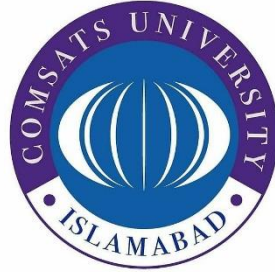# Synthesis of Novel Nanocomposite Based Electrochemical Sensing Platform for Water Remediation

MS Thesis

By

Samreen Riaz

CIIT/FA22-R06-005/LHR

COMSATS University Islamabad

Lahore – Pakistan

Fall 2022 - Spring 2024

Synthesis of Novel Nanocomposite Based Electrochemical Sensing Platform for Water Remediation

A thesis submitted
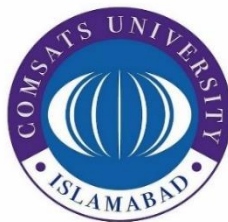
To

COMSATS University Islamabad

In partial fulfillment of the requirements for the degree of
Mater of Science
in
Chemistry

By

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Fall 2022 - Spring 2024

Synthesis of Novel Nanocomposite Based Electrochemical Sensing Platform for Water Remediation

This thesis is submitted to the Department of Chemistry in partialfulfillment of the requirements for the award of the degree of Master of Science in Chemistry.

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Dedication

To My Beloved Parents and Siblings

This thesis is dedicated to my parents and siblings, whose unwavering support and encouragement have been instrumental in my academic journey. My parents' endless sacrifices and steadfast belief in my potential have provided me with the strength and determination to overcome every obstacle. To my siblings, thank you for your constant encouragement, understanding, and for always being there to cheer me on. Your companionship and support have been a source of immense motivation and joy. If a violation of HEC rules on research has occurred in this thesis, I shall be liable to punishable action under the plagiarism rules of HEC.

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In the name of *Allah,* the Most Compassionate, the Most Merciful, I begin by expressing my deepest gratitude to *Allah,* the source of all wisdom and strength, for guiding and sustaining me throughout the arduous yet rewarding journey of my research work. His blessings have been my constant inspiration and foundation.

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Abstract

Synthesis of Novel Nanocomposite Based Electrochemical Sensing Platform for Water Remediation

By

Samreen Riaz

One resilient element that is frequently utilized in many manufacturing operations is lead. Because of its enduring nature, it can linger in the atmosphere for quite a while and is harmful to the functioning of biological systems. Mining operations, along with incineration, are the main sources of copper release. As your liver is the first organ to access copper accumulation when it enters the bloodstream, chronic copper poisoning primarily affects it. The supposed advantages of electrochemical sensing are the simplicity of the apparatus, the extreme sensitivity and robust specificity of the test, mobility, and the ability to analyze the target analyte on-site. A nanocomposite of UiO-66-NH$_2$@Ppy-NWs@CoFe$_2$O$_4$ was prepared to determine trace amounts of copper and lead ions in water. The atomic structure and physicochemical properties of the prepared material were examined using XRD. The electrochemical behavior of the GCE modified with UiO-66-NH$_2$@Ppy-NWs@CoFe$_2$O$_4$ was studied by means of cyclic voltammetry (CV). It was demonstrated that, with the UiO-66-NH$_2$@Ppy-NWs@CoFe$_2$O$_4$, Pb^{2+} and Cu^{2+} could be sensed via differential pulse voltammetry (DPV). As the concentration increased from 10 to 100 nM, a substantial linear response was achieved, with a lower limit of detection. The high sensitivity of the UiO-66-NH$_2$@Ppy-NWs@CoFe$_2$O$_4$/GCE towards the electroanalytical applications marked its use for real-world applications in its as-prepared state.

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List of Abbreviations

AAS	Atomic Absorption Spectroscopy
XRF	X-ray Fluorescence Spectrometry
ICP-AES	Inductively Coupled Plasma-Atomic Emisssion Spectrometry
HMIs	Heavy Metal Ions
1D	One Dimensional
2D	Two Dimensional
3D	Three Dimensional
CNTs	Carbon Nanotubes
GO	Graphene Oxide
NC	Nanocomposite
NP	Nanoparticles
PANI	Polyaniline
MOF	Metal Organic Framework
MIL	Material of Institute Laviser
FTIR	Fourier Transform Infrared
XRD	X-ray Diffraction
ABS	Acetate Buffer Solution
MWCNTs	Multi -walled Carbon Nanotubes
Ppy-NWs	Polypyrrole Nanowires
GCE	Glassy carbon electrode
RE	Reference Electrode
WE	Working Electrode
CV	Cyclic Voltametry
DPV	Differential Pulse Voltametry

Chapter 1

Introduction

1.1 HMIs Contamination

The environment is an area that is populated or used by humans, microbes, plants, and animals. It is composed of water, air, and land. The lithosphere (land), biosphere (living things), hydrosphere (water), and atmosphere (air) are the four spheres that comprise the Earth's system. Environmental contaminants or pollutants are substances that are found in some parts of the environment at higher or more abundant levels than others [1].The last century's rapid industrialization, skyrocketing utilization of energy, and careless resource exploitation are the main causes of the environmental pollution crisis, which is at present expected to seriously threaten biodiversity and ecological mechanisms. The discharge of various harmful pollutants, both organic and inorganic, into water bodies triggers subsequent pollution of the soil and sediments.

Heavy metals are among the most potentially damaging to the environment [2]. A pollutant is any material present in the surrounding that has detrimental effects, impacting the health of the ecosystem, diminishing the quality of life, and potentially leading to fatalities. This substance must exceed a specified limit or threshold in the environment that is potentially seen as palatable and tolerable. Consequently, Pollution of the environment occurs when a pollutant is present in the surroundings, specifically in the air, water, or soil. These Pollutants can be harmful and hazardous and pose a threat to Biota within the spoiled ecosystem[3]. Water, often perceived as commonplace, is an incredibly remarkable substance. It serves a multitude of purposes in our daily lives, including cooking, drinking, washing, swimming, and fishing. As human beings are composed of roughly 2/3 of water, its vital role in our survival cannot be overstated. Water is indispensable for the existence and evolution of life as we understand it. Droughts led to hunger crises, while floods result in illness and fatalities. Its significance is evident from the extensive research it garners, making it the most extensively studied material on our planet. As the primary component of all living things, liquid water has many uses and is never just a passive solvent [4].

Although there is a substantial the Earth contains an estimated volume of approximately 1.4 billion cubic kilometers of water, the majority, over 97%, is located within the Earth's oceans, while the

unconsumed portion exists in polar icecaps and glaciers. Consequently, less than 1% of the world's water is continental freshwater available for our use. The astronomical rise in the global population has led to an increasing requirement for fresh water in our daily lives, resulting in severe global water scarcity [5]. There is a global challenge in water resource management because of the growing demand for freshwater bodies of water for daily needs brought on by Earth's population growth. Water dearth and declining water quality can have a significant impact on agricultural production, the economy, and the ability to provide thousands of people in emerging nations with basic health and hygiene aid if current pollution trends continue. Due to outdated wastewater treatment systems and rising waste from cities and factories, the freshwater supply in emerging nations is constantly in danger of pollution [6] . Deadly effluent has been released into the environment without restriction, resulting in extensive pollution.

A variety of contaminants, including metallic ions, household cleaners, medications, pesticides, colorants, leaking oil, and aromatic/organic substances, have been shown to be present in the water recently [7]. HMIs are among the most perilous of these contaminants because of their high toxicity, difficulty to decompose naturally, and propensity to build up and intensify through the food chain [8]. The Presence of HMIs in aquatic ecosystems has negative impact on living organisms in one way or another. Furthermore, although in the ground, metallic ions pose a significant danger to both plants as well as animals, as these are taken up by plants and eventually make their way into the bodies of living organisms. As a result, the effects of water pollution have driven researchers to devise appropriate methods for identifying and quantifying the concentrations of heavy metal pollutants [9].

Metals aren't utilized. As opposed to specific natural insect poisons, metals can't be rotted into less harmful structures [10]. Lead and cadmium have a variety of applications; for examples, lead is used in coatings, fuel, insecticides, electricity, and water pipes, while cadmium is used in the production of TV panels, portray pigments, steel zinc plating, optical fibers, and aircraft parts. Anemia, neurological conditions, renal and hepatic damage, hearing dysfunction, digestion-related harm, lower intelligence scores, emotional and intellectual issues in youngsters, memory loss, tumors, and the development of illnesses like tumors in breasts are among the detrimental impacts of lead build-up in various organs. In the exact same way, cadmium may harm the renal system, the hepatocytes, mammary glands, reproductive system, pulmonary system, epidermis, and pancreas, in addition to causing harm to these organs [11].

1.2 Sources of Heavy Metal Ions

Normally accessible substances with enormous sub-atomic masses and thicknesses, essentially an element of five greater than water's, are known as heavy metal ions. Their widespread dispersion in the environment as a result of their numerous manufacturing, home, farming-based, therapeutic, and technology-related uses has ignited stresses over their potential outcomes on environmental factors and general wellbeing. Their poisonousness depends on various factors, including the synthetic substance species, dosage, and method of contact, in addition to the physical condition, genes, and nutrition state of those who are exposed. Arsenic, cadmium, chromium, lead, and mercury are viewed as critical to human wellbeing because of their serious level of poisonousness. Indeed, even at lower fixations, these metal-based substances have been accounted for to cause various unfriendly consequences for organs and are delegated foundational poisons [12]. Bug anti-agents, synthetic composts, and related synthetic compounds for cultivating still contribute very little to ecological harm with regards to heavy metal ions. Besides, heavy metal contamination can likewise result from normally occurring occasions like soil disintegration, regular rot, rusting of metals, metallic material escape from water and the ground, and molecule recuperation[13-16].
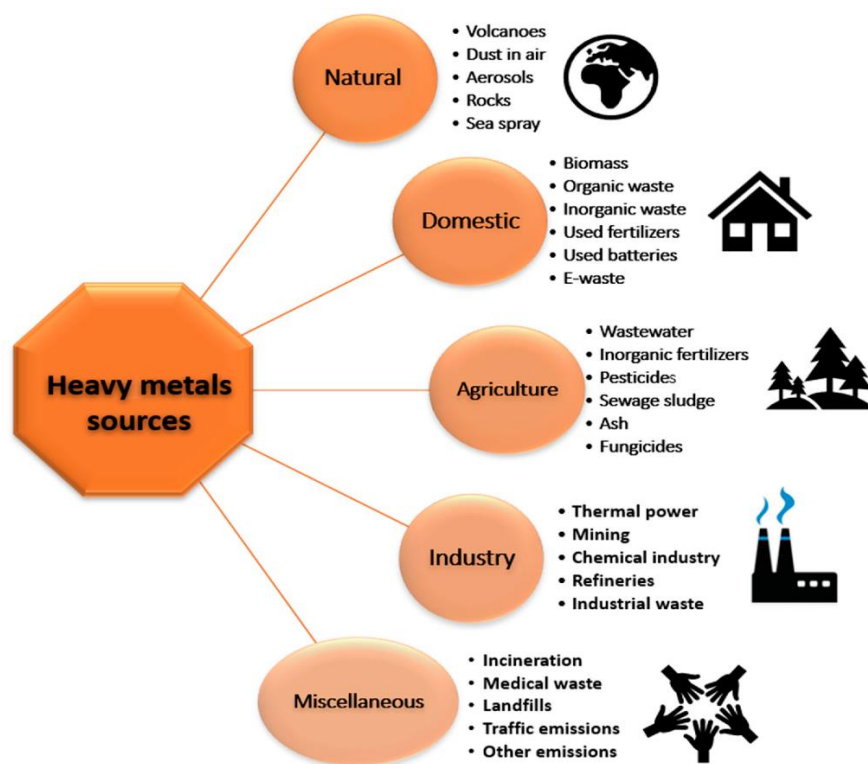
Figure 1 : Showing sources of HMIs [17]

1.3 Impact of HMIs on environment

Polluting substances may reach the environment in a variety of ways besides the hydrosphere, lithosphere, and air. Polluting substances penetrate the atmosphere gradually through a variety of means, including aging rocks and lava flows, but the actions of humans also play a significant role. Accidental discharges can happen because of mining-related activities, explosions, wreckage, and leaking oil. Moreover, there may be deliberate uses, such as those generated when biological agents are employed to manage pathogens. The pace at which metallic substances or other pollutants of any kind move is influenced by humidity, water's surface flow and course, the mass of air distribution, the velocity of wind, and a variety of other factors. Apart from these, other factors that influence the dispersion and movement of the pollutants are the split coefficient, the orientation, pressure of the vapors, and molecule permanence [18].

1.3.1 Air Pollution of HMIs

The unseen ecological HMIs in the exterior atmosphere pose a major hazard to the lives of creatures of all kinds. Foliage transfer is the process by which HMs in the surrounding air gather in the cells of plants after being settled on the leaves by aerosols. HMIs from the polluted air moved into agricultural webs due to elevated HMI levels in flora near melting plants, suggesting that foodstuffs in the area may be easily accessible to humans and pose a health risk[1, 19]. Furthermore, HMs in the atmosphere have the ability to enter the bodies of individuals through the layers of skin, mouth, and nose[20, 21]. According to Clarkson and Mago's [22] Mercury (0) enters a person's body through the airways, where it accumulates and seriously damages organs, including the liver, kidneys, and brain. Indoor dust is a major source of danger to individuals, especially children, as it is a carrier of both organic and inorganic pollutants, including HMIs. Some researchers claim that the amount of lead, nickel, cadmium, cobalt, copper, and chromium in the air increases as the size of sand particles reduces [23]. Some researchers claim that the amount of lead, nickel, cadmium, cobalt, copper, and chromium in the air increases as the size of sand particles reduces [24].

1.3.2 Soil Pollution of HMIs, Its sources and effects

The area where humans reside and engage in agriculture is not devoid of metals; heavy metals from raw materials and many human-related activities seep into the soil. Soil is an essential part of the

ecosystem. Because of its absorbing and releasing characteristics, soil is susceptible to contamination from a wide range of sources.

Contamination of soil can occur accidentally or on purpose. Intentional pollution includes things like leaded color, chemical fertilizers, insecticides, biological waste, hydrocarbon distillate leaks, byproducts of coal-fired power plants, rubbish disposal, sewage irrigation, and mining tailing. The prevalence of heavy metals in our countryside has grown due to unchecked wastewater and sewage consumption. These metals are subsequently absorbed by vegetables that are often eaten by humans. Non-intentional pollution can arise from both automobile accidents involving the transportation of dangerous chemicals and river and ocean flooding, which disperses sewage and contaminated water onto land [25-30].

Because heavy metals cannot be degraded by chemical compounds or bacteria, they remain in the earth for a very long time. Heavy metals are destroying the biosphere by making their way up the food chain. Heavy metals also affect the rate of decomposition of organic pollutants, which reduces their ability to decay and has a double-negative effect on the ecosystem. The whole biosphere is at risk from these metals, which are found in the soil. They alter the pH, color, porosity, and natural chemistry of the soil, which reduces the quality of the soil and contaminates water. They are also directly consumed by creatures and absorbed by plants, which can be hazardous to the species and the entire food web that consumes them [9, 31-33].

1.3.3 Water pollution of HMIs, Its sources and effects

Water pollution is a result of both ocean and freshwater contaminants. Eventually, manufacturing, the buyer, and industrial waste, chemical fertilizers and insecticides, and acidic precipitation that falls on the land all leach heavy metals into freshwater and soil water[34]. Metal contaminants in lakes and streams can linger as droplets or as persistent particulates. Aquatic animals transmit these poisons into their sinks [35]. A serious environmental issue that has an immediate impact on all living things is water contamination. A couple of the several factors that determine how hazardous HMIs are include their availability, kind, functionality in the organism exposed, and the duration of the cell's life at the moment of exposure [36]. If one of the creatures in the food network is affected, then all of them will be. Since humans are frequently at the base of the food web, this might have a bigger effect on us since we were going to absorb more metal as the amount increased up the food chain [37, 38]. Water pollution of HMIs is our main area of interest and explained in detail in upcoming paragraphs.

1.3.3.1 Volcanic eruptions

Volcanic ash-like material, which may fall many kilometers from an erupting volcano, is the most widely spread result of explosive volcanic eruptions. Ash, even in small concentrations, can interfere with the water supply system [39]. When volcanic ash gets into drinking water, it harms the water by acidifying it, increasing its pH, and creating turbidity. Freshly generated volcanic ash has extremely acidic layers on its surface because of the presence of droplets in the plume that are composed of the strong acidifying minerals H_2SO_4, HCl, and HF. Because of this, water that has recently seen an eruption may experience a pH decrease that is harmful to aquatic life [40]. Increasing population and industrialization throughout the world have led to a rise in the quantity of HMIs in the earth's air that are caused by human activities [41].

1.3.3.2 Agriculture activities

Agricultural systems have expanded and developed to accommodate the rising demand for food. Abuse and overuse of farming-related herbicides, water, animal feed, and production-enhancing pharmaceuticals have resulted in elevated concentrations of contamination in ecosystems, such as streams, freshwater, dams, and shoreline waterways. Aquatic ecosystems are also impacted by agricultural pollution; for example, fisheries and biodiversity are negatively impacted by eutrophication, which is caused by an accumulation of organic matter in lakes and coastal rivers [42]. Farms discharge a lot of chemical pesticides, organic waste, leftover medications, rocks, and salinized effluent into rivers and lakes. As a result, water pollution endangers aquatic environments, the well-being of humans, and business activity [43]. Fish have suffered from a variety of harmful effects because of agricultural waste being deposited in aquatic environments. It steadily raises pollutants in the food cycle by concentrating those that are already in the water. Chemicals used in agriculture—herbicides and fungicides—are widely used in agriculture in many countries. When picked and handled irresponsibly, they can pollute waterways with cancer-causing substances and other harmful substances that can damage humans [44].

1.3.3.3 Industrial effluents

The immediate discharge of household waste, business garbage, and municipal rubbish into the bodies of the aquatic system is one of the primary sources of pollution. The discharge of leftover garbage leads to water contamination. The untreated disposal of industrial emissions into water bodies is the main source of pollution, both on the surface and in groundwater [45]. Water pollution is brought on

by contaminants such as acid, hazardous metals, agricultural pesticides, coloring agents, and other forms of untreated waste released from businesses. Discharged materials, which frequently lead to pollution, can cause a decline of species in the marine environment and may put individuals at risk for cholera, diarrhea, etc.

1.3.3.4 Mining

The process of extracting rock, minerals, and other geographical elements from earth layers is known as mining. The mining sector works to extract the metallic substances and minerals that our society needs for building, sound, phone companies, food production, housing, and medical purposes, as well as for space exploration. Water pollution is a major problem raised by mining activity [46]. When you have a plenty of water created during mining activities, including the extraction procedure, mine cooling down, mine drainage, and other extraction procedures, these substances are subjected to pollute ground and surface water. Degradation of surface water is mostly caused by mining water discharge, waste material erosion, and unintentional discharges of hazardous chemicals [47].
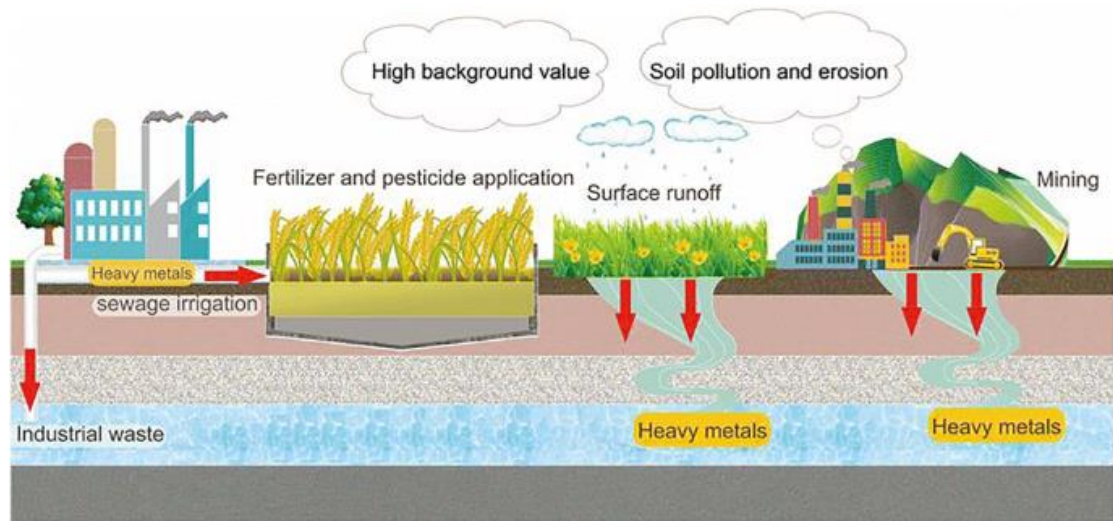
Figure 2 : Showing Discharge of heavy metal ions from various sources[48]

1.4 Effect of HMIs water pollution on aquatic environment & aquatic health

One characteristic of metals is that they are not biodegradable, meaning that, unlike organic materials, most of them cannot be converted into less dangerous compounds through metabolism. After being added to an aquatic environment, metals are either used by aggregation or distributed throughout the water column [49]. The mineral deposits provide a semi-persistent invitation for natural phenomena to become polluted by metals through mechanisms of response and retention. Metallic wastes can be

bioaccumulated by aquatic organisms [50]. The mineral deposits provide a semi-persistent invitation for natural phenomena to become polluted by metals through mechanisms of response and retention. Metallic wastes can be bioaccumulated by aquatic organisms [51, 52]. Metal bioavailability is the term used to describe the part of the total amount of a metal that has the potential to gather over time in the body. The body's ability to soak up metals depends on the following factors: Physical and chemical parameters include things like saltwater, humidity, pH ranges, osmotic ability, the amount of biological carbon in water-based solutions, total particles floating, and the organism's condition [53, 54]. When it comes to dissolved metals, intake happens through the receptive stratum; for suspended metals, intake happens through food. Metal-related biological processes, the presence of inorganic or organic substances, saltiness, temperature, pH, and reaction variables are the primary factors that affect the toxicology of metals. Similar factors that impact intake uptake include feeding pace, enteral transit time, and digesting efficacy [55]. Numerous studies have demonstrated that the most readily accessible form of HMIs like cadmium, zinc, and other elements is the free, hydrated metallic particle, although some deviations have been noted [56]. When it comes to dissolved metals, intake happens through the receptive stratum; for suspended metals, intake happens through food. Metal-related biological processes, the presence of inorganic or organic substances, saltiness, temperature, pH, and reaction variables are the primary factors that affect the toxicology of metals. Similar factors that impact intake uptake include feeding pace, enteral transit time, and digesting efficacy [57]. In comparison to toxic sublimate, which is not soluble in lipids, the mercurial organic substances are macromolecules-soluble and quickly penetrate the lipid membranes, increasing the toxicity [58]. The level of metals in water generally is influenced by the impact on suspended particles.

The relationship between solid substances and metals is crucial for the absorption of metals into living things through consumption of food [59]. Although ineffective metal complexes pile up in the floating particles, the metal dissipates in the gap water in the presence of appropriate conditions. Because they are abundant in the water, a relatively small percentage of these notable concentrations of metal from suspended debris is also a highly important supply for the absorption of metal in animals and benthic species [60]. Due the dynamics of different types of metals at different periods throughout water context are not fully understood, further research is required to examine the many cumulation and bioaccumulation supply facilitated by floating or submerged M^+ forms. Many studies have demonstrated that the availability of M^+ in bivalve mollusks is controlled by the sedimentary size of particles, which is explained by the animals' filter-feeding activity.

If organisms that exist, polymers, or fulvic acids were added to the particles, the absorbed capacity of Cd, Zn, and Ag would be significantly enhanced. Metal binding frequently reduces the bioavailability of metals in the sediment. Both underground and marine habitats are threatened by pollution [61]. Because the dynamics of different types of metals at different periods throughout an aquatic context are not fully understood, further research is required to examine the many accumulation and bioaccumulation routes supported by floating or submerged metal forms. Variou studies have explained that the availability of metals in bivalve mollusks is controlled by the sedimentary size of particles, which is explained by the animals' filter-feeding activity. If organisms that exist, polymers, or fulvic acids were added to the particles, the absorbed capacity of Cd, Zn, and Ag would be significantly enhanced. Metal binding frequently reduces the bioavailability of metals in the sediment. Both underground and marine habitats are threatened by pollution [62].
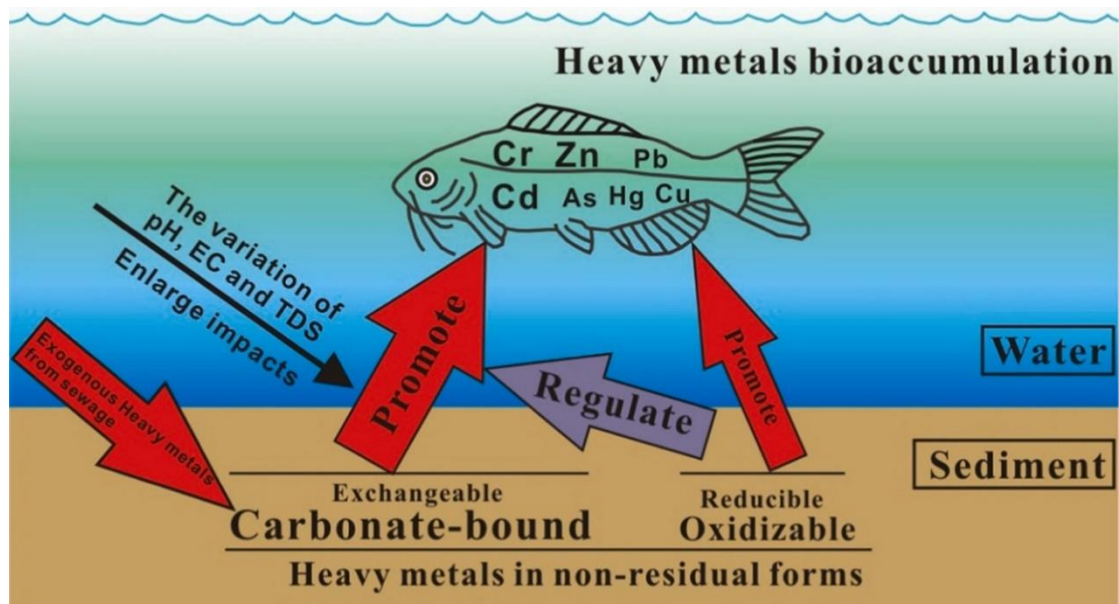
Figure 3: Showing toxicity of HMIs on aquatic ecosystem [63]

1.5 Different HMIs and their contamination

1.5.1 Effect of Lead (Pb) contamination

One resilient element that is frequently utilized in many manufacturing operations is lead. Because of its enduring nature, it can linger in the atmosphere for quite a while and is harmful to the functioning of biological systems. Numerous investigations have connected higher illness prevalence in a variety of species to chemical lead-based chemicals. There is a connection between lead poisoning and the prevalence of brain diseases such as high blood pressure, Alzheimer's disease, etc. By attaching to

amino acid proteins, lead obstructs the formation of skeletal amino acids, hinders the uptake of minor minerals, and blocks the reactions of enzymes.

1.5.2 Effect of Cadmium (Cd) contamination

Cd^{2+} is a highly prevalent version of the toxic substance. Typically, the earth, the water, and the atmosphere contain it. Cadmium is an unnecessary metal for our bodies. Its gradual method of elimination means that it can nevertheless be harmful at minimal levels. In addition to being present in the atmosphere, it is also released by metallurgical operations and the businesses that create materials used to make fuel cells and polymers. It builds up in the tissue layers of the human kidneys, liver, respiratory tract, skeleton, and nerves, causing harm and dysfunction. Although it is difficult to eliminate from the kidneys, where they are primarily kept, cadmium causes harm to them. It travels to the liver via protein in the circulation, where it binds to metallothione [64].

1.5.3 Effect of Arsenic (As) contamination

As a toxic substance, arsenic pollution of the water that is consumed is regarded as a major global health risk to the well-being of humans. Being exposed to arsenic over an extended period can lead to a number of medical conditions, including irregularities in the circulatory system, insulin resistance, kidney damage, and neurological. Furthermore, hepatic damage and altered hepatic function have been linked to the ingestion of arsenic. Additionally, only a small number of studies showed that prolonged contact with arsenic might cause malignancies like cancer of the epidermis, urinary tract, and pulmonary system [65].
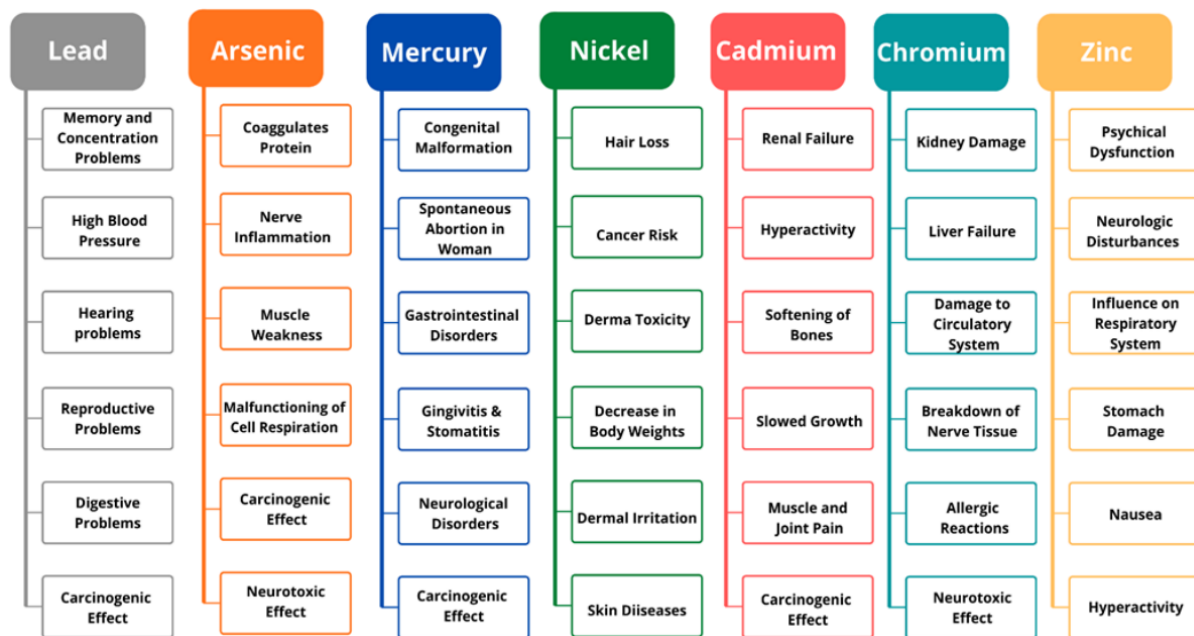
Figure 4 : Showing toxic effects of HMIs on human health [66]

Table 1 : Classification of HMIs on the basis of carcinogenicity [67, 68]

GROUP	HAEVY METAL	LEVEL OF CARCINOGENICITY	EVIDENCE
1	Aluminum, arsenic inorganic compounds, cadmium, chromium, nickel and their compounds	Carcinogenic	Many evidence in humans

2	Divide into two categories:
	  A. Lead and its compounds.
	  B. Methylmercury, lead, cobalt, alloys of nickel and oxides of vanadium and molybdenum.
		Probably carcinogenic
		
		Possibly carcinogenic
			Enough evidence in animals but limited in humans.
			Limited evidence in humans and animals

3	Copper, mercury, selenium and their compounds. Arsenic organic compounds	Carcinogenicity not classifiable	Insufficient evidence in both humans and animals
4	Manganese, silver, and zinc	Probably not carcinogenic	Sufficient evidence

1.5.4 Effect of Mercury (Hg) contamination

As an illustration, the term "whole ambient mercury compounds" is often used to refer to both atmospheric mineral mercury (Hg^0) and gaseous oxidizing mercury (Hg^{2+})[69]. After mercury is formed as particulate-bound mercury, Hg^{2+} can be secondary formed by oxidizing Hg^0. Except in regions of pesticide use or microbiological activity, organic forms of HMs in the air are thought to be of minor consequence. When discharged in bigger amounts, mercury exhibits neurotoxicity; the CNS is the element's main target for its vapors. When mercury gets into the body in higher doses, spontaneous accumulation in pregnant women is prevalent. There are many different types of declared cognitive, personality, sensory, and motor abnormalities. A lasting encounter to elemental mercury vapors has been linked to decrease psychomotor performance, shaky gait, poor focus, trembling speech, and clouded eyesight. In those who were subjected to elemental mercury vapors for a while, chronic cough has been documented [70].
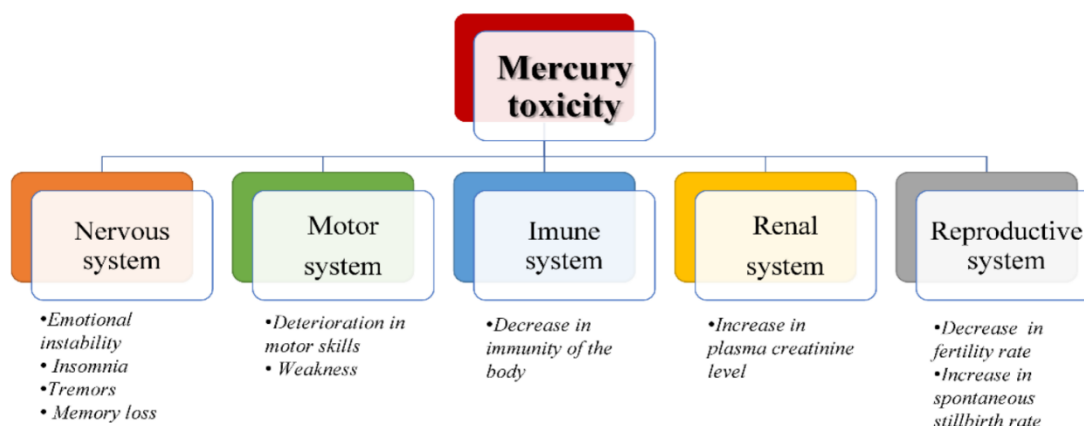
Figure 5 : Showing major mercury toxicity in human body [71]

1.5.5 Effect of Aluminum (Al) contamination

The most prevalent naturally occurring metal-based substance in the uppermost layer of the Earth is aluminum (Al). It concentrates in 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 histology alterations in neurons. Unfortunately, little is known about how being exposed to aluminum affects the growth of water species during its

infancy [72].

1.5.6 Effects of Chromium (Cr) contamination

The environment is becoming contaminated by this metal as a result of human activity. Chromium is negatively impacted by a few species of fish [34]. Chromium compounds have been shown to increase the risk of lung cancer, according to several studies [73-75]. There is also evidence of circulatory injury and nerve tissue breakdown in the system. According to reports, the presence of Cr alongside other metals increases the quantity of glycogen in numerous organs that are under stress from metal exposure [75].
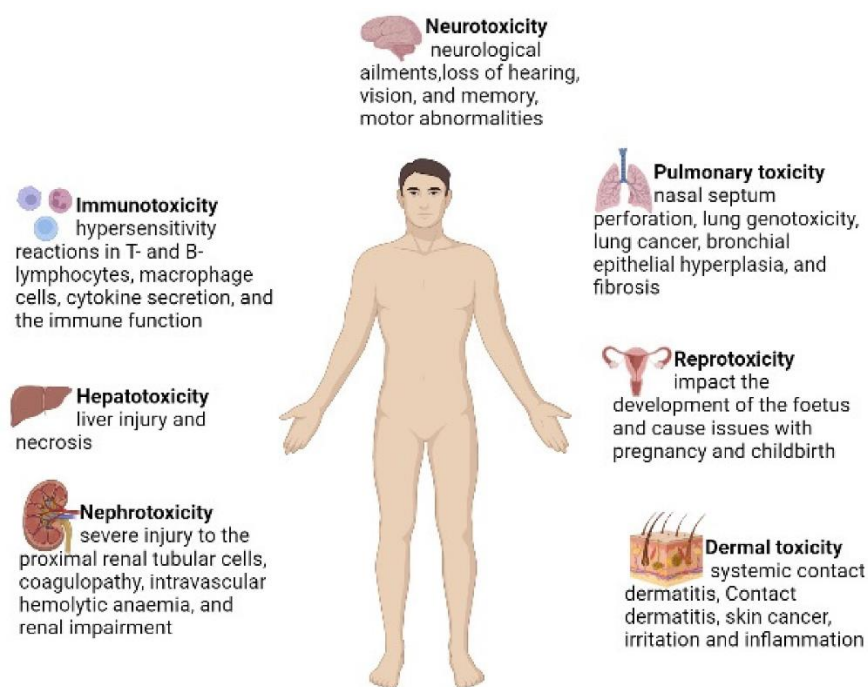
Figure 6 : Showing outcomes of chromium poising in humans [75]

1.5.7 Effects of Nickel (Ni) contamination

Two common sources of nickel in the surrounding environment are the weathering of rocks and soil and dust particles emitted during volcanic eruptions. Dermatology association, swallowing, and inhalation appearances occur in nickel and nickel alloy production plants in addition to the welding process, electroplating, compression, and cutting procedures. Nickel is well known for its capacity to induce human malignant cells, in addition to several other pathologic effects. When dissolved or inorganic nickel complexes are exposed to the skin, allergic dermatitis may result. Consuming nickel causes a considerable fall in body weight [76]. The most obvious side effect of nickel poisoning is hair

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loss. Exposure to inhaled dust containing certain nickel compounds has resulted in the most severe unfavorable effects from nickel contact, such as pulmonary and nasal sinus cancer, persistent pneumonia, and reduced lung functioning [77-80].

1.5.8 Effects of Zinc (Zn) contamination

Zinc fluids may originate via the organic erosion of rocks and human-caused processes such as animals and household and business wastewater outputs. Zinc is essential for maintaining cell structure under these conditions. Zinc is considered to be necessary for the immune system to function. Zinc raises the possibility of heart disease and stroke. It might cause digestive problems, nausea, and elevated blood pressure. It is also responsible for the neurological impact it has on humans. Excessive use of zinc may result in psychological impairment. The neurological system experiences several changes when zinc is ingested by humans [81, 82].

1.5.9 Effect of Copper (Cu) contamination

Copper is a part of jewelry, along with various compounds utilized to produce imitated jewelry. It is applied as a primary metal in defense weaponries, 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. Severe gastrointestinal pain is associated with the ingestion of food or water contaminated with copper. 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 [83].

1.5.10 Effects of Silver (Ag) contamination

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^+ interacts 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 [84].
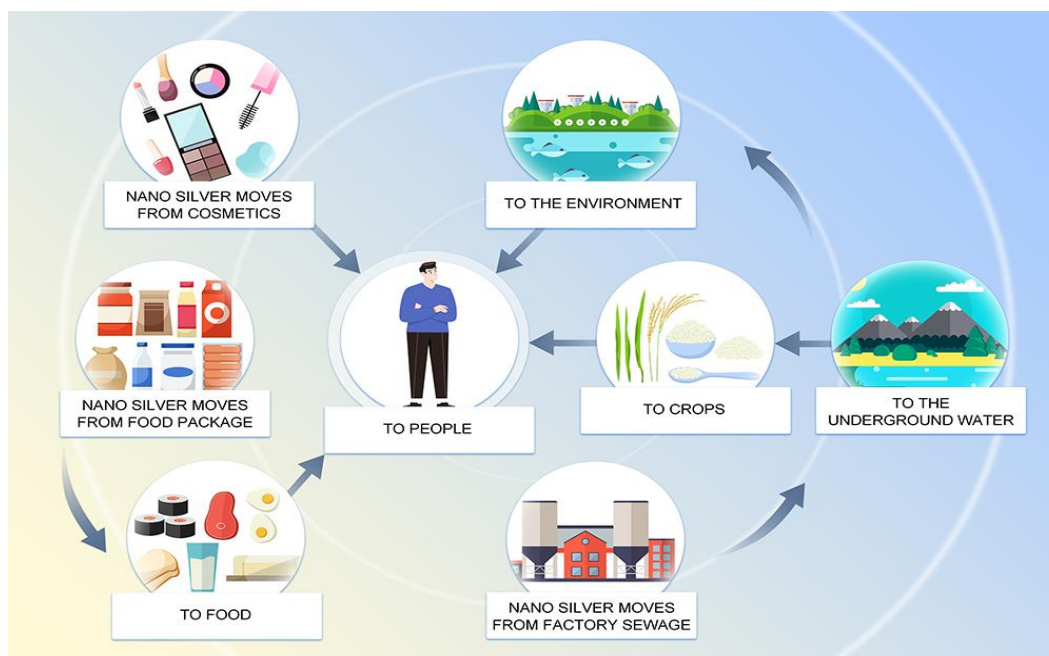
Figure 7 : Showing toxic effects of silver on humans [85]

Additionally, nano silver could enter at the cellular level and cause cellular toxicity. This impact may be brought on by any one of the following consequences that have been noted in mammalian cells: a negative allergic reaction, stunted development, mitochondrial disruption, DNA and structural damage, and alterations in cell shape. Nano silver generates a hazardous reaction in a range of cell types, although those reactions might differ depending on the kind of cell [86].

1.6 Accumulation of heavy metal ions in food chain

These HMIs can also find their way into our bodies through our food, drink, and air in smaller amounts. Few of these dangerous metals—like copper, Zn, and selenium—are necessary to maintain the body's metabolic rate. However, they could become dangerous at larger concentrations [87]. Using a food chain, breathing in high natural air concentrations near emission sources, or using contaminated water to drink (lead pipes) can all cause heavy metal intoxication. Toxic metals can be harmful to people since they enter the body directly. Bioaccumulation is the process by which an organism accumulates an element at a pace commensurate with its concentration in the atmosphere [88]. Actually, the effects of food-related consumption of metals on human wellness are a topic of great concern globally. However, studies on trends in the environment may help us determine the degree to which they affect the wellness of people. The difficulties may vary from country to country, as may the poorly known source of metallic pollutants [89].

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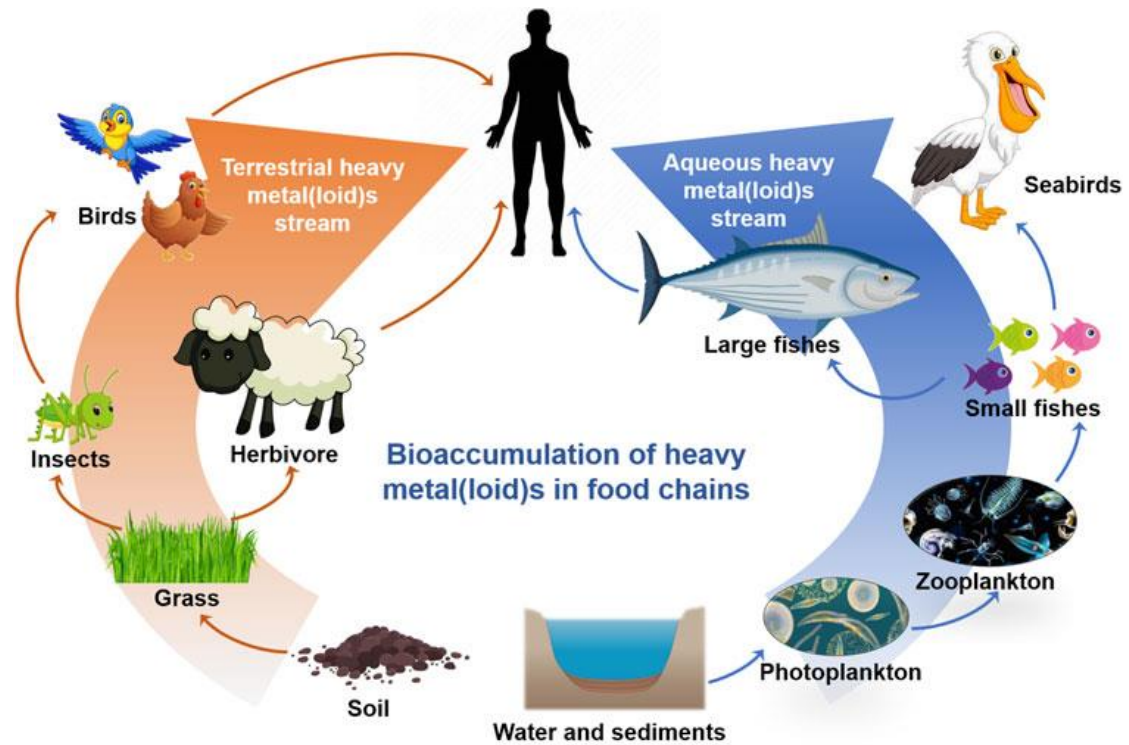
Figure 8 : Explain the route of bioaccumulation of different metal ions in Food Chain [31]

If known to be poisonous heavy metals are present in their environment, aquatic creatures have acute issues. Through the food webs of marine life, it may get into the body and produce a variety of clinical diseases in humans, such as occasional fever, cramps, decreased kidney function, and high blood pressure. Since fish are at the highest level of the food chain and are suitable transporters of pollutants for individuals, they are essential to the biodiversity of metals [90]. Because of their toxic and carcinogenic effects as well as their ability to cause the oxidative degradation of biological macromolecules, heavy metals could potentially be very dangerous to humans as shown in figure [31, 91].

1.7 Regulations and guidelines for HMIs limits in drinking water

By nation and location, there may be differences in the rules and recommendations for maximum levels of heavy metal ions in drinking water. Here are some instances of the restrictions imposed by various organizations, though:

In the US, EPA has set maximum contamination limits for a number of heavy metals in drinking water. The MCLs for lead are 0.015 milligram per liter, cadmium is 0.05 milligram per liter, chromium is 0.1 milligram per liter, copper is 0.05 milligram, nickel is 0.05 milligram per liter, and arsenic is 0.01

milligram per liter.

European Union: For a few heavy metal ions, the European Union has established limit values in drinking water. Lead is restricted to 0.01 milligram per liter, cadmium to 0.005 milligram, chromium to 0.05 milligram per liter, copper to 2 milligram per liter, and arsenic to 20-gram per liter.

WHO: The WHO has set standards for several ions of heavy metals in water used for drinking. The standards provide for lead levels of 0.01 milligram per liter, cadmium levels 0.003 milligram per liter, chromium levels of 0.05 milligram per liter, copper levels of 2 milligram per liter, and arsenic levels of 10 gram per liter [92].

1.8 Detection of environmental pollutants

A pollutant sensor is a piece of machinery synthesized to detect the presence of metal ions in the surrounding air. On rare occasions, these pollutants can also be measured with it. It is critical to develop a strategy that will keep lakes and rivers safe for use by living creatures, since the importance of pollutant-free water supplies has already been highlighted. Prior to removing these dangerous M^+ from water specimen, we need to be able to detect their presence. This will enable us to select the best removal method and offer a numerical estimate of the level of pollution. To achieve this, environmentally friendly detection procedures that are also time and cost efficient should be devised. Additionally, a detection method needs to be accurate enough to pick up even minute amounts of metal ions. Although there are several methods for detecting heavy metal ions, there isn't one that can be used to detect all ions [93].

1.9 Detection

There are three primary methods for detection of pollutants.

Spectroscopic techniques

Optical techniques

Electrochemical techniques

1.9.1 Spectroscopic techniques

Highly sensitive methods for the spectroscopic determination of environmental pollutants are neutron activation analysis, ICP-ES [94, 95], atomic absorption spectroscopy [96], inductively coupled plasma mass spectroscopy [94], and XRF spectrometry [97]. They are adaptable when it comes to simultaneously determining the concentration of different pollutants and metallic ions for an extensive

limit of materials with incredibly low LOD value. However, all of them are highly costly, and skilled workers are needed to operate the sophisticated machinery. Limits of detection for lead, copper, and cadmium ions, respectively, have been stated to be 3, 2, & 0.2 g/dm3 when using the flame atomic. absorption spectroscopic means to quantify the presence of these ions in water [98]. Limits of detection for Copper, lead, and mercury ions have been detected at ppm to subdivisions per billion levels using high-resolution surface plasmon resonance spectroscopy and anodic stripping voltammetry [99]. The following is an explanation of a few significant spectroscopic techniques for determining the presence of HMIs.

1.9.1.1 Atomic absorption spectrometry

The magnitude of energy captured during the excitation process is evaluated in atomic absorption spectroscopy and correlates to the number of atoms that exist in the sample. Isolated atoms are stimulated from their ground state to their excited state using a particular wavelength. It is made up of a main light source, an atomizer that creates gaseous ions or atoms for evaluation, the monochromator, an analyzer, and a digital "readout" device.

A gas medium containing individual atoms or ions that are suitably separated from one another may often be employed for spectroscopic identification in atomic absorption. Flames, plasma-like fluids, and electro-thermal are used to create gaseous phase atoms and ions. The breakdown and volatilization of a substance to produce atoms and ions in the gaseous is known as atomization. A light source, such as an empty electrode or an electrodeless discharge lamp made of the element under study, is used to ignite the nuclei or ions.

It is possible to use numerous lights to determine multiple components without changing the bulb. Transistors are utilized in PMTs and solid-state detectors in atomic absorption spectroscopy. Mercury is detected via flow injection mercury methods, which are a modified version of atomic absorption spectroscopy [93].

Table 2 : Detection of HMIs by atomic absorption spectroscopic technique

SPECTROSCOPIC TECHNIQUES	ANALYTE DETECTION	SOURCES	REFERENCES
AAS	Cr, Cd, Mn, Pb	Arbaminch, Ethiopia	[100]
AAS	Pb, As, Sb, Al,	Water from Balochistan, Pakistan	[101]
AAS	Cd, Ni, Pb, Cu, Fe, Zn, Tl	Seawater	[102]

GF-AAS	Co, Ni	Water samples	[103]
GF-AAS	Pb	Water samples	[104]
GF-AAS	Pt	Rocks	[105]
GF-AAS	V	Wine	[106]
GF-AAS	Cd	wine	[107]
GF-AAS	Cr	wine and grapes	[108]
GF-AAS	Hg	Muscles of fish	[109]
AAS	Fe	mineral waters	[110]
AAS	Nitrate and nitrite	Meat	[111]

1.9.1.2 Graphite furnance atomic absorption spectrometry

A graphitic tube with holes on either side and a middle hole for the introduction of samples is the main component of a graphitic furnace. The sample, after the heat treatment that discards the liquid and other elements of the analyte, is transferred directly to a graphite tube for atomization. Subsequently, the substance is atomized and evaluated using the same procedure as flame atomic absorption spectroscopy results. In graphitic furnace AAS, the substance being studied is no more directly on the surface of furnance; rather, the process of atomization occurs in a temperature-secure environment, resulting in more accurate results. The disadvantages to being a heavy metal ions identification method include the longer processing time compared to flame sampling and fewer elements can be identified. In this case, copper, mercury, cadmium, lead, and arsenic were determined whose detection thresholds were 0.49, 0.061, 0.014, 0.28, and 0.19 mg/ L, respectively [112].

1.9.1.3 Atomic fluorescence spectrometry

Compared to atomic absorption spectrometry, atomic fluorescence spectroscopy performs and operates differently. In atomic fluorescence spectrometry, similar to atomic absorption spectroscopy, material is first converted into atomic form. Then, the atomized materials are activated by an outside light source by irradiating them. As these excited atoms settle on the detector because of electromagnetic decomposition and emission of certain radiations, the detector monitors atomic fluorescence. Mercury is frequently detected via cold vapor atomic fluorescence spectroscopy, which transfers free mercury atoms to the column where they are excited by a collimated UV light source. The excited atoms light up again and release the absorbed energy, which is detected using an UV photodiode detector or a photomultiplier tube sensor.

Table 3 : Detection of HMIs by using atomic fluorescence spectroscopy

SPECTROSCOPIC TECHNIQUE	ANALYTE DETECTION	SOURCES	REFERENCE
AFS	Pb	Water samples	[113]
XRFS	Cu, Pb	Aqueous solution	[114]
XRFS	Fe, Ni, Zn, Mn, Cu, Pb	Coastal seawaters	[115]
XRFS	As, Pb, V, Cr, Cu, Ni, Zn	Soil	[116]
XRFS	As, Ni, Zn, Cd, Cr, Cu, Pb	Soils	[117]
XRFS	Cr, Zr, Ni, Cu, Zn, Rb, Ga, V, Y, Ba, Pb, Sr, Nb.	surface soil samples	[118]
AFS	Hg	Water	[119]
XRFS	Pb, Zn, As, Cu	Soil samples	[120]
XRFS	Pb, Ni, Cu, Zn, Cr, Hg	Fish tissues	[121]

1.9.2 Optical techniques of detection

Techniques such as absorption, reflection, or luminescence spectroscopy can determine the visual impact of the materials with ease. Most normally, the detection of HMIs by optical methods. Optical ion sensing is useful for detecting some heavy metal ions, but it suffers from a number of limitations [122].

1.9.2.1 Indicator dye-based sensors

It is based on the heavy metal cation binding interaction with the colorant dye that modifies the binding reagents' absorbance or fluorescence. In this line of HMI detectors, the indicator becomes a HMI transducer as straight visual analysis is impractical. Another class of the indicators utilize heavy metal ions as "quenchers" that, when combined with indicator dye [123].

Due to their inferior analytical wavelengths, insufficient stability, requirement for ancillary reagents, and inability to be found in the pure form needed for sensing applications, numerous indicators are ill-suited for use in optical sensing for heavy metal ions. Many indicators complex only at extreme pH or at values that are irreversible. This general problem pertains to indicator dye-based systems. One

advantage to using sensors is the availability of an analytical wavelength that is distinguishable because with every different dye to be used, the entire procedure for detection becomes more complicated. [124].

1.9.2.2 Ionophore-based sensors

Because marker substances and ion-complexing organic molecules have several limitations, ionophores have been utilized for HMIs tracking using optical techniques. Because these ionophores are ion carriers, ion combinations, and binders that carry ions, they may be utilized to identify the ions HMIs. Ionophores can be functionalized as M^+ sensors by a range of sensing methods, including the addition of fluorogenic or chromogenic groups or the coupling of the appropriate dyes. The most effective technique for detecting HMIs is to use ion carriers to extract ions into membranes [125, 126]. In these optical sensors, the visible light signal is produced by a proton-selective chromo-ionophore, and the identification of heavy metal ions is made possible by selective heavy metal binding with ionophores [127].
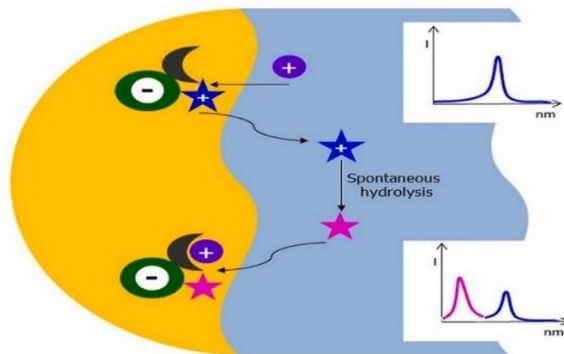
Figure 9 : Showing ionophore based sensor [128]

1.9.3 Electrochemical techniques

Conventional detection methods, such as ICP-AES, X-ray fluorescence spectrometry (XRF), ICP-mass spectrometry (ICP-MS), and AAS, are practical for identifying trace-level HMIs with high reliability. However, these methods required time-consuming sample prior preparation procedures and pricey test apparatus. For HMIs sensing in this area, electrochemical analytical methods are the best option because to their high sensitivity, user-friendliness, and simultaneously multi-element sensing capability [129].

1.9.3.1 Potentiometry

It is feasible to reliably identify trace-level HMIs using traditional analysis techniques. However, these

techniques require costly test equipment and tedious sample preparation steps beforehand. The ideal alternative for HMI sensing in this field is to employ electrochemical analytical techniques due to their exceptional sensibility, ease of use, and parallel multi-element sensing capacity [130]. This approach has some limitations, including greater detection limits and limited sensitivity, however work has been done to address these issues [131, 132].

Table 4 : Detection of HMIs with application of modified electrodes via potentiometric approach

METAL ION	MODIFICATION	LOD (MOL/L)	REF
Hg^{2+}	modification of carbon paste electrode with silica that is factionalized with thiourea	7×10^{-8}	[133]
Hg^{2+}	zirconium antimonate ionophore for modification of Screen-printed electrode	5×10^{-8}	[134]
Pb^{2+}	carboxymethyl cellulose/ Sn (IV) phosphate/ PVC composite	1×10^{-6}	[135]
Pb^{2+}	Zirconium (IV) iodosulphosalicylate	$4.07 \times 10{-6}$	[136]
Pb^{2+}	Polypyrrole	7.0×10^{-7}	[136]

1.9.3.2 Amperometry

A potentiostatic method called amperometry uses the flow of minuscule electricity that is produced when certain HMIs are reduced and are being monitored. This approach involves placing the initial and active electrodes in a buffer containing conductive ions, with a constant potential difference between them. Since the voltage is calculated as an indicator of time, these kinds of tests are referred to as amperometry techniques. This technique makes it possible to identify a particular metal ion within other electroactive forms because of the steady voltage that is present on the working electrode [137].

Table 5 : Electrochemical detection of HMIs by amperometric approach

METAL	MODIFICATION	LOD	REFERENCE
Hg^{2+}	Pt/CeO$_2$/urease.	1.8×10^{-8}	[138]
Hg^{2+}	PVF/ platinum electrode	5×10^{-10}	[139]
Pb^{2+}	carbon fiber electrode	1.3×10^{-6}	[140]

1.9.3.3 Voltammetry

One popular electrochemical technique for monitoring HMIs is voltammetry. Voltammetric techniques

measure electricity at different applied potentials and generate a graph of current versus voltage. Voltammetry enjoys a wide application in the detection of HMIs because of its good reliability, low detection limit, and large sensitivity. Even though there are many modes of voltammetry, they have the same basic way of scanning potential for the current generation. Some of the voltammetry modes among several for analysis of HMIs are summarized herein.

1.9.3.3.1 Cyclic voltammetry

In cyclic voltammetry, the given potential is the variation of the potential in two directions, that is, one way followed by the other. A record of electricity for a forward and back scan, plotted against the applied voltage, produces a cyclic volta gram. This cyclic volta gram is used to ascertain various important parameters like the related currents and peak potentials for the reduction and oxidation processes. Cyclic voltammetry was used for the specific detection of Hg^{2+} by Au NPs and rGO-functionalized GCE, which is referred to as an Au/rGO-SH/GCE composite[141].
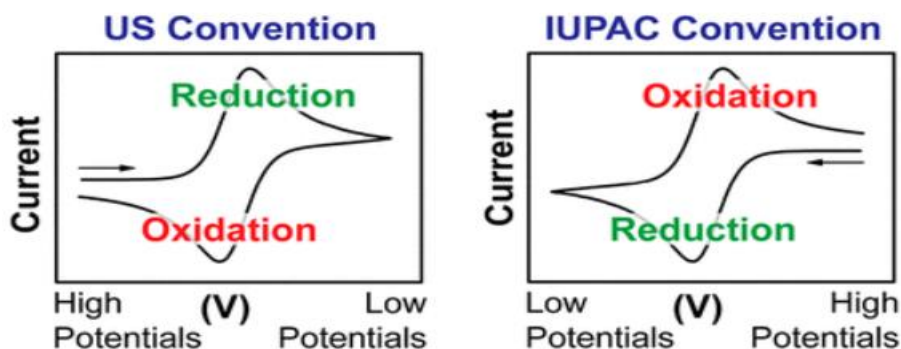
Figure 10 : Showing CV curves [142]

1.9.3.3.2 Pulse voltammetry

Pulse voltammetry is a distinct sort of voltammetry that is created when voltage signals with varying shapes and amplitudes are used in voltammetry measurement. Additional subcategories of pulse voltammetry include normal pulse voltammetry, differential pulse voltammetry, reverse pulse voltammetry, etc. Due to its excellent sensitivity for detecting ions of heavy metals, the differential pulse is the most popular pulse voltammetric technique. Cd^{2+}, Pb^{2+}, and Hg^{2+} ions were simultaneously detected by differential pulse voltammetry [143].
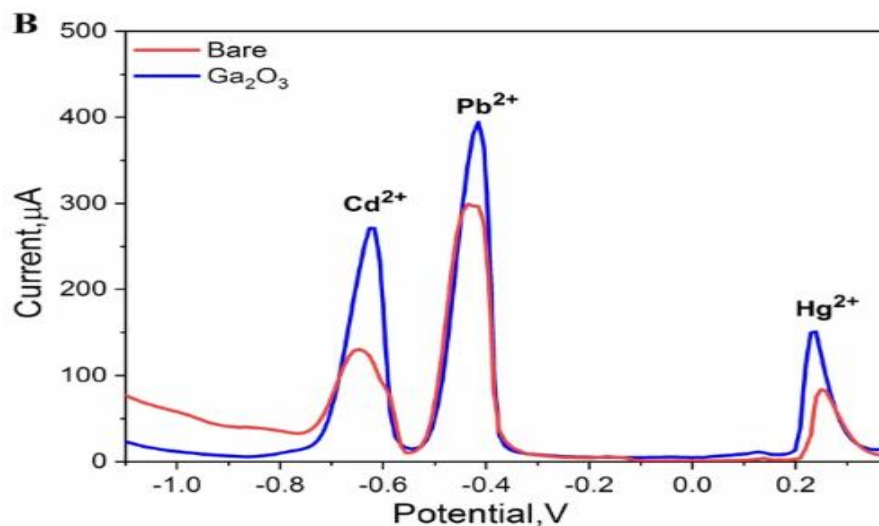
Figure 11: Showing voltametric response Ga2O3/CPE and bare carbon paste electrode [143]

1.9.3.3.4 Electrochemical impedance spectroscopy (EIS)

Perhaps the most significant electrochemical method is EIS, which uses ohms (a resistance unit) to assess the resistance of a circuit. Because it uses small signal examination, and can detect signal relaxations over a very wide range of employed frequencies, from less than 1 mHz to greater than 1 MHz, through easily accessible electrochemically employed stations, EIS offers several advantages over the other electrochemical technique (potentiostat) [144].
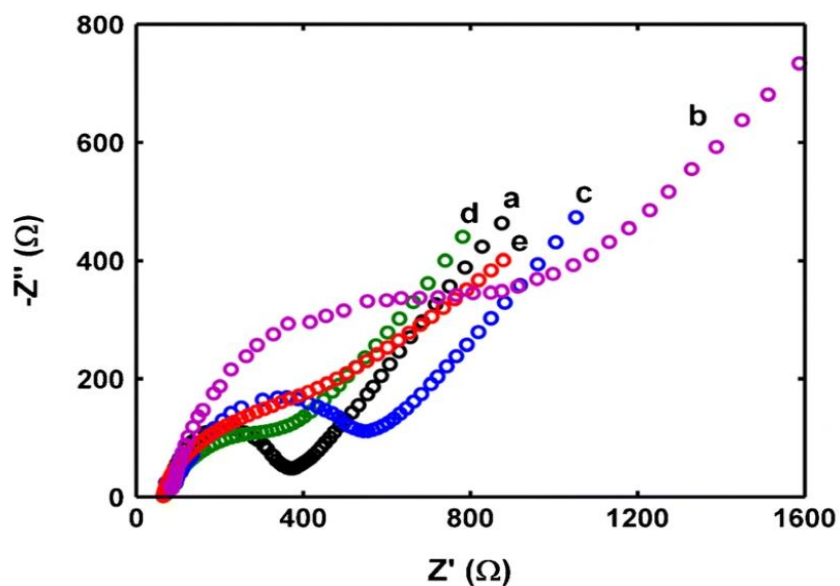
Figure 12 : Showing results of Electrochemical impedance spectroscopy (EIS) on different modified electrodes [145]

1.10 Basic construction of electrochemical sensors

The electrochemical sensors are made up of a receptor that acts as a recognizing component and an amplifier that is attached to it. Some recognition elements can engage only with compounds, changing their physicochemical properties [146]. To enable qualitative as well as quantitative identification, the sensor converts and amplifies these modifications into an electrical or optical signal, such as an electrical current or a change in appearance. As a result, a chemical sensor is an instrument created to react with and evaluate a specific analytic agent [147].

Because of their ease of use, low cost, and exceptional sensibility, electrochemicalectors are extremely appealing. Usually, three-electrode cell configurations with potentiostat control are used in electroanalytical detectors [148]. When redox processes, chemical energy is transformed into electrical power at the working electrode (WE). The voltage that is applied differential at the operational electrodes is maintained or stabilized by the source electrodes (RE). Finally, a comparable redox semi-reaction is facilitated by the counter electrodes. The solution of electrolysis in this electrochemical cell improves its ionic conductivity [149].

1.11 Principle of electrochemical detection of HMIs

Electrochemical monitoring is a frequently used method for detecting heavy metal ions because of its outstanding sensibility, simplicity, and low cost [149]. The working electrode (WE), a reference electrode (RE), and the counter electrode (CE) are the three electrodes that make up the typical electrochemical monitoring system [150]. Heavy metal ions on the outermost protective layer of the working electrode undergo reductions or the oxidation process throughout the electrochemical measuring process by either gaining or losing electrons. Chemical impulses are converted to electrical impulses to establish a link between the quantity of HMIs and the consequent current. The characteristics of the functioning of the electrode are important in determining the results during the entire measurement process. The surface modification of the electrode greatly influences the sensitivities and accuracy of the identification process. Therefore, the electrode could be modified by adding different substances or using composite components so that it is made more sensitive with its detection limitation lowered and its detecting aptitudes widened [151].

1.12 Metal organic frameworks (MOFs)

Moreover, many different organic-inorganic composites can enhance sensors designed to detect heavy metal ions. These composites enable the sensors to be modified. Metal-organic frameworks constitute typical organic-inorganic hybrid materials realized by linking metal ions with organic linkers, and researchers have looked into their potential in improving electrochemical signal amplification and detection [152]. Most MOFs possess expansive surface areas, porous structures, and easily adjustable surface properties [153]. They also could host selectively molecules of specific sizes. The numerous research efforts toward these MOF-based nanomaterials have significantly enhanced the fundamental properties of the electrochemical sensors for various applications, such as sensitivity, durability, selectivity, and precision. In addition, MOFs also have great potential for the sensing of heavy metal ions since they can efficiently immobilize substances on their surface and entrap different nanoparticles.[154].

Altering properties like pore volume, pore dimensions, surface area, and crystal size are achievable by manipulating synthesis parameters such as pH, concentration, temperature, and reaction time. Metal-Organic Frameworks (MOFs) are gaining popularity as a versatile material in numerous applications, including energy storage, catalysis adsorption/desorption, sensors, and the separation of vapors and light hydrocarbons. Metal ions exhibit diverse geometries and coordination numbers, which encompass linear, T- shaped, Y-shaped, hexagonal, square-planar, square-pyramidal, octahedral, trigonal-prismatic, trigonal-bipyramidal, and pentagonal-bipyramidal arrangements. UiO-66, formed by connecting $Zr_6O_4(OH)_4$ clusters with terephthalate ligands, possesses a robust three-dimensional structure with multiple defects and a significant surface area. This MOF has been used in the capture and detection of HMIs, such as Pb^{2+}, Hg^{2+}, and Cd^{2+}, due to its outstanding capacity to draw heavy metal ions and its extraordinary resistance to hydrolysis [155]. MOF-74 is a group of metal-organic frameworks that are created by combining 2,5- dihydroxyterephthalic acid ligands with metals such as Mg, Co, and Ni to create a strong and porous framework [156].

The large surface areas and remarkable resistance to chemical reactions of these MOF-74 materials make them highly esteemed. By making use of the metal binding sites, they have shown to be successful in identifying heavy metal ions in aquatic environments, particularly Cd^{2+} and Hg^{2+}. $Fe_3O(OH)$ clusters in MIL-100(Fe), an iron-based metal-organic framework, are linked by

terephthalate ligands in a three- dimensional configuration. It has a large surface area and mesoporous cavities. MIL- 100(Fe) is highly regarded for its exceptional stability and adsorption power. In aquatic environments, it has been used for the detection and elimination of metallic ions it it has been used for the detection and elimination of metallic ions such as As^{3+} and Cr^{6+} [157]. UiO-66 is known by the designation Oslo University. Zirconium serves as a metal cluster in UiO-66, while 1,4-benzene dicarboxylic acid serves as a linker, resulting in a structure resembling a cuboctahedron. Octahedral and tetrahedral cages are joined by triangular windows in the material UiO-66. In the presence of a protic solvent, such as water and alcohol, UiO-66 is highly stable. It was discovered that UiO-66's crystallinity was preserved even after being treated with aqueous HCl (pH=1) or water-based NaOH (pH = 14) [158].

1.13 Conducting polymers

The work done on PEDOT: PSS, poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) by modifying electrode, has been done considerably because of its exceptional conductance, strong chemical reactivity, wide redox window, and effective film-forming procedure. The PSS, present in PEDOT, plays a major role in polymer stability and may provide an electrostatic contact with abundant oxygen functionality in graphene oxide substances. Therefore, in order to identify the presence of uric acid, a homogeneous dispersion of rGO with PEDOT: PSS is prepared [159]. PEDOT: PSS is a conducting polymer consisting of many electrolytes that is sold cost-effectively. The strong interaction of two polymeric materials results in the complex structure of poly. The well-recognized model for the structure in solution features small PEDOT segments that are in close proximity to PSS bundles [160]. More importantly, PEDOT: PSS film has been used as an excellent electrode modification material for the modification of battery cells, supercapacitors, and sensors for analyses [161]. GCE modified composite of ErGO and PEDOT: PSS could exhibit excellent analytical performances for use as a hydrazine sensor [162].

Due to its relatively superior conductivity, rigidity, ease of manufacture, cost effectiveness, and electrochemical characteristics in comparison to other CPs, polyaniline has gained the interest of several investigators [163]. Polyaniline (PANI) is a conducting polymer showing strong thermal stability, high electrical conductivity, excellent potential capacitance, and ecological durability. Besides, it is easily prepared. Therefore, modified polyaniline materials are considered the right choices for the development of electrochemical sensors. For example, the cobalt copper MOF/PANI

combination is a very exact GCE for the detection of lead and cadmium ions [164].

One of the most common conducting polymer compounds is polypyrrole, which is cost-effective, easy to synthesize, and exhibits good electrochemical reversibility, good environmental stability, good biocompatibility, and great conduction when loaded [165]. The use of PPy as an electrode material for heavy metal detection is very advantageous since PPy has a high binding capacity with metal ions, coupled with superior conductance and ecological durability. Polypyrrole molecules, since they link among themselves, disperse poorly in an aqueous solution and congregate readily [166].

1.14 Ferrites

Ferrite nanoparticles are those which follow the generic formula with the internal structure of spinel because of the attractive, versatile features of MFe_2O_4, where M denotes a divalent cation, it has a long list of applications, particularly as a sensor [167].One of ferrites' main benefits is that they are porous, which is essential for a sensor [168]. Cobalt ferrite, $CoFe_2O_4$, is one of the several spinel ferrites that show potential for magnetic applications because of its strong mechanical properties, strong magneto-crystalline anisotropy, a mild saturation magnetic field, high electrical characteristics, and chemical resistance [169].

Chapter 2

Literature Review

The use of MOFs in the electrochemical detection of heavy metals has been extensively researched, revealing their outstanding effectiveness in identifying and extracting these ions. A rapidly evolving area of scientific exploration involves the study of MOFs and their composite materials, specifically aiming to detect arsenic in water [170].

The L-Cystine/MWCNTs/N-MoS$_2$@GCE sensor, interaction of L-Cys, carbon nanotubes (CNTs), and nitrogen-doped molybdenum disulfide, at a limit of detection in nanomolars, has proven to be an effective electrochemical sensor for the simultaneous detection of lead and cadmium in common water sources and freshwater. The sensor has excellent anti-interference performance, high stability, repeatability, and a wide linear range. It is possible to identify metal ions in aquatic environments simultaneously by using actual water samples [171].

The present work aims to develop a simple analytical method for the measurement of hazardous HMIs like lead and mercuric ions, considering the possible health hazards. Electrochemical investigation of these ions was carried out by synthesizing NH$_2$-functionalized magnetic nanoparticles, namely, Fe$_3$O$_4$@SiO$_2$-NH$_2$. The sensor was constructed using Fe$_3$O$_4$@SiO$_2$-NH$_2$, and metal ions were electrodeposited onto the electrode surface. The sensitivity and detection limits were improved by optimization of the sensor. The sensor was successfully able to detect these ions, with recoveries in milk from 95.1% to 114% [172].

A novel electrolytic sensor for the simultaneous unmasking of Cd^{2+} and Pb^{2+} was designed by utilizing nanocomposites of AuNPs on L-Cys functionalized MOF and graphene oxide (L-Au-MOFs-GO). A one-step hydrothermal process was adopted for the synthesis of the composite on GO nanosheets; then, AuNPs were generated by reaction with HAuCl4. The hydrophilic groups interacted with metal cations to enhance the conductivity in the composite and act as a medium for the enrichment of HMIs. L-Au-MOFs-GO composite showed better electrochemical properties compared to graphene oxide material or MOFs-graphene composite. The sensor showed very good selectivity and sensitivity to determine cadmium and lead in an ABS solution [173].

This chapter presents the surface modification of a glassy carbon electrode using MIL-88B(Fe)-NH$_2$,

an amine-functioned MOF, to enhance the oxidation sensing of metal ions for electrochemical detection. The sensor was prepared through the solvothermal method and deposited onto GCE to analyze find out the levels of Cd^{2+}, Pb^{2+}, and Cu^{2+} ions using DPV. The sensor proved to be a viable application method for assessing heavy metal ions in water, since it provides outstanding electrochemical performance, high dependability, and good selectivity [174].

An electrochemical sensor called Bi-BDC-NH$_2$@NMCS was designed to determine Cd^{2+} and Pb^{2+} content in shrimp, fish, and liver specimens. Unstructured and granular Bi-BDC-NH$_2$ sensors were immobilized onto N-doped mesoporous carbon nanosphere. Compared with classical bismuth film electrodes, the sensor has a higher specific area and more exposed sites for the adsorption and transmission of the electrons of metal ions, resulting in a higher charge transfer rate, stability, and conductance. The stripping performance of the approach was proved to be excellent, with a limit of detection of 0.36 nanogram permililiter for Pb^{2+} and 0.44 nanogram permililiter for Cd^{2+} [175].

A brand-new, very sensitive sensor has been created for the rapid identification of harmful Pb^{2+} ions in aquatic surroundings. A carbonized metal–organic framework nanocomposite and Bi_2O_3 nanoparticle-based sensor were manufactured by a one-step annealing method. Bi_2O_3 and carbonated Ui O-66-NH$_2$ modified GCE were used for the Pb detection using differential pulse anodic stripping voltammetry (DPASV). It has a low detection limit and large linear range under ideal conditions. Besides, it has outstanding anti-interference, stability, and repeatability qualities [176].

The aim of the work is to develop an electrochemical sensor capable of detection of heavy metal ions, cadmium and lead ion, from water samples using the cobalt copper-MOF/polyaniline sensing electrode. A one-step in-process polymerization process was developed to fabricate the sensor, and many methodologies were implemented to characterize it. By using differential pulse voltammetry, the concentrations of Pb^{2+} and Cd^{2+} were determined at optimal pH. Multiple detection of Pb^{2+} and Cd^{2+} was done at the lowest detection. In addition, anti-interference and repeatability tests were conducted in the present study that showed efficient targeted sensor technology. Therefore, the outcomes of this work are the functional design of CoCu-MOF/polyaniline materials and the establishment of a competent approach towards the detection of HMIs [164].

The study used a Ti$_3$C$_2$/Fe$_3$O$_4$/g-C$_3$N$_4$ nanocomposite to provide an ultra-sensitive and efficient nanosensor for the multiplex measurement of multi-metal ions. A co-precipitation method was employed in the synthesis of the small material, and afterwards it was sonicated. The Simultaneous detection of zinc, copper, lead, and mercury ions was performed using the DPSAV. To achieve

maximum sensitivity, the electrolyte parameters were optimized. The $Ti_3C_2(HF)/Fe_3O_4/g\text{-}C_3N_4$ sensor exhibited good sensitivity for Zn^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, and Hg^{2+} ions in a micromolar concentration with the detection limit below recommendations of WHO in optimal conditions. The sensor also showed excellent selectivity in a complicated alien species matrix and specificity in the detection of multiple targets, respectively. The high electroanalytical performance and accuracy may be attributed to the heterostructure and coherence provided by precision [177].

Being fast-responding, easy to use, highly sensitive, and applicable with portable devices, the advantages of electrochemical sensor technology can provide many benefits for making heavy metal ion detection on-site and online. In the present work, a novel hetero-shelled hollow MOF hybrid material, HCZ@ UiO–66–NH₂, is presented. This material is synthesized by growing UiO–66–NH₂ on the ZIF-8 substrate. Because of the hollow carbon polyhedron design of HCZ, the dissolution of UN was enhanced, and the transferred e⁻ capacity increased to offer a more precise detection accuracy and sensing capability for lead ions measurement [178].

This work provides a composite for accurate and precise analysis of copper and lead ions through a Field Effect Transistor that is constructed and enriched with L-Cysteine: PEDOT: PSS/ rGO. This sensor works at low voltage with a great sensitivity to such metal ions. In this respect, it is found out that lead and copper screening levels fall short of WHO guidelines [179].

Electrochemical detection of 4-nitrophenol, a highly dangerous organic contaminant dangerous to the ecosystem, is described here. Solvothermal synthesized $CuBi_2O_4$ nanorods are deposited on electrodes in this process. The electrode offers excellent selectivity against both organic and inorganic interferences. From the above study, $CuBi_2O_4$ material is promising for the electrochemical assessment of 4-NP [180].

A modified Au electrode with a nanomaterial poly-pyrrole/NH2-MIL-53(Al) has been used for the construction of a novel electrolytic sensor for trace detection of lead and copper ions. The developed nanocomposite material was electrochemically deposited onto the polypyrrole nanosubstrates via an on-site electrochemical technique after being synthesized by the polymeric procedure. This novel electrochemical characteristic will give a new turn to heavy metal ion identification [181].

After the modification of GCE with polypyrrole, metal organic framework, and bismuth film (BF), a new electro-chemical sensor to analyze of Pb^{2+} ions in water was constructed. MOFs expanded the particular area of coverage and attachment site of the electrode, while PPy improved the conductance of the composite materials. The electrochemical functionality of the electrode could be tuned by

changing the applied voltage, coating duration, solution pH, and amount of bismuth ions. The electrode has strong anti-interference, consistency, strength, and a broad linear range with a LOD. The conclusions provide information regarding future effective and quick screening for Pb^{2+} ions in aquatic settings [182].

Applying polypyrrole, MOFs, and bismuth film (BF) modified GCE, a novel electrochemical sensor has been constructed for analysis of lead ions in water. MOFs expanded the particular area of coverage and attachment site of the electrode, while Ppy enhanced the conductance of the combined materials. The electrochemical performance of the electrode could be modulated by changing the applied voltage, coating time, solution pH, and amount of bismuth ions. The electrode has good anti-interference, consistency, strength, and LOD. The findings give insight into future effective and rapid screening for lead ions in aquatic environments [183].

This project, based on a Sm-BTC MOF, stresses the detection of trace-level mercury (Hg^{2+}) with an ultrasensitive electrolytic method. Electrochemical experiments reveal that the Sm-BTC functionalized glassy carbon electrode shows excellent sensitivity and selectivity to mercury ions (Hg^{2+}). The limit of detection of the sensor was as low as 10 nanomolar, which is lower than the recommended value of 30 nanomolar by the World Health Organization. The study in the real sample demonstrates that the sensor has a good recovery percentage and is useful to detect Hg^{2+} ions [184].

The bismuth cuprous oxide@Aluminum-MOF@UiO-67 nanocomposite material was utilized to construct a novel and highly accurate electrochemical sensor. This sensor will concurrently detect several HMIs, such as cadmium, lead, copper and mecury ions. Such a sensor is made possible through the preparation of many small-particle aluminum-MOF and UiO-67-MOF nanomaterial hybrids on the surface of Bi_2CuO_4. In this way, it can selectively identify and enhance metal ions on different substrates. This sensor is excellent in electrocatalytic redox capacity, exhibiting excellent selectivity, good robustness, and repeatability. Moreover, the sensor electrode further enhances the absorbent capacity toward (mercury) Hg^{2+} ,(lead) Pb^{2+}, (cadmium) Cd^{2+}, and (copper) Cu^{2+} [185].

A novel electrochemical sensing method was manifested for the sensing of mercury ions (Hg^{2+}) in tap water and tinned tuna fish. Cu-MOF nanoparticles are perfect for the preliminary concentration and adsorption of mercury ions (Hg^{2+}) due to their porous design. The electrochemical characteristics of the sensor were analyzed; at optimal settings, the mercury ions (Hg^{2+}) detection limit was about 0.0633 nanomolar. Mercury ions (Hg^{2+}) present in tap water and canned tuna seafood were examined using Cu-MOF nanoparticles. Its anti-interference, reliability, stability, and application were good enough,

and this was the first step toward the ultrasensitive and precise detection of mercury. This proof of concept shall mark the first step in encouraging mercury sensing [186].

Presently, this research has developed a new electrochemical sensor for the diagnosis of hazardous heavy metal trades in foods. The sensor utilized a 3DGO screen-printed electrode modified to incorporate nanocomposite nanomaterials of UiO-66-NH$_2$. The sensor can detect cadmium, copper, lead and mercury ions in 150 seconds with some detection limitations. The sensor provides a new avenue in the determination of electrochemical presence of heavy metal ions in foods through enhancement of electrical properties and electrochemical behavior of the UiO-66-NH$_2$ material [187].

A powerful pesticide, glyphosate, is used in agriculture, which enhances the output of crops. However, due to its hazardous effects and capacity to cause cancer, powerful, quick, and extremely selective sensors have been developed. The method developed research employs light enhancement to locate glyphosate doses within the nM range. The researchers synthesized NH$_2$-MIL-88B(Fe), MOF-based nanocrystals (NCs) through a hydrothermal technique and used them for the detection of glyphosate in an aqueous medium. The coordinative ligands and metal clusters present in the MOF NCs act as photon quenchers and prevent emission triggered by photoinduced electron transfer from the ligand to ferric ions. A high degree of preference toward glyphosate is evident from the luminescence enhancement with negligible interference from M$^+$ ions and insecticides [188].

We produced a diversity of NH$_2$-functionalized MIL-53 with various metals acting as nodes. Metal organic framework flexibility is modulated by the contact between the amines in the organic linker and the μ2-OH in the inorganic scaffold; the intensity of this interaction is connected with the electrical properties of the metal [189].

An electrochemical biosensor for hydrogen peroxide was prepared by means of a molybdenum sulfide nanosheet on nitrogen-doped carbon nanowires (MoS$_2$/CN NWs). A few layers of nanosheets composed of MoS$_2$ were hydrothermally grown over polypyrrole NWs to produce the nanohybrid. Due to the synergy in numerous active sites contained in nanosheets composed of MoS2 and the high stability of CN NWs, the MoS2/CN nanohybrid enhanced the performance of hydrogen peroxide electrochemical reaction. Due to the framework effect brought in by the CN NWs, the rigidity and conductance of the MoS$_2$ nanocomposite were improved. The probe developed also detected the release of H$_2$O$_2$ from A549 live cells, showing the electrochemical sensing potential of MoS$_2$/CN NWs [190].

Detection of lead ions is very important, as it is a dangerous heavy metal, which can easily be found

everywhere in everyday needs and food. With an aim to produce an excellent detection technique for lead in the surroundings and food, an electrochemical monitoring platform was fabricated based on a dopamine polymer-doped polypyrrole hydrogel-modified SPCE. The compounds showed remarkable conductivity and ability for selective adsorption. For the development of hydrogel, dopamine hydrochloride and pyrrole were hybridized. For the detection of lead ions, the PDA-PPy/SPCE showed excellent sensing capabilities. Moreover, it showed respectable recoveries in real sample analyses, indicating potential applications [191].

his work presents a new sensing platform for the electrochemical detection of luteolin, one of the antitumoral drugs widely used, based on MoO_3-polypyrrole nanowires/MWCNTs composite. By the solvothermal process, the composite is fabricated into a material with a huge specific surface. The surface layer of MoO_3-PPy prevented MoO_3 NW clumping and improved electrical conductivity. MWCNTs act as electrically conducting wires, enhancing the electron transport and catalyst oxidation reduction performance. The sensor demonstrates good long-term robustness, selectivity, and repeatability, and the detection limit for luteolin can reach as low as 0.03 nM [192].

In this research, a nitrate selective flow-through electrochemical sensor was developed by the electropolymerization process. Polypyrrole nanowire electrodes were fabricated. The sensor performances were evaluated by CV, amperometry, and flow-through analysis in two calibration solutions. The electrodes have shown improved selectivity toward ions such as phosphate, chloride, sulfate, and perchlorate without losing any of the interfering ions [193].

This paper describes the one-pot production of triethanolamine-functionalized AuNP-metal-organic framework-graphene oxide nanocomposites for the analysis of cadmium, copper and lead ions in river water. In the case of GO nanosheets, the UiO-66-NH2 is synthesized in situ, reducing the protons of 2-NH_2 BDC by TEOA acting as the base, in which the composite can enhance the electrochemical signals and accelerate the transmission of electrons. Furthermore, the composite acts as a reducer and enhances electrochemical signals, resulting in an increase in electron transmission. This TEOA@AuNPs-GO-UiO-66-NH_2-modified electrode is utilized for independent and simultaneous electrochemical measurement in an ABS with good selectivity and accuracy. Electrochemical sensors can have widespread use in environmental monitoring and assurance of food safety [154].

The accumulation of heavy metals through water and medicinal herbs poses a health risk to the world. A hybrid material consisting of MWCNTs and methylene blue-functionalized metal-organic framework was used to build a ratiometric electro sensor. For the detection of mercury, cadmium and

lead ions, the sensor performs better than other options. The probe generates a ratio signal and uses methylene blue as the internal reference. This sensor, more than the others, enhances repeatability, dependability, and removes interference, especially in complicated situations. This detector has been successfully used in actual water and herbal product sample analysis, hence providing a new method in the evaluation of the risk of heavy metal buildup and the protection of people's health and lives [194].

In this study, the redesigned material carbon-Dots/UiO-66-NH2 for glassy carbon electrodes was prepared to electrochemically detect lead and cadmium ions in water. A blend of carbon dots and frameworks was realized through the use of m-phenylenediamine as a source of CDs and NH2-functionalized-based Zr frameworks. The NH2 groups created a favorable adsorption contact with the complexation of metal ions. The sensor also has strong resistance to interfering and stable detection [195].

The release of heavy metal ions into the natural world has raised serious problems with the toxicity of pure fresh water. A nanomaterial known as Ni@UiO-66 has been synthesized to analyze such ions with low detection limits, all in a bid to solve this problem. Excellent fluorescence detection was made possible by the Ni-doped MOF structure in the UiO-66 network, which exhibited turn-off or and Fe^{3+} analytes and turn on for Cr (6) and Al^{3+} analytes. The lowest Hg^{2+} ion detection limit values were in the aqueous phase. These results suggest that the Ni@UiO-66 metal-organic framework can be applied in the detection of Hg^{2+}, Al^{3+}, Cr^{6+}, and Al^{3+} ions in trace amounts [196].

Chemical structural modifications have been employed to enhance the photochemical and electrochemical properties of graphene derivatives. Through amidation modification of RGO with L-Arg, an effective photonic chemosensor for Cd^{2+}, Co^{2+}, Pb^{2+}, and Cu^{2+} ions discrimination was prepared. L-Arginine-RGO was used as an electrode modifier to fabricate an L-Arginine-reduce graphene oxide-modified glassy-carbon electrode (L-Arginine-RGO/GCE) for DP-ASV-based Pb^{2+} ion selective detection. Depending on the type of modification, the study shows that reduce graphene oxide could be a suitable platform for optical and electrochemical sensors for efficient and selective determination of metallic transition. One common amino acid possessing the capability to be used for both optical and electrical metallic transition detection is L-arginine [197].

Chapter 3

Material and Methods

3.1 Chemicals required

Pyrrolemonomer, Hydrochloricacid, Ammoniumpersulphate(APS), Hexadecyltrimethylammonium bromide (CTAB), Distilled water, Deionized water, Ethanol, Dimethyl formamide (DMF), Acetic acid, 2-aminoterephthalic acid, Zirconium chloride, Cobalt nitrate hexahydrate and ferric nitrate nonahydrate ,Citric acid , Ammonia .

3.2 Glassware required

Beakers (100 mL, 250 mL, 500 mL), Measuring cylinder (100 mL), Pipette (10 mL), Funnel, Spatula, Magnetic stirrer.

3.3 Instruments required

Hot Plate (Wiggens WH2240-HT), Weighing Balance (Pioneer ^{TM}), Fume Hood, Ultrasonicator (great Sonic), Microwave oven (Samsung), Centrifuge Machine, Refrigerator, Muffle furnace.

3.4 Methodology

3.4.1 Synthesis of Polypyrrole nanowires (PPy NWs)

0.91g of CTAB was dissolved into 125ml HCl of 0.2M solution.0.3ml of pyrrole monomer were added and reaction was stirred for 2 hrs. Precooled APS solution (prepared by dissolving (1.14g APS in 10ml of 0.2M HCl solution) was dropped into above mixture solution. Reaction was further stirred for 30 mins. Reaction mixture was kept at 4-degree temperature for 5 days. The obtained product was washed with ethanol and deionized water. Obtained black precipitates were dried at 50-degree temperature for 24 hrs.
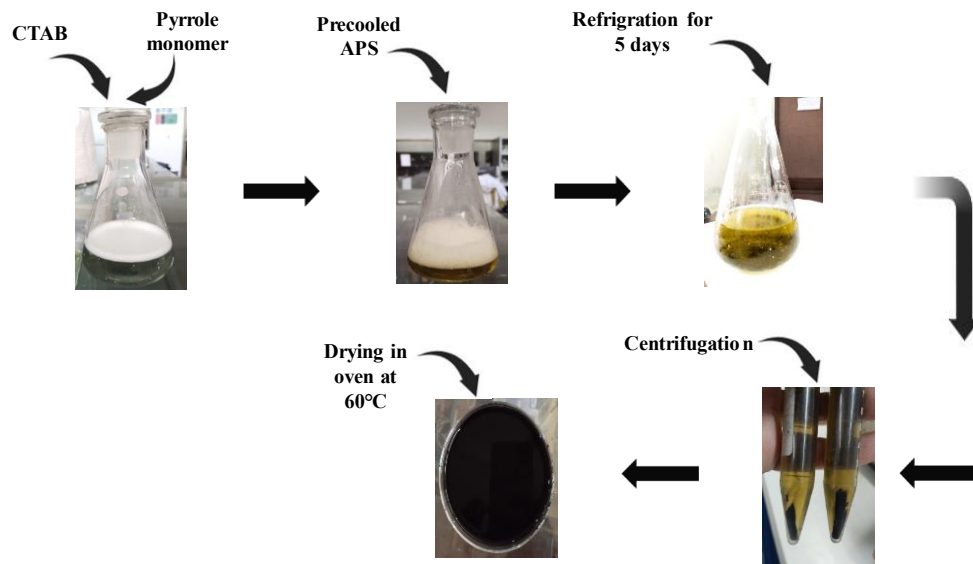
Figure 13 : Showing synthesis of polypyrrolenanowires

3.4.2 Synthesis of UiO-66-NH₂ MOF

215 mg of 2-Aminoterepthalic acid and 75 mg of zirconium chloride were added to 30 ml of DMF.1.5ml of acetic acid was added to above solution and solution sonicated for 30 minutes. The solution was heated in microwave for 3 minutes at 120 °C and kept for 2 mins at room temperature. After restin at room temperature, the product was centrifuged 3X with ethanol via centrifugation. The desire product was dried in oven at 60 °C for 12hrs.
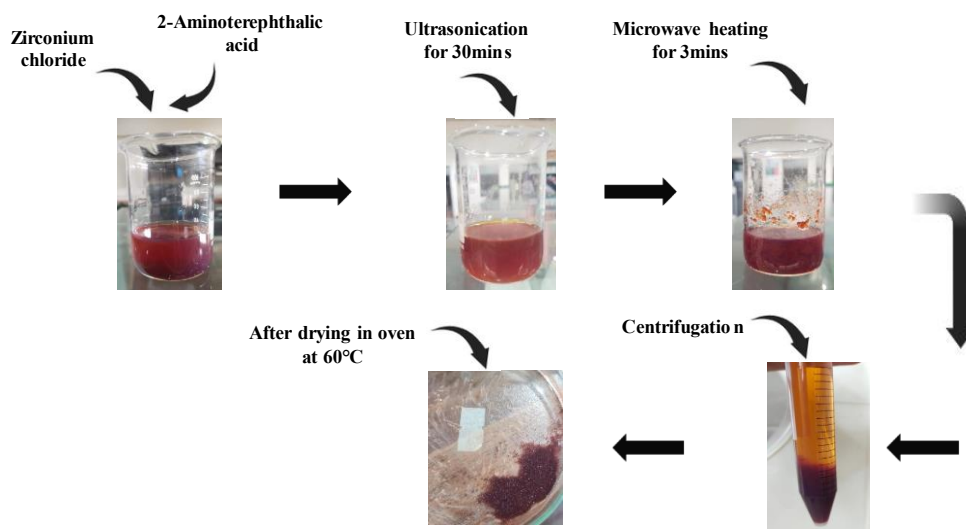
Figure 14: Showing synthesis of UiO-66-NH₂

3.4.3 Synthesis of Cobalt ferrites
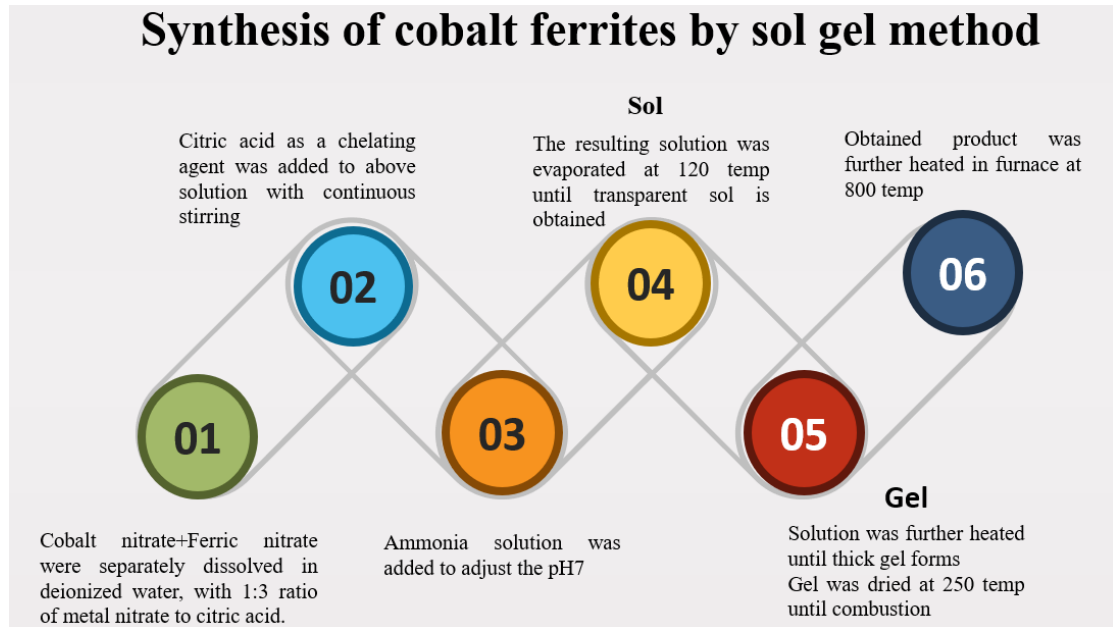
Figure 15 : Showing synthesis of cobalt ferrites

3.4.4 Synthesis of UiO-66-NH$_2$@Ppy-NWs@CoFe$_2$O$_4$

An equal amount of UiO-66-NH$_2$ MOF, Ppy nanowires, and cobalt ferrites were dispersed in ethanol. The resulting solution was sonicated for 3 hours in order to obtain a homogenous solution. After sonication, the mixture was poured into a petri dish and dried in an oven at 60°C for 12 hours. The product was obtained and ground into a fine powder for further characterization and electrochemical sensing.
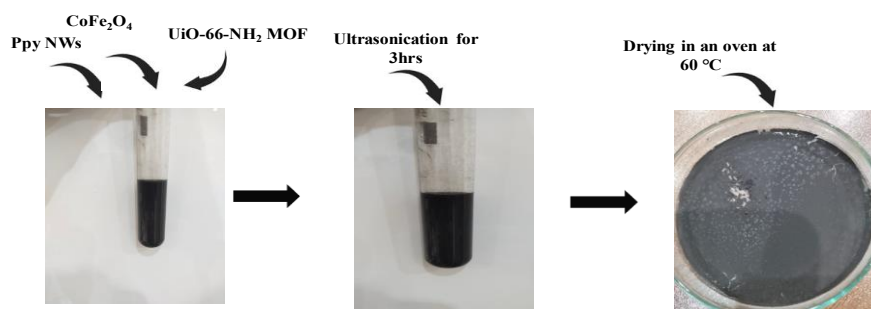
Figure 16 : Synthesis of UiO-66-NH$_2$@Ppy-NWs@CoFe$_2$O$_4$

3.5 Modification of Glassy carbon electrode (GCE)

The Glassy carbon electrode was modified with UiO-66-NH$_2$@Ppy-NWs@CoFe$_2$O$_4$ by the drop casting method using micropipette. The composite was dispersed in 1 ml of ethanol, and uniform slurry was formed by ultrasonication. The resulting solution was deposited on GCE by the drop-casting method.Functionalized GCE was dried in an oven and used for further electrochemical analysis.

Chapter 4

Results and Discussions

4.1 X ray diffraction (XRD)
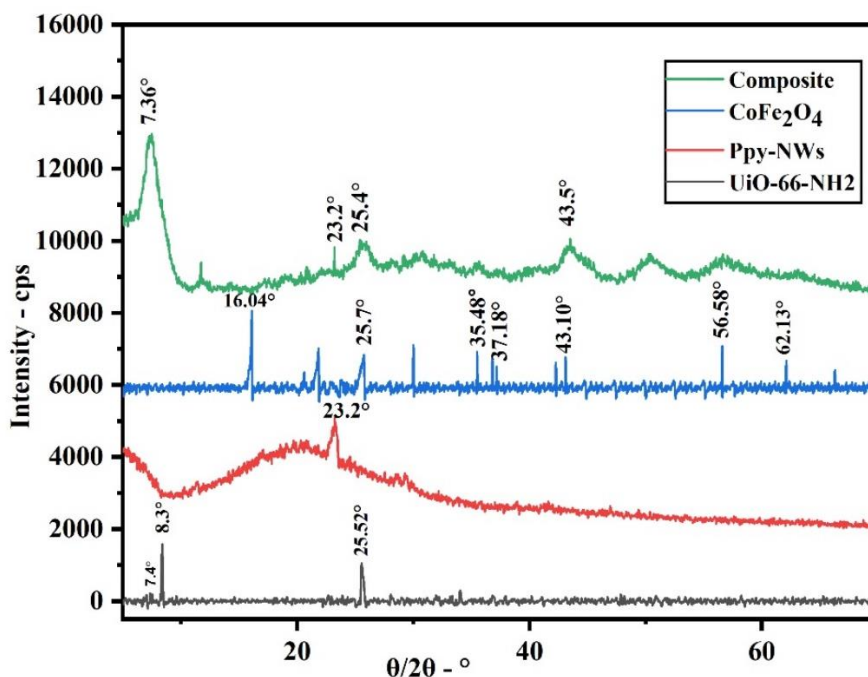
Figure 17 : XRD graph of UiO-66-NH$_2$ MOF, CoFe$_2$O$_4$, and UiO-66-NH$_2$@Ppy-NWs@CoFe$_2$O$_4$

X-ray Diffraction (XRD) analysis was performed to investigate the crystalline structure of the synthesized samples. The XRD analysis of UiO-66-NH2 MOF shows characteristics peaks at 7.4°, 8.4° and 25.6° showing crystal plane at (111), (200), and (600) confirming crystal structure of UiO-66-NH$_2$ MOF. The XRD analysis of ferrites indicates peaks at 16.04°, 25.7°, 35.48°,37.18°, 43.10°,56.58°, and 62.13°. The XRD analysis of Ppy-NWs indicates peaks at 23.2°, showing formation of Ppy-NWs and their amorphous nature. The reduction in overall peak intensity show that amorphous behavior of final composite, which enhances the overall electrochemical sensing of composite.

4.2 Cyclic voltammetry (CV)
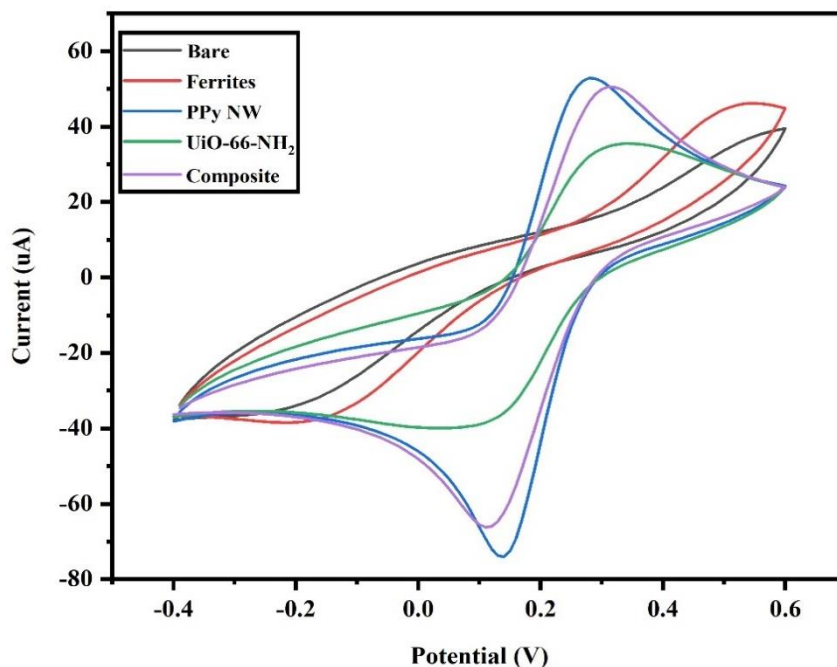
Figure 18 : CV of Bare electrode, CoFe2O4, Ppy-NWs, UiO-66-NH$_2$, and UiO-66-NH$_2$@Ppy-NWs@CoFe$_2$O$_4$

The CV study will help in determining the occurrence of a particular electrochemical process through a characteristic onset of current or peak. An electrochemical study was conducted using GCE as a working electrode, onto which UiO-66-NH$_2$@Ppy-NWs@CoFe$_2$O$_4$ material was deposited. 5 mM potassium ferricyanide ([K3(FeCN)6]) and 0.1 M KCl solution were used as electrolyte solutions. An electrochemical analysis was performed at a scan rate of 10 mV/s. Oxidation and reduction peaks of UiO-66-NH$_2$@Ppy-NWs@CoFe$_2$O$_4$ were compared with those of bare glassy carbon electrode. Increased in redox peaks of UiO-66-NH$_2$@Ppy-NWs@CoFe$_2$O$_4$ as compared to bare suggests the improved and enhanced conductivity of composite material. This notable rise in current for the nanocomposite UiO-66-NH$_2$@Ppy-NWs@CoFe$_2$O$_4$ suggests that Ppy-NWs enhances the conductivity of nanocomposite while CoFe$_2$O$_4$ provides large surface area and more active sites for analyte interaction. Thus, interactions between the electrolyte and the composite all cooperate in the promotion

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of the electron-transfer rate, hence enhancing conductivity.

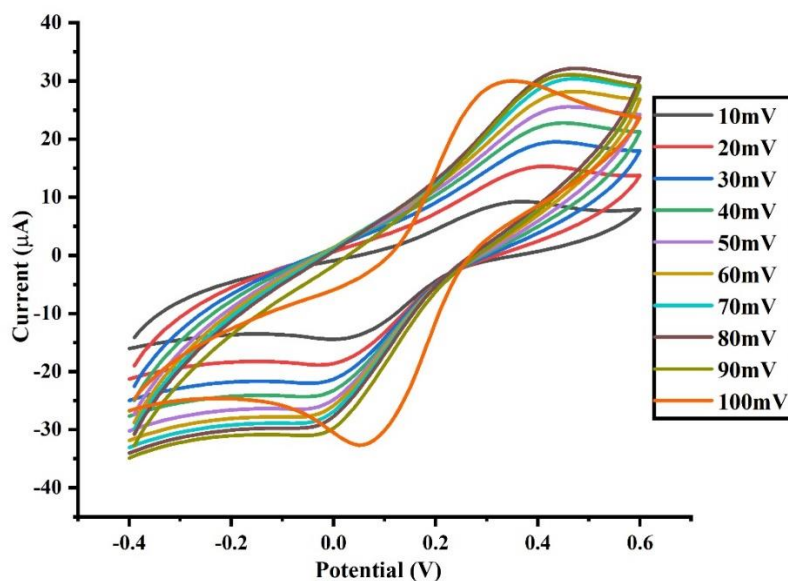Figure 19 : CV of UiO-66-NH2@Ppy-NWs@CoFe$_2$O$_4$ composite at different scan rate

The CV of Composite UiO-66-NH2@Ppy-NWs@CoFe$_2$O$_4$ is taken at different scan rates from 10 mV/s to 100 mV/s. The enhanced oxidation peak current in UiO-66-NH2@Ppy-NWs@CoFe$_2$O$_4$ indicates the enhanced conductivity of the composite as shown in Fig 4.4 (A). Plot 4.4 (B) represents the dependence of peak current on the square root of the scan rate and its linear fit for the anodic and cathodic peaks observed in the CV records of UiO-66-NH2@Ppy-NWs@CoFe$_2$O$_4$ modified GCE in 5 mM solution of potassium ferricyanide containing a 0.1 M KCl solution. The increase in the scan rate from 10 to 100 mV/s shows an increase in both oxidative peak current and reductive peak current, both showing a linear relationship, indicating that electrocatalytic activity at the UiO-66-NH2@Ppy-NWs@CoFe2O4 /GCE-modified electrode is a surface-controlled process.

4.3 Differential pulsive voltammtery (DPV)

The determination of lead (Pb^{2+}) and copper (Cu^{2+}) ions was carried out utilizing differential pulse voltammetry (DPV) as a highly sensitive electrochemical technique with a low detection limit. These experiments were conducted in a solution characterized by a pH of 5.0 and 0.1 M ABS, with variations in Pb^{2+} and Cu^{2+} concentrations at scan rates of 100 mV/s. It was demonstrated that when the analyte concentration increased in the electrochemical cell, both the pulse current and the actual current of

each peak steadily improved in concentration.

To optimize experimental conditions, the determination of copper was carried out utilizing differential pulse voltammetry (DPV) as a highly accurate electro-chemical technique with a low detection limit LOD 17.30µg/L, at concentration 10-100nM.

Figure 20 : DPV of UiO-66-NH$_2$@Ppy-NWs@CoFe$_2$O$_4$ electrode against Cu^{2+} ions
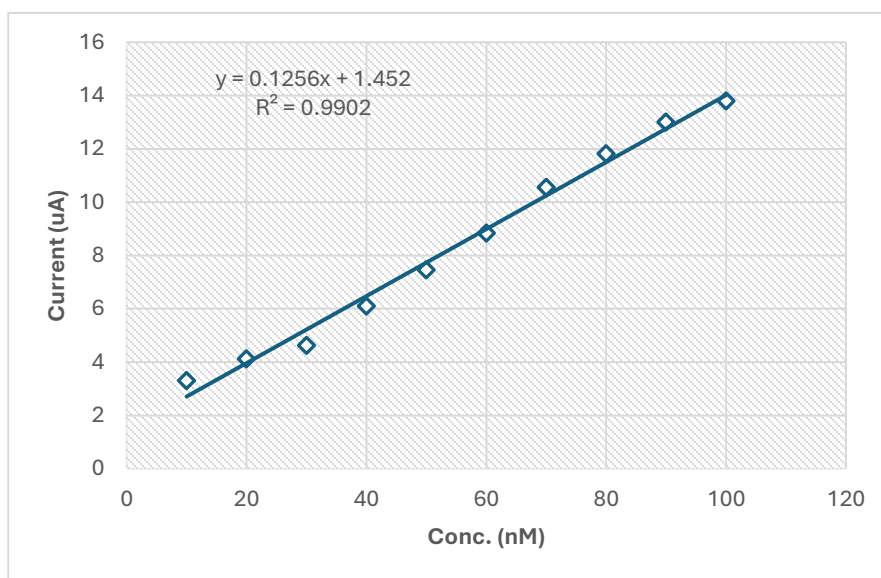
Figure 21 : Current peak of UiO-66-NH$_2$@Ppy-NWs@CoFe$_2$O$_4$ against Cu^{2+}

To optimize experimental conditions, the determination of lead was carried out utilizing differential pulse voltammetry (DPV) as a highly accurate electro-chemical technique with a low detection limit, LOD 12.75µg/L at concentration 10-100nM.

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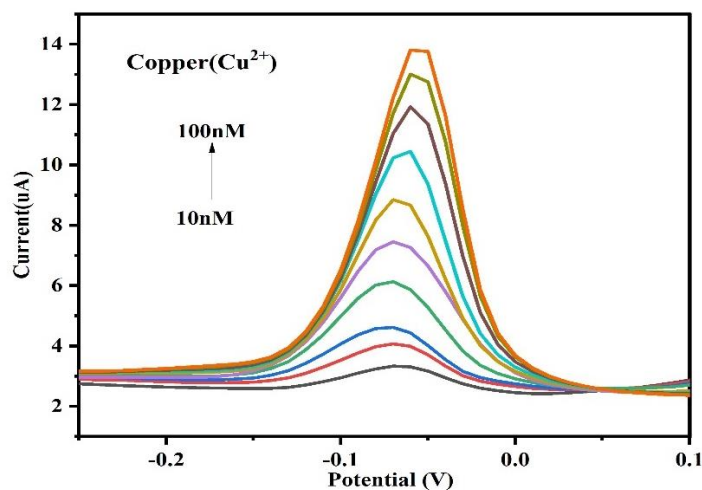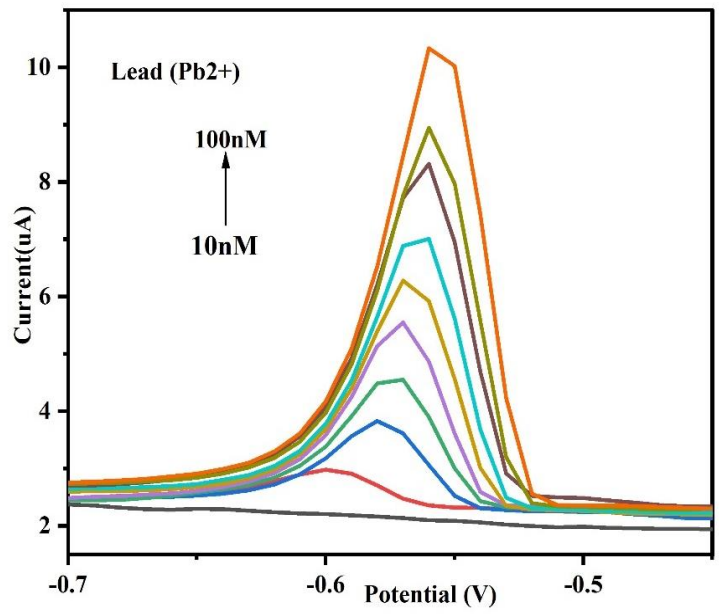Figure 22 : DPV of UiO-66-NH$_2$@Ppy-NWs@CoFe$_2$O$_4$ electrode against Pb^{2+}ions
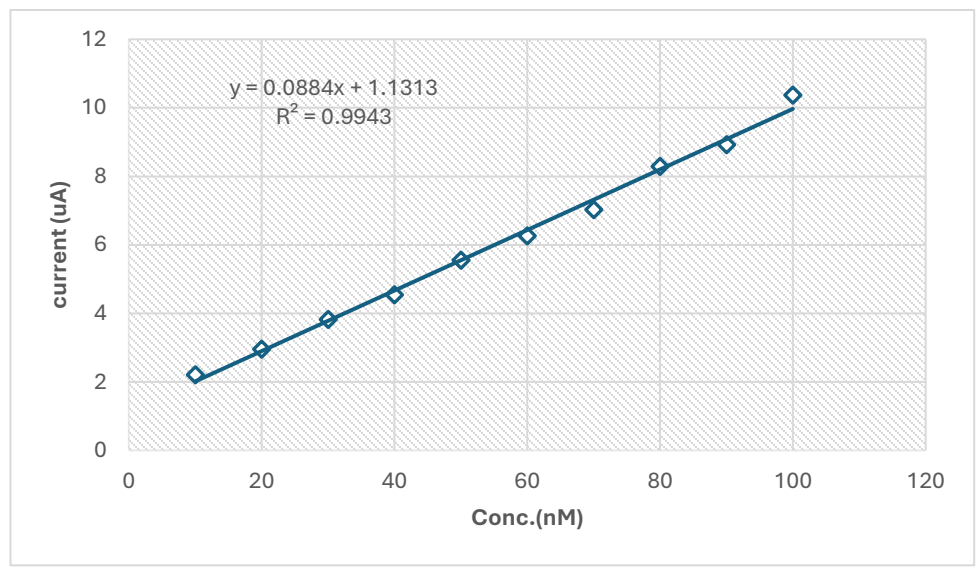
Figure 23 : DPV of UiO-66-NH$_2$@Ppy-NWs@CoFe$_2$O$_4$ electrode against Pb^{2+}

Chapter 5

Conclusion

This thesis presents synthesis of UiO-66-based NH_2@Ppy-NWs@$CoFe_2O_4$ using microwave for an advanced and conducting nanocomposite. The formation of this multi-faceted composite was from a step-wise synthesis strategy. The method followed for the synthesis was, synthesis of PpyNWs (polypyrrle nanowires), Cobalt ferrites $CoFe_2O_4$ and UiO-66-NH_2 with assistance of microwave. Thorough validation of the synthesis carried out through X-ray diffraction (XRD) authenticated the structural integrity of the composite. The conductivity of the UiO-66-NH_2@Ppy-NWs@$CoFe_2O_4$ composite was established to be advanced in the studies conducted through electrochemical strategies cyclic voltammetry (CV). These results signify its usage over a wide range of electroanalytical applications. The detection in the effective estimation of lead and copper ions by the composite, proved by differential pulse voltammetry (DPV) was exceptional and established the scope for the nanocomposite in environmental estimation and decontamination. The utilization of microwave-assisted synthesis distinguishes this study, offering a rapid and efficient method for producing advanced materials.

The research offers significant input in the field of electrochemical sensing by showing the adaptability and effective synergistic composites synthesized through microwave methods. The given findings advance not only the understanding of these materials but also open the avenue to conceive innovative solutions in electroanalytical chemistry.

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