REMOVAL OF LEAD, CADMIUM, AND CHROMIUM IONS FROM AQUEOUS SOLUTIONS USING IRON(III) OXIDE

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by

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LIST OF SYMBOLS AND ABBREVIATIONS

×	Multiplication
-	Minus
=	Equal
>	Higher than
ºC	Degree Celcius
%	Percentage
µg/g	Microgram per gram
µL	Microliter
A	Ampere
AAS	Atomic Absorption Spectroscopy
ATSDR	Agency for Toxic Substances and Disease Registry
cm^{-1}	Per centimetre
cm^{-3}	Per cubic centimetre
et al	And others
FAAS	Flame Atomic Absorption Spectroscopy
FAO	Food and Agriculture Organization
FTIR	Fourier-Transform Infrared Spectroscopy
g	Gram
g/cm^3	Gram per cubic centimetre
g/L	Gram per litre
H_2SO_4	Sulfuric acid
ICP-MS	Inductive Coupled Plasma-Mass Spectrometry
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
KBr	Potassium bromide
m^{-1}	Per meter

m^2/g	Meter square per gram
mg-equ/L	Milligram equivalent per litre
mg/kg	Milligram per kilogram
mg/L	Milligram/litre
mL	Millilitre
mmol/g	Millimole per gram
nm	Nanometer
pm	Picometer
ppm	Parts per million
V	Voltage

LIST OF APPENDICES

PENYNGKIRAN ION-ION PLUMBUM, KADMIUM, DAN KROMIUM DARIPADA LARUTAN AKUEUS DENGAN MENGGUNAKAN FERUM(III) OKSIDA

ABSTRAK

Plumbum (Pb), kadmium (Cd), dan kromium (Cr) diklasifikasikan sebagai logam berat yang telah mencemarkan alam sekitar, terutamanya sumber air. Oleh hal yang demikian, matlamat kajian ini adalah untuk menyingkirkan logam berat, khususnya ion Pb, Cd, dan Cr daripada larutan akueus menggunakan ferum(III) oksida dan turut menyumbang kepada pengurangan bahan buangan yang boleh mencemarkan alam sekitar. Kajian ini direka bentuk untuk menggunakan teknik penjerapan untuk menyingkirkan ion Pb, Cd, dan Cr daripada larutan akueus dengan bantuan penjerap kos rendah, ferum(III) oksida, Fe_2O_3. Kepekatan ion Pb, Cd, dan Cr dalam larutan akueus kemudiannya ditentukan oleh instrumen Spektroskopi Penyerapan Atom Nyalaan (FAAS). Pelbagai parameter seperti suhu pengkalsinan bahan penjerap, dos penjerap, dan masa sentuhan digunakan untuk menjalankan proses penyingkiran ion Pb. Kesan penjerapan ke atas logam berat yang berbeza, Cd dan Cr serta penjanaan semula penjerap turut dikaji dalam penyelidikan ini. Penemuan FTIR mendedahkan bahawa logam berat tertentu lebih terkemampuan untuk terikat dengan penjerap ini atas kehadiran kumpulan berfungsi penting seperti hidroksil (-OH) dan karbonil (C=O). Daripada kajian ini, keadaan penyingkiran optimum ialah suhu pengkalsinan bagi penjerap 400ºC, 0.2 g dos penjerap, dan 60 minit masa sentuhan. Keputusan menunjukkan bahawa penjerap Fe_2O_3 telah menyingkirkan 0.912 mg/L, 0.540 mg/L, dan 0.489 mg/L ion Pb, Cd, dan Cr daripada larutan akueus, menunjukkan bahawa ia adalah lebih cekap ke arah penyingkiran ion Pb. Kajian kebolehulangan penjerap pula

menunjukkan bahawa penjerap Fe_2O_3 boleh digunakan semula untuk tiga kali dan mempunyai potensi besar untuk menyingkirkan logam berat daripada larutan akueus. Oleh itu, kajian ini menunjukkan bahawa teknik penjerapan menggunakan penjerap Fe_2O_3 mampu menyingkirkan ion Pb, Cd, dan Cr daripada larutan akueus. Pengurangan kepekatan logam berat ini oleh bahan penjerap juga boleh membantu mengekalkan kualiti air yang baik yang tidak melebihi had dibenarkan oleh WHO.

REMOVAL OF LEAD, CADMIUM, AND CHROMIUM IONS FROM AQUEOUS SOLUTIONS USING IRON(III) OXIDE

ABSTRACT

Lead (Pb), cadmium (Cd), and chromium (Cr) have been classified as heavy metals that have polluted the environment, mainly water sources. Therefore, the aim of this present study is to remove heavy metals, specifically Pb, Cd, and Cr ions from aqueous solutions using iron(III) oxide while, also contributing to the reduction of waste products that might ultimately cause environmental pollution. This study was designed to adopt adsorption technique to remove Pb, Cd, and Cr ions from the aqueous solutions with the help of low-cost adsorbent, iron(III) oxide, Fe_2O_3. The concentrations of Pb, Cd, and Cr ions in the aqueous solutions were then detected by Flame Atomic Absorption Spectroscopy (FAAS) instrument. Various parameters such as calcination temperatures of adsorbents, adsorbent dosages, and contact time were used to carry out the removal process of Pb ions. The effects of adsorption on different types of heavy metals, Cd and Cr as well as repeatability of adsorbents were also studied in this research. The FTIR findings revealed that certain heavy metals were more likely to bind to these adsorbents due to the presence of crucial functional groups such as hydroxyl (-OH) and carbonyl (C=O). From this study, the optimum removal conditions were calcination temperature of adsorbents of 400ºC, 0.2 g dose of adsorbent, and 60 minutes of contact time. The results showed that Fe_2O_3 adsorbents removed 0.912 mg/L, 0.540 mg/L, and 0.489 mg/L of Pb, Cd, and Cr ions from the aqueous solutions, suggesting that it was more efficient towards the removal of Pb ions. Repeatability study demonstrated that Fe_2O_3 adsorbent can be reused for three consecutive periods and thus, has a great potential for eliminating heavy metals from

aqueous solutions. Hence, this study showed that the adsorption technique using Fe_2O_3 adsorbents was capable of removing Pb, Cd, and Cr ions from aqueous solutions. The reduction of these heavy metals' concentration by adsorbents can also assist to preserve good water quality that does not exceed the permissible limit by WHO.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Water is a liquid that has no colour and odour that forms the oceans, rivers and even lakes. Water is one of the most basic necessities for human survival. Bodies of water including streams, reservoirs, groundwater and collected rainwater provide water supplies to the community. It also benefits humans in many ways, especially for domestic, agricultural and commercial activities. However, these activities impose a significant burden on the environment, which is growing as a result of water pollution, scarcity, and restricted supply due to the depletion of natural water supplies (Carolin *et al.*, 2017).

The rapid rise of urbanisation and industrialisation advancements are the reasons for the increasing environmental issues by dumping huge quantities of pollutants, including toxic and hazardous waste, organic contaminants and most importantly heavy metals. The level of water pollution due to heavy metal discharges by the chemical industries is intensifying and it is beyond the permissible limit. Moreover, it is causing tremendous fear owing to the detrimental effects it may have on the human population.

The term ‘heavy metal’ refers to a group of high-density elements that comprise metals and metalloids (Vareda *et al*., 2019). The most typical heavy metals that cause water contamination are lead (Pb), arsenic (As), copper (Cu), cadmium (Cd), nickel (Ni), chromium (Cr), zinc (Zn), cobalt (Co), and mercury (Hg) (Renu *et al*., 2017). High quantities of these heavy metals in the natural environment are caused by anthropogenic activities such as electroplating, alloy manufacture, and mining. Living organisms are capable of absorbing heavy metals because they are highly water-soluble. When heavy metals enter the food chain, they may accumulate in high amounts in the human body, causing major health consequences such as cancer, organ damage, nervous system impairment, and, in extreme circumstances, death (Barakat, 2011).

Most of the heavy metals are extremely toxic to biota, but their toxicity is determined by the dosage and duration of exposure. According to Rezaee Ebrahim Saraee *et al*. (2011), the concentration of heavy metals on the east coast of Peninsular Malaysia was as followed: 46.40 mg/kg of Cr, 37.40 mg/kg of Pb, 20.10 mg/kg of Ni, 0.25 mg/kg of Cd, and 44.30 mg/kg of Zn. For manganese, the range concentration of Mn on the east coast of Peninsular Malaysia ranged between 207.58 and 491.33 μg/g (Shaari *et al.*, 2015). These heavy metals are typically present in an insoluble form or in precipitated or complex forms that are not readily available for living organisms' uptake since they have an excellent adsorption capacity (Ayansina and Olubukola, 2017).

Due to the noxious effects of these metals, there is a rising awareness of environmental and societal concerns, as well as the necessity to treat the heavy metal-polluted environment. To overcome this problem, several techniques to remove heavy metals from aqueous solutions were introduced by some researchers such as ion-exchange (Gunatilake, 2015), coagulation-flocculation (Pang *et al.*, 2011), chemical precipitation (Zhang and Duan, 2020), electrochemical treatment (Trellu *et al.*, 2016), electrodialysis (Carolin *et al.*, 2017), and membrane filtration (Patil *et al.*, 2016). Each method has its own pros and cons, and they are used dependent on the type of heavy metals (Carolin *et al.*, 2017). Advantages include convenient process, ease of operation and control, a wide range of input loads, less sludge production and many more (Gunatilake, 2015). Yet, their advantages are hindered by several drawbacks, like incomplete removal of pollutants, high operational costs, high-energy requirements, and generation of contaminated sludge (Anjum *et al.*, 2019).

Therefore, the adsorption technique has been introduced by researchers as a potentially favoured alternative approach for an effective elimination of toxic metals in various samples. Adsorption is a mass transfer process by which the heavy metal ions are transferred from the liquid phase to the surface of a solid, the adsorbent and subsequently bounded by a physical or chemical attraction (Ojedokun and Bello, 2016). Its main advantage is the effectiveness at both high and low pollutant concentrations, the ability to regenerate spent adsorbents, selectivity through the use of customized adsorbents and a comparatively low cost (Sharma *et al.*, 2016). This method can be improved through some interventions with the help of advancements in nanotechnology (Anjum *et al.*, 2019).

Nanotechnology advancement has demonstrated tremendous potential for treating heavy metal polluted environments, as well as various other environmental issues (Gupta *et al.*, 2015). Nanotechnology is a sub-discipline of nanoscience that utilizes nano-materials that have structure components with one dimension at least less than 100 nm (Amin *et al*., 2014). Lately, nano-particle materials have been studied for their potential as adsorbents for the effective elimination of toxic metals (Anjum *et al.*, 2019). Increasing surface area by using smaller sizes of nano-particles leads to enhancement in the chemical reaction and adsorption capacity of nanoparticles for the heavy metal ions adsorption on their surfaces. Oxides including manganese oxide, magnesium oxide, zinc oxide, ferric oxides, titanium oxides, and graphene, activated carbon and carbon nanotubes, are the most often employed nano-particles for adsorption of heavy metals (Gupta *et al.*, 2015).

Iron oxides had been utilised as the adsorbent in this study to remove Pb, Cd, and Cr from aqueous solutions. Iron oxide is a low-cost material and an environmentally safe substance that can be applied directly in a polluted environment with a reduced risk of subsequent contamination.

1.2 Problem Statement

In recent times, the pollution of the environment with heavy metals has become a severe environmental hazard since the ions cannot be reduced to non-toxic forms and hence tend to persist in the ecosystem. Industrialization and urban civilisation are the major contributors to this phenomenon probably due to the unethical disposal of waste products into various bodies of water.

The bioaccumulation of heavy metal ions in the ecosystem and its toxicity may inflict a detrimental impact on the ecosystem. The unmanageable discharge of toxic wastes and the persistence of heavy metals can cause deleterious health troubles for aquatic fauna, but it also troubles the health of humans through the prevailing ecological food chain (Gupta *et al.*, 2015). The build-up of heavy metal ions in the living human body can result in severe illnesses and diseases such as cancer, birth defects, gastrointestinal dysfunction, nervous system disorder even death.

Furthermore, heavy metal pollution may indirectly affect the quality of drinking water, especially by the contamination of lead (Pb), chromium (Cr), cadmium (Cd), zinc (Zn), mercury (Hg) and arsenic (As) ions. Since the ions are non-degradable in nature and cannot be removed easily, they tend to degrade the quality of water. Consequently, it will cause brutal health effects on living organisms for consuming such contaminated water. Thus, an initiative to protect the environment and lower the health risks to living creatures by treating the heavy metal contaminated water should be taken into consideration.

Several removal techniques for the removal of noxious heavy metals, notably, membrane filtration, flotation, coagulation and flocculation, chemical precipitation, and ion exchange have shown effective results (K. Singh *et al*., 2017). However, they suffered some drawbacks like incomplete removal of heavy metals, production of toxic sludge, high operational costs and many more. Meanwhile, the use of adsorbents in the size of smaller particles is found to be simpler, economical, effective and most preferable in treating heavy metal ions in an aqueous solution. Therefore, this study was conducted to remove Pb, Cd, and Cr ions from aqueous solutions by applying an adsorption technique using iron oxides as the adsorbent.

1.3 Objectives

A general objective and three specific objectives have been generated in this study.

1.3.1 General objective

The general objective of this research study is to remove Pb, Cd, and Cr ions from aqueous solutions using iron(III) oxide.

1.3.2 Specific objectives

The three specific objectives of the study are listed as follows:

1. To synthesise iron(III) oxide as an adsorbent from iron(III) nitrate nonahydrate.
2. To perform the removal process of Pb, Cd, and Cr ions from aqueous solutions using iron(III) oxide.

3. To determine the concentration of Pb, Cd, and Cr ions in the aqueous solutions after the removal process.

1.4 Significance of Study

The findings from the study are of utmost importance for developing a more powerful, cost-effective technique for treating heavy metal ions in aqueous solutions using an adsorption technique. The procedure developed in this study can be used to spread information to others, especially in agricultural and industrial sectors regarding the effectiveness of this method in removing heavy metals accumulated in water resources. In addition to that, this study would also assist some chemical industries in treating noxious metals before being disposed into the water bodies like streams and rivers. Moreover, the treatment of heavy metals is vital to ensure a high quality of water based on regulations of the World Health Organization (WHO) and make sure the content of heavy metals in the water bodies is not exceeding the permissible limit.

In this study, the use of iron oxides as adsorbents was implemented as it is considered a convenient method to design and carry out with efficient, effective and varied capabilities. Iron oxides are known to be eco-friendly and low-cost adsorbent due to their natural occurrence may help to spread awareness to the public on how the heavy metals can be treated efficiently and eventually create a cleaner and safer environment for living organisms.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metals

The word heavy metal refers to the element that is generally considered to have a density that exceeds 5g per cubic centimetre (Gunatilake, 2015) and an atomic weight between 63.5 and 200.6 (Carolin *et al.*, 2017). These toxic metals include As, Pb, Cu, Hg, aluminium (Al), barium (Ba), chromium (Cr), uranium (U), bismuth (Bi), cadmium (Cd), nickel (Ni), tin (Sn), manganese (Mn) and others. They are very carcinogenic and dangerous pollutants due to their flexibility, non-biodegradable, accumulation, and endurance. In other words, even at extremely low concentrations of heavy metals, there is a considerable risk to ecological systems and human health. Thus, heavy metal pollution is a major environmental burden as they persist in the ecosystem and cause adverse effects on living organisms.

2.1.1 Lead

Lead (Pb) is the second most lethal heavy metal after As, accounting for 0.002% of the earth's crust and having a natural level of less than 50 mg/kg (Kumar *et al.*, 2020). It is a naturally occurring bluish-grey metal that is highly noxious, non-disintegrative, has an atomic number of 82, a molecular weight of 207.2, a density of 11.34 g/cm^3 and a melting point of 327.5 °C. Anthropogenic activities such as mining, combusting fossil fuels and cable making have increased the release of Pb in high concentrations despite its natural occurrence.

Rapid industrialization is one of the major contributors to the effluent discharge from industrial units which is contaminated with Pb. Lately, the production of lead-acid batteries has become the primary source of Pb in effluent discharges from industries

(Carolin *et al.*, 2017). In general, Pb can be exposed to humans through automobile exhaust, atmospheric dust and even paint. Recently, Pb is regarded as a ‘Group 2’ human carcinogen since the uptake of Pb through lead-contaminated dust particles causes terrifying health effects on humans.

2.1.2 Cadmium

According to the ATSDR list, cadmium is the seventh most hazardous heavy metal (Pfeifer and Škerget, 2020). Cadmium (Cd) is one of the naturally occurring metals that can be seen in the Earth's crust that contains barely 0.1 ppm of Cd, according to estimates (Pfeifer and Škerget, 2020). Heavy metals such as Cd can also be encountered in polluted water resources, which are frequently characterized as a toxin, despite serving no physiological functions. It has an atomic number of 48, a molecular weight of 112, a melting temperature of 321°C, a boiling point of 765°C, and is described as being soft, malleable, silvery-white with a bluish colour, and shiny (Rafati Rahimzadeh *et al.*, 2017). It is generally observed as a mineral associated with other elements like oxygen (Cd oxide), chlorine (Cd chloride), or sulphur (Cd sulphate, cadmium sulphide) (Singh Thakur *et al.*, 2013). Cadmium is often used in polyvinyl chloride plastic production, nickel-cadmium batteries, paint making, electroplating, and also as a pigment.

A study was performed by Idrees *et al.* (2018) to measure the concentration of Cd ions in the underground water in western Uttar Pradesh regions, India. Four districts were selected for the study, including Shahjehanpur, Bareilly, Moradabad, and Rampur, the water samples were taken from six locations in each district. The findings revealed that the raised Cd concentration was at an alarming level in all of the selected areas. According to World Health Organization, it is suggested that the Cd content in drinking water should be less than 0.05 ppm (Paul, 2017). However, the investigation showed that the levels of hazardous metal were over the recommended limit in every one of the places that were examined.

Moreover, Naseem *et al*. (2014) conducted a study on the Cd concentrations in the groundwater of Pakistan, specifically in Winder Town, Balochistan. About 48 samples of soil and water were gathered, and they were examined for the presence of Cd and other elements. The results of the current investigation demonstrated that Cd ions were found in water samples, and a majority of the samples, nearly 60% had concentrations above the recommended WHO guidelines, that was 0.05 mg/L for drinking purposes.

2.1.3 Chromium

As per Mohanty and Patra (2013), the seventh most prevalent metal on earth is chromium. Chromium, which makes up around 0.037% of the earth's crust, is a hard, silver-coloured metal with an atomic number of 24, a density of 7.19 g cm^{-3}, and a molecular weight of 51.10 g M^{-1} (Singh *et al.*, 2022). Even though chromium exists in a variety of oxidation states, trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) are the most stable forms. When comparing the two chromium forms, Cr(VI) is more hazardous than Cr(III), which is uncommon that can have adverse effects on human health (Pfeifer and Škerget, 2020). Whereas humans consume only a very little amount of Cr(III) as it is a vital mineral in the diet.

Mani Tripathi and Chaurasia (2020) have conducted an investigation to detect Cr in ground and surface water. The study was performed in Unnao, a district of Uttar Pradesh, India. Unnao is a sizeable industrial area with a high concentration of tanneries and chemical plants that contaminate the surface water around these water bodies by dumping their waste products into them which eventually had an impact on the local flora and wildlife. 47 samples of water from the Unnao district were taken for investigation and parameters such as the presence of Cr(VI) and total Cr were tested. As a result of the investigation, one of the locations, Dharamkata, has a concentration of Cr(VI) that was discovered to be 2070 mg/L, which has a remarkable efficacy for contaminating abandoned streams and thus, polluting both surface water and groundwater.

2.2 Sources of Heavy Metals

Heavy metals are natural contaminants which reside in the environment for a long period. They can be introduced into the ecosystem by natural and anthropogenic sources. Natural sources include surface water, groundwater, soil erosion, volcanic activities, and urban runoffs. While anthropogenic sources of heavy metal contamination are agricultural activities like herbicides and pesticide usage, mining extraction operations, electroplating processes and municipal waste used for fertilization.

2.2.1 Sources of Lead

Nowadays, the contamination of Pb is one of the greatest concerns of all because it creates harmful effects on both humans and plants. Various natural sources led to the contamination of Pb in air, soil, and water resources such as geochemical weathering, sea spray emissions, volcanic activity, and remobilization of sediment, soil, and water from mining areas (Kumar *et al.*, 2020).

Harvey *et al*. (2015) revealed that water contamination happened due to the use of Pb metal in the tank supplies roof catchments and corrosion of plumbing fittings in small study cohorts. In addition to that, drinking water has been contaminated with Pb as a consequence of plumbing fittings and taps. Ferati *et al*. (2015) stated that Pb metal contamination originates from anthropogenic sources like the discharge of industrial water from mining flotation and the mine waste eroded from the riverbanks, urban discharge and industrial waste.

According to Maheshwari *et al*. (2020), the reasons for Pb contamination in water were due to the changes in disinfectant chemicals from chlorine to chloramine, inappropriate pH modifications, and the cessation of corrosion inhibitors in treatment facilities. As a result, Pb was dissolved in the water, harming water consumers.

As per Othman *et al*. (2013), the heavy metals discovered in waste were sourced from the electroplating and metal processing or fabrication industries residing along the West coast of peninsular Malaysia, including Klang Valley, Penang, Ipoh, and Johor Bahru. Pb pollution was also discovered in various industries, including petrochemicals, paints, and battery production. According to Statista Research Department (2020), up to 11.6 million metric tonnes of lead were produced globally in 2018. According to Zahra (2012), 60% of Pb output has been used in the manufacturing of batteries, with the remaining 40% used in numerous industrial goods such as pigments and plastics.

2.2.2 Sources of Cadmium

Contamination with heavy metals such as Cd compounds has the potential to cause significant health issues to human beings. Almost all foods contain cadmium, however, the amount varies greatly depending on dietary preferences. As a result of anthropogenic activities like the burning of waste and the usage of fossil fuels, it is ubiquitous in the environment (Rafati Rahimzadeh *et al.*, 2017). About 75% of Cd production is due to the manufacturing of alkaline batteries (Abd El-Hameed *et al.*, 2021). In addition, another 25% of Cd is employed in the production of coatings, pigments, and plastic stabilisers (Jaishankar *et al.*, 2014).

Research conducted by Yuan *et al*. (2019) in a town in Southeast China, reported that the major source of anthropogenic Cd emissions was due to industrial production (IP), accounting for 62.1% of total emissions. Followed by other sources such as aquaculture (AQ), wastewater treatment (WT), living consumption (LC), crop farming (CF), and animal breeding (AB), which each represented less than 10% of total emissions. In addition, the research has discovered that anthropogenic activities contributed to the highest Cd emissions into the water, which was 90%, followed by the soil and atmosphere which were 9% and 1%, respectively.

The major source of industrial production was pigment production, which accounts for more than 98.4% and it generates the most environmental pollutants of any industry representing about 61.1% of total anthropogenic Cd emissions. Moreover, Cd discharged into water will be carried downstream by mixing with local watercourses, resulting in no-point source contamination during irrigation and contaminating the vital supply of drinking water for that region, the Taihu Lake.

2.2.3 Sources of Chromium

The increased concentration of Cr in soil and water as a result of natural and anthropogenic sources is garnering attention. Cr is produced naturally as a by-product of coal and oil combustion, petroleum from ferro chromate refractory material, fertilisers, pigment oxidizers, metal plating tanneries, and chromium steel (Jaishankar *et al.*, 2014). Chromium is used widely in industries, particularly for the production of chrome-steel or stainless steel and other alloys, dyes and pigments as well as bricks in furnaces chrome plating, wood preservation, and leather tanning (Singh Thakur *et al*., 2013). These industries contribute significantly to Cr contamination, which ultimately has a negative impact on biodiversity. Dumping of sewage and fertilizer utilization are the anthropogenic sources of Cr emission into the ecosystem that increases environmental contamination by Cr.

Neelam (2018) conducted an experiment to test the wastewater quality of tanneries effluent in Korangi, Karachi, Pakistan. Korangi town is well-known for its leather production that uses chromium sulphate. After the analysis, it was reported that the concentrations of Cr were not within acceptable limits. The main contributor to the high level of Cr in the wastewater is the wastes released from the tanneries in Korangi.

Cheng *et al*. (2014) conducted research in which they compiled an inventory of Cr emissions into the atmosphere and water from anthropogenic activities in China between 1990 and 2009. Oil and coal combustion, production of ferrochromium, cement production, iron and steel industry, and waste incineration were the sources of Cr emissions into the atmosphere. Among them, coal combustion produced the highest emission of Cr, which was up to 46.6%. Whereas, the sources that caused the discharge of Cr into water bodies were industrial sectors, including the leather industry, fabricated metal industry, chemical manufacturing industry, and nonferrous metals mining industry. Of all, the fabricated metal industry discharged the most percentage of Cr into the water, which was about 68%.

2.3 Effects of Heavy Metals

Heavy metals are well known for their toxicity. Each heavy metal has its toxicity levels and causes deadly effects on others. They may pose serious threats to the human community as they can be absorbed and accumulated in the human body. Noxious diseases and disorders would turn up as the result of bioaccumulation in human body cells and tissues.

2.3.1 Effects of Lead

Human exposure to Pb can occur through inhalation of lead-contaminated dust particles and ingestion of lead-contaminated water, foods and also paints. The effect of toxicity due to Pb is known as lead poisoning. Lead poisoning can be either acute or chronic and it usually affects our central nervous system and gastrointestinal tracts in adults as well as in children (Azeh Engwa *et al.*, 2019). Acute exposure can cause headaches, loss of appetite, abdominal pain, hypertension, renal dysfunction, sleeplessness, fatigue, arthritis, vertigo, and hallucinations. In contrast, chronic exposure can cause mental retardation, congenital disabilities, psychosis, autism, allergies, dyslexia, weight loss, hyperactivity, paralysis, muscular weakness, brain damage, kidney damage, and death.

According to Kumar *et al.* (2020), Pb absorption is observed to be greater in children rather than in adults, approximating that adults may absorb 3 to 10% of an oral dose of water-soluble Pb, whereas for children, it may be as high as 40 to 50%. According to WHO, Pb metal can cause significant environmental contamination and health problems because it is widely spread mostly in developing countries. Based on the study conducted by Tanja Kragulj (2015), about 0.6% of Pb metal exposure accounted for the global burden of disease, and the highest burden of the disease happened in developing countries.

Pb exposure will have a negative impact not only on humans but also on aquatic species, especially fish as they are more vulnerable to the hazardous effects of Pb exposure (Lee *et al.*, 2019). Metal toxicity in fish is induced largely through bioaccumulation in tissues as well as metabolic, excretory, and detoxifying methods triggered by metal intake and eventually leads to oxidative stress (Eroglu *et al.*, 2015). Pb-induced oxidative stress causes synaptic damage and neurotransmitter dysfunction in fish, resulting in neurotoxicity (Zhu *et al.*, 2016). Furthermore, as an immuno-toxicant, Pb exposure affects immune responses in fish.

2.3.2 Effects of Cadmium

Due to its detrimental effects on human bodily organs, cadmium poisoning has grown to be a significant global health problem. The leakage of sewage sludge into agricultural soil may result in the transfer of Cd compounds taken up by the plants, which may play a significant role in the food chain. They could then be ingested by humans and cause the accumulation of Cd metals in numerous organs.

Long-term Cd exposure via air, water, soil, and food may cause carcinogenicity which then leads to cancer and degradation of the organ systems, including the skeletal, urinary, reproductive, cardiovascular, central and peripheral neurological systems, and respiratory systems (Rafati Rahimzadeh *et al.*, 2017). While short-term cadmium exposure through inhalation can lead to serious lung damage and respiratory problems (Azeh Engwa *et al.*, 2019). Yet, ingesting high quantities of Cd might irritate the stomach and cause vomiting and diarrhoea.

A review presented by Kumar *et al*. (2019) summarized the recent information on the reproductive hazardous potential of Cd in humans based on data that have been collected through many sources, including websites, books, reports, and other publications. The results showed that human male reproductive organs were affected by Cd exposure, which causes spermatogenesis, semen quality, specifically sperm motility, and hormonal synthesis to be compromised. It also affects female reproduction and reproductive hormonal balance, as well as menstrual cycles, according to experimental and clinical research. In addition, the exposure to Cd might have adverse impacts on human pregnancy or its outcome, where it affects the development of infants such as low birth weight and length, decreased head circumference, and others.

Itai-itai disease, which first appeared in Japan in the 1960s, was predominantly brought on by long-term exposure to Cd as a result of industrialization-related activities (Nishijo *et al.*, 2017). Osteomalacia with agonizing bone pain is an effect of itai-itai disease, which is also related to renal tubular failure. The disease mainly affected women Women who live in rice farming regions in Toyama, Japan that are fed by the poisoned Jinzu River are the majority of those affected by the itai-itai disease.

Cd will not only have negative effects on humans but also marine life such as Heteropneustes fossilis when being subjected to a high concentration of Cd for 24, 48, 72, and 96 hours. A study conducted by Kumar *et al*. (2019) on this type of fish has resulted in an accumulation of Cd that can be found mostly in the gills and liver of the fish. The sequence of Cd accumulation rates in these tissues was determined to be liver > gills > kidney. In addition, Cd inhibits oxidative metabolism in tissues, resulting in an altered energy status in fish due to the toxicant's influence on carbohydrate metabolism in the liver, brain, and gills. Because of the toxic stress, glucose and lactate levels increased dramatically, whereas glycogen and pyruvate levels declined significantly.

2.3.3 Effects of Chromium

Both Cr(III) and Cr(VI) have harmed the lives of humans as well as flora and species. Cr is the most hazardous species when it is in hexavalent form, while other species such as Cr(III) compounds are far less toxic and hence produce little or no health consequences. Irritation of the nose, eyes, lungs, intestines, and stomach is one of the acute toxic effects that can happen when there is an extremely high level of Cr(VI) in the environment (Singh Thakur *et al*., 2013). Moreover, people who are sensitive to chromium may get asthma episodes after inhaling elevated concentrations of either Cr(VI) or Cr(III). According to Mohamed *et al*. (2019), exposure to high doses of Cr(III) could even induce DNA damage due to the high accumulation of Cr in body cells. Excessive Cr(VI) compound exposure in humans can cause serious cardiovascular, haematological, pulmonary, renal, hepatic, gastrointestinal, and neurological complications, but also death (Azeh Engwa *et al.*, 2019).

Sharma *et al*. (2012) investigated the health consequences of hexavalent chromium groundwater pollution caused by tanneries and chrome sulphate manufacture in Kanpur, India. The health status of residents living in regions with high Cr(VI) groundwater pollution was compared to residents with identical sociodemographic features residing in communities with no increased Cr(VI) levels. As a result, individuals exposed to Cr(VI) groundwater experienced severe health repercussions such as gastrointestinal disorders, dermatological diseases, and haematological defects.

Caparros-Gonzalez *et al*. (2019) performed a study on the association of chromium exposure with neuropsychological development in children in Spain. In 2010 and 2012, 393 children aged from 6 to 11 years old were randomly recruited from schools in two southern Spanish regions and their urine and hair samples were collected for the determination of Cr levels. According to the findings, hair and urine chromium levels decreased neurobehavioral function in both boys and girls. Moreover, urine chromium levels seemed to have an effect on cognitive function exclusively in boys.

2.4 Determination of Heavy Metals in Polluted Water

Heavy metals impose a major threat as hazardous contaminants to both aquatic and terrestrial ecosystems because of their noxiousness and tenacity in minuscule amounts (Aquisman *et al.*, 2019). Determination of concentrations of heavy metals in soil, and water samples in aquatic and terrestrial ecosystems has been a challenge in recent times. A community-wide effort to identify the presence of heavy metals in wastewater, soil, or aquatic species is essential in preventing disease, especially among individuals who live near industrial or mining areas. Several modern analytical techniques are available for the study of heavy trace metals, including FAAS, AAS, ICP-MS, ICP-OES, liquid-liquid extraction, anodic stripping voltammetry, polarography and ultrafiltration.

A study was conducted by Dagne (2020) to determine the concentration of heavy metals (Cr, Cd Zn, Fe, Pb, and Cu) in wastewater and identify their toxicological effects around the Eastern Industrial Zone, Central Ethiopia. Flame atomic absorption spectroscopy (FAAS) was used for the identification of toxic heavy metals present in the wastewater. From the results, it showed that the total concentrations of Cr, Cd, Zn, Fe, Pb, and Cu were ranged from (0.20-1.04 mg/L), (0.04-0.08 mg/L), (0.07-0.21 mg/L), (2.89-5.15 mg/L), (3.11-45 mg/L), and (0.30-0.99 mg/L) respectively. Overall, the concentration for each of these heavy metals has exceeded the permissible limit recommended by the WHO and FAO.

Another investigation has been conducted by Wijaya *et al*. (2019) to determine the metal concentrations of Pb, Cd, Zn, As, Cu, Ca, Fe and Mn in the contaminated sediments of the Sumida River in Tokyo, Japan and the Chao Phraya River in Bangkok, Thailand. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was employed for the analyses of heavy metal concentration in the samples collected. The results of both sediment samples displayed the maximum leached levels of Cd (38.6 %), Ca (55.2%), Mn (41.3%), Pb (52.1%), Zn (56.7%), Cu (61.2%), As (47.1%) and Fe (55.9%). In sum, the levels of Pb, Zn and Cu metals in both the rivers were reported to be higher than the permissible limits guided by WHO.

Besides that, Gashi *et al*. (2020) performed a case study on the estimation of the heavy metals' content in the stream of Llapi River, Kosovo. Atomic absorption spectroscopy (AAS) was utilised as the instrumental technique to detect and trace heavy metal ions in the river water samples. From the results, it was found that the concentration of Cr, Ni, Zn, Cu and Fe metals in all samples were under the recommended limits of WHO. However, the concentration of Cd and Pb in all samples and concentrations of Mn in several samples exceeded the norms fixed by WHO.

2.5 Techniques for Removal of Heavy Metals

Many techniques have been introduced and implemented by researchers to treat toxic heavy metals present in effluents. These techniques include chemical precipitation, ion exchange, membrane filtration, coagulation-flocculation, adsorption and electrochemical treatment. Generally, each method aforementioned has its pros and cons.

2.5.1 Chemical precipitation

Chemical precipitation is considered a mature and reliable method where it is used broadly in many industries. In this conventional process, chemicals are added to the contaminated water to adjust the pH to convert the soluble heavy metal ions into insoluble precipitates. These precipitates include hydroxide, sulphide, carbonate and phosphate (Zhang and Duan, 2020) which can then be removed by sedimentation, flotation or filtration methods and the cleared water is used for other purposes. This process is divided into two types of precipitation, hydroxide precipitation and sulphide precipitation.

The hydroxide precipitation process can be described as adding a hydroxide to the stirred wastewater to form insoluble metal hydroxide precipitates (Qasem *et al.*, 2021). The common types of precipitants that are accessible and can be used to treat heavy metals are lime, calcium hydroxide ($Ca(OH)_2$), and sodium hydroxide (NaOH) which can produce hydroxide precipitates by releasing the hydroxide ion bonded with heavy metal ions (Carolin *et al.*, 2017). Meanwhile, sulphide precipitation distinguishes itself in terms of higher removal efficiency and lower solubility of metal compounds than hydroxide precipitates (Qasem *et al.*, 2021). A variety of precipitants such as sodium sulphide (Na_2S), sodium hydrosulphide (NaHS), calcium sulphide (CaS), ammonium sulphide ($(NH_4)_2S$) and barium sulphide (BaS) for sulphide precipitation (Bejan and Bunce, 2015).

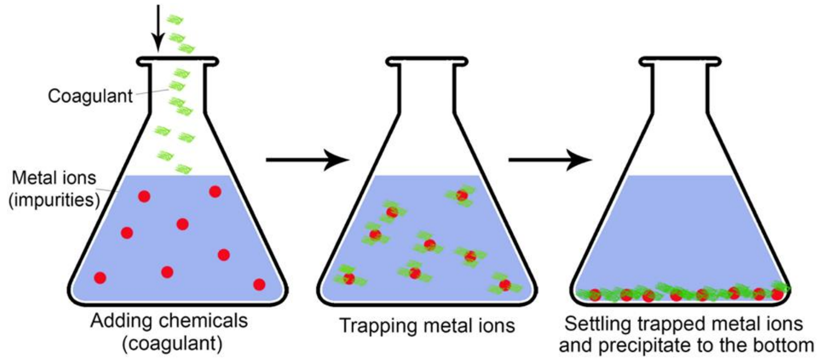

Figure 2.1 Treatment of heavy metals by chemical precipitation (Qasem *et al*., 2021)

Chen *et al*. (2018) studied the removal of heavy metals, which were Zn (II), Cu (II), and Pb (II) from aqueous solutions using lime ($Ca(OH)_2$), soda ash (Na_2CO3) and sodium sulphide (Na_2S) as the precipitants. At an initial concentration of 100 mg/L, these precipitants successfully removed up to 99.99 percent of Cu and Zn. In contrast, the removal rate of Pb (II) ion was 99.75% when being treated with sodium sulphide, 76.14% of Pb (II) ion when being treated with lime and 97.78% of Pb (II) ion when being treated with soda ash.

Uddin *et al*. (2020) examined the removal of Cr (III) from chrome tan wastewater using three precipitating agents that were calcium carbonate ($CaCO_3$), sodium bicarbonate ($NaHCO_3$), and magnesium oxide (MgO) to treat chrome tan wastewater. After treating with $NaHCO_3$ and $CaCO_3$, the removal percentage of Cr (III) at optimum pH was found to be 99.97% and 99.95% respectively. Meanwhile, the removal rate of Cr (III) after being treated with MgO was found to be 99.98%.

Zhang and Duan (2020) have synthesized magnesium hydroxy carbonate as the precipitating agent using low-grade magnesite. Three metals, vanadium oxide, VO_2^+, Cr^{3+}, and Fe^{3+} were successfully eliminated from wastewater in a declining concentration with the optimal parameters of 20 minutes contact time, 0.3 g of precipitant dose and a pH of 7.1. Using magnesium hydroxy carbonate, the precipitated amounts of VO_2^+, Cr^{3+}, and Fe^{3+} were 0.7, 0.133, and 3.47 g/g, respectively. The precipitate was somewhat made up of iron(III) oxide, Fe_2O_3, vanadium pentoxide, V_2O_5, and chromium(III) oxide, Cr_2O_3, and it may be utilized as a substitute material in the metalworking industry.

2.5.2 Ion exchange

The ion exchange approach is a reversible chemical process that is used to replace the toxic heavy metal ions with the similarly charged ions attached to a water-insoluble substance, known as ion exchanger resin. Ion exchange resin is an immobile solid particle which absorbs positively or negatively charged ions from an electrolyte solution and releases other ions with the same charges (Gunatilake, 2015). The materials of ion exchange resins are categorized into two kinds, natural and synthetic resins (Bilal *et al.*, 2013). Of these resins, synthetic resins are preferred over natural resins for eliminating heavy metal ions.

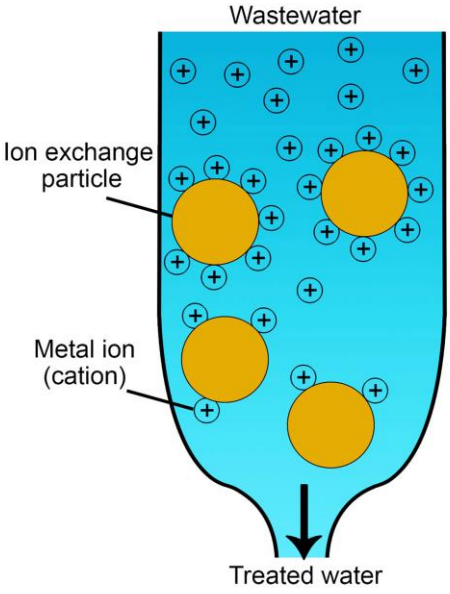

Figure 2.2 Heavy metal removal by ion exchange treatment (Qasem *et al.*, 2021)

Tan *et al*. (2017) conducted an investigation on the removal effect of Cu and Ni in the wastewater by D001 resin. The used D001 ion exchange resin was a strongly acidic styrene cation exchange resin. The removal rate of Cu and Ni was 99.14% and 99.33% respectively when the initial concentrations of Cu and Ni in the wastewater were 100 mg/L and the pH was 5.

Shaidan *et al*. (2012) employed a fixed bed with strong acidic cation exchange resin to remove Ni from wastewater effluents. The author has achieved a removal rate of 97% Ni from the wastewater. Meanwhile, Zewail and Yousef (2015) have conducted an investigation on removing Ni and Pb from wastewater spouted beds with AMBERJET 1200 Na resin. The reported result was 99% and 98% removal for Pb and Ni respectively.

Moosavirad *et al*. (2015) studied the removal of Pb(II), Zn(II), Cd(II), Cu(II), and Ni(II) from wastewaters in industrial areas of Iran and Kerman by ion-exchange method. Dowex 50WX8 (H^+) resin was chosen as an appropriate adsorbent for the elimination of hazardous components in the wastewater. The optimum condition for this adsorption study was a flow rate of 4 mL min^{-1}, a dose of 200 mg resin, and a pH of 4–6. Pb(II), Zn(II), Cd(II), Cu(II), and Ni(II) adsorptive capacities were 60, 50, 50, 45, and 40 mg/g, respectively. The findings show that exchanger resin is particularly helpful in decreasing the heavy metal concentrations of wastewater.

2.5.3 Membrane filtration

Membrane filtration is one of the techniques used widely in wastewater treatment applications that uses pressure to separate or filtrate undesired substances. The membrane is generally composed of a specific porous substance that promotes the remediation of heavy metals from polluted water (Patil *et al*., 2016). Inorganic contaminants like heavy metals, organic compounds and suspended solids can be eliminated using this method. Membrane filtration comes in a variety of types such as ultrafiltration, microfiltration, nanofiltration and reverse osmosis that can be utilized for heavy metal removal from wastewater. Among these, nanofiltration (NF) has attracted many researchers as the operation is simple, energy consumption is low and requires low pressure.

Zhu *et al*. (2014) have fabricated dual-layer nanofiltration hollow membranes using polyethersulfone (PES)/polyvinylpyrrolidone (PVP), and polybenzimidazole (PBI) for the removal of toxic metal ions, Cd, Cr and Pb. As a result, the membrane successfully rejected 95% Cd, 98% Cr and 93% Pb. Mehdipour *et al*. (2015) conducted an experiment using polyamide NF membrane for Pb removal and it was found that an inclination in initial feed concentration and pressure boost the removal of Pb up to 97.5%.

2.5.4 Coagulation-flocculation

The mechanism of coagulation-flocculation is based on the electrostatic attraction between pollutants and coagulant-flocculant agents (Gunatilake, 2015). Coagulants such as aluminium sulphate (alum), magnesium chloride, and aluminium hydroxide are used to destabilize the colloidal particles present in the wastewater (K.