



JIMMA UNIVERSITY
JIMMA INSTITUTE OF TECHNOLOGY
FACULTY OF CIVIL AND ENVIRONMENTAL ENGINEERING
SCHOOL OF GRADUATE STUDIES ENVIRONMENTAL ENGINEERING CHAIR

REMOVAL OF HEXAVALENT CHROMIUM FROM TANNERY WASTEWATER
USING MAGNETIC RECOVERABLE ZEOLITE: OPTIMIZATION USING
RESPONSE SURFACE METHODOLOGY (RSM)

BY
MOHAMMED ASANU MOKONON

A THESIS SUBMITTED TO JIMMA UNIVERSITY, JIMMA INSTITUTE OF
TECHNOLOGY, FACULTY OF CIVIL AND ENVIRONMENTAL ENGINEERING,
ENVIRONMENTAL ENGINEERING CHAIR IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTERS OF SCIENCE IN
ENVIRONMENTAL ENGINEERING

JIMMA, ETHIOPIA
MARCH 2022

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ENVIRONMENTAL ENGINEERING**

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MARCH 2022

DECLARATION

I, Mohammed Asanu, hereby declare that this study entitled “Removal of Hexavalent Chromium from Tannery Wastewater Using Magnetic Recoverable Zeolite: Optimization using Response Surface Methodology (RSM)” is my original work. It composed by myself, with the guidance of my advisors, that the work contained herein is my own except where explicitly stated otherwise in the text and that all sources of materials used for the study have been fully acknowledged.

Name	Signature	Date
Mohammed Asanu		March 8, 2022

As member of the Board of examiner of M.Sc. Thesis open defense examination, we certify that, we have read and evaluate the study prepared by Mohammed Asanu and examined the candidate. We approved that the thesis be accepted as fulfilling the thesis requirement for degree of masters of Science in Environmental Engineering

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ABSTRACT

A recoverable adsorbent of magnetic natural zeolite has prepared by co-precipitation techniques for enhanced removal of Cr (VI), from aqueous solution. MZ adsorbents prepared by the technique characterized and its performance evaluated for the removal of Cr (VI) from tannery discharge. Furthermore, the effects of different fractions of MP on the adsorption capacity and recoverability of the adsorbents investigated. Medium fraction of MP (33.3%) give a promising adsorption efficiency and recoverability

The optimum adsorbent dose, pH, agitation speed and contact time at which maximum Cr (VI) adsorbed from aqueous solution experimentally determined. Finally, the adsorption kinetic that best fits to the maximum adsorption rate as well as the adsorption isothermal model that well describes the adsorption capacity of the adsorbents were determined.

In this study, a response surface methodology (RSM) approach using central composite design (CCD) was investigated to develop a mathematical model and to optimize the effects of pH, adsorbent dose, and initial concentration and contact time related to the hexavalent chromium removal by magnetic zeolite (MZ). The highest removal percentage of 93.57% was found by the predicted model under the optimum conditions (pH of 3, 1.6g of MZ, 30 mg/l of Cr (VI) and 60 min of contact time). The maximum percentage of Cr (VI) removal using natural magnetic Zeolite was found 94.88%. The MZ characterized by FTIR, BET, and analyses. Moreover, a Langmuir isotherm fitted well ($R^2 = 0.9966$) with the experimental data, and the maximum adsorption capacity was discovered to be 43.859 mg/g. Kinetic data were well foreseen by pseudo second order. In summary, the Cr (VI) removal onto economic, sensitive and selective MZ was optimized using CCD to study MZ behaviors.

Keywords: *Co-precipitation, Hexavalent Chromium, Magnetic Natural zeolite, Recoverability*

TABLE OF CONTENTS

DECLARATION	ii
ACKNOWLEDGMENTS	iv
ABSTRACT.....	v
TABLE OF CONTENTS.....	vi
LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF ACRONYMS	xi
1. INTRODUCTION	1
1.1. Background.....	1
1.2. Statement of the Problem.....	4
1.3. Objectives	5
1.3.1. General objective	5
1.3.2. Specific objectives	5
1.4. Research Questions.....	5
1.5. Significance of the Study.....	5
1.6. Scope of the Study	6
2. LITERATURE REVIEW	7
2.1. Overview of Tannery Wastewater	7
2.2. Occurrences of Chromium.....	8
2.3. Toxicity of Chromium	9
2.4. Aqueous Medium Hexavalent Chromium Removal Methods.....	9
2.4.1. Adsorption Using Magnetic Natural Zeolite for Removal of Cr (VI).....	11
2.4.2. Magnetic Zeolite adsorbent.....	15
2.6. Parameters Effecting Adsorption.....	17
2.6.1. Effect of Contact time.....	17
2.6.3. Effect of initial concentration	17
2.7. Response surface methodology.....	18
2.8. Adsorption Equilibrium Models	18
2.8.1. Langmuir isotherm.....	19

2.8.2. Freundlich Isotherm model	19
2.9. Adsorption kinetics Models	20
3. MATERIALS AND METHODS.....	21
3.1. Study Design.....	21
3. 2. Study variables.....	22
3.2.1. Independent variables	22
3.2.2. Dependent variables.....	22
3.3. Chemicals and Instruments	22
3.3.1. Chemicals.....	22
3.3.2. Materials used	22
3.4. Data Collection Process	22
3.5. Preparation of adsorbent	22
3.5.1. Raw Zeolite preparation.....	22
3.5.2. Magnetic Nano particle preparation.....	23
3.5.3. Magnetization of zeolite	23
3.6. Characterization of Adsorbent	23
3.6.1. FTIR analysis adsorbent	23
3.6.2. Surface characterizing adsorbent	23
3.6.3. Point of zero charge determination adsorbent	23
3.6.4. Characterizing recoverability of adsorbent.....	24
3.7. Experimental Design.....	24
3.8. Batch Adsorption Process	26
3.9. Adsorption isotherms	26
3.10. Kinetic parameters	27
3.11. Data Analysis	27
4. RESULT AND DISCUSSION	28
4.1. Adsorbent Characteristics Analysis	28
4.1.1. Surface characters	28
4.1.2. Recoverability of adsorbents.....	29
4.1.3. Point of zero charge determination	30
4.1.4. Fourier transform infrared spectroscopy (FTIR)	31

4.2. Choosing adsorbent from different adsorbents	33
4.3. Optimization of the adsorption process.....	34
4.3.1. Models validation.....	34
4.3.3. Development of regression model equations using CCD	37
4.3.3. Statistical and graphical analysis	37
4.4. Effect of experimental parameters on adsorption of Cr (VI).....	39
4.4.1. Effect of Adsorbent dose on adsorption.....	39
4.4.2. Effect of contact time on adsorption.....	40
4.4.3. Effect of initial concentration of Cr (VI) on adsorption	41
4.4.4. Effect of solution pH on adsorption.....	41
4.5. Combined effects of the factors on adsorption of Cr (VI) on MZ	41
4.6. Optimum point by CCD Design	45
4.7. Adsorption isotherm studies	47
4.8. Adsorption kinetic studies.....	48
5. CONCLUSION AND RECOMMENDATION.....	50
5.1. Conclusion	50
5.2 Recommendations.....	51
References.....	52
APPENDIXES	58

LIST OF TABLES

Table 2:1.	IUPAC classifications of pore sizes	13
Table 3:1.	Ranges of Independent variables and their levels	24
Table 3:2.	DoE matrix layout values	25
Table 4:1.	Surface and pore properties of the adsorbents prepared	28
Table 4:2.	Frequencies and respective functional groups present on the surface of MZ	32
Table 4:3.	Validation of adsorption process variables under optimum conditions.	34
Table 4:4.	Actual and predict value of response from experiment	35
Table 4:5.	Model summary statistics	36
Table 4:6.	Fit Statistics for removal efficiency	37
Table 4:7.	ANOVA for Quadratic model of removal efficiency	38
Table 4:8.	Comparison of optimum process variables and removal efficiency using experimental and software predictions	46
Table 4:9.	The adsorption isotherm	47
Table 4:10.	Comparison of maximum Adsorption capacity of magnetic zeolite with other adsorbents	48
Table 4:11.	The adsorption kinetic parameters	49

LIST OF FIGURES

Figure 2:1.	Natural Zeolite	12
Figure 2:2.	Zeolite pore structure	13
Figure 2:3.	(a) TO_4 tetrahedron. (b) Tetrahedral sharing a common oxygen vertex	14
Figure 2:4.	Schematic presentation of synthesis of MZ by co-precipitation technique	17
Figure 3:1.	Research design	21
Figure 4:1.	Clarity of filtrate and ability of Adsorbents	29
Figure 4:2.	pH of zero charge of the Adsorbents	30
Figure 4:3.	Fourier Transform Infrared Red spectra graph	32
Figure 4:4.	a) Predicted versus actual values of response b) Normal probability plot of residual	39
Figure 4:5.	Effect of parameters on adsorption of Cr (VI) on MZ adsorbent	40
Figure 4:6.	Figure 4:6. Response surface 3D plots for the CCD of interaction effect parameters for Cr (VI) adsorption: (A) effect of adsorbent dose and contact time, (B) effect of adsorbent dose and initial concentration, (C) effect of adsorbent dose and pH and (D) effect of contact time and initial concentration (E) effect of contact time and pH (F) effect of initial concentration and pH	42
Figure 4:7.	Optimum points by ramp graph	46
Figure 4:8.	Adsorption isotherms a) Langmuir model graph b) Freundlich model graph	47
Figure 4:9.	Adsorption Kinetics graph a) pseudo first Order b) Pseudo Second order model graph	48

LIST OF ACRONYMS

AAS	Atomic Adsorption Spectrophotometry.
ANOVA	Analysis of variance
BBD	Box-Behnken design
BET	Brunauer Emmett and Teller analysis
CCD	Central composite design
EEPA	Ethiopian Environmental Protection Authority
FTIR	Fourier transform infrared spectroscopy
IUPAC	International Union of Pure and Applied Chemistry
IZA	International Zeolite Association
MP	Magnetic particle
MZ	Magnetic zeolite
pH	potential of hydrogen
PRESS	Predicted residual error sum of squares
Pzc	Point of zero charge
RSM	Response surface methodology
WHO	World Health Organization

1. INTRODUCTION

1.1. Background

Population growth has led to rapid industrialization and urbanization, which resulted in the pollution of water, air and land of the world. Heavy metals are elements having a density greater than 5 g/cm^3 in their elemental form. The incredible increase in the use of the heavy metals over the past decades has eventually resulted in an increased flux of metallic substances in the environment (Koller and Saleh, 2018). Therefore, it received attention of researchers all over the world, mainly their harmful effects on human beings. Heavy metals that are discharges into rivers and lakes from different sources directly exposed to water bodies, in addition to the discharge of different liquid wastes (Meybeck *et al.*, 1996).

In the world, environmental pollution has been a major area of concern. Agricultural and industrial processes released toxic substances such as heavy metals to the environment which retaken by animals as well as by plants into their body systems that cause another distribution of toxicants to the environment(Okereafor *et al.*, 2020).

Chromium is a naturally occurring element present in water, sediments, rocks, soils, plants, animals and volcanic emissions. It exists in a number of oxidation states though only Cr (III) and Cr (VI) are biologically and environmentally stable in natural aqueous medium(Tchounwou *et al.*, 2012). Chromium is a common pollutant found in industrial effluents because chromium salts such as chromate and dichromate have many industrial applications such as in textile, electroplating, leather tanning, dyeing, cement preservations, paints and pigment and metallurgy industries(Choppala, Bolan and Park, 2013). At trace level Cr (III) is considered as an essential nutrient for living organisms whereas hexavalent chromium, is a more poisonous, carcinogenic, teratogen and mutagenic to biological systems(Nur-E-Alam *et al.*, 2020).

Researches show that many place of the world are becoming the victims of heavy metals specifically Cr (VI) (Koller and Saleh, 2018). Cr (VI) contaminated soils, were reported in different soils around the globe(Bemben, Bemben and Hartman, 2005). As (Sheffer, 2013) document describes in many industries of the world Cr (VI) emissions into the environment are significantly higher than the international guidelines values. These are not the only documents which are suggesting the message of how alarming rate of Cr (VI) accumulation rise our world is facing, but the aforementioned literatures are ample to use as evidence.

Water contamination with heavy metals is a serious pollution problem because these metals tend to persist and accumulate in the environment. Industrial and mining wastewaters are important sources of heavy metals pollution. Heavy metals like Zn, Cr, Pb, Cd, Cu, Mn, Fe considered potentially harmful and can cause physiological and neurological disorders (Koller and Saleh, 2018).

Water pollution is a big problem in the world. Natural water is one of the natural resources that are important not only to our life but also to other animals. Natural water quality has affected by different activities like urbanization, industrialization, rapid population growth that make our environment polluted (Metcalf and Eddy., 2003) (Liyanage and Yamada, 2017). Either surface water or underground water can be polluted due to the discharge of wastes from the leather industry especially chromium oriented industry (Genawi, Ibrahim and El-naas, 2020). The problem that faced to human and the environment is because of water pollution. The polluted water distributes a wide range of diseases so, safe drinking water is a necessity for human development, and health (Zewdu and Amare, 2018).

Leather processing Tannery industry wastewater effluent characteristically contains a complex mixture of both organic and inorganic pollutants like chlorinated phenols and Heavy metals. The tanning operation discharges hexavalent chromium, which causes a serious environmental pollution problem (Yakubu *et al.*, 2018).

In conclusion, the discharge of Cr (VI) opulent water to the environment can lead to potential hazards on humans and affect the worth of the natural resources nearby the tanning industry. This study also revealed significant contamination of the surrounding downstream water bodies showing that the treatment process of the tannery was not able to remove the chromium perceived in the downstream surrounding water bodies.

The above and related studies are in common agreement that our world is in high risk of accumulation of chromium due to the disposal of wastage from industries. Therefore, to resolve this problem, industries should take treatment process before they release to the environment. As the Cr (VI) is a hazardous metal to the environment, the leather industries in Ethiopia have to plan some more effective averting mechanisms to make an environmentally unthreatening tannery industry.

Knowing the effect of chromium on the environment even on the health at large people has been trying different mechanism to remove chromium. Different techniques have applied to remove Cr

(VI) from the industrial effluent such as chemical precipitation, ion exchange, reduction, electrochemical precipitation, solvent extraction, membrane separation, cementation, electro-dialysis and adsorption (Ye *et al.*, 2019); (Murthy and Rao, 2020). Efficient methods of chromium removal from wastewater are important to attain environmental quality standards. From these techniques, adsorption has identified as one of the most promising method for removal of dissolved heavy metal from wastewater for the reason that of its high efficiency, easy handling and cost effectiveness as well as availability of different adsorbents (Gorzin and Bahri Rasht Abadi, 2018). Currently, adsorption has believed to be a simple and effective technique for water and wastewater treatment and the success of the technique largely depends on the development of an efficient adsorbent. Activated carbon, clay minerals, biomaterials, zeolites and some industrial solid wastes have been widely used as adsorbents for adsorption of ions and organics in wastewater treatment (Wang and Peng, 2010).

Even though, the presence of all these different techniques and adsorbents, chromium (VI) accumulation is highly increasing in our world. The use of natural as an adsorbent appears as a viable and eco-friendly option for the removal Cr (VI) polluted wastewaters because zeolite is one of the most abundant, effective and low cost materials (Gandhi, Sirisha and Sekhar, 2013).

Characteristically, an ideal adsorbent must possess high surface area, good physical, mechanical, and chemical stability, and high affinity to bind with pollutant molecules (Wang and Peng, 2010) (Popov *et al.*, 2010). Also, an effective adsorption process depends on several factors such as pH (Saranya *et al.*, 2017) and temperature, concentration of the adsorbate, degree of ionization of the adsorbate, the adsorbent dosage (Sika, Liu and Chen, 2010), and the structure and surface charge of the adsorbent (Pandey, Sharma and Sambhi, 2010b).

Since recent times, natural zeolites have time-honored attention for the removal of various pollutants due to their excellent properties as adsorbent including high adsorption capacity, low cost, high chemical stability and worldwide abundance (Pambudi, Wahyuni and Mudasir, 2020). Adsorption technique using natural zeolites one of the most recommended processes due to its economic and technical advantages (Wang and Peng, 2010). Due to their superior properties, zeolites have frequently used to remove various contaminants such as phenol, dyes (Sánchez-Hernández *et al.*, 2018) and heavy metals (Kadja and Ilmi, 2019).

Optimization is improving the performance of processes and increasing the yields of the systems without increasing the associated costs. RSM defines the effects of the important factors, alone or

in combination with the involved processes (Bayuo, Abukari and Pelig-Ba, 2020). Hence, in this study Statistical optimization of independent variables influencing the adsorption process was examined with central composite design (CCD), a subset of response surface methodology (RSM) in Design-Expert software 13.0.5.0. Furthermore, four parameter adsorption isotherm and kinetic models were explored to determine the models that best represent the equilibrium data in removal of hexavalent chromium from aqueous solutions by using magnetic zeolite as adsorbent.

1.2. Statement of the Problem

Because of its multipurpose, Chromium is one of the heavy metals wasted from different industries like textile, leather, and steel industries. Due to this reason, the amount of chromium accumulated in our earth is increasing.

Discharge from Leather industry contain Chromium based waste, both in liquid and solid form such as chromium sludge, chrome tanned leather shavings, and chrome leather trimmings. These wastes are unavoidable due to adaptability of chromium, and possess a serious threat to the environment like; deteriorating the water underground, air, and soil of our world, which leads to affect both fauna and flora in adversely.

Since, Cr (VI) catches its place in the priority list arranged by the Agency of Toxic substances and diseases registry, it can cause mutation and cancer, and hinder enzymes and nucleic acid synthesis. Therefore, to tackle this problem immediate action necessity be taken.

In order to prevent of Cr (VI) contamination in water, removal of Cr (VI) to a permissible level is a top agenda to be carry out. Therefore, it is imperative to develop financially viable, efficient, secure and environmentally friendly technologies to remove Cr (VI) from contaminated water and industrial wastewaters. One such alternative technique that has attracted a lot of attention in recent years because of its competitiveness, effectiveness and low cost is adsorption using easily available adsorbent.(Margeta *et al.*, 2013).

Decreasing Cr (VI) concentration in water has been currently studied by adsorption method using a numerous of adsorbents(Gorzin and Bahri Rasht Abadi, 2018), because it is an effective, economical and flexible in design and operation. However, adsorption of Cr (VI) using magnetic natural zeolite is not been explored yet.

Therefore, to solve these problems, I investigate adsorption of Cr (VI) by using zeolite-Fe₃O₄. This is because zeolites has special characteristic, which can be useful to implement in improving

adsorption efficiency of Cr (VI). These are porosity, abundant availability, low cost and easily preparation procedure

1.3. Objectives

1.3.1. General objective

The main objective of this study is to use magnetic recoverable natural zeolite adsorbents for the removal of hexavalent chromium from tannery discharge.

1.3.2. Specific objectives

The specific objectives of the study are:

- ☒ To prepare and characterize of magnetic recoverable zeolite adsorbents.
- ☒ To find out the optimum process conditions, using CCD in RSM approach for the removal of chromium (VI) from wastewater by MZ as adsorbent.
- ☒ To determine the kinetic behavior and isotherm models for the adsorption of Cr (VI) onto MZ adsorbents.

1.4. Research Questions.

The researches questions of this study addressed as follows:

1. How can magnetic recoverable zeolite adsorbents be prepared and characterized?
2. How can the optimum process conditions be found using CCD in RSM approach for the removal of chromium(VI) from wastewater by MZ as adsorbents?
3. How the kinetic behavior and isotherm models are determined for the adsorption of Cr (VI) onto MZ adsorbents?

1.5. Significance of the Study

This study presents a novel approach for the removal of Cr (VI) from leather industries wastewater by using locally available adsorbent. This study endeavors to introduce a new, simple, and cheap process on removing of heavy metal Cr (VI) from aqueous waste.

Cr (VI) is one of the world's most versatile materials having a wide range of uses in the metals and chemical industries although it is harm if it is not handling properly. For example, its alloys enhance metal resistance to impact, corrosion, and oxidation. Due to the many industrial uses of Chromium, Ethiopia, have sites with Cr (VI) contaminant problems. With all these applications of chromium, it is going be barred unless low cost, simple, and viable treatment process is developed soon. Therefore, this work will play a big role on keeping the versatility of chromium in industries usage.

What is common to many Cr (VI) sites are questions that continue to arise regarding the safety of the drinking water supply. As with most environmental challenges, questions of science compete with emotional responses and financial interests. Many Researchers have tried various methods for removal of heavy metals from wastewater. Adsorption process provides wide scope for the elimination of heavy metals from Industrial wastewater using low cost adsorbents. In addition, low cost adsorbents should use to minimize cost and maximize heavy metal removal efficiency. The study would be important because adsorption of Cr (VI) using magnetic natural zeolite has not explored yet. Hence, this study is significant since it seeks to address the characters and efficiency of magnetic natural zeolite prepared by the co-precipitation techniques.

The findings are useful to the Ethiopian leather industries. Moreover, it used as a reference for Cr (IV) by adsorption methods adsorbent recovered by magnetic bar. It is also the baseline for further detail study of comparison of the characters and adsorption capacity of the magnetic natural zeolites for removal of hexavalent chromium by adsorption process. It may also help to contribute to the already existing body of knowledge as well as help to inform policy makers in government to limit standard effluent of Cr (IV) in tannery industries.

1.6. Scope of the Study

The scope of this study bounded to investigation of removal of the Cr (VI) by magnetized natural zeolite adsorbents. Since it is difficult to begin the task from the mark, the literature provides few experimental data for preparation of adsorbent from zeolite and Ferro- material. Herein, the prepared adsorbent is going to be study in detail for the Cr (VI) removal from aqueous wastewater of tannery effluent. Address the characters and efficiency of magnetic natural zeolite prepared by co-precipitation. The parameters affecting the adsorption efficiency (i.e., Contact time, Concentration, pH, adsorbent dose). Further, the adsorption kinetic parameters pseudo first & pseudo second order and the equilibrium data was analyzed using Langmuir and Freundlich isotherms. Moreover, the optimization of working conditions of adsorption investigated. For the characterization of the adsorbent different analysis techniques performed. Among this, point of zero charge, Fourier transform infrared and surface analyses are the basic ones. It performs to evaluate the surface charge, chemical band form, and surface of adsorbent, respectively.

2. LITERATURE REVIEW

This chapter provides a brief literature review related to the overview of tannery industries wastewater, Chromium (VI) pollutant in tannery discharge and its effect on Environment and relevant results obtained about their removal from water matrices by adsorption. Later, the mathematical modeling for adsorption equilibrium data presented for both, isotherm models and adsorption kinetics

2.1. Overview of Tannery Wastewater

Water is the most important natural resources and its pollution is commonly associated with the discharge of effluents from sewers or sewage treatment plants, drains and industrial plants to the water body of rivers, seas and marine(Vi and Water, 2014). Heavy metals are among the most common pollutants found in wastewater. Heavy metals are elements having atomic weights between 63.5 and 200.6 and have a specific gravity greater than 5.0 g/cm³(Shalaby *et al.*, 2018).According to World Health Organization(WHO) the heavy metal ions of the most immediate concern to human beings are Chromium(Cr), Nickel(Ni), Lead (Pb), Copper (Cu), Mercury(Hg), Arsenic(As) and Zinc(Zn). This study mainly focused on removal of hexavalent Chromium from discharge of effluents from tanning industries.

Tanning is a process of converting putrescible outer coverings of animals to non-putrescible leathers with definite physical, chemical and biological properties so that they used in our daily life and industries. Major stages of tanning process were Soaking, de hair & liming, de liming, bating, pickling, tanning and re tanning.

Leather processing involves a huge amount of water in its different stages and therefore it produces a considerable amount of wastewater, which demands high investments and operational cost for effluent treatment to satisfy the discharge standards required by environmental legislation.(De Araujo Silva, 2018).

There are two types of tanning vegetable tanning and chrome tanning. Chrome tanning is the commonly used tanning agent since, longtime but still now it is the main mineral tanning material. The most widely used tanning substances are Chromium salts. Unfortunately, skins react with only 60-70% of the chromium salts used in the tanning process and the remainder left over in aqueous phase. Sulfide and chromium are the two major chemical constituents of the wastewater ejected from the tanning industry. These chemicals mixed with water are discharged from the tanneries, pollute the groundwater permanently, and make it unfit for drinking, irrigation and general

consumption. Chromium has also a very bad effect on human health. A little amount of trivalent chromium (50 to 200 micrograms) has recommended for good health but hexavalent chromium is common factors for causing cancer inhuman body (Chew *et al.*, 2019).

With solid wastes representing about 70% of the wet weight of the original hides, the tanning process comes at a considerable strain on water treatment installations. In addition to the other environmental impacts of leather, the production processes have a high environmental impact, most notably due to the heavy use of polluting chemicals in the tanning process and air pollution because transformation process (Hadgu and Amare, 2016).

Currently in Ethiopia Tanning industry, thought to be one of the sectors supporting economic development of the country significantly by generating foreign currency but pollutant intensive sector that threatens the environment at large. Ethiopian tanneries are now on a new path of g values to the products that therefore requires a series of additional individual process steps and varieties of chemical input that possibly intensifies the pollution load of the wastewater effluent. The environment and development integration in a leather industry should strengthen to achieve the intended sustainable economic benefit for human wellbeing.

2.2. Occurrences of Chromium

Chromium enters into the environment by natural and anthropogenic sources. Volcanic eruptions, geological weathering of rocks, soils and sediments are the natural sources of chromium, whereas anthropogenic contributions were due to result of chromium is widely used, there are many sources of leaching the chromium into the natural water system. These are from industrial applications, including electroplating, tanning, industrial water cooling, paper pulp production, petroleum refining, paint and pigments, laboratory oxidant, and wood preservatives. (Mitra, Sarkar and Sen, 2017)

Chromium is existing in oxidation states ranging from Cr (-II) up to Cr (+VI) but, the most common, stable and abundant forms are chromium (III) and chromium (VI). Chromium (III) exists as cation, Cr^{3+} and it occurs naturally in the environment while chromium (VI) exists in the anionic form (chromate) produced by industrial process for laboratory reagents and manufacturing intermediates(Yogeshwaran and Ak, 2021). Each of both forms has a unique chemistry and behavior.

2.3. Toxicity of Chromium

Cr (III) is actually an essential micronutrient, benefits to the human body, it not been reported as toxic(Rollinson, 1973).On the other hand, Cr (VI) known to be harmful when inhaled and when dermally exposed. If ingested via contaminated drinking water, effects can occur on the liver, kidney, gastrointestinal and immune systems, and possibly the blood (Rollinson, 1973),(Report, 2013). Various problems such as severe diarrhea, eye and skin irritation, kidney defection and probable long carcinoma hastened due to Cr (VI) concentration(Upadhyay *et al.*, 2018) and hence, treatment needed before discharging. Therefore, restriction of chromium concentration in discharged water enforced for public health protection and animals.

Chromium is inorganic chemicals listed as a primary drinking water standard regulated by the Environmental Protection Agency (EPA, 2016). In order to prevent toxic impacts of chromium, EPA has established a maximum contaminant level (MCL) for this compound. The maximum concentration limit for Cr (VI) is not more than MCL(Krishna, Krishna and Sree, 2013). However, the industrial wastewater contains concentrations that are beyond the permissible limit. The Regulations enforces limitations for industries discharging chromium.

The maximum allowable amount chromium disposal differs from country to country and from organization to organization. According to United States Environmental Protection Agency, the maximum Cr (VI) level for discharging into potable water is 0.05 mg/L (Krishna, Krishna and Sree, 2013)and for inland surface waters is 0.1 mg/L.

WHO states regarding maximum allowable chromium. As a result of the health effects determined largely by the oxidation state, different guideline values for chromium (III) and chromium (VI) should be derived. However, current analytical methods and the variable speciation of chromium in water favor a guideline value for total chromium. Leather Tanning and Finishing Point Source Category, which shall comply with limitations before introducing process wastewater pollutants into a publicly owned treatment works.

2.4. Aqueous Medium Hexavalent Chromium Removal Methods

In the aqueous solutions, Cr (VI) is very soluble, exists as form of chromic acid (H_2CrO_4)and as dichromate ($\text{Cr}_2\text{O}_7^{2-}$) while in neutral solutions, Cr(VI) is present as form of HCrO_4^- and CrO_4^{2-} (Ulatowska and Stala, 2021).

Ethiopia shows rapid industrial expansion implies economic progress these affect environment, particularly due to the discharge of wastewater. Leather industry ranked as the most polluting

activities in Ethiopia due to the high growth rate and discharge of wastewater to the water bodies. At present there is more than thirty-one tanning industries in Ethiopia, fully operated. Most of them discharge their wastewater into nearby water bodies and open land without any form of treatment.

Hence, discharge of tannery wastewater into the environment pose severe threat in aquatic plants, animals and human health due to their toxicity, high oxygen demanding, eutrophication and persistence in the environment. Therefore, treatment of the effluent to remove the pollutant before discharging into the environment becomes inevitable. (Hadgu and Amare, 2016)

A number of methods to remove chromium ions from aqueous solutions have been reported mainly reduction, ion exchange, filtration(Chew *et al.*, 2019), coagulation(Vi and Villabona-ortíz, 2021), Ion exchange, fluidized bed reactor, ion flotation, flue gas purification, solvent extraction, reverse osmosis, chemical precipitation, and. electro dialysis(ED), photo catalysis, and biological processes, adsorption (Gomes, Kumar Gupta and Kumar Sinha, 2017).

Each method has its own merits and limitation. The versatility, simplicity, cost effectiveness and technical feasibility are a few factors that must considered while selecting a particular method. Precipitation is not applicable when low concentrations of heavy metal ions are present in large volumes of water. Flocculation or coagulation needs to accompany precipitation, which usually results in large volumes of sediments containing heavy metal ions forming. High cost and technical complication are the problem associated with reverse osmosis and electro dialysis. Ion exchange is also comparatively costly whereas chemical precipitation leads to sludge generation and involve high capital costs. Photo catalysis process is still in the developmental stage. Based on the above factors mentioned for the comparative purpose of the techniques, adsorption is preferable technique for the removal of chromium.

Adsorption methods were found to be more effective and attractive due to its less investment in terms of initial cost and land, simple design, easy operation, higher efficiency of heavy metal ions removal from wastewater and no effect of toxic substances compared to conventional biological treatment processes (Gomes, Kumar Gupta and Kumar Sinha, 2017).

Some adsorbents, used to adsorb Cr (IV) (Yogeshwaran and Ak, 2021) investigated in prior research include cashew nut shells, olive cake, date pits and fruits, Carbon, micro silica composite, Barberry Leaf, Zeolite and Agro industrial Waste, by Microorganism, Rice husk silica. Tea factory waste, maize cobs, and wood saw dust, waste products and other natural products. Hence, allowing

for an inexpensive and feasible method of removing Cr (IV) from wastewater. The problem lies in obtaining the optimal adsorbent and corresponding conditions that effectively remove a large percentage of a known metal.

The primary requirements of adsorbents for economic and commercially attractive were adsorbent must have a large internal surface area; this surface area should be accessible through pores big enough to allow certain molecules passage during adsorption that is it should be highly selective. The adsorbent should be mechanically strong, enough to withstand bulk handling and vessel vibrations. The adsorbent should be easy to regenerate. There should not be any rapid exhausting (that is, loss of adsorptive capacity) of the adsorbent due to continual recycling(Li *et al.*, 2010).

Cost is actually an important parameter for comparing adsorbent materials. A solid can be considered as low-cost adsorbent if it is required little processing and abundant in nature. To achieve this aim natural adsorbent for adsorbing chromium investigated in batch system. Following subsections discusses applications of magnetic natural zeolite of the adsorbents reported in literature for removal of hexavalent chromium from wastewater.

2.4.1. Adsorption Using Magnetic Natural Zeolite for Removal of Cr (VI)

Zeolites are crystalline, hydrated alumino-silicates of alkali and alkali earth metals principally sodium, potassium, magnesium, lithium, barium and calcium, that possess infinite, three dimensional crystal structures(Exchange *et al.*, 2019). They characterized by an ability to lose and gain water reversibly and to exchange some of their constituent elements without major change of structure.

Zeolites occurred naturally as well as they are prepared in industries. Natural zeolites are the most important inorganic cation exchangers that exhibit high ion exchange capacity, selectivity and compatibility with the natural environment(Exchange *et al.*, 2019)(Wang and Peng, 2010). The potential applications of both synthetic and natural zeolites depend of course on their fundamental physical and chemical properties. Clinoptilolite is the most abundant natural zeolite that occurs in relatively large minable sedimentary deposits in sufficiently high purity in many parts of the world. There are many types of synthetic zeolite such as type A, X, Y, mordenite, ZSM, Molecular sieve, etc. (Kyeyune and Mulamba, 2015).



Figure 2:1. Natural Zeolite

The main zeolite formula is $M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$ with M defining the compensating cation with valence n.

The structures of zeolites consist of a three-dimensional framework of SiO_4 and AlO_4 tetrahedral. The fundamental building blocks of all zeolites are a tetrahedron of four oxygen anions surrounding a small silicon or aluminum ion. The crystal lattice extends in three dimensions and the 2-oxidation state of accounted by each oxygen (Review, 1800). The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Al^{3+} for Si^{4+} raises a negative charge in the lattice. The net negative charge balanced by the exchangeable cation (sodium, potassium and calcium). These cations are exchangeable with certain cations in solutions such as lead, cadmium, zinc and manganese. The fact that zeolite exchangeable ions are relatively innocuous makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters.(Wang and Peng, 2010).

The very regular structure and pore sizes give these materials a sponge-like appearance. Their pores hold water and or other molecules. Differences in zeolites arise from pore diameter, pore shape and the way these pores are interconnected. The pore size plays a significant role in the use of zeolites: allowing or prohibiting the entrance of the molecules to the system.(Popov *et al.*, 2010).

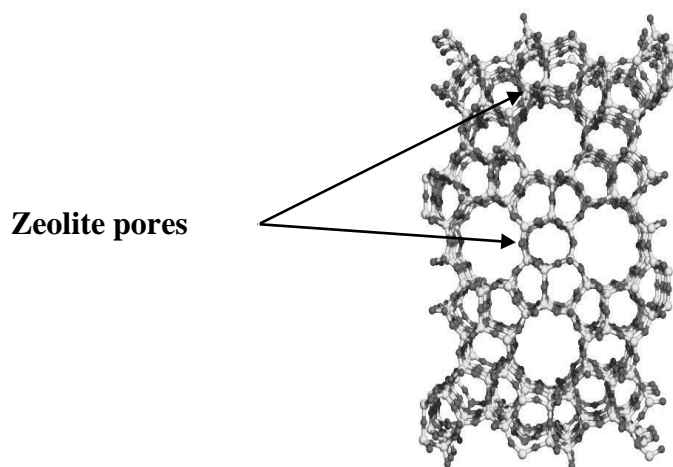


Figure 2:2. Zeolite pore structure

The zeolite is responsible for the physical adsorption of the molecule to the surface and therefore it is necessary to develop the largest possible internal surface obtained by the presence of well-defined pores and cavities. Zeolite type adsorbents applied in two ways: Separation according to molecular size: only those molecules with a diameter smaller than the zeolite pore will enter and adsorbed. Secondly, Separation according to molecular polarity: zeolite adsorbents tend to adsorb molecules of higher polarity by affinity. (Wołowiec *et al.*, 2019)

The range of pore sizes which is defined according to the IUPAC is shown in table 2:1.

Table 2.1: IUPAC classifications of pore sizes

Pores	Pore size (nm)
Micropores	<0.2
Mesopores	2-50
Macropores	>50

Zeolites are crystalline materials that have a composition very similar to sand, mainly comprising of Si and O₂. The zeolite structure contains (Si – O – Al) linkages that form surface pores of uniform diameter and enclose regular internal cavities and channels of discrete sizes and shapes depending on their chemical composition and crystal structure of the specific zeolite. Pore size start from about 2Å. The enclosed cavities contain both the metal cations and water molecules. The cations are loosely bound to the lattice and thus engage in ion exchange. Their open pore structure makes

them very useful for solving the mobility of toxic elements in a number of environmental applications.(Gatta and Lotti, 2019)

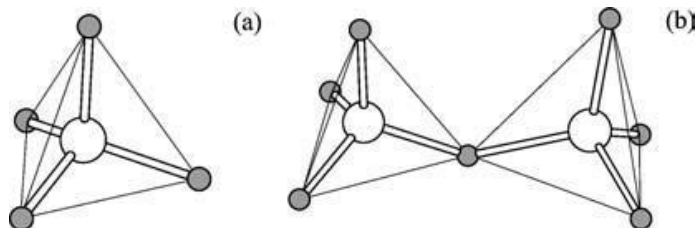


Figure 2:3. (a) TO_4 tetrahedron. (b) Tetrahedral sharing a common oxygen vertex

Zeolites are widely used in industry for water purification, as catalysts, as molecular sieve and in nuclear reprocessing. Their biggest use is in the production of laundry detergents. They also used in medicine, in agriculture, gas purification and catalysis. (Joanna and Kazimierz, 2013)

Zeolites natural have strong affinity for heavy metals. Zeolite was shown to have high selectivity heavy metal ions such as Pb^{2+} , Cd^{2+} , Zn^{2+} and Cu^{2+} . According to Zeolite is an inexpensive material as its commercial price is cheaper than commercial activated Carbon. Zeolite has received considerable interest for metals removal due to its high cation exchange capacities with certain metal ions in the aqueous solutions (Blute and -Hazen, 2012).

Many researchers have used natural zeolites for metal ion adsorption. conducted a series of experiments using a natural zeolite and modified forms for removal of several metal ions such as Ni^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+} . In Ni^{2+} adsorption, natural and modified zeolites have tested in a batch process. Zeolite modification can increase Ni^{2+} adsorption by 25–30%.

In general, natural zeolites in wastewater treatment are quite effective in comparison with other methods mentioned above. Thus the possible regeneration of the zeolite, re-use of the zeolite and reuse of the obtained concentrate metal ions after regeneration of the zeolite, very positively impact on the environment without creating new waste. One of the heavy metal that has been a major focus in wastewater treatment is chromium.

As, investigated by (Sivakumar, 2015) the comparisons of adsorption potential of zeolite and agro industrial wastes, grape and olive wastes, in removal of Cr (VI) from aqueous solution. This shows that of the interest in natural zeolite is the zeolite can serve as adsorbent materials in fields such as pollution control. Generally, Zeolite can serve as to remove contaminant from water like Cr (IV) as I planned to remove these ions by adsorption from tannery effluent.

Investigations using natural zeolites in removing chromium Show that as-received zeolite has better removal capabilities at lower Cr concentrations (5 and 10 mg/l) with adsorption capacities of 4.20 and 3.55 mg/g, respectively. thus, suggesting that zeolite is also suitable for the treatment of chromium effluents at lower concentrations (5 and 10mg/l) (Sheffer, 2013).

2.4.2. Magnetic Zeolite adsorbent

In fact, zeolites are micro porous aluminosilicates that are widely employed for cation exchange and remediation of metals in wastewaters but not powerfully adsorbed anion on unmodified zeolite due to permanent, structural negative charge of the crystal lattice. Since zeolite contain oxides of aluminum and silicon, its surface adsorbs Cr^{6+} , as it may also acquire positive charge in acidic medium however, in aqueous medium chromium exist as oxyanions forms such as chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) in the solution. Therefore, modification of natural zeolite is required to enhance adsorption process.

The metal nanoparticle has been the topic of many research because of the unique properties of nanoscale metals and their potential utility in advanced catalysis, adsorption and electronic systems. Migration of reduced metals from the zeolite channels to the external crystal surfaces Metal oxide nanoparticles are made of purely metal precursors. Examples of these metal oxide nanoparticles are titanium dioxide, silver, zinc oxide, cerium dioxide, copper, copper oxide, aluminum, nickel, and iron are most commonly used. Iron oxide nanoparticles are iron oxide particles with diameters between about 1 and 100 nanometers. The magnetic nanoparticles with sizes smaller than 100 nm are due to their surface efficiency, easily attach ligands and small settling velocities, which give a high stability in suspension and improve tissue diffusion. Various forms of iron oxides such as FeO, Fe₂O₃ and Fe₃O₄. The unit cell of Fe₃O₄ has interesting properties because the presence of non-equivalent cations in two valence states, Fe²⁺ and Fe³⁺, in the crystal structure leads to formation of a unique magnetic structure.

Magnetite nanoparticles are one of the most widely studied materials in multi-disciplinary research including biotechnology, biomedicine, magnetic resonance imaging, separation, catalysis, etc. In addition, magnetite nanoparticles have used in various hybrid systems such as magnetite–polypeptide hybrid, carbon nanotube–magnetite composites and silicon–iron oxide hybrid nanoparticles (Lopez *et al.*, 2010).

It is important to understand the main reason for the special interest in the synthesis and application of magnetite-supported nanomaterials: their characteristics and behavior are quite different with

respect to bulk materials with the same composition. Consequently, the range of parameters that has to be assessed to characterize these materials is large. (Maharana and Sen, 2021)

Both natural zeolite and magnetic particles are adsorption materials. In adsorption, bulk materials suffer from enormous mass transfer resistance due to large surface areas and large diffusion lengths. To overcome these limiting factors in adsorption, adsorption media could be designed to have some Nano features in order to enlarge mass transport kinetics by providing contaminants with rapid access to high surface area and by encouraging internal mass transport. One way of achieving this is by developing nanocomposites in which nanoparticles are coated materials. This study explores the use of magnetic natural zeolite composite as a strong adsorption media for hexavalent chromium removal from water.

Several preparation methods of MZ nanocomposites have developed, including co-precipitation, hydrothermal, thermal decomposition, impregnation, micro emulsion, chemical vapor deposition, electrochemical synthesis and laser pyrolysis. Co-precipitation method was known as the most conventional method for obtaining Fe_3O_4 because of its simplicity and low cost than others. Composite have obtained Fe_3O_4 nanoparticles using chemical co-precipitation method within 30 minutes at $60\text{-}70^\circ\text{C}$

Magnetite is an ideal oxide support, easy to prepare, having a very active surface for adsorptions of metals, which can be separated by magnetic decantation after the reaction, thus making it a more sustainable technology for greener remediation of contaminated sites. Lately, he has been focusing on greener approaches to assembly of nanomaterials and sustainable applications of magnetically retrievable Nano-composite

Generally, sorption activity increased with magnetic nanoparticles of smaller size, as they contain a large amount of active catalytic sites compared to bigger particles. MNPs have more functional surface compared.

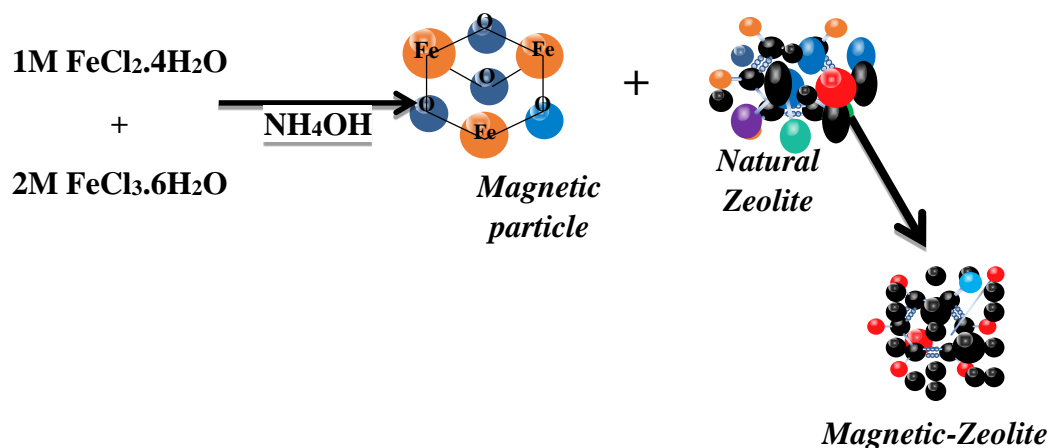


Figure 2:4. Schematic presentation of synthesis of MZ by co-precipitation technique

2.6. Parameters Effecting Adsorption

From the literature study it is found that adsorption is affected by parameters like contact time, solution pH, amount of adsorbent, initial concentration of Cr (IV). The following paragraph discusses the effects of various parameters.

2.6.1. Effect of Contact time

Contact time is important factor in batch adsorption process that determines extent of adsorption. Effects removal of chromium ions has been studied using different adsorbents by various authors. In most of the cases it was observed that the removal percentage increases with increase of contact time and reached a constant value (Pang, Kano and Imaizumi, 2015)

2.6.2. Effect of pH

The pH is an important parameter that affects the adsorption behavior of Chromium ions in aqueous systems. The pH determines the speciation of metal ions and affects the surface charge of the solid adsorbents. In addition, it is possible to manage metal uptake from aqueous solutions by changing the pH value (Pang, Kano and Imaizumi, 2015).

2.6.3. Effect of initial concentration

Equilibrium percentage removals of metal ions versus initial concentrations of solutions have examined using different adsorbents. Increase in the removal efficiency with because of the higher adsorbate concentration provided by higher driving force to overcome various mass transfer resistances from the aqueous to the solid phase, resulting in higher probability of collision between metal ions and the active sites (Jor *et al.*, 2017).

2.6.4. Effect of adsorbent dosage

The various researchers studied the effects of adsorbent dosage on the adsorption of metal ions removal. They have found that the removal efficiency of Chromium ions increases with adsorbent dosage increase. This is due to the greater availability of the exchangeable adsorption sites at the available larger sorbent surface area (Pandey, Sharma and Sambhi, 2010a)

2.7. Response surface methodology

Response surface methodology is an empirical statistical technique employed for multiple regression analysis by using quantitative data obtained from properly designed experiments to solve multivariate equations simultaneously. There are two main types of response surface designs: Central Composite designs (CCD) and Box-Behnken designs (BCD). Central Composite designs can fit a full quadratic model. They often used when the design plan calls for sequential experimentation because these designs can include information from a correctly planned factorial experiment and has five levels in CCD and include runs at their extreme setting, such as all of the low settings. Box-Behnken designs usually have fewer design points than central composite designs, thus, they are less expensive to run with the same number of factors. They can efficiently estimate the first- and second-order coefficients; however, they cannot include runs from a factorial experiment. Box-Behnken designs always have 3 levels per factor.

2.8. Adsorption Equilibrium Models

Equilibrium study is important in determining the efficacy of adsorption. It is also necessary to identify the adsorption mechanism for a given system. If the adsorbent and adsorbate contacted long enough, equilibrium established between the amount of adsorbate adsorbed and the amount of adsorbate in solution.

The adsorption isotherm is also an equation relating the amount of solute adsorbed onto the solid and the equilibrium concentration of the solute in solution at a given temperature. These relationships depend on the type of adsorption that occurs, chemical, or physical adsorption etc. The adsorption isotherm is widely used to examine adsorbent performance and can provide information on the feasibility of removing Cr(VI) and the surface properties and affinity of the adsorbent.

There are several models for predicting the equilibrium distribution. However, the most commonly used are, Langmuir, Freundlich, linear, and BET (Brunauer, Emmet, and Teller). Related documents, were performed the adsorption isotherm on the first two. The concept of the

adsorption isotherm is very important, because how much you load the surface at equilibrium depends on how much left in water. To determine which model to use to describe the adsorption for a particular adsorbent/adsorbate isotherms experiments typically run. Data from these isotherm experiments then analyzed.

2.8.1. Langmuir isotherm

In 1916, Langmuir proposed Adsorption Isotherm known as Langmuir Adsorption isotherm. Use different assumptions such as dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. The general form of Langmuir isotherm model has given by the following formula (Gomes, Kumar Gupta and Kumar Sinha, 2017).

$$q_e = \frac{q_{max} * b * C_e}{1 + b * C_e} \dots\dots\dots \text{Equation 2:1.}$$

While the linearized form of Langmuir isotherm has given using the following formula.

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{b * q_{max}} \dots\dots\dots \text{Equation 2:2}$$

Where, q_{max} (mg/g) is the Langmuir monolayer adsorption capacity and b (L/mg) is the Langmuir adsorption intensity constant as the ratio of the adsorption rate to the desorption rate, indicating the solid surface affinity and ability. (Gandhi et al. 2014).

Q_e calculated from the following equation.

$$q_e = \left(\frac{C_0 - C_e}{w} \right) V \dots\dots\dots \text{Equation 2:3}$$

Where, C_0 (mg/L) is initial concentration of adsorbate and C_e (mg/L) is concentration of adsorbate at equilibrium whereas V (L) is the volume of the adsorbate and w is the mass of the adsorbent in g. In order to evaluate the feasibility of the process, the Langmuir isotherm has described in terms of the dimensionless constant; separation factor or equilibrium parameter (R_L) (Srinath, 2012)

$$R_L = \frac{1}{1 + b C_0} \dots\dots\dots \text{Equation 2:4}$$

Where, b (L/mg) is the Langmuir isotherm constant and C_0 (mg /L) is the initial concentration of adsorbate. There are four probabilities for the R_L value: For favorable adsorption $0 < R_L < 1$, unfavorable adsorption $R_L > 1$, linear adsorption $R_L = 1$ and irreversible adsorption for $R_L = 0$

2.8.2. Freundlich Isotherm model

In 1909, Freundlich gave an empirical expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Isotherm (Miyazaki, 2013) This model is suitable for

heterogeneous surfaces with non-uniform distribution over the adsorbent. The Freundlich isotherm equation assuming that the adsorption takes place on heterogeneous surfaces of solids and in a multilayer sorption manner. This isotherm, Freundlich isotherm model, given by the following formulas:

$$q_e = K_f C_e^{\frac{1}{n}} \dots \dots \dots \text{Equation 2:5}$$

Freundlich isotherm model, K_f (mg/g) is the Freundlich isotherm constant representing the adsorption capacity and n_f is the adsorption intensity, reflecting the degree of difficulty for adsorption. When n exceeds 2 but no more than 10, the adsorption process is easy to proceed. Comparatively, the ability for adsorption will be too weak when n is less than 0.5 (Strom, 1976).

2.9. Adsorption kinetics Models

Kinetic models have been exploited to test the experimental data values then to find the mechanism of adsorption and its potential rate-controlling step that include mass transport and chemical reaction. Adsorption kinetics expressed as the solute removal rate that controls the residence time of the sorbate in the solid– solution interface

Adsorption kinetic parameters were determined based on the data of the contact time variation by following equations for pseudo-first order and pseudo-second order. The parameters obtained will be adsorption capacity at equilibrium (q_e) and adsorption rate constant (k).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \dots \dots \dots \text{Equation 2:6.}$$

$$\frac{t}{q_t} = \frac{1}{k_2 (q_e)^2} + \frac{t}{q_e} \dots \dots \dots \text{Equation 2: 7.}$$

Generally, from related literature review discussed above, Removal of Heavy metal ions from aqueous solution before discharging to water bodies are hot topic by many scholars. In my opinion in case of removal by using zeolite, have been tried by many researchers and reported suitable for metal ion removal due to their regeneration capacity. Further, there was not found that magnetic natural zeolite yet, hence I have selected this study to cover the gap mentioned above.

3. MATERIALS AND METHODS

3.1. Study Design

In this study, laboratory based experimental study design conducted in Jimma Institute of Technology of Jimma University, and Environmental Engineering laboratory. The study conducted from January 2021 to mid-July 2021. Natural Zeolite sample was bought and taken to laboratory, preparation by washing and dry in oven. Magnetization of Natural zeolite and produce various adsorbent, after those important preparation and characterization of MZ, the powder of adsorbent used for synthetic laboratory test. Then by dissolving potassium dichromate prepare synthetic wastewater, finally, the performance of each adsorbent compared.

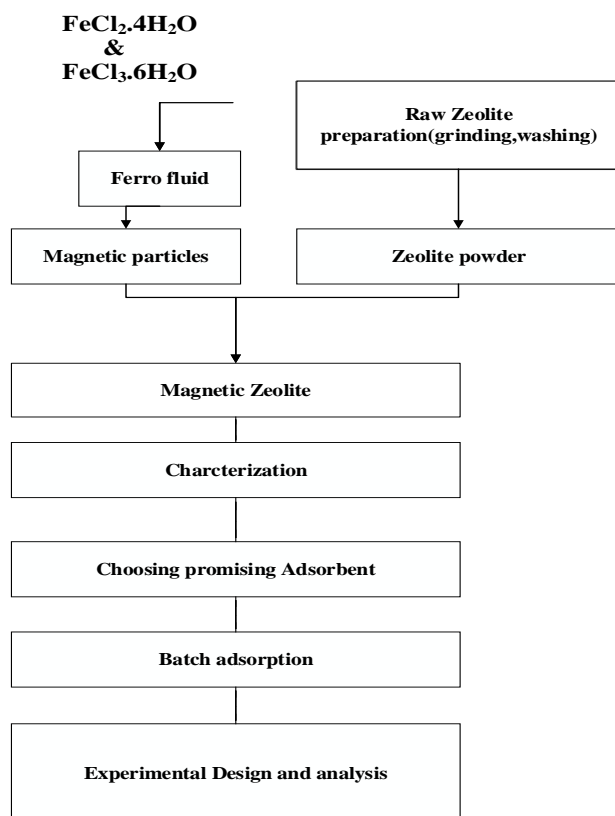


Figure 3.1. Research design

3. 2. Study variables

3.2.1. Independent variables

In this study, there are four independent variables. These are pH, contact time, Initial chromium concentration, and adsorbent dose.

3.2.2. Dependent variables

In this study, dependent variable is adsorption removal efficiency of Cr (VI)

3.3. Chemicals and Instruments

3.3.1. Chemicals

Natural zeolite is used adsorbent for this study Zeolite powders purchased from Sigma Aldrich Private limited company. In addition, for the preparation of MZ adsorbents $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ purchased from alpha company. $\text{K}_2\text{Cr}_2\text{O}_7$, distilled water, HCl and NaOH.

3.3.2. Materials used

Among many materials and equipment's used in this study, the majors were, Fourier Transform Infra-Red Spectroscopy (FTIR) by PerkinElmer Spectrum Two, surface area analyzer, turbid meter and UV-Vis Spectroscopy (Spectrophotometry) apparatuses used to analyze and characterize prepared magnetic zeolite adsorbents.

3.4. Data Collection Process

The study conducted first by identification of the mechanism of chromium removal through literature review and desk study on selected journal articles then from the findings. All the experiments carried in batch process with synthetic effluents at ambient condition.

Synthetic tannery wastewater was prepared in laboratory conditions by simulating real tannery wastewater whose selected constituents were of Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). 1000 mg/L was added in order to prepare the stock solution and to improve the Cr (VI) concentration in the solution. For pH, contact time, initial concentration and adsorbent dosage on the adsorption capacity of Cr (VI and optimization studies.

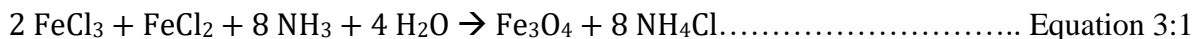
3.5. Preparation of adsorbent

3.5.1. Raw Zeolite preparation

- ⊗ Wash raw zeolite by distilled water.
- ⊗ The raw natural zeolite has dried in the oven at 80-100°C for a day (24 hours).
- ⊗ The prepared zeolite was kept in a closed plastic bag and labeled as Natural zeolite

3.5.2. Magnetic Nano particle preparation

The magnetic particles in a Ferro fluid were formed from crystal called magnetite, which has a formula Fe_3O_4 . The magnetite particles synthesized by mixing iron (II) and iron (III) ions with ammonia in the presence of water, to form the iron oxide by Schikorr's equation. (Gunn, 2015)



3.5.3. Magnetization of zeolite

A recoverable adsorbent of magnetized natural zeolite has prepared by co-precipitation (Yazid and Joon, 2019). Four adsorbents are prepared of having different MP fraction (25, 33.3, 50, and 75) % w/w on the adsorption capacity and recoverability has also studied. And choose the best adsorbent for removal of Cr (VI) from prepared adsorbent.

3.6. Characterization of Adsorbent

After the preparation of MZ adsorbents, the next step was characterizing it to know the details about the MZ adsorbents. Characterization of MZ adsorbents can tell if the specified materials recommended for adsorbent development or not. Hence, point of zero charge, surface area determination using surface area analyzer and Fourier Transform infrared spectroscopy analysis performed as characterization of adsorbent.

3.6.1. FTIR analysis adsorbent

FTIR analysis has performed to identify functional group of adsorbents. For FTIR analysis of the MZ prepared from natural zeolite, a small amount of powdered adsorbent sample was, mixed with dry KBr. After pressure applied, the sample scanned over a wavelength of 4,000 - 400/cm by attenuated total reflection FTIR and the results presented in form of graphs.

3.6.2. Surface characterizing adsorbent

The surface characters including pore diameters, surface area, and pore volume of the adsorbents prepared with various MP fractions characterized by BET mechanisms.

3.6.3. Point of zero charge determination adsorbent

The point of zero charge (PZC) has determined by the salt addition (drift) method. (Jiao *et al.*, 2017) NaCl solutions were prepared in 5 Erlenmeyer flasks. By using NaOH and HCl pH of each container adjusted to values of 2, 5, 7, 9 and 11. Then add 0.2 g of adsorbent material into the flask and keep it for shaking for 24 hrs. in an air tight condition at 200 rpm and 25°C. Finally, Samples were filtered and the final pH value was measured. The point of zero charge corresponded to the pH at which the curve crosses the line $pH_{final} = pH_{initial}$

3.6.4. Characterizing recoverability of adsorbent

The clarity of the filtrates separated from zeolite of various adsorbent magnetically studied qualitatively to correlate with the improvement in adsorbent recoverability. Quantitatively recoverability determined by measuring turbidity of the filtrates from which separated, higher turbidity indicates lower clarity of the filtrate, which shows the lower recoverability of the corresponding adsorbents

3.7. Experimental Design

In this study, four factors and five level central composite response surface experimental design (CCD) was used to optimize and investigate the influence of process variables such as Contact time, pH, adsorbent dosage and initial Concentration in the treatment of synthetic tannery discharge wastewater using adsorption by MZ. Process variables and their ranges were determined based on previous studies, which shown in Table 3:1.

Table 3:1. Ranges of Independent variables and their levels

Independent variable	Unit	Symbol	Coded levels				
			$-\alpha$	-1	0	+1	$+\alpha$
Adsorbent dosage	g/L	A	0.4	0.8	1.2	1.6	2.0
Contact time	Min	B	15	30	45	60	75
Initial concentration	mg/L	C	10	30	50	70	90
pH	g/L	D	1.5	3	4.5	6	7.5

After selection of process variables and their ranges, experiments were established based on CCD which consists a total of 30 experimental runs having sixteen factorials, eight axial and six central points were generated using central composite design (CCD) shown below in table 3:2.

Table 3 :2. DoE matrix layout values

Run	S/type	dosage(g/L)	time(min)	C _o (mg/l)	pH	R (%)
1	Center	1.2	45	50	4.5	
2	Axial	0.4	45	50	4.5	
3	Center	1.2	45	50	4.5	
4	Factorial	0.8	60	70	3	
5	Factorial	0.8	60	30	3	
6	Axial	1.2	45	90	4.5	
7	Center	1.2	45	50	4.5	
8	Factorial	1.6	30	30	3	
9	Axial	2	45	50	4.5	
10	Center	1.2	45	50	4.5	
11	Center	1.2	45	50	4.5	
12	Center	1.2	45	50	4.5	
13	Factorial	0.8	30	30	3	
14	Factorial	1.6	30	70	6	
15	Factorial	1.6	30	30	6	
16	Factorial	0.8	60	70	6	
17	Factorial	0.8	30	70	6	
18	Factorial	0.8	30	70	3	
19	Axial	1.2	45	10	4.5	
20	Factorial	1.6	60	30	3	
21	Axial	1.2	45	50	1.5	
22	Factorial	0.8	60	30	6	
23	Factorial	1.6	60	30	6	
24	Factorial	1.6	60	70	3	
25	Factorial	1.6	60	70	6	
26	Axial	1.2	15	50	4.5	
27	Axial	1.2	75	50	4.5	
28	Axial	1.2	45	50	7.5	
29	Factorial	0.8	30	30	6	
30	Factorial	1.6	30	70	3	

Total 30 runs were conducted by the same adsorbent for optimization purpose in the laboratory of environmental engineering, Jimma University

The experiments with different adsorbent dosage, contact time, initial concentration and pH employed simultaneously covering the spectrum of variables for the removal of chromium in CCD. The regression analysis was performed to estimate the response functions as a second order polynomial as shown in (Equation 3:2.) (Anderson *et al.*, 2017).

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4 \dots \dots \dots \text{Equation 3:2.}$$

Where, Y is the predicted response, X₁, X₂, X₃, X₄ are linear effects, X₁², X₂², X₃², X₄² are squared effects, X₁X₂, X₁X₃, X₁X₄, X₂X₃, X₂X₄, X₃X₄ are interaction effects and. β₀ is constant coefficient, β₁, β₂, β₃, β₄ are linear coefficients, β₁₁, β₂₂, β₃₃, β₄₄ are squared coefficients, and β₁₂, β₁₃, β₁₄, β₂₃, β₂₄, β₃₄ are interactive coefficients.

3.8. Batch Adsorption Process

Cr (VI) adsorption by MZ adsorbent conducted in batch experiment, following procedure: preparation of raw zeolite, magnetization by Co-precipitation and produce various adsorbent with different fraction of MP (25%, 33.3% ,50%, and 25%) w/w by changing the zeolite weights.

100 mL of Cr (VI) stock solution with concentration of 50 mg/L mixed with 15 mg of MZ for MZ₂₅ adsorbent. Then the mixture stayed under constant rate for 30 minutes. The recover adsorbent using magnetic bar and analyze filtrate by UV-vis Spectrophotometer to determine Cr (VI) concentration remain in the solution. The same procedure where used for different adsorbents of MZ. Then compare performance of adsorbents. From adsorbents, the best adsorbent where used for adsorption with various doses (0.2 g/L-2.0 g/l), solution pH (1.5-7.5), contact time (15–75 minutes) and initial Cr (VI) concentrations (10–90 mg/L). The pH value of the solution where adjusted by adding 0.10 N of NaOH to raise pH or 0.10 N HCl to lower the pH as desired that maintained with the corresponding buffer.

3.9. Adsorption isotherms

Equilibrium isotherms analyzed using the Langmuir and Freundlich, isotherms. By plotting the data into the equations for Langmuir and Freundlich models(Chen, 2015), n_f,b,q_{max} parameters would have obtained.

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \dots \dots \dots \text{Equation 3:3.}$$

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \dots \dots \dots \text{Equation 3:4.}$$

3.10. Kinetic parameters

Adsorption kinetic parameters were determined based on the data of the contact time variation by following equations for pseudo-first order and pseudo-second order. The parameters obtained will be adsorption capacity at equilibrium (q_e) and adsorption rate constant (k).

$$\log(q_t - q_e) = \log q_e - \left(\frac{k_1 t}{2.303}\right) \dots \dots \dots \text{Equation 3:5.}$$

$$\frac{t}{q_t} = \frac{1}{k_2 (q_e)^2} + \frac{1}{q_e * t} \dots \dots \dots \text{Equation 3:6.}$$

3.11. Data Analysis

After Adsorption process of each run, sample taken after treated carefully, then recover adsorbent using magnetic bar and analyze filtrate. Then removal efficiency was determined according to the standard methods for the Examination of Water and Wastewater (APHA, AWWA, 2017). The removal efficiency, R (%) was calculated using (Equation 3:7).

$$\% \text{ Removal } (R) = \frac{C_0 - C_e}{C_e} \times 100 \dots \dots \dots \text{Equation 3:7.}$$

Then the adsorption capacity labeled as Q_e (mg/g) has calculated using the following equation (Equation 3:8)(Chen, 2015).

$$Q_e = \left(\frac{C_0 - C_e}{m}\right)V \dots \dots \dots \text{Equation 3:8.}$$

Where, C_0 and C_e are the initial and final Cr (VI) concentrations (mg/L), V is the Cr (VI) solution volume (L) and m is the adsorbent dose (g).

The experimental values obtained by using equation 3:7. exported to DoE software version 13.0.5.0 to investigate and evaluate the experimental results obtained and eventually to establish optimum values of operating parameters that results desirable responses. The equations validated by the statistical test called ANOVA. The significance of each term in the equation is to estimate the goodness of fit in each case.

4. RESULT AND DISCUSSION

In this chapter the results of the study including, the adsorbent preparation and characterization, the mechanism and efficiency of chromium removal from synthetic tannery wastewater by prepared MZ adsorbent, effects of four studied variables (pH, initial concentration, time, and adsorbent dose) and adsorption isotherms were discussed with respect to literature in details.

Knowledge of the characteristics of natural zeolite is important. This reveals information on the nature of adsorbent, which related to removal efficiency of heavy metals ions from solution. In this study, different characterization where used to study adsorbent (natural zeolite and magnetic product samples) including, point of zero charge pzc, Fourier Transform Infrared (FTIR), surface area and recoverability of adsorbents.

4.1. Adsorbent Characteristics Analysis

4.1.1. Surface characters

Surface characteristic determined by the BET surface area, pore volume and pore size. This result shown in Table 4:1 indicates that natural zeolite was an excellent meso porous material. It exhibited a BET surface area was 21.21 m²/g and pore volume of 0.09 cm³/g.

The result shows that as result of magnetization, process start fills MP by increasing fraction in the zeolite pores, results in dropping the pore size observed. This is because of that increasing MP gives smaller size by hindering the pores Zeolite.

Table 4:1. Surface and pore properties of the adsorbents prepared

Adsorbent	S (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (Å)
NZ	21.21	0.09	186.7
MZ ₂₅	78.66	0.26	134.0
MZ _{33.3}	88.24	0.22	100.7
MZ ₅₀	77.68	0.14	73.9
MZ ₇₅	68.23	0.04	21.3

The improvement of the surface area indicates that magnetic particles also afford surface active into the adsorbents. Although, more magnetic loaded in the adsorbent contributes larger surface area extra addition possibly form aggregate with larger size that drops the surface area.

The increment of the pore volume of monolayer observed from NZ to magnetized adsorbents except for MZ₇₅ indicates that MP and NZ combined in to one and used as adsorbent. For instance, I observed as more fraction of MP loaded pore volume of adsorbent increased until saturated capacity reached, volume start to decrease beyond saturation. The diameter of pore is range of (2nm-50nm) which agree with zeolite is Mesoporous substance prove that it is a Nano porous material. The result agreed (Ramesh *et al.*, no date). Mesoporous materials are excellent host supports due to large, uniform pore diameters and a high surface area

4.1.2. Recoverability of adsorbents

Acyclic adsorption application relies on recoverability of adsorbent.so that adsorbent can operate in consecutive process with same performance. Since adsorbable component i.e. MZ and Cr (VI) physic-sorb process they attract weakly we can separate easily by magnetic. The regeneration of adsorbent affects original capacity of adsorption and clarity of solution.

Magnetically adsorbents separated from solutions. Figure 4:1 shows the adsorption ability of the adsorbents and turbidity of the filtrates resulted from the separation of each adsorbents. It takes to note that higher turbidity represents lower clarity of the filtrate; hence, it demonstrates the reduced recoverability of the corresponding adsorbent (Grobbelaar, 2009). The figure shows that increasing fraction of MP in the adsorbents, has improved the recoverability, however in divergence it causes the adsorption capacity slightly dropped.

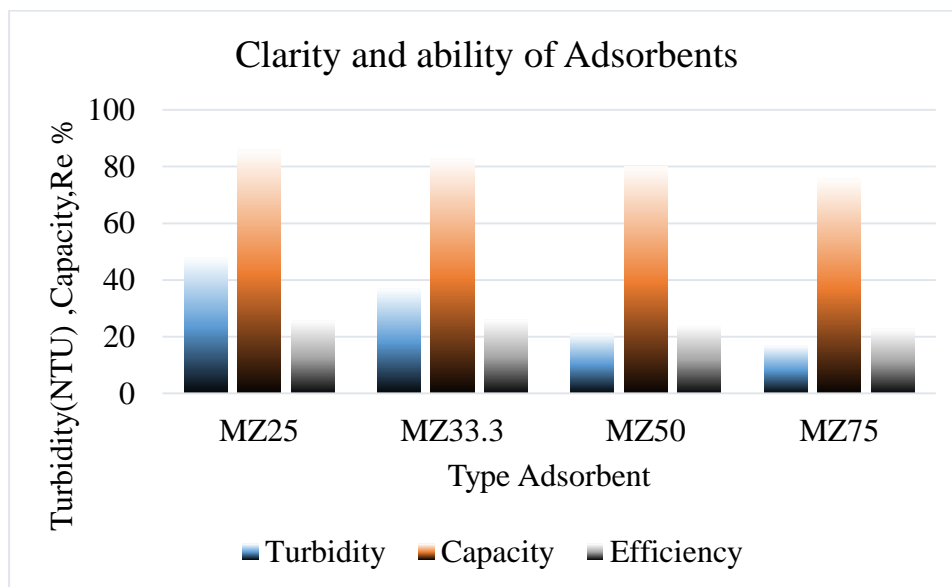


Figure 4.1: Clarity of filtrate and ability of Adsorbents

The presence of MP can contribute the magnetic property on the adsorbents, allowing them easier to recover magnetically. At the same time, MP also covers some part of the zeolite surface that reduced the adsorption active sites. It is clear that although MP can extent the surface area of the adsorbents, but it does not always enlarge the adsorption surface.

4.1.3. Point of zero charge determination

It is obvious; pH has a great importance in cation sorption because it influences chemical speciation of the metal in solution and on the ionization of chemically active sites on the sorbent. Thus, the net charge of sorbent surface might play a crucial role in sorption processes, and the characterization of protonation-deprotonating behavior of sorbent materials in aqueous media could be useful to explain sorption mechanism.

The point zero charge determines the surface charge of the sorbent at a given pH and its knowledge informs about the possible electrostatic interactions between sorbent and chemical species of metal. The intersection of the curve $\text{final pH} = f(\text{initial pH})$ (Neag *et al.*, 2020) with the bisector corresponds to the pH of adsorbents as shown in Figure 4:2 was equal to Pzc.

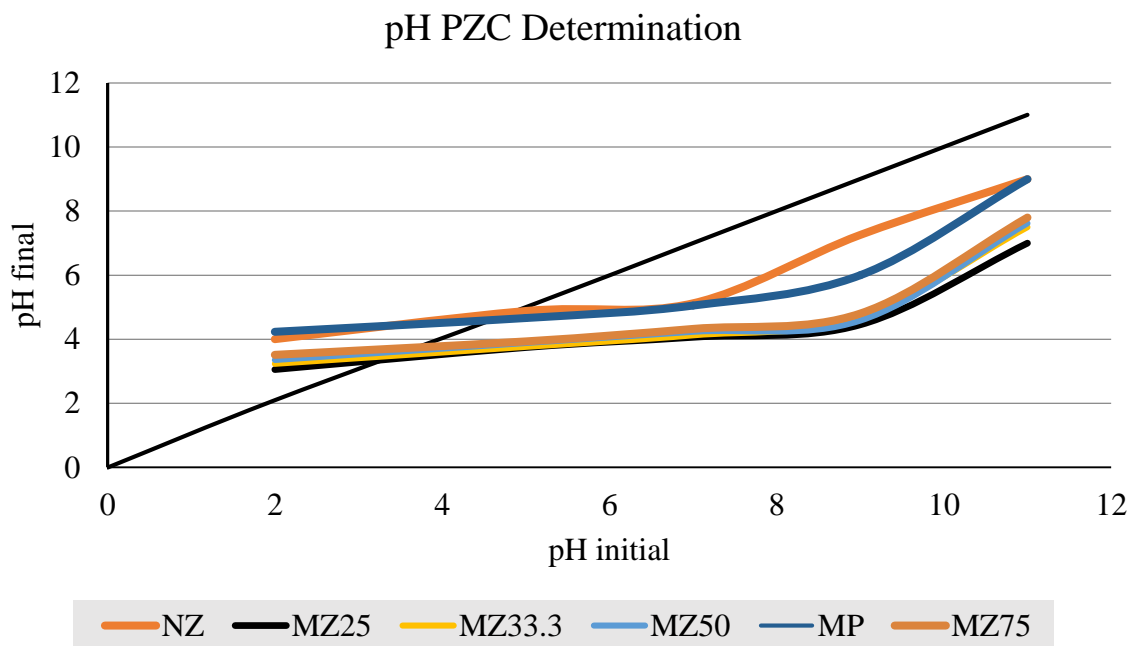


Figure 4:2. pH of zero charge of the Adsorbents

The uptake adsorption of the Cr (VI) by zeolite and magnetic zeolite can be explained by their point zero charge (pzc). Each adsorbent has its pzc. If the pH is higher than pzc, the net charge is

negative charged and could interact with metal positive species. If the measured pH of the solution system is lower than the pzc, the net charge of the surface is positive. Hence, positively charged surface ($\text{pH} < \text{pH}_{\text{pzc}}$) tends to repulse with cations in the solution, and lower metal adsorption on the surfaces. Therefore, at low pH, adsorptions of cations tend to be low.

The pzc of MZ is lower than that of MP and NZ, at the same pH solution above their pzc, the positive charges on the surface of magnetic zeolite would expected to be greater than natural zeolite (Václavíková *et al.*, 2009). Similar experiment using zeolite synthesized for the adsorption of Cr (VI) gave the optimum condition at pH close to 4 (Cr and Li, 2020) yields highest removal. Hence, In the subsequent investigations, experiments performed at pH solution value 3.5 of to avoid any possible hydroxide precipitation. (Cr and Li, 2020)

The MP, NZ, MZ₂₅, MZ_{33.3}, MZ₅₀ and MZ₇₅ used in this study have pzc values of 4.63, 4.9, 3.47, 3.50, 3.64, and 3.76, respectively as can be seen in Figure 4:2. The result indicates that Cr (VI) adsorption is favorable at pH value lower than pH_{pzc} , since, it occurred as anion in solution adsorption is favored at pH values lower than pH_{pzc} . This suggests that adsorption of Cr(VI) is highly favorable at the value of pH less than 4 and this might be attributed to strong electrostatic attraction between anion (HCrO_4^-) and protonated oxygen-containing functional groups (Si-O and Si-O-Al) present on the surface of zeolite. The result obtained here is in agreement with the findings of many researchers who reported higher adsorption of Cr (VI) at pH values 2–6. (Krishna and Kumar, 2017)

4.1.4. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra have recorded, to detect the interaction between MP with the zeolite structure that may happened, as shown in Figure 4:3. The spectra, it can illustrate various peaks of zeolite appear different of the wavenumbers.

Absorption band at 4000-3740 regions resent stretching bond of Si-OH. Band region of 3740-3610 stretching bond of Si-OH-Al. 3430-3410 cm^{-1} region represents stretching vibration of O-H bonds of water molecules in zeolites. This band is overlap with the stretching vibration of the O-H bonds of hydroxyl terminal group in zeolite. Absorption band at 3410-1638 cm^{-1} indicates the bending vibration of the H-O-H bond from water. Sharp and strong absorption band at 1638-1078 cm^{-1} correspond to O-Si-O and O-Al-O asymmetry stretching.

Table 4:2. Frequencies and respective functional groups present on the surface of MZ

Frequencies(Cm^{-1})	Bond	Functional group
4000-3740	Si-OH	framework of zeolite
3740-3610	Si-OH-Al	framework of zeolite
3430-3410	stretching vibration of O-H	Water, hydroxyl zeolite
3410-1638	bending vibration of the H-O-H	Water
1638-1078	O-Si-O and O-Al-O asymmetry stretching	tetrahedral framework of zeolite
Magnetic particle (Fe_3O_4)		
1420	O-H vibrations	MP
590	Fe-O vibrations	MP

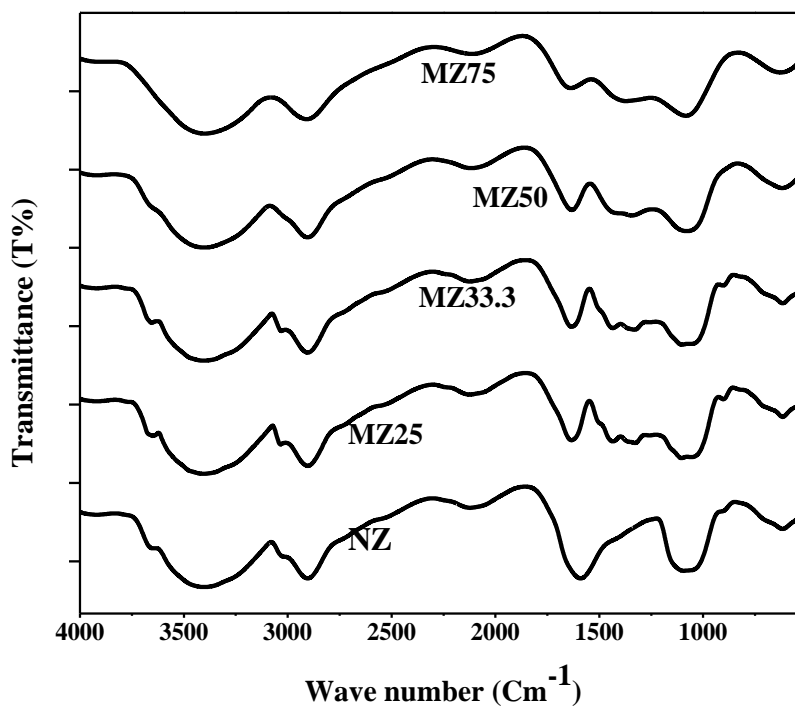


Figure 4:3. Fourier Transform Infrared Red spectra graph
 Furthermore, the absorption peaks of all MZ adsorbents prepared understood as combination peaks of zeolite and MP It suggested that MP particles have covered the zeolite structure. In the

spectra of MZ, adsorbent prepared, a new peak at around 1420 cm^{-1} is observed, this peak understood to be present provided by Fe-O-Si bond. It implies that in synthesizing tolerating Fe atoms of MP to attach with Si-O of the zeolite, indicating the successful coating of Magnetic particles on the zeolite surface.

4.2. Choosing adsorbent from different adsorbents

The primary requirements of adsorbents for economic and commercially attractive were adsorbent must have a large internal surface area; this surface area should be accessible through pores big enough to allow certain molecules passage during adsorption that is it should be highly selective. The adsorbent should be mechanically strong, enough to withstand bulk handling and vessel vibrations. The adsorbent should be easy to regenerate. There should not be any rapid exhausting (that is, loss of adsorptive capacity) of the adsorbent due to continual recycling(Li *et al.*, 2010).

The performance of MZ adsorbents which were produced in the laboratory having four different grades for each adsorbent depending on the fraction of MP used during this Preparation has been evaluated critically. The basis for the critical evaluation of the performance of the adsorbents is parametrical studies. It is interesting to note that the performance of each adsorbent under consideration appear to be comparable by their removal efficiency of Cr (VI) and recoverability after the process.

Adsorbents of MZ prepared by co-precipitation MZ_{33.3} possess better characters with respect to the surface characters in terms pore surface character compared to the other adsorbent prepared.

Cr (VI) removal may depend not only on the surface area and pore size distribution of the adsorbent but also on the specific adsorbate-adsorbent interactions that can be established. In my case, adsorption is due to specific interactions as well as to non-specific interactions, which still exist. The non-specific interactions will depend on the surface and solution pH and on the nature, amount and dispersion of metallic nanoparticles.

In recoverability comparing their turbidity, attend of adsorption as MP increase turbidity decrease which in turn solution was clear and higher recoverability increase with fraction of MP. But removal efficiency was nearly the same after MP fraction was 33.3%. Hence, I choose, MZ_{33.3} adsorbent for this study.

4.3. Optimization of the adsorption process

In order to obtain the maximum response that jointly satisfies all process conditions, optimization carried out using the Design Expert software under RSM. In numerical optimization, I chose the desired goal for each factor and response. The goal was to maximize responses only and set to an in range value factors. A low and a high level must provide for each parameter included. The goal seeking begins at a random starting point and proceeds up the steepest slope to a maximum. Starting from several points in the design space improves the chances of finding the best local maximum. In the optimization analysis, the goal criterion was set as in range values for the four independent variables, (A- adsorbent dosage, B-Contact time, C-Initial concentration and D-pH) and a dependent variable of removal efficiency for the adsorption of Cr (VI) ion as summarized in Table 4:3.

4.3.1. Models validation

The model validated by conducting a batch experiment under optimum operating conditions to compare the experimental values with predicted values under optimum operating condition.

Table 4:3. Validation of adsorption process variables under optimum conditions

Constraint name	Goal	Lower limit	Upper limit	Lower weight	Upper weight	Importance	
Adsorbent dose	In range	0.4	2	1	1	3	
Contact time	In range	15	75	1	1	3	
Initial concentration	In range	10	90	1	1	3	
pH	In range	1.5	7.5	1	1	3	
Removal efficiency	Maximize	38.88	94.88	1	1	3	
<i>Solution</i>							
Solution №	Dose	Contact time	Initial Conce.	pH	Y (%)	Desirability	Status
1	2	75	10	1.5	93.57	0.977	Selected

The predicted optimal values for the four variables obtained from the software were adsorbent dose = 2 mg/L, contact time = 75 min, initial concentration = 10 mg/L, and pH = 1.5 The model predicted that the maximum removal efficiency under these optimum conditions is 93.57% which is very close to the experimental result as shown in Table 4:4.

Table 4:4. Actual and predict value of response from experiment.

Run	S/type	dosage(g/L)	time(min)	Initial Concentration	pH	Removal efficiency (%)	
						Actual	predicted
1	Center	1.2	45	50	4.5	55.74	56.87
2	Axial	0.4	45	50	4.5	53.99	52.98
3	Center	1.2	45	50	4.5	54.24	56.87
4	Factorial	0.8	60	70	3	73.25	73.15
5	Factorial	0.8	60	30	3	76.66	77.43
6	Axial	1.2	45	90	4.5	55.28	55.61
7	Center	1.2	45	50	4.5	57.65	56.87
8	Factorial	1.6	30	30	3	73.23	71.64
9	Axial	2	45	50	4.5	55.13	57.85
10	Center	1.2	45	50	4.5	57.27	56.87
11	Center	1.2	45	50	4.5	55.36	56.87
12	Center	1.2	45	50	4.5	60.98	56.87
13	Factorial	0.8	30	30	3	65.87	64.91
14	Factorial	1.6	30	70	6	39.81	38.64
15	Factorial	1.6	30	30	6	57.92	56.72
16	Factorial	0.8	60	70	6	63.45	64.63
17	Factorial	0.8	30	70	6	49.91	49.91
18	Factorial	0.8	30	70	3	55.95	55.55
19	Axial	1.2	45	10	4.5	76.59	77.97
20	Factorial	1.6	60	30	3	94.88	93.57
21	Axial	1.2	45	50	1.5	87.28	88.99
22	Factorial	0.8	60	30	6	66.38	66.38
23	Factorial	1.6	60	30	6	75.76	75.76
24	Factorial	1.6	60	70	3	78.29	78.06
25	Factorial	1.6	60	70	6	63.12	62.77
26	Axial	1.2	15	50	4.5	38.88	41.43
27	Axial	1.2	75	50	4.5	78.91	78.07
28	Axial	1.2	45	50	7.5	65.55	65.55
29	Factorial	0.8	30	30	6	56.92	56.75
30	Factorial	1.6	30	70	3	52.35	51.04

The model summary statistics Tables 4:5 showed that the quadratic models of the response selected as suggested by the software because the additional terms were significant and the model was not aliased. The quadratic model for the response, Y is not aliased implying that the quadratic models could hire to describe the relationship between responses Y and the interacting factors.

Table 4:5. Model summary statistics

Source	Std. Dev.	R ²	Adjusted R ²	Predicted R ²	PRESS	Comment
Linear	6.96	0.7497	0.7096	0.6363	1758.06	
2FI	6.92	0.8120	0.7130	0.6729	1581.56	
Quadratic	2.01	0.9874	0.9757	0.9528	228.30	Suggested
Cubic	2.32	0.9922	0.9677	0.7058	*	Aliased

Table 4:5 showed that the quadratic model had a small standard deviation of 2.01 and high R² (0.9874) with predicted R² (0.9528) that is in reasonable agreement with adjusted R² (0.9677). The R² value of response was close to unity with smaller standard deviations indicating the suitability of the model in predicting the response. However, a large value of R² as posited by does not always imply that the regression model is a good one and such inference can only have made based on a similarly high value of adjusted R². For the regression model to be in good agreement, the adjusted R² and predicted R² should be within 20%. This requirement was satisfied in this study because the difference between the values of the adjusted R² and predicted R² for response was within 20%. This confirmed that the model for response is highly significant and indicated a good agreement between the experimental and predicted values of the removal efficiency.

Tables 4:6 showed that the adequate precisions of response were greater than 4.0 which implies that the model was in good agreement and highly significant. The Predicted R² of 0.9528 showed that the model was adequate and offer 63.22% variability in prediction removal efficiency. In addition, R², R²_{adj} and R²_{pred} having values of 0.9874, 0.9757 and 0.9528, respectively, indicated that the predicted model and experimental values are in good agreement. The CV value of 3.18% indicates a high precision and a good agreement of reliability with the experimental values. The obtained model may designate as reproducible concerning the value of CV (3.18).

Table 4:6. Fit Statistics for removal efficiency

Std. Dev.	2.01	R²	0.9874
Mean	63.22	Adjusted R²	0.9757
C.V. %	3.18	Predicted R²	0.9528
		Adeq. Precision	38.6060

The results in Table 4:6 showed that the quadratic model was selected as suggested by the software and Equation 4:1 provided the response surface model equation in its coded values.

4.3.3. Development of regression model equations using CCD

The quadratic response surface model determines the relationship between responses and independent parameters as follows.

$$Y=56.87+1.22A+9.16B-5.59C-5.86D+2.35AB-2.81AC-1.69AD+1.27BC-0.7206BD+0.6319CD - 0.3645A^2+0.7193B^2+2.48C^2+5.10D^2.....Equation 4:1.$$

Where,

- ✓ Y is the removal efficiency,
- ✓ A is Adsorbent dosage,
- ✓ B is the Contact time,
- ✓ C is the Initial Conc. Cr (VI), and D is the pH.

The negative values in response Y model equations indicated hostile effect and positive values favored the response of the process conditions. In the response Y Model Equation 4:1, the factors that have a positive effect on the removal efficiency of Cr (VI) are Constant(c), B, AB, BC, CD, B², C² and D². The factors that have a negative effect on the removal efficiency of Cr (VI) are C, D, AC, AD,BD,A². It concluded that from Equation 4:1 and Table 4:5 that the Cr (VI) removal percentage from Synthetic wastewater could be fitted well with the developed quadratic model. In Equation The terms with negative sign shows antagonistic effect, while the terms with positive sign show the synergistic impact on the Cr (VI) removal efficiency.

4.3.3. Statistical and graphical analysis

The model equation selected for removal efficiency (response Y) was further analyzed using ANOVA component of the software to validate the importance and the adequacy of the models. In Table 4:7, the model terms for responses have p-values less than 0.05 and F-values of 84.21.

Table 4:7. ANOVA for Quadratic model of removal efficiency

Source	Sum of square	df	Mean squares	F-Value	P-value	Remark
Model	4773.64	14	340.97	84.21	< 0.0001	Significant
A-Adsorbent dose	35.65	1	35.65	8.80	0.0096	Significant
B-Contact time	2014.65	1	2014.65	497.56	< 0.0001	Significant
C-Initial Concentration	749.40	1	749.40	185.08	< 0.0001	Significant
D- pH	824.50	1	824.50	203.63	< 0.0001	Significant
AB	88.60	1	88.60	21.88	0.0003	Significant
AC	126.28	1	126.28	31.19	< 0.0001	Significant
AD	45.80	1	45.80	11.31	0.0043	Significant
BC	25.88	1	25.88	6.39	0.0232	Significant
BD	8.31	1	8.31	2.05	0.1725	
CD	6.39	1	6.39	1.58	0.2283	
A ²	3.64	1	3.64	0.8999	0.3578	
B ²	14.19	1	14.19	3.50	0.0808	
C ²	168.60	1	168.60	41.64	< 0.0001	Significant
D ²	713.21	1	713.21	176.14	< 0.0001	Significant
Residual	60.74	15	4.05			
Lack of Fit	32.60	10	3.26	0.5794	0.7837	<i>not significant</i>
Pure Error	28.13	5	5.63			
Cor Total	4834.37	29				

The $p < 0.05$ implied that the models were highly significant and higher F-values indicated that the model terms have the most significant effect on the response function. The significant model terms in response surface quadratic model for removal efficiency response were found to be A,B, C,D, AB, AC, AD, BC and C², D². The model term that is most significant effect on the response is B with F-value of 497.56. The effect of the model terms is in the order B>D>C>D²>C²>AC>AB>AD>A>BC. It was observed that, the lack of fit F-value 0.5794 of response Y was not significant as the p-value was >0.05 indicating that the model was valid.

ANOVA diagnostic plots showing the correlation between actual experimental values and predicted values guide us to justify the model competence. Figure 4.4a displays the scattering amid the data points for predicted against actual values of the Cr (VI) obtained by the model, and the diagonal line presented satisfactory agreement, showed a minimal divergence of points from the diagonal indicating that the model equations can used to adequate represent the interaction of

the four factors. For high-quality agreement with actual value, the predicted Cr (VI) removal percentage should lie near the $Y = X$ line.

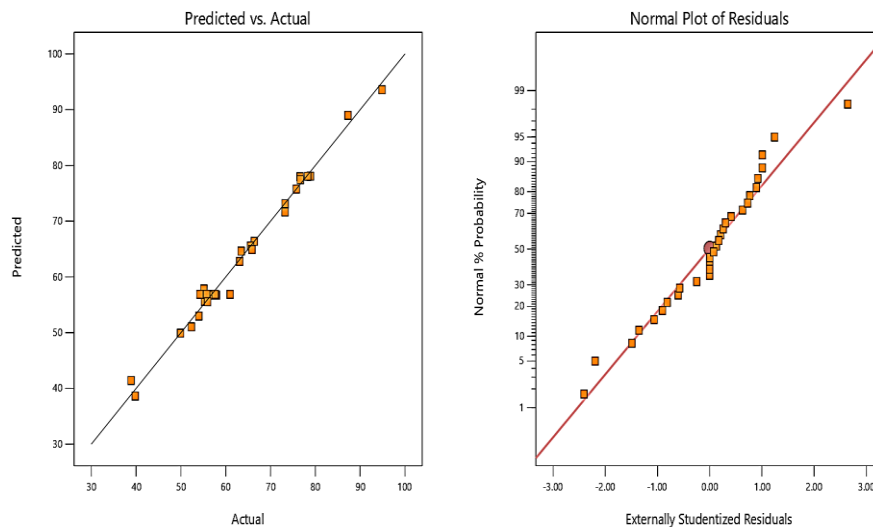


Figure 4:4 a) Predicted versus actual values of response b) Normal probability plot of residual.

Figure 4:4b., shows the normal probability plot indicates that the residuals observed value more of following to normal distribution, this indicates the experiment points in the plots fit a straight line this show that the quadratic polynomial model satisfies the assumptions of analysis of variance and it shows a reasonably straight line.

4.4. Effect of experimental parameters on adsorption of Cr (VI)

4.4.1. Effect of Adsorbent dose on adsorption

As shown in Figure 4:5A. The study on the effect of the amount of adsorbent on the process of adsorption were carried out by varying adsorbent dose from 0.8 to 1.6 g in the 50mg/l concentration of Cr(VI) solution of pH 3 and 45 min contact time. The removal efficiency of Cr (VI) becomes increase from 55.25 to 57.75 with increase in the dosage 0.8 g to 1.6 g of adsorbent. This may possibly due to the availability of more adsorption sites for the metal ions. However, additional increase in dose of MZ leads to decrease in the removal efficiency. This is due to saturation of the active sites on the adsorbent surface and combination resulting from high Cr (VI) concentrations. The maximum removal efficiency achieved with an adsorbent dosage of 1.6 g/L of solution. This finding is also consistent with other studies.

4.4.2. Effect of contact time on adsorption

As shown in Figure 4:5. B. The removal efficiency of MZ increases with increasing the contact time. However, it starts to fall down for an increase in time beyond the equilibrium time. This is because the extent of adsorption increased rapidly at the early stages due to the presence of large number of vacant active sites of an adsorbent. However, after a certain time, most sites may possibly occupy and the remaining sites may be difficult to occupy because of repulsive forces between Cr (VI) ions on the solid and in the solution. The maximum removal efficiency achieved at the equilibrium point after 60 min. This finding is also in agreement with other studies conducted on zeolite adsorbent.

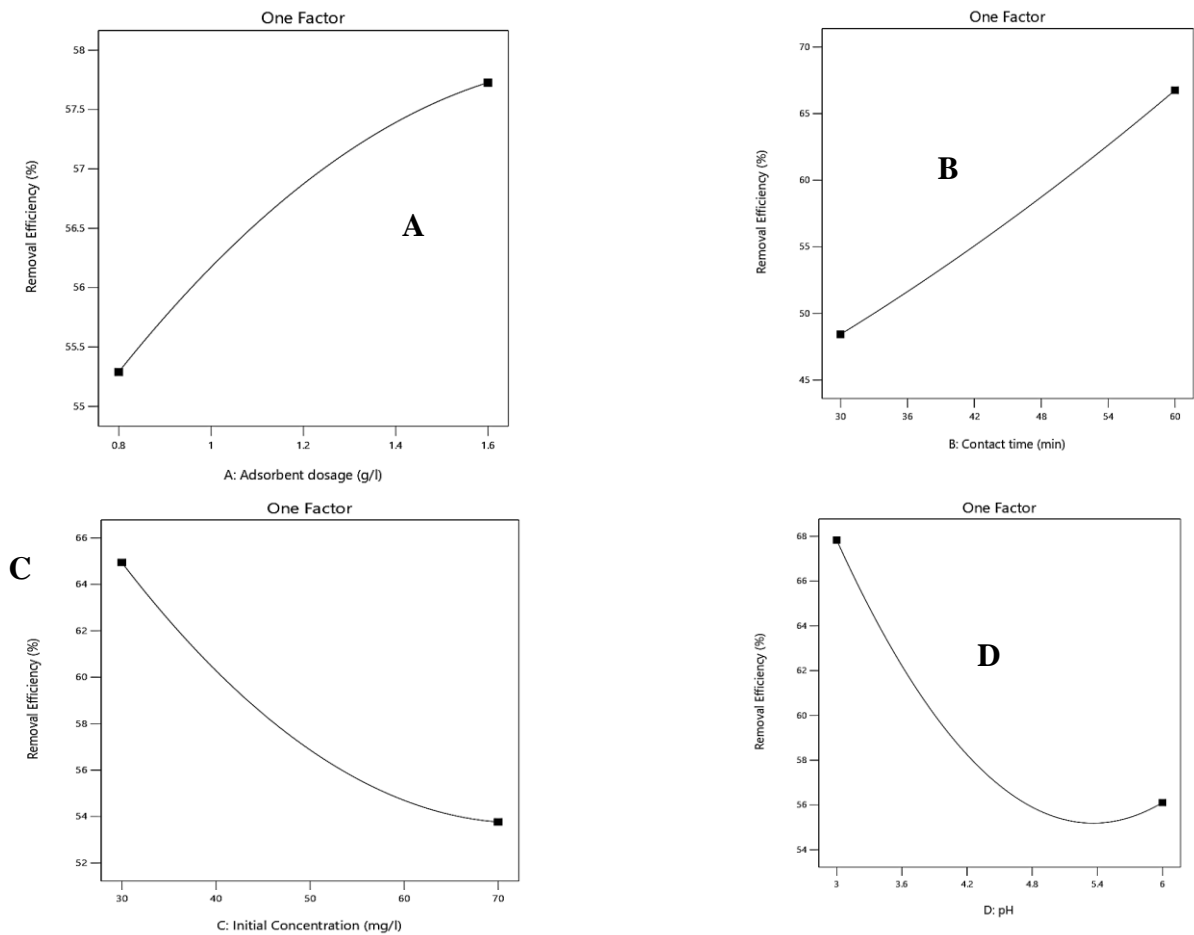


Figure: 4:5. Effect of parameters on adsorption of Cr (VI) on MZ adsorbent A) Adsorbent dosage B) Contact time C) initial Concentration D) pH

4.4.3. Effect of initial concentration of Cr (VI) on adsorption

As shown in Figure 4:5C. The as initial concentration increases, its removal efficiency becomes decrease. At higher concentration, the available sites of adsorption to initial concentration of metals become less and the removal efficiency come to be decrease. The maximum removal efficiency achieved at 30 mg/L initial concentration of the ions. This result is also in agreement with other studies conducted on different adsorbent.

4.4.4. Effect of solution pH on adsorption

The current study depicted that uptake of Cr (VI) decreases with increasing pH as shown in Figure 4:5D. This might be due to at lower pH, number of OH⁻ groups becomes decrease, and the net positive charge of MZ becomes increase. This leads to high electrostatic force for the adsorption of chromate anions (acid chromate (HCrO₄⁻), chromate (CrO₄²⁻), and dichromate (Cr₂O₇²⁻) ions) on the surface of MZ. Maximum Cr (VI) removal efficiency obtained at pH 3, which is in mark with the actual pH of most industrial effluents such as tannery and electroplating effluent. This depicts that MZ can be used as the best choice for removal of Cr (VI) from most industrial effluents. However, for treatment of effluents with higher pH, earlier to adsorption, correction of the pH by acid would be required. The finding was in close agreement with other studies.

4.5. Combined effects of the factors on adsorption of Cr (VI) on MZ

By making other variables constant, the effect of interaction of two variables at a time on the responses presented below using 3D response surface. Optimized condition for Cr(VI) removal and validation experiments. An experiment conducted to evaluate the optimization result under optimum conditions predicted by the model. The actual experimental removal efficiency of MZ at the optimum condition was in close agreement with model predicted value. Therefore, the optimization conditions validated.

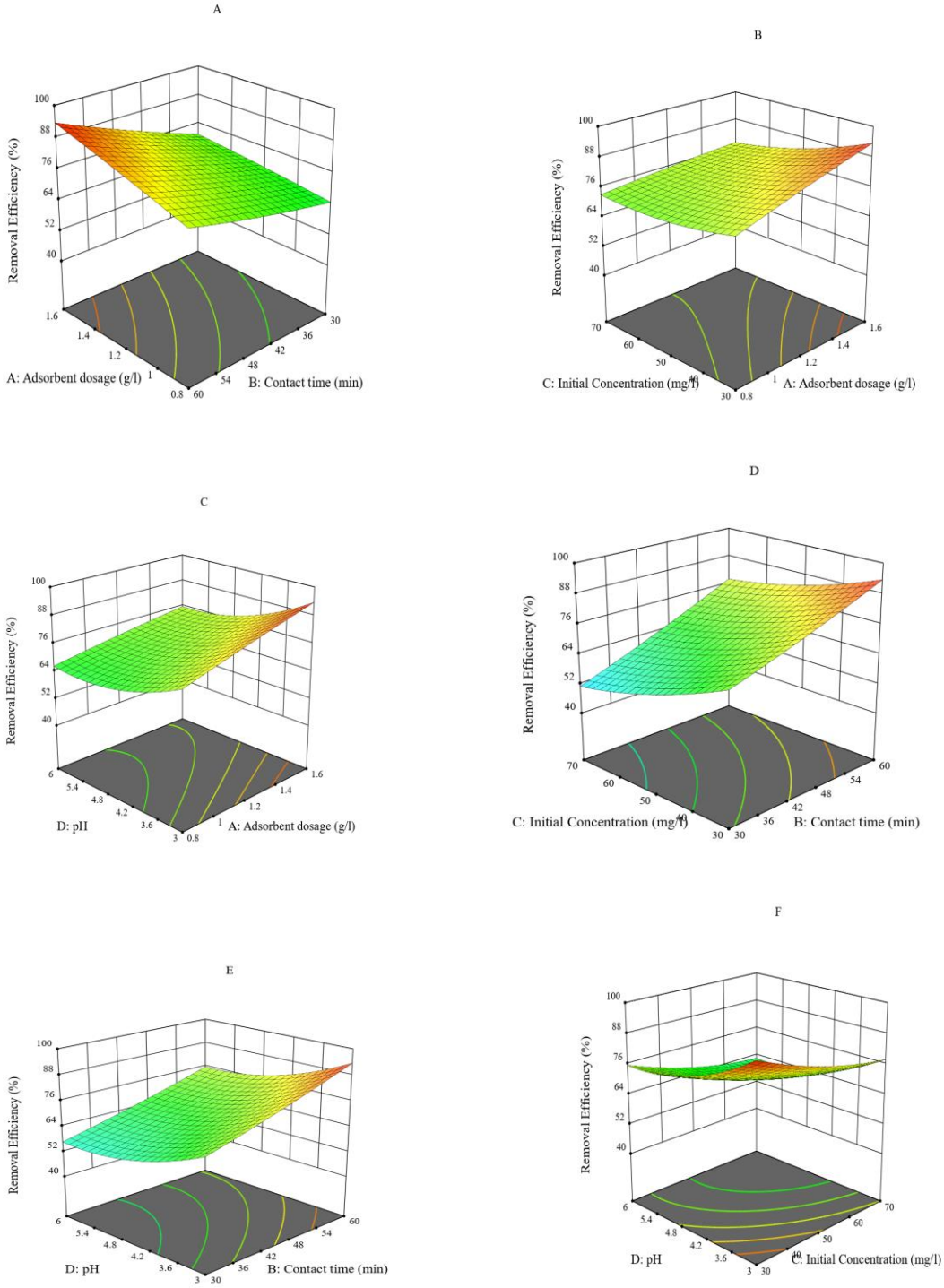


Figure 4:6. Response surface 3D plots for the CCD of interaction effect parameters for Cr (VI) adsorption: (A) effect of adsorbent dose and contact time, (B) effect of adsorbent dose and initial concentration, (C) effect of adsorbent dose and pH and (D) effect of contact time and initial concentration (E) effect of contact time and pH (F) effect of initial concentration and pH

The interaction effect of process variables for percentage removal of Cr (VI) ions using MZ were visualized through 3D plots of three dimensional views of response surface as a function of two independent variables, maintaining all other variables at fixed or different level. These plots can be helpful in understanding both the main and interaction effects of the independent variables on the response variable.

A. The Interaction Effect of Adsorbent Dosage and Contact Time(AB)

Figure 4:6A shows mutual interaction effect of adsorbent dose and contact time on the removal efficiency of MZ. From the surface response plot, it shows that the removal efficiency increases with adsorbent dose 62.43 % chromium (VI) removal was obtained at sorbent dosage 0.8 g/l, and contact time 60 min at fixed PH 4.5 But, removal increased up to 69.95 % at sorbent dosage increased to 1.6 g/l, and 30 % chromium (VI) removal was obtained at sorbent dosage 0.8 g/l, and contact time 30 min at fixed PH 4.5 But, removal increased up to 47.95 % at sorbent dosage increased to 1.6 g/l, The increase in removal percentage of chromium due to increase in adsorbent dose, this increases the availability of more surface area.

As stated from coded equation of the response variable, the combined effect of adsorbent dose and contact time (AB) affects the removal efficiency positively with the coefficient of +2.35 (Equation 4:1). It also revealed that the maximum removal efficiency attained at an adsorbent dose of 1.6 g/L and 60 min contact time. From the figures, as contact time increase at lower adsorbent dosage gives positive effects on the efficiency of chromium removal and decreases in efficiency at a higher dose with lower contact time.

B. The Interaction Effect of adsorbent dose and initial concentration(AC)

Combined interaction of concentration initial with adsorbent dosage on removal efficiency of MZ shown in Figure 4:6B. From the plots, it elucidated that the removal efficiency increases with decrease in the initial Cr (VI) concentration from 70 to 30 mg/L and increase in adsorbent dose from 0.8 to 1.6 g/L. From the surface response plot, it shows that the removal efficiency decrease with initial concentration of Cr (VI) 70 % chromium (VI) removal was obtained at initial concentration 30 mg/l, and contact time 30 min at fixed PH 4.5, contact time 45 min but, removal decrease to 54 % at initial concentration increased to 70 mg/l.

As stated from coded equation of the response, the combined effect of initial Cr(VI) concentration and adsorbent dose (AC) affect the removal efficiency negatively with the coefficient of - 2.81 (Equation 4:1). It also has a significant effect on removal efficiency of MZ with p value of less

than 0.001 (Table 4:7). The maximum removal efficiency attained at initial Cr (VI) concentration from 30 mg/L and adsorbent dose of 1.6 g/L.

C. The interaction effect of adsorbent dosage and pH (AD)

3D plot graph showing predicted the response of chromium (VI) ion removal efficiency as a function of adsorbent dosage and pH were shown in Figure 4:6C. The maximum percentage removal of Cr (VI) ion using MZ was obtained at lower pH and higher adsorbent dosage. The graph shows that the maximum adsorption (70 %) occurs under acidic conditions, pH 3 and adsorbent dose of 1.6 g/l. increasing the solution pH from 3 to 6, decreasing removal to 55 % for Cr (VI). This may be due to the surface positive oxygen-containing functional groups of the MZ adsorbent carried the oxyanions (negatively charged) of Cr (VI) ions by electrostatic force of attraction. At higher pH, the increased negative charges on the adsorbent surface decreased the attraction of oxyanions of Cr (VI) on the adsorbent.

As stated from coded equation of the response variable, the combined effect of pH and adsorbent dose (AD) affects the removal efficiency negatively with the coefficient of - 1.69 (Equation 4:1). The maximum adsorption of Cr (VI) ion attained at pH 3 and dose of 1.6 g/L.

D. The Interaction Effect of contact time and initial concentration (BC)

3D plot graph showing predicted the response of chromium (VI) ion removal efficiency as a function of initial concentration and contact time were shown in Figure 4:6D, The figure revealed that as the contact time increases from 30 to 60 min, the removal efficiency becomes increased and becomes decreased for extended time. The graph shows that the maximum adsorption (72 %) occurs at 30 mg/l initial concentration and contact time of 30 min. increasing initial concentration 30 to 70, decreasing removal to 65 % for Cr (VI).

As stated from coded equation of the response variable, the combined effect of initial ion concentration and contact time (BC) affects the removal efficiency positively with the coefficient of + 1.27 (Equation 4:1). This result supported by the ANOVA result, which showed that the interaction of initial concentration and contact time has significant effect on the removal efficiency. Hence, the interaction between contact time and initial metal concentration has a significant effect on the removal efficiency of MZ.

E. The Interaction Effect of pH and Contact Time (BD)

3D plot graph showing predicted the response of chromium (VI) ion removal efficiency as a function of solution pH and contact time were shown in Figure 4:6E. The graph illustrated that, as contact time increase to the first 60 min removal efficiency chromium increases, and reach peak value beyond that removal efficiency decreases slowly. Also, as pH value decrease from 6 to around 3 the chromium removal efficiency increases, this indicates pH value of solution strongly affect the site of dissociation of the MZ surface and solution chemistry of the heavy metals. General, when contact time increase at lower of pH and when PH of the solution increases at lower contact time have negative effects on the efficiency of chromium(VI) ion removal using MZ. As stated from coded equation of the response variable, the combined effect of contact time and pH (BD) affects the removal efficiency negatively with the coefficient of -0.7206 (Equation 4:1). The maximum removal efficiency attained at pH 3 and contact time of 60 min.

F. The Interaction Effect of initial concentration and pH. (CD)

3D plot graph showing predicted the response of chromium (VI) ion removal efficiency as a function of initial concentration and pH were shown in Figure 4:6F. The graph illustrated that, the removal efficiency gets increase with decrease in pH. The removal efficiency also becomes decrease with initial concentration.

From the surface response plot, 76.869 % chromium (VI) removal was obtained PH 3, and initial concentration 30 mg/l but, removal decreased up to 51.708 % at PH increased to.6, and 70 mg/l initial concentration. Decrease in removal percentage of chromium due to increase in initial concentration and pH, this combined effect. As stated from coded equation of the response variable, the combined effect of initial concentration and pH (CD) affect the removal efficiency positively with the coefficient of $+0.6319$ (Equation 4:1). The maximum removal efficiency at all the studied concentrations takes place at pH 3 and at initial concentration of 30 mg/L.

4.6. Optimum point by CCD design

Optimization of the response using Stat-Ease Design Expert Software version 13.0.5.0 and the operating condition with the highest desirability considered as selected by the software. Experimental condition with the highest desirability selected. Confirmed to maximize the removal efficiency of Cr(VI) in terms of the lowest allowable values of the experimental parameters to obtain a reasonably specific optimum zone. As shown in Figure 4:7 optimum operating conditions for the adsorption of Cr (VI) using magnetic zeolite were; A- adsorbent dosage=1.6g/L, B-Contact

time=60 min, C-Initial concentration=30 mg/L, D-pH=3 and with the desirability of 0.977 after looking for 100 solutions to optimize operating conditions for Cr (VI) adsorption. The removal efficiency Cr (VI) under this operating condition was found to be 93.572%.

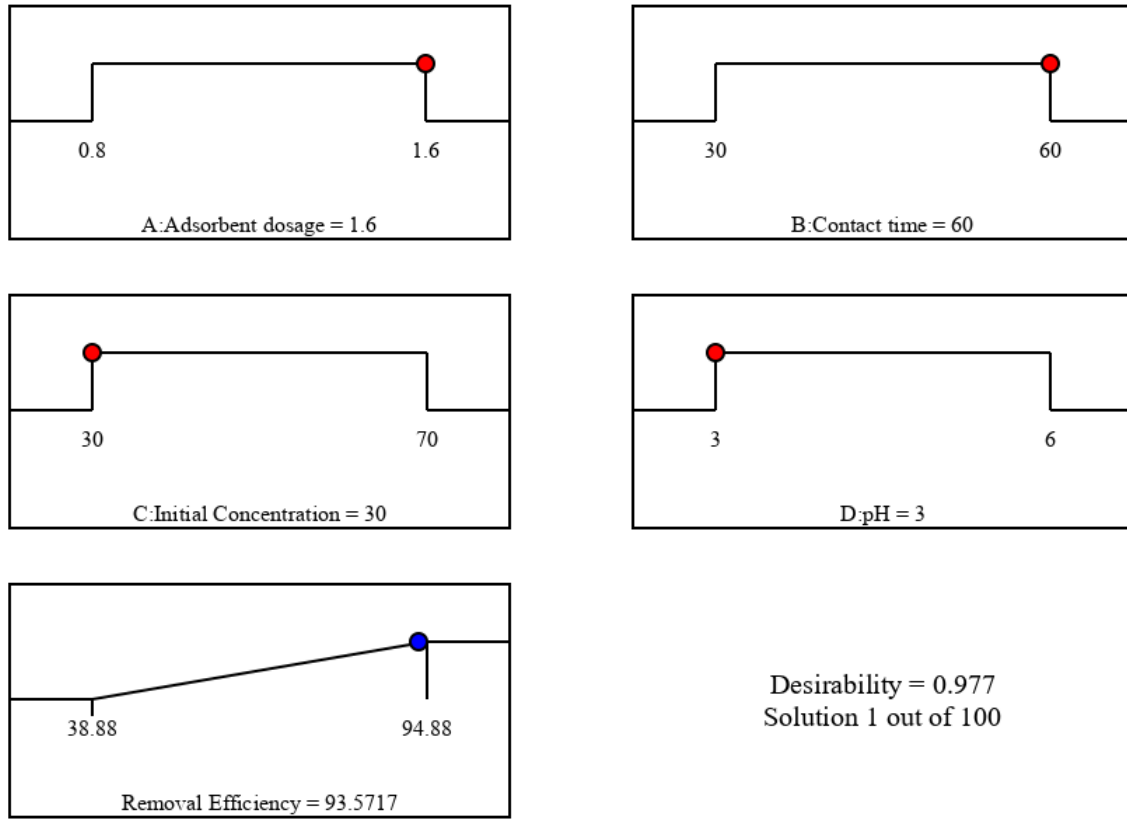


Figure 4:7. Optimum points by ramp graph

Table 4:8. Comparison of optimum process variables and removal efficiency using experimental and software predictions

Optimization	Optimum process variables				Optimum removal efficiency (%)
	Adsorbent dose (%)	Contact time (Min)	Initial concentration (mg/L)	pH	
Experimental	1.6	60	30	3	94.88
Software prediction	2	75	10	1.5	93.57

4.7. Adsorption isotherm studies

The adsorption isotherm model approached based on the data of the initial concentration. By plotting, the data into the equations for Langmuir and Freundlich models, some parameters could have obtained, as displayed in Figure 4:8. In Langmuir isotherm model, q_{\max} (mg /g) is the Langmuir monolayer adsorption capacity and b (L/ mg) is the Langmuir adsorption intensity constant as the ratio of the adsorption rate to the desorption rate, indicating the solid surface affinity and ability.

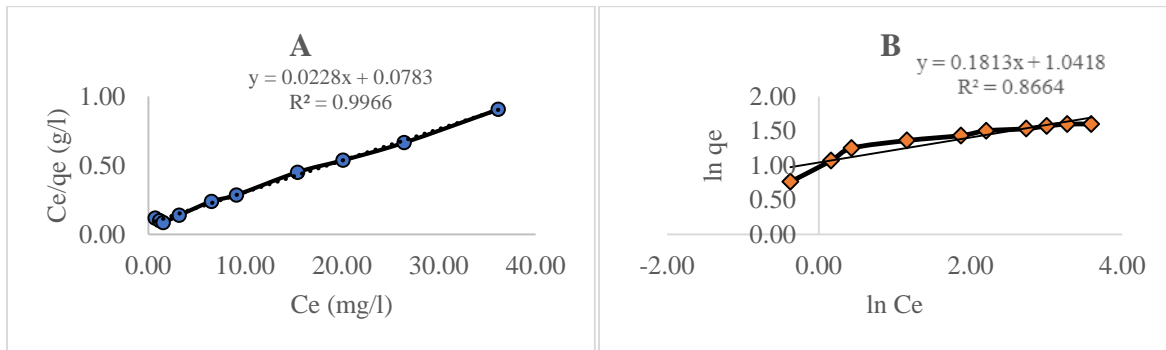


Figure 4:8. Adsorption isotherms a) Langmuir model graph b) Freundlich model graph

Meanwhile in Freundlich isotherm model, K_F (mg/g) is the Freundlich isotherm constant representing the adsorption capacity and n_F is the adsorption intensity, reflecting the degree of difficulty for adsorption. When n exceeds 2 but no more than 10, the adsorption process is easy to proceed. Comparatively, the ability for adsorption will be too weak when n is less than 0.5.

Table 4:9: The adsorption isotherm

Isotherm Langmuir			Isotherm Freundlich		
q_{\max} (mg/g)	B (L/mg)	R^2	K_F (mg/g)	n_F	R^2
43.859	0.29	0.9966	2.83	5.52	0.8664

Table 4:9, investigations the correlation of the Langmuir model of the Cr (VI) adsorption is $R^2=0.9966$, confirming that the adsorption follows the Langmuir isotherm. It suggests the monolayer adsorbed Cr (VI) ion formed on the surface of the adsorbent. The adsorption capacity of Cr (VI) is 43.859 mg/g. The same finding also obtained and reported by other scholars’

Separation factor or equilibrium parameter (R_L)

$$R_L = \frac{1}{1 + bC_0} = \frac{1}{1 + (0.29 \times 30)} = \frac{1}{9.7} = 0.103$$

As R_L is less than 1, the present data satisfies for favorable adsorption as per Langmuir isotherm condition $0 < R_L < 1$

Table: 4:10. Comparison of maximum Adsorption capacity of magnetic zeolite with other adsorbents

No	Adsorbents	q_e (mg/g)	References
1	paper mill sludge AC	30.21	(Gorzin and Bahri Rasht Abadi, 2018)
2	Natural zeolite	30.45	(Álvarez, Guerrón and Montero Calderón, 2021)
3	Natural zeolite clinoptilolite	10.42	(Jor <i>et al.</i> , 2017)
4	Synthetic zeolite/ Amine-Functionalized Zeolite	12.2	(Nasanjargal <i>et al.</i> , 2021)
5	Zeolite NaX	6.414	(Pandey, Sharma and Sambhi, 2010a)
6	Magnetic zeolite	43.859	In this study

4.8. Adsorption kinetic studies

Adsorption kinetic parameters were determined based on the data of the contact time variation by following equations for pseudo-first order and pseudo-second order. The parameters obtained were adsorption capacity at equilibrium (q_e) and adsorption rate constant (k) that were presented in figure 4:9.

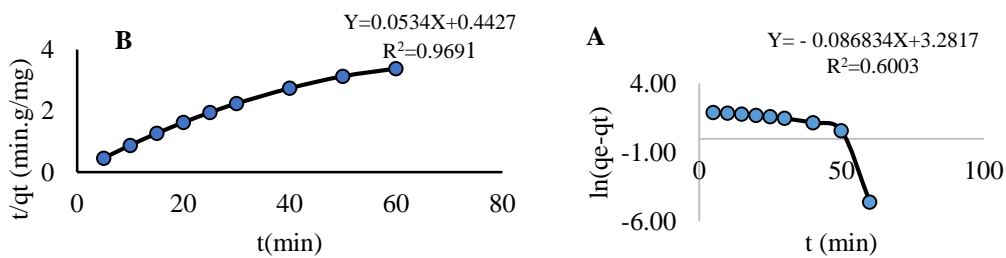


Figure 4:9. Adsorption Kinetics graph a) pseudo first Order b) Pseudo Second order model graph

Table 4:11. The adsorption kinetic parameters

Pseudo first order Lagergren			Pseudo second order Ho		
q_e (mg/g)	K_1 (min ⁻¹)	R^2	q_e (mg/g)	K_2 (g.mg ⁻¹ . min ⁻¹)	R^2
0.916	3.28	0.6003	18.73	6.441×10^{-3}	0.969

It shows that the adsorption kinetics of Cr (VI) ions well fits with the pseudo second-order model as indicated by R^2 (correlation coefficient) as much as 0.999. Some studies found same results. Pseudo second-order model represents that the rate-controlling step for the adsorption involves chemisorption by covalent forces or ion exchange between the adsorbent with Cr (VI) ions. The adsorption capacity is found to be 18.73 mg/g with the adsorption rate constant of $6.441 \times 10^{-3} \text{g mg}^{-1} \text{min}^{-1}$ that show good ability of the adsorbent and promising potential to industry application.

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

Removal of Cr (VI) form of tannery wastewater were possible using MZ at batch adsorption study. The sorbent prepared by co precipitation techniques using Fe_3O_4 -zeolite MZ_{33.3} appears to be a promising sorbent for the removal of Cr (VI) ion from aqueous solution with respect to the surface characters and recoverability compared to the other adsorbent prepared.

The adsorption kinetics studies indicated at equilibrium in the adsorption of Cr (VI) ion has reached in 60 min of contact between the zeolite- Fe_3O_4 and the solution. It has found that the kinetics of the adsorption on MZ followed by pseudo-second-order. Langmuir isotherms showed a better fit to the process ($R^2= 0.9966$) with adsorption capacity of 43.859 mg.g^{-1} . The adsorption of Cr (VI) ions on the adsorbent has well fitted to pseudo second-order model with reaction rate constant of $6.44 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$.

The FTIR analysis describes that the adsorbent natural contain functional groups such as hydroxyl (O-H-O), Fe-O, O-Si-O/O-Al-O groups. Based on the graph of FTIR spectra, those functional groups participate on chromium binding on to surface of zeolite.

Regression results showed that A,B, C,D, AB, AC, AD, BC and C^2 , D^2 have a statistically significant impact on the process of removing Cr (VI), It was observed that, the lack of fit of response was not significant as the p-value was >0.05 indicating that the model was valid ANOVA the analysis it had been concluded that quadratic model is the best model to describe the relationship between response and input variables. The Experimental values and the predicted values are in perfect match with R^2 value of 0.967.

The optimal adsorption of chromium (VI) was obtained as (A- adsorbent dosage, B-Contact time, C-Initial concentration and D-pH) and these were found to be 1.6 g/L, 60 min, 30 mg/L,3 and, respectively, resulting in 93.572% of maximum predicted adsorption of chromium (VI) with the desirability of 0.977. The results clearly demonstrated that RSM with a central composite design was one of the reliable methods to model and optimize the operational variables.

Generally, the results showed that MZ_{33.3} has high possibility and efficiency in removing Cr (VI) ion in wastewater. It is an alternate adsorbent and poses as an environmental friendly adsorbent to society and environment.

5.2 Recommendations

Based on this study, the MZ have a high potential to remove chromium ion from tannery wastewater, therefore, the following direction of work is recommended in the MZ for the removal of chromium (VI) ion from tannery effluent.

Based on the present study, some recommendations for future work stated. First, I recommended that alternative techniques such as sonolysis, Sogel and impregnation be used in the MZ synthesis. A lot of work has done in this area and has successfully produced high quality as-magnetic zeolite. This will cut down time considerably as conventional adsorbent. Increasing the reaction temperatures would enhance the equilibrium point. Working at different temperatures will help to understand the process more. The use of alternate methods other than the batch method is highly recommended. Columns or beds could use to measure the efficiency of zeolites and produce a water of higher quality. In the batch method, a long contact time may be required to reach equilibrium. Finally, I suggested that to determine the maximum contact time when equilibrium has achieved I should increase the time of exposure.

In this study only the effect of adsorbent dosage, pH, initial concentration and contact time were analyzed and concluded on the efficiency of chromium (VI) ion uptake, but further research recommended to the concluded effect of temperature and shaker speed of on adsorption efficiency. Correspondingly, synthetic wastewater has used to evaluate the adsorption test process. However, I recommended, using real tannery wastewater for the more exactness of the studies because synthetic wastewater does not contain other interacting constituent's ions which can compete with adsorbent sites.

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APPENDIXES

Appendix A: Calculation of Potassium Dichromate Requirement

I prepared 1000 mg/l standard chromium solution for that I needed from chromium salt (Potassium dichromate is $K_2 Cr_2 O_7$)

Molecular wt. of chromium = 52 mg/mol

Molecular wt. of potassium dichromate ($K_2Cr_2O_7$) = $(2*39) + (2*52) + (7*16) = 78 + 104 + 112 = 294$ g/mole,

$$103.992 \frac{\text{mg}}{\text{mol}} \text{Cr is present in } 294.185 \text{ K}_2 \text{Cr}_2 \text{O}_7$$

$$1 \text{g Cr is present in } \frac{294.185}{103.992} = 2.82 \text{ g of K}_2\text{Cr}_2\text{O}_7$$

In 1000 mg/L, it came out to be 2828.91 mg/L = 2.828 g/L

Finally, I have to dissolve 2.828 g in 1 L water to get 1000 mg/l solution

Appendix B: Dilution of Cr (VI) Stock Solution from 1000 mg/l

After preparing standard solution, I get samples of required concentration from this solution by using dilution law, $C_1V_1 = C_2V_2$ and V_2 is fixed 50 ml flask volume then find V_1

- ✗ Initial concentration of Cr(VI) 10 mg/l $C_1V_1 = C_2V_2 = 1000 \times V_1 = 10 \times 50$ then, $V_1 = 0.5$ ml
- ✗ Initial concentration of Cr(VI) 20 mg/l $C_1V_1 = C_2V_2 = 1000 \times V_1 = 20 \times 50$ then, $V_1 = 1.0$ ml
- ✗ Initial concentration of Cr(VI) 30 mg/l $C_1V_1 = C_2V_2 = 1000 \times V_1 = 30 \times 50$ then, $V_1 = 1.5$ ml
- ✗ initial concentration of Cr(VI) 40 mg/l $C_1V_1 = C_2V_2 = 1000 \times V_1 = 40 \times 50$ then, $V_1 = 2.0$ ml
- ✗ Initial concentration of Cr(VI) 50 mg/l $C_1V_1 = C_2V_2 = 1000 \times V_1 = 50 \times 50$ then, $V_1 = 2.5$ ml
- ✗ initial concentration of Cr(VI) 60 mg/l $C_1V_1 = C_2V_2 = 1000 \times V_1 = 60 \times 50$ then, $V_1 = 3.0$ ml
- ✗ initial concentration of Cr(VI) 70 mg/l $C_1V_1 = C_2V_2 = 1000 \times V_1 = 70 \times 50$ then, $V_1 = 3.5$ ml
- ✗ initial concentration of Cr(VI) 80 mg/l $C_1V_1 = C_2V_2 = 1000 \times V_1 = 80 \times 50$ then, $V_1 = 4.0$ ml
- ✗ initial concentration of Cr(VI) 90 mg/l $C_1V_1 = C_2V_2 = 1000 \times V_1 = 90 \times 50$ then, $V_1 = 4.5$ ml

After preparing the all samples, I went for AAS. I measured before adsorption absorbance of each required initial concentration sample. Now I added 1.5 gram MZ to each sample, left for 30 min. Adsorption of chromium had taken place, and again I measured absorbance of sample after adsorption by Magnetic zeolite adsorbent by AAS.

Appendix C: Experimental layout of Design Expert 13.0.5.3 and lab result data

Run	S/type	dosage(g/L)	time(min)	C _o (mg/l)	pH	C _f .(mg/L)	R (%)	Q(mg/g)
1	Center	1.2	45	50	4.5	22.13	55.74	17.42
2	Axial	0.4	45	50	4.5	23.01	53.99	16.87
3	Center	1.2	45	50	4.5	22.88	54.24	16.95
4	Factorial	0.8	60	70	3	18.73	73.25	32.05
5	Factorial	0.8	60	30	3	7.00	76.66	14.37
6	Axial	1.2	45	90	4.5	40.25	55.28	31.10
7	Center	1.2	45	50	4.5	21.18	57.65	18.02
8	Factorial	1.6	30	30	3	8.03	73.23	13.73
9	Axial	2	45	50	4.5	22.44	55.13	17.23
10	Center	1.2	45	50	4.5	21.37	57.27	17.90
11	Center	1.2	45	50	4.5	22.32	55.36	17.30
12	Center	1.2	45	50	4.5	19.51	60.98	19.06
13	Factorial	0.8	30	30	3	10.24	65.87	12.35
14	Factorial	1.6	30	70	6	42.13	39.81	17.42
15	Factorial	1.6	30	30	6	12.62	57.92	10.86
16	Factorial	0.8	60	70	6	25.59	63.45	27.76
17	Factorial	0.8	30	70	6	35.06	49.91	21.84
18	Factorial	0.8	30	70	3	30.84	55.95	24.48
19	Axial	1.2	45	10	4.5	2.34	76.59	4.79
20	Factorial	1.6	60	30	3	1.54	94.88	17.79
21	Axial	1.2	45	50	1.5	6.36	87.28	27.28
22	Factorial	0.8	60	30	6	10.09	66.38	12.45
23	Factorial	1.6	60	30	6	7.27	75.76	14.21
24	Factorial	1.6	60	70	3	15.20	78.29	34.25
25	Factorial	1.6	60	70	6	25.82	63.12	27.62
26	Axial	1.2	15	50	4.5	30.56	38.88	12.15
27	Axial	1.2	75	50	4.5	10.55	78.91	24.66
28	Axial	1.2	45	50	7.5	17.23	65.55	20.48
29	Factorial	0.8	30	30	6	12.92	56.92	10.67
30	Factorial	1.6	30	70	3	33.36	52.35	22.90

Appendix D: Data for adsorption isotherm models

C_o	C_e	q_e	$1/C_e$	$1/q_e$	$\ln C_e$	$\ln q_e$	C_e/q_e
10.00	0.69	5.82	1.45	0.17	-0.37	0.76	0.12
20.00	1.18	11.77	0.85	0.08	0.16	1.07	0.10
30.00	1.54	17.79	0.65	0.06	0.43	1.25	0.09
40.00	3.20	23.00	0.31	0.04	1.16	1.36	0.14
50.00	6.51	27.18	0.15	0.04	1.87	1.43	0.24
60.00	9.08	31.82	0.11	0.03	2.21	1.50	0.29
70.00	15.39	34.13	0.06	0.03	2.73	1.53	0.45
80.00	20.11	37.43	0.05	0.03	3.00	1.57	0.54
90.00	26.41	39.75	0.04	0.03	3.27	1.60	0.66
100.00	36.14	39.91	0.03	0.03	3.59	1.60	0.91

Appendix E: Data for adsorption kinetics models

Run	Time(min)	C_o (mg/l)	C_f (mg/l)	q_t	$\ln(q_e - q_t)$	t/q_t
1.	5	30	12.258	11.09	1.90	0.45
2.	10	30	11.634	11.48	1.84	0.87
3.	15	30	10.947	11.91	1.77	1.26
4.	20	30	10.1964	12.38	1.69	1.62
5.	25	30	9.384	12.89	1.59	1.94
6.	30	30	8.508	13.43	1.47	2.23
7.	40	30	6.567	14.65	1.15	2.73
8.	50	30	4.374	16.02	0.58	3.12
9.	60	30	1.536	17.79	-4.61	3.37

Appendix F: Turbidity data

Type of Adsorbent	Turbidity(NTU)	Capacity(mg/mg)
MZ25	48	86
MZ33.3	41	83
MZ50	21	80
MZ75	17	76

Appendix G: mass of zeolite & fraction of MP used for formulation of composite

Fraction of MP	Mass of MP	75%	50%	33.3%	25%
	<i>total mass composite</i>				
Mass of zeolite		0.5g.	1.5g.	3.0g.	4.5g.
Adsorbent type		MZ75	MZ50	MZ33.3	MZ25

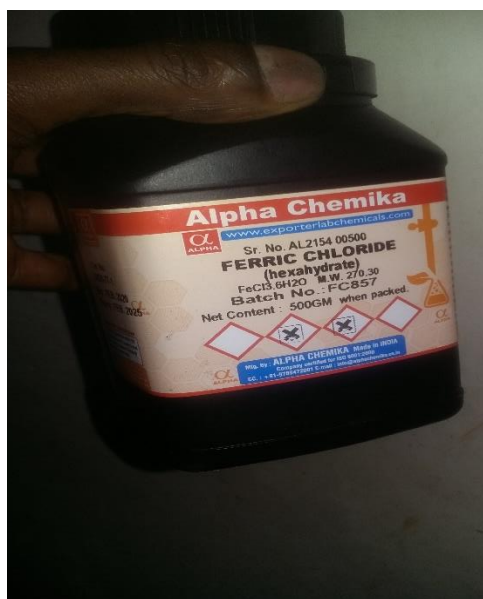
Appendix H: important figures captured in laboratory



Potassium Dichromate powder



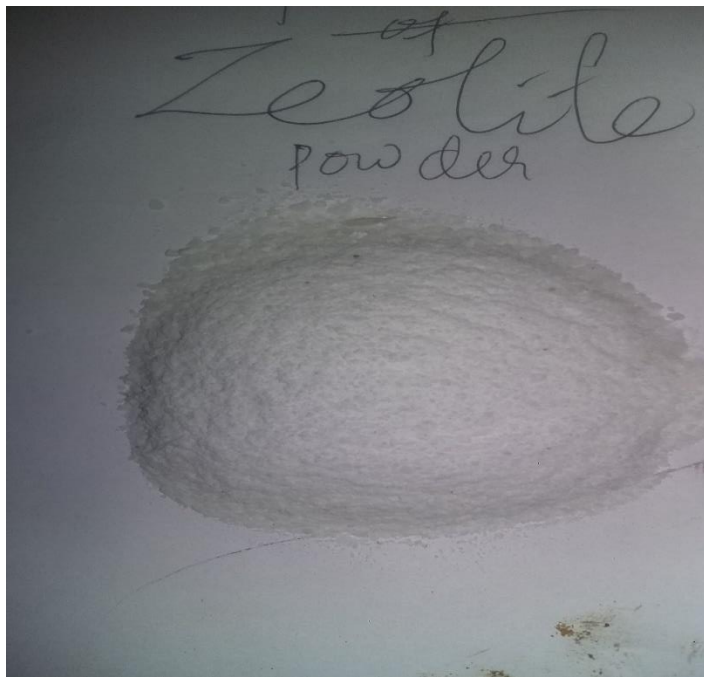
Standard solution of potassium dichromate



Ferric Chloride hexa-hydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$)



Ferros Chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$)



Zeolite powder





Some Apparatus used

