Chapter 1

Introduction

1.1 Background

Water is the most precious gift from the nature, and it is essential for a long and healthy existence. India is a large and densely populated country and its economy is largely based on agriculture. Industrialization has potential to become a dominant component of the economy, displacing agricultural production. The practice of discharging untreated industrial waste into rivers and other water sources is endangering the traditional livelihoods of occupational groups. These unmanaged disposals have a severe influence on local natural resources and have long-term consequences. A large number of industrial units' release wastewater into the environment without treatment. The contamination of water has an impact on the environment. Living organisms acquire heavy metals from industrial wastes in their tissues, especially in human beings. Industrial waste can be reactive, corrosive, flammable or hazardous, depending on its composition. Typhoid, dysentery and cholera are caused by untreated sewage that is dumped into rivers without being treated beforehand. Natural elements and plant supplements, such as nitrate and phosphate, encourage the growth of algae on the water's surface by stimulating the production of oxygen. Eutrophication is caused by algal blooms, which lower the amount of oxygen in the water. It is detrimental to the aquatic ecology. Drinking water of high quality is the most basic necessity for people all over the world, yet even this basic need has not been addressed due to environmental contamination caused by the usage of heavy metals in manufacturing. Heavy metals have atomic weights ranging from 63.5 to 200 and a specific gravity of more than 5. Even at low concentrations, they are a source of concern due to the substantial risk they pose to the environment and human beings health. The primary source of pollution that affects people all around the world is industrial wastewater [1]. Heavy metals have drawn concern since they are non-biodegradable, harmful and even persistent for a long time in the environment. These heavy metals are highly soluble in water that are consumed by fish and vegetables and finally get accumulated in the body of human beings and animals through the food chain [2]. Furthermore, natural resources have been polluted by mixing of industrial pollutant discharge into fresh water which ultimately causes the lack of clean and fresh water even in areas with an abundance of water [3]. Due to their frequent occurrence in wastewater and toxicological profile, hazardous heavy metals such as copper (Cu), zinc (Zn) and nickel (Ni) must be removed from aqueous solutions. These issues have received much interest in recent years because heavy metals in wastewater can be absorbed quickly by marine animals and then reach the human food chain, providing a considerable health concern. Table 1.1 depicts the permissible limit for each metal in drinking water [4].

Table 1.1: Permissible limit (mg/ L) of Copper, Nickel and Zinc in drinking water [5]–[7]

Standard	Copper	Nickel	Zinc
WHO	1.0	0.02	5.0
BIS (Desirable limit)	0.05	0.02	5.0
BIS (Permissible limit in absence of alternate source)	15	No relaxation	15.0
USEPA	1.3	0.1	5.0
ICMR	1.5	0.02	0.10
CPCB	1.5	-	15.0

Among heavy metals, Ni, Cu and Zn belong to the fourth period of the periodic table. Due to industrial contamination, their concentration is steadily increasing, resulting in significant health problems. Cu is typically present predominantly in wastewater as it is regarded as the most desirable and widely used metal in several industrial applications like metal processing, electroplating and etching. Cu is non-biodegradable and therefore bio-accumulate in animals and plants. As a result, Cu-contaminated wastewater must be treated before it may be released into the natural environment [8]. Similarly, Zn is an important metal and a part of the human diet, with a recommended daily consumption of 10 to 20 mg, but an excessive amount of Zn can cause a variety of chronic disorders. Workers exposed to Zn fumes in galvanizing unit suffer from high fever and mouth dryness. Ni is a common component in meteorites along with iron and can even be present in crops, livestock and seawater in tiny amounts [9]. Its prominent use is in alloying-especially with chromium and other metals to develop steels that are stainless and heat-resistant [10], [11].

1.2 Sources of Heavy Metals

Sources of toxic pollutants may be natural (volcanoes, earthquakes) or anthropogenic. The primary sources of Ni contamination in water bodies are pipes and fittings, Ni ore bearing rocks, metallurgical and steel industries, combustion of coal and volcanic eruptions [12].

Table 1.2: Concentration (mg/ L) of copper, nickel and zinc in various industrial discharge

Industrial Discharge	Copper	Nickel	Zinc	References
Galvanization	0.009	0.05	18.1	[13]
Pharmaceutical	0.08-0.38	-	1-1.3	[14]
Textile	0.007-0.15	-	-	[14]
Tannery	0.018-0.26	-	-	[14]
Electroplating	4.5	-	4.2	[14]
Dye	3	-	5	[14]
Electroplating	1.45	3.01	0.03	[15]
Chrome containing wastewater	35	78	-	[16]
Effluent from plating industry	1.1	0.5	-	[16]
Electroplating	23.6	54.8	-	[17]
Plating (Acid rinse)	15.52	12.32	-	[18]
Plating (Nickel rinse)	0.2	1.06	6.4	[18]
Electroplating	20.54	-	7.17	[19]

The concentration of Ni in industrial effluent discharging into potable water bodies ranges from 2-900 mg/L [20]. Contamination due to Cu is of huge concern in agricultural lands due to the adverse impact on its fertility. Main sources of Zn contamination in various water bodies are effluent discharged from metal processing and alloy industries, metallurgical units, disposed Zn manganese batteries and electric utilities [21].The effluent emanating from mining and metallurgical unit, steel and coal combustion plant, paint and pigment industry contains very high level of Zn [22]. Table 1.2 reveals the concentration of Ni, Cu and Zn discharges from various industries.

1.3 Heavy Metals Exposure and Poisoning

Ni is responsible for cancer of the kidney and lung. Zn causes fatigue, lethargy, neurological symptoms, dizziness and increased thirst [23] and finally, Cu is genotoxic, induces alopecia and damages the liver or kidney [24]. Other health issues associated with Ni intake in human beings include dermatitis, nausea, chronic asthma, coughing, nephrotoxic, hemolysis and anaphylaxis [25]–[27]. Cu overdose leads to its accumulation in liver, kidney, pancreas and brain which ultimately leads to death. Other adverse effects of Cu poisoning in human beings includes gastrointestinal distress and geno-toxicity [28]. Excessive exposure of Zn results in mental depression, neurological disorders and polydipsia.

1.4 Mechanism of Heavy Metals Toxicity

Toxicity is a term that refers to the extent to which a substance can harm an organism. The mechanism of Cu, Ni and Zn toxicity have been discussed below.

It has been reported that Cu ions, such as cupric (Cu^{2+}) and cuprous (Cu^{+}) have been involved in forming reactive oxygen species (ROS) and these ions are capable of participating in both oxidation and reduction reactions. It is possible to reduce Cu^{2+} to Cu^{+} in the presence of glutathione (GSH) or ascorbic acid and then Cu^{+} catalyze the breakdown of H_2O_2 to generate OH by the Fenton reaction [29]. The OH radical has the capability of interacting with a variety of biomolecules.

$$Cu^{+} + H_2O_2 \rightarrow Cu^{2+} + OH^{\bullet} + OH^{-} \tag{1.1}$$

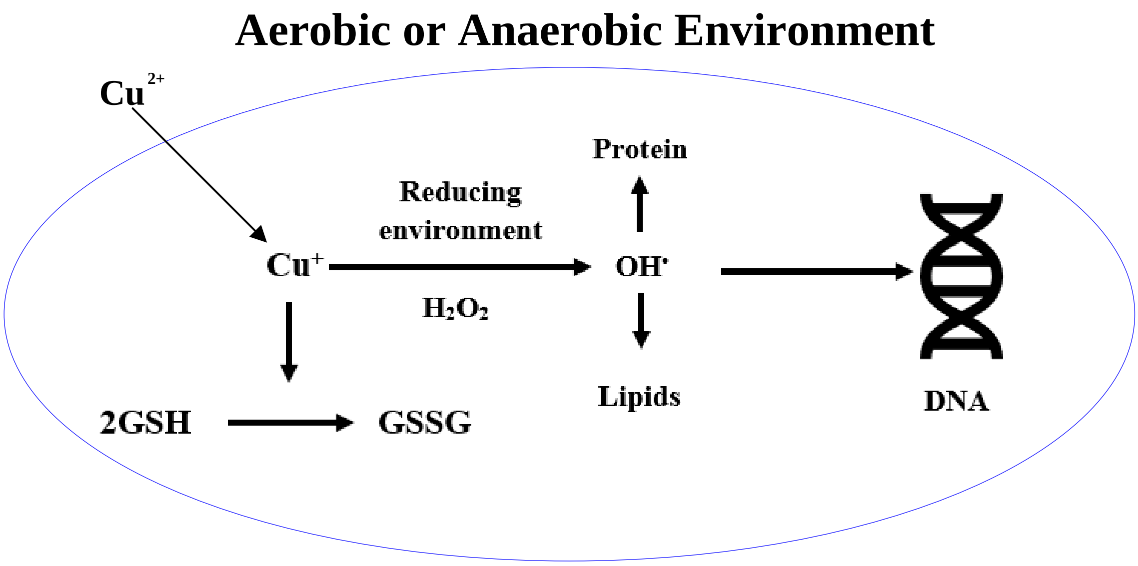


Figure 1.1: Copper toxicity and its mechanisms of action

As shown in Figure 1.1, Cu enters the bacterial cell through a variety of routes. A reduction state in the cytoplasm reduces Cu to Cu^{+}, which can be subsequently engage in Fenton type reactions, resulting in the formation of extremely reactive hydroxyl radicals. Nucleic acids and lipids are among the substances that can react nonspecifically with these radicals. Cu^{+} can also cause thiol depletion in the GSH pool, proteins and free amino acids [30]. Cu has the ability to cause DNA strand breakage and base oxidation through the usage of oxygen free radicals [31]. While Cu-induced oxidation of low density lipoprotein (LDL) has not been shown in vivo, in vitro studies have successfully established Cu-induced LDL oxidation [32].

Nickel promotes carcinogenesis by a variety of mechanisms, including transcription factor regulation, directed gene expression and the formation of free radicals. Ni has been demonstrated to control the expression of long non-coding RNAs, as well as messenger RNAs and microRNAs. Ni has been shown to enhance methylation of the promoter and to stimulate the downregulation of maternally expressed gene 3 (MEG3), resulting in the upregulation of hypoxia-inducible factor-1α (HIF-1α). These two proteins are associated with carcinogenesis (Figure 1.2) [33]. Ni is known to produce free radicals, which have been linked to the development of cancerous diseases [34].

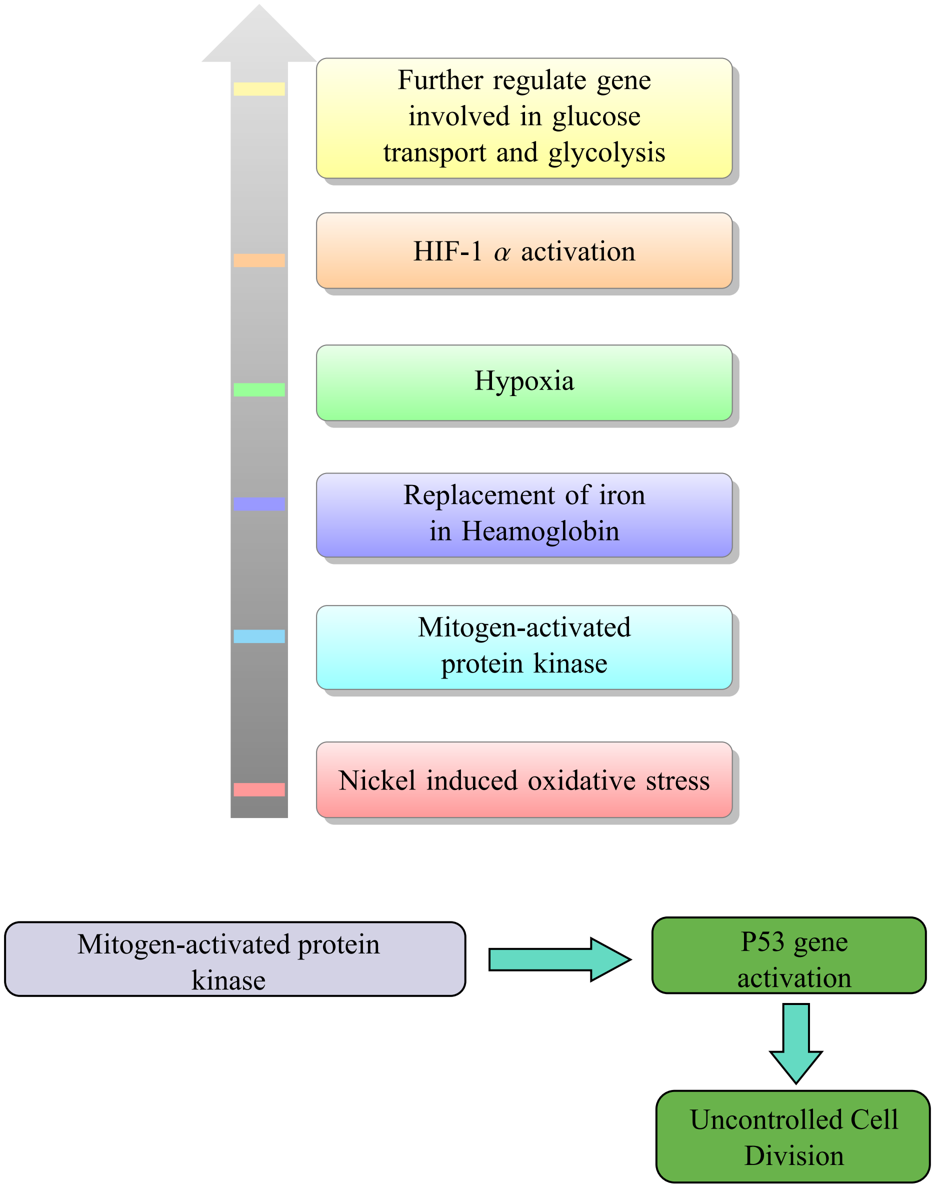
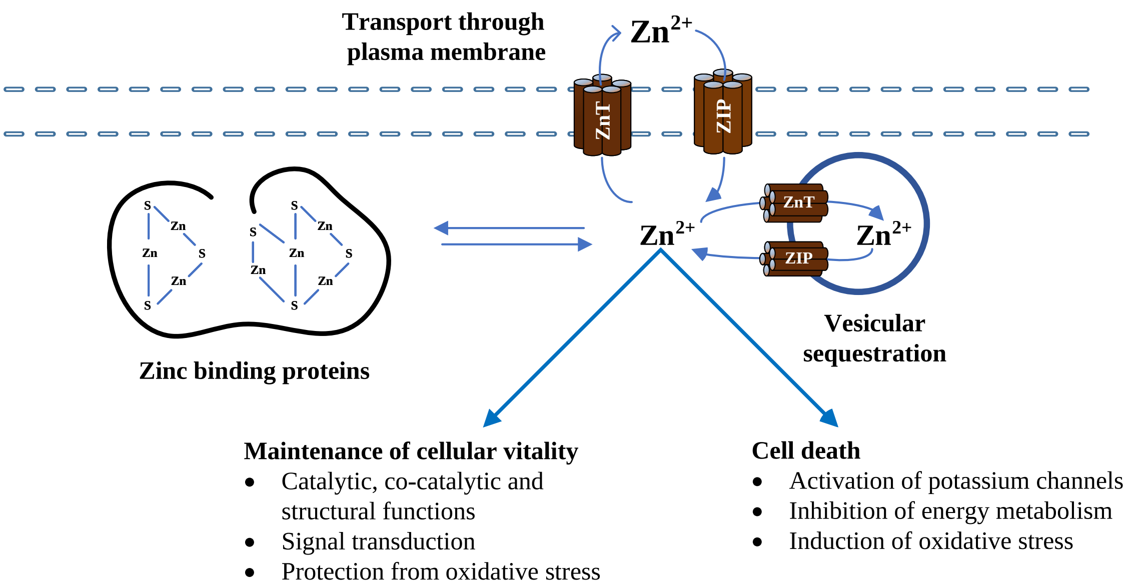
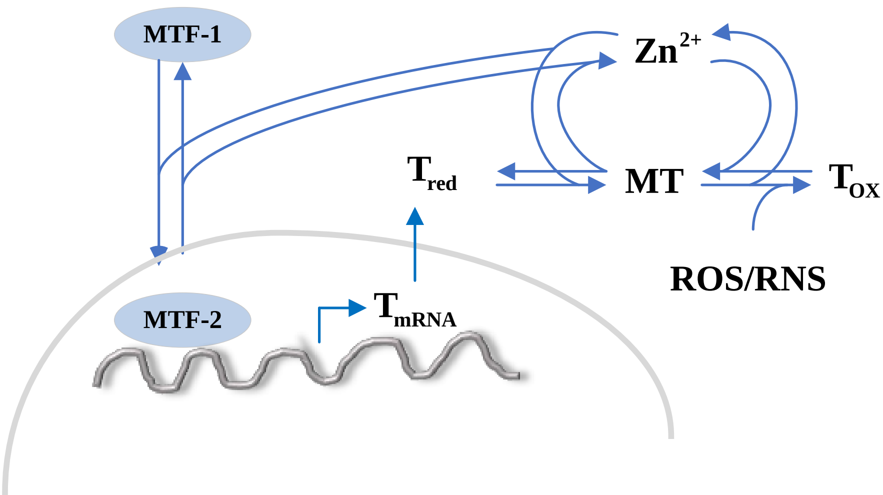


Figure 1.2: Nickel-induced oxidative stress

At the cellular level, Zn is found in the nucleus in concentrations ranging from 30 to 40%, in the cytosol it is 50% and remaining portion is found in membranes [35]. Cellular Zn is required for effective homeostatic regulation, which avoids excessive Zn buildup (Figure 1.3a). The zinc importer (Zip) and zinc transporter (ZnT) families both play a function in cellular Zn homeostasis. Zip family consists of fourteen Zn-transporting proteins to transport Zn to cytosol. ZnT family consists of ten proteins that are involved in the transfer of Zn from cytosol to extracellular space [36]. Eventually, metallothioneins (MTs) play a critical role in Zn homeostasis by forming complexes approximately to 20% of intracellular Zn (Figure 1.3b) [37], [38]. MTs have been shown to be involved in the regulation of Zn homeostasis. MTs are proteins with molecular weight of 6-7 kDa that are widely distributed and have a high cysteine content and also possesses an ability to complex with metal ions. Up to seven Zn ions can be bound by a single MT molecule. It can act as a cellular Zn buffer over a wide concentration range due to the various affinities of the metal ion binding sites [39].



(a) Major pathways involved in maintaining zinc homeostasis in the cell



(b) Important roles played by the metallothionein

Figure 1.3: Regulation of zinc homeostasis in cells and its effects on cytotoxicity

Figure 1.3a demonstrates three major pathways are involved in maintaining Zn homeostasis in the cell. First, importers from the Zip-family export proteins from the ZnT-family and are transported across the plasma membrane. Secondly, metallothionein, a Zn-binding protein is involved in the process. In a third instance, transporter-mediated sequestration within intracellular organelles such as the Golgi apparatus, endoplasmic reticulum and lysosomes is accomplished. It is necessary to maintain rigorous control over Zn homeostasis in order to maintain cellular viability, whereas dysregulation results in the cell death.

The metallothionein/thionein-system plays a vital function in maintaining intracellular Zn homeostasis Figure 1.3b. The apo-protein thionein (Tred) binds Zn ions, both free and loosely bound, culminating in the production of MT. When free Zn ions are available in large amounts, they can bind to the Zn finger structures of the metal-regulatory transcription factor (MTF)-1, causing the protein thionein to be expressed. Furthermore, thiol oxidation by reactive oxygen (ROS) or nitrogen (RNS) species results in the creation of the oxidised protein thionein (Tox), which releases Zn as a byproduct [40].

Uncertainty exists over Zn's precise role in regulating apoptosis (cell death). Many studies proven that Zn can have either a pro- or anti-apoptotic effect depending on its quantity and that both Zn deprivation and excess can cause apoptosis in the same cell line [41]–[44]. In different tissues and cell types, elevated intracellular Zn levels have shown to induce apoptosis [44]–[46].Several investigations have shown that intracellular Zn accumulation, whether from exogenous delivery or release from intracellular reserves via ROS or RNS, activates pro-apoptotic molecules including p38 and potassium channels, resulting in cell death [44], [47]–[49]. Increased Zn concentrations within cells have the potential to trigger cell death by interfering with the cells' energy metabolism [50], [51].

1.5 Heavy Metal Removal Technologies

There have been extensive studies of several physicochemical methods, including ion exchange and membrane filtration, as well as photochemical and electrochemical processes, coagulation and flocculation, in the past (Figure 1.4) [8] However, the majority of these methods are expensive, time-consuming and generates secondary chemical sludge as a result of their use.

The disposal of secondary chemical sludge in environment is another critical issue. On the contrary, adsorption technique has gained exceptional attention by scientists in the last few decades [52]. Adsorption is particularly concerned for removal of heavy metals due to its high efficacy, ease of handling/ use, reliability and the availability of various materials as adsorbents [53]. Adsorption has been observed to be inexpensive and more effective than other chemical techniques in the recent years [54].

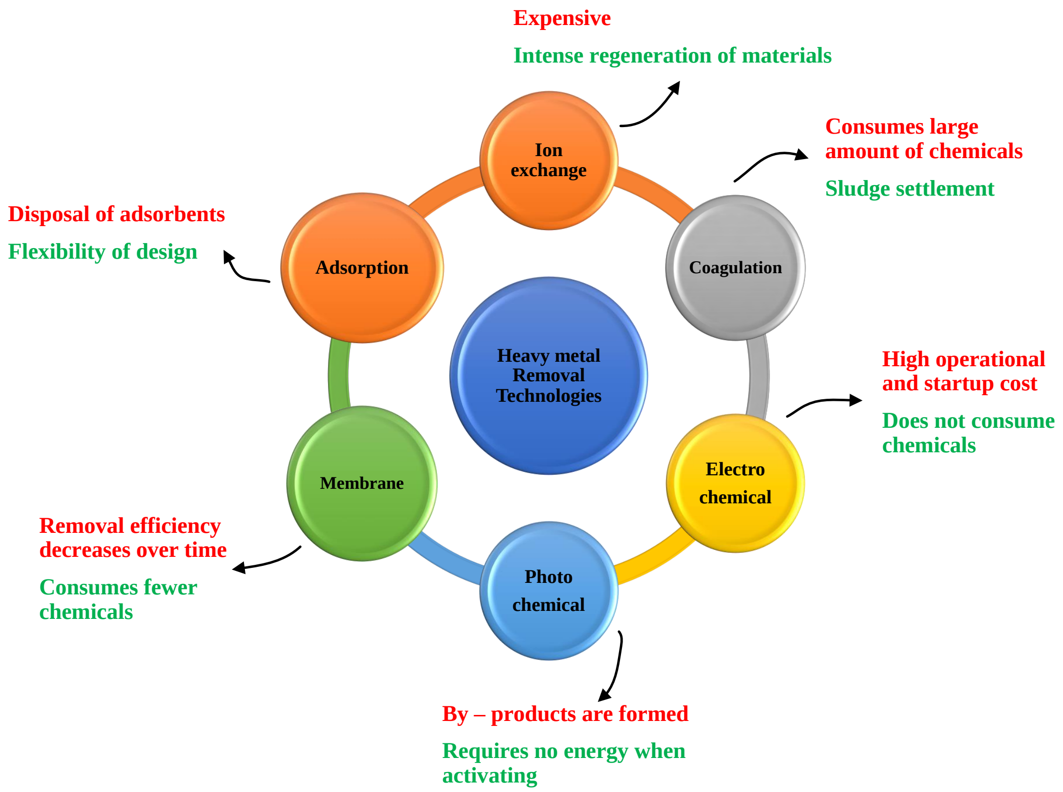


Figure 1.4: Removal technologies for heavy metals from contaminated water

Low cost, significant decrease in chemical and biological sludge production and high efficiency are the benefits of the adsorption [55]. The binding of metal ions on the surface of adsorbents relies on the chemical species of metal ions (charge and size), type of biomass and environmental conditions (pH, temperature) [56].

Natural materials which are abundantly available and agro-waste have the potential for becoming an inexpensive adsorbent. It is commonly known in the industry that the use of activated carbon for the adsorption of heavy metals is a quick and efficient method of removal. Additional chemicals (acids and bases) may also be required to improve the effectiveness of adsorption in wastewater. Due to these limitations, a more efficient approach must be taken that should not only be less costly but also more productive. Adsorption based on natural resources demonstrates a more efficient process with low operating costs.

1.6 Motivation

Heavy metals are toxic and have a detrimental effects on the health of millions of people all over the world. A large number of researchers are working on finding ways to remove them from contaminated water. Metal working and electroplating industries, which discharges heavy metals into its effluents, including Ni, Cu and Zn that have been identified as a major source of concern for the human beings health and aquatic life in the past few decades.

Cu is extremely dangerous due to the fact that it is not biodegradable and is carcinogenic. Cu has been found to induce neurotoxicity, also known as Wilson's disease and kidney failure in human beings. Ni exposure causes skin irritation, damage to the lungs, injury to neurological system and impairment in mucous membranes. Zn poisoning as a result of excessive intake is rare, however it can result in gastrointestinal discomfort and diarrhoea in some cases.

Heavy metal pollution must be reduced to a level of a few parts per million or less in order to retain compliance with existing wastewater and drinking water requirements, according to the current regulatory framework. Heavy metal concentrations in wastewater can be reduced by employing a range of treatment strategies, that can be discussed in this study. While some studies employ precipitation, coagulation methods, others are investigating adsorption technique. However, treatment by precipitation or coagulation procedure results in secondary pollution and raises the expense of sludge handling. As a result, this approach is not advised for heavy metal removal.

Adsorption using inexpensive adsorbents is an environmentally friendly and cost-effective technology that many researchers are investigating to address the issue of heavy metal toxicity. According to the literature review, there is a need for a method that is not only inexpensive but also does not contaminate the environment again. Numerous novel adsorbents are used in this study to remove Cu, Ni and Zn from contaminated water. Novel adsorbents seems to be an efficient solution to address this issue and ensure that people drink pure, contaminant-free water as soon as possible to avoid being afflicted by the threatening problem of heavy metal poisoning.

1.7 Objectives of the Present Work

Numerous approaches have been investigated and reported in the literature, but the majority of them are hindered from being implemented in practice due to a number of technological limitations. The development of a more environmentally friendly approach for providing heavy metal-free and pure drinking water is required. The main objective of this research was to remove copper, nickel, and zinc from contaminated water using novel adsorbents, which was accomplished in this context. The present study was planned to conduct via batch adsorption of copper, nickel and zinc onto novel adsorbents.

Additionally, the study was expanded to examine the effect of operating conditions in a batch study. Thus, the main objective was broken into various individual objectives, which are shown below.

1. Characterization of novel adsorbents
2. Adsorption of copper, nickel and zinc using novel adsorbents
3. To study the effects of operating parameters (pH, adsorbent dose, initial concentration, temperature and contact time)
4. To study the adsorption kinetics, adsorption isotherms and thermodynamics for each of the above cases
5. Utilization of dimensionless numbers to study adsorption dynamics
6. Artificial Neural Network Modeling
7. Regeneration of spent adsorbent

1.8 Thesis Outline

This work is summarily outlined in chapters as mentioned below:

Chapter 1: Sources of exposure, heavy metal poisoning, toxicity mechanisms, and removal technologies were discussed after an overview of the entire work.
A glance at copper, nickel and zinc contamination was followed by a description of the fundamental aims of this work and finally, the thesis structure was given.

Chapter 2: A thorough review of the literature was discussed. This chapter covered a wide range of topics related to heavy metal contamination, allowing the reader to gain a comprehensive understanding of the topic.

Chapter 3: The materials that were used, as well as the research technique and the testing methods that were used, were all documented. The physico-chemical characterisation of the adsorbent was included in this section.

Chapter 4: The results and discussion of the adsorption study obtained by using composite material.

Chapter 5: The results and discussion of the adsorption study obtained by using *Azadirachta indica* twig ash.

Chapter 6: The results and discussions of the adsorption study obtained by using activated carbon.

Chapter 7: The results and discussion of the adsorption study obtained by using mould.

Chapter 8: Comparison of novel adsorbents, desorption and application of spent adsorbent were discussed in this chapter.
This chapter compares various adsorbents, with the goal of determining which adsorbent works better in less time and with a higher percentage of removal from the solution.

Chapter 9: A critical analysis has been made about the most important findings and conclusions. The experimental results of novel adsorbents have been described in this chapter.

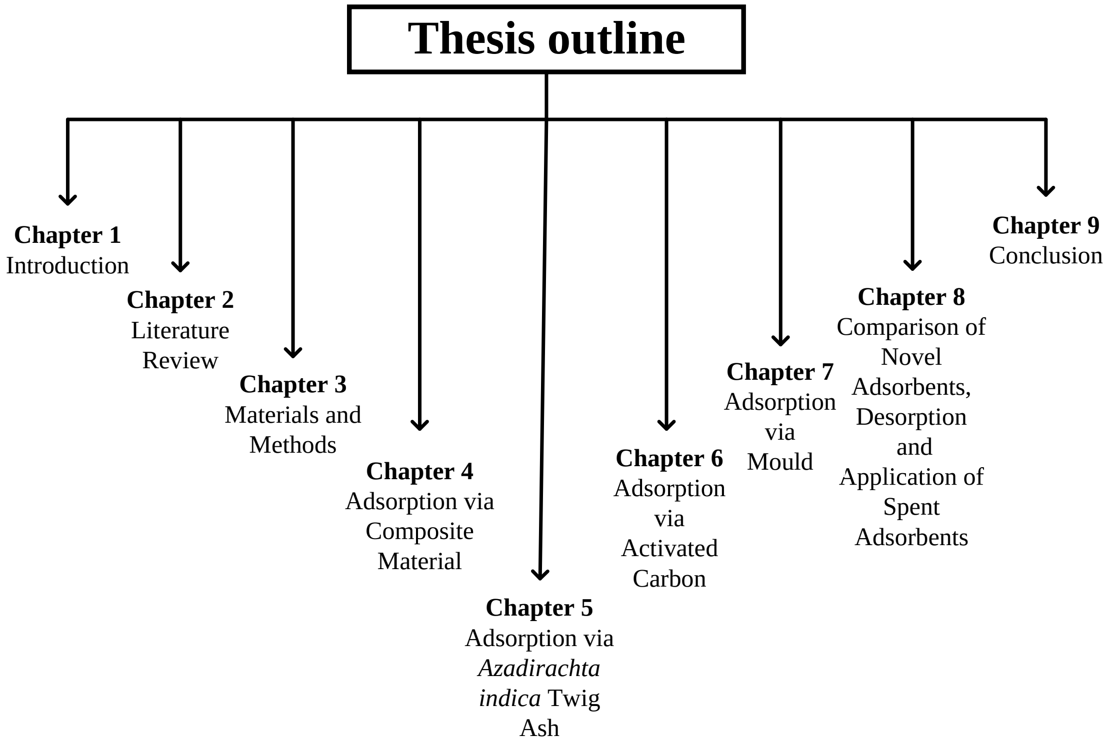


Figure 1.5: Outline of this work