Evaluation of removal performance of hexavalent chromium species using montmorillonite clay and iron coagulant

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DEDICATION

This endeavour would not have been possible without the support of my exceptional parents, adored sibling, and my friends whose tremendous support and cooperation led me to this wonderful accomplishment.

“By virtue of whose prayers, we have been able to attain this position and whose hands are always raised for prayers, for our well-being.”

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ABSTRACT

Chromium ion contamination in surface and groundwater is a pressing global issue that demands urgent improvements in treatment systems to lower toxic levels. In accordance, conventional water treatment processes like coagulation, flocculation, and sedimentation (C/F/S) offer practical pathways to ensure public safety. Therefore, in current research, single and combined effect of ferric chloride (FC) coagulant and montmorillonite clay for hexavalent chromium (Cr(VI)) removal from water was examined. The results indicated greater Cr(VI) removal performance of FC coagulant (93.9% at a dosage of 0.12 g/L) at pH 5 than montmorillonite clay (13.27%, at 0.1 g/L) and combined system with 0.12 g/L FC and 0.1 g/L montmorillonite clay (84.3%). Maximum Cr(VI) removal was observed in acidic conditions (93.49% at pH 4) while removal potential of FC coagulant continuously decreased with increase in pH (64.31% at pH 6, 49.57% at pH 7, 36.34% at pH 8 and 28.71% at pH 9). Single and combined interfering ions effects were evaluated where results showed maximum Cr(VI) removal of 87.97% in presence of chloride and minimum Cr(VI) removal of 52.52% in presence of phosphate, while in presence of mixture of interfering ions, 64% Cr(VI) removal was observed. Moreover, turbidity removal was also monitored before and after FC coagulation, with results showing a significant decline in turbidity from (41.4 NTU to 492 NTU) to below 0.01 NTU, thus showing excellent coagulation performance. Sorption data showed better fitting with the Freundlich model (R^2: 0.92), indicated multilayer Cr (VI) adsorption on heterogeneous sites of the FC coagulant, surpassing the Langmuir model (R^2: 0.85). In general, this research underscores the promising application and usage of FC coagulant in removing particulates as well as dissolved metal ions from aqueous solutions, thereby providing critical insights to drinking water treatment industries.

Keywords: Hexavalent chromium removal, ferric chloride coagulant ,montmorillnite clay, coagulation/flocculation/sedimentation,water treatment.

CHAPTER 1

INTRODUCTION

Water covers over 70% of the Earth's surface. However, despite its prevalence, more than 97% of this water is saline, leaving only 3% as fresh water, and even less than 1% of that is considered usable freshwater. Rivers and lakes, which are common sources of water and vital for fulfilling daily water requirements, contain just 0.3% of the world's freshwater. Pakistan is currently categorized as a water-stressed country. The nation's total renewable water resources have decreased from 2,961 cubic meters per capita per year in 2000 to 1,420 cubic meters per capita annually in 2015, further plummeting to 1,139 cubic meters per capita per year in the same period(Mekonnen Engida and Sanjrani, 2017).Access to clean drinking water is not only a pressing social and economic concern but also a fundamental necessity for human survival. The global trend for clean water access is presented in ***Figure 1***.

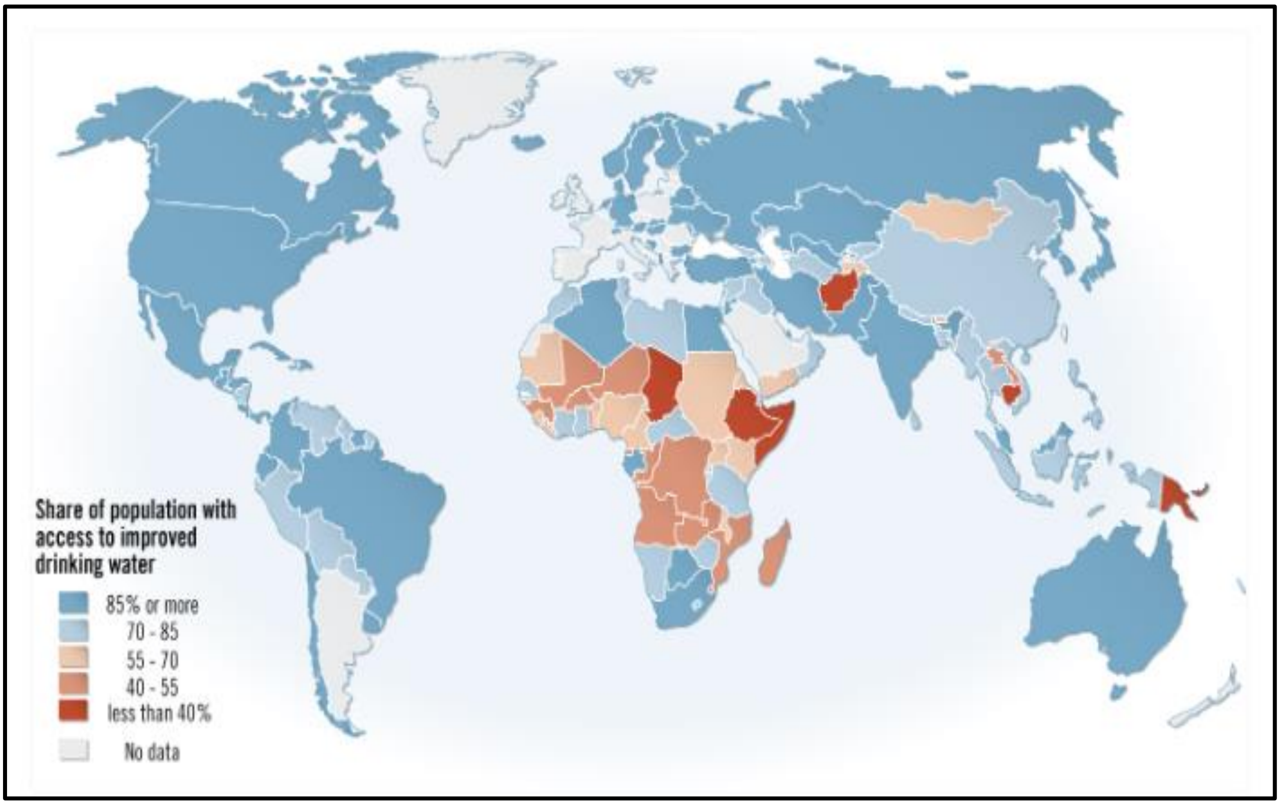

Figure 1 Global Clean Water Access Trends

For global development, ensuring access to clean water is essential. Millions, however, lack access to clean drinking water because it is scarce and contaminated. This poses significant risks to health and obstructs societal advancement. The reliance of billions on groundwater emphasizes the scale of the challenge. Addressing this issue requires collaborative efforts at both local and global levels to develop sustainable solutions. Such collaborative efforts are crucial to ensure access to safe water for everyone,thereby fostering resilience and prosperity. (Khan et al., 2015).

1.1 Background

Chromium, a transition metal denoted by the symbol Cr and atomic number 24, boasts unique properties that make it highly valuable in industrial applications, particularly in metallurgy and material fabrication. ***Figure 2*** presents the global distribution of chromium resevesand also highlights the leading countries in chromium production. This figure presents the geographic dicersity of chromium production and provides the strategic importance of these nations in meeting the worldwide requirement for chromium, an important element of multiple industrial applications, from stainless steel production of aerospace engineering.

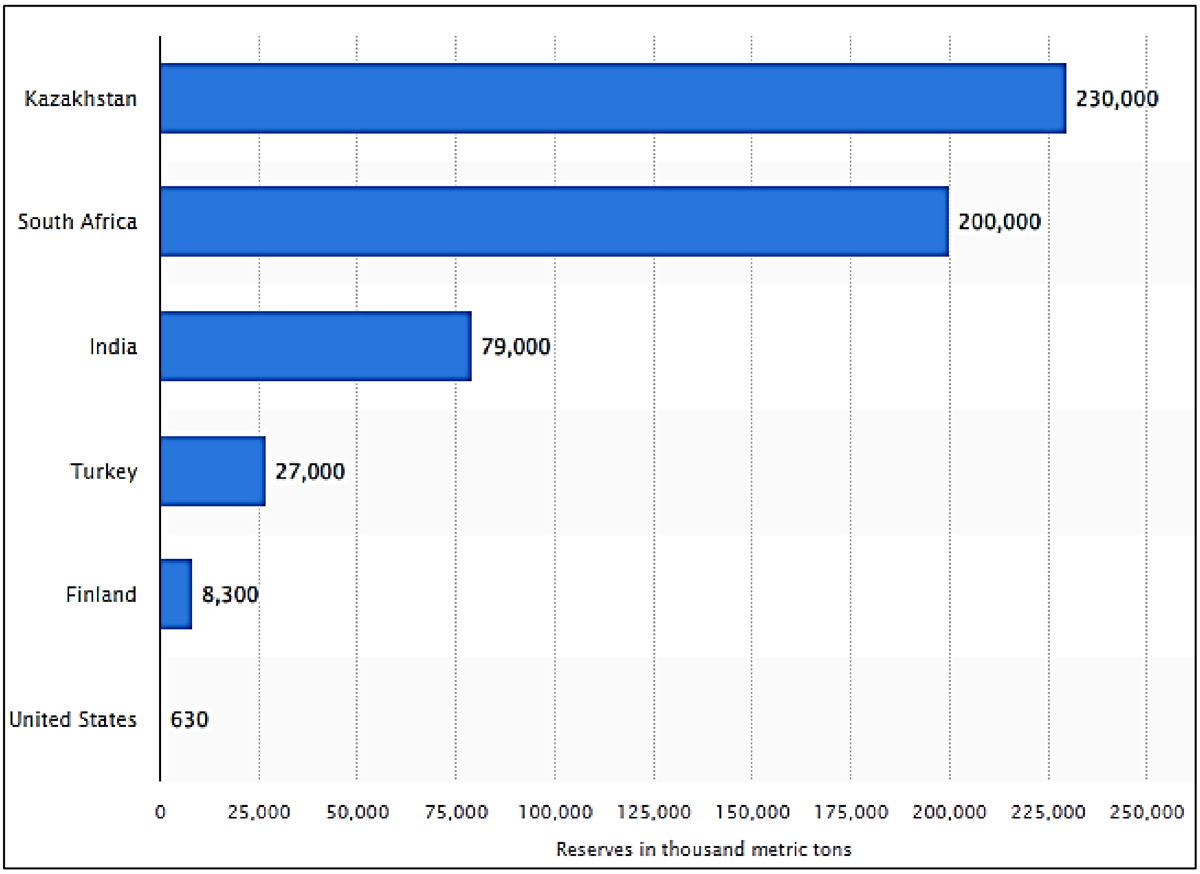

Figure 2 Leading countries with chromium reserves in 2023

Chromium, was discovered in 1798, and has become vital for the production of various alloys in which it improves the strength and resistance to the corrosion. Primary uses of chromium includes the production of ferrous alloys which helps in the production of stainless steels.Ferrochromium which is an alloy of iron and chromium, is a key component in stainless steel production, contributing to its durability and resistance to corrosion (Saha et al., 2022).

Usually, stainless steel contains 10-26% chromium, and increased chromium concentration promotes corrosion resistance. This is particulary advantageous for the industries where exposure to harsh environmnets or corrosive substances is common. For instance, stainless steel products that are madeup of chromium-enriched alloys, are widely utilized in the production of oil tubing, automobile trim and many other consumer goods. Here, chromium helps in prolonging the lifespan of products through rust and corrosion prevention which ultimately reduces the maintenance cost of products (Hayashi et al., 2021).Owing to the corrosion resistant properties of chromium, it is also used in electroplated protective coatings across multiple industries**.** The process of electroplating involves the deposition of thin layer of Cr(VI) on the metal based surfaces following an electrochemical process, which creats a shield againt the corrosion, abrasion and wear. This process not only improves the aesthetic attraction of these products but also enhances the durability and performance. Additionally, chromium is also used in multiple industrial processes including chemical manufacturing and electronics. The compounds of chromium are useful in the processes like electroplating, leather tanning and pigment production since they have the ability to make stable complexes and catalyze certain reactions.

1.2 Environmental cycling of Chromium

The environmental cycle of chromium, as presented in ***Figure 3***, involves various processes that influence its distribution and transformation in the environment(Johnson et al., 2006).

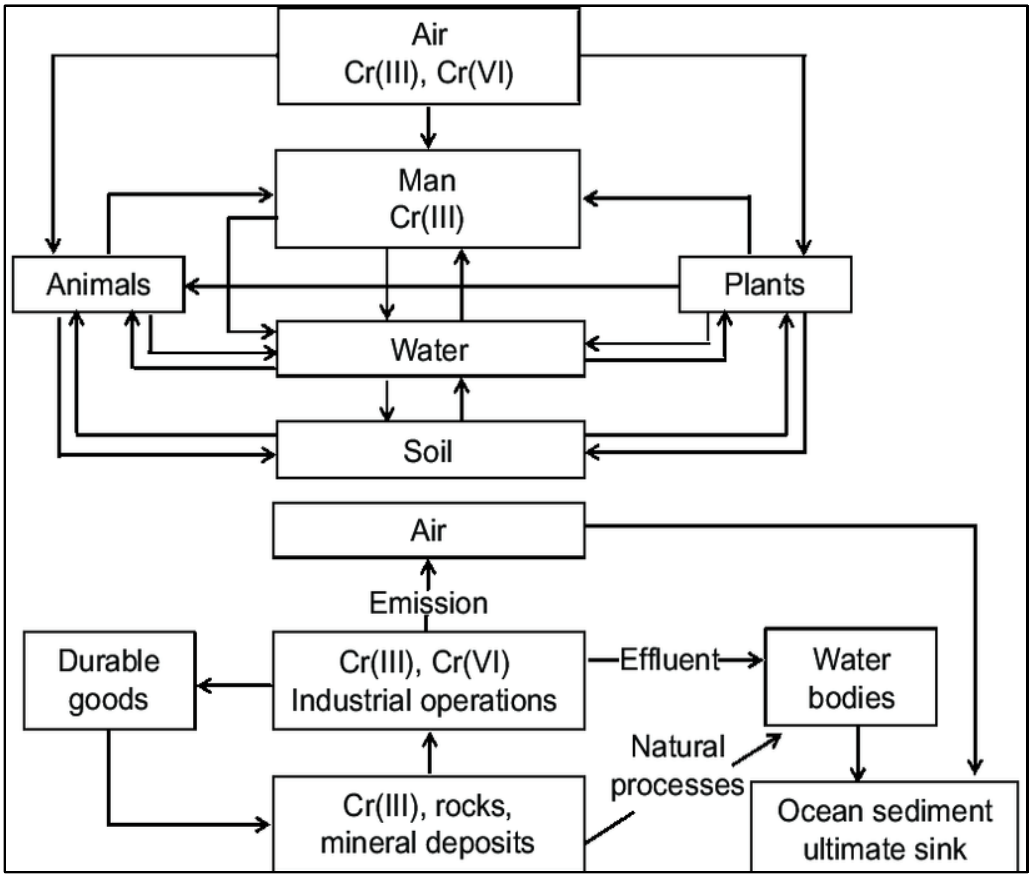

Figure 3 Environmental Cycling of Chromium

Chromium exists in different oxidation states, primarily chromium (III) and chromium (VI), with each form having distinct environmental behaviors(Johnson et al., 2006).

(i) Sources

Chromium enters the environment through natural processes like weathering of chromium-containing rocks and volcanic emissions, as well as anthropogenic activities such as industrial processes (e.g., metal plating, leather tanning, and stainless steel production), coal combustion, and waste disposal.

(ii) Mobility in Soil

: In soils, chromium can bind to soil particles or dissolve in soil water depending on its oxidation state. Chromium (III) tends to adsorb strongly to soil particles and is relatively immobile, while chromium (VI) is more mobile and can leach into groundwater

(iii) Water Transport

Chromium can be transported through surface water and groundwater. Surface water may become contaminated with chromium from industrial discharges or runoff from contaminated soils. In groundwater, chromium (VI) can persist for long periods and spread to distant areas.

(iv) Bioaccumulation and Biomagnification

Chromium can bioaccumulate in aquatic organisms like fish and invertebrates, particularly in its more toxic form, chromium (VI). Additionally, in food webs, chromium can biomagnify, meaning its concentration increases at higher trophic levels.

(v) Chemical Reaction

In aquatic environments, chromium undergoes various chemical reactions, including reduction and oxidation processes. These reactions can transform chromium between different oxidation states, influencing its toxicity and mobility.

(vi) Sedimentation

Chromium may precipitate and accumulate in sediments, especially in areas where water flow slows down. Sediment-bound chromium can serve as a long-term reservoir and potential source of contamination if disturbed.

(vii) Volatilization and Atmospheric Transport

Certain chromium compounds can volatilize into the atmosphere from soil, water, or industrial processes. Once airborne, chromium particles can travel long distances before depositing onto soil or water bodies

(viii) Biological Processes

Microorganisms play a significant role in the environmental cycling of chromium. Some bacteria have the ability to transform chromium (VI) to less toxic chromium (III) through reduction processes, while others can utilize chromium as an electron acceptor in metabolic pathways.

(ix) Human Exposure and Health Risks

Human exposure to chromium primarily occurs through inhalation, ingestion of contaminated food and water, and dermal contact. Chromium (VI) is of particular concern due to its carcinogenic properties and adverse health effects on the respiratory system, skin, and gastrointestinal tract.

1.3 Sources of Chromium

Understanding the sources of chromium contamination requires thorough investigation into the numerous factors influencing its occurrence in the environment. Chromium, occurring naturally, can assume different forms in both natural and human-influenced settings. Some common sources of chromium are presented in ***Figure 4***.

Figure 4 Common sources of chromium.

Naturally occurring chromium is predominantly found within chromite ore, which boasts significant deposits across regions like South Africa, India, Kazakhstan, and Turkey. Chromite ore is one of the primary sources of chromium and is commercially mined for the extraction of this vital element. It exhibitis an average concentration of of around 140 parts per million (ppm) (Johnson et al., 2006).Chromium isfound in multiple environmental mediums, including rocks, soil, fresh water and air. Nonetheless, naturally occurring chromium is found in different concentrations in different mediums, with relatively lower concentrations in seawater and higher concentrations in sediments. Anthropogneicsources are man-made activities which release the chromium into the environment. For instance chromium plating of metal parts(Yu et al., 2018), industrial manufacturing of pigments(Danilov et al., 2006), and the production of tanned leather, rubber, and ceramic raw materials.These activities ultimately lead to the contamination of soil, water, and air with chromium, affecting environmental health and necessitating measures to mitigate the effects of chromium pollution(MacAdams et al., 2005).

1.4 Impacts of Chromium

Chromium is a transition metal which has significant industrial applications but caiusessubstantial environmental and health risks(Usmani et al., 2023).Chromium is widely used in industries including leather tanning, electroplating, and steel production. It is often released into the environment, leading to contamination of soil, water, and air. Chromium exists in different oxidation states,among which hexavalent chromium Cr(VI) is more toxic and carcinogenic. Chromium exposure, particularly Cr (VI) exposure leads to health issues like respiratory issues, skin irritation and increased risk of cancer. In addition, persistent nature of chromium and its potential of bioaccumulation in living bodies further increases the risk on ecosystems, which necessistatestringent regulatory measures and effective remediation techniques to mitigate the detrimental effects of Cr(VI).***Figure 5***presents a brief overview of some impacts of chromium.

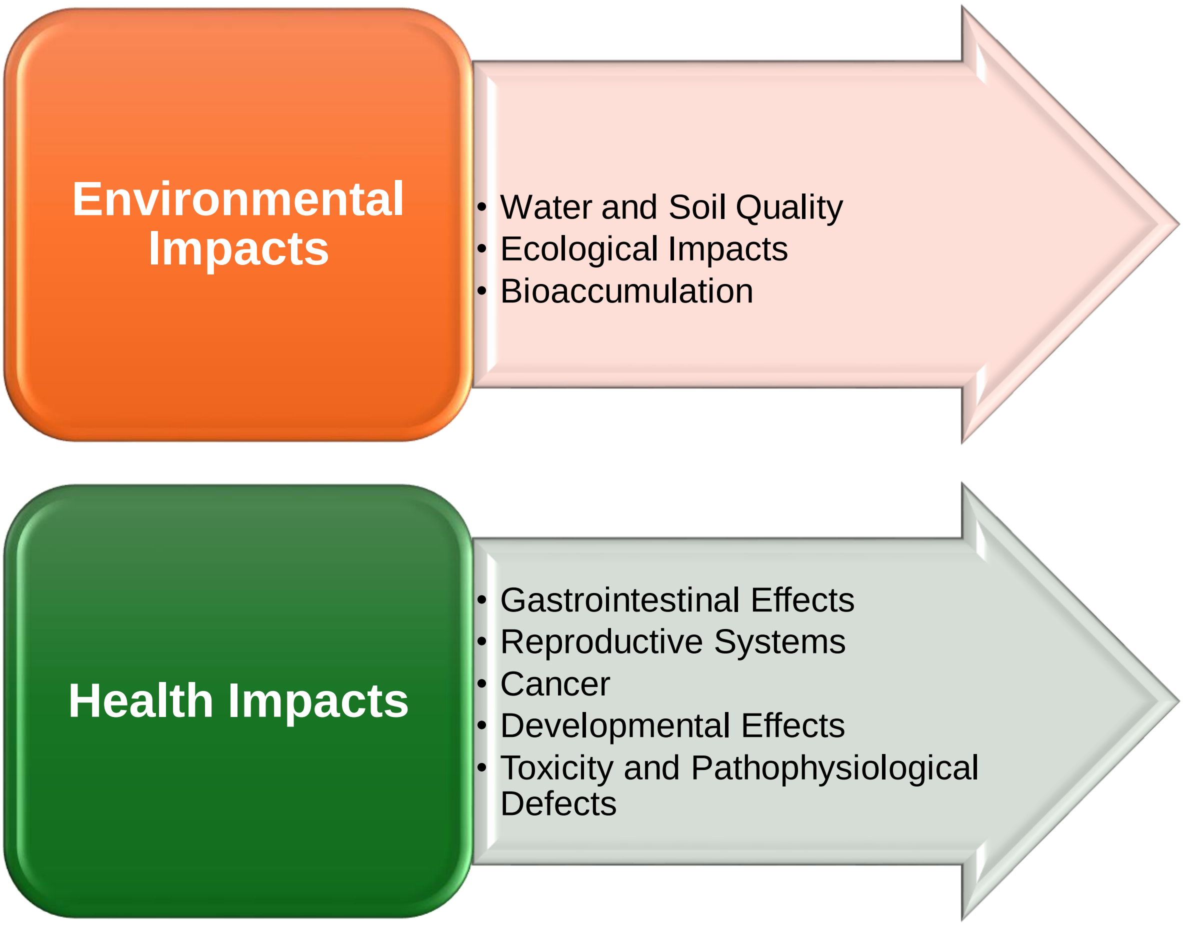

Figure 5 Impacts of Chromium

Following are some key impacts of chromium based on the provided sources:

1.4.1 Impacts on Environment

Water and soil quality

Chromium pollution causes a serious threats to both water and soil quality. The primary sources include electroplating, leather tanning and textile manufacturing. Chromium exists in different oxidation states, among them hexavalent from of Cr is the most hazardous. Owing to its high solubility and mobility which ultimately leads to serious environmental degradation. In aquatic bodies, chromium contamination poses damaging effects. Cr(VI) is extremely soluble therefore it gets readily soluble and disperses in water bodies. This leads to widespread contamination. This contamination disrupts the ecosystems by imparing the respiratory finctions of fish and other aquatic organisms, which causes higher rates of mortality. In addition, Cr(VI) also effects the chemical balance of water, affects the availability of essential nutrients and leads to the decline of aquatic plant life. Overall water quality is compromised, thereby impacting its use for recreational activities, agricultural and other ecological functions.

In land, chromium Cr(VI) affects soil health by changing the microbial composition and activity. It inhibits the growth of beneficial growth of valuable soil bacteria and fungi. These elements are essential for the nutrient cycling and maintenance of soil fertility. This disruption leads to loss of soil fertility, poor crop growth, and curtailed growth of plants. Plants exposed to the chromium contamination may also encounter, chlorosis, root damage, and impaired photosynthesis which significantly affects agricultural productivity. Soil remiditation also becomes challenging and expensive, since chromium binds with the soil and persist in the environment. Moreover, chromium-contaminated water can penetrate groundwater supplies,thereby posing significant risks to water quality. This contamination leads to widespread environmental degradationwhich affects the availability and quality of groundwater for various uses. Owing to the persitant nature of chromium, it remains hazardous for long periods, hence necessitating extensive remediation efforts to restore the affected areas.

Ecological Impacts

Higher levels of chromium in sediments, such as the Aberjona River watershed, underscores the ecological affects which are linked to chromium pollution. It also threatens the aquatic food webs and fauna(Prasad et al., 2021).This contamination poses a serious threat to aquatic ecosystems, which affects the structure and function of food webs and harms aquatic fauna. Since ChromiunCr(VI) is highly soluble and mobile in nature, it easily gets dispersed in water bodies and accumulate in sediments. Once it gets attached with the sediments, chromium disrupts the benthic environment, and hence affects the overall health of ecosystem. Benthic organisms are those,which live in or on the sediments and they are essential components of the aqautic food web. They play a critical role in nutrient recycling and decomposition of organic matter. They are also a food source for higher trophic levels like fish and aquatic birds. Higher levels of chromium present in sediments leads to damaging effects on the these benthic organisms and causes the reduction in their population and biodiversity. It eventually has a cascading effect on the aquatic food web as a whole. For instance, the fish that feed on benthic organisms may encounter reduced availability of food and also leads to the compromisedgrowth, reproduction, and survival rates. Resultantly, predators relying on these fish as a food source, such as larger fish, birds, and mammals, are also affected. Besides, chromium contamination can change the chemical composition of sediments and affects the availability of essential nutrients along with the overall health of the aquatic environment. Likewise, chromium minds with the sediments and organic matteri, changes their properties and makes them unsuitable for aquatic life. Chromium contamination also leads to the long term ecological degradation, as chromium persists in the environment and continues to impact ecosystems over extended period of time. In conjunction with the direct effects on aquatic organisms, chromium disrupts the interactions between species and their habitats. For example, chromium-contaminated sediments can damnagethe development and behavior of aquatic larvae, thereby leading to population declines and altered community dynamics. These disruptions can make the resilience of aquatic ecosystems weak, and makes them more vulnerable to other environmental stressors, like climate change and pollution from other sources.

Bioaccumulation

Bioaccumulation of chromium involves the absorption of chromium present in the environment which results in higher concentrations of the metal in their tissues than in the surrounding environment(Sharma et al., 2020). This phenomenon primarily takes place by two pathways: direct absorption from contaminated water and ingestion of contaminated food.In aquatic ecosystems, chromium, particularly in its hexavalent form (Cr (VI)), is extremnelys soluble and easily enter the bodies of organisms. The process starts with primary producers like algae and phytoplankton, which absorbs chromium directly from the water. These primary producers serve as the base of the food web, and when they are consumed by herbivores such as zooplankton, the chromium is transferred and concentrated within these organisms. Since, herbivores are eaten by larger predators, the concentration of chromium continues to intensify at each trophic level. This process, known as biomagnification, results in the highest concentrations of chromium being found in top predators, such as large fish and birds.Thebioaccumulation of chromium can have severe toxic effects on aquatic organisms. At increased concentrations, chromium causes oxidative stress, damages cellular components like proteins, lipids, and DNA. This leads to a range of adverse health effects, including impaired growth, reproductive issues, and increased mortality. For instance, fish exposed to high levels of chromium may exhibit compromised swimming performance, which makes them more susceptible to predation and less effective at foraging.In terrestrial ecosystems, bioaccumulation of chromium may occur through the contamination of soil and plants. Plants absorb chromium from the soil, which can afterwards enter the food web when herbivores consume these plants. Similar to aquatic systems, chromium concentrations increase at each trophic level, affecting herbivores and their predators. The persistence of chromium in the environment implies that it can remain in soils and sediments for long periods, continuing to pose a risk to ecosystems.Bioaccumulation of chromium also presents risks to human health, particularly for communities that depend on contaminated water and food sources. Consumption of fish and other aquatic organisms with high levels of chromium can lead to chronic exposure, resulting in prospective health issues.

1.4.2 Impacts on human health

Gastrointestinal Effects

Chromium, particularly in its hexavalent form (Cr (VI)), causes significant risks to human health. In particular,the gastrointestinal (GI) system is particularly vulnerable to the toxic effects of chromium (VI)(Wang et al., 2017). When ingested, chromium causes a range of acute and chronic gastrointestinal issues, which depends on the dose and duration of exposure.Acute exposure to high levels of chromium leads to instant and severe gastrointestinal problems. These include intense abdominal pain, nausea, vomiting, and diarrhea. The corrosive nature of Cr (VI) damages the lining of the stomach and intestines, which leads to ulcerations and bleeding. In severe cases, this damage can cause life-threatening conditions such as gastrointestinal hemorrhage and perforation, which requires urgent medical intervention.Chronic exposure to lower levels of chromium can result in persistent gastrointestinal problem. Individuals that are exposed to chromium over long periods may encountercontinuing stomach pain, indigestion, and chronic gastritis. This chronic irritation and inflammation of the stomach lining can impair digestive functions and lead to malabsorption of nutrients, resulting in nutritional deficiencies and weight loss.The mechanisms behind the gastrointestinal toxicity of chromium are primarily linked to its oxidative properties. Cr (VI) can create reactive oxygen species (ROS) within the gastrointestinal tract, that causes oxidative stress and damage to cellular components like lipids, proteins, and DNA. This oxidative damage disrupts normal cellular functions and triggers inflammatory responses, further worsening tissue injury and symptoms.Furthermore, chromium exposure can change the gut microbiota, the community of microorganisms living in the digestive tract. A disrupted microbiota can compromise the barrier function of gut, which allows toxins and pathogens to enter the bloodstream more easily. This condition can contribute to systemic inflammation and a range of other health issues beyond the gastrointestinal system.Long-term gastrointestinal effects of chromium exposure can also increase the risk of more serious conditions, like gastric ulcers and even stomach cancer. The persistent irritation and cellular damage caused by Cr (VI) leads to the development of pre-cancerous lesions and eventually malignant tumors in the gastrointestinal tract.

Reproductive system

Chromium exposure causes serious problems to reproductive health which affects sperm and egg quality, hormonal balance, and fetal development and thus necessitates further research and regulatory measures for the mitigation of its impact(Alvarez et al., 2021).Exposure to chromium (VI) is also linked to sperm damage and harm to the male reproductive system, as seen in laboratory animals, highlighting the reproductive health risks linked with the exposure of chromium. Chromium, particularly in its hexavalent form (Cr (VI)), causes detrimental effects on the reproductive system, which affects both males and females through different mechanisms. The toxic effects of chromium on the reproductive system are of significant concern due to its potential to cause infertility, developmental defects, and hormonal imbalances.In males, chromium exposure causes a range of reproductive issues. Studies show that Cr (VI) can induce oxidative stress in the testes, resulting in damage to sperm cells and reduced sperm count and motility. This oxidative stress harms the DNA within sperm cells, leads to genetic mutations that can be passed on to offspring. Also, chromium can upsets the production of testosterone, a crucial hormone for male reproductive health, leads to lowered libido and fertility.Females are also adversely affected by chromium exposure. Chromium can interfere with the normal functioning of the ovaries, impairing oocyte (egg cell) development and maturation. This can result in decreased fertility, and an increased risk of spontaneous abortions. Chromium exposure during pregnancy is particularly concerning as it can cross the placental barrier, andexposes the developing fetus to its toxic effects. This exposure leads to developmental abnormalities, low birth weight, and increased neonatal mortality.

Likewise, chromium has been shown to disturb endocrine function by mocking or inhibiting the action of natural hormones. This endocrine disruption leads to hormonal imbalances, affects the regulation of the menstrual cycle, ovulation, and other reproductive processes. In both sexes, chromium-induced oxidative stress and DNA damage can lead to a higher risk of reproductive cancers, such as testicular cancer in men and ovarian cancer in women. Animal studies have confirmed these findings, displaying that chromium exposure results in reduced fertility, abnormal reproductive organ development, and changed sexual behavior. These studies provide a model for understanding the potential effects on human reproductive health.

Cancer

Chromium, particularly in its hexavalent form (Cr (VI)), is a well-known carcinogen that establishes significant risks of cancer to various parts of the body. When inhaled, ingested, or absorbed through the skin, Cr (VI) leads to the development of cancer through several biological mechanisms, including oxidative stress, DNA damage, and disruption of cellular processes. The primary pathway for chromium-induced carcinogenesis is its ability to produce reactive oxygen species (ROS). Cr (VI) can penetrate cells and undergo reduction to lower oxidation states, such as Cr (III), within the cell. This reduction process produces ROS, which can cause significant oxidative damage to cellular components, including lipids, proteins, and DNA. The resultant oxidative stress leads to alterations, genomic instability, and altered cell signaling pathways, all of which are key factors in the development of cancer. Cr (VI) is alsocorrelated with an increased risk of lung cancer, especially among workers in industries such as electroplating, welding, and leather tanning, where exposure to chromium dust and fumes is common. Inhaled Cr (VI) particles can affect the respiratory tract, leading to chronic inflammation and continuous oxidative stress, which over time can convert normal lung cells into malignant ones. Epidemiological studies have proven a higher prevalence of lung cancer among workers exposed to Cr (VI), underlining the severe risk posed by this compound. In addition to lung cancer, chromium exposure has been linked to other forms of cancer, likenasal and sinus cancers. These cancers are often linked with direct contact of chromium compounds with the mucous membranes of the respiratory tract, which leads to local carcinogenic effects. There is also evidence suggesting a possible linkage between chromium exposure and cancers of the stomach and gastrointestinal tract, particularly when chromium is uptakenthrough contaminated water or food. Chromium's interaction with cellular DNA is a serious factor in its carcinogenic potential. Cr (VI) can directly attach to DNA or cause the formation of DNA adducts and cross-links, which disrupt normal DNA replication and repair processes. These disruptions lead to mutations and chromosomal aberrations, driving the transformation of healthy cells into cancerous ones.

Developmental Effects

Although no direct studies have conclusively presented that chromium causes birth defects in humans, animal studies suggest that exposure to increased doses during pregnancy could result in miscarriage, low birth weight, and developmental alterations in the skeleton and reproductive system. This underscores the potential developmental risks related with chromium exposure.Chromium, particularly in its hexavalent form (Cr (VI)), poses significant developmental risks to humans and animals due to its toxic and mutagenic properties. Exposure to Cr (VI) during critical periods of development, such as gestation and early childhood, can lead to a range of adverse effects, impacting both prenatal and postnatal development.

During pregnancy, Cr (VI) can cross the placental barrier, exposing the developing fetus to its toxic effects. This exposure can lead to developmental abnormalities and birth defects. Studies in animals have shown that pregnant females subjected to chromium have offspring with a variety of developmental issues, including low birth weight, skeletal deformities, and impaired organ development. The mechanisms behind these effects are primarily related to chromium's ability to induce oxidative stress and DNA damage in developing tissues, which are specifically vulnerable during rapid cell division and differentiation.Chromium's oxidative properties can generate reactive oxygen species (ROS) within fetal tissues, leading to oxidative damage of cellular components such as lipids, proteins, and DNA. This oxidative stress can inhibit normal cellular functions and signaling pathways critical for development, resulting in malformations and growth retardation. Moreover, chromium-induced DNA damage causes mutations and chromosomal abnormalities, further contributing to developmental defects.

Postnatal exposure to chromium can also poorly affect development, particularly in young children. Chromium disrupts endocrine function, leading to hormonal imbalances that affect growth and development. For instance, disruption of thyroid hormone levels can impair brain development and cognitive function, which results in learning disabilities and developmental delays. Chromium exposure has also been linked with immunotoxic effects, weakening the immune system and making children more susceptible to infections and illnesses.In humans, epidemiological studies have presented that populations exposed to high levels of chromium, often through contaminated water or industrial emissions, exhibit higher rates of developmental issues. These include neurodevelopmental disorders, reduced cognitive abilities, and improved incidence of congenital anomalies. The persistence of chromium in the environment means that it can have long-lasting effects on exposed populations, hence necessitating ongoing monitoring and remediation efforts.

Toxicity and Pathophysiological Defects

Chromium toxicity, particularly from its hexavalent form (Cr (VI)), can prompt various pathophysiological defects beyond direct health impacts. One primary area of concern is its effect on cellular integrity and genetic stability. Cr (VI) readily enters cells where it experiencesreduction to Cr (III), a process generating reactive intermediates such as reactive oxygen species (ROS). These ROS can induce oxidative stress, causing damage to cellular components like lipids, proteins, and DNA. The resulting DNA damage may lead tochanges , chromosomal aberrations, and genomic instability, which impacts cellular functions and potentially contributing to the development of malignancies. Likewise, chromium's interference with cellular signaling pathways can interrupt essential processes like cell proliferation, differentiation, and apoptosis. Disruption in these pathways may lead to abnormal cell growth and tissue remodeling, further aggravating pathological conditions. For insistence, chromium exposure isrelated to alterations in the signaling pathway, which plays a crucial role in cell fate determination and tissue homeostasis. Distraction of this pathway can promote aberrant cell proliferation and tumorigenesis. Additionally cellular effects, chromium toxicity can affect organ function and tissue morphology. Chronic exposure to high levels of chromium is also associated with tissue damage, inflammation, and fibrosis, particularly in organs exposed to direct contact, such as the respiratory and gastrointestinal systems. These structural alterations can damage organ function, leading to symptoms like respiratory distress or gastrointestinal disturbances. Besides, chromium's ability to bind to cellular proteins and enzymes can restrict with their normal function, disrupting metabolic processes and cellular homeostasis. For example, chromium can prevent enzymes involved in DNA repair mechanisms, aggravating the accumulation of DNA damage and genomic instability.

1.5 Problem Statement

Hexavalent chromium (Cr (VI)) contamination in water sources is a substantial global environmental and public health concern, which originates from industrial activities and natural processes. Chromium has carcinogenic properties and persistence in aqueous environments. Traditional treatment methods often fail to remove Cr (VI) efficiently and economically, which therefore necessitates the development of innovative remediation strategies.

Regardless of extensive research, challenges persist in development sustainable and ascendable approaches to reduce Cr (VI) contamination effectively. Current technologies have limitations like excessive costs, secondary pollutant generation, and insufficient removal efficiencies, especially in complex water matrices with competing ions.

The use of natural adsorbents like montmorillonite clay and iron-based coagulants demonstrate promising effeciency in addressing these challenges. Montmorillonite clay, known for its abundant availability and excellent adsorption characteristics, presents a practical solution for Cr (VI) removal. Similarly, iron coagulants can form insoluble complexes with Cr (VI) ions, henceaiding in their removal from aquatic matrices.

However, gaps exist in understanding the synergistic effects and best use of montmorillonite clay and iron coagulants for Cr (VI) removal. Further research is needed to discover the mechanisms of Cr (VI) adsorption and coagulation, optimize treatment conditions, and evaluate the scalability of these methods for real-world applications.

This thesis aims to address the acute need for a comprehensive study into the efficacy of montmorillonite clay and iron coagulant in removal of hexavalent chromium from aquatic matrices. By bridging this knowledge gap, the research seeks to contribute to the development of sustainable, cost-effective solutions for Cr (VI) remediation, ultimately protecting human health and the environment.

1.6 Objectives

Continuing, the objectives of this research are delineated as follows:

- Evaluate the effectiveness of iron, clay, and combined iron-clay coagulants for removing chromium contaminants from water through coagulation processes.
- Investigate the impact of varying parameters including pH, dosage, initial chromium concentration, temperature, and contact time on the coagulation efficiency of each coagulant.
- Identify optimal conditions for chromium removal using each coagulant by systematically altering parameters and analysing their influence on chromium removal.
- Compare the performance of individual iron and clay coagulants with that of their combined form to figure out the most effective coagulant for chromium removal.
- Contribute to the development of efficient and sustainable water treatment strategies for mitigating chromium pollution in groundwater.

CHAPTER 2

LITERATURE REVIEW

2.1 Available Technologies for removal of Cr (VI)

Various treatment methods, such as coagulation (Xu et al., 2019), membrane separation(Mondal and Saha, 2018), electrochemical processes (Peng et al., 2019), and bioremediation (Ayele and Godeto, 2021), have been previously used to remove heavy metals like Cr (VI) from water. But, high capital and operating costs, higher sludge production, and microbial toxicity,reducetheir widespread application and scalability(Karimi-Maleh et al., 2021).Therefore, the exploration of indigenous and cost-effective sorbents for treating targeted Cr (VI) species could offer a practical solution for the drinking water.

Numerous techniques are available for the removal of chromium from water. Common methods for eliminating chromium include:

- Chemical precipitation
- Electrocoagulation
- Ion exchange
- Membrane filtration
- Adsorption
- Coagulation-flocculation

2.1.1 Chemical Precipitation

Chrmoium contamination poses a significant challenge in industries like tanneries. For the treatment of this kind of waste water, chemical precipitation stands out as a prevalent technique (Basavaraju and Ramakrishnaiah, 2012). This method uses chemical precipitants such as sodium hydroxide, calcium hydroxide, and calcium magnesium carbonate to accelerate the removal process by transforming soluble chromium ions into insoluble compounds that can be removed from the water. Many key parameters influence the precipitation process. The choice of precipitation agent is crucial, with each chemical offering different efficiencies and expenditures.Sodium hydroxide, for instance, is efficient in raising pH to optimal levels (7.5 to 9.5) for chromium hydroxide precipitation.Calcium hydroxide is yet another common choice owing to its cost-effectiveness and ability to increase alkalinity.Magnesium oxide and calcium magnesium carbonate are options based on specific characteristics of wastewater. pH levels are also important, since the solubility of chromium compounds depends greatly on pH. Maintaining the pH within the optimal range confirms maximum removal efficiency. Stirringspeed affects the distribution of the precipitant and the development of flocs, with proper mixing stimulating the aggregation of particles for easier separation, though excessive agitation can break up flocs and delay settling. The volume of sludge produced during precipitation must be considered for efficiency and environmental impact. Efficient precipitation makes compact sludge that is easier to dewater and dispose of. The duration of mixing is also substantial, as sufficient retention time ensures complete reactions between the precipitate and chromium ions, increasing removal efficiency without excessiveconsumption of energy. Complexing agents in wastewater can make soluble complexes with chromium, which ultimately resists precipitation. Identifying and managing these agents is important and sometimes needs additional treatment steps.

2.1.2 Electrocoagulation

Electrocoagulation (EC) emerges as aeffective technique for the removal of chromium from wastewater, specially targeting hexavalent chromium (Cr (VI)), a harmful pollutant. Extensive research has identified the efficiency of electrocoagulation using aluminum or iron electrodes in accomplishing substantial removal percentages of Cr (VI) from contaminated solutions (Genawi et al., 2020). This metthodinfluences the electrochemical dissolution of metal electrodes to yield coagulants in situ, which aid in the aggregation and removal of pollutants.

Key factors influencing the efficiency of chromium removal via electrocoagulation include residence time, voltage levels, and the number of electrodes used. Studies show that lesser voltages and prolonged residence times improve the removal process of chromium through electrocoagulation (Li et al., 2019). Particularly, lower voltages lessen energy consumption and heat generation, which ultimately promotes the stability of the formed coagulants and improving the overall removal efficiency. Prolonged residence times allow more systematic interaction between the generated coagulants and chromium ions, facilitates more effective pollutant aggregation and subsequent removal. Likewise, the configuration and movement of electrodes substantiallyaffect the efficiency of electrocoagulation. Favorable outcomes have been observed with the use of rotating aluminum electrodes, which show advanced removal efficiencies compared to stationary electrodes. The rotation of electrodes improves the mixing and distribution of coagulants, preventing the passivation of electrode surfaces and confirming continuous production of active coagulants. This dynamical action advances the contact between coagulants and pollutants, leading to better removal rates of Cr (VI).

The underlying mechanism of electrocoagulation implies the formation of metal hydroxide sludge, which showsaimportant role in the adsorption and precipitation of chromium. As electric current passes through the electrodes, metal ions are liberated into the solution, where they hydrolyze to generate metal hydroxides. These hydroxides act as coagulants, thereby capturing and precipitating chromium ions, this significantly contributes to their removal from wastewater. The resultant sludge, including the removed chromium, can be afterwards separated and disposed of, rendering the wastewater free of chromium contaminants.

2.1.3 Ion Exchange

Ion exchange emerges as a very efficient method for the removal of Cr (VI) from water sources. Both strong-base anion (SBA) and weak-base anion (WBA) exchange resins have shown wonderful efficacy in reduction of hexavalent chromium concentrations to safe levels in drinking water. Research findings present that using anion exchange technology in a lead-lag column configuration can generate treated drinking water with hexavalent chromium concentrations below 1 µg/L. This process involves the replacement of hexavalent chromium ions with chloride ions on the resin, which effectively removes the contaminant from the water. Ion exchange technology, principallyuses anion exchange resins, stands out as a dependable and widely used method for Cr (VI) removal. It also ensures the delivery of safe and pristine drinking water.

The two primary types of ion exchange resins include cation exchange resins and anion exchange resins. Cation exchange resins show functional groups containing a negative charge, such as sulfonate or carboxylate groups. These groups attract and exchange positively charged ions present in the solution. Common cations that can undergo exchange include calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}). In reverse, anion exchange resins have functional groups with a positive charge, like quaternary ammonium or amine groups. These positively charged groups attract and exchange negatively charged ions in the solution. Typical anions that can be exchanged include chloride (Cl^{-}), sulphate (SO_4^{2-}),and carbonate (CO_3^{2-}).

In the ion exchange procedure, the solution is added in a column or bed having an ion exchange resin. As the solution and resin interact, the ions exhibit in the solution are exchanged with ions attached to the functional groups on the resin. The original ions are so released into the treated solution, while the exchanged ions are bound to the resin. Researchers have used multiple ion exchange resins, like alkaline anion resin (Ahmed et al., 2020)achieving high removal efficiencies of 98%. Although ion exchange is anflexible and efficient water treatment process, it is not without its drawbacks and limitations. These include issues such as the presence of competing ions like phosphate, sulphate, and carbonate, which can reduce removal efficiency(Kocaoba et al., 2022). In addition, factors like excessive cost, the need for resin regeneration, and the disposal of waste pose challenges to its prevalent application.

2.1.4 Membrane Filtration

Membrane filtration is extremely effective and promising method for removal of hexavalent chromium (Cr (VI)) contamination in water sources. Recent research has focused on utilizing advanced composite membranes to improve the removal efficiency of Cr (VI) from wastewater (Korus and Loska, 2009). One noteworthy study proposed a novel chitosan-coated iron oxide nanoparticle-immobilized hydrophilic poly(vinylidene) fluoride membrane. This innovative composite membrane showed exceptional adsorption capacity for Cr (VI) in both batch and continuous in-flow systems. Importantly, the membrane's removal efficiencies remained high even in the presence of challenging competing ions such as Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-}(Çimen, 2015).The instant and effectiveremoval of Cr (VI) by this composite membrane features its potential as a feasible and reliable solution for the treatment of water contaminated with hexavalent chromium (Zolfaghari and Kargar, 2019). The chitosan coating on iron oxide nanoparticles improves the adsorption process by providing many active sites for Cr (VI) binding, while the hydrophilic poly(vinylidene) fluoride base assuressuperior permeability and mechanical strength. This synergy results in a membrane capable of maintaining better removal efficiency under varying water quality conditions. Membrane filtration, via the use of advanced composite membranes, not only offers a scalable and competent approach for large-scale water treatment but also represents a significant step forward in reducing chromium contamination in water sources (Dos Santos et al., 2019). The modular nature of membrane systems allows for easy integration into existing water treatment infrastructure, which facilitates the adoption of this technology across different scales and settings.Likewise, the use of such advanced membranes addresses both current and future challenges in water treatment, including the need for better selectivity and resistance to fouling. Recently, the development of even more sophisticated membranes ensures to enhance the sustainability and efficiency of water purification processes. Eventually, membrane filtration stands out as a critical technology in the global effort to confirm safe and clean water, efficiently tackling the persistent issue of hexavalent chromium contamination in water bodies.

2.1.5 Adsorption

Adsorption is a widely used method for the removal of hexavalent chromium (Cr (VI)) from aquatic matrices. Numerous studies have showed the efficiency of ion exchange resins in adsorbing Cr (VI) ions from aqueous solutions. For example, the use of Indion GS-300 ion exchange resin accomplished a remarkable 98% removal of hexavalent chromium from simulated wastewater, highlighting the high adsorption capacity of this resin for Cr (VI). This impressive performance highlights the potential of ion exchange resins in efficiently treating chromium-contaminated water.Also, cation exchange resins like IRN77 and SKN1 have been found to be efficient in the removal of chromium from water and wastewater through adsorption processes (Rai et al., 2016). These resins present high removal efficiencies for chromium across a wide pH range, making them applicable for different water conditions. The adsorption process of these resins follows the Freundlich adsorption isotherm, which implies that the adsorption occurs on heterogeneous surfaces and involves multilayer adsorption (Park et al., 2022). This model shows that as the concentration of Cr (VI) ions increases, the adsorption sites on the resins become progressively occupied, leading to a more complex adsorption mechanism.The kinetics of chromium adsorption by these ion exchange resins follow first-order reversible kinetics. This indicates that the rate of adsorption is directly related to the concentration of Cr (VI) remaining in the solution, and the desorption rate is linked with the amount of Cr (VI) adsorbed on the resin. This behavior shows a stable adsorption process, where chromium ions are essentially captured and held by the resins.The adsorption abilities and intensities of these resins highlight their strong attraction for chromium, thereby making them valuable for the removal of hexavalent chromium from water sources. Their effectiveness across various conditions and their robust adsorption kinetics make ion exchange resins a practical and reliable choice for treating Cr (VI) contamination. These characteristics ensure that ion exchange resins remain a critical tool in the ongoing effort to ensure safe and clean water by effectively removing hazardous chromium pollutants.

2.1.6 Coagulation-Flocculation

The coagulation-flocculation method is a prominent technique in water and wastewater treatment, valued for its efficiency in removing suspended particles and diverse contaminants. This process engages the addition of chemical coagulants to target wastewater, assisting the aggregation of small particles into larger flocs. These flocs can then be removed through numerous separation techniques. Widely used to address organic substances, suspended particles, and heavy metals like chromium, its importance is underscored by chromium's adverse effects on biological treatment efficiency in municipal wastewater treatment facilities. Therefore, coagulation-flocculation acts as an indispensable preliminary step to lessen chromium contamination (Khan et al., 2021). The detailed mechanism of coagulation-flocculation is shown in ***Figure 6***.

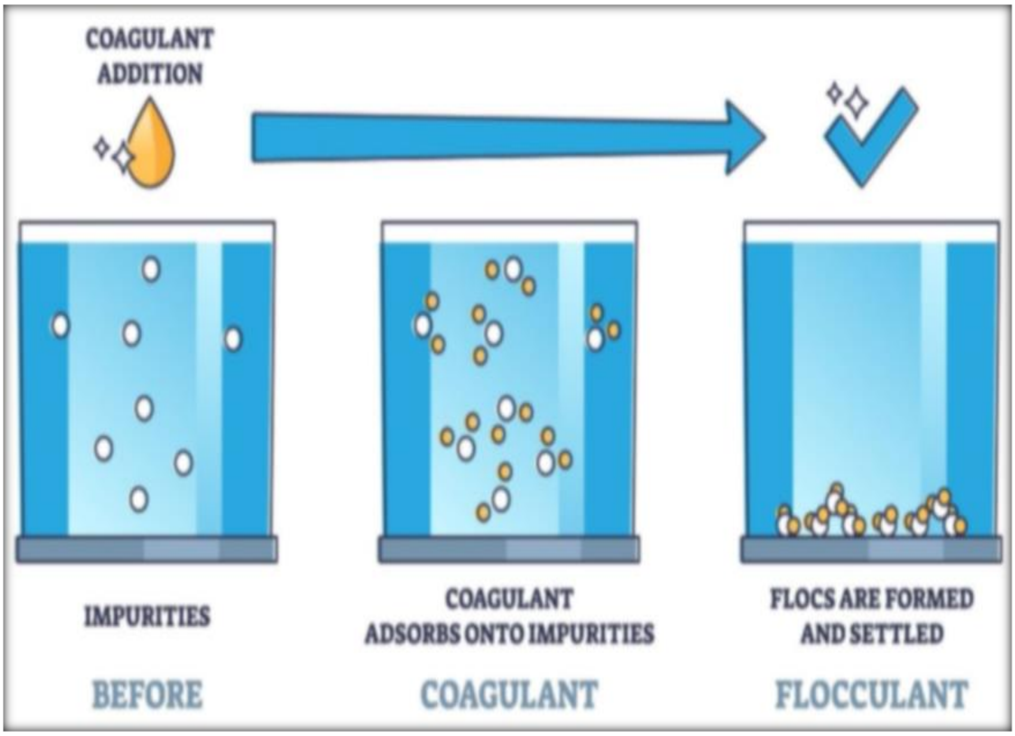

Figure 6 Mechanism of Coagulation-Flocculation

This process incorporatesnumerous vital steps fundamental for effectiveremoval of contaminants like hexavalent chromium (Cr (VI)) from water matrices . Coagulation starts the sequence, wherein coagulants are introduced to counteract particle charges, promoting the development of larger agglomerates for better removal. This stage disturbs the repulsive forces between particles, improving their aggregation into micro-flocs. The choice of coagulant, dosage, pH, and mixing intensity significantlyinfluences the effectivenessof coagulation.

Coagulation is followed by the flocculation, where flocculants are instituted to further raise the growth of these micro-flocs into larger, visible particles called pin-flocs. Flocculants are typically long-chain polymers that facilitate in particle entanglement, enhancing van der Waal's forces and hydrogen bonding between particles. The gentle mixing during flocculation advances the development of macro-flocs through other collisions between pin-flocs.

Once the flocs reach an optimal size and strength, the water is ready for solids-liquid separation through processes like filtration, centrifugation, sedimentation, or flotation. Polymers, whether natural or synthetic, play a fundamental role in improving the flocs and increasing their settling weight during the flocculation process. The use of polymers helps in stabilizing or enhancing the flocculation of particles, ensuring effective removal of contaminants from the water.

Conclusively, the mechanism of coagulation-flocculation involves a strategic combination of coagulants and flocculants to neutralize charges, help particle agglomeration, and ease the formation of larger flocs that can be proficiently separated from the water, leading to the successful removal of contaminants like Cr (VI) from water sources.

In different research, coagulation-flocculation has been investigated for Cr (VI) removal, using ferric chloride and polymeric ferric sulphate as coagulants, achieving notable removal efficiencies of 91%, 95%, and 98.3%, respectively (Amuda et al., 2006). However, this process is time-consuming and generates substantial sludge, needs proper disposal or further treatment, andincreases overall costs and complexity.

In this study, investigating the effectiveness of using a combination of iron (Fe) and montmorillonite clay as a novel coagulant for the removal of hexavalent chromium (Cr (VI)) from contaminated water sourcesis intended. The selection of iron and montmorillonite clay is based on their known adsorption and coagulation properties, which have shown favourableefficiency in earlier studies for the removal of various contaminants from water. The synergistic effect of iron and montmorillonite clay is assumed to enhance the coagulation-flocculation process, thereby improving the removal efficiency of Cr (VI) ions. Iron is known for its ability to precipitate and adsorb heavy metal ions, including chromium, by forming insoluble hydroxide complexes. Montmorillonite clay, on the contrary side, offers a high surface area and cation exchange ability, and eases the adsorption and aggregation of contaminants.This approach could capitalize on the individual benefits of iron and montmorillonite clay, potentially addressing limitations associated with each material when used independently(Khan et al., 2021).Overall, this study seeks to help in the development of efficient and sustainable water treatment strategies for the removal of hexavalent chromium, with the aim of safeguarding environmental and human health.

2.2 Comparison of Cr (VI) Removal Technologies

A brief comparison of most widely used technologies for the elimination of Cr(VI) removal from aquatic matrices is presented below in ***Table 1***.

Table 1 Comparison of Cr (VI) removal technologies

TECHNOLOGY	ADVANTAGES	DISADVANTAGES
CHEMICAL PRECIPITATION	Chemical precipitation offers high removal efficiency and is cost-effective for lowering chromium (VI) concentrations in water sources.	The process generates high volumes of sludge, that needs proper disposal, and its efficiency is highly pH dependent.
ELECTRO-COAGULATION	It offers a highly efficient solution for reducing Cr (VI) levels in water, and provides versatility across various water sources.	Electrocoagulation needs substantial energy consumption and produces sludge, which necessitates proper disposal.
ION EXCHANGE	Ion exchange provides effective removal of Cr (VI) from water, ensures high removal rates and compliance with regulatory standards.	Ion exchange can be costly to operate and needs frequent regeneration of the resin, which leads to increased operational costs and complexity.
MEMBRANE FILTRATION	Membrane filtration offers superior efficiency and selective removal of contaminants from water sources.	Membrane filtration systems can be susceptible to fouling, requires regular maintenance which eventually increases operational costs and downtime.
ADSORPTION	Adsorption is a highly effective method for Cr (VI) removal, offers high removal efficiencies and versatility for various water sources.	Adsorption may need frequent regeneration of the adsorbent material, leads to increased operational costs and complexity.
COAGULATION-FLOCCULATION	Coagulation-flocculation presents a strong approach for Cr (VI) removal, effectively reducing chromium levels and enhances water clarity through the aggregation of contaminants.	It produces significant sludge volumes, requires proper disposal and potentiallyincreases operational costs. It also demands careful parameter monitoring for optimal performance.

CHAPTER 3

MATERIALS AND METHODS

This chapter covers the materials used, explains the coagulation-flocculation procedures, and analyses the process using instrumental methods. It includes initial planning, equipment, resources, and methodology for ensuring quality research work.

3.1 Chemicals

3.1.1 Stock Solution of Chromium (VI)

The 1000 mg/L Cr (VI) stock solution was prepared by dissolving 0.285 g $K_2Cr_2O_7$ in 100 mL distilled water. The working solutions of desired Cr (VI) concentration were then prepared by spiking the required volume of stock solution in distilled water, as per experimental conditions. Moreover, 0.1 M HCl and 0.1 M NaOH solutions were prepared to adjust the solution pH. In addition, all glassware and sampling vessels were washed with 15% HNO_3 solution, followed by rinsing with distilled water prior to experiments.

3.1.2 $FeCl_3$ Solution

To prepare 1000 mL of a 0.1 mol/L solution of Iron(III) chloride was dissolved 27.029 g of FeCl3×6H2O (100 % purity) in deionized or distilled water. After the solid is completely dissolved, the solution was diluted to a final volume with deionized (distilled) water.

3.1.3 Montmorillonite Clay

Montmorillonite clay solutions are typically prepared by dispersing the clay in water to form a suspension. The chemical formula of montmorillonite clay is(Na,Ca)0.33(Al,Mg)2(Si_4O_{10}) (OH)2·nH2O. To prepare a solution, the montmorillonite clay is added to water and mixed thoroughly to ensure the clay particles are well dispersed in the liquid. The resulting suspension can be used for various applications, such as in the oil drilling industry as a part of drilling mud, in soil additives to keep water in drought-prone soils, and in catalytic processes.

3.2 Equipment

3.2.1 Jar test Apparatus

This apparatus is used to simulate and perfect the coagulation and flocculation process in water treatment, ***Figure 7***. It generally consists of a series of glass beakers, usually six, with changeable paddles or stirrers inside. Each jar is filled with a sample of water to be treated, and various coagulants or chemicals are added in varying concentrations to each jar. The paddles or stirrers stir the water to simulate mixing, allowing the coagulants to work together with the particles in the water. By monitoring the formation of flocs and measuring parameters such as turbidity or settling rates, water treatment operators can determine the most effective coagulant dosage and treatment conditions to achieve optimal water quality.

Figure 7 Jar Test Apparatus

3.1.2 UV Visible Spectrophotometer

A UV-visible spectrophotometer (AAS, NovAA 800D, Analytik Jena, Germany) wasemployedto measure how much UV and visible light a sample absorbs or transmits, ***Figure 8***. It is based on the principle that different molecules absorb light at specific wavelengths. The instrument contains a light source, a monochromator to isolate light wavelengths, a sample holder, and a detector. It is used in chemistry, biochemistry, and other fields for analysing substances and studying molecular structure. Quartz cuvettes were used as sample holders owing to their transparency to UV and visible light, thereby allowing accurate measurement of samples.

Figure 8 UV Visible Spectrophotometer

3.1.3 Turbidity Meter

This study assess the efficacy of coagulation process. Turbidity metr plays a crucial role in assessing the performance of the treatment in lowering turbidity levels, ***Figure 9***.Primarily, baseline turbidity measurements are recorded to develop the initial turbidity levels of the water sample prior to any treatment applied.This step presents a baseline for subsequent comparisons. All through the coagulation process, turbidity measurements are regularly supervised to monitor changes in turbidity levels. These values arebeneficial for the assessing theeffectiveness of coagulation processes, turbidity reduction and water clarification. Following the conclusion of the coagulation process, final turbidity measurements are achievedfor the evaluation of the overall reduction in turbidity levels accomplished by the treatment.Analysis of the tangible data describes the efficiency of the coagulation process. Turbidity meter, used in this study, can perfectlyaccess the efficiency of the coagulation process in treating water and reducing turbidity levels.Such information extendsimportance for water treatment facilities, environmental engineers, and researchers trying to improve water quality and advance treatment procedures.

Figure 9 Turbidity meter

3.3 Experimental Condition and Procedure

To evaluate the removal efficiency of $FeCl_3$ and Montmorillonite Clay, batch experiments were carriedout using 20 mg/L Cr (VI) suspensions. The study first examined the effect of Iron coagulant dosages between 15-200 mg/L at pH 5 with an initial chromium concentration of 20 mg/L. The sorption performance of both adsorbents was assessed under different pH conditions (4, 5, 6, 7, 8, and 9), using a Fe coagulant dosage of 120 mg/L and/or Montmorillonite Clay dosage of 0.1 g/L at pH 5.Experiments were conducted using single and binary coagulant dosage to access their efficacy in Cr (VI) removal. Afterwards kinetics, isotherms and thermodynamic studies were employed to determine the underlying mechanisms involved in Cr (VI) removal.After experiments, all samples were filtered using 0.22µm GE cellulose nylon membrane filter. A reagent was made by the addition of 0.5 g of 1,5-diphenylcarbazide into 100 mL of acetone (Rattanarat et al., 2013). Subsequently, 2 mL of this reagent wasadded into the filtrate along with 3 to 4 drops of phosphoric acid (H_3PO_4). The filtrate was then analyzed at 540 nm wavelengthusing a UVVisible spectrophotometer (SPECORD 200, Analytikjena, Germany).

3.4 Calibration Curve

The calibration curve is important for emperminets employing UV-Visible spectrophotometer, since this allows the assessment of samples having unknown concentrations through correlation of absorbance readings to the solutions of known concentrations. This assures the accuracy and precision in determination of theanalytes'sconcetration. Through the use of standard solutions, the calibration curve confirms the performance and reliability of the UV Visible spectrophotometer. In addition, it helps in the identification of the detection limits for this method and the linear range of the instrument, considering that absorbance is directly proportional to concentration. Moreover, any disparities in instrument response, and ensure consistent and reliable results over time. In general, the calibration curve is vital for precise and accurate concentration measurements in UV experiments.

Calibration curve was constructed using the solutions of different Cr(VI) concetration (ranging from 0.1-2 mg/L). The coefficient of determination (R^2) for the curve was found to be 0.999. ***Table 2*** and ***Figure 10*** below show the data comparable to the calibration curve.

Table 2 Calibration Curve of Chromium (VI)

Concentration (mg/L)	**0.0**	**0.1**	**0.2**	**0.5**	**1.0**	**1.5**	**2.0**
Absorbance	0.0000	0.0997	0.2246	0.4630	0.8744	1.2793	1.6792

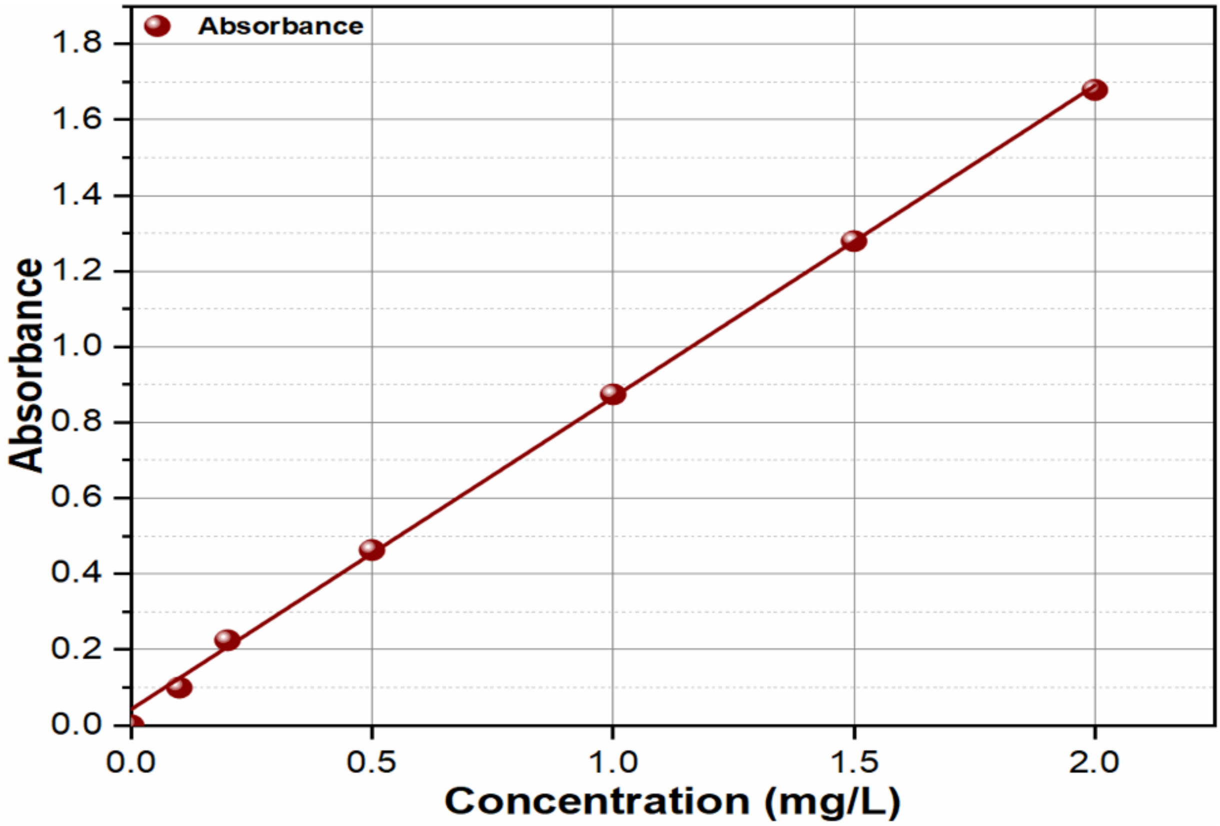

Figure 10 Calibration Curve

3.5 Final Concentration and Adsorption Capacity

Following equations were employedfor the calculation the residual chromium concentration:

Adsorption capacity: $q_e = \frac{(C_o - C_e)V}{m}$ **(1)**

Removal efficiency: $R = \frac{(C_o - C_e)}{C_o} * 100\ \%$ **(2)**

Here C_e and $C_o$are the residual and initial Cr (VI) concentrations (mg/L) in the solutions,m is the mass of coagulant (g), and V is the initial volume of suspension (L).

3.6 Isotherm Models

For the study of isotherms of the adsorbent, Eq. (5) and Eq. (6) were utilized which are as follows:

Langmuir equation: $q_e = \frac{q_m k_L C_e}{1 + k_L C_e}$ **(5)**

Freundlich equation: $q_e = k_F C_e^{\frac{1}{n}}$ **(6)**

Here adsorption capacity of the coagulant at equilibriumis labelled as q_e(mg/g),final chromium concentration is C_e (mg/L) , the maximum adsorption capacity of the coagulant is q_m (mg/g) is, Langmuir constant is labelled as k_L(L/mg), k_F [(g/mol) (L/mg)]$^{1/n}$is a constant related to the adsorption capacity, while n is an index of heterogeneity.

CHAPTER 4

RESULTS

4.1 Effect of Varying Coagulant dosage

Experiments were conducted to access the impact of varying dosage on the removal of Cr (VI) from aqueous solutions. Employing the systematic adjustment of combined coagulant comprising iron and montmorillonite clay, the relationship between coagulant dosage and chromium removal efficiency was observed. A series of controlled experiments were used to for careful monitoring ofchanges in chromium concentration in response to different coagulant dosages. This study was sought to determine the optimal coagulant dosage required for maximum chromium removal while minimalizing excess coagulant usage.

4.1.1 Effect of Varying Iron coagulant dosage on Cr (VI) removal

Primary objective of this study was to interpret the impact of varying iron coagulant dosage, spanning a range from 0.015 to 0.2 g/L. Synthetic aqueous samples containing an initial Cr (VI) concentration of 20 mg/L were used, for the analysis of the efficiency of varying coagulant dosages in the eleminationof chromium contaminants. The complicated interplay between iron coagulant dosage and their respective chromium removal potential was performedfor the determination of optimum coagulant dosage for Cr (VI) removal form aquatic matrices.The effects of varying iron coagulant dosages on Cr(VI) removal are shown below in ***Table 3***.

Table 3 Effect of Varying Iron coagulant dosage on Cr (VI) removal

Initial Cr (VI) Conc. (mg/L)	Final Cr (VI) Conc. (mg/L)	% Removal	Adsorption Capacity (mg/g)	Fe Coagulant (Dosage) (g/L)
20	18.078	11.83	26.40	0.073
20	16.64	16.8	34.61	0.097
20	13.52	32.4	33.37	0.194
20	7.7	61.5	50.68	0.243
20	6.42	67.9	46.62	0.291
20	4.2	79	40.69	0.388
20	2.62	86.9	35.80	0.485
20	1.22	93.9	32.24	0.583
20	0.82	95.9	28.22	0.680

20	0.66	96.7	24.90	0.777
20	0.64	96.8	22.16	0.874
20	0.54	97.3	20.04	0.971

4.1.2 Effect of Varying Montmorillonite Clay dosage on Cr (VI) removal

In this study, the individual impact of varying Montmorillonite clay dosageon the removal of Cr (VI) was studied.Montmorillonite clay dosage was adjusted in a range from 0.1 to 1 mg/L, to analyze its efficacy in elimination of chromium contamination. A series of controlled experiments were used for monitoring the relationship between clay dosage and chromium removal efficacy. These findings presentfundamental insights into the efficiency of Montmorillonite clay as a potential solution for chromium removal in water treatment processes.

Table 4 Effect of Varying Montmorillonite Clay dosage on Cr (VI) removal

Initial Cr (VI) Conc. (mg/L)	Final Cr (VI) Conc. (mg/L)	% Removal	Adsorption Capacity (mg/g)	Montmorillonite Clay (Dosage) (mg/L)
20	17.346	13.27	26.54	0.1
20	18.604	6.98	6.98	0.2
20	18.614	6.93	3.47	0.4
20	18.64	6.76	2.25	0.6
20	18.776	6.12	1.53	0.8
20	18.796	6.02	1.20	1

4.1.3 Effect of Varying Montmorillonite Clay dosage and fixed dosage of Fe-coagulant on Cr (VI) removal

This experiment was aimed to access the impact of changing Montmorillonite clay dosage, while maintaining a fixed dosage of Fe-coagulant, on the removal of Cr (VI) from aqueous solutions was examined.This study focusesto determine the relationship between Montmorillonite clay dosage and Cr (VI) removal efficiency. The systemiatic adjustment of the dosage of Montmorillonite clay across a range of concentrations, the addition of clay changes the efficiency of chromium removal processes in water treatment applications. In this experiment, a fixed dosage of Fe-coagulant at 0.12 g/L was maintained while the

Montmorillonite clay dosage was thoroughly varied from 0.1 to 1 g/L.Effect of differentdosages of Montmorillonite Clay and a Fixed Dosage of Fe-Coagulant on removal of Cr (VI), are presented in ***Table 5***.

Table 5 Effect of Varying Montmorillonite Clay dosage and fixed dosage of Fe-coagulant on Cr (VI) removal

Initial Cr (VI) Conc. (mg/L)	**Final Cr (VI) Conc.(mg/L)**	**% Removal**	**Adsorption Capacity (mg/g)**	**Coagulant Dosages**	
				Montmorillonite Clay (Dosage) (mg/L)	**Fe-Coagulant (Dosage) (mg/L)**
20	0.282	84.3	76.64	0.1	0.12
20	1.958	83.7	52.31	0.2	0.12
20	2.908	82	31.54	0.4	0.12
20	3.936	79.7	22.14	0.6	0.12
20	6.318	79.8	17.35	0.8	0.12
20	10.536	77.1	13.77	1	0.12

4.2 Effect of varying pH

4.2.1 Speciation diagram

Speciuation diagram of Chromium:

A speciation diagram of chromium for Cr (VI) was plotted using visual MINTEQ, as presented in ***Figure***11. It illustrates the distribution of different chemical species of chromium as a function of pH(Kocaoba and KselAkcin, 2002).

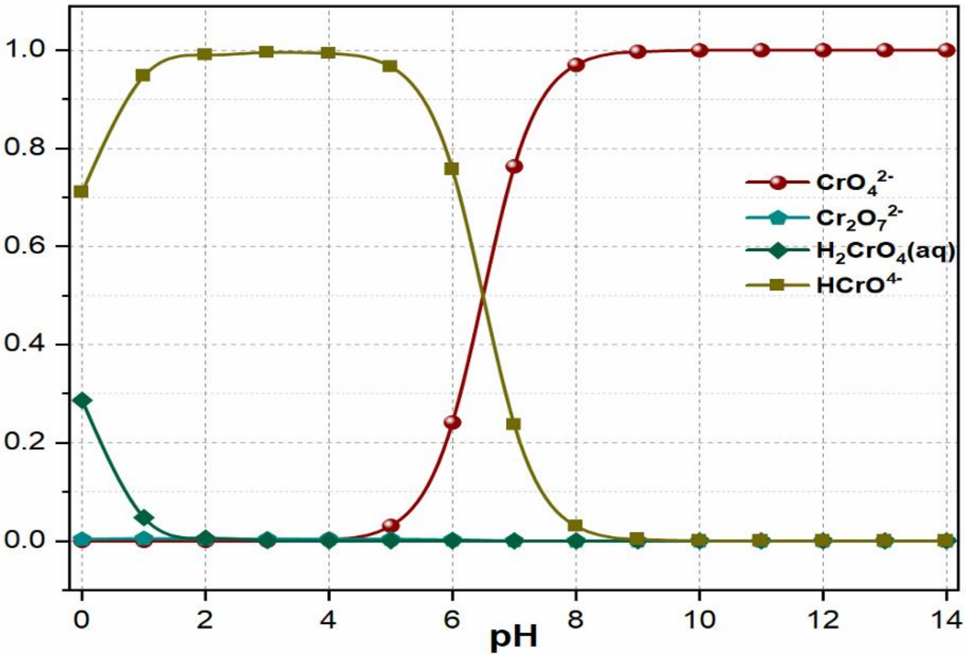

Figure 11 Speciation Diagram of Chromium

Chromium primarily exists in two oxidation states in aqueous environments: Cr(III) and Cr(VI). Each state has distinct chemical behaviors and environmental impacts. In acidic conditions (low pH), the trivalent form Cr^{3+} is dominant. As the pH increases to neutral and slightly alkaline conditions, chromium(III) forms hydroxide complexes such as $Cr(OH)^{2+}$, $Cr(OH)^{2+}$, and $Cr(OH)_3$. $Cr(OH)_3$ can precipitate out of solution, making Cr(III) less mobile and less bioavailable. In very alkaline conditions, chromium(III) can form soluble hydroxyl complexes like $Cr(OH)_4^-$. Chromium(VI) species behave differently; in acidic to neutral conditions, Cr(VI) primarily exists as $HCrO_4^-$ and $Cr_2O_7^{2-}$, while in alkaline conditions, CrO_4^{2-} becomes the dominant species. The speciation diagram helps in understanding the environmental mobility, toxicity, and remediation strategies for chromium, as Cr(VI) is more toxic and mobile compared to Cr(III).

Speciation diagram of Iron

A speciation diagram of chromium for Iron(Fe) was also plotted using visual MINTEQ, as presented in ***Figure*12**. It illustrates the distribution of different chemical species of chromium as a function of pH.

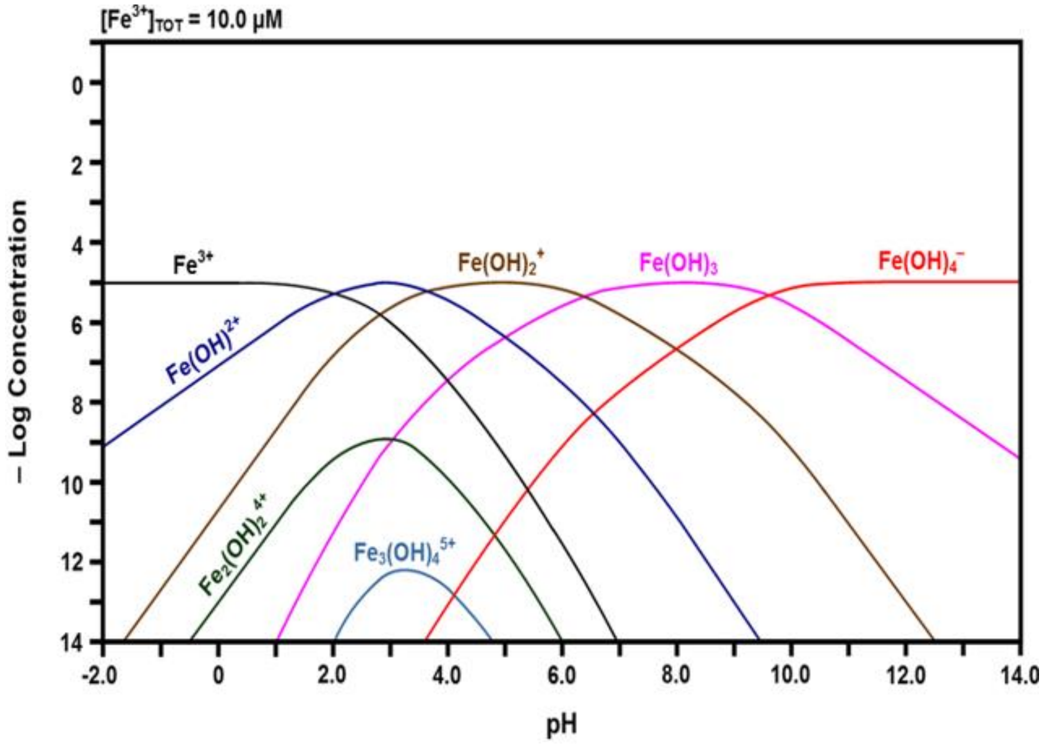

Figure 12 Speciation Diagram for Iron

Iron primarily exists in two oxidation states in aqueous environments: Fe(II) and Fe(III). Each state has distinct chemical behaviors and environmental impacts. In reducing conditions and acidic to neutral pH, Fe(II) is dominant and exists mainly as Fe^{2+}. As the pH increases, Fe^{2+} can form complexes with hydroxide ions, such as $FeOH^{+}$ and $Fe(OH)_2$, though these are less common in natural waters. In oxidizing conditions, Fe(III) is more stable and forms a variety of species depending on the pH. In acidic conditions, Fe^{3+} is the primary form. When the pH of the solution os increased to neutral, Fe^{3+} hydrolyzes to generate species like $FeOH^{2+}$, $Fe(OH)^{2+}$, and ultimately $Fe(OH)_3$. $Fe(OH)_3$ can precipitate out of solution, creating solid iron hydroxides that are relatively insoluble and reduced bioavailability. Further increase in the pH of solution, soluble complexes such as $Fe(OH)_4^{-}$ can generate. The speciation diagram is important for understanding the behavior of iron in environmental and industrial processes, manipulating factors like solubility, mobility, and the potential for forming precipitates, which are crucial for water treatment and soil chemistry.

4.2.2 Effect of varying solution pH on Cr(VI) removal

The impact of altering the pH of the solution was examined while keeping fixed dosages of both Fe-coagulant and Montmorillonite clay. The pH of the solution was systematically adjusted across a range of values, including 4, 5, 6, 7, 8, and 9, to interpret its impact on the removal efficiency of Cr (VI) contaminants. By keeping the constant dosages of Fe-coagulant(0.12 g/L) and Montmorillonite clay (0.1 g/L) constant and changing the pH of the solution, understanding the changes in pH impact the efficacy of the treatment process in the removal of chromium contaminants from aquatic matrices.The impac of changing solution pH on the removal of Cr(VI) from water is represented in ***Table 6***.

Table 6 Effect of varying pH

Initial Cr (V) Conc. (mg/L)	Final Cr (VI) Conc. (mg/L)	% Removal	Adsorption Capacity (mg/g)	pH
20	1.302	93.49	32.07	4
20	1.23	93.85	32.20	5
20	1.7845	64.31	5.52	6
20	5.043	49.57	8.50	7
20	9.549	36.34	9.35	8
20	14.258	28.71	9.85	9

4.3 Effect of Varying initial Cr (VI) Concentration on Cr (VI) removal using Fe Coagulant

This experiment aimed to elucidate the influence of varying initial concentrations of Cr (VI) on the efficacy of montmorillonite clay as a coagulant for Cr (VI) removal from aqueous solutions. The study aimed to determine the relationship between the initial contaminant concentration and the chromium (VI) removal efficiency of Fe coagulant. Experimental procedures involvedadding fixed Fe-coagulant dosage of 120 mg/L in the aqueous solutions containing differing initial concentrations of Cr (VI). The removal efficiencies were meticulously monitored and are presented below in ***Table 7***.

Table 7Effect of Varying initial Cr (VI) Concentration on Cr (VI) removal using Fe Coagulant

Initial Cr (VI) Conc. (mg/L)	Final Cr (VI) Conc. (mg/L)	% Removal	Adsorption Capacity (mg/g)	Fe- Coagulant Dosage (g/L)
1	0.0309	96.91	1.66	0.12
2	0.0844	95.78	3.29	0.12
5	0.2515	94.97	8.14	0.12
10	0.526	94.74	16.2	0.12
15	0.804	94.64	24.3	0.12
20	1.22	93.9	32.2	0.12

25	3.455	86.18	36.9	0.12
50	19.465	61.07	52.3	0.12
100	40.24	59.76	102.50	0.12

4.4 Isotherm Models

Isotherm models were employedfor the characterization the interaction between adsorbate molecules and adsorbent surfaces under equilibrium conditions. These models present valuable insights into the adsorption behaviour, allowing researchers to understanding the adsorption mechanism, evaluating the adsorption capacity, and prediction of the equilibrium conditions(Usmani et al., 2023). By fitting experimental data to isotherm models, multiple parameters like the adsorption capacity, equilibrium constants, and surface area could be accessed, enabling the quantification and comparison of chromium (VI) removal performances. Furthermoreisotherm models facilitate the design and optimization of adsorption processes by providing a framework for prediction of the adsorption behaviourin different operating conditions and controlling the selection of appropriate adsorbents for specific contaminants. ***Figure 13***and***Table 8***presents the isotherm models for this study.

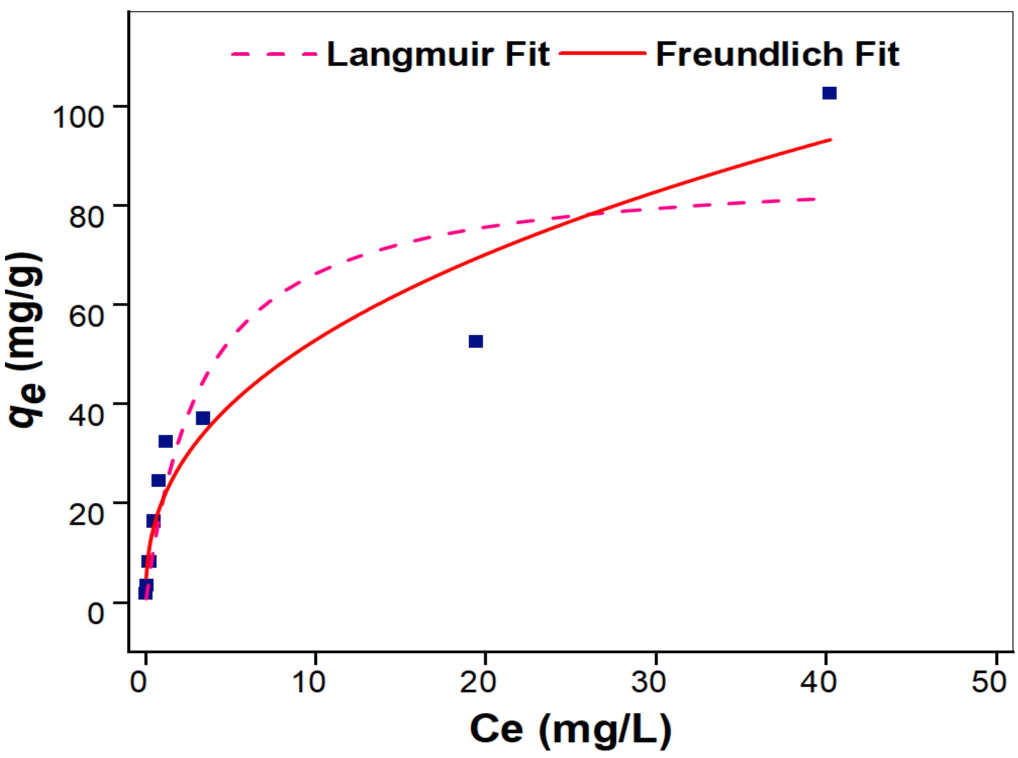

Figure 13 Isotherm Models

Table 8 Isotherm Model

Adsorbent	**Isotherm Model**		
Fe Adsorbent	Langmuir Model		
	q_m (g/mol)	**K_L (L/mg)**	**R^2**
	88.12	0.304	0.85
Fe Adsorbent	Frendulich Model		
	n	**K_F $[(g/mol)(L/mg)]^{1/n}$**	**R^2**
	2.46	99.24	0.92

In the evaluation of the Freundlich and Langmuir models for adsorption, the coefficient of determination (R^2) acts as a measure of how well the model fits the experimental data. A higher R^2 value indicates a better fit of the model to the data. The Freundlich model explains adsorption onto heterogeneous surfaces where there is no specific adsorption energy(Irfan et al., 2023). On the contrary, the Langmuir model follows monolayer adsorption onto a homogeneous surface with a fixed number of identical adsorption sites.

4.5 Effect of Interfering species on Chromium removal

The presence of interfering ions in aquatic media has the ability to substantiallyaffect chromium removal, which makes it important to understand their impacts(Usmani et al., 2023). Chromium is a lethal and carcinogenic metal that presents significant risks to human health and the environment, and its exclusion from aquatic matrices is a critical process. Nonetheless, the efficacy of chromium removal could be affected by the interference of other ions, like chlorides, phosphate, nitrate, sulphate, and bicarbonate, which are usually found in aquatic media.

For the investigation of the impacts of these interfering ions on chromium removal, an experiment was conducted where an initial concentration of 20mg/L of chromium ions was selected, along with 20mg/L of individual interfering ions. The impact of each interfering ion on chromium removal along with the combined effect of all ionswas measured and presented in ***Table 8***.

Table 9 Effect of Interfering ions

Intefering ions	Interfering ions conc. (mg/L)	Cr (VI) ions conc. (mg/L)	% Removal
Chloride	20	20	87.97
Phosphate	20	20	53.52
Nitrate	20	20	78.77
Sulphate	20	20	82.39
Bicarbonate	20	20	86.04
Combined	20	20	64.05

The results showed that chloride (87.97%), phosphate (53.52%), nitrate (78.77%), sulphate (82.39%), and bicarbonate (86.04%) all had significant effects on chromium removal, with the combined presence of all ions resulting in a removal efficiency of 64.05%. Notably, the removal efficiency of chromium in the absence of interfering ions was 93.9%, highlighting the significant impact of interfering ions on chromium removal.

CHAPTER 5

DISCUSSION

5.1 Effect of varying dosage

5.1.1Effect of Varying Iron coagulant dosage on Cr (VI) removal

The effect of varying iron coagulant dosage on the elimination of Cr(VI) from water has been presented in ***Figure 14***.

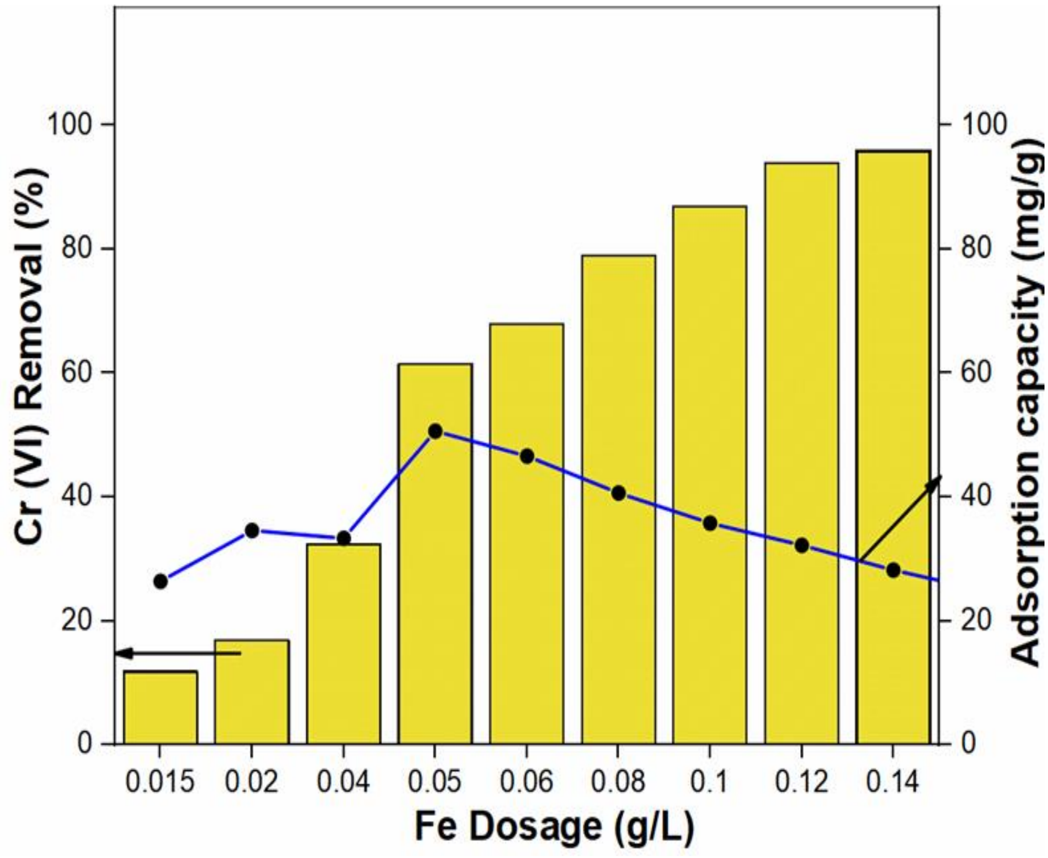

Figure 14 Effect of Varying Iron coagulant dosage on Cr (VI) removal

This graph illustrates the relationship between the coagulant dosage and both the percentage removal of Cr (VI) and the adsorption capacity (mg/g). As the coagulant dosage increases from 0.073 to 0.971, the percentage removal of Cr (VI) improves, starting at 11.83% and reaching up to 97.3%. This trend shows that higher coagulant dosages enhance the removal efficiency of chromium from the solution, as more coagulant provides additional active sites for chromium adsorption.

However, the adsorption capacity (mg/g) exhibits a different trend. Initially, it increases with the coagulant dosage, peaking at a dosage of 0.243 g/L with an adsorption capacity of 50.68

mg/g. Beyondthis point, the adsorption capacity starts to declineslowly, while the percentage removal continues to rise. This suggests that increased dosages of coagulants improve the overall removal of chromium, the effectiveness in terms of the amount of chromium adsorbed per unit weight of the coagulant diminishes. This reduction might be related to saturation of adsorption sites or other limiting factors in the adsorption process.

These results appeareda compelling correlation between iron coagulant dosage and chromium removal efficiency. This experimental trend highlights the pivotal role of dosage optimization in raising the efficacy of iron coagulant for chromium removal in aqueous environments. A critical dosage threshold of 0.12 g/L appeared as the optimal dosage for achieving the highest removal efficiency. Surprisingly, this dosage not only exhibited superior chromium removal capabilities but also relieved excess coagulant usage, thereby presenting itself as an efficient and economically viable solution for chromium removal in water treatment applications.

5.1.2 Effect of Varying Montmorillonite Clay dosage on Cr (VI) removal

The impact of changingMontmorillite clay dosage on Cr(VI) removal is presented in ***Figure 15.***

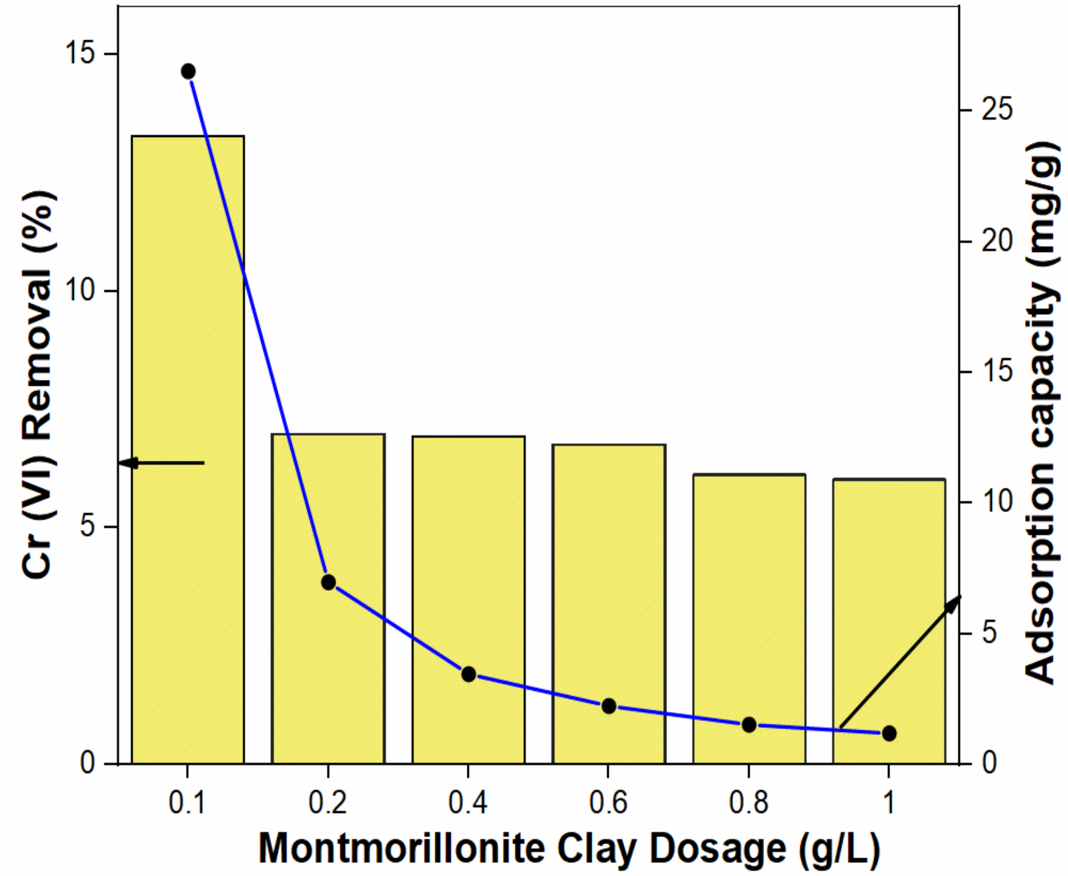

Figure 15 Effect of Varying Montmorillonite Clay dosage on Cr (VI) removal

The data indicates the effect of varying dosages of Montmorillonite clay on the removal efficiency and adsorption capacity for Cr (VI) at an initial concentration of 20 mg/L. As the Montmorillonite clay dosage increases from 0.1 to 1 g/L, the percentage removal of Cr (VI) presents a notable trend. At a dosage of 0.1 g/L, the removal efficiency is 13.27%. However, with increasing dosages, the increase in percentage removal becomes less significant, with values around 6.98% to 6.02%. Likewise, the adsorption capacity (mg/g) also shows a discrete pattern. At the lowest dosage of 0.1 g/L, the adsorption capacity is 26.54 mg/g, but as the dosage increases, the adsorption capacity decreases sharply, reaching 1.20 mg/g at the highest dosage of 1 g/L. The initial high adsorption capacity and significant removal efficiency at lower dosages of Montmorillonite clay suggest that a small amount of clay is highly effective in adsorbing Cr (VI). As the clay dosage increases, the total removal of chromium still improves slightly, but the efficiency in terms of adsorption capacity per unit mass decreases. This indicates reduced Cr (VI) removal efficiency with higher dosages which may be related to excess of adsorption sites available for chromium ions, leading to competition among chromium ions for binding sites on the clay particles. As a result, not all chromium ions may be effectively adsorbed onto the clay surface, reducing removal efficiency. Likewise, the incidence of excess Montmorillonite clay particles in the solution mightlead to increased turbidity or suspended solids, which can interfere with separation and sedimentation processes, further inhibiting chromium removal efficacy. Furthermore, the improved dosage of Montmorillonite clay mightchange the solution's pH owing to the presence of basic functional groups on the clay surface. Alterations in pH can effect the speciation of chromium ions, making some species less prone to adsorption onto the clay surface, thus reducing removal efficiency. Besides, elevated clay dosages may indicate the formation of clay agglomerates or aggregates, delaying the access of chromium ions to active adsorption sites on the surface of clay.The data suggests an optimal point at lower dosages where the balance between removal efficiency and adsorption capacity is most favourable. Beyond this point, additional clay dosage does not significantly improve removal efficiency and leads to lower adsorption capacity per unit mass, thereby highlighting the importance of optimizing clay dosage for effective chromium removal.

5.1.3 Effect of Varying Montmorillonite Clay dosage and fixed dosage of Fe-coagulant on Cr (VI) removal

The efficacy of varying Montmontriliite Clay dosage in combination with the fixed dosage of Fe-coagulant was also accessed for the remova of chromium from aquatic matrices and the observation are presented in ***Figure 16***.

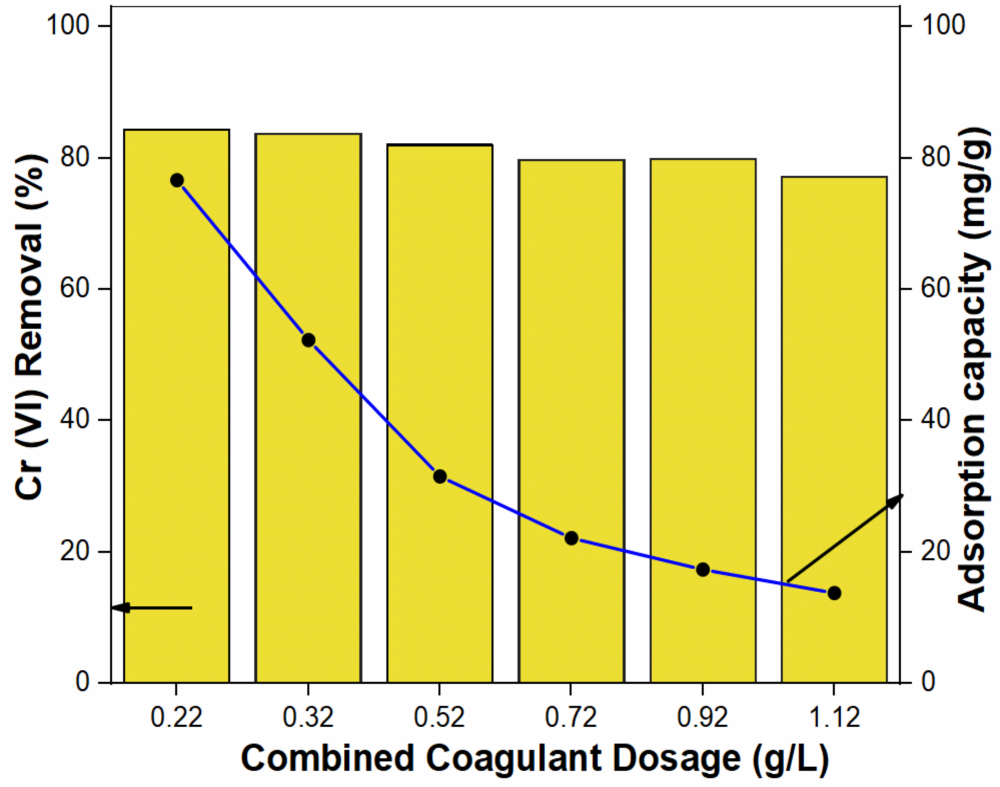

Figure 16 Effect of Varying Montmorillonite Clay dosage and fixed dosage of Fe-coagulant on Cr (VI) removal

The trend of chromium removal efficiency and adsorption capacity was studied using varying dosages of Montmorillonite clay (0.1, 0.2, 0.4, 0.6, 0.8, 1 g/L) along with a fixed Fe coagulant dosage of 0.12 mg/L. The removal efficiency of Cr (VI) showed a slight decline as the clay dosage increased, starting at 84.3% with 0.1 g/L clay and gradually decreasing to 77.1% at 1 g/L clay. Correspondingly, the adsorption capacity decreased more sharply with increasing clay dosages, from 76.64 mg/g at 0.1 g/L to 13.77 mg/g at 1 g/L.

This trend indicates that while the total chromium removal remains relatively high, the efficiency in terms of the amount of chromium adsorbed per unit mass of clay significantly diminishes as the clay dosage increases. Initially high adsorption capacity at lower coagulant dosage suggest the effective usage of the clay. However, as the dosage increases, the saturation of adsorption sites lead to lower adsorption capacity per unit mass. This elucidates the importance of maintaining the balance between removal efficiency and adsorption capacity.It assures the effective and efficienct chromium removal. The improved efficacy of the 0.12 g/L Fe-coagulant combined with 0.1 g/L Montmorillonite clay could be related to multiple factors. Initially Firstly, the fixed dosage of Fe-coagulant stipulated a stable baseline for chromium removal, whereas the addition of Montmorillonite clay at 0.1 g/L improved the adsorption capacity of the treatment system. The corresponding interaction between Fe-coagulant and Montmorillonite clay assisted the development of larger flocs, improving the removal efficiency of chromium contaminants from the aquatic matrices .Also, the optimized dosage combination minimized potential drawbacks like excess clay dosage, which might lead to congestion of adsorption sites and reduced removal efficiency. Therefore, the combination of 0.12 g/L Fe-coagulant with 0.1 g/L Montmorillonite clay dosage was selected for follow-up experiments.

5.2 Effect of varying pH

The effect tof varying solution pH was also accessed and data obtained has been presented in ***Figure 17***.

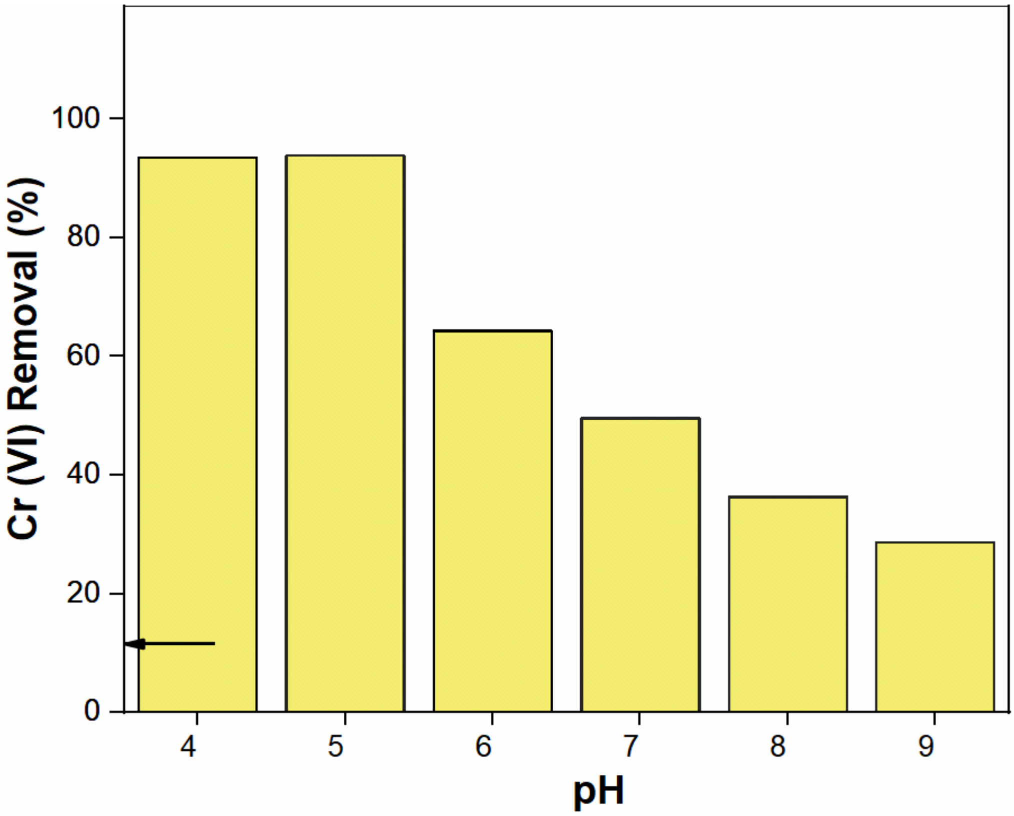

Figure 17 Effect of varying pH

The data illustrates the effect of pH on the percentage removal and adsorption capacity of Cr (VI) using a fixed dosage of Montmorillonite clay. At a pH of 4, the percentage removal of chromium is 93.49%, which slightly increases to 93.85% at pH 5. However, as the pH continues to rise, the removal efficiency drops significantly, with 64.31% at pH 6, 49.57% at pH 7, 36.34% at pH 8, and finally 28.71% at pH 9. The adsorption capacity follows a different trend, starting at 32.07 mg/g at pH 4 and slightly increasing to 32.20 mg/g at pH 5. As the pH increases further, the adsorption capacity drops drastically to 5.52 mg/g at pH 6, but then it slightly recovers, reaching 9.85 mg/g at pH 9.

These results suggest that the removal efficiency of Cr (VI) is highest at lower pH values, with optimal performance at pH 4 and 5. As the pH increases, the effectiveness of the clay in removing chromium decreases significantly. Conversely, the adsorption capacity is highest at low pH levels and shows a marked decline as the pH increases, although there is a slight improvement in adsorption capacity at higher pH values. This shows that acidic conditions (lower pH) are more beneficial for both high removal efficiency and adsorption capacity. The data highlights the significance of pH in the performanceoptimaztion of Montmorillonite clay for chromium removal, with lower pH levels being more efficient for accomplishing higher removal rates and adsorption capacities.

5.3 Effect of Varying initial Cr (VI) Concentration on Cr (VI) removal using Fe Coagulant

The impact of varying initial chromium concentration on the removal efficiency of chromium has been presented in ***Figure 18***.

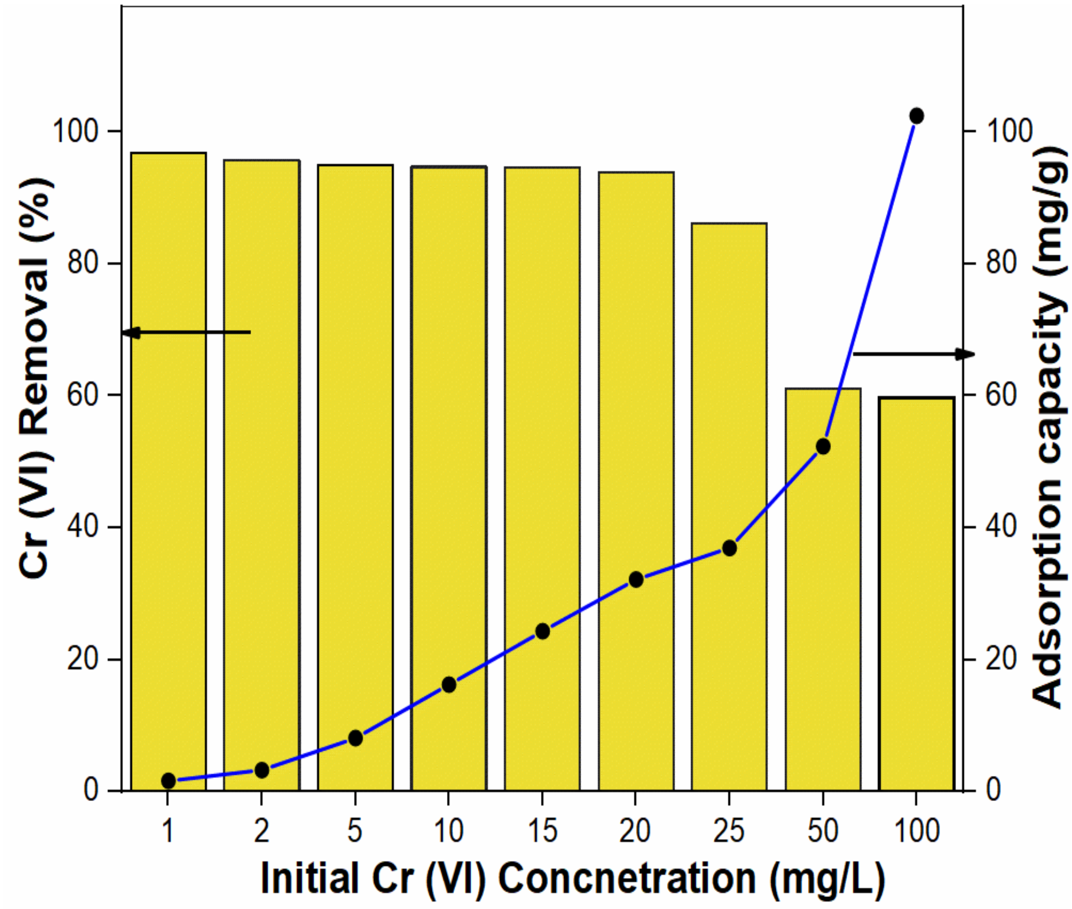

Figure 18 Effect of Varying initial Cr (VI) Concentration on Cr (VI) removal using Fe Coagulant

With the increase in the initial concentration of chromium the proficiency of Cr (VI) removal by the Fe- coagulant reducessteadily. This decline in removal efficiency indicates that the coagulant’s capacity to adsorb chromium ions lowers at higher concentrations, because of saturation of adsorption sites or alterations in the chemical environment. Concurrently, the adsorption capacity of the coagulant encounters a remarkableincrease with increasing initial chromium concentrations. This shows that while the overall removal efficiency declines, the ability of clay to capture chromium ions per unit mass improvessubstantially. This indicates that higher chromium concentrations grant more chances for chromium ions to interact and bind with the clay particles. Therefore, the data features the complicated balance between removal efficacy, adsorption capacity, and the effect of coagulants in chromium removal procedures using Fe-coagulant. Estimation of these relationships is critical for optimization of treatment processes and development of effective strategies for addressing chromium contamination in aquatic matrices.

5.4 Isotherm Models

The comparison of the R^2 values of the Freundlich and Langmuir models, it becomes obvious that the Freundlich model, with an R^2 value of 0.92, offers a substantially better fit to the experimental data than the Langmuir model, which has an R^2 value of 0.85.This observation implies that the adsorption process within the system presents characteristics that align more closely with the assumptions and principles of the Freundlich model. Specifically, the Freundlich model indicates a heterogeneous adsorption process, where the energy distribution across the adsorption sites is not uniform. The higher R^2 value correlated with the Freundlich model indicates that it takes the inconsistency in the experimental data more essentially and provides a more precise representation of the adsorption dynamics. This upper fit indicates that the adsorption process is manipulated by multiple sites of varying resemblances on the adsorbent surface. The heterogeneous nature of the adsorption process can be accredited to the distinct characteristics of the adsorbent material, which exhibits a range of binding sites with different adsorption capacities and similarities.

Unlike the Langmuir model, which affects a monolayer adsorption onto a surface with a predictable number of identical sites, the Freundlich model accounts for the complexity and irregularities commonly found in real-world adsorbent surfaces. The Langmuir model suggests that all adsorption sites have identical affinity for the adsorbate and that once a site is occupied, no further adsorption can occur at that site. On the contrary, the Freundlich model does not undertake a finite number of identical sites and agrees for the adsorption process to occur on a heterogeneous surface with varying energy levels.

In practical terms, the finer fit of the Freundlich model implies that the adsorption process does not influence a saturation point directly, and the adsorption capacity improves indefinitely with increasing concentration. This proposes a more complex interaction between the adsorbate and the adsorbent, manipulated by the presence of various adsorption sites with different energy levels. The Freundlich model's higher R^2 value underlines its capability to provide a more detailed understanding of the adsorption process, indicating the intricate nature of the interactions occurring on the heterogeneous surface of the adsorbent. Besides, the ability of adsorption phenomena to adjust a wider range presents it particularly appropriate for systems where the adsorbent surface is not uniform, and the adsorption sites keep different correspondences and capacities. This flexibility allows the Freundlich model to more accurately describe the real-world scenarios where adsorption occurs on complex and irregular surfaces. Thus, the higher R^2 value for the Freundlich model not only signals a better fit but also highlights the robustness and versatility of this model in acquiring the true nature of the Cr(VI) removal process in heterogeneous systems.

5.5 Effect of interfering ions

The outcome of this testemphasize the substantial affect of interfering ions on chromium removal from aquatic matrices as shown in ***Figure 19***. The individual impacts of chloride, phosphate, nitrate, sulphate, and bicarbonate on chromium removal were considerable, with removal efficiencies ranging between 53.52% and 87.97%. The combined occurrence of all ions presented a removal efficiency of 64.05%, which is pointedly lower than the removal efficiency of chromium without interfering ions (93.9%).

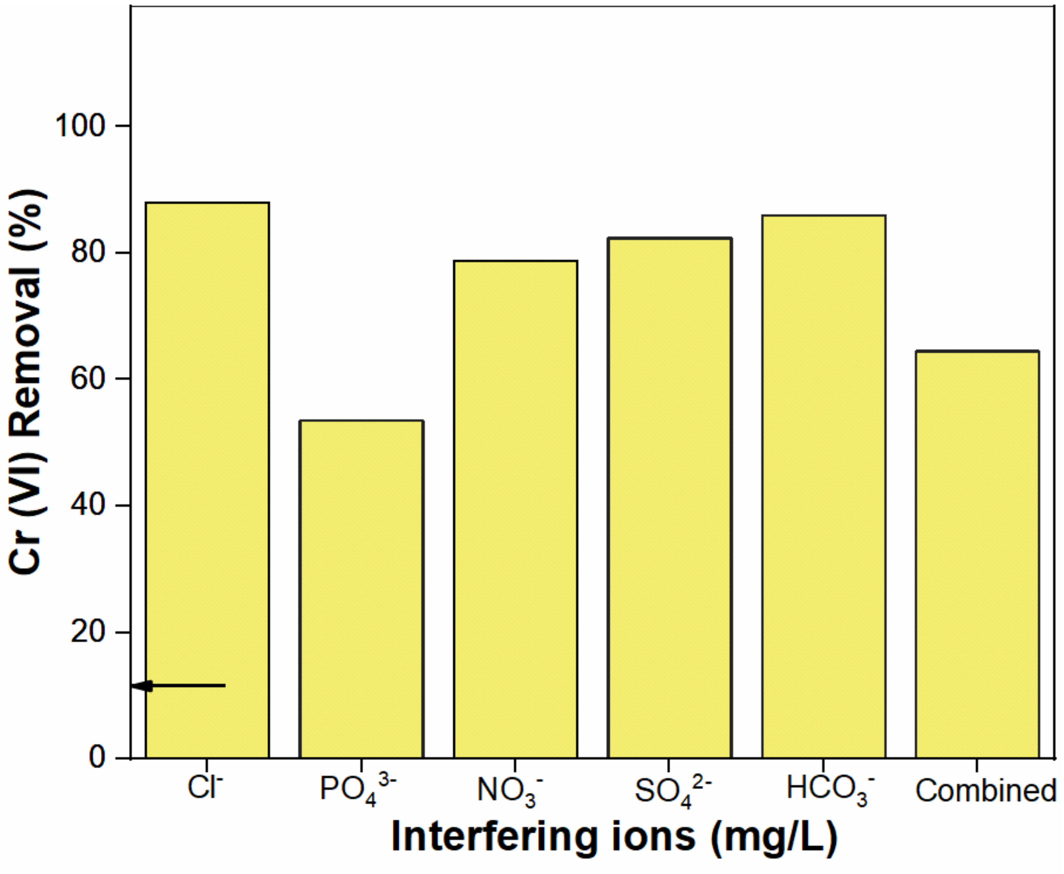

Figure 19 Effect of Interfering ions

These outcomesindicate that the occurrence of interfering ions can notablydecrease the efficiency of chromium removal, and that a thorough approach is needed to understand their impacts. The results also highlights the significance of considering the combined effects of interfering ions, as their individual effects may not perfectlycalculate their combined effect. The processes of chromium removal in the existence of interfering ions are complex and may embrace multiple interactions, including competition for binding sites and formation of precipitates or complexes. Further research is required to completely understand these mechanisms and to develop efficient remediation strategies that consider the presence of interfering ions. Overall, this experiment determines the significance of considering the occurrence of interfering ions in chromium removal, andsupplies valuable insights into the development of effective remediation approaches. The findings of this study have central implications for the development of sustainable and efficient technologies for chromium removal from water.

5.5 Turbidity before and after coagulation

Initial and final turbidity of different samples was evaluated to determine the efficiency of coagulation process and results are presented in ***Table 10.***

Table 10 Turbidity before and after coagulation

Sample	Initial turbidity (NTU)	Final Turbidity (Ntu)
1	41.4	< 0.01
2	83.4	< 0.01
3	175	< 0.01
4	255	< 0.01
5	380	< 0.01
6	492	< 0.01

The coagulation treatment presentedincredibleefficacy in eliminating suspended particles, by significantly enhancing water clarity. The significant reduction in turbidity levels, from initial values ranging between 41.4 to 492 NTU to less than 0.01 NTU, emphasizes the effectiveness of the process. This major decrease in turbidity proves the ability of coagulation to competently aggregate and precipitate suspended particles, resulting in extremely clear water. These results not only emphasize the success of the coagulation treatment in completing water quality objectives but also underline its ability for additionaloptimisation. Notwithstanding the already impressive results, additional adjustments to process parameters could possiblyimprove treatment effectiveness even further. Fine-tuning factors such as coagulant dosage, pH levels, and mixing intensity could indicate to even greater turbidity reduction, thereby ensuring consistently high water quality standards are met or exceeded. Likewise, the agreement with regulatory standards strengthens the suitability of coagulation treatment for addressing turbidity concerns in water treatment processes. By constantly producing water with turbidity levels well below regulatory limits, coagulation arises as a reliable and effective method for achieving water quality goals directed by governing bodies.Theconsiderable reduction in turbidity levels observed across the six samples treated in the jar test apparatus, coupled with agreement with regulatory standards, provides robust evidence supporting the adoption of coagulation as a dependable solution for turbidity removal in water treatment processes. The efficiency demonstrated in this study underlines the importance and efficiency of coagulation treatment in preserving and enhancing water quality, further improving its position as a cornerstone of modern water treatment practices.

CHAPTER 6

CONCLUSION

The efficiency of Fe-based coagulants in eliminating Cr (VI) ions from water, as compared to montmorillonite clay and their combination, is ascribed to numerousfundamentalaspects. These coagulants have been remarked to advance the formation of larger and denser precipitates, improve surface adsorption capacity, optimize pH conditions, and stabilize flocs, all contributing to effective chromium removal. In opposition, an increased dosage of montmorillonite clay hampered the proficiency of chromium removal, probably due to interference with floc formation and settling processes.

The study found optimal process parameters for having the highest Cr (VI) removal rates, including a pH of 5, Fe dosage of 0.12 g/L, clay dosage of 0.1 g/L, combined coagulant dosage of 0.22 g/L, and a temperature of 25°C. Moreover, the sorption data, best fitted with the Freundlich model, proposed multilayer sorption onto heterogeneous sites of the Fe-based coagulant.This research underlines the promising potential of Fe-based coagulants for efficient chromium removal from polluted water matrices. These findings present valuable insights for water treatment processes and environmental remediation strategies, highlighting the significance of considering Fe-based coagulants in addressing water pollution challenges. The findings of this study align with broader research signifying the proficiency of Fe-based materials in eliminating of Cr(VI) from water-based solutions, further supporting the implication of this study in the field of water treatment and environmental remediation.

This research also contributes to the ongoing discovery of novel materials and methods for addressing heavy metal pollution in water bodies. The potential toxic impacts of chromium in drinking water emphasize the importance of advancing effective removal strategies, making the insights from this study particularly relevant. In addition, the study's identification of optimal process parameters contribute to the advancement of knowledge in water treatment processes and environmental remediation strategies.

CHAPTER 7

RECOMMENDATION

After analyzing the findings of the study, some recommendations have been suggested to further advance the acceptance and application of Fe-based coagulants in chromium removal. These recommendations involve areas such as long-term stability, scalability, process optimization, and real-world performance evaluation. By addressing these recommendations, future research can contribute substantially to the field of water treatment and chromium remediation. These recommendations include:

Exploring Long-Term Stability and Sustainability:

Further research must focus on assessment of the long-term stability and sustainability of Fe-based coagulants in chromium removal applications. This could require extended monitoring and analysis to recognize the stability and efficiency of these coagulants over time. Key areas of study should incorporate the chemical stability of Fe-based coagulants under varying environmental conditions, their potential for secondary pollution, and their interactions with other treatment processes. Additionally, research should explore the economic feasibility and environmental impact of large-scale use, as well as potential improvements through the integration of functional materials or nanomaterials. Pilot-scale studies and real-world applications will be critical for confirming laboratory findings and assuring practical pertinence in diverse wastewater treatment scenarios.

Scalability and Cost-Effectiveness:

Examining the scalability and cost-effectiveness of applying Fe-based coagulants on a larger scale in water treatment plants is vital. This research should include comprehensive economic analyses to estimate costs and benefits, as well as pilot studies to test practical application in real-world. Assessments should focus on the logisticchallenges of large-scale implementation, potential savings from advanced chromium removal efficiency, and the overall sustainability of using Fe-based coagulants. Such studies will help verify the feasibility and long-term viability of this approach for widespread adoption in municipal and industrial water treatment facilities.

Optimization of Process Parameters and Dosages:

Continued optimization of process parameters and coagulant dosages is fundamental for proficient chromium removal and cost reduction in wastewater treatment. Experimentation and modeling are crucial to identifying sustainable operating conditions. By fineadjustingthese variables, plants can increase performance while decreasing environmental impact. Leveraging advanced techniques streamlines the optimization process, aiding in decision-making. Assimilation of experimentation and modeling yields tailored strategies for determined efficiency. This proactive approach sides withwith environmental stewardship goals. Eventually, optimized operations benefit ecosystems and communities alike.

Real-World Performance Evaluation:

Detailedstudies evaluating Fe-based coagulants' effectiveness in real-world contexts, spanning diverse water qualities and environmental settings, are vital. These tests offer invaluable insights into the feasibility and reliability of these coagulants for chromium mitigation across different scenarios. By studying their performance in varied conditions, researchers can gathernecessary data for improving treatment strategies. Understanding how Fe-based coagulants fare in actual applications advisesmost suitable processes for wastewater treatment units. This empirical approach assures the reliability and effectiveness of chromium remediation efforts in a multitude of environments. Such comprehensive research aligns with the goal of achieving sustainable and efficient water treatment practices.

By addressing these recommendations, future research can contribute substantially to the understanding and practical application of Fe-based coagulants for chromium elimination in water treatment processes.

ssCHAPTER 8

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