@mFe_3O_4@mC nanocomposite displayed very good electrochemical activity, high stability and surface area, which allowed it to bind strongly with the aptamer strands that were designed to double-cross heavy metal ions. The apt sensor that was developed took advantage of the conformational transition that is caused by G-quadruplex formation between single-stranded

aptamers and the metal ions that are absorbed, thus producing a linear response to the log of Pb^{2+} and As^{3+} concentrations in the range of 0.01-10.0 nM. The LOD were found to be 2.27 pM for Pb^{2+} and 6.73 pM for As^{3+}. Moreover, the apt sensor exhibited good regenerability, remarkable selectivity, and decent reproducibility which are the features that make it applicable for both environmental monitoring and biomedical use [159].

Liu et.al. produced a new Fe-Co-based metal-organic framework (Fe-Co-MOF) by using the traditional hydrothermal method. The amalgamation of the Fe-Co-MOF with acid-functionalized multi-walled carbon nanotubes (MWCNT-COOH) resulted in a nanomaterial that has high electrical conductivity, superb electrochemical activity, and plenty of catalytic active spots. The component's synergistic effect was applied to heavy metals ions detection. They mapped out the composite's morphology and microstructure in detail using SEM, XRD, and XPS. They found that a GCE modified with the Fe-Co MOF@MWCNT-COOH composite showed excellent performance. Low detection limits of 2.49 ppb for Pb^{2+} and 2.60 ppb for Cd^{2+} were achieved with linear ranges of 20-1000 ppb and 100-1000 ppb, respectively. More impressively, it showed strong stability in the determination of heavy metals in real water samples, with an error of less than 8%. This suggests promising real-world use for environmental monitoring [160].

Saleem et.al. reported a new type of ratiometric electrochemical sensor based on a ferrocenedicarboxylate modified bismuth metal-organic framework (Fc-Bi-MOF) for the simultaneous analysis of Pb^{2+} and Cu^{2+}. The Fc-Bi-MOF was used to modify a glassy carbon electrode to prepare a new type of sensor named Fc-BiMOF/GCE and differential pulse anodic striping voltammetry (DPASV) was used for precise quantitation. The sensor offered a limit of detection of and 0.002 μg/L for Cu^{2+} based on the concentration range of 0.1-20 μg/L, and it was successfully utilized for the accurate simultaneous detection of both ions in tap water samples. The remarkable sensitivity is attributed to the high porosity, high surface area, as well as the high oxidative ability of Fc-Bi-MOF, which synergistically promotes the sensitivity of electrochemical analysis of Pb^{2+} and Cu^{2+} through their preconcentration. Furthermore, the modification of BiMOF with Fc enhances the conductivity of BiMOF as well as offers an internal standard for the ratiometric analysis resulting in both accurate and precise data. This work presents a new

biosensing platform for the detection of heavy metal ions with high accuracy and depicts the enhanced practicality of Bi-MOFs in electrochemical sensing missions. This study showcases the effectiveness of Bi-MOF-2 [161].

Dhayanithi et.al. discussed the extent to which the widespread use of the fluoroquinolones family of antibiotics, prevalent in living organisms and the environment, poses serious concerns. This is due to the need to detect the antibiotics quickly and accurately. In our study, the application and combination of nickel rods (NiR) and a nickel-based metal-organic framework (Ni-MOF) could enhance the electrochemical sensing of gatifloxacin (GAT). This is owing to the synergistic effects realized from the combination. To verify the hypothesis, the NiR/NiMOF composite materials were synthesized in different proportions of 2:1, 1:1, and 1:2 and tested for the electrochemical sensing of GAT. The electrochemical sensor based on the NiR/Ni-MOF composite on the Glassy Carbon Electrode (GCE) could distinguish between similar antibiotics and perform effectively on real sample materials like river water, serum, and urine, which reveals the possibility of using this material in actual applications. On the whole, the study introduces a new sensor platform and provides guidance on how MOF hybrids can be designed for improved electrochemical sensing as well as a scalable method for tracing pollutants in the environment. [162].

Chapter 3
Materials and Methods

3.1. Instruments Required

All materials were synthesized through hydrothermal or solvothermal reactions. The surface morphology of the synthesized materials was examined using field emission scanning electron microscopy (FESEM, Nova NanoSEM 230, FEI, USA). The crystalline structure was determined using an X-ray diffractometer (XRD, MiniFlex 600-C, Rigaku, Japan). Fourier-transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo Fisher Scientific, USA), operated in attenuated total reflection (ATR) mode, for the identification of the functional groups and surface terminations. Electrochemical measurements, like cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), were performed using a potentiostat (Gamry Interface 1010E) workstation in a three-electrode configuration.

3.2. Chemicals Required

Ytterbium (III) acetate tetrahydrate [Yb $(OAc)_3 \cdot 4H_2O$, 99.9% purity], benzene-1,3,5-tricarboxylic acid (H_3BTC, ≥99% purity), N, N-dimethylformamide (DMF, ≥99.8% purity), deionized water (DI), and ethanol (≥99.5% purity) were used in this study. Ammonium heptamolybdate tetrahydrate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, ≥99% purity] and thiourea (CH_4N_2S, ≥99% purity) were also used as received. All reagents were of analytical grade and employed without additional purification.

3.3. Methodology

3.3.1. Synthesis of MoS_2

Hydrothermal method was used for the synthesis of MoS_2 nanoflowers. 1g of ammonium heptamolybdate tetrahydrate and 2.5g of thiourea were dissolved in 60ml Deionized water (DI) by continuous stirring for 30min. After stirring, a homogenous colorless solution was poured into Teflon-lined stainless steel autoclave reactor for 24h under 180°C. After centrifugation black-coloured MoS_2 solution was repeatedly washed with DI $H_2O$and ethanol. After that it was subjected to drying in an oven for 24h at 80°C [164].

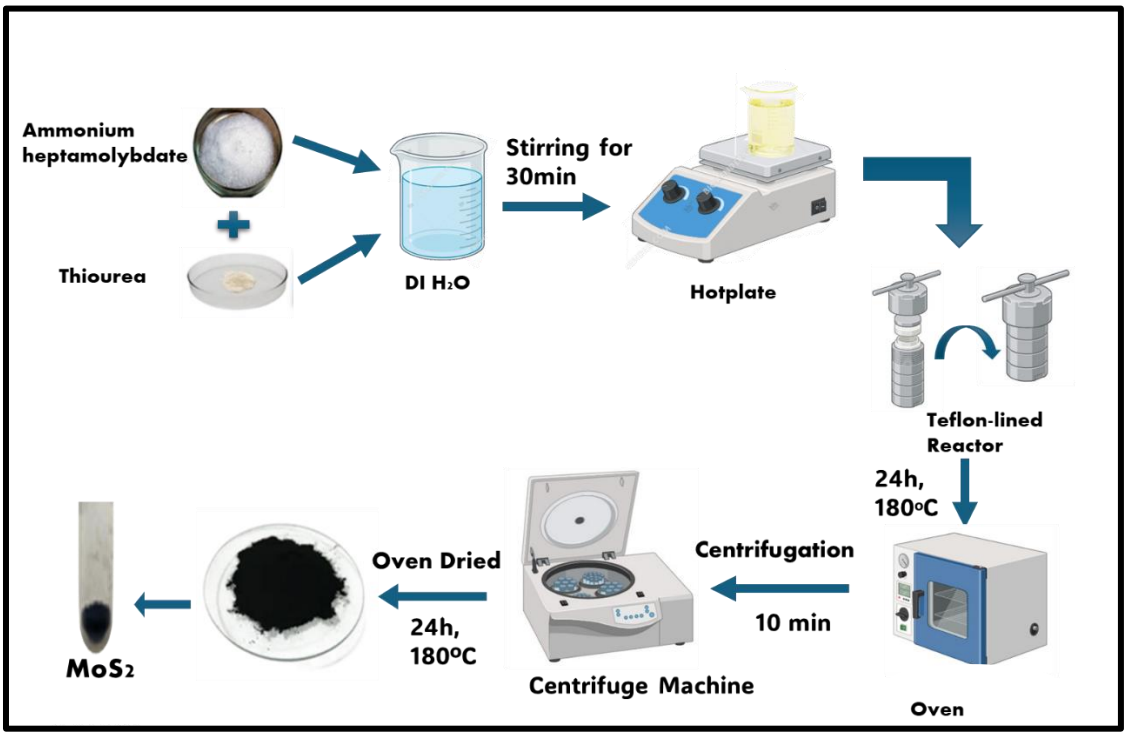

Figure 3.1: Synthesis of MoS_2

3.3.2. Synthesis of Yb-MOF

A solution of 1.125 mmol Yb $(OAc)_3.H_2O$ in 10mL H_2O, and 0.375 mmol H_3BTC in 20 mL DMF, and 10 mL H_2O were stirred with a magnetic stirrer at room temperature and under neutral conditions during 2h. The heating of the autoclave was then done at 140°C and then left to cool to room temperature. The mixture was then repeatedly washed with DMF and ethanol, respectively, and dried at 60°C in the end [147].

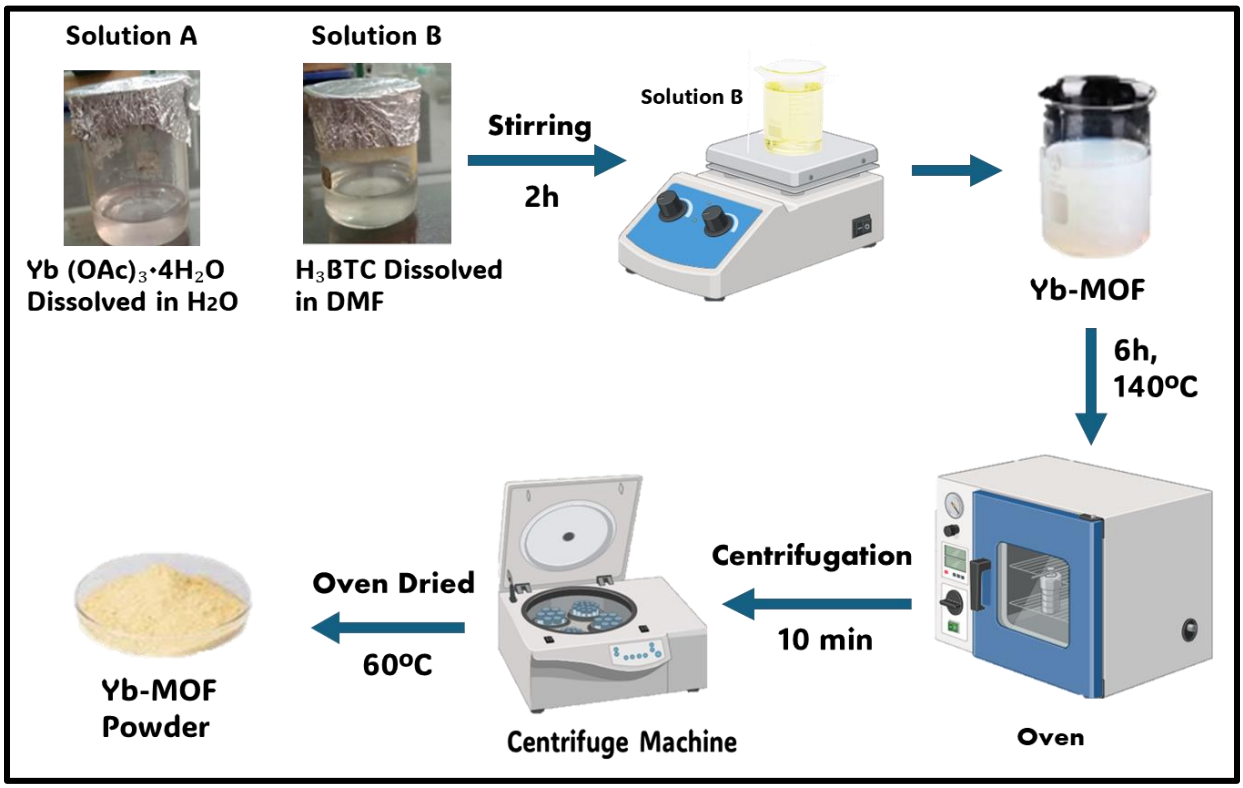

Figure 3.2: Synthesis of Yb-MOF

3.3.3. Synthesis of MoS_2@Yb-MOF Composite

Solution of 1.125 mmol Yb $(OAc)_3$.H2O in 10mL of H_2O, and 0.375 mmol H_3BTC in 20 mL of DMF, and 10 mL of H_2O were stirred using a magnetic stirrer at room temperature and in a neutral environment for 2 hours. The heating of the autoclave followed, which was carried out at a temperature of 140°C and later cooled to room temperature. The product was later cleaned using DMF and ethanol, separated, and dried at a temperature of 60°C [165]

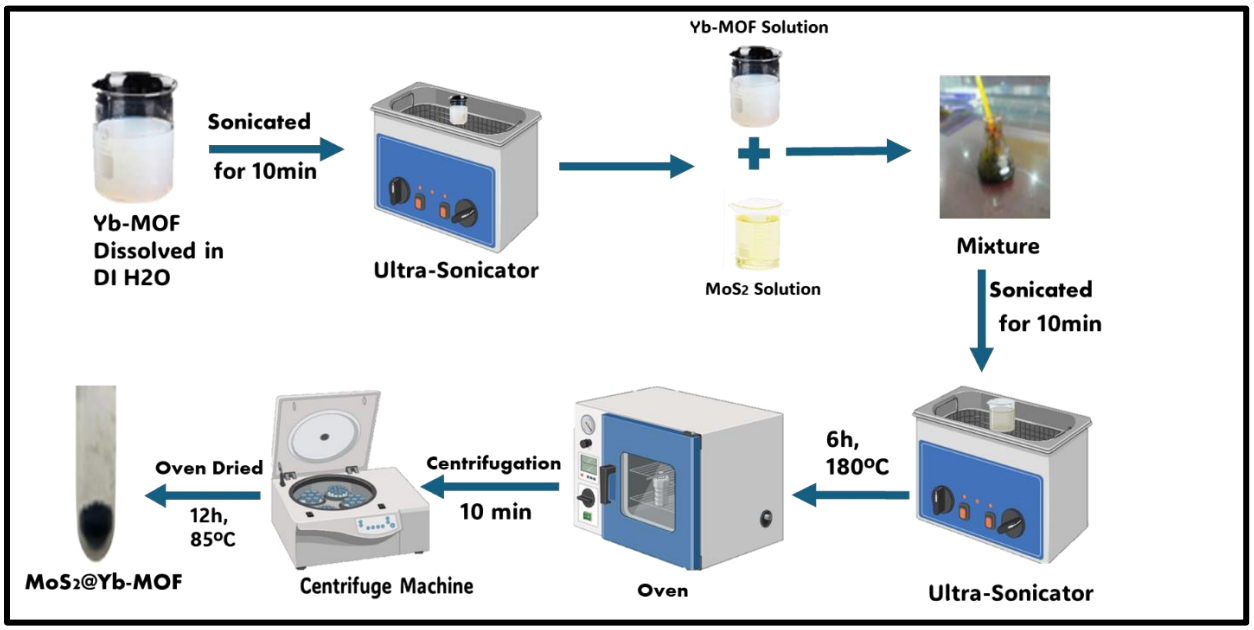

Figure 3.3: Synthesis of MoS2@Yb-MOF

3.3.4. Electrode Preparation

The working electrode was prepared using the synthesized material as an active component. A homogeneous slurry was obtained by mixing the synthesized material (80 wt%) with polyvinylidene fluoride (PVDF, 10 wt%) and carbon black (10 wt%). Dimethyl sulfoxide (DMSO) was added as the solvent, and the solution was ultrasonicated for 20 min to obtain a uniform suspension. The resulting suspension was carefully cast onto a pre-cleaned carbon cloth substrate (1 × 1 cm^2). The coated electrode was then dried under 60 °C for 3 h to evaporate the solvent completely. Mass loading of the electrode material on the carbon cloth was approximately ~2 mg/cm^2.

Chapter 4
Results and Discussion

4.1. Field- Emission Scanning Electron Microscopy (FE-SEM)

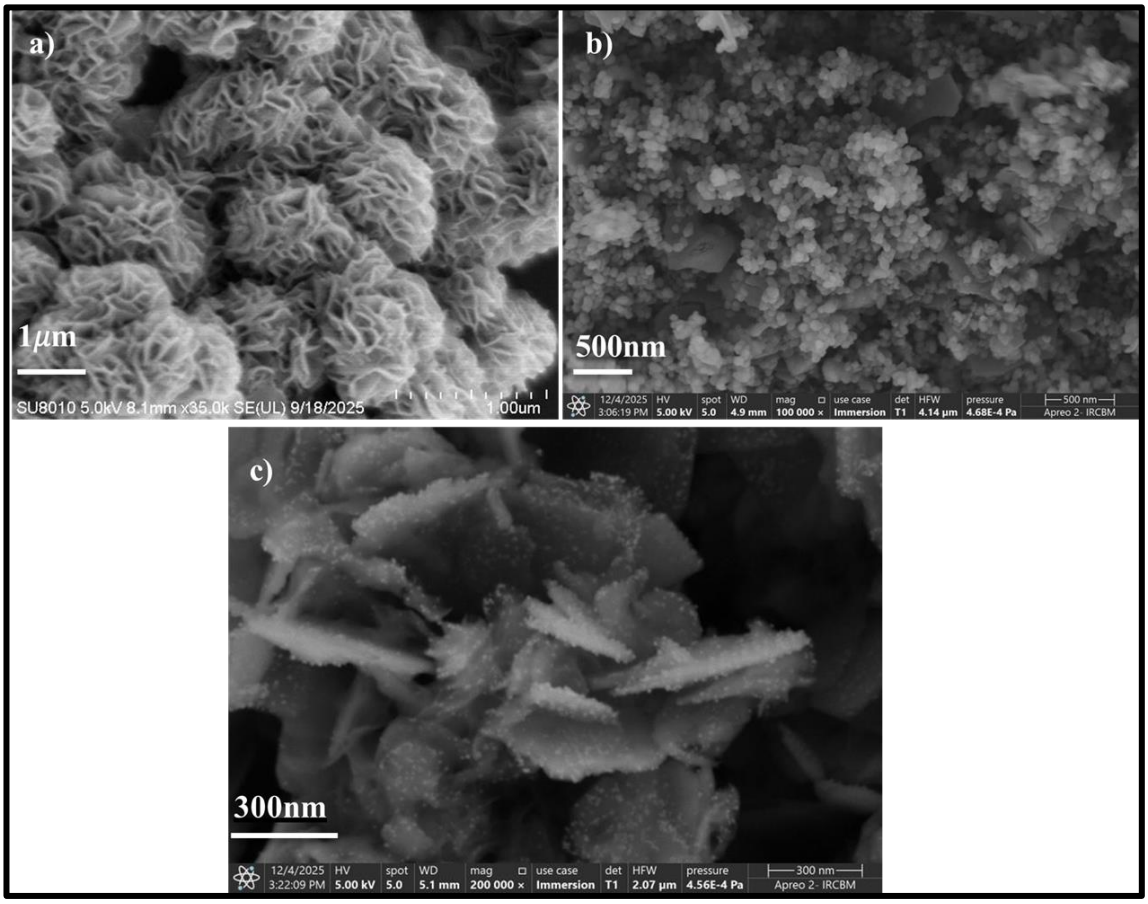

Figure 4.1: FE-SEM of MoS_2 (**a**), Yb-MOF (**b**), MoS2@Yb-MOF composite (**c**)

FE-SEM was used to study the surface morphology and structural features of the MoS_2. The SEM image Figure 4.1(a) clearly reveals a 3D-flower-like structure, comprised of densely packed, petal-shaped nanosheets radiating outward from a central core. This hierarchical morphology is a characteristic feature of MoS_2 synthesized via hydrothermal routes and has been widely reported in literature [166]. The magnified images show that individual flower-like structures are made up of ultrathin, curved structures that entwine to form a porous structure. This implies that MoS_2 starts

growing along the basal planes before self-assembling into flower-like structures as a means of minimizing surface energy during synthesis. Similar layered, petal-like assemblies have also been observed for hydrothermally prepared MoS_2, where the nanosheets grow outward to form flower-like or hierarchical microsphere structures [167]. At higher magnification, MoS_2 nanoflowers consist of thin, wrinkled, and curved nanosheets that overlap and interconnect, forming a porous network with loosely stacked petals. This morphology arises from anisotropic growth along the basal planes followed by radial assembly, where nanosheets nucleate and aggregate to minimize surface energy. The high density of exposed edges and inter-petal voids increases the accessible surface area and active sites [168].

The Figure 4.1(b) shows FE-SEM of Yb-MOF have clustered nanostructured morphology composed of numerous quasi-spherical nanoparticles loosely aggregated into larger assemblies. At high magnification (100 000×, 500 nm scale), these primary particles exhibit a uniform nanoscale size distribution and rough surface texture, which is characteristic of nanoparticulate metal-organic frameworks formed under solvothermal or wet chemical conditions. Such dense aggregation of nanoparticles is often observed in MOF materials when rapid nucleation and growth lead to numerous small crystallites that coalesce into larger clusters, contributing to a high external surface area and potential interparticle porosity. This morphology occurs due to anisotropic growth on the basal planes. This is followed by radial assembly, where the nucleation and accumulation of the nanosheets occur. Such morphological properties correlate well with other MOF materials that had been documented to improve through nanoparticle assembly, which increases surface access and diffusion channels in adsorption applications and catalysis [169].

Figure 4.1(c) of the FE-SEM image of the MoS_2@Yb-MOF composite reveals distorted and nonuniform flower-like structures of the reduced symmetry of MoS_2 in comparison to the pristine samples of MoS_2. The petal-shaped structures of MoS_2 are seen to be destroyed and disproportionately partially and this is a clear indication that there were strong interactions between MoS_2 and the MOF material during the preparation of the composites. The petals of the MoS_2 are not as homogenous as pure MoS_2, which is a sign of morphological change due to the formation of the composite. The fact that the sheet surfaces possess small granular features which enable the incorporation of Yb- MOF components to be successful also supports it. The loosely stacked and wrinkled sheets form a porous network, which may enhance surface area and provide additional active sites for electrochemical applications. Overall, the morphological changes indicate a strong

interaction between MoS_2 and Yb-MOF, leading to a composite structure that combines the advantages of both components [156, 170, 171].

4.2. Fourier Transform Infrared Spectroscopy (FTIR)

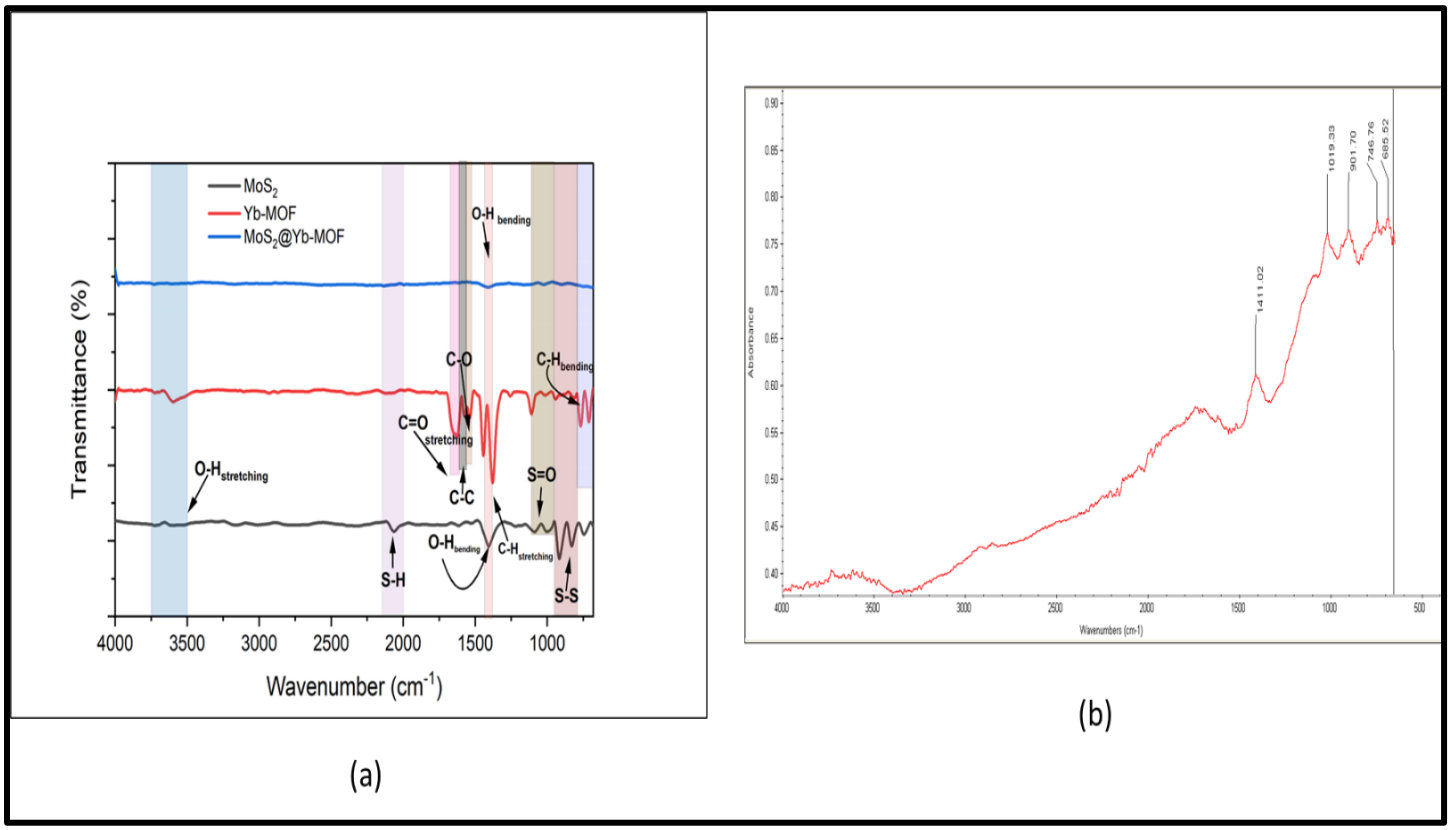

Figure 4.2: FTIR of (a) MoS_2, Yb-MOF, MoS_2@Yb-MOF (b) MoS_2@Yb-MOF

The FTIR spectroscopy of the synthesized Yb-MOF and MoS_2@Yb-MOF composite was used to determine the chemical bonding and functional moieties of the compound as illustrated in Figure 4.2. The FTIR spectrum of synthesized Yb-MOF exhibited the O-H stretching vibration at 3396cm^{-1} because of the presence of coordinated water molecules and HO bonds [172]. This intense band at 1625 cm^{-1} was assigned to the vibration of the C=O bond of the carboxylate groups in the BTC ligand. Asymmetric and symmetric vibration of the deprotonated COO^- groups was found to appear at 1423 cm^{-1} and 1382 cm^{-1}, respectively. These characteristic bands proved the coordination of the BTC units to the Yb^{3+}ions. The absence of absorption bands at 2650cm^{-1} for

O-COOH and 1690 cm^{-1} for C-COOH suggested the complete deprotonation of the carboxylic acid functional groups after the synthesis of the MOF. Out-of-plane-out bending vibration for aromatic C-H was assigned to the absorption bands at 759 cm^{-1} and 713 cm^{-1}. However, the absorption band at 620 cm^{-1} was assigned to the Yb-O vibration to confirm the interaction between the ytterbium ion and the carboxylate group [147, 173] .

The FTIR spectra of the resulting MoS_2@Yb-MOF also showed that the characteristic vibrational bands of Yb-MOF were not affected, which means that no damage occurred to the Yb-MOF during the synthesis of the composite material. Moreover, a new peak at 625 cm^{-1}, ascribed to Mo-S lattice vibration, which can be seen as a characteristic peak of MoS_2, further supported the presence of MoS_2 in the composite material. The peaks related to S-H stretch (2550-2600 cm^{-1}) and S-S vibrations (900-800 cm^{-1}) also supported that MoS_2 material was indeed produced [174].

The slight shifts of the peaks and the intensity in the composite spectrum compared to the pristine Yb-MOF and MoS_2 suggested successful interfacial interactions.

4.4. Cyclic Voltammetry

The electrochemical characteristics of the manufactured sensors are evaluated using cyclic voltammetry on both bare and modified electrodes. CV is applied to investigate electrochemical activity (redox reaction, active surface area, peak position, reversibility stability, etc.) of fabricated sensors. Through comparing different modified electrode, we come to know about which type of modified electrode material exhibits better redox activity and performance during reaction. Using reference electrode (Ag/AgCl), CV performed to determine electrochemical activity of MoS_2, Yb-MOF, and MoS_2@Yb-MOF in 1.0 mM potassium ferricyanide with 0.1M potassium chloride as supporting electrolyte. Figure 4.3. elaborated that potential was scanned from -0.2V to 0.6V at scan rate of 100mVs^{-1}.

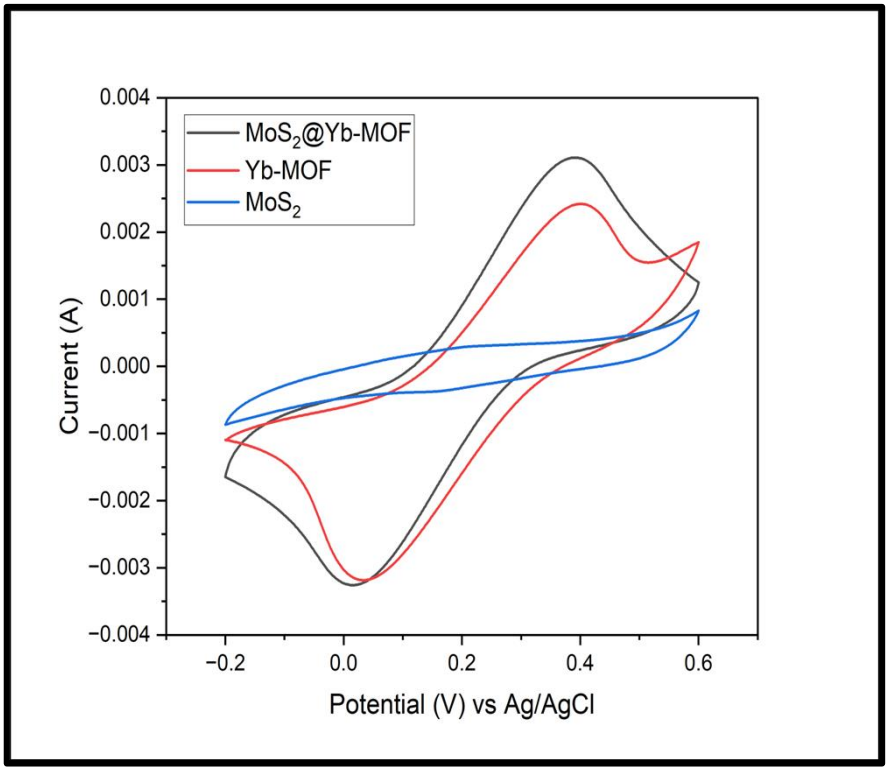

Figure 4.3: CV comparison of MoS_2, Yb-MOF and MoS_2@Yb-MOF

The MoS_2 electrode displayed the lowest anodic and cathodic peak currents, indicating limited electron-transfer capability and fewer electroactive sites much higher redox activity sites [175]. The CV curve of pristine MoS_2 exhibits a relatively low enclosed area with a quasi-rectangular shape accompanied by weak redox features. This is typical of layered MoS_2, in which charge storage is due to a combination of both electric double-layer capacitance (EDLC) and low faradaic reactions related to reversible ion intercalation between MoS_2 layers. The low current response can be attributed to restacking of nanosheets and moderate intrinsic electrical conductivity. The Yb-MOF-modified electrode showed higher peak current responses compared to MoS_2, there were redox peaks which indicating that they have capability to undergo oxidation and reduction processes which can be attributed to its porous structure that facilitates redox species diffusion and provides additional active centers. Redox peaks generally show the movement of electrons within a working electrode between its various oxidation states [147]. These peaks arise from reversible redox transitions of Yb metal centers coordinated within the MOF framework. However, despite the presence of redox activity, the overall current density is limited due to the poor electrical conductivity typically associated with MOFs. The MoS_2@Yb-MOF composite electrode showed

the largest current response among all electrodes tested, depicting a synergistic effect between Yb-MOF and MoS_2. The redox peaks in the CV curve of the composite were sharper than those of the individual components, indicating better charge transfer kinetics. However, MoS_2@Yb-MOF signified that the introduction of Yb-MOF into the MoS_2 structure even improved the conductivity and stability for redox reaction of final composited electrode many times. Thus, final MoS_2@Yb-MOF exhibited best and desired electrochemical response.

4.5. CV at Different Scan Rate

As depicted in Figure 4.4. the cyclic voltammograms of modified electrode were recorded over scan rates from $10mVs^{-1}$ to $100mVs^{-1}$. A rapid electron transfer and surface diffusion-controlled reaction, in which more species undergo oxidation and reduction at the same time, is indicated by the linear increase in redox peak currents with scan rate.

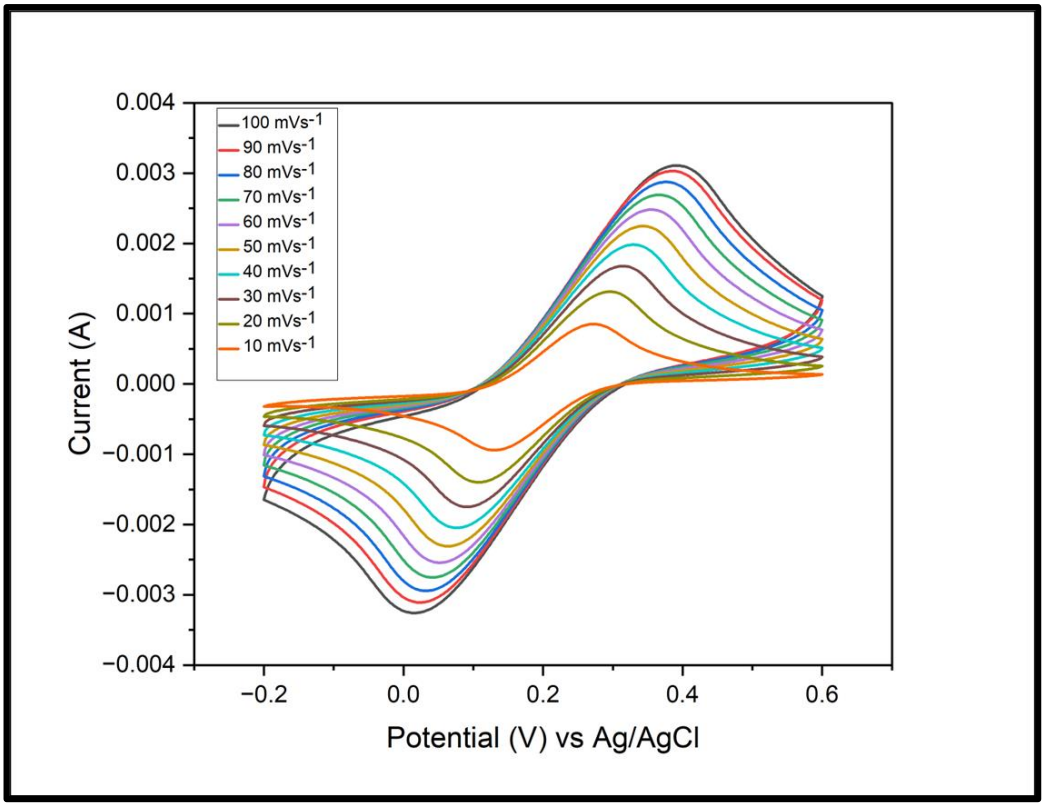

Figure 4.4: CVs of MoS_2@Yb-MOF at different scan rate

Overall outcome of CV at various scan rates shows optimum electrochemical behavior. As the current increases linearly and enhances redox activity of modified electrode without even blocking the surface.

4.6. Electrochemical Impedance Spectroscopy

EIS was used to determine the interfacial charge transport behavior, ion diffusion characteristics, and double-layer capacitance of modified carbon cloth electrodes. The measurements were conducted in an aqueous electrolyte containing 1.0 mM potassium ferricyanide and 0.1 M potassium chloride, over a wide frequency range from 0.01Ω to 80kΩ.

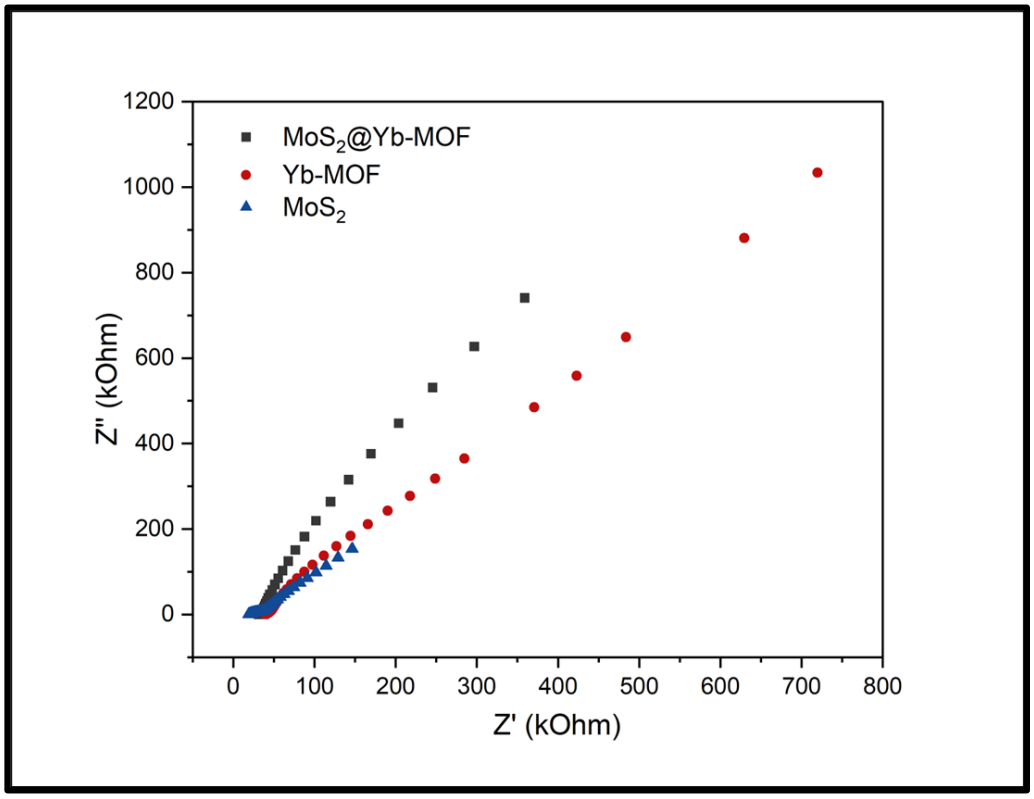

Figure 4.5: EIS comparison of MoS_2, Yb-MOF and MoS_2@Yb-MOF

From Fig.4.5, Nyquist plots of all the electrodes are linear in the lower frequency regions, indicating diffusion-control phenomena in the Warburg impedance region, and this means that the transportation of ferricyanide ion to the electrode surface is dominant in the electrochemical kinetics.

Among the studied electrodes, MoS_2 exhibited a more extended and less steep linear region in the low-frequency domain, indicating faster and more controlled Warburg diffusion of electroactive species at the electrode–electrolyte interface. This is in conformity with the layered character of MoS2 that facilitates easy accessibility of ions and facilitates rapid movement of electrons along the basal planes therefore permitting electrochemical kinetics that are dominated by diffusion.

On the other hand, the diffusion line of the Yb-MOF electrode was relatively steeper, which means that the diffusion resistance was higher and the ion transport was slower. Although porous structure of Yb-MOF has a high number of channels through which electrolytes can pass through the structure, its low intrinsic conductivity restricts continuous charge flow, which results in less desirable diffusion processes. The restriction of the ferricyanide ions mobility in the MOF structure is reflected in the diffusion-controlled impedance response at lower frequencies.

On the other hand, the MoS_2 Yb-MOF composite is a successful integration of the porous structure of Yb-MOF and the layered conductive structure of MoS_2, resulting in regulated Warburg diffusion and enhanced ion mobility at the electrode electrolyte interface. The high interfacial contact between the nanosheets of MoS_2 and the MOF structure provides continuous diffusion channels, providing ferricyanide ions to diffuse more efficiently through the composite structure.

Overall, the EIS results demonstrate that the electrochemical properties of the MoS_2 electrode at Yb-MOF are more diffusion-controlled than those of MoS_2 and Yb-MOF. The increased diffusion response of the Warburg diffusion is an indication of increased rate and stability of ion transport in the composite electrode, which is particularly useful in electrochemical sensing instruments that require effective diffusion of analytes to accessible active sites.

4.7. Differential Pulse Voltammetry

It was used for detection of Cd^{2+} separately and in combination in 0.1 M sodium acetate with pH 5.0 over a potential range of -1.7V to – 0.4V. Carbon cloth used as the working electrode, Pt wire as the counter, and Ag/AgCl as the reference in the three-electrode setup. At their respective potentials, peaks emerged.

4.7.1. Detection of Cadmium Cd^{2+}

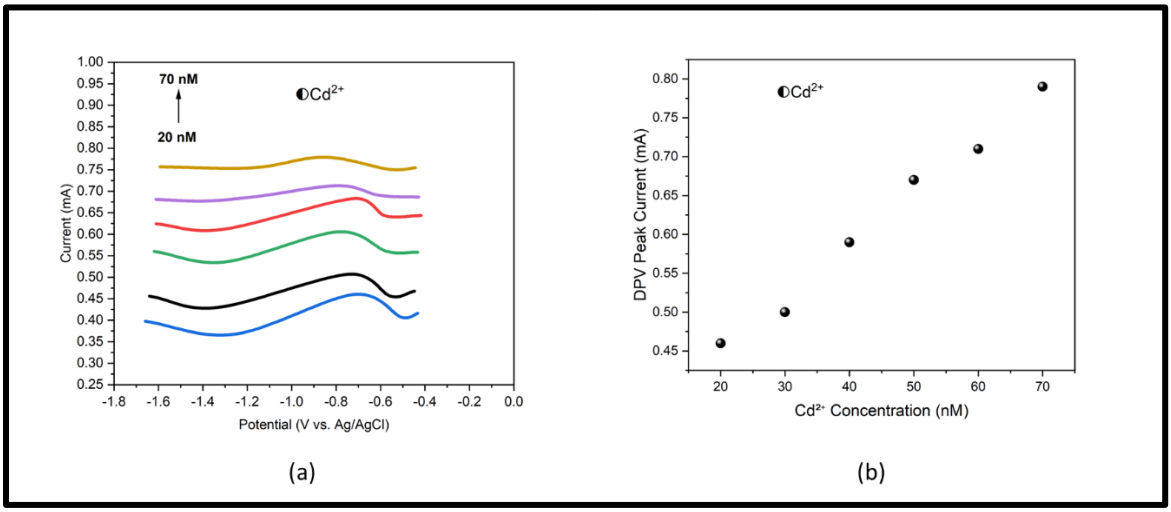

Figure 4.6 (a) DPV detection signals of a Cd (II) ions by MoS2@Yb-MOF on carbon cloth at different nM concentrations. (b) Linear regression graph of Cd (II)ions detection

Firstly, the MoS_2@Yb-MOF composite was deposited on the carbon cloth surface for the fabrication of a sensing platform. A three-electrode apparatus was immersed in buffer solution, containing cadmium ions in concentration range from 20 nM-70 nM. The potential window at which measurements were taken ranged from -1.7 V to 0.4 V. With the increase in the concentration of Cd^{2+}, the detection peak at -0.77 V increased linearly. The results showed the sensor has given its linearity in the range from 20 nM-70 nM with the detection of Cd^{2+}.

The calibration equation was I (mA) = 0.00674C (nM) + 0.3166 with a correlation coefficient (R^2) of 0.9896, suggesting high linearity. The sensitivity was 6.74 μA·nM-1, which indicated the efficient electron transfer on carbon cloth, strong Cd^{2+} adsorption by MoS2, and additional active sites from Yb-MOF. The **LOD** was estimated to be **0.89 nM** (S/N = 3) using "LOD"=3σ/m, where: σ = standard deviation of blank signal (DPV without Cd^{2+}) and m = slope of calibration curve.

Chapter 5
Conclusion

A MoS_2@Yb-MOF composite was synthesized and characterized using techniques FTIR, XRD, and SEM, confirming the formation and structural integrity of the hybrid material. Cyclic voltammetry and electrochemical impedance spectroscopy were performed to study electrochemical studies i.e. charge transfer characteristics and electrochemical stability.

The synergistic interaction between MoS_2 and Yb-MOF provides enhanced surface properties and improved electrochemical behavior, highlighting the potential of the composite for environmental and electrochemical applications.

Chapter 6
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