

Chapter 2

Literature Review

2.1 Background

Water contamination is a major global issue that affects everyone. It has been stated that it is the most common source of illness and misery in human beings, and that it is responsible for the deaths of more than 14,000 people every day in the world [57]. Groundwater pollution is defined as, modification in physical, chemical and biological characteristics of water, which may cause detrimental effects on human and aquatic biota [58]. Environmental pollution as a result of technological advancements in current industrial activity is one of the most critical challenges of the twenty-first century. Significant attention has been drawn to the issue of the contamination of water resources by hazardous substances in this context. This is mostly owing to the hazardous and chronic health consequences of these substances.

At the moment, water resources are the most mismanaged natural system since man firstly stepped on the earth. Water contamination is gradually increasing as a result of rising population, industrial exploitation, urbanisation, rising standards of living, and a diverse range of human activities.

It is possible that the day will not be far away when clean and pure water will be in short supply in highly populated industrialised water-limited areas, making it impossible to maintain normal living standards. It is difficult to restore the aquatic water quality after

groundwater pollution has occurred since contamination is often irreversible once it has occurred. Due to their toxicity, the majority of heavy metals are categorised as hazardous contaminants. Certainly, the presence of dissolved heavy metals in the environment represents a significant health hazard for the general public. They accumulate in living tissues at all levels of the food chain, with humans occupying the pinnacle of the food chain [59]. Heavy metal ions must be removed from wastewater due to their severe toxicity towards aquatic life and humans. Environmental demands have resulted in tougher rules regarding the limit of metal discharges, particularly in the developed countries. This necessitates limiting heavy metal release into the environment.

Everybody knows that metals are essential for the normal functioning of living beings; they are required for sustenance and have a physiological purpose, respectively. Although its accumulation in the environment over certain concentrations is one of the most serious global environmental hazards. Numerous sectors, including mining, tannery, fertilizer, batteries, electroplating, and paper manufacturing, have expanded tremendously in recent years, leading to contamination. Biological accumulation of Ni, Cu, and Zn has been observed in organisms, which has the potential to lead to a reduction in the diversity of species.

Table 2.1: General information about copper, nickel and zinc with their possible toxic effects [1], [4]

Heavy metals	Nickel (Ni)	Copper (Cu)	Zinc (Zn)
MCL (mg/L)	0.2 [60]	2.0 [60]	5 [61]
Substance priority number in ATSDR	57	118	75
Atomic number	28	29	30
Atomic mass (u)	58.6934	63.546	65.38
Density (g/cm^3)	8.96	8.96	7.14
Oxidation state	+2	+1, +2	+2
Electronic configuration	[Ar] $4s^2 3d^8$	[Ar] $4s^1 3d^{10}$	[Ar] $4s^2 3d^{10}$
Appearance	silver, metallic	reddish, metallic	bluish white, metallic

Health effect	dermatitis, nausea, chronic asthma, coughing, a human carcinogen (lung cancer), destroy RBCs, nephrotoxic, anaphylaxis [25]–[27]	acute effect: Gastrointestinal distress chronic effect: liver or kidney damage, Genotoxic and alopecia [62]–[66]	depression, lethargy, neurological signs, dizziness, and increased thirst [66]–[68]
Sources of contaminant in drinking water	pipes and fittings, nickel-ore bearing rocks [69]	corrosion of household plumbing systems; erosion of natural deposits [70], [71]	coal-fired power station, by-product of steel production and from burning of waste material [71]
Techniques to remove contaminants	Adsorption Cementation Membrane Filtration Electrochemical method Photocatalysis	Adsorption Membrane Filtration Biological treatment Chemical Precipitation Ion Exchange Electrocoagulation [72]	Chemical Precipitation Ion exchange Membrane Filtration Ozonation Technique Bacterial, fungal and algal bio-sorbents [73], [74]
Uses	production of non-ferrous alloys, stainless steel, super alloys; electronic products; electroplating; food supplement [75], [76]	making of electrical wires, pipes, valves, fittings, cooking utensils, building materials and coins. Its compounds are used as wood preservative, fungicides, insecticides and algicides. Also used in electroplating, petroleum refining, food additives, azo-dye manufacturing, animals and plant growth regulator [76]	used in making of corrosion resistant alloys, as pesticides and in galvanization of steel and iron products [69], [76], [77]

2.2 Nickel

Ni is a metallic element with a silver-white, shiny appearance that occurs naturally. It is the fifth most prevalent component on earth and is widely found in the crust and core of the earth. Ni is also a prevalent component in meteorites and discovered in crops, livestock and seawater in tiny amounts [9]. It has exceptional physical and chemical properties, making it vital for various industrial products such as high melting point (1453 °C), high ductility, resistant to corrosion, helps in alloy formation and behaves like a magnet at room temperature. It is deposited by electroplating, possesses catalytic activity and has a potential to get recycled. It's greatest use is in alloying especially with chromium and other metals to develop steels that are stainless and heat-resistant [78].

Naturally, It occurs primarily as oxides, sulfides and silicates. The world produces and utilizes more than two million tons of fresh or primary Ni annually. There are many Ni ores that require a range of extraction methods. In more than 25 nations around the world, Ni-containing ores are presently being mined. Its first use is to convert Ni products into intermediate products, which are the foundation of end-use products [9]. These first-use products are further processed prior to their use. Its first use applications are in the production of stainless steel, batteries, Cu/Cr-Ni alloys and many other Ni compounds. It is used in a diverse range of end-use domains due to its exceptional physical and mechanical characteristics. End use domains such as engineering, metal goods, building and construction, transport, electronics and many others. It is fully recyclable without loss of its quality that supports circular economy models [9].

2.2.1 History

In 1751, it was initially acknowledged and isolated as an element by the Swedish chemist "Axel Cronstedt". Plates and alloys such as Ni-silver in the 19th century was brought to the fore in which they were alloyed with Cu and Zn. It was named due to its color and does not comprise of silver.

Initially, Ni alloyed with Cu, it was used to manufacture coins in the USA in 1857. At that time, It was not produced from pure Ni. Conversely, in 1881 pure It was used for

coins manufacturing in Switzerland [78]. In the beginning of the 20th century, stainless steel was discovered and Ni played a very important role in many ordinary grades. The Ni-based alloys have been identified as high corrosion and temperature resistant, making them ideal for chemical plants and jet engines.

2.2.2 Properties

Approximately 69% produced is used in the manufacturing of stainless steel. Another 15% is used in manufacturing of other steel and non-ferrous alloys-often used in aviation or military sectors with high specializations.

Table 2.2: Key characteristics of Nickel

Atomic number	28
Atomic radius	1.97 Å
Atomic weight	58.69
Block	d
Boiling Point	2730 °C
Chemical Symbol	Ni
Covalent radius	1.17 Å
Density	8.90 g/cm ³ at 25 °C
Discoverer	Axel Fredrik Cronstedt (1751)
Electron affinity	111.537 kJ/mol
Electronegativity	1.91 (Pauling scale)
Electronic shell	[Ar] 3d ⁸ 4s ²
Energy of first ionisation	735 kJ/mol
Energy of second ionisation	1753 kJ/mol
Energy of third ionisation	3395 kJ/mol
Group	10
Ionic radius	0.069 nm (+2), 0.06 nm (+3)
Isotopes	10
Melting Point	1453°C
Name	Nickel
Period	4
Standard potential	-0.25 V
van der Waals radius	0.124

Approximately 8% of total Ni produced is used for plating and another 3% is consumed

in foundries and castings. Around 3% of it is used in electronic batteries and in mobile and hybrid vehicles and round 2% is used in chemical, catalytic and coloring applications [78]. Additionally, key characteristics of Ni are shown in Table 2.2 [9], [79].

2.2.3 Nickel's presence in the Environment

Most of the Ni is unapproachable on earth, as it is locked into the iron-Ni molten core of the earth. Around 8 billion tons of it is thought to be dissolved in the ocean. Because organic matter can absorb metal; coal and oil both contain significant amounts of it. In clay and loamy soils, the Ni content is 0.2 mg/L or 450 mg/L. The average is approximately 20 mg/L, which is another prolific source of nickel [80], [81].

It is found in millerite in association with sulphur, in niccolite in combination with arsenic, and in Ni glance in combination with arsenic and sulphur. The iron Ni sulfides such as pentlandite are the most important ores from which it is extracted. In 2017, the world produced 2.1 metric tonnes of Ni. Philippines, Russia, Canada, New Caledonia, Indonesia, Australia, and Brazil are the top Ni producers [80], [82].

2.2.4 Health Effects

It is naturally found in trace amounts in foods and abundant in chocolate and fat. It's consumption is increased when individuals consume a significant amount of vegetables grown in polluted soils. Plants and vegetables accumulate it in large quantity. Smokers are more susceptible for uptake Ni through their lungs. Detergents also contains tremendous amount of Ni. Human beings are exposed to it by air, potable water, food or smoking. One is also exposed when skin comes in contact with Ni-contaminated soil or water. It is important in small quantities (25-35 µg/day) [83], but it may pose a risk to human health if intake is too high (170 µg/day) [84].

The following complications could be developed if too much Ni is taken [79], [85]:

1. Higher probability of lung, nose, larynx, and prostate cancer
2. Ni gas exposure results in sickness & dizziness

3. Lung embolism
4. Heart disorders
5. Allergic responses such as skin rashes, primarily from jewelry
6. Asthma and chronic bronchitis
7. Birth defects

Ni fumes are a respiratory irritant and can cause pneumonitis in some people. Its exposure and components have the potential to cause a dermatitis known as Ni itch in persons who are sensitive to it [85]. The first symptom is typically itching that lasts up to seven days before the skin eruption occurs. When an erythematous or follicular skin eruption occurs, it is followed by an ulcer that lasts for a long time.

It's exposure may occur by handling Ni-containing items (including jewelry or coins) or by the intake of contaminated food. This does not have a significant adverse effect on health in most of the instances, although it will depend on the type of Ni compounds one is exposed with. Certain compounds (but not the sheer metal itself) are considered to be carcinogenic-most of them are lung cancer [86].

It has been identified as carcinogenic in the National Toxicology Program (NTP). The International Agency for Cancer Research (IARC) list Ni compounds in group 1 (adequate proof for human carcinogenicity) and in group 2B (substances that may be carcinogenic to humans) [87]. Ni is reported to be human carcinogen in the American Conference of Governmental Industrial Hygienists (ACGIH) intended notice as a Category A1 [79], [85].

2.2.5 Environmental Impacts

It is released into the atmosphere by trash incinerators and power plants. After reacting with raindrops, it settles down or falls to the ground of its own accord. In most cases, it takes a significant period of time for contaminants to be eliminated from the air. When it is present in wastewater streams, it has the potential to possibly end up in surface water. In the environment, the majority of the nickel and its derivatives that are discharged adsorb on sediment or soil particles and remain immobile at the end [79]. Ni, on the other hand, is more mobile in acidic soils and is washed away into the ground water. In the case of

creatures other than humans, there is little information available on the impacts of nickel [81]. The elevated levels of Ni in sandy soil harm crops, and elevated Ni level in surface water reduce algae growth [79].

Microorganisms can also experience growth inhibition as a result of Ni exposure; however, they often develop resistance to Ni over a period of time. It is a necessary nutrient for animals in trace concentrations. But, it is not only beneficial as an essential element; it can also be dangerous if the maximum permissible concentration (0.02 mg/L, according to WHO) is exceeded. As a result, a range of different types of cancer (lung cancer and nasal cancer) can develop in humans, with the most severe cases occurring in people who live near refineries [79].

2.3 Copper

2.3.1 Background

It occurs naturally in a variety of environments, both as a pure metal in basaltic lavas and in reduced form such as chlorides, sulphides, arsenides, and carbonates. It is found in combination with other elements in a number of minerals like chalcocite and malachite. It acts as an oxygen transporter in the hemocyanin of blue-blooded mollusks and crustaceans similar to iron's role in the hemoglobin of red-blooded animals. As a trace metal found in humans, aids in the catalysis of haemoglobin synthesis. The world's largest known deposit of porphyry Cu is located in the Chile's Andes Mountains [88].

It is mostly produced commercially through smelting or leaching, followed by electrodeposition from sulphate solutions. A large portion of Cu is used in the electrical industry while the rest is alloyed with other metals. Additionally, it is also used for electroplating. Brass, bronze, and Ni silver are major series of alloys in which Cu is the main component. Cu and Ni alloys, particularly Monel, are extremely valuable since the two metals are fully miscible. Additionally, It is a major alloying component in aluminum bronze and coins. It is one of the most ductile metals, it is neither too strong nor very hard. It has two stable isotopes in nature: Cu-63 (69.15%) and Cu-65 (30.85%) [88].

2.3.2 History

The word derives from the Old English term *coper* which is derived from the Latin word *Cyprium aes* which denotes a metal from Cyprus. Since prehistoric times, it has been a necessary component of human life. In fact, one of human history's major ages is named after a Cu alloy: bronze. Early human beings discovered that it could be easily hammered into sheets and more intricate shapes as their skill level improved [89].

2.3.3 Properties

About 60% of Cu is used in electrical equipment, while about 20% is used in construction, such as roofing and plumbing.

Table 2.3: Key characteristics of copper

Atomic number	29
Atomic radius	1.96 Å
Atomic weight	63.546
Block	d
Boiling Point	2560 °C
Chemical Symbol	Cu
Covalent radius	1.22 Å
Density	8.96 g/cm ³ at 20 °C
Electronegativity	1.90 (Pauling scale)
Electron affinity	119.16 kJ/mol
Electronic shell	[Ar] 3d ¹⁰ 4s ¹
Energy of first ionisation	743.5 kJ/mol
Energy of second ionisation	1946 kJ/mol
Energy of third ionisation	3554.62 kJ/mol
Group	11
Ionic radius	0.096 nm (+1), 0.073 nm (+2), 0.069 nm (+3)
Isotopes	6
Melting Point	1084.62 °C
Name	Copper
Period	4
Standard potential	+0.345 V
van der Waals radius	0.128 nm

In the industrial sector, approximately 15% of it is utilized for machinery, most of which is used in heat exchangers. Only 5% of Cu is used to form alloys [90]. Its key characteristics are shown in Table 2.3. It is the primary conductor of electricity in appliances and electronic devices [91]. It is utilized in a variety of durable and ornamental applications, including Cu roofing, door hardware, railings and trim. It is employed in automobiles, aeroplanes and plumbing systems. Various other metals are included into the fabrication of shaped Cu products to enhance metal characteristics. These alloying elements impart additional qualities such as strength, ductility, durability and resistance against the corrosion [89]–[91].

2.3.4 Copper's presence in the Environment

It is widely distributed in the environment and migrates via natural mechanisms. People utilize due to its abundance in the earth's crust. It is widely utilized in industry and agriculture. Its production has increased significantly in the past few decades. As a result, the amount of contamination in the environment has increased [90].

Rivers are depositing toxic-Cu-contaminated sludge on their banks as a result of discharging metal contaminated wastewater. It can make its way in the atmosphere via the combustion of fossil fuels. In the air, it remains buoyant and sets over soil after rain [90].

It is typically found in effluents emanating from mines, industrial facilities, landfills, and waste disposal sites (Cu slag and Cu tailings) [90]–[92]. Water-soluble compounds represent the biggest threat to human health. Water-soluble Cu compounds frequently accumulate in the environment from agricultural wastewater [90].

2.3.5 Health Effects

Excessive exposure induces nasal, mouth, eye irritation, headaches, stomach pains, dizziness, nausea, and diarrhoea. Its overdose may result in renal and hepatic damage leading to death [90]–[93]. People exposed to industrial-grade Cu may experience metal fume fever, is characterized by atrophic alterations in the nasal mucous membranes. Wilson's Disease is caused by chronic Cu poisoning and is characterized by cirrhosis of the liver,

demyelization, brain damage and renal disease [90], [93].

2.3.6 Environmental Impacts

It bonds with organic molecules and minerals as it reaches the soil. As a result, it does not circulate widely and rarely enters groundwater. It can move long distances via suspended sediment or free ions in surface water. In soils, it accumulates in plants and animals [90]. That is why there is little plant diversity in close proximity to Cu-disposal factories. It has the ability to disorganize soil activity by negatively affecting the activity of microorganisms and earthworms. As a result, the degradation of organic substances is significantly slowed down. When agriculture soils become contaminated with Cu, animals absorb toxic levels that are harmful to their health. Specifically, sheep are severely harmed by its poisoning, as the effects of Cu emerge at relatively low quantities [90].

2.4 Zinc

2.4.1 Background

It is a metallic element that is bluish-white in colour and has a high lustre. It is a member of the periodic table's group IIB. It becomes ductile and malleable between 110-150 °C. At room temperature, it is crystalline and brittle [94].

Around half of metallic, it is utilized in galvanizing steel and is employed in the creation of certain alloys. It is utilized in both the creation of American pennies and in automobile industry for die casting. Zn oxide is a white pigment used in watercolors and in rubber formulations. Zn metal is contained in the majority of single tablet formulations, and it is theorized to help the skin and muscles guard against premature ageing [94].

2.4.2 History

It was known to the Romans but rarely used. There are evidences that a large-scale Zn smelter at Zawar, Rajasthan in the 1100 and 1500 century produced large amounts of Zn

concentrate [94], [95].

China started producing/ refining plenty by the end of 1500 century. Investigation on the remains of a sunken East India Company ship in Sweden in 1745 revealed that the ship was carrying thousands of pounds of Chinese Zn, and all the recovered ingots tested proved nearly pure [94], [95].

P. Moras de Respour, published a paper describing the extraction of metallic Zn from Zn oxide in 1668, inspite of being Flemish metallurgist. However, it was German chemist Andreas Marggraf who correctly identified it as a new metal [95].

2.4.3 Properties

It is widely used in various galvanization (55% of overall Zn produced) sectors, brass and bronze manufacturing ingests 16%, other alloys 21% and miscellaneous 8% [95]. The key characteristics are shown in Table 2.4.

Zinc is extensively used to galvanize iron in order to avoid rusting. Galvanized steel is utilized in the construction of automobile bodywork, street lighting posts, pedestrian barriers, and suspension bridges [94].

It is consumed in huge volumes in the manufacturing of die-castings, which are essential in numerous sectors, including automobiles, electrical and hardware units. Additionally, it is found in a range of alloys, such as brass, Ni silver and aluminum solder [94].

Zn oxide is a popular constituent in a broad variety of commodities, including paints, tyres, cosmetic products, pharmaceuticals, polymers, inks, soaps, batteries, textiles, and electrical equipment. Zn sulphide is commonly used to manufacture luminescent paints, fluorescent lights and X-ray screens [94].

2.4.4 Zinc's presence in the Environment

It is frequently found in nature. Numerous food items contain varying amounts of Zn. It is naturally found in the air, water, and soil but increasing concentrations of Zn are being added unnaturally due to human influence. In industrial operations, like mining, coal and waste combustion, and steel manufacturing, it is most commonly used as a supplemental

Table 2.4: Key characteristics of Zinc

Atomic number	30
Atomic radius	2.01 Å
Atomic weight	65.37 g.mol ⁻¹
Block	d
Boiling Point	907 °C
Chemical Symbol	Zn
Covalent radius	1.20 Å
Density	7.11 g/cm ³ at 20 °C
Discoverer	Andreas Marggraf (1746)
Electronegativity	1.65 (Pauling scale)
Electronic shell	[Ar] 3d ¹⁰ 4s ²
Energy of first ionisation	904.5 kJ/mol
Energy of second ionisation	1723 kJ/mol
Energy of third ionisation	3832.69
Group	12
Ionic radius	0.074 nm (+2)
Isotopes	10
Melting Point	420 °C
Name	Zinc
Period	4
Standard potential	-0.763 V
van der Waals radius	0.138 nm

ingredient. The soil samples from Zn mine or processing facility, an industrial sewage sludge facility, where it is used as a fertilizer contain tremendous amount of Zn [94].

2.4.5 Health Effects

It is a trace element that is necessary for the human body. Individuals who do not consume enough Zn may have a loss of appetite, reduced sensations of taste and smell, delayed wound healing, and skin ulcers as a result of their deficiencies. Its deficiency can result in birth defects in some cases [94].

While humans can handle relatively high Zn levels, an overabundance can result in major health concerns like stomach cramps, skin irritations, nausea and anemia. Levels that are too high can cause havoc on the pancreas, impair protein metabolism and result in

arteriosclerosis. Zn chloride exposure for an extended period of time can cause respiratory difficulties [94].

Zn pollution at the workplace can result in metal fever, which is similar to the flu. This is a transient condition produced by over sensitivity [94].

It may be toxic to unborn and newborn infants. When a women absorb excessive amounts of Zn, their infants may be exposed to it via their mother's blood or milk [94].

2.4.6 Environmental Impacts

Its production is still growing over the world. This simply indicates that an increasing amount of Zn is released into the environment. Its presence in huge amount in the wastewater of industrial units pollutes the water. This effluent has not been sufficiently cleaned. The effect of this is that Zn-polluted sludge is being deposited on the banks of rivers. It can also make water more acidic. When fish reside in contaminated streams, their bodies can collect Zn. It can bio magnify up the food chain when it enters the bodies of these fishes and also, it is abundant in soils. If agricultural soils are contaminated with Zn, animals will absorb high quantities of it that are hazardous to their health. It is water-soluble and found in soils can contaminate groundwater. Zn poses a harm not just to cattle, but also to plant species. Its accumulation in soils causes plants to frequently consume an amount of Zn that their systems are unable to handle. Only a few plants have a possibility of surviving in Zn-rich soils. That is why plant diversity near disposable facilities is limited. It poses a major danger to farmland production due to its impacts on plants. Despite this, Zn-rich manures are still used. Finally, it can cause soil activity to be disrupted by interfering with the activities of microorganisms and earthworms in the soil. As a result, it is possible that the degradation of organic matter will be markedly slowed.

2.5 Techniques for removal of copper, nickel and zinc from contaminated water

The maximum contaminant level of Cu, Ni and Zn is shown in Table 2.5.

Table 2.5: Permissible limit (mg/ L) of Copper, Nickel and Zinc in drinking water [5]–[7]

Standard, Country	Cu	Ni	Zn
World Health Organization, The United States of America	1.0	0.02	5.0
Bureau of Indian Standards, India (Desirable limit)	0.05	0.02	5.0
Bureau of Indian Standards, India (Permissible limit in absence of alternate source)	15	No relax- ation	15.0
United States Environmental Protection Agency, The United States of America	1.3	0.1	5.0
Indian Council of Medical Research, India	1.5	0.02	0.10
Central pollution Control Board, India	1.5	-	15.0

A significant number of industries discharge metal-containing effluents that exceed the permissible limit [5]–[7]. As a result, it becomes important to remove heavy metals from industrial effluent before discharging it into rivers that contaminate river water. There have been several convectional approaches to the removal of Cu, Ni, and Zn from wastewater. These include ion exchange, chemical precipitation, electrochemical methods and adsorption.

2.5.1 Ion Exchange

The principle of ion exchange is based on the reversible exchange of ions between the solid and liquid phases [96]. The mechanism begins with ion exchange reactions, followed by physical absorption of the heavy metal ions and formation of a complex between the counterion and the functional group. Finally, hydration happens at the solution's surface or within the pores of the adsorbent [97]. The cost of a conventional ion exchange system for treating wastewater is too expensive [98].

Revathi et al., 2011 [99] evaluated the cationic exchange resin's ability to remove Cu^{2+} , Ni^{2+} and Zn^{2+} ions from simulated electroplating rinse water (Ceralite IR 120). At optimal experimental conditions, the Langmuir model predicted a maximum adsorption capacity of 109 mg g^{-1} for Ni^{2+} , 164 mg g^{-1} for Cu^{2+} and 105 mg g^{-1} for Zn^{2+} ions. The kinetic data for the adsorption of metal ions followed pseudo second-order dynamics. Similarly,

Jerroumi et al., 2020 [100] investigated the removal of Ni from industrial electroplating wastewater using sulphide precipitation. The results indicate that when an initial pH of 5 was used with an equimolar ratio of $[S^{2-}]/[Ni^{2+}]$:1/1, the removal efficiency of Ni^{2+} ions approached 91 and 94%, respectively, for industrial and synthetic solutions. Under the same pH value and supersaturation conditions $[S^{2-}]/[Ni^{2+}]$:1.5/1), the removal effectiveness for industrial and synthetic solutions was 62 and 92%, respectively. The ideal dosage of sulphide ions was determined for successful metal removal. Ni^{2+} has a clearance effectiveness of roughly 90% at 33 mg/L $[S^{2-}]$.

Alyuz and Veli, 2009 [101] investigated the use of ion exchange resins to remove Ni^{2+} and Zn^{2+} ions from aqueous solutions. Under ideal conditions, it was reported that more than 98% removal efficiency was obtained for Ni^{2+} and Zn^{2+} ions. The removal of Ni^{2+} and Zn^{2+} ions was determined to be well-fit by the Langmuir isotherm and pseudo-second-order reaction kinetics model.

Shek et al., 2009 [102] determined the equilibrium exchange capacity of ion exchange resins used to remove Zn ions from effluent to be 2.7 mmol/g resin. Zhou et al., 2019 [103] worked on manganese-Zn chloride waste liquor from cobalt smelting which is an important source of manganese sulphate. The separation of Zn^{2+} from waste liquor is critical for manganese recovery. The purpose of research was to establish an ion-exchange method for selectively extracting and separating Zn from waste liquor. Zn^{2+} was found to be adsorbed on D201 resin in the form of Zn chloride complex. Murray and Ormeci, 2019 [104] investigated the removal of Zn^{2+} from natural waters using polymeric sub-micron ion-exchange resins and obtained a removal of 55% for Zn^{2+} in river water spiked with 500 $\mu\text{g/L}$ of Zn^{2+} . Similarly, Murray and Ormeci, 2019 [104] were capable of removing 28% of Zn^{2+} ions from wastewater.

2.5.2 Chemical Precipitation

Chemical precipitation is a simple and easily mechanized form of wastewater treatment [105]. Chemical precipitation requires a high concentration of chemicals (Sulfide, carbonate and lime) to remove metal ions to an acceptable level for discharge, although it

occasionally fails to do so [106], [107]. These chemicals contribute significantly to additional contamination. Chemical precipitation procedures include the reaction of chemical precipitant agents with heavy metal ions to form insoluble solid particles. Sedimentation or filtering is used to separate the solid phase from the solution [106]. This process is relatively complex as well as expensive [107].

Zainuddin et al., 2019 [18] investigated the removal of Ni(II), Zn(II), and Cu(II) from industrial raw effluent from plating processes through hydroxide and sulphide precipitation. The efficiency of sulphide and hydroxide precipitation in removing Ni(II), Zn(II), and Cu(II) from industrial wastewater, specifically acid and Ni(II) rinse samples were evaluated. Ni(II) was removed from the acid rinse sample up to 95.32% and 76.66% by sulphide and hydroxide precipitation, respectively. Zn(II) was removed from the Ni(II) rinse sample by 93.75% and 68.8% using sulphide and hydroxide precipitation method. Both sulphide and hydroxide precipitation methods were used to extract 65.75% of the Ni(II). Cu(II) was completely removed from acid rinse and Ni(II) rinse samples by using both hydroxide and sulphide precipitation.

Chen et al., 2018 [108] used typical chemical precipitation methods using lime ($\text{Ca}(\text{OH})_2$), soda ash (Na_2CO_3) and sodium sulfide (Na_2S) for the removal of Zn^{2+} and Cu^{2+} from aqueous solutions. A removal of 99.99% from aqueous solution with these precipitants was achieved for Cu(II) and Zn(II) at an initial concentration of 100 mg/L.

Ghosh et al., 2011 [109] removed Zn^{2+} ions from rayon industry effluent using electro-Fenton treatment in conjunction with chemical precipitation. The initial concentration of Zn^{2+} ions in the wastewater was determined to be 32 mg/L. 99.3% Zn^{2+} ion removal was obtained. Liu et al., 2011 [110] used hydrocalumite to remove Zn^{2+} ions from contaminated water and reported that the maximum uptake capacity of Zn^{2+} ions was 6.72, 7.34 and 7.57 mmol L^{-1} with NO_3^- , SO_4^{2-} and Cl^- , respectively. Nemeth et al., 2016 [111] used natural porous rocks to remove Zn^{2+} ions from wastewater and observed a removal of 92-99% for metal uptake. Natural porous rocks, such as limestone and rhyolite tuff, are capable of reducing heavy metal contamination by adsorbing or precipitating them from heavy metal-containing solutions due to their favorable physical and chemical properties.

Wang and Chen, 2019 [112] eradicated Zn^{2+} ions from industrial effluent by using hydroxide precipitation. Zn^{2+} ions was then precipitated with a recovery rate of 96.1%. This enabled metal recovery and eliminated the need for sludge disposal.

2.5.3 Electrochemical Methods

Numerous electrochemical wastewater treatment technologies have been developed . In the subject of wastewater purification, emphasis has been placed on clarifying, disinfection, and phosphate removal in order to reduce costs in comparison to more traditional techniques. Electrochemical treatment is highly efficient and significantly reduces process detention periods, allowing for the construction of smaller plants [113]. Additionally, electrochemical treatment of wastewaters is a capital and energy-intensive technique [114].

Sankaranarayanan et al., 1991 [115] investigated the electrochemical removal of Ni(II). Electrochemical industries such as metal finishing and electroplating add significantly to the metal pollution load in water sources. Heavy metals and a variety of chemical and inorganic substances are among the contaminants. Ni(II), a well-known heavy metal contaminant, is found at concentrations ranging from 10 to 200 mg/L in plating effluent. Electrolysis took place in a batch recirculating system. The flow rate was varied between 5 and 60 L/h, and it was determined that 5 L/h is the ideal flow rate with 84% current efficiency and 97% conversion efficiency [115]. Hunsom et al., 2005 [116] evaluated an electrochemical approach for removing Ni^{2+} from plating industry effluent on laboratory scale. The investigations were conducted in a 1 L membrane reactor. The electrolyte was flowed with a constant rate of 0.42 L/min and the pH was maintained at 1. Current densities of 10 and 90 A/m^2 were used. More than 99% metal reduction was achieved, with final Cu(II) concentrations in treated water ranging between 0.05-0.13 mg/L. Golder et al., 2007 [117] investigated the electrochemical treatment of Ni-containing plating rinse effluents using mild steel and aluminium electrodes. Direct electrochemical treatment of industrial wastewater is capable of removing 80-85% Ni(II). Combining chemical precipitation at pH 8.7 with electro treatment reduces Ni(II) to the permissible discharge limit.

Hunsom et al., 2005 [116] evaluated an electrochemical approach for removing Cu^{2+} from plating industry effluent on a laboratory scale. The investigations were conducted in a 1 L membrane reactor. The electrolyte was flowed at a constant rate of 0.42 L/min and the pH was maintained at 1. Current densities of 10 and 90 A/m^2 were used. More than 99% metal reduction was achieved, with final Cu(II) concentrations in treated water ranging between 0.10 and 0.13 mg/L.

Ajzeroud et al., 2018 [118] explored the electrocoagulation-electroflotation (ECEf) technique in conjunction with the mucilage of the *Opuntia ficus indica* (OFI) plant in order to increase the efficiency of Cu(II) removal. ECEf study using aluminium electrodes were undertaken to determine the effect of mucilage on Cu(II) metal ion removal, aluminium and hydrogen Faradaic yields, settling process and specific electrical energy consumption. It was observed that Cu(II) removal efficiency reached 100% in 5 minutes when 30 mg/L OFI mucilage was used at a pH of 7.8. Konstantinos et al., 2011 [119] investigated the removal of Zn(II) from synthetic aqueous aliquot solutions and actual electroplating effluent using electrocoagulation with aluminium electrodes. The pH range 4-8 exhibited the greatest potential for the metal removal. Zn(II) ions were totally eliminated from the solution after 50 minutes. Increased current density, on the other hand, hastened the electrocoagulation process at the expense of increased energy consumption. Ghaya et al., 2019 [120] recovered Zn(II) by electrowinning from an acidified zinc sulphate and electrorefining Zn dross anodes in an alkaline ammonia solution. Both methods addressed a variety of parameters, involving current density and deposition time. A Zn powder with a purity of about 100 percent was achieved.

While all of these wastewater treatment procedures are capable of removing heavy metals, they each have their own inherent advantages and disadvantages. Chemical precipitation is a simple and economical procedure that has been historically used to remove heavy metals from aqueous solutions. However, chemical precipitation is only successful when wastewater contains a high concentration of heavy metal ions and is inefficient when the metal ion concentration is low. Additionally, chemical precipitation generates a huge volume of sludge that must be managed with great care [121].

Ion exchange has been widely used to treat wastewater for the removal of heavy metals. On the other hand, when ion-exchange resins become exhausted, they must be regenerated by using chemical reagents, which can result in significant secondary pollution and as they are expensive, particularly when dealing with vast amounts of wastewater containing low concentrations of heavy metals, they cannot be used on a mass scale [122].

Electrochemical approaches for heavy metal removal are believed to be the most quick and precise, requiring fewer chemicals, producing higher reduction yields, and generating less sludge. However, because electrochemical methods require a significant initial capital investment and consume huge electricity, their progress is constrained [123].

Disadvantages of all of the preceding processes prompted a search for a process capable of overcoming all of the preceding process's challenges. One such process is adsorption.

2.5.4 Adsorption

Adsorption is another physico-chemical approach for removing the heavy metals from wastewater that has been shown to be effective in lowering metal concentrations. Adsorption is a process that involves mass transfer between the liquid phase and the adsorbent/solid phase. These adsorbents have a wide surface area and a high capacity for adsorption. The advantage is that the process is reversible, with the adsorbents being regenerated by desorption. Adsorbents can be made from agricultural waste, industrial byproducts, or naturally occurring materials. Ong et al., 2017 [124] investigated the potential for reusing groundwater treated sludge for Ni²⁺ ion adsorption from aqueous solutions. As the initial Ni²⁺ concentration was increased from 10 to 200 mg/L, the amount of Ni²⁺ adsorbed increased from 1.3-11.6 mg/g. As per the coefficient of determination, the Freundlich isotherm and pseudo second order kinetic model best fitted the experimental data. Bartczak et al., 2018 [125] demonstrated the removal of Ni²⁺ from aqueous solution using peat. The experimental results were highly consistent with Langmuir's isotherm model. Peat adsorption capacity for Ni²⁺ ions was 61.27 mg/g. Thanh et al., 2018 [126] produced a magnetic hydroxyapatite nanocomposite and evaluated it for Ni²⁺ removal from the aqueous solution. The nanocomposite was found to have nanostructure and had a spe-

cific surface area of 101.2 m²/g. The Langmuir adsorption isotherm was found to be a suitable model for describing the adsorption processes, indicating that nanocomposite has an adsorption capacity of 29.07 mg g⁻¹. Mahdi et al., 2018 [127] examine the elimination of Cu²⁺ ions using biochar derived from date seeds. Batch tests demonstrated that the best adsorption occurred around pH 6, with 0.421 mmol/g of uptake capacity. The Sips isotherm and pseudo-second order kinetics model best fitted the experimental data. More than two-thirds of the ions were removed via the ion exchange mechanism. Additionally, complexation with carboxyl and hydroxyl group aided in the ion removal.

Rani et al., 2018 [128] emphasized on Cu²⁺ ions removal from aqueous solution utilizing laterite as an adsorbent. The equilibrium, kinetics and adsorption behavior at various pH and temperature values was examined. Approximately 90% removal efficiency was obtained. The kinetics was consistent with pseudo second order model. The Langmuir model well represented the adsorption equilibrium. Jung et al., 2019 [129] produced hydroxyapatite/biochar nanocomposites (HAP/BC-NCs) by a straightforward one-pot hydrothermal technique and used them as an adsorbent for Cu²⁺ removal from aqueous phase. Langmuir isotherm model was used to precisely depict the adsorption isotherms, and the maximum adsorption capacity was calculated to be 99.01 mg/g at 298 K, which indicated towards efficient Cu²⁺ adsorption.

Kara et al., 2017 [130] utilized metakaolin-based geopolymer as an adsorbent for removal of Zn²⁺ ions from the aqueous solution. With the increase in contact time, the amount of Zn²⁺ ions adsorbed onto geopolymer increased, and the adsorption equilibrium was established within 40 minutes at an optimized initial pH of 6.39. Mousavi et al., 2018 [131] described a new generation of silica-based mesoporous adsorbents for Zn²⁺ ions removal with a goal of developing new adsorption methods for the water treatment. The authors observed a high Langmuir uptake capacity of 107.21 mg/g for Zn²⁺ ions. Karri and Sahu, 2018 [132] evaluated the efficacy of a low-cost adsorbent made from palm oil kernel shell-derived from agricultural waste in terms of Zn²⁺ ions removal from waste water and aqueous solution. The response surface methodology (RSM) and artificial neural network (ANN) techniques were used to determine the ideal values of process variables

for maximum percentage removal. With R^2 values of 0.91 and 0.92, the optimized trained neural network accurately portrayed the testing and validation of data. The results proved the effectiveness of ANN based model predictions over RSM based quadratic model.

2.6 Properties of an Adsorbent

The adsorbent is critical in the adsorption process. A good adsorbent should possess the following characteristics: distinct pore structure that facilitates rapid interaction between adsorbate and adsorbent, high thermal stability, large surface area, supports reversible adsorption, selective, recyclable and should be of low cost. Also it must be easy to handle and readily available [133].

2.7 Adsorption Mechanisms

Adsorption is a process that involves the adsorbate binding on the adsorbent surface. Numerous natural materials can be utilized in adsorption of metal ions via physical (electrostatic interactions or van der Waals forces) or chemical binding (displacement of either bound metal cations (ion exchange) or protons), precipitation, chelation, diffusion and transport (2.1). The functional groups found in adsorbent are mainly amine, imidazole, imine, thioether, carboxyl, sulfonates as well as carbonyl, phosphate and sulfhydryl groups. It is possible to trap the metal in a variety of ways due to the diversity in chemistry and structure of the adsorbents. Consequently, the adsorption mechanisms are numerous and varied. Important characteristics that control and define these aforementioned mechanisms are as follows [134], [135].

- Stereochemical, chemical and coordination properties of metal ions such as their ionic radius, molecular weight and oxidation state
- Adsorbent's attributes (its structure and composition)
- Process parameters like pH, adsorbate concentration, adsorbent dose, other competing metal ions and temperature

- Binding site's type and availability are important considerations
- The cumulative effect of the mechanisms has an effect on the metal speciation (the adsorption-induced generation of new metal species)

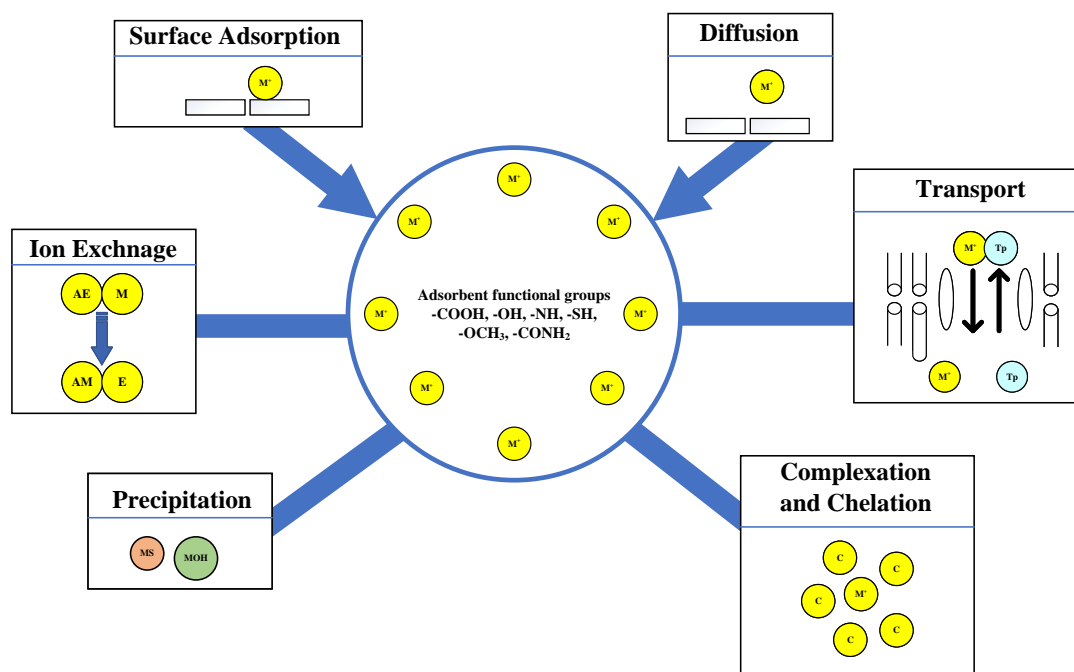


Figure 2.1: Different mechanisms of Adsorption (AE and AM: molecules with exchangeable ions and metal ions, C: chelating agents, M^+ : heavy metal ions, Tp: transport protein)

They can be classified according to the following distinct criteria.

2.7.1 Chemical Adsorption

Chemisorption occurs only when the adsorbent and adsorbate have the ability to bind with a chemical bond, such as when oxygen and hydrogen adsorb on metal to form metal oxides hydride. Chemisorption is a mono-molecular layer adsorption that happens at a high temperature and requires a high activation energy and high heat of adsorption. Chemisorption is irreversible and has a high enthalpy value (80-240 kJ/mol). The chemisorption process, like physisorption, is influenced by the adsorbent surface area and adsorption temperature and it improves with increase in temperature and adsorbent surface area [136].

According to Lasheen et al., 2016 [137], metal adsorption onto nano magnetite (Fe_3O_4) composites with kaolinite occurs by chemical adsorption rather than physical adsorption.

Zhong et al., 2021 [138] investigated the adsorption properties of modified kaolin for heavy metals (Pb, Cd, Zn, and Cr) obtained from coal combustion using a mix of experimental and theoretical study. Acid/alkali modification efficiently enhances electron transport between modified kaolin and heavy metals, resulting in stable chemical adsorption.

2.7.2 Physical Adsorption

The physical adsorption mechanism is based on van der Waals forces between the metal and the cell surface, which are independent of the cell metabolism. Chen et al., 2001 [139] studied the mechanism by which heavy metals such as Cr, Cu, Pb and Cd adsorb on the adsorbent during incineration. They found that the principal mechanisms are physical molecular adsorption and particle growth for the extremely volatile metal Cd and the majority of metal chlorides.

The majority of volatile metal species are adsorbed/distributed on the adsorbent's surface. Chemical and physical adsorption mechanisms are critical for Pb (which has been characterized as having a medium to high volatility), based on the reacting environment. Additionally, physical adsorption was accountable for the adsorption of Cu^{2+} onto Carbon Black [140].

2.7.3 Ion Exchange

Ion exchange is a crucial concept in the adsorption of heavy metals. Ion exchange occurs when functional groups on the adsorbent surface contact with metal ions. Yasemin and Zeki, 2007 [141] implied that the shells of hazelnut and almond adsorb Ni^{2+} , Cd^{2+} , and Pb^{2+} from aqueous solution via ion exchange. The adsorption of heavy metals onto spent coffee grounds was investigated by Guzman et al., 2016 [142]. The equilibrium adsorption of Cd^{2+} , Cu^{2+} , and Pb^{2+} in a batch system was described using an ion-exchange model based on heavy metal ion exchange with calcium and protons bonded to active sites on the coffee ground surface. Using the ion-exchange model, the greatest amount of adsorbed metal ions was 0.12, 0.21, and 0.32 mmol/g of Cd^{2+} , Cu^{2+} , and Pb^{2+} ions respectively.

2.7.4 Precipitation

Natural zeolites were studied by Motsi et al., 2009 [143] for their capacity to adsorb heavy metals derived from acid mine drainage. In nature, natural zeolites are moderately acidic and sodium mediated exchangers are hydrogen selective $R - Na + H_2O \ll RH + Na^+ + OH^-$, leading to a high pH values once the exchanger is equilibrated with dilute electrolyte solutions, allowing for the metal hydroxide precipitation to take place. As a result, the pH of the solution rises as the reaction proceeds in its course. In all of the metal adsorption reactions, a little amount of precipitate was observed, indicating that heavy metal ions were removed from solution both via ion exchange and by precipitation in addition to adsorption. It was observed that the presence of competing cations had an effect on the individual adsorption of Cu^{2+} , Fe^{3+} , Zn^{2+} , and Mn^{2+} by natural zeolites. There were no significant effects on the adsorption of Fe^{3+} due to the presence of competing ions other than the presence of Fe^{3+} . This could be due to the fact that precipitation is widely regarded to be the principal process by which Fe^{3+} is removed from solution [143]. Using montmorillonite and calcium montmorillonite, Pablo et al., 2011 [144] studied the adsorption of heavy metals by the minerals in a range of acid to alkaline environments. Cr^{3+} , Pb^{2+} and Cu^{2+} oxides and hydroxides precipitated at pH below 5, while Hg^{2+} , Zn^{2+} , Ba^{2+} , Cd^{2+} , Ni^{2+} , Mn^{2+} and Ag^+ remain in solution and were adsorbed as simple and hydroxyl cations by the clay, with the selectivity sequence being $Hg^{2+} > Zn^{2+} > Ba^{2+} > Cd^{2+} > Ni^{2+} > Mn^{2+}$.

2.7.5 Complexation and Chelation

Complexation is described as the association of two or more species that results in the generation of a complex. Between the metal ion and the ligands, mononuclear (monodentate) complexes are produced in which the metal atom occupies the centre position. Polynuclear (multidentate) complexes are composed of more than one metal ion in the centre, with the metal atom carrying a positive, negative, or neutral charge depending on the number of binding ligands. The monodentate ligand complex formation is superior to the multidentate ligand complex formation, as the latter comprises numerous ligands, which

may result in multiple species binding. By means of covalent bonds, the metal ion links with ligands [145]. Hu et al., 2012 [146] observed a similar process of adsorption when they used alkali-modified sewage sludge to remove Cd (II). Chelation is the process by which a chelating agent binds to a metal ion in multiple places at the same time to form a ring structure; this complex is referred to as a chelate. The reaction is dominated by polydentate ligands that participate in the formation of stable structures via multiple bonding. Increasing the number of ligand binding sites makes the structure more stable. Because the metal ion binds to the chelate in several places, chelates are more stable than complexes [145]. Ding et al., 2012 [147] investigated the use of rice straw as a possible adsorbent to remove Cd (II) from wastewater. There are functional groups like C=C, O-H and C-O, and carboxylic acids present on the adsorbent's surface that chelate with adsorbed Cd (II).

2.8 Raw Adsorbents

2.8.1 Bentonite

Bentonite is a term that refers to a naturally occurring, extremely fine-grained material that is predominantly formed of clay minerals such as montmorillonite [148]. Depending on the composition of bentonite, a description and discussion of montmorillonite is important. Along with montmorillonite, bentonite contains trace amounts of other minerals, most commonly quartz, feldspar, volcanic glass, organic debris, gypsum, or pyrite [149].

2.8.1.1 History

In 2018, China was the world's largest producer of bentonite, accounting for more than a quarter of worldwide output, followed by the United States and India. Globally, bentonite production totaled 24,400,000 metric tonnes [150]. The Tokat Resadiye region of Turkey and an area between the Black Hills of South Dakota and the Bighorn Basin of Wyoming generate the majority of high-grade natural sodium bentonite. Greece, Australia, India, Russia and Ukraine are among the countries that mine mixed sodium/ calcium bentonite [151].

2.8.1.2 Chemical Properties of Bentonite clay

Montmorillonite is a hydrous aluminium silicate with minor concentrations of alkali and alkaline-earth metals, as per its chemical composition. The aluminium octahedral sheet and the silica tetrahedral sheet are the two primary building components of montmorillonite (Figure 2.2). A single montmorillonite unit cell is made up of two silica tetrahedral sheets with an aluminium octahedral sheet sandwiched between them (Figure 2.2).

Montmorillonite flakes have lengths and widths between 10 and 100 times their thick-

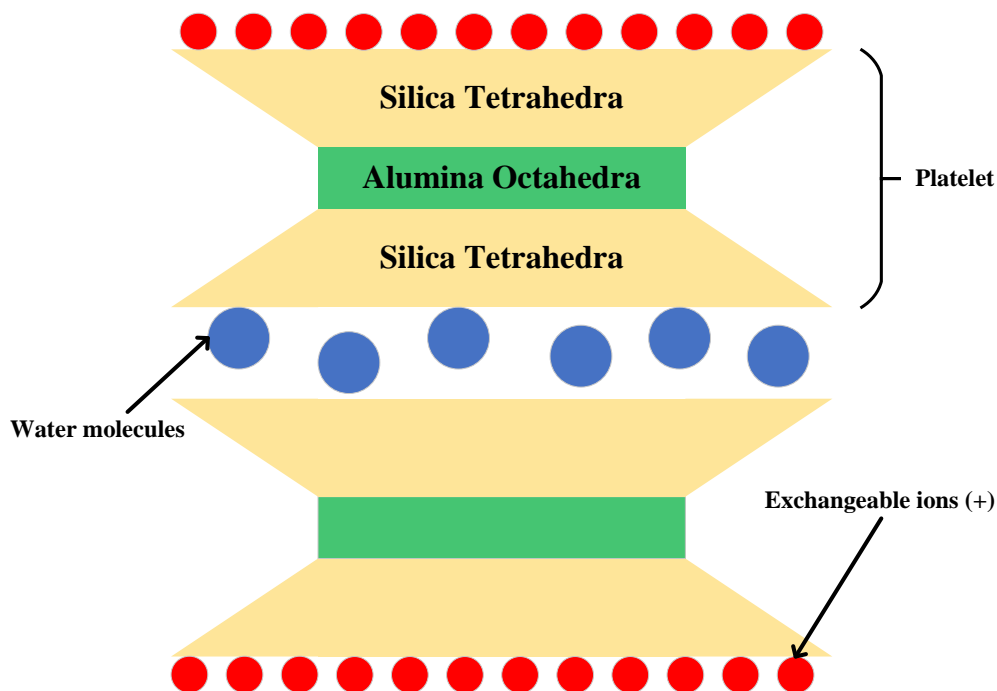


Figure 2.2: Structure of bentonite clay

nesses. The charge of the montmorillonite lattice is negative, owing to isomorphous substitutions of ions within the structure. This negative character is balanced by the presence of cations on the surface of the flakes. The clay quickly exchanges cations held in this manner. The most abundant cations in nature are sodium and calcium.

The aluminium octahedral sheets and the silica tetrahedral sheets are the two the primary building components of bentonite clay (Figure 2.2). One aluminium octahedral sheet is placed between two tetrahedral silica sheets in a single unit cell. The exchangeable cations in the intermediate layers compensate for the modest negative charge of these silicate layers. The cations (Na^+ , Mg^{2+} , or Ca^{2+} ions) can be adsorbed with an accompanying hydra-

tion shell since the charge is weak. Ion exchange easily replaces the cations held in this form in the clay [152].

2.8.1.3 Application of Bentonite Clay

- **Foundry**

Bentonite is used in the manufacturing of moulding sand, which is utilized in the production of iron, steel, and nonferrous castings. It is also utilized in the production of ceramics. Bentonite's special properties result in green sand mould that have excellent flow ability and thermal stability, which are ideal for the creation of high-quality castings [153].

- **Pelletizing**

When iron ore pellets are being manufactured, bentonite is utilized as a binding agent. Iron ore fines are transformed into spherical pellets, which can be used as raw materials in blast furnaces for the production of pig iron [154].

- **Environmental markets**

The adsorption/absorption capabilities of bentonite are extremely beneficial for wastewater treatment. EU directives encourage the usage of low permeability soils, which naturally include bentonite, as a sealing material during landfill construction and restoration to protect groundwater from pollution. Bentonite is the geosynthetic clay liners' active protective layer [155].

- **Drilling**

Bentonite is used as a component of drilling mud for oil and water wells. It is primarily responsible for sealing the borehole walls, removing drill debris and lubricating the cutting tip [156].

- **Oils / Food markets**

Bentonite is used to remove contaminants from oils and is critical in the processing of edible oils and fats (soya / palm / canola oil). Bentonite is employed as a clarifying agent in

beer, wine and mineral water, sugar and honey. Refinement of mineral oils, such as lubricating oils and other hydrocarbons, is accomplished through the use of activated bleaching clays. These oils are bleached at a variety of temperatures, from 40°C to 250°C. At these elevated temperatures, an inert environment must be maintained above the oil to prevent oxidation [157].

- **Agriculture**

When it comes to animal feed supplements, bentonite can be utilized as a pelletizing help for animal feed pellets. It can also be used as an ion exchanger to enhance and condition the soil, which is beneficial. It has the ability to act as a porous ceramic carrier for a wide variety of herbicides and insecticides, when thermally processed [158].

- **Detergents**

Laundry detergents and liquid hand cleaners/soaps rely on bentonite to extract pollutants from solvents and to soften fibers [159].

- **Paper**

Bentonite is critical in paper manufacturing because it is employed in pitch control, which is the absorption of wood resins that tend to clog machines. This increases the efficiency of pulp conversion into paper and improves the paper's quality. Acid activated bentonite is also used in the creation of carbonless copy paper, and it is a major element in the process [160].

2.8.2 Red Ochre

The French scientist Jean-Etienne Astier invented the industrial procedure for making ochre pigment in the 1780s. He was from Roussillon, in the Vaucluse province of Provence, and was drawn to the region's red and yellow clay cliffs. He discovered a way for mass manufacturing the pigment. Initially, clay was extracted from mines or open pits. The raw clay contained around 10% to 20% ochre [161]. He separated the sand grains from the ochre particles by cleaning the clay. To separate the ochre from the sand,

the remainder of the mixture was decanted into large basins. After draining the water, the ochre was dried, crushed, sorted, and finally classified according to colour and grade.

The finest paints were reserved for artists [162], [163]. In the United Kingdom, ochre was mined in Brixham. It developed into a significant commodity for the British fishing industry, where it was blended with oil and used to coat sails to protect them from seawater, imparting a crimson hue color to them. The ochre was boiled in large caldrons along with tar, tallow and oak bark, known as barking yards due to oak bark. These yards were used to paint the hot mixture onto the sails [163]. In 1894, a theft case shed light on the pigment's use as a food adulterant in the making of sausage rolls, where the accused apprentice was instructed to soak brown bread in red ochre, salt, and pepper to simulate beef sausage for the filling [162], [163]. The Ochre pigments from Vacluse were sold throughout Europe and the world as a result of the process created by Astier and refined by his successors. Not only was it utilized in artists' and house paintings but also it became a critical component of the rubber industry [162], [163].

Red ochre is a natural red iron oxide that contains hematite as dominant iron oxide. It also comprises of several white pigments such as alumino-silicate (kaolinite or illite), quartz and calcium compounds (calcite, gypsum and dolomite). The varying proportion of hematite and goethite determines the color of ochre from red to yellow and few shades in between. Red ochre is shaped from various natural and anthropogenic sources namely from the natural aerobic decomposition of iron-bearing minerals and as precipitate obtained from coal mine water [164]–[170]. The worldwide production of red ochre is 192,000 tonnes per year [171].

2.8.3 *Tectona grandis* Sawdust

The Lamiaceae family of tropical hardwood trees includes the *Tectona* genus. *Tectona grandis*, *Tectona hamiltoniana* and *Tectona philippine* are three species that make up the *Tectona* genus. *Tectona grandis*, for example, is widely dispersed in Bangladesh, Thailand, China, India, and Pakistan. In Kerala, Andhra Pradesh, Karnataka, Orissa, Madhya Pradesh, Maharashtra, Gujrat, Rajasthan, Uttar Pradesh, and Manipur, *Tectona grandis*

grows natively below 24°N latitude. *Tectona grandis* woods cover roughly 8.9 million hectares in their natural state [172]. Due to its exceptional wood quality, most appealing grain, texture, and colour, it is used for furniture, carving, cabinet making, door and window making. Each of India's teak-growing states has marketplaces and depots for *Tectona grandis* wood [172]. It is estimated that waste sawdust accounts for 15% to 20% of total production in the lumber sector [173], [174]. That is a significant amount of data, yet its utilization is not optimised. The wood of the *Tectona grandis* species has 47.5% cellulose and 29.9% lignin. The fact that cellulose exists shows that it has been used as an adsorbent [173]. The sawdust from *Tectona grandis* is inexpensive, unusable, and is often discarded [175]. TG contains a high carbon content of roughly 50%, indicating that it may be a natural precursor to activated carbon [176].

2.8.4 *Azadirachta indica* Twig Ash

Azadirachta indica twigs are used to treat cough, asthma, hemorrhoids, bowel worms, urinary illness and diabetes [177]. *Azadirachta indica* belongs to Meliaceae family and is widely available in India, Bangladesh, Pakistan, Nepal and Sri Lanka.

In India, the major *Azadirachta indica* producing states are Uttar Pradesh, Tamil Nadu, Karnataka, Madhya Pradesh, Maharashtra, Andhra Pradesh and Gujarat. It has enormous potential in the field of pesticide control, protection of the environment and medicine. This is one of the most studied trees in the world and is the most promising tree of the twenty-first century [177]. *Azadirachta indica* products have water purification capability. *Azadirachta indica* twigs have antiseptic properties. *Azadirachta indica* has now gained international popularity as natives of all countries are inclined towards green technology. *Azadirachta indica* products do not harm humans or livestock. The total number of *Azadirachta indica* trees in India is about 18 million [178].

2.8.5 Natural Soil

Adsorption takes place in soil when solution components cling to the surface of soil particles. This process is influenced by the inorganic and organic components of the soil and

environmental conditions. Soil particles include a wide variety of compounds, including soil components, plant nutrients, surfactants, insecticides and environmental pollutants. Soil is amphoteric, with a broad spectrum of negative and positive charge and magnitude [179].

Soil maintain a steady negative charge due to structural flaws caused by ion replacements or site vacancies in crystalline clay minerals and non-crystalline hydrous oxides of silica, iron and aluminium [180]. Cations are adsorbed explicitly or nonspecifically by inorganic and organic constituents of soils in terrestrial environment [181]. Due to the intrinsic structure and properties such as smaller ionic dimension and load, Zn^{2+} is heavily absorbed by soils. The highest adsorption potential is found in Zn^{2+} ion, which has the smallest ionic radius [182]. It was further observed by Akay and Doulati, 2012 [182] that clay rich soils have higher absorption capacity.