Addis Ababa University
Addis Ababa Institute of Technology
School of Chemical and Bio Engineering

Chromium Removal from Tannery Wastewater using Calcinated Eggshells as an Adsorbent: A Case study of Ethiopian Tannery Share Company, Ethiopia.

By: Berihu G/cherkos

A Thesis

Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemical Engineering (Environmental Engineering Stream)

Advisor: Dr. Ing.Berhanu Assefa

Addis Ababa University

Addis Ababa, Ethiopia

July 2019

ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIOENGINEERING

Chromium Removal from Tannery Wastewater using Calcinated Eggshells as an Adsorbent: A Case study of Ethiopian Tannery Share Company, Ethiopia.

A thesis Submitted to the Research and Graduate School of Addis Ababa University, Addis Ababa Institute of Technology, School of Chemical and Bioengineering in partial fulfillment of the requirements for the attainment of the Degree of Masters of Science in Chemical Engineering under Environmental Engineering Stream.

By: Berihu G/cherkos

Approved by Board of Examiners

Examiners name:	**Signature**
----------------------	-------------------------
School Director (Graduate Program Coordinator**)**	
Dr. Ing.Berhanu Assefa	-------------------------
Advisor	
Dr. Shegaw A.	--------------------------
Internal Examiner	
Prof.Dr.Ing. Belay Weldeyes	--------------------------
External examiner	

DECLARATION

I, the undersigned, declare that this thesis entitled "Chromium Removal from Tannery waste water using Calcinated Eggshells as an Adsorbent: A Case study of Ethiopian Tannery Share Company, Ethiopia" is my original work, and has not been presented by any other person for an award of a degree in this or any other University, and that all resources of materials used for this thesis have been duly acknowledged.

Name: Berihu G/cherkos

Signature -----------------------------

Date of submission July, 2019

This thesis has been submitted to the University with my approval as the University Advisor.

Name Dr. Ing.Berhanu Assefa
(Advisor)

Signature ----------------------------

ACKNOWLEDGEMENTS

- First, I would like to thank my almighty God for helping me to complete this research paper and to reach to stage in my life after passing difficulties.
- Great Thanks go to my able and sincere adviser Dr. Ing.Berhanu Assefa for his valuable guidance during this research paper by giving critical comments and advices.
- My deepest thanks and gratitude also go to my family especially My Aunt Mana Weldu and her Family who light the path of my life for their love, financial support and encouragement.
- I would like to say thanks to all the technical staff members of School of Chemical and Bioengineering, especially environmental engineering laboratory staff members.
- I extend my gratitude to my class mates and my friends.
- I am also grateful to Addis Ababa University, Department of Chemistry, especially to Dr. Negash and Dr. Yonas for helping me in the analysis of samples.
- Last, but not least, appreciation also goes to Ethiopian Tannery Share Company, especially Tesfaye under quality control Department of Ethiopian Tannery Share Company for his supporting me during sample collection.

Table of Contents

List of Tables

List of figure

List of Acronyms

AAS	Atomic absorption spectrophotometer
APHA	American Public Health Association
ANOVA	Analysis of variance
ASTM	American society for testing and materials
BOD	Biological oxygen demand
CCD	Central composite design
COD	Chemical oxygen demand
Co	Initial metal concentration (mg/L)
Ce	Concentration of the sorbate at equilibrium (mg/L),
EEPA	Ethiopian Environmental Protection Authority
ETSC	Ethiopian Tannery Share Company
FTIR	Fourier transform infrared radiation
JCPDS	Joint Committee on Powder Diffraction Standards.
K_f	Freundlich adsorption capacity (mg/g)
K_L	Langmuir equilibrium constant (L/mg).
K_1	Pseudo first order rate constant
K_2	Pseudo second order rate constant
Ppm	parts per million
MESP	Modified eggshell powder
RESP	Raw eggshell powder
TS	Total solids
TSS	Total Suspended Solids
TDS	Total dissolved solids
XRD	X- ray diffraction
WW	waste water

Abstract

Discharge of untreated chromium containing tannery wastewater into the environment poses a serious environmental and health problem. Finding an environmentally safe and cost effective method which is efficient enough to meet the regulatory standards of industrial wastewater discharge presents unique challenges. There is need for environmentally friendly and cost effective methods for their removal. The present study investigated the adsorptive removal of chromium ions from Ethiopian tannery share company site using thermally modified chicken eggshells because it is high removal capacity, low cost and easy accessibility. Characterization of the adsorbent such as proximate analysis, surface charge, Fourier transform infrared radiation spectroscopy, surface area and X- ray diffraction was done prior to bio sorption process. Thermally modified eggshell was assessed in batch mode adsorption experiment for percentage chromium removal and milligrams per gram chromium uptake as a function of contact time, pH, and dose of the adsorbent and initial concentration. The effect of factors such as one factor effect and interaction effects were investigated by central composite design (CCD). The maximum percent removal was obtained 99.505 % at optimum pH =7, adsorbent dose=1g/100ml, contact time 120min and 80mg/L of initial chromium ion concentration. Sorption kinetics of chromium adsorption by Thermally modified eggshell was predicted reliably using a pseudo-first order, pseudo-second order and intra particle diffusion model. The kinetic adsorption data well fitted to pseudo-second order. Equilibrium uptakes were evaluated using Langmuir, Freundlich and Temkin adsorption isotherm models. The equilibrium data well fitted into Langmuir isotherm. The study demonstrated the efficacy of Thermally modified chicken eggshells and presents it as a viable low-cost adsorbent for bioremediation.

Keywords Chromium, Calcinated eggshell, Adsorption isotherm, Adsorption kinetics.

1. Introduction

1.1 Background

Although rapid industrial expansion in Ethiopia is viewed as an indicator of economic progress, they are greatly associated with environmental degradation, particularly due to the discharge of untreated or partially treated wastewater. Industrial expansion coupled with a weak regulatory mechanism in the country has led to widespread degradation of environmental resources. Due to low profit margin, many industries failed to afford investment costs in pollution remediation equipment and technologies(EEPA, 1997a). Those who have better capital are not willing to install efficient treatment technologies, due to lack of governmental control and weak implementation to environmental policies.

Leather tanning has been ranked as one of the most polluting sector in Ethiopia due to the high growth rate and discharge of untreated wastewater to the environment(EEPA, 2003).Tanning is the chemical process that converts animal hides and skin into leather and related products. The transformation of hides into leather is usually done by means of tanning agents and the process generates highly turbid, colored and foul smelling wastewater. The major components of the effluent include sulfide, chromium, volatile organic compounds, large quantities of solid waste, suspended solids like animal hair and trimmings. For every kilogram of hides processed, 30 liters of effluent is generated. The various components present in the effluent affect human beings, agriculture and livestock besides causing severe ailments to the tannery workers such as eye diseases, skin irritations, kidney failure and gastrointestinal problems (Midha & Dey, 2008).

At present there are more than thirty one tanning industries in Ethiopia, operating fully(LIDI, 2013). Eleven of these tanning industries are found around Modjo town on the shore of the Modjo River(LIDI, 2012). Only a few of the industries in Ethiopia have the treatment facilities and can treat their wastewaters to any degree, while most of them discharge their wastewater into nearby water bodies and open land without any form of treatment(EEPA, 2003, Seyoum Leta,2004).

The untreated release of tannery effluents containing high COD, BOD levels, trivalent chromium, sulfides, sodium chloride, organics and other toxic ingredients, to the natural water bodies effect flora and fauna of the ecosystem and increases the health risk of human beings. It is in the interest of tanneries to produce as much tanned leather as possible, to the lowest possible cost, avoiding paying added costs for the reduction of the effects of pollution, which will increase proportionally to the commercial success of the tannery, while it is unacceptable for the surrounding communities. Postponing the solution of this problem will bring serious problems to the management of the environment, up to the extreme consequence of the impossibility to live in the area(Favazzi, 2003).

Heavy metal pollution can affect all environment but its effects are most long lasting in soils because of the relatively strong adsorption of many metals onto the humid and clay colloids in soils. Unlike organic pollutants, which will ultimately be decomposed, metals will remain as metal atoms or ion, although their separation may change with time as the organic molecules binding them decompose or soil conditions change(Trivedi and Goel, 1984). All metals are most soluble and bio-available at low pH and therefore, toxicity problems are likely to be more severe in acid environments. Therefore, chromium is one of the heavy metal highly affected the environment.

A number of methods are available to remove Cr (III) and Cr (VI) from aqueous solutions.

The most important of these technologies include; chemical precipitation, filtration, ion-exchange, electrolysis, lime coagulation, solvent extraction, reverse osmosis and electrocoagulation. However, all these technologies have their inherent advantages and limitations in application. Most of the methods suffer from some drawbacks such as incomplete chromium removal, low selectivity, high reagent and energy requirement, high capital and operational cost and generation of toxic sludge or other waste product that require careful disposal has made it imperative for a cost effective treatment method (Rao and Datta, 1987).

In the present investigation, to estimate the amount of chromium ions present in its aqueous solutions before and after treatment and the removal of chromium from wastewater using calcinated eggshell as an adsorbent is attempted. Though many conventional adsorbents are used for the effective removal of heavy chromium ions, calcinated egg shell has been chosen as adsorbents as they are thrown as kitchen waste materials from hotels, restaurants, bakery and from the hatchery of the poultry farms with an aim to use waste/ pollutant material as adsorbent. The present work is also aimed at fixing the optimal conditions such as adsorbent amount, initial concentration, pH and equilibrium time (for batch mode technique) for effective removal of chromium.

1.2 Problem Statement

Discharge of untreated or partially treated chromium containing tannery wastewater from ETSC to the water bodies pose greater health risks to the downstream users and ecological degradation in water bodies. Many people in the Rift Valley basin could face shortages of clean water and many of them are depending on Lake and river water for a variety of purposes such as drinking, fishing, livestock watering, irrigation, and recreation. Extensive use of chromium in leather tanning can result in release of chromium containing effluents to the environment. Chromium exists as two stable oxidation states, Cr(III) and Cr(VI). Cr(III), which is often used in tanning of leather, is considered as an essential element for living organisms when it is below 2mg/L but can be toxic in large doses. By contrast, Cr(VI) is highly toxic, mutagenic and potentially carcinogenic to living organisms. Accumulation of Cr(VI) in aqueous waste streams is therefore of great concern. Chromium carcinogenicity to humans and other living organisms has promulgated extensive research on its treatment technologies with varying levels of success; generally, the most efficient methods come with a significantly higher cost burden(Kimbrough, Cohen et al.1999)
These showed that the presence of higher concentration of chromium in the Ethiopian Tannery Share Company effluents affects the nearby water body communities of plants and animals. The effect also may further extend to the soil and human beings. Therefore, it is urgently needed to develop cost effective and efficient treatment technology, by increasing research interest by using alternative low cost adsorbent and effective removal of chromium from waste water. Adsorption processes have received significant attention due to several reasons, especially for those chromium ions that cannot be removed efficiently by other technique. Hence, it is expedient to device or seeks alternative methods of removing chromium ions from tannery wastewaters by using locally available and cheap adsorbent. To this effect, the research examines potential of calcinated waste eggshell to be prepared as adsorbent to remove Cr(III) and Cr(VI).

1.3 Objectives

1.3.1 General Objective

The general objective of this work was to remove chromium from tannery waste water using Calcinated eggshell as an Adsorbent

1.3.2 Specific objectives

- ➢ To prepare and characterize locally available calcinated chicken eggshell adsorbent
- ➢ To study isotherm of the adsorption process using different models and optimize the effect of pH, contact time, initial Chromium concentration and adsorbent dose on adsorption efficiency of the adsorbent in adsorbing chromium

1.4 Significance of the study

So far various wastewater treatment techniques have been used to remove heavy metals from industrial wastewater. Wastewater treatment through adsorption is one treatment technique used. Different adsorbent has been used to remove chromium from wastewater. But those adsorbent which have high removal capacity, low cost and easy accessibility are no question in being a choice for industrial wastewater treatment process. This research is intended to use low cost adsorbent called waste eggshell material for removal of chromium. Eggshell which is a byproduct of chicken egg processing industries and fast foods can be easily available without any charge. Knowing its chrome removal capacity and its application can be beneficial, because:

- ✓ It's a low cost adsorbent which can be easily prepared from materials that can be collected without charge.
- ✓ Its application in industrial wastewater treatment can be a choice and at the same time
- ✓ reduce its accumulation in the environment, because the eggshell is simply discharged into the nearby environment or landfill from restrunts and different food processing industries from which sample of eggshell in these study has been taken.
- ✓ Re-usability of these by product is a n environmental friendly approach of waste management.

2. Literature review

2.1 Previous Studies for chromium Removal using different adsorbent

- **Saw dust**

Saw dust was investigated as a low cost adsorbent for removal of Cr (VI) from tannery industries. The experimental results demonstrate that the sawdust adsorbent has a significant capacity for adsorption of Cr (VI) from wastewater streams. The maximum adsorption of Cr (VI) on sawdust was obtained at pH 1. The equilibrium time obtained was 105 min for Cr (VI) adsorption on sawdust(Papita Das Saha, Apurba Dey, 2012).

- **Coconut shell**

The use of wheat shell was examined as a potential adsorbent for Cr (VI) removal from aqueous solution (Papita Das Saha, Apurba Dey, 2012). The experimental results showed that the adsorption process is pH dependent and have maximum removal 97.4% at pH less than 3 at 35^{o}c.

- **Commercial coffee waste**

Commercial coffee waste was investigated for the removal of Cr (VI) and Cu (II) metal from aqueous solution. The experimental results revealed that for the formaldehyde treated commercial coffee waste at pH 2, the percentage Cr (VI) removal was 5% and for untreated commercial coffee waste it was 4%. However, increasing the pH from pH 2 to 5 increased the adsorption capacity to 62% for the formaldehyde treated waste. After pH 5 the percent removal stays constant (Kyzas, 2012).

- **Algal biomass**

Green micro algal isolate, Chlorella Miniata was used for biosorption and bioreduction of Cr (VI) from aqueous solutions(Han X, Wong YS, 2007) . The experimental results showed that, at initial pH of 1.0 and biomass dose of 2g/L, nearly 98% Cr(VI) was removed within 58 hours while increase the pH to 4 resulted in decrease of the removal capacity to 10%. However, at pH 2 with 1g/L ,2g/L and 5g/L of biomass dose, the Cr (VI) removal percentages obtained were 60%, 85% and 98%respectively with respective equilibrium time of 240, 215 and 150 hours.

- **Eggshell**

Mashangwa (2016) investigated the removal of zinc, lead, copper and nickel ions from synthetic aqueous solutions using chicken eggshells. Process parameters were evaluated and the optimum conditions obtained were pH 7, adsorbent dose of 7 g and contact time of 360 minutes at 100ppm metal ions. Under these conditions the percentage adsorptions were; 97% for lead, 95% for copper, 94% for nickel and 80% for zinc.

Table 2. 1:Adsorption capacity of Cr using various natural adsorbents

Adsorbent	Max. Adsorbent capacity (mg/g)	pH	Initial Concentration (mg/L)	Percent Removal efficiency	Reference
Coconut coir	8.9964	6	100	< 81.999%	(Shrivastava & Gupta, 2015)
Coconut shell	16.300998	2	100	81.999%	
Rice Husk	12.6226	2	100	< 81.999%	
Sugar Cane Bagasse	12.8760	6	100	< 81.99%	
Tulsi Branches	8.3908	2	100	< 81.999%	
Tulsi Leaf	4.6680	2	25	23.340%	
Fly ash	10.4208	6	100	< 81.999%	
Sawdust bio char	8.5	6-7	6.5	99%	(Gunatilake, 2016)
Rice straw bio char	5.5	6-7	6.5	87%	
Calcinated eggshell					This study

2.2 Gaps in the Literature

Literature review indicates that different forms of biomass can be used for the removal of chromium pollutants in the industrial effluents. Investigation has been carried out to evaluate the performance of easily available adsorbent for removal of chromium from waste water. Undoubtedly, such low-cost adsorbents offer a lot of promising benefits for their commercial use in the future. However, only few researches were done on biosortpion studies using eggshell as bio adsorbent. Initial concentration effects on biosorption process have been insuffiently discussed. Interaction effects that could occur among process variables were neglected. Removal efficiency does not fit the permissible discharge limit for chromium total (Gunatilake, 2016; Shrivastava & Gupta, 2015).

2.3 Solution for the gab in literature

The current research was conducted with the main objective of filling the identified gaps. The search for new technologies involving the removal of toxic chromium from wastewaters has directed attention to natural biomass. The use of calcinated eggshell as a bio adsorbent has a lot of merits over other bio adsorbents. It is low coast, easily available and non-degradable by microorganism. The purpose of calcination is to increase the porosity of the surface. There for calcinated eggshell as adsorbent at varying initial concentration of sample, pH of the solution, contact time and adsorbent dose overcome the gabs for the previous studies and also adsorb chromium below its discharge limit (2ppm), the main target for this study.

2.4 Environmental problem associated with industrial wastewater discharge

Growing attention is being directed towards environmental and health hazards caused by accumulation of heavy metals in aqueous environment. Rapid population growth, urbanization and industrial development have been adversely degrading human environment by their effect through loss of biodiversity and pollution from wastes. Industrialization, like other activities that impact on the environment, often results in pollution and degradation. It carries inevitable costs and problems in terms of pollution of air, water resources and general degradation of the natural environment. Industrial waste is the most common point source of water pollution in the present day and it increases yearly due to the fact that industries are increasing because most countries are getting industrialized(Ogedengbe & Akinbile, 2004).

Industrial effluents which discharged from textile and tannery contains a higher amount of metals especially chromium, copper and cadmium. These effluents released on the land as well as dumped into surface water which ultimately leaches to ground water and lead to contamination due to accumulation of toxic metallic components and resulted in a series of well documented problems in living things because they cannot be completely degraded. Hence, industrial effluents offer a wide scope of environmental problems and health hazards are becoming more complex and critical not only in developing countries but also in developed countries(Malarkodi, Krishnasamy et al.2007).

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0. With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc., heavy metals through wastewaters are directly or indirectly discharged into the environment, especially in developing countries. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium(Fenglian & Qi, 2011).

Essentially it is now recognized that direct contact with some industrial chemicals can potentially cause disability, illness (toxigenic/carcinogenic) and death in humans. Minor exposures can cause the buildup of toxic levels within humans. Solvents from degreasing and finishing are a source of exposure through vapors. Human health can also be affected by toxic hazards through the unskilled and unprotected handling of pesticides, tanning chemicals and treated hides and skins (Mwinyihija, Meharg et al .2005).

2.5 The tanning sector

In primitive times, man used animal skins to cover himself in order to protect him from the environment. Although skins were resistant and available, they had some weaknesses: they were damp, they would decompose and when trying to avoid purification by drying they lost their mechanical properties such as flexibility and softness due to drying. Because of this, leather production became an important craft dated more than 3000 years old. This process of turning skin into leather product is called tanning.

Tanning is a process where putrefaction is avoided while maintaining or enhancing the mechanical properties of being flexible and soft even when dry. Hides and skins gain durability and can be used in a wider range of products because of this process. These skins usually come from large and medium size mammals such as the ox, cow, calf, buffalo, sheep, goat, pig and horses; although marine animals and some reptiles are also processed. Leather processing is a technology that is composed of a series of step Operations that aim at isolating collagen by removing non-collage nous components of skin and then improving the material by making it more resistant to environmental and use factors(Favazzi, 2003)

Processing hides ad skins to convert them into leather has evolved through the years from a manual craft process into chemical intensive industrial process. According to (Sharphouse, 1983),it is composed of the following three main stages:-

1. Pre-tanning (also known as beam house operations): this consists of unit operations from skinning the animal and preparing the skin for transport by curing, to treating the skin prior to tanning (washing, liming treatment, unhearing, fleshing, de liming, bating and pickling).

2. Tanning. (Also known as tannery operations): Tanning through chemical or vegetable treatment of the skin.

3. Post-tanning (finishing operations): That consists of operations to obtain the finishing mechanical and esthetic characteristics usually containing steps such as splitting to gain uniformed thickness, washing residue form tanning process, pH neutralizing, dyeing, flattening, oiling, drying and rolling. These steps require many natural resources such as water, metals, and derived chemicals in order to achieve the desired quality. If better manufacturing practices and control systems are not in place the tanning process can become an important environmental issue. Because of its potential and the many companies that have poor manufacturing practices, the tanning industry has generally been identified as a source of pollution and described as a problematic industrial sector in terms of environmental performance.

These steps require many natural resources such as water, metals, and derived chemicals in order to achieve the desired quality. If better manufacturing practices and control systems are not in place the tanning process can become an important environmental issue. Because of its potential and the many companies that have poor manufacturing practices, the tanning industry has generally been identified as a source of pollution and described as a problematic industrial sector in terms of environmental performance. Western countries this has been met by legislation that outline and delimit industrial environmental performance. According to the European Commission in order to remain competitive in the global market place, European leather producers must exploit more efficiently their raw materials and avoid wasting collage nous material (hides and skins) that constitutes valuable raw material for other industries and agriculture, as well as, have high adverse environmental and cost implications. By-products should be either reused/recycled or converted into new, higher value Products(DGEI, 2012).

2.6 Use of chromium in tanneries

Tanning is the process in which hides and skins are converted into different stable materials by using different tanning agents(Wang et al., 2005). Chromium is one of the many chemicals used during tanning process for the treatment of skin and hides(Barnhart, 1997). It is used in tanneries as chromium (III) sulfate because of its processing speed, low cost, and light color and greater stability of the resulting leather.

2.7 Environmental challenges

Due to its rapid expansion, in Ethiopia, Agro-processing Industries are considered to be a major source of pollution and tannery wastewater in particular, is a potential environmental concern (Ros and Ganter, 1998). Tanning industry wastes poses serious environmental impact on water, soil and atmospheric systems. The impacts of tannery wastewater in water bodies are due to its high oxygen demand, discolorations and toxic chemical constituents (such as sulfide, ammonia and chromium) (Song et al .2000). The conversion of raw hides and skins into finished leather requires three distinct processes; beam house (pre tanning), tanning (chrome tanning) and finished steps (post tanning). Each has its own wastewater characteristic wastes. Effluents generating from Beam house process (liming, deliming/bating, fleshing and splitting machines) have high BOD (80%), sulfides, pH (11-12.5), COD, salt, pesticides, flesh, hair, suspended solids, ammonia, base and chloride but they are Cr free (figure 2.1). The tanning processes generate the high content of chromium, BOD, COD, salt, acid, suspended solids. The finishing process generates BOD, COD, salt, chromium, oil (Seyoum Leta et al., 2003; UNIDO, 2011) . Soaking and other general effluents, mainly from post tanning operation (fat-liquoring, dying) has low Cr content.

The main Problem of high organic loading, discharge in water bodies is the depletion of dissolved oxygen content from stream waters caused by microbial decomposition(Mwinyihija et al., 2006). These encourage anaerobic activity, which leads to release of noxious gases (such as H_2S) in the water bodies (Song et al. 2000; Mwinyihija et al., 2006). The primary biochemical effects of H_2S exposure are inhibition of the cytochrome oxidase and other oxidative enzymes(Nicholson et al., 1998; Reiffenstien et al., 1992). Chromium as chromium polynicotine, chromium chloride and chromium picolinate (CrP) is a micronutrient and have been proven to exhibit a significant number of health benefits both in animals and humans(Anderson, 2000).

Chromium as a basic sulfate is the most widely used tanning substance today(UNEP, 1994). Chromium as inorganic pollutant exists in several oxidation states (oxidation numbers from 0 to VI). The most common forms are stable trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) species(Kotaś & Stasicka, 2000). Chromium hazards, due to environmental contamination, depend on its oxidation state (i.e. Cr^{6+} is more toxic than the Cr^{3+}) which precipitates at higher pH. The presence and ratio between these two forms depend on various processes; chemical and photochemical, redox transformation and precipitation/dissolution. Cr^{3+} is the dominant form in tannery effluents, but with Redox reactions occurring in the sludge, an increase in the hexavalent form can occur. Discharge of untreated tannery effluent containing all these pollutants causes environmental and health problems in the downstream community(Kotaś & Stasicka, 2000).

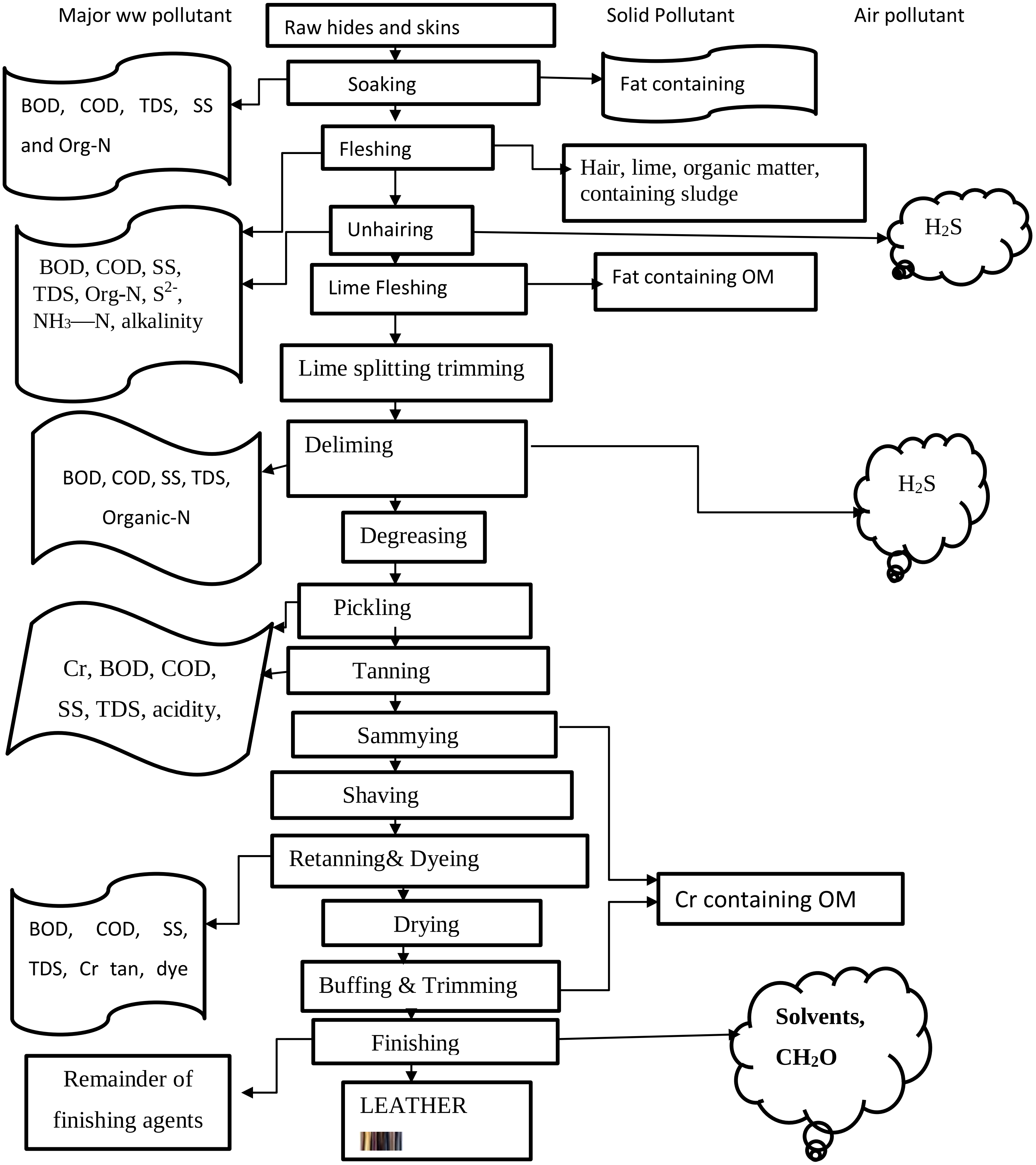


Figure 2. 1:Tanning process flow chart, source and type of pollutant(Source, UNIDO: 2011; UNEP, 1994)

Environmental pollution prevention and control regulations no. 159/2009 (2) (Article 15) arms competent environmental agencies with the power to slap administrative measures on miscreants contravening the proclamation. Therefore, Ethiopia can be said to be endowed with good and almost complete environmental laws, however, their implementation is questionable. 90% of industrial enterprises, whether existing or new, discharging their waste, sometimes hazardous, into the environment without any attempt to treat them (EPA, 2003).

Table 2. 2:Tannery effluent standards of EPA Pollutant

Pollutant Parameters	**Limit values for discharge to water**
Temperature	40^{o}C
pH	6-9
BOD5 at 20^{o}C	90% removal or 200mg/L at 20 ^{o}C, whichever is les
COD	500 mg/L
Suspended solids	50 mg/L
Total ammonia (as N)	80% removal or 30 mg/L, whichever is les
Total nitrogen (as N)	80% removal or 60 mg/L, whichever is les
Chromium (as Total Cr)	2 mg/L
Chromium (as Cr VI)	0.1 mg/L
Total phosphors	10 mg/L
Chlorides (as Cl)	1000 mg/L
Sulfides (as S)	1 mg/L
Oils, fats, and grease	15 mg/l

(SourceEthiopia EPA,2005)

2.8 Conventional technologies for Chromium removal and their Limitation

Chromium removal processes are carefully considered as not only toxic heavy metal removal in environmental aspects, but also precious chromium recovery in industrial aspects. Chromium contamination is common all over the world. For water resources, the impact of this contamination is severe. Consequently, it is desirable to remove chromium from the contaminated water. Many treatment processes have been developed to remove chromium from wastewater. The most important of these technologies include; chemical precipitation, filtration, ion-exchange, electrolysis, lime coagulation, solvent extraction, reverse osmosis and electrocoagulation. However, all these technologies have their inherent advantages and limitations in application. Most of the methods suffer from some drawbacks such as incomplete metal removal, low selectivity, high reagent and energy requirement, high capital and operational cost and generation of toxic sludge or other waste product that require careful disposal has made it imperative for a cost effective treatment method.(Rao, M.N. Datta, 1987)

2.8.1 Chemical Precipitation

Chemical precipitation is the method, in which dissolved and suspended chromium ions are transformed to the insoluble solid through a chemical reaction. Usually a precipitating agent accelerates this conversion from metal ions into insoluble solid. The commonly used precipitation agents are lime and magnesia. This technique has been proven as an effective way to remediate chromium from wastewater. It is a simple, inexpensive, convenient, and safe method. However, this technique requires large amounts of chemicals, and excessive toxic sludge is produced. Sludge filtration and disposal increase the overall cost of the process. Sometimes chromium precipitation is slow, and aggregation of chromium precipitates take place(Kurniawan, Chan et al.2006).

2.8.2 Ion exchange

Ion exchange is a procedure in which mobile ions from the solution of interest are substituted for ions that are electrostatically bound to the functional groups contained within a solid matrix. Ion exchange resins are categorized as cationic or anionic depending on whether they exchange positive or negative ions. Acidic functional groups, such as sulphonic groups are components of cation exchange resins, whereas anion exchange resins have basic functional groups like amine. Ion exchange resins, either synthetic or natural solid resin, has the specific ability to exchange its cation or anion with chromium ion in wastewater treatment. High cost and the need for appropriate pre-treatment systems seem to be the primary limiting factors on the use of ion exchange for chromium effluent treatment. The matrix easily gets fouled by organics and other solids in the wastewater. This makes it unable to handle concentrated metal solution. Furthermore, ion exchange is nonselective and extremely sensitive to the pH of the solution(Mashangwa, 2016).

2.8.3 Reduction

Reduction is a treatment process in which the higher valance state of chromium ion is converted or reduced to the lower valance state using reducing agents. This technique offers several advantages such as recovery of chromium from contaminated wastewaters; recycle of treated water and short treatment times. However, the limitation includes additional chemicals requirement, and hazardous sludge formation. It is also quite expensive(Martinez and Rodriguez, 2007).

2.8.4 Membrane process

The ability of membrane filtration to remove suspended solids, organic compounds and also inorganic pollutants such as chromium makes it extensively useful for the treatment of inorganic effluent (Fei et al., 2005).Reverse osmosis and eletrodialysis are pivotal models of membrane process relevant to chromium wastewater treatment.

2.8.4.1 Reverse osmosis

The reverse osmosis process depends upon a semi-permeable membrane through which pressurized water is forced. Reverse osmosis, simply stated, is the opposite of the Natural osmosis process of water. Osmosis is the name for the tendency of water to migrate from a weaker saline solution to a stronger saline solution, gradually equalizing the saline composition of each solution when a semi-permeable membrane separates the two solutions. In reverse osmosis, water is forced to move from a stronger saline Solution to a weaker solution, again through a semi-permeable membrane. Because molecules of salt are physically larger than water molecules, the membrane blocks the Passage of salt particles(Barakat, 2011). The result is desalinated water on one side of the membrane and a highly concentrated, saline solution of water on the other side. The drawback of reverse osmosis are Limited flow rates, two to four gallons of water flushed down the drain for each gallon of filtered water produced, high pressure inflow requirement, membrane scaling and expensive to install(Mishra, 2007).

2.8.4.2 Electro dialysis

Electro dialysis (ED) is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cat-ions toward the cathode, crossing the anion exchange and cat-ion exchange membranes(Chen, 2004). The limitation is the formation of metal hydroxides, which clog the membrane.

2.8.5 Coagulation and flocculation

Coagulation, sedimentation, flocculation and filtration can also be used to eliminate chromium from wastewaters. Coagulation is the destabilization of colloids by counteracting the forces that keep them away from each other. Aluminum, ferrous sulfate and ferric chloride are the most common coagulants used in the conventional chromium containing wastewater treatment processes. This results in the effective elimination of chromium by charge neutralization of chromium (El Samrani et al., 2008).Flocculation is the feat of polymers to create bridges between the flocs and bind the particles to form large agglomerates. When particles aggregated into larger particles, get suspended they are generally detached or separated by filtration, straining or floatation. Though poly ferric sulfate and polyacrylamide are the most common flocculants and are commonly used in the treatment of chromium(Chang et al. 2002).Coagulation and flocculation are relatively simple technology ,high chromium removal efficiency and relatively low coat. Production of sludge, continuous chemicals requirement and transfer of toxic compounds into solid phase for disposal are the main drawbacks of coagulation and flocculation.

2.8.6 Solvent extraction

The introduction of selective complexing agents led to routine use of the liquid-liquid extraction or solvent extraction of chromium from solutions on a large scale in waste reprocessing and effluent treatment. Solvent extraction encompasses an organic and an aqueous phase whereby the aqueous solution that contain the chromium is mixed with the right organic solvent. This causes the chromium to be transferred into the organic phase (Ramachandra et al., 2005). Liquid–liquid (solvent) extraction is one of the most efficient methods of concentrating and separating chromium ion from aqueous solutions. The recovery of the extracted chromium involves contacting the organic solvent with sulphuric acid (Wionczyk et al., 2006).The cost of organic solvent is limitation of solvent extraction treatment method. In comparison with the conventional methods for the removal of chromium from wastewater, the bio sorption process offers potential advantages such as low operating cost, minimization of the volume of chemical and/or biological sludge to be disposed of, high efficiency in detoxifying very diluted effluents, and so on. Therefore, the search for new cost effective technologies for the removal of chromium from wastewater has been directed towards low cost adsorbents (biosorbents) from eggshell wastes(Basc et al., 2004; Kobya et al, 2005; Talouizte et al., 2013).

2.9 Chromium removal using bio sorption

The conventional heavy metal removal processes have several limitations such as less effective removal of metal ion, high reagent requirement, high costs, the generation of toxic sludge ‘s, and the problem of the safe disposal of the materials. Compared with conventional methods for removal of toxic chromium ions, bio sorption process offers the advantages of low cost, minimization of the volume of chemical and biological sludge to be disposed of, high efficiency in detoxifying very dilute effluents, chromium recovery and high removal efficiency.

2.9.1 Adsorption

The adsorption technique has several benefits. It is effective and economical. It can remove the contaminating chromium as well as recovery and recycle of sorbet chromium from sorbent. It has evolved as the suitable alternative for those metal ions that cannot be removed easily by other techniques. The removal efficiency is excellent for this process and depends on pH ,adsorbate concentration, contact time and adsorbent dosages(Mohan, Singh et al. 2005).

Adsorption is the process through which a substance originally present in one phase is removed from that phase by accumulation at the interface between that phase and a separate solid phase. The driving force for adsorption is the reduction in interfacial (surface) tension between the fluid and the solid adsorbent as a result of the adsorption of the adsorbate on the surface of the solid(Mohan et al., 2005).

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements be they ionic, covalent or metallic of the constituent atoms of the material is filled. But atoms on the clean surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favorable for them to bond with whatever happens to be available. Adsorption can result either from the universal Vander Waals interactions (physisorption) or it can have the character of a chemical process(chemisorption). Contrary to physisorption, chemisorption occurs only as a monolayer.

Physorption is a reversible process that occurs at a temperature lower or close to the critical temperature of an adsorbed substance. Chemisorption's occur usually at temperatures much higher than the critical temperature(Ferrari, Kaufmann et al.2010).The presence of suspended particles, oils, and greases reduces the efficiency of the process and, therefore, pre-filtration is sometimes required. When a finely divided solid is shaken with the contaminated or polluted water, the pollutants adhere to the solid surface and a stage of equilibrium is established. At this stage, the concentration of pollutant adsorbed and in the water become constant. The relationship, at a given temperature, between the equilibrium amounts of pollutant adsorbed and in the water is called an adsorption isotherm. Langmuir, Freundlich and other models are well known and can explain the adsorption efficiency of a pollutant systematically and scientifically.

2.9.1.1 Adsorption mechanism

The classical mechanism of adsorption is divided into three steps Figure (2.2) a) diffusion of adsorbate to adsorbent surface, b) migration into pores of adsorbent c) monolayer build-up of adsorbate on the adsorbent. Figure (2.2) presents the process of adsorbate distribution. The first step occurs diffusion of adsorbate on the adsorbent surface by intermolecular forces between adsorbate and adsorbent. The second step involves migration of adsorb-ate into pores of adsorbent. Tributed on the surface and filled up the volume of pores, particles of adsorbate are building up the monolayer of reacted molecules, ions and atoms to the active sites of adsorbent.

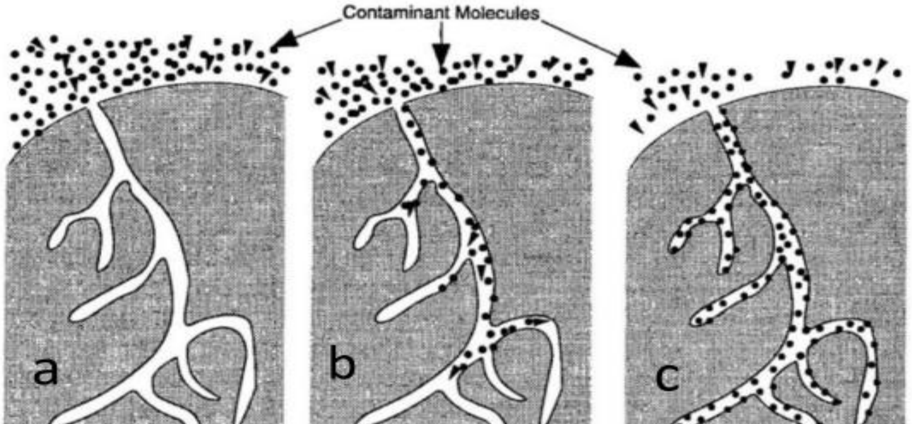


Figure 2. 2:Three steps of adsorption mechanism(a) diffusion of adsorbate to adsorbent surface b) migration into pores of adsorbent c) monolayer build-up of adsorbate on adsorbent (Repo, 2011).

2.9.1.2 Physisorption and chemisorption

The nature of adsorption depends upon the forces, which act between adsorbent and adsorbate. The adsorption forces are a key factor in defining whether the adsorption is physical or chemical. Occasionally, it is complicated to identify what type of adsorption is predominating in a certain situation. Sometimes it might be a combination of chemisorption and physisorption(Fomkin, 2009).

Physisorption

Physical adsorption is reversible and rapid. Molecules are holding to the surface by van der Waals forces of attraction (intermolecular forces and inter atomic interactions with the energy of 10-20 kJ/mol). Therefore, the lack of interaction energy may break the bond between adsorbent and adsorbate, for example by mechanical movement of the interface. Consequently, the most valuable parameters for physisorption are the pore size, pore structure, pore volume, and surface area. Physisorption prevails at low temperatures, and activation energy is 5-10 Kcal/mol.

Chemisorption

A specific surface area of phases, types of active sites, number of active sites, and stability of active sites are predominantly valuable for chemisorption. Chemical adsorption occurs because of chemical reaction between molecules and atoms of the adsorbate and adsorbent. Chemisorption is irreversible because chemically adsorbed molecules are not able to move on the surface of within interface. The main advantages are high selectivity of separation and the ability to treat exceptionally small concentrations of solute. Chemisorption accelerates by elevated temperature where activation energy varies between 10-100 Kcal/mol(Sharma, 2013).

2.9.1.3 Factors affecting adsorption process

2.9.1.3.1 pH

The pH value of the metal solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The pH of the solution would affect both aqueous chemistry and surface binding sites of the adsorbents. The effect of pH in turn depends on the charge on the adsorbent surface. If the adsorbent surface is negatively charged, at lower pH, the large number of H^+ ions present neutralizes the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion, and a better adsorption is obtained. If the surface charge of the adsorbent is positively charged, the H^+ ions may compete effectively with the cations of the solution causing a decrease in the amount of metal ion adsorbed(Jiaping, 2012).

2.9.1.3.2 Contact Time

The amount adsorbed on to the adsorbent is in a state of dynamic equilibrium with the amount desorbed from the adsorbent. The time required to attain this state of equilibrium is termed as the equilibrium time. The amount adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under the operating conditions(Jiaping, 2012).

2.9.1.3.3 Adsorbent Dosage

The concentration of both the metal ion and the sorbent is a significant factor to be considered for effective adsorption process. The adsorbent dosage is an important parameter because this determines the capacity of an adsorbent. It determines the sorbent and sorbate equilibrium of the system. The effect of adsorbent dosage on adsorption was studied by varying the amount of adsorbents and keeping the other parameters constant. According to(Joshi, Lokeshwarl, & Keshava, 2009) investigation, chromium uptake rose with an increase in sorbent. This appears to be due to increase in the available binding sites, which is the surface area of adsorbent in the biomass for the compellation of chromium. However, the chromium uptake decreased gradually when the sorbent concentration exceeding more. Accordingly, the chromium ion in solution has been decreased drastically with the increase in the sorbent dosage.

2.9.1.3.4 Concentration

The metal concentration plays a pivotal role in the sorption process. At higher initial metal ion concentrations, the amount of adsorbed ions is greater than the amount at lower concentrations since there are more binding sites for interaction, thus there is a greater driving force at higher concentrations between the solid and liquid interface which may enable mass transfer(Iram & Abrar, 2015). It is also of note that other sorbable ions in the solution possibly will compete with the metal ion of interest for the different surface sorption sites thus the binding of the metal ion of interest is lowered however the amount of inhibition would also depend on the binding strength of the different metal ions to the biomass (Zheng et al., 2016). The initial and final concentrations of the solutions were measured by Atomic absorption spectrophotometer.

2.9.1.3.5 Effects of temperature adsorption

Aksu et al.(1992)reported that temperature in the range of 20 to 35 degree centigrade does not have an effect on the bio sorption process but decreases with an increase of temperature above a critical value. The metal ions kinetic energy may increase as the temperature increases, which would make it easier for the metal ions to be attached to the bio sorbent surface.

2.9.1.3.6 Effect of Porosity

The adsorption performance is dependent on the condition of internal surface accessibility. A very important and decisive property of adsorbent materials is the pore structure. The total number of pores and their shape and size determine the adsorption capacity and even the rate of adsorption. According to the IUPAC recommendation, microspores are pores of a width not exceeding 2 nm, meso pores are pores of a width between 2 and 50 nm, and Macro pores are pores of a width greater than 50 nm. A further classification involves ultra-micro pores, which are pores of a width less than 0.7 nm. The specific surface area of Macro pores adsorbents is very small. Therefore, adsorption on this surface is usually neglected. In the case of meso pores, the adsorbent surface area has a distinct physical meaning. Mono- and multilayer adsorption takes place successively on the surface of meso pores, and adsorption proceeds according to the mechanism of capillary adsorbate condensation. Specific surface area, pore volume, and pore size distribution are basic parameters characterizing meso pores. Meso pores and Macro pores play an essential role in the transport of adsorbate molecules through the micro pores. The sizes of micro pores are usually comparable to those of adsorbate molecules. Consequently, adsorption in micro pores is essentially a pore-filling process. Therefore, the volume is the main controlling parameter for adsorption in micro pores. Considering also that most of the total surface area is found in the micro pores and the contribution of Macro pores to the total surface area is very low, the contribution of micro pores to adsorption would be expected to be higher(Ferhan Cecen, 2012).

2.9.1.4 Adsorption process modeling

Adsorption modeling helps to identify the removal efficiency of adsorbent. Adsorption modeling is applied to describe the experimental data by using adsorption isotherm and kinetic models(Repo, 2011).

2.9.1.5 Adsorption Isotherms

Equilibrium isotherm model equations such as Langmuir, Freundlich and Temkin Isotherms are used to describe experimental adsorption data in the batch model to describe the relation between adsorbate on the surface of adsorbent that is the amount of species adsorbed per unit mass of adsorbent and concentration solute left in the solution (Gautam et al., 2014**).** The equilibrium adsorption isotherms were depicted by plotting solid phase concentration (qe) against liquid phase concentration (Ce) of solute. Adsorption isotherm explains the interaction between adsorbate and adsorbent with critical for design of adsorption process. Each adsorption equilibrium state is uniquely defined by the variables adsorbate concentration, adsorbed amount also referred to as adsorbent loading and temperature. For a single-solute system, the equilibrium relationship can be described in its general form as equation 2.1.

$$q_{eq} = f\,(C_{eq}, T) \text{ -- } 2.1$$

Where Ceq is the adsorbate concentration in the state of equilibrium, q_{eq} is the adsorbed amount (adsorbent loading) in the state of equilibrium, and T is the temperature.

2.9.1.5.1 Langmuir Adsorption Isotherm

Langmuir adsorption isotherms are widely used to describe the relationship between the amount of adsorbate adsorbed onto the adsorbent, its equilibrium concentration in aqueous solution and based on three assumptions: (i) the surface of the adsorbent is in contact with a solution containing an adsorbate which is strongly attracted to the surface; (ii) the surface has a specific number of sites where the solute molecules can be adsorbed; (iii) the adsorption involves the attachment of only one layer of molecules to the surface, i.e. monolayer adsorption (Gautam et al.,2014).The Langmuir equation is:

$$q_e = \frac{q_{max} K_L Ce}{1+K_L Ce} \text{ --- } 2.2$$

Where qe is the amount of metal ions adsorbed per gram of adsorbent at equilibrium (mg g^{-1} dry weight), q_{max} is the maximum amount of the metal ion per unit weight of the adsorbent to form a complete monolayer on the surface-bound at high Ce, Ce is concentration of metal ions in solution at equilibrium and K_L is a Langmuir constant. The linear form is

$$\frac{Ce}{q_e} = \frac{Ce}{q_{max}} + \frac{1}{K_L q_{max}} \text{ --------------------------------2.3}$$

The value of q_{max} and K_L computed from slope and intercept of the Langmuir plot of Ce/q_e versus Ce. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant [separation factor] (Dada et al., 2012)

$$R_L = \frac{1}{1+K_L Co} \text{ ---2.4}$$

Where Co initial concentration R_L value indicates the adsorption nature to be either unfavorable if $R_L>1$, linear if $R_L=1$, favorable if $0<R_L<1$ and irreversible if $R_L = 0$.

2.9.1.5.2 Freundlich Adsorption Isotherm

At lower concentrations, an alternate isotherm developed by Herbert F. Freundlich frequently describes the data better. Freundlich isotherm describes that the ration of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of solute in the solution is not constant at different concentrations. The empirical Freundlich model also considers monomolecular layer coverage of solute by the adsorbent. However, it assumes the adsorbent has a heterogeneous surface so that binding sites are not identical. This model takes the following form for a single component adsorption.

$$q_e = K_f Ce^{1/n} \text{ --2.5}$$

Where Ce = the equilibrium concentration of adsorbate (mg/L), qe = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g), K_f and 1/n are Freundlich constants. K_f and 1/n are indicators of adsorption capacity and adsorption intensity respectively. The linear form is:

$$\log q_e = \log K_f + \frac{1}{n} \log Ce \text{--2.6}$$

If n =1 then the partition between the two phases are independent of the concentration. If the value of 1/n is below one, it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption.

2.9.1.5.3 Temkin Adsorption Isotherm model

This isotherm model is based on the assumption that the decline of the heat of sorption as a function of temperature is linear and this decrease is due to adsorbate-adsorbent interaction. This model is expressed as

$$q_e = \frac{RT}{b}\ln(ACe) \text{--} 2.7$$

The linearized form of Temkin equation is expressed as follows

$$qe = \frac{RT}{b}\ln A + \frac{RT}{b}\ln Ce \text{--} 2.8$$

$$q_e = B\ln K_T + B\ln Ce \text{ --} 2.9$$

Where, R is gas constant (8.314 J/mol/K), T is Temperature (K), qe is the amount of chromium adsorbed at equilibrium, Ce equilibrium concentration in mg/L, A is Temkin isotherm constant (L/g) and b is heat of sorption (J/mol).

2.9.1.6 Adsorption kinetics

The prediction of adsorption rate gives important information for designing batch adsorption systems (King P etal 2007).In order to determine the rate limiting step during the adsorption process different kinetic models have been used to analyze the experimental data. These models include first- order, pseudo second-order and intra-particle diffusion as the most important kinetic models (Balarak, Pirdadeh, & Mahdavi, 2015).Adsorption kinetics describes the rate of solute uptake, which is also responsible for the residence time needed for an adsorption study. Therefore, it is an important characteristic in defining how fast the sorption processes is carried out.

2.9.1.6.1 Pseudo first order model

First order model which is believed to be the earliest model, was developed by Lagragren in 1898 (Qiu et al., 2009). To describe the kinetic process of liquid-solid phase adsorption he presented first order model as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \text{ --} 2.10$$

Where q_e and q_t(mg/g) are the adsorption capacities at equilibrium and time t (min), respectively. K_1 (min^{-1}) is the pseudo first order rate constant for the kinetic model. Integration of the equation with the boundary conditions of q_t=0 at t=0 and q_t=q_t at t=t, gives,

$$\ln\left(\frac{q_e}{q_e - q_t}\right) = k_1 t \text{ --} 2.11$$

The linear form of equation 2.10 expressed in the form of:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \text{ --} 2.12$$

The plot of log (q_e – q_t) versus t should give a linear relationship from which K_1 and q_e can be determined from the slope and intercept of the plot, respectively.

2.9.1.6.2 Pseudo-second-order model

The adsorption kinetic data can be further analyzed using Ho's pseudo second-order kinetics (McKay and Ho, 1999). This is represented by:

$$\frac{dq_t}{dt} = K_2(q_e-q_t)^2 \text{ --2.13}$$

Integrating the equation for the boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_t, gives:

$$\frac{1}{q_e-q_t} = \frac{1}{qe} + k_2t \text{ ---2.14}$$

This can be linearized as follows:

$$\frac{t}{q_e} = (\frac{1}{q_e^2 k_2}) + (\frac{1}{q_e})t \text{ ---2.15}$$

q_e is the amount of chromium sorbed at equilibrium, mg/ g; k_2 is the equilibrium rate constant of pseudo-second order sorption, g /mg min

The constants, q_e and K_2, are obtained from the slope and intercept of t/q_t versus t linear plot, respectively.

2.9.1.6.3 Intra-particle diffusion model

In the case of intra-particle diffusion model it is assumed that an uptake of metal ions from the solution by an adsorbent varies almost proportionally with the square root of t (i.e. $t^{0.5}$) rather than t, nearly linear variation of the quantity is sorbed with $t^{0.5}$and is predicted for a large initial fraction of reactions controlled by rates of intra-particle diffusion (Ho and McKay, 1998). An equation for this model can be written as:

$$q_t = k_i t^{0.5} + C \text{ ---2.16}$$

Where, q_t is the amount of metal adsorbed at time t '(mg g^{-1}), K_i is intra-particle diffusion rate constant (mg g^{-1} $min^{-1/2}$) and C is intercept. The value of K_i and C were obtained from slope and intercept of the linear plot of q_t versus ($t^{0.5}$) at different initial metal concentrations and room temperature 25^0c. When the metal ion solution is mixed with the adsorbent, transport of the metal ions from the solution through the interface between the solution and the adsorbent occurs into pores in the particles. There are four main stages in the process of adsorption by porous adsorbents (i) solute transfer from the bulk solution to the boundary film that surrounds the adsorbent ‘s surface, (ii) solute transport from the boundary film to the adsorbent ‘s surface, (iii) solute transfer from the adsorbent ‘s surface to active intra particular sites, and (iv) interactions between the solute molecules and the available adsorption sites on the internal surfaces of the adsorbent. One or more of these four steps controls the rate at which solute is adsorbed.

2.9.2 Preparing Eggshells as a bio adsorbent

The egg-shell is constituted of a number of layers of calcium carbonate. The mammillary layer is the innermost layer measuring close to 100 µm and grows on the outer egg membrane. The innermost layer creates a base upon which the palisade layer is created to constitute the thickest part of about 200 µm of the egg-shell. The top layer is the vertical layer that is about 5-8 µm and is enclosed by the organic cuticle(Chojnacka, 2005).

Egg shell has an outstanding mechanical performance, such as an excellent combination of stiffness, strength, impact resistance and toughness. The composition is about 95% calcium carbonate (which occurs in two crystal forms: hexagonal calcite and rhombohedral aragonite) and 5% organic materials. The amine and amide groups of the proteins on the surface of particulate egg shell are a potential source of hardening agent and help in chromium removal via chelation(Guru & Dash, 2013) and this hardening agent (providing strength to the adsorbent) has an affinity for chromium. Egg shells have been used for the removal of chromium from water in both modified and non-modified forms. Modification is carried out by calcinating at high temperatures. After calcination the structure changes due to the development of pores via the emission of carbon dioxide gas(Rohim et al. 2014).

As a pre-treatment process for the preparation of the reused material from the waste eggshell, calcination was performed in the furnace at 800°C for 2hr after crushing the dried waste eggshell(Baisakh & Patnaik, 2002). From the application of the calcined eggshell in the treatment of industrial wastewater, the calcined eggshell showed a promising removal capacity of heavy metal ions as well as it had a good neutralization capacity in the treatment of strong acidic wastewater.

2.10 Availability of Eggshell

Although chicken eggs are a worldwide daily food they also pose environmental problems. For example, in Ethiopia, about 9555.48 tons of eggshell is generated every year(Moges et al.,2010). This Eggshell is mostly sent to the landfill with a high management cost. Therefore it is economical to transform this eggshell waste to create new values such as effective adsorbent in this study. Hatchery, bakery shops and hotels are the major areas where eggshell is more generated.

2.10.1 Eggshell produced from hatchery

There are poultry farms in Bishoftu in which high amount of eggshell is generated during hatching. Among these Elefora produces average of 10.84 ton per year eggshell waste. Alema poultry farm also found in Bishoftu produces an average eggshell of 6.02 ton per year. The other also produces waste eggshell depend on their capacity.

2.10.2 Eggshell produced from bakery

There are many bakery shops in Addis Ababa which produces waste eggshell daily. On average eggshell produced from bakery in Addis Ababa was estimated as 144.54 ton per year. Therefore, eggshell is more enough available and easy to collect

2.11 Description of the study area

Ethiopian Tannery Share Company (ETSC) is located in Edjersa Kebele of Lome Wereda, near to Mojjo Town about 90km, South of Addis Ababa with an altitude between 1788 to 1,825 m above sea level. The tannery was erected about one kilometer from Awash River, with 650,000 square meters of area and a quarter of it is covered by infrastructures. The annual rainfall varies between 680 to 2,000 mm (EEPA, 1997) with an average annual temperature is 22.2^{0}c and riches up to 30^{0}c.

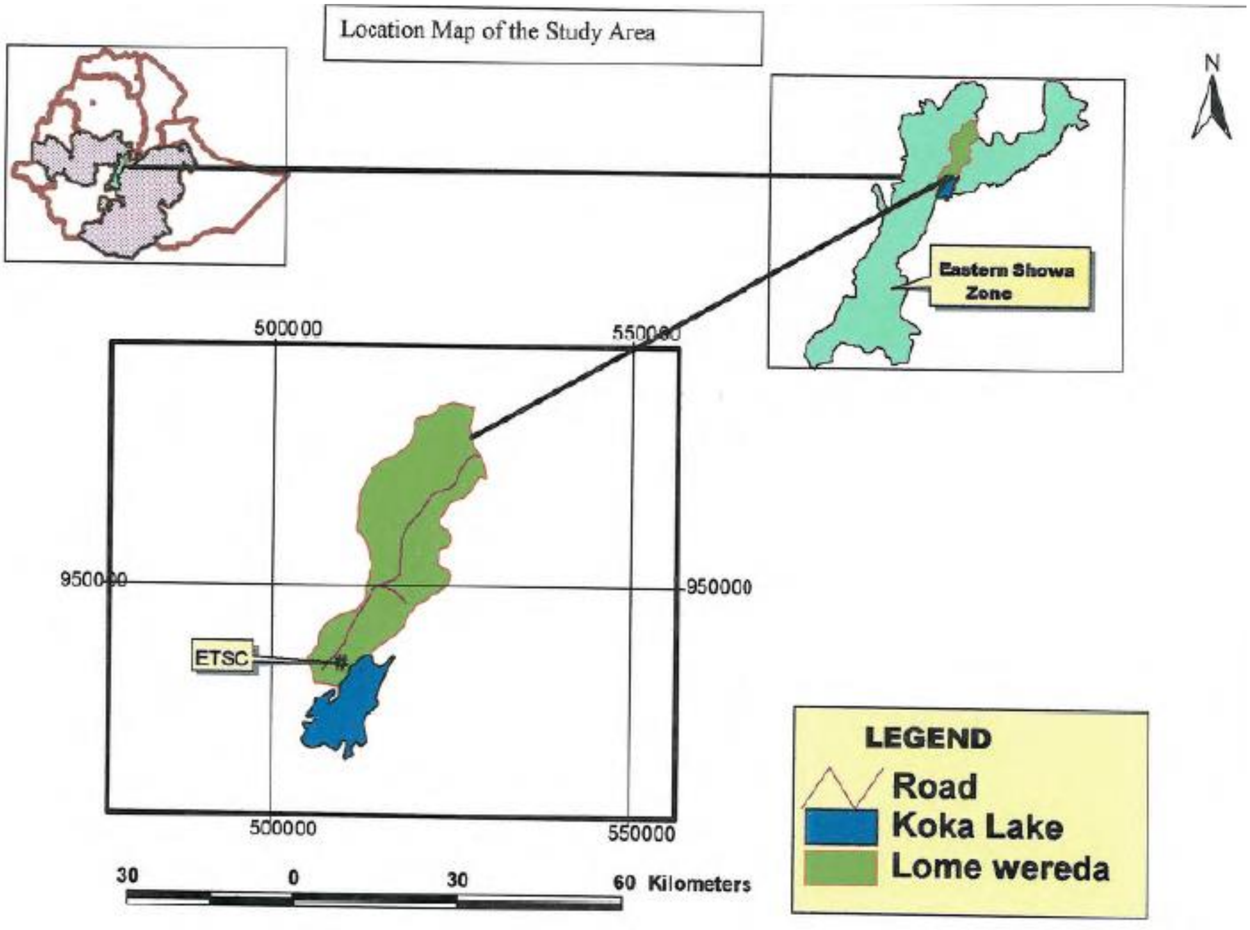


Figure 2. 3:Location of the study area

3. MATERIALES AND METHODES

3.1 Preparation and characterization of Eggshell as bio adsorbent

3.1.1 Materials and equipment

The major equipment's and apparatus that were used during this thesis work includes Analytical balance (Ohaus, EP 214C Switzerland), grinder, 250ml plastic bottles, Orbital shaker (GFL 3074 Model), Sieves (75 – 210 µm size), pH meter (model: JENWAY; 3505 pH meter), magnetic stirrer, FTIR (model: Perkin Elmer Spectrum 65), XRD, drying oven (model: Memmert,100- 800 Germany) and Furnace (Nebertherm LHT 02/16 Germany). All of the chemicals were analytical grade. Nitric acid (HNO_3), hydrochloric acid (HCl), potassium nitrate (KNO_3) and sodium hydroxide (NaOH) were purchased from chemical shop in Addis Ababa.0.1MNaOH and 0.1MHCl were used for PH adjustment of the zero-point charge determination. Potassium Nitrate was used to determine zero-point charge of the adsorbent.

3.1.2 Experimental Methods and procedures

The collected eggshell was washed several times with distilled water to remove dirt particles. Following the method of Kumaraswamy, et al. (2015), the eggshells were dried for three hours in an oven at 150 ºC and then allowed to cool to 24 ºC (room temperature). The dried eggshells were ground into small particles using a grinder and sieved to obtain under 75µm mesh size.

The suitable temperature for calcination process was 800ºC to ensure complete conversion of $CaCO_3$ to CaO (Baisakh & Patnaik, 2002).Then calcination was performed in a furnace at 800ºC for 2hr and the calcinated eggshell powder was packed into desiccator

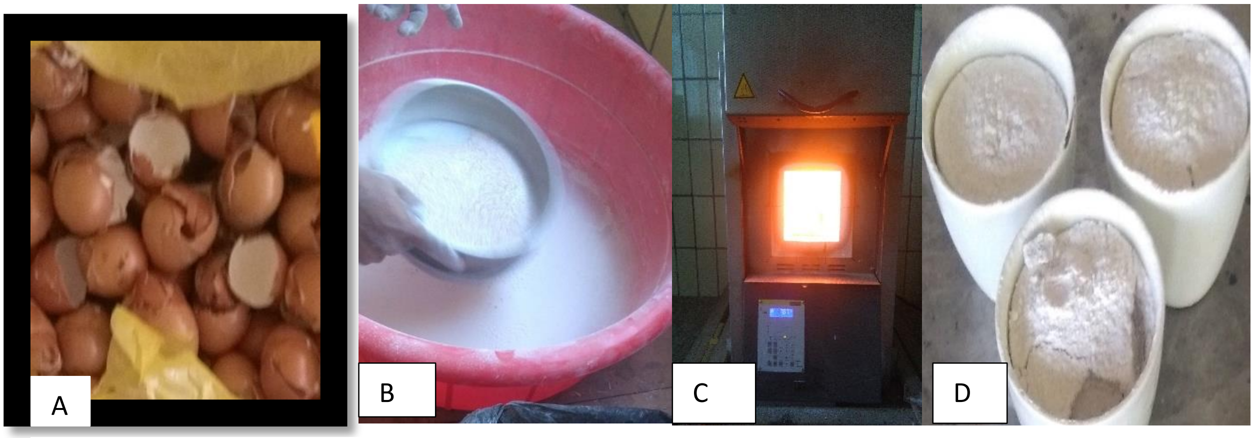


Figure 3. 1:Adsorbent preparation(A) Raw eggshell, (B)powder eggshell, (C) calcination process and (D) Calcinated eggshell powder(MESP)

3.1.3 Characterization of the bio sorbent

The samples were characterized by proximate analysis; Fourier transform infrared spectroscopy (FTIR) & X-ray diffraction (XRD) analysis.

3.1.3.1 Proximate analysis

It consists determination of moisture content, ash value, fixed carbon and volatile matter contents. The details of this analysis was carried out on Eggshell ground to fine powder that passed 75µm mesh size. Sample was run in triplicate and the average values have been taken.

Moisture content: moisture content was determined using ASTM D2867-91 method. This was determined by loss on drying method. A crucible amount weighed, for each adsorbent of eggshell and calcinated eggshell was taken and then the crucible was placed in an electric hot air oven maintained at 105^0C. The sample was weighed at regular intervals of 30 minutes and once the weight observed became constant, the moisture content was calculated using the equation 3.1.

$$\text{Moisture content(\%)} = \frac{(w_2 - w_1)-(w_3-w_1)}{w_2-w_1} *100 \text{ ------------------------------------}3.1$$

Where, W_1= weight of the crucible, W_2 = weight of the sample and crucible before drying, W_3 = weight sample and crucible after drying

Ash content: Ash is defined as the quantity of mineral matter which remains as incombustible of testing substance (Cauvain and Young, 2009). Ash content determination was done according to the ASTM D2866-94 standard procedure. A 10gram sample of eggshell powder from the oven dried sample was placed in a crucible and transferred into muffle furnace at a temperature of 650^oC(Al-awwal & Ali, 2015). Then the crucible was cooled at room temperature in desiccator and its weight was recorded. The heating, cooling and weighing cycle was repeated until constant weight was obtained. Once a constant weight was observed, the % ash content (dry basis) was calculated as:

$$\text{Ash content} = \frac{(w_3-w_1)}{w_2-w_1}*100 \text{ ---}3.2$$

Where, W_1 = weight of the crucible, W_2 = weight of the crucible and sample before igniting, W_3 = weight of crucible and sample after igniting

Volatile Matter content: 10g of oven-dried, powdered sample was taken in crucible. Then the crucible was kept in furnace for 10 min at the temperature of 550°C(Baisakh & Patnaik, 2002).

The crucible was taken out of the furnace and allowed to cool in a dissector.

The % volatile matter content in the sample was calculated by using the formula given below:

$$\%\text{volatile matter (VM)} = \% \frac{(w_2 - w_1) - (w_3 - w_1)}{w_2 - w_1} \text{------------------------------} 3.3$$

Where, w_1 represents weight of crucible, w_2 weight of sample and crucible, w_3 represents weight of crucible and sample after incineration for the given time.

Fixed Carbon Content: Fixed carbon was the combustible residue left after removing the moisture content, volatile matter and ash from the sample. The fixed carbon of samples was calculated by subtracting the sum of moisture content, ash content (%) and volatile matter (%) from 100.

Fixed carbon (%) = 100 – (moisture, % + ash, % + volatile matter, %)-------------------------3.4

Bulk density: The bulk density was determined according to ASTM D2854-96 standard testing procedure. 10 gram of raw ground and calcinated eggshell powder were placed into 100 ml graduated cylinder and record the volume occupied by the solid sample. The experiment run twice and the average value was taken. The bulk density of both samples were calculated as follows:

$$\text{Bulk density } (\text{g}/\text{cm}^3) = \frac{\text{weight of dry sample(g)}}{\text{volume of packed sample(cubic centimeter)}} \text{--------------} 3.5$$

Particle density: The particle density of both ground eggshell and calcinated eggshell powder were determined using Pycnometer. The procedure was written as follows;

1.First the weight of the dry Pycnometer was measured.

2.The Pycnometer was filled by distill water and weighed.

3. The Pycnometer was filled by eggshell powder to some extent and measured the weight.

4.Filled the remained space in step 3 with distill water and measured the weight.

$$\text{Particle density of eggshell} = \frac{M_{sample}}{V_p - V_{wa}} \text{--} 3.6$$

Where, M_{sample} represents mass of eggshell in Pycnometer, V_p represents volume of Pycnometer and V_{wa} represents volume of water added

Porosity: Porosity is the fraction of the total powder volume that is taken up by the pore (Nimmo, 2004). The porosity of the Eggshell powder was determined based on the particle density and bulk density of the powder. The porosity of Eggshell powder and calcinated eggshell powder were obtained from bulk and particle density using equation 3.7:

$$\text{Porosity} = \frac{\text{Particle density} - \text{Bulk density}}{\text{particle density}} \text{--} 3.7$$

3.1.3.2 Characterization of Eggshell powder using FTIR and XRD analysis

Functional groups in raw, calcinated eggshell and chromium loaded calcinated eggshell powder were examining by using the Fourier Transform Infrared (FTIR) method of analysis. The FTIR spectrophotometer was analyzed based on changes in dipole moment resulting from bond vibration upon absorption of IR radiation. It was carried out at room temperature using Spectrum 65FT-IR (Perkin Elmer) in the average range 4000-400 cm^{-1} using KBr pellets. The wave numbers associated to signals in the FTIR spectra from chemical functional groups were determined. XRD analysis was carried out to know the crystal phase composition of calcinated eggshell. The diffraction patterns were obtained in the 2θ range from 10-60°.

3.1.3.3 pH of zero charge determination

The point of zero charge of the adsorbent was determined by the solid addition method. A50ml of 0.1M KNO_3 solution transferred into a series of 100 ml conical flask. The initial pH(pH_0) values of the solution was adjusted from 1.0 to 10.0 by adding either 0.1M HCl or0.1M NaOH. Then 1.5 g of eggshell powder was added to each flask which was securely capped immediately. The flasks were then placed into a constant temperature water bath shaker and shaken for 24 h. The pH values of the supernatant liquid were noted after 24 h. The difference between the initial and final pH (ΔpH) values in y-axis was plotted against the initial pHi (x-axis). The point of intersection of the resulting curve with the x-axis gave the pHpzc. The pH of the solution affects the surface charge of the adsorbents as well as the degree of the ionization and speciation of different pollutants. Change in the pH affects the adsorptive process through dissociation of functional groups as the active sites on the surface of the adsorbent. This subsequently leads to a shift in the reaction kinetics and the equilibrium characteristics of the adsorption process. Adsorption of the various anionic and cationic species on such adsorbents can be explained on the basis of the competitive adsorption of H^+ and OH^- ions with the adsorbate.

It is a common observation that the surface adsorbs anions favorably at lower pH due to presence of H^+ ions, whereas the surface is active for the adsorption of cations at higher pH due to deposition of OH^- ions. (Bhaumik et al., 2012).

3.1.3.4 Specific surface area

The ESP and calcinated eggshell specific surface area was determined using the method described by Yadav et al, 2012. 1.0 g of adsorbent was mixed with 100 ml of distilled water and 20 g NaCl. The mixture was shaken for five minutes. Its final pH was adjusted to 4 with 0.1 M HCl. It was then titrated against 0.1M NaOH to raise the pH from 4 to 9 and the volume (ml) of 0.1M NaOH used was measured in replicate and the average value was taken for the surface area calculation by sears method. Specific surface area of adsorbent was calculated using the formula Sears method(Yadav O et al., 2012):

S = 32 x V-25------------------------------------3.8

Where, S is surface area of bio adsorbent per gram ($m^2\ g^{-1}$), V is volume (ml) of 0.1M NaOH required to raise the pH of the sample from 4 to 9. The numbers 32 and 25 are physical constants.

3.2 Study and optimizations the adsorption process parameter

3.2.1 Material and equipment

All of the chemicals were analytical grade. Nitric acid (HNO_3), hydrochloric acid (HCl), potassium nitrate (KNO_3) and sodium hydroxide (NaOH) were purchased from chemical shop in Addis Ababa.0.1MNaOH and 0.1MHCl were used for PH adjustment of the solution. Concentrated Nitric acid was used for both acidifying the sample during collection to prevent precipitation of heavy metal and also it was used during digestion of solution in order to freely ionized which was suitable to analysis using AAS.

The major equipment's and apparatus that were used during this thesis work includes ,250ml plastic bottles, Orbital shaker (GFL 3074 Model) , pH meter (model: JENWAY; 3505 pH meter), magnetic stirrer, Hot plate,FAAS (AA-6300 (SHIMADZU)) gases: acetylene + air obtained from Ezana (Mekelle, Meli) model NovAA400P, Germany for estimation of metal ion concentration electrical conductivity , turbidity tube Micro pipette (10-25ml), volumetric flasks (50-250 ml), pipettes, test tubes, glove and whats man filter paper etc.

3.2.2 Experimental Methods and procedures

Composite sample of wastewater that was obtained from Ethiopia Tannery share company (chrome line) was analyzed for the amount of chromium using FAAS prior to the experiment. After obtaining the result of the amount of chromium from analysis of the sample wastewater it was diluted to 80mg/L ,120mg/L and 160mg/L then adsorption efficiency of Thermally modified eggshell powder was evaluated under different pH, contact time, initial concentration of chromium and dose of adsorbent. Adsorption efficiency in percent and milligram of Cr adsorbed per gram of adsorbent was calculated using the equations 3.11 and 3.12, respectively. Finally, average of the triplicate results was presented.

$$\%R = \left(\frac{C_o-C_f}{C_o}\right)*100 \text{ --}3.11$$

Where, %R is percent removal, Co is initial concentration and C_f concentration after adsorption

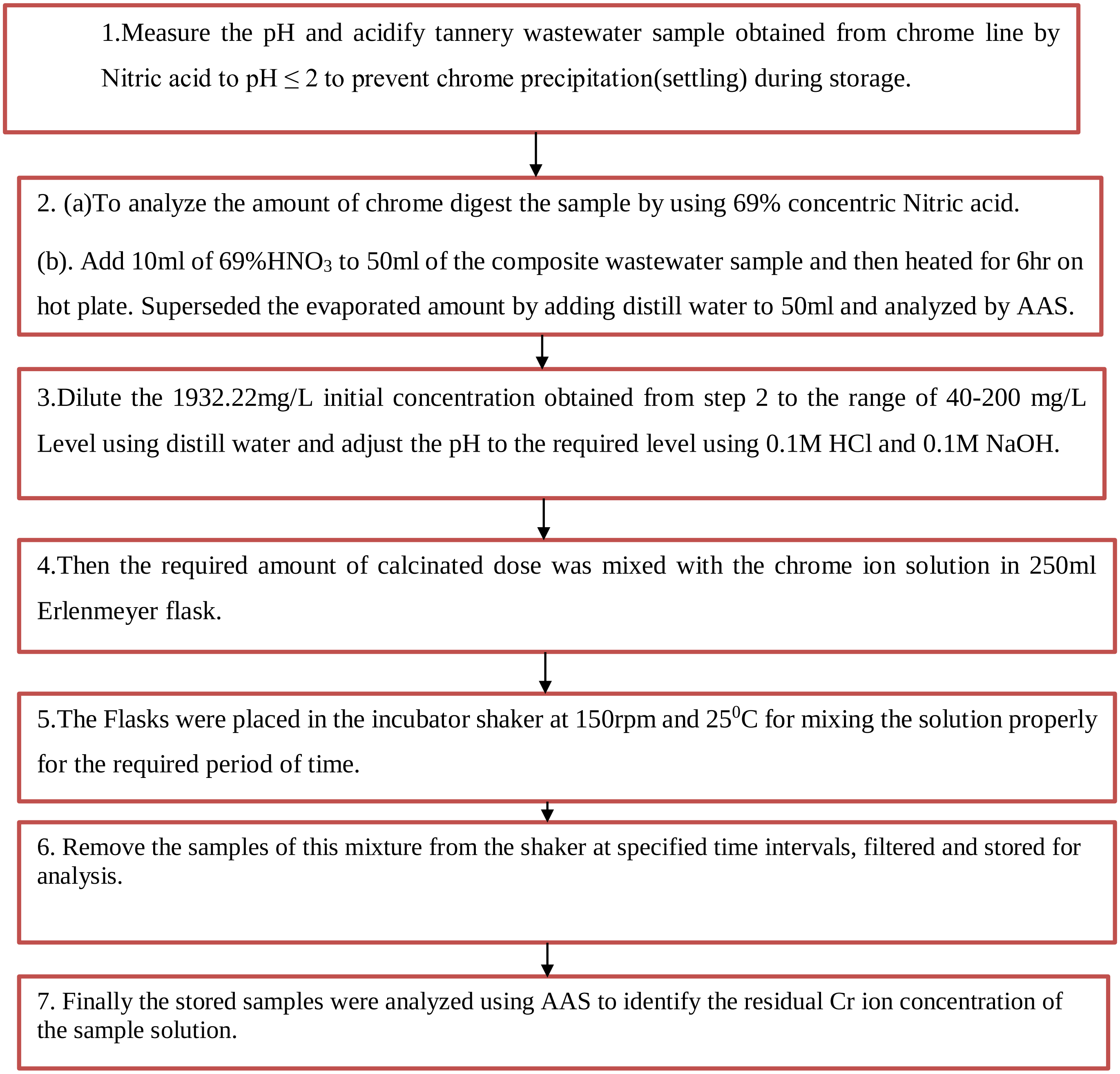
$$q = \frac{V(C_o-C_f)}{m} \text{ --}3.12$$

Where q is metal removal in mg/g, C_o is initial concentration, C_f concentration after adsorption, m is adsorbent mass in gram and v is volume of wastewater used during the experiment.

Figure 3. 2:Cr analysis (A) waste water sample, (B)Digestion and (C)Cr analysis using AAS

3.2.3 Batch adsorption studies

All experiments were carried out in batch mode. The batch adsorption studies were conducted at room temperature by agitating (150 rpm) weighed quantities of the adsorbent in 100 ml of chrome water solutions at the required pH, contact time, initial concentration and dose of adsorbent. These experiments were run in different Erlenmeyer glass flasks of 250 ml of capacity. In each flask first determined amount of adsorbent was added. After shaking the sample was taken and filtered by What man membrane filter paper of pore size 0.45 μm using a syringe. Finally, the sample was analyzed by FAAS for the remaining chromium in the solution. Equilibrium of this experiment was studied using Langmuir, Temkin and Freundlich, isotherm models. The kinetics was also studied by Pseudo- first order, Pseudo-second order and intra particle diffusion models. The detailed description of experimental procedure of batch adsorption studies was shown in the Figure below.



1.Measure the pH and acidify tannery wastewater sample obtained from chrome line by Nitric acid to pH ≤ 2 to prevent chrome precipitation(settling) during storage.

2. (a)To analyze the amount of chrome digest the sample by using 69% concentric Nitric acid.

(b). Add 10ml of 69%HNO_3 to 50ml of the composite wastewater sample and then heated for 6hr on hot plate. Superseded the evaporated amount by adding distill water to 50ml and analyzed by AAS.

3.Dilute the 1932.22mg/L initial concentration obtained from step 2 to the range of 40-200 mg/L Level using distill water and adjust the pH to the required level using 0.1M HCl and 0.1M NaOH.

4.Then the required amount of calcinated dose was mixed with the chrome ion solution in 250ml Erlenmeyer flask.

5.The Flasks were placed in the incubator shaker at 150rpm and 25^0C for mixing the solution properly for the required period of time.

6. Remove the samples of this mixture from the shaker at specified time intervals, filtered and stored for analysis.

7. Finally the stored samples were analyzed using AAS to identify the residual Cr ion concentration of the sample solution.

Figure 3. 3:Experimental procedure of batch adsorption studies

The effect of four parameters such as pH. contact time, initial concentration and dose were investigated as follows.

3.2.3.1 pH

The effect of the solution pH on chromium metal ions removal using calcinated eggshell as an adsorbent was conducted, using a 100 mL solution of 80 ppm of metal ion solution in the pH range of 1 to 11 with 2 pH interval at 25^oC and adsorbent dosage used was 0.75 g per 100ml solution. Flasks were shaken on an incubator shaker for 150rpm shaking speed and 120 min contact time to make sure equilibrium is reached. After equilibrium was reached, the solutions were filtrated and analyzed to determine the metal ion concentration.

3.2.3.2 Contact time

The effect of contact time on the adsorption efficiency and the optimum contact time for the process was studied by conducting the experiment from 15 to 135 minutes with 15minute time interval keeping other parameters such as pH, initial concentration and dose constant at 7, 80ppm and 0.75g respectively. The experiment was carried out at150 rpm incubator shaker and room temperature. After the time required for adsorption was arrived the adsorbent and the solution was filtered by wat man 0.45 filter paper. The filtered solution was analyzed using AAS for the remaining chromium in the solution.

3.2.3.3 Dose of adsorbent

The effect of adsorbent dose was studied by conducting the experiment from 0.25 to 1.5g/100ml of calcinated eggshell with 0.25g difference while keeping the parameter such as initial concentration, pH and contact time constant at 80ppm, 7 and 120 minute respectively. The experiments were conducted at room temperature and 150rpm incubator shaker. After the adsorption was accomplished the solution and adsorbent was filtered. The filtered solution was analyzed using AAS to determine the remaining chromium solution, then followed estimation of removal efficiency plot vs adsorbent dose used.

3.2.3.4 Initial concentration of chromium

Another most important factor in the adsorption process was the initial concentration of chromium. Samples in the concentration range of 40-200 mg/L with 49mg/L interval were prepared for the sake of determining the effect of initial concentration of chromium on the removal efficiency. Then it was put on the orbital shaker at 150rpm and room temperature by maintaining pH, dose and contact time constant at 7 ,7.5g and 120 minute respectively. Then the residual chromium ion concentration was recorded.

3.2.4 Kinetics study

It is very important to know the rate at which the process takes place and the factors that control the rate of the process, for this purpose kinetics of the process were evaluated. These experiments were conducted by varying the contact time from 15 to 135 min at room temperature, keeping constant other parameters such as pH, adsorbent dose and initial metal ion concentration at 7, 0.75g and 80ppm respectively. The samples were shaken at 150 rpm and withdrawn at 15minute time interval to determine the residual chromium ion in the solution. Then data from the experiment was introduced into pseudo-first order model of Lagergren, intra particle diffusion and pseudo-second order models of Ho and McKey (Dagmawi & Mekibib, 2013; De Souza Macedo et al.,2006; Gulipalli et al, 2011).

3.2.5 Adsorption Isotherm

When a solution is contacted with a solid adsorbent, molecules of adsorbate get transferred from the fluid to the solid until the concentration of adsorbate in solution as well as in the solid phase are in equilibrium. At equilibrium, equal amounts of solute eventually are being adsorbed and desorbed simultaneously. This is called adsorption equilibrium. The equilibrium data at a given temperature are represented by adsorption isotherm and the study of adsorption is important in a number of chemical processes ranging from the design of heterogeneous chemical reactors to purification of compounds by adsorption. Adsorption isotherm models such as Temkin, Langmuir and Freundlich models were used to fit the experimental data. It helps to find out the best fitting isotherm model in order to evaluate the efficiency of the prepared adsorbent and to develop a suitable batch adsorber design.

The adsorption capacity at equilibrium, qe (mg/g) was calculated by the following relationship:

$$qe = \frac{Co-Ce}{w} * v \text{-------------------------------------} 3.13$$

Where, Co and Ce (mgL^{-1}) are the initial and equilibrium metal ion concentrations respectively

3.2.6 Response surface design

The experimental design for optimization of Cr adsorption onto thermally modified eggshell was done by applying Response Surface Methodology (RSM) through three levels Central Composite

Design (CCD). Design Expert (Stat-Ease, Inc., version 11.1.0.1,) software was used for statistical data analysis. In order to investigate the effect of various independent process parameters such as initial concentration (A), pH (B), adsorbent dose (C) and contact time (D) on % removal of Cr, batch experiments were conducted based on the central composite design (CCD). A CCD with 30 experiments was used for the optimization of process parameters.

$N = 2^k + 2k + n_o = 2^4 + 2(4) + 6 = 30$

Where N is the total number of experiments required, K is the number of factors and n is the number of replications. Experimental results obtained are analyzed using response surface regression procedure of statistical analysis system. Correlation between responses and independent variables is obtained by fitting them into second order polynomial equation(Kasiri, Aleboyeh, & Aleboyeh, 2008). Design expert software version 11.1.0.1 was used for ANOVA analysis and for the optimization of adsorption process parameters.

Table 3. 1:Experimental factors and levels used in CCD

Independent Variables	Coded factor	Coded levels		
		-1	0	+1
Initial metal Concentration (mg/L)	A	80	120	160
PH meter	B	3	5	7
Adsorbent dose (g)	C	0.5	0.75	1
Contact time (min)	D	60	90	120

4. Result and Discussion

4.1 Preparation and Characterization of adsorbent

0.5kg of calcinated eggshell was obtained from the calcination process.

4.1.1 Moisture content

Measuring the moisture content of the adsorbent is one of the important features in order to know the adsorbent quality. The laboratory results of the moisture content of raw ES and MES were determined to be 0.99 and 0.133 % respectively, whereas dry matter content of MES samples greater than that of raw ES. The moisture content of a sample refers to the percentage of water content of the sample. These gave a tangible and substantial amount of organic matter needed was removed during modification. The moisture content of both raw and modified ES were slightly lower than the value reported in the literature, 1.174% (Bhaumik et al., 2012). The lower the moisture content, the higher its adsorption efficiency since water molecules can have the potential effect in the pores of an adsorbent through filling the adsorbent binding site before it contacts with the solution.

4.1.2 Ash value

The ash content is a measure of total amount of inorganic compounds such as minerals in the eggshell (Der-Jiun et al., 2012; Segura-Campos et al., 2013). The chicken eggshell was found to contain 76.3% ash. This value was greater than with the ash content of eggshell reported in literature 45.29 (Ajala et al., 2018).The high ash content was needed as adsorbent for this study.

4.1.3 volatile mater and fixed carbon content of eggshell powder

The laboratory result of volatile matter amount of eggshell was 2.6%. Hence this value is low it has no negative effect on the amount of calcinated eggshell powder produced.

Fixed carbon is the solid combustible residue that remains after the eggshell was heated and the volatile matter was expelled. The fixed-carbon content of eggshell was determined by subtracting the percentages of moisture, volatile matter, and ash from a sample and it was obtained 20.11%.

4.1.4 Bulk density

Bulk densities (g/cm^3) for raw ESP and calcinated were 0.769 g/cm^3 and 0.425 g/cm^{3}respectively.The obtained bulk density of this study were less than the bulk density reported by (Bhaumik et al., 2012). It was observed that the bulk density of calcinated eggshell was less than the ground raw eggshell powder.

The smaller bulk density the higher porosity of adsorbent was obtained.

4.1.5 Particle density

The particle density laboratory result for both ESP and calcinated eggshell were 1.03 g/cm^{3}and 2.06g/cm^3 respectively. From those overview the bulk density decreased from the raw to the modified whereas the particle density increases from the raw to the calcinated eggshell powder and this indicates the porosity is high with high value of particle density and low with high value of bulk density.

4.1.6 Porosity

In the current study powdered ES and calcinated were found to have 25.34 and79.36% of porosity. According to Malik et al. (2006) for activated carbon there is a direct relation between porosity and adsorptive property. An increase in porosity means the adsorbent has relatively large potential of adsorbing the adsorbate. Therefore, calcination (thermal modification) of eggshell increased its porosity.

4.1.7 Fourier transform infrared (FT-IR) spectrum analyses of eggshell powder

The Fourier transfer infrared spectroscopy (FTIR) analysis has been considered as a kind of direct mean for identifying the characteristic functional groups on the surface of the eggshell, which are responsible for adsorption of metal ions(Bhaumik et al., 2012). The FTIR spectrum of eggshell powder was recorded to obtain the information regarding the stretching and bending vibrations of these functional groups. Figure 4.1 illustrates the FTIR analysis for chicken ESP and chicken calcinated eggshell through numerous bands from 4000 to 400 cm^{-1}.

From Figure 4.1 it can be distinguished that in both spectra appears a prominent peak of carbonate CO_3^{2-} at 874 and 875 cm^{-1}respectivly. According to Hariharan et al., (2014) similar absorption peak for ESP is reported at 875 cm^{-1}. The presence of these bands justifies the carbonate content in ESP. The band at 1416 cm^{-1} is much sharper compare to the raw eggshell in in the Figure 4.1below indicates the stretching of C-H bond. The peak 713 cm^{-1} is referred to the vibration bands of the carbonate CO_3^{2-} molecular ion for C-O symmetric stretching (Cree & Rutter, 2015). Shan et al., (2015) reported that calcium oxide has a strong broad band between 250 cm^{-1}and 600 cm^{-1} corresponding to a stretching vibration of the Ca-O group. The peak at 466 and 479 cm^{-1} figure4.2 indicates the presence of Ca-O band.

A peak at 3643 cm^{-1} in figure 4.1 for calcinated eggshell is due to the OH^{-}group which corresponded to calcium hydroxide ($Ca(OH)_2$) from adsorption of moisture in the sample by calcium oxide (CaO) and similar result was reported by Cree & Rutter, (2015). The similarity of peaks for RESP, MESP and Cr loaded MESP were due to absorbance of moisture and carbon dioxide from environment.

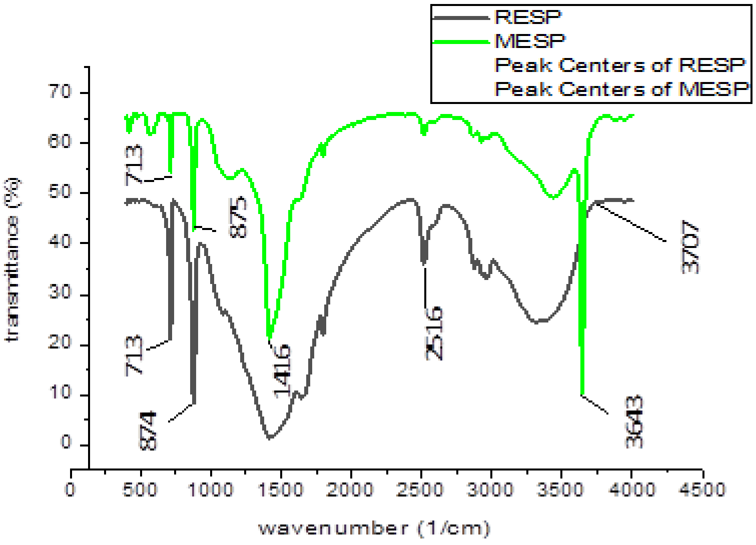


Figure 4. 1:FTIR for raw Eggshell and Modified eggshell

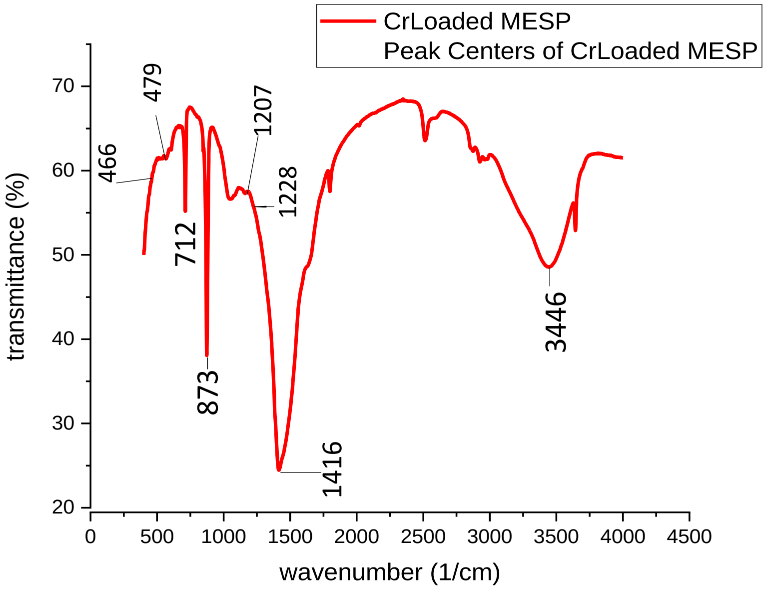


Figure 4. 2:FTIR for Cr loaded calcinated eggshell

4.1.8 X-ray diffraction analysis (XRD)

The peaks relating to the CaO phase were detected for the eggshells calcined at 800˚C for 2hr. The 2θ values of CaO peaks are 29.74,34.42 and 47.82 and these peaks indicates the conversion of calcium carbonate to calcium oxide and well much with (JCPDS No. 00-004-0777). Similar result was obtained by (Mohadi et al.,2016).From figure 4.3 the narrow diffraction peaks indicates the phase composition have crystalline structure.

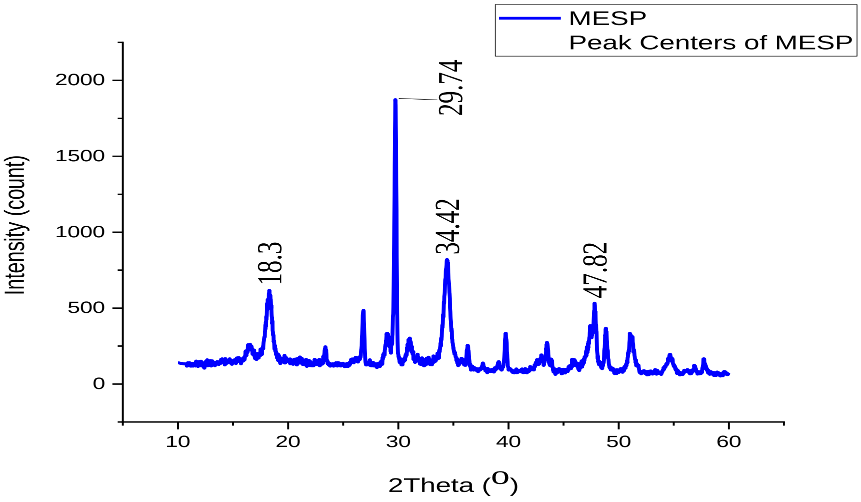


Figure 4. 3: XRD pattern of calcinated eggshell

4.1.9 Point of zero charge value

To understand the adsorption mechanism, it is necessary to determine the point of zero charge (pHp_{zc}) of the adsorbent because the point of zero charge is the pH value at which the surface charge of an adsorbent equals to zero. At pH value less than pH_{pzc}, the surface charge on the adsorbent is a net positive charge, while at pH value greater than pH_{pzc} the surface charge on the adsorbent is a net negative charge (Bhaumik et al., 2012). Therefore, cations adsorption on surface of any adsorbent is favorable at pH value higher than pH_{pzc}. Here, the experimental result of pH_{pzc} of modified eggshell powder was obtained as 6.71 as shown in the figure below

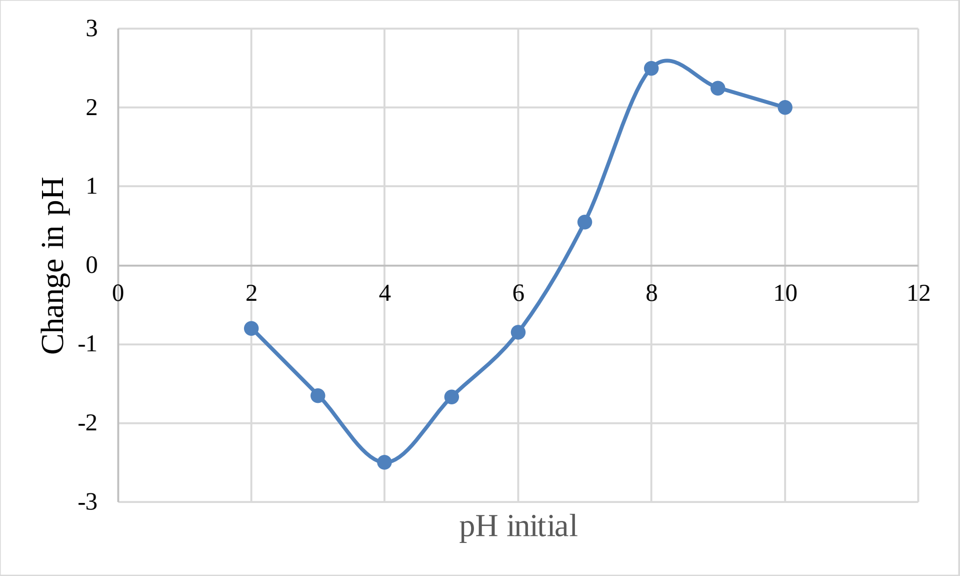


Figure 4. 4:Zero Point charge of calcinated eggshell powder.

This indicates that pH values should be maintained greater than 6.71 to ensure a predominant negatively charged surface resulting in electrostatic attraction between adsorbate molecules and biomass of adsorbent. Below this pH, the surface charge of the adsorbent biomass acquires positively charged due to protonation of functional groups which making H^+ ions compete effectively with the Cr cations as a result these a decrease in the expected amount of adsorbate adsorbed.

4.1.10 Specific surface area determination

The surface area was calculated using equation 3.8 under the materials and methods section. The titrated volume of NaOH required to raise the pH of the solution from four to nine was 1.8 and 2.9 ml for ESP and calcinated eggshell respectively. The resulting specific surface area of eggshell was 32.85 m^2per gram and this was greater than 21 m^2 per gram which was reported in the literature(Bhaumik et al., 2012). The specific surface area of thermally modified eggshell was 68m^2 per gram. This result was between 50 and 90 the specific surface area for calcinated calcium carbonate obtained by(Borgwardt, 1985).From the laboratory result observed calcination increases the surface area of the adsorbent.

tannery wastewater was measured and reported in table 4.1. In addition, chromium ion the characterization indicates chromium line waste water also have BOD, COD, TS etc. above discharge limit value.

4.2 Study and optimize the effect of the selected adsorption parameters

4.2.1 Effect of pH

The graph in figure 4.5 showed that the percentage removal of Cr increased with pH. This was due to the fact that the Point of zero charge of the calcinated eggshell was at pH = 6.71. The cationic adsorption is favored at pH greater than pHpzc. Minimum percent removal of Cr was observed 32.47 at pH 1 and the maximum removal was 98.53 % at pH 7. At low pH, H_3O^+ ion competes with Cr^{3+} ions mostly the trivalent chromium for binding and surrounded hydronium ions (H^+) preventing the metal ions from approaching the binding sites and it could be responsible for low adsorption capacities. Protonated adsorption sites were incapable of binding metal ions due to electrostatic repulsion between positively charged metal ions and positive charged sites. Hence, only low percentage of Cr $^{3+}$ions were adsorbed. As the pH increased, there were fewer H^+ ions present in the solution and consequently more negatively charged sites were made available and this facilitated greater metal ions uptake by electrostatic attraction. Since more hydroxyl groups are in thermally modified eggshell surface when pH higher than 7, adsorption was reduced due to production of Polynuclear species $Cr_2(OH)_2$ and $Cr_3(OH)_4^{5+}$(Gunatilake, 2016). (Gunatilake, 2016) also found similar results.

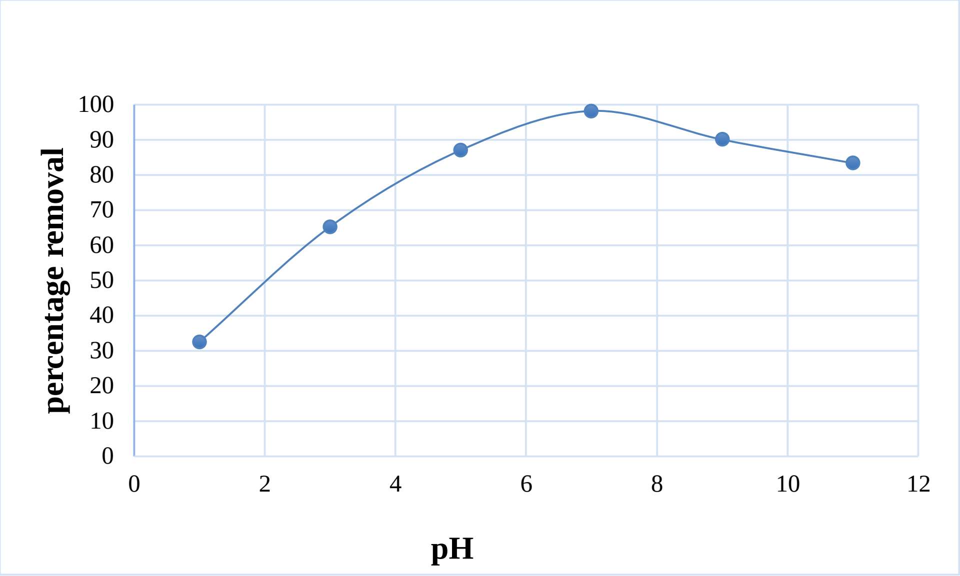


Figure 4. 5: Effect of pH on Cr adsorption

4.2.2 Effect of adsorbent dose

The percentage adsorption of Cr(III) was studied by increasing the adsorbent dose from 0.25 to 1.5 g/ml in 0.25g dose interval at neutral pH,120minute contact time and 80 mg/L initial concentration of Cr(III) solution. The results indicated more than 99.56 % removal of Cr(III) with 1 g/100ml adsorbent dose after 120 min of contact time. It is observed that within the range of adsorbent dose studied, the percent removal increases with an increase in the amount of adsorbent up to an optimum amount of the adsorbent beyond which the percent removal remains nearly the same (Fig 4.6). The increase in the percentage adsorption with increase in the adsorbent dosage is due to the increase in the number of adsorption sites. Similar effect is estimated by (Bedemo, Chandravanshi, & Zewge, 2016).

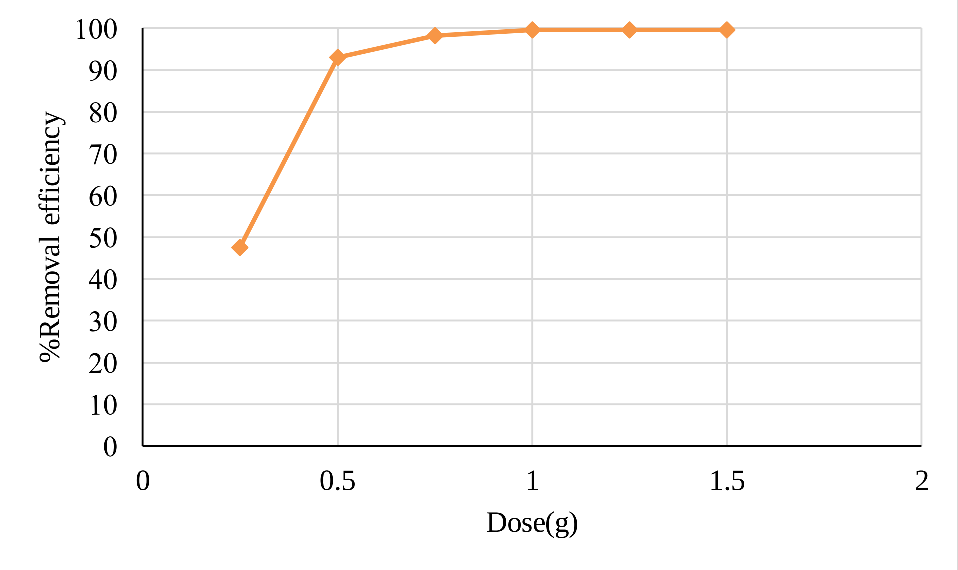


Figure 4. 6:Effect of calcinated eggshell dosage on Cr adsorption

4.2.3 Effect of contact time

Generally, the adsorption capacity and the removal efficiency of metal ions by adsorbents will increase with increase in contact time. However, in practice it is necessary to optimize the contact time, considering the adsorption process. The effect of contact time on the adsorption of Cr^{3+} ions using calcinated eggshell adsorbents investigated over time interval of 15 to 135 minute. Fig 4.7 represent the results of the effects of contact time on the Cr adsorption. As illustrated in fig 4.7 it can be concluded that as the contact time increases removal efficiency and capacity increases until equilibrium was reached at 120 min. It is clear that increasing the contact time beyond the 120 min had not significant impact on adsorption performance, it was wastage of time.

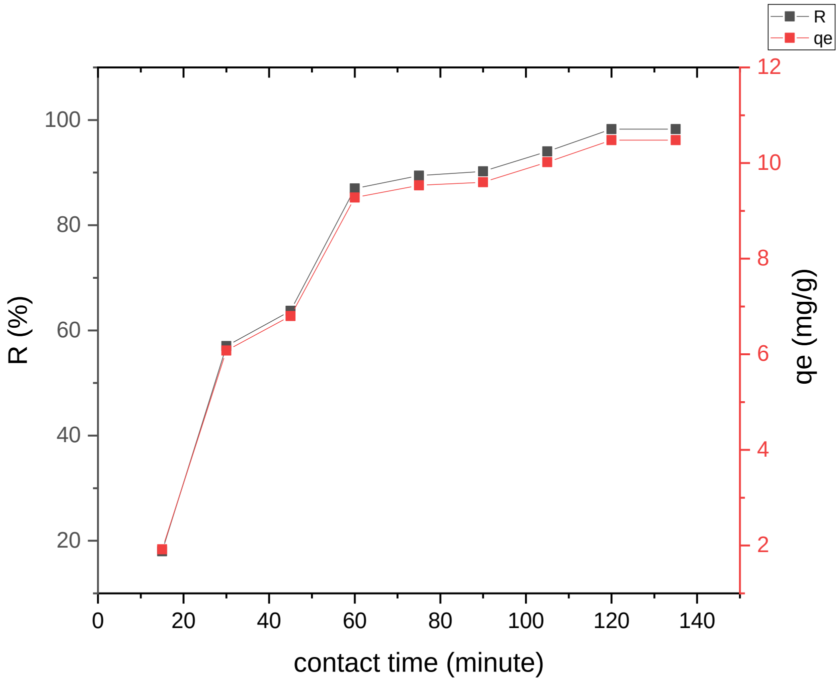


Figure 4. 7:Effect of Contact time on Cr adsorption

4.2.4 Effect of initial concentration

Adsorption experiments at varying initial Cr concentrations from 40 to 200 mg/L were performed with fixed doses of adsorbent. The result indicates that percentage Cr(III) removal decreases as the initial concentration of Cr(III) was increased. Cr(III) removal ranged from 99.75 to 65.53 % at initial Cr(III) concentration of 40–200 mg/L (Fig. 4.8). This can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration. Since percent removal = (Co − Ce)/Co, another reason for decrease in percent removal is larger increase in the denominator (Co) value in comparison to that of (Co − Ce) value. But, the actual amount of chromium removed (mg) per gram of the adsorbent is lager for higher concentration. This is because of the increased driving force for mass transfer between aqueous solution of metal ions and the solid adsorbent.

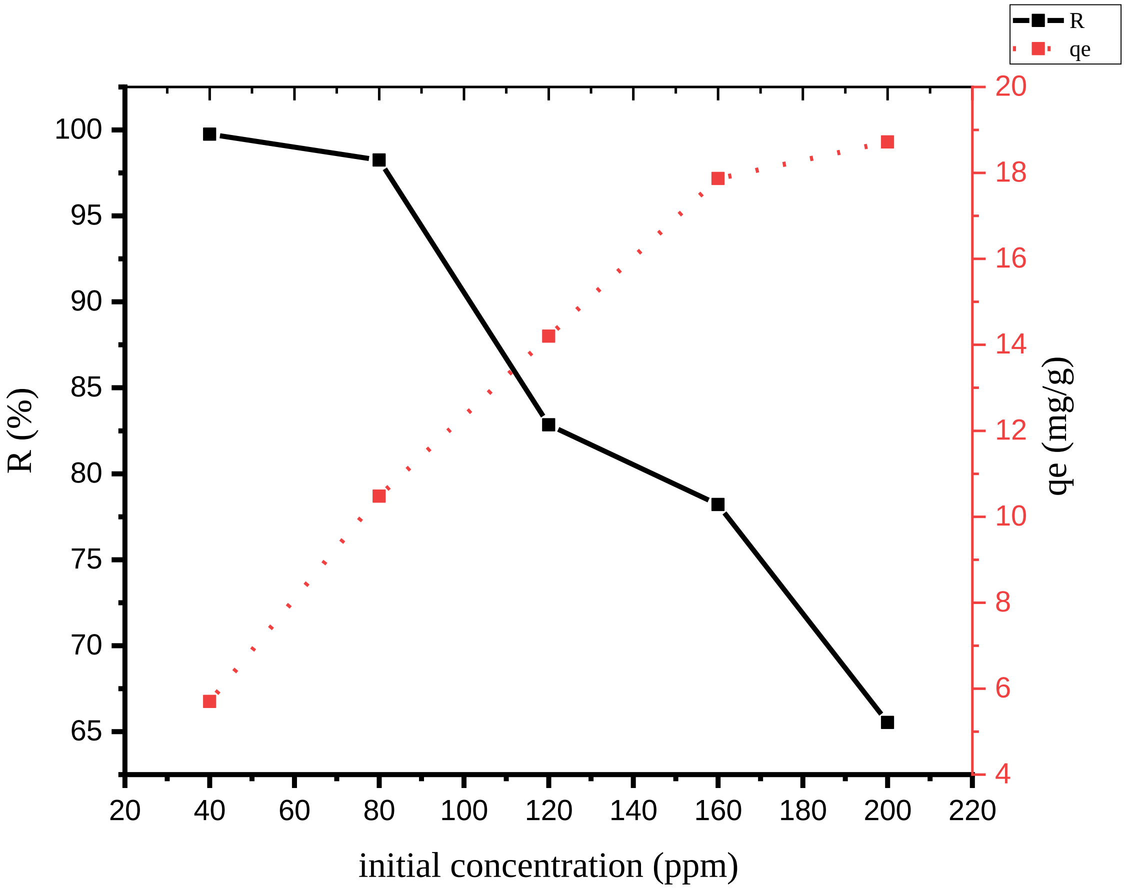


Figure 4. 8:Effect of initial concentration on adsorption

4.2.5 Evaluation of the adsorption isotherm models

Equilibrium isotherms model equations such as Langmuir, Freundlich and Temkin isotherms are used to describe experimental adsorption data in the batch model to describe the relation between adsorbate on the surface of adsorbent that is the amount of species adsorbed per unit mass of adsorbent and concentration solute left in the solution. The suitability of a certain adsorption isotherm to describe the obtained data depends on the correlation coefficient (R^2) of the profile representing the obtained data.

The analysis of the isotherm data is important to develop an equation which accurately represents the results and could be used for design purposes. In order to investigate the adsorption isotherm, the adsorption data can be interpreted using several relationships which describe the distribution of Cr ion between the aqueous and solid phases. In order to investigate the adsorption isotherm, the experimental data of equilibrium isotherms were interpreted using three equilibrium models;

the Langmuir, Freundlich and Temkin isotherm in equation 2.3,2.6 and 2.9 respectively.

These isotherms relate metal uptake per unit mass of adsorbent, *qe*, to the equilibrium adsorbate concentration in the bulk fluid phase *Ce*. The linearized Langmuir, Freundlich and Temkin adsorption isotherms were used in order to check the best fitting model. Langmuir model fitted very well to the sorption data in the studied concentration range with a higher correlation coefficient R^2 value 0.991 as shown in fig.4.9. The Langmuir model assumes that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the surface of the identical (specific) adsorbent, the energy of adsorption is fixed and molecules of the adsorbent will not migrate in the surface plane. The q_m and K_L values of the Langmuir constants were calculated from Ce/qe vs Ce plot as 19.011 mg/g, 0.43 L/mg respectively. R_L a separation factor given as

$1/\ (1+K_LC_0)$ also showed a result between 0 and 1 which explains a favorable adsorption (N. rajamohan *et al*, 2013).

Table 4. 1:Langmuir separation factor RL

Concentration (ppm)	Langmuir Separation factor R_L
	Cr as total
40	0.055
80	0.0282
120	0.019
160	0.014
200	0.011

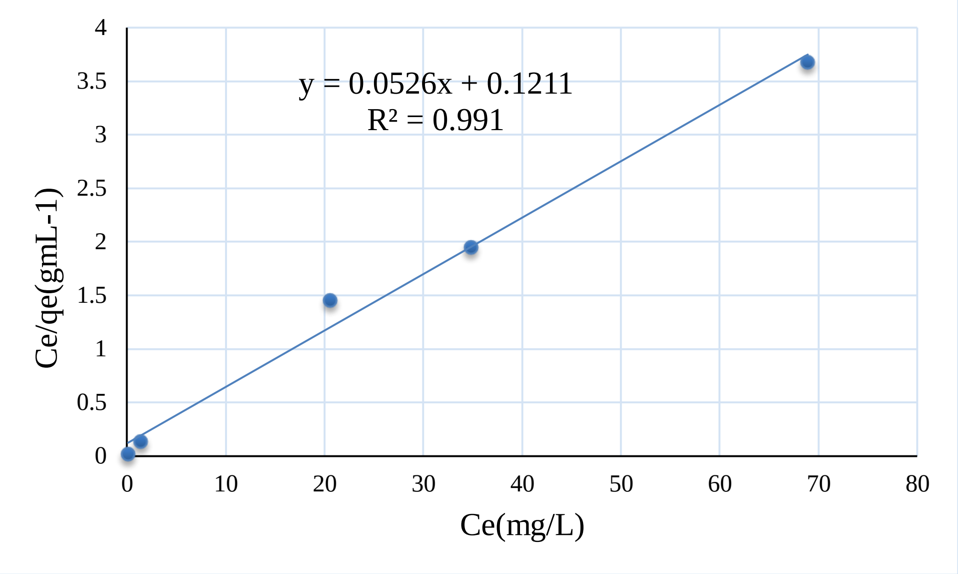


Figure 4. 9:Langmuir isotherm of Cr removal

Freundlich isotherm model was plotted as log Ce versus log qe on figure 4.10 to test the validity generate the values of freundlich constants K_f indicator of adsorption capacity and n adsorption intensity. The freundlich constants K_f and n were 8.97mg/g and 5.63 The correlation coefficient R^2obtained was 0.9775.

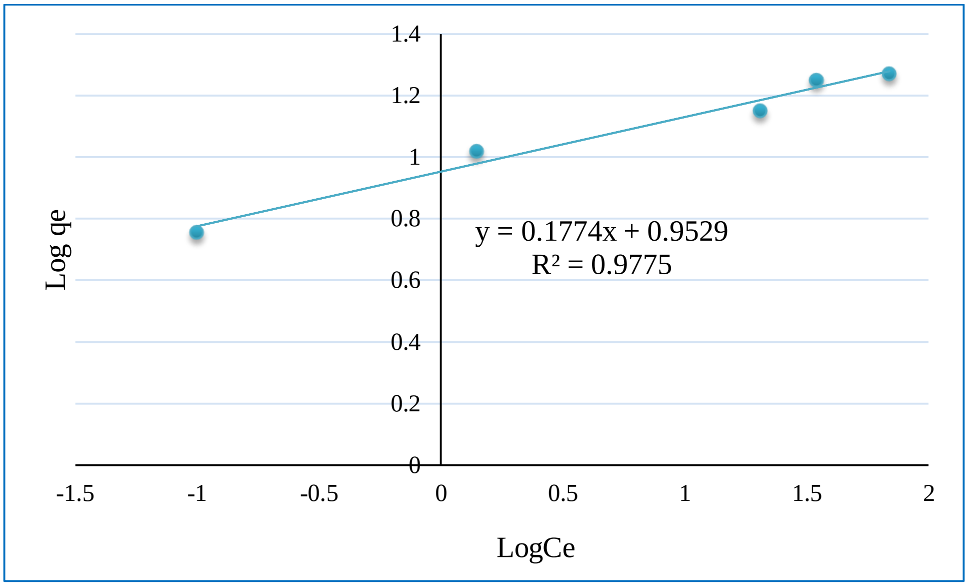


Figure 4. 10:Freundlich isotherm of Cr removal.

A plot of qe versus ln Ce is depicted on figure 4.11 to test the validity of Temkin isotherm and determine the equilibrium constants. B_1 and K_T. K_T is the equilibrium binding constant (l/mol) corresponding to the maximum binding energy and constant B1 is related to the heat of adsorption. As seen on the graph below the R^2 value is 0.9655. This is smaller than the correlation coefficient obtained by Langmuir isotherm and Freundlich isotherm which means the isotherm experimental data deviates the linear regression equation however, the Langmuir isotherm fits well. The highest correlation coefficient (R^2) the best fit isotherm model. Similar isotherm model is investigated for chromium adsorption using various agricultural waste(Shrivastava and Gupta, 2015).

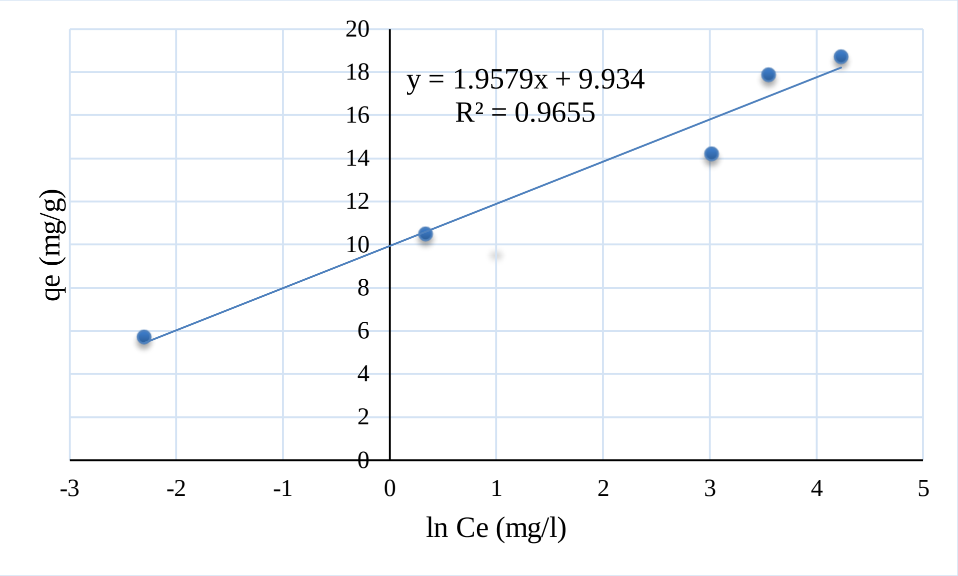


Figure 4. 11:Temkin isotherm of Cr removal

Table 4. 2:summary equilibrium parameter value of Cr with different isotherms.

Heavy Metal ions	Langmuir Isotherm			Freundlich Isotherm			Temkin Isotherm		
	q_m (mg/g)	K_L(L/mg)	R^2	n	K_f (mg/g)	R^2	K_T(mg/L)	B(L/g) (RT/b)	R^2
Cr as total	19.011	0.43	0.991	5.63	8.97	0.9775	40371.2	1.95	0.9655

Comparison of Cr ion uptake capacity by the adsorbent used in this study and those reported elsewhere in literature is shown in Table 4.5. From table 4.5 the higher adsorption capacity of chromium ion was 16.300998 mg per gram of coconut shell. Maximum percentage removal of

81.999% was investigated using coconut shell adsorbent than the other adsorbents used by these authors(Shrivastava & Gupta, 2015). The adsorption capacity of chromium ion using calcinated eggshell was found 10.48 mg/g. Even though this adsorption capacity is less than 16.300998mg/g, it's removal efficiency was greater than 81.999%. It can be concluded that the sorption capacity of the calcinated eggshell is still higher than some of the available ones in the literature.

4.2.6 Kinetic studies

The kinetic models pseudo first order, pseudo-second-order and intra-particle diffusion were used to analyze the kinetic behavior of the metal sorption process. The kinetic rate constants, adsorption capacities and correlation coefficient were calculated from the slope and intercept of their corresponding graphs (table 4.5). The calculated, q_{cal} values derived from the pseudo second order model for sorption of metal ions were close to the experimental (q_{exp}) values. The pseudo second order equation appeared to be the best fitting model than both first order and intra particle diffusion equations because it has highest R^2 value. This kinetic study confirmed that bio sorption of Cr ions on calcinated eggshell was a multistep process involving adsorption Cr ions on the external surface (diffusion of metal ions from the bulk solution to the surface of the adsorbent) and diffusion into the interior (diffusion of metal ions from the surface to internal sites(Nguyen et al., 2013). Therefore, the adsorption process can be approximated more favorably by the pseudo-second order kinetic model, suggesting the adsorption process to be a chemisorption process involving exchange or sharing of electrons between adsorbent and adsorbate.

The pseudo-first order rate equation was the first to describe the adsorption rate based on adsorption capacity of the adsorbent (solid phase) (Ho, 2006). This model considers that the rate of occupation of adsorption sites is proportional to the number of unoccupied sites. The linearized pseudo-first order kinetic model is expressed in equation 2.12. A straight line of $\ln(q_e-q_t)$ versus t indicates the applicability of this kinetic model as show in fig.4.12. q_e and k_1 values can be determined from the intercept and the slope of the plot, respectively. In most cases, the pseudo-first order model does not fit well along the range of contact time and is usually applicable over the initial 20-30 min of the adsorption process(Aksu et al,.1992).

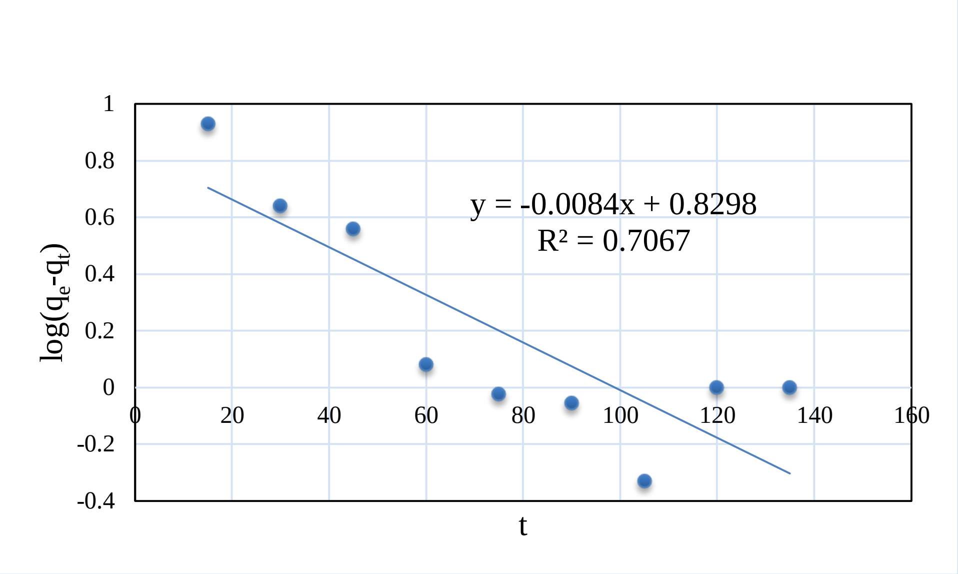


Figure 4. 12: Pseudo -first-order kinetic model plot of Cr adsorption

The pseudo-second order kinetic model is also based on the sorption capacity of the adsorbent and it assumes that bio sorption follows a second-order mechanism, so the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites(Netzahuatl-Muñoz et al., 2010). The pseudo-second order kinetic model is expressed in equation 2.15. The value q_e and k_2 was calculated from the plot t/qt vs t corresponding slope and intercept respectively.

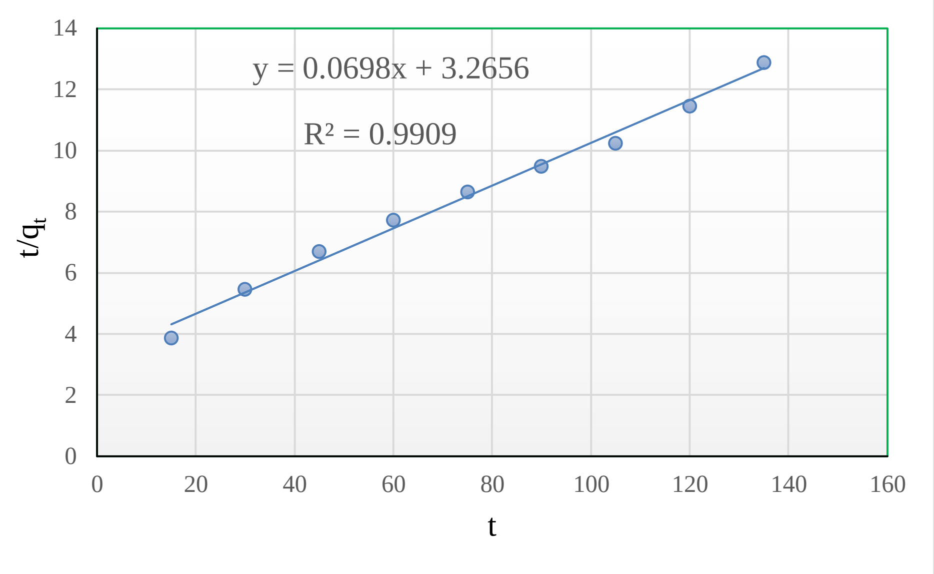


Figure 4. 13:Pseudo–second-order kinetic model plot of Cr adsorption.

According to (Lakshmi et al., 2009) if a plot of q_t versus $t^{1/2}$ is linear and passes through the origin, then intra-particle diffusion is the sole rate-limiting step. However, Figure 4.14 revealed the linear plots did not pass through the origin. Although intra-particle diffusion was involved in the adsorption process, it was not the sole rate- controlling step.

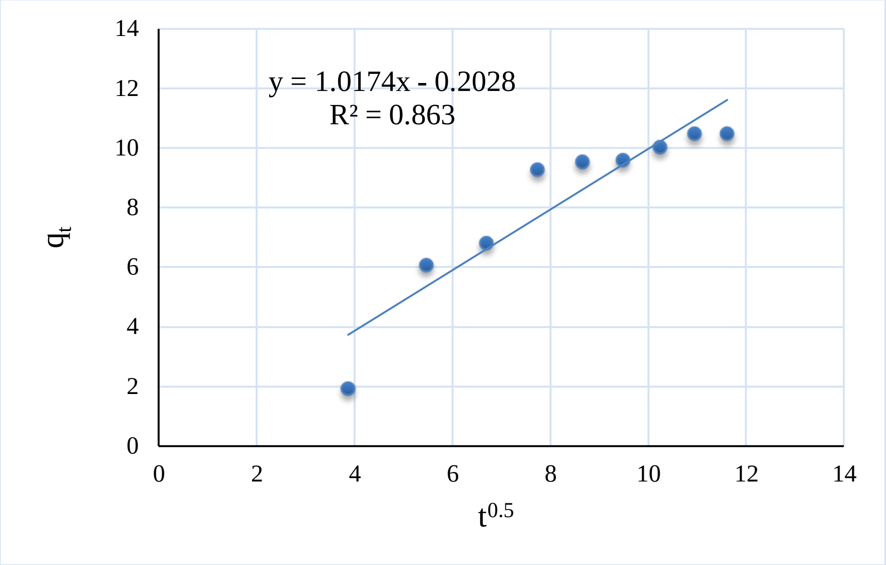


Figure 4. 14:Intra particle diffusion kinetic model plot of Cr adsorption.

Table 4. 3:pseudo first order, pseudo second order and intraparticle Diffusion parameters for chromium bio sorption on to calcinated eggshell.

Heavy Metal ions	First order kinetic model			Pseudo Second order			Intraparticle Diffusion		
	q_e (mg/g)	K_1 (mg/g*minute)	R^2	qe(mg/g)	K_2 (mg*min)/g	R^2	Ki $mgg^{-1}min^{-1/2}$	C	R^2
Cr as total	6.75	0.019	0.706	14.32	0.0015	0.9909	1.017	-0.2028	0.86

The pseudo-first-order model rendered the lowest correlation coefficient, in contrast, the pseudo-second order model satisfactorily described the experimental kinetic data (Figure 4.13). This tendency comes as an indication that the rate-limiting step in bio sorption of chromium ions onto calcinated eggshell is a chemical sorption (chemisorption) involving valence forces through the sharing or exchange of electrons between sorbent and sorbate.

4.3 Analysis of variance (ANOVA) for the design model

Design expert software was used to design the experiment and randomize the runs. Randomization ensures that the conditions in one run neither depend on the conditions of the previous runs nor predict the conditions in the subsequent runs. Randomization is essential for drawing conclusions from the experiment, in correct, unambiguous and defensible manner.

RSM was applied to model and optimize different process parameters effect of pH, adsorbent dose, contacting time and initial concentration in adsorption percentage of the response chromium as total. The operational parameters with optimum adsorption % were predicted using developed model. Accordingly, first model development and evaluation was discussed. Second, the effect of independent variables on response variables were examined. Then finally using the model optimum points of operational parameters were identified.

4.3.1 Chromium adsorption modeling and model analysis

For each of experimental runs adsorption percentage was determined using the methodology described. Experimental results of adsorption percentage were fed to design expert 11.1.0.1 version, for ANOVA, graphical and multiple regression fitting sequential or extra sums of squares for the linear. A quadratic and cubic terms in the model there is a warning message concerning aliasing in the cubic model because the CCD does not contain enough runs to support a full cubic model. The small P value for quadratic term we decided to fit the second-order model to the removal efficiency of Cr response. The ANOVA summary percentage removal of Cr is given in Table4.7. The parameters with probability value less than 0.05 are said to be significant. The probability of the model when it is<0.0001 showing that the suggested model is highly significant. AS shown in table 4.8 quadratic model is suggested by the software.

Table 4. 4: Analysis of variance (ANOVA) for Quadratic model

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	15025.80	14	1073.27	309.55	< 0.0001	Significant
A-A	2778.45	1	2778.45	801.34	< 0.0001	
B-B	7475.48	1	7475.48	2156.04	< 0.0001	
C-C	911.80	1	911.80	262.98	< 0.0001	
D-D	1207.43	1	1207.43	348.24	< 0.0001	
AB	5.21	1	5.21	1.50	0.2392	
AC	0.2186	1	0.2186	0.0630	0.8052	
AD	1.54	1	1.54	0.4453	0.5147	
BC	254.80	1	254.80	73.49	< 0.0001	
BD	28.92	1	28.92	8.34	0.0113	
CD	0.0077	1	0.0077	0.0022	0.9631	
A^2	22.64	1	22.64	6.53	0.0220	
B^2	1830.13	1	1830.13	527.83	< 0.0001	
C^2	695.61	1	695.61	200.62	< 0.0001	
D^2	317.72	1	317.72	91.63	< 0.0001	
Residual	52.01	15	3.47			
Lack of Fit	40.28	10	4.03	1.72	0.2862	not significant
Pure Error	11.73	5	2.35			
Cor Total	15077.81	29				
R^2 = 0.9966 Adjusted R^2 = 0.9933 Predicted R^2 = 0.9835 Adeq Precision =66.0046						

The Model F-value of 309.55 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, D, BC, BD, A^2, B^2, C^2, D^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

The Lack of Fit F-value of 1.72 implies the Lack of Fit is not significant relative to the pure error. Non-significant lack of fit is good in order to fit the selected model. The Predicted R^2 of 0.9835 is in reasonable agreement with the Adjusted R^2 of 0.9933; i.e. the difference is less than 0.2. Adeq Precision measures the signal to noise ratio is 66.005. The ratio determined is greater than

4, representing that the quadratic model can be used to navigate the design space and to find the optimal conditions of this process. Furthermore, the fitting of the experimental data to the regression model was checked and suitably explained by the value of the adjusted determination coefficient (R^2Adj= 0.9933). This result means that 99.33 % of the total variation on Cr adsorption data can be explained by the selected model.

Final Equation in Terms of Coded Factors:

%Cr Removal = $80.57-10.76A+17.65B+6.16C+7.09D-3.99BC-1.34BD -0.908A^2-8.17B^2-5.04C^2-3.40D^2$ --------------------------------------4.1

The above equation describes how Cr adsorption onto thermally modified eggshell was affected by the individual variables (linear and quadratic) or double interaction. Negative coefficient values indicate that individual or double interactions factors negatively affect Cr adsorption while positive coefficient values represent that factors increase Cr removal percentage. For instance, among all linear factors initial concentration had a negative effect but pH, adsorbent dose and contact time had a positive effect on Cr removal.

Table 4. 5: model summary statistics

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	< 0.0001	0.0001	0.7919	0.7586	
2FI	0.8818	< 0.0001	0.7556	0.7258	
Quadratic	**< 0.0001**	**0.2862**	**0.9933**	**0.9835**	**Suggested**
Cubic	0.1533	0.5733	0.9960	0.9710	Aliased

4.3.2 Model diagnosis

Model diagnostic plots are graphical summaries for case statistics. The plots of residuals showed that how well the model satisfies the residual assumptions of the analysis of variance. Different model diagnostic plots were plotted are the normal probability plot compares the distribution of the residuals to a normal distribution (the straight line). Expect some scatter even with normal data. Look only for definite patterns like an s-shaped curve, which indicates that a transformation of the response may provide a better analysis. The residuals vs. predicted plot checks for constant variance across the range of predictions. Non-constant variance is indicating by a pattern in the plot (upward or downward curves, etc.). If the plot appears randomly scattered between the red lines, then the assumption of constant variance is confirmed.

The predicted vs. actual a graph of the predicted response values versus the actual response values. It primarily used to detect a value, or group of values, that are not predicted well by the model. These values for the model are close indicating a correspondence between the mathematical model and the experimental data (actual value). Normal probability plot of the studentized residuals are used to check for normality of residuals. Figure 4.15b shows the relationship which is the straight line means that no response transformation was required and that there was no apparent problem with normality. The relationship between actual values and predicted values (Fig.4.15a) showed that the actual values are overlaps to the straight line, indicating good fitness of the model. Again in Fig4.15(c&d), the plot of studentized residuals vs predicted (run number) was tested and the residuals were scattered randomly around ±3.00. This was an indication of better fitment of the model with the experimental data.

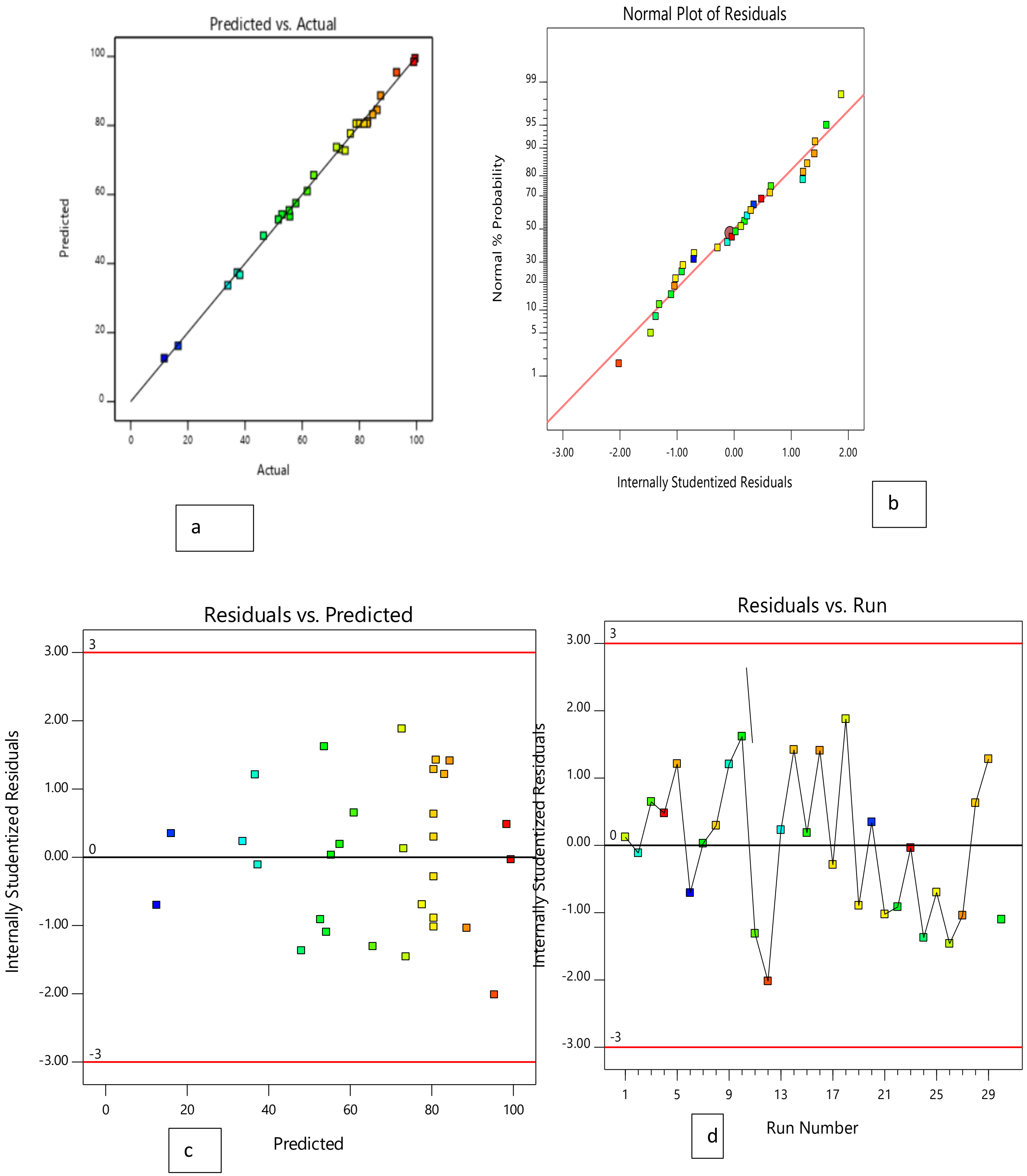


Figure 4. 15:Model diagnostic plots of Cr adsorption on calcinated eggshell

4.3.3 Effect of significant model terms for Chromium Removal using calcinated eggshell

4.3.3.1 Single effects of A, B, C and D model terms

The main and interaction effects observed on the analysis of variance were furtherly studied with the help of single and interaction graphs of design expert. Design expert version 11.1.0.1 reflects the main single effects in a linear model tem by considering one factor vary starting from its low level to high level while the other factors at their medium level. As shown in figure 4.16 the percentage removal of chromium ions decreased with increasing initial concentration of sample. A maximum percent removal,77.304% was obtained at 80ppm and minimum percent removal, 55.78 % was obtained at 160ppm.For pH minimum percent removal, 48.88% was obtained at pH 3 and a maximum percent removal,84.2% was obtained at pH 7. This is due to adsorption at different pH can be explained by the species distribution of chromium in water and the nature of adsorbent surface. In acidic pH, the predominant species of Cr(III) cations are: $Cr^{3+,}$ $CrOH^{2+}$ and $CrOH^{2+}$ and under acidic conditions, the surface of the adsorbent becomes protonated and hence there is a decrease in the electrostatic attraction between the Cr(III) species and the adsorbent surface, with a consequent decrease in percentage adsorption. But as pH increases, the adsorbent surface becomes less protonated and will have strong attraction for cationic species of Cr(III). A minimum percent removal of 60.38 was obtained at 0.5g for factor adsorbent dose and maximum removal of 72.7% was obtained at 1g. This is due to high availability of active sites. The effect of contact time vs percent removal shows direct relationship until the removal percent reaches equilibrium. From the graph below a minimum percent removal,59.45% was obtained at 60 min and a maximum percent removal,73.64% was obtained at 120 min. These values generally agreed with vales reported under the literature(Bedemo et al., 2016).

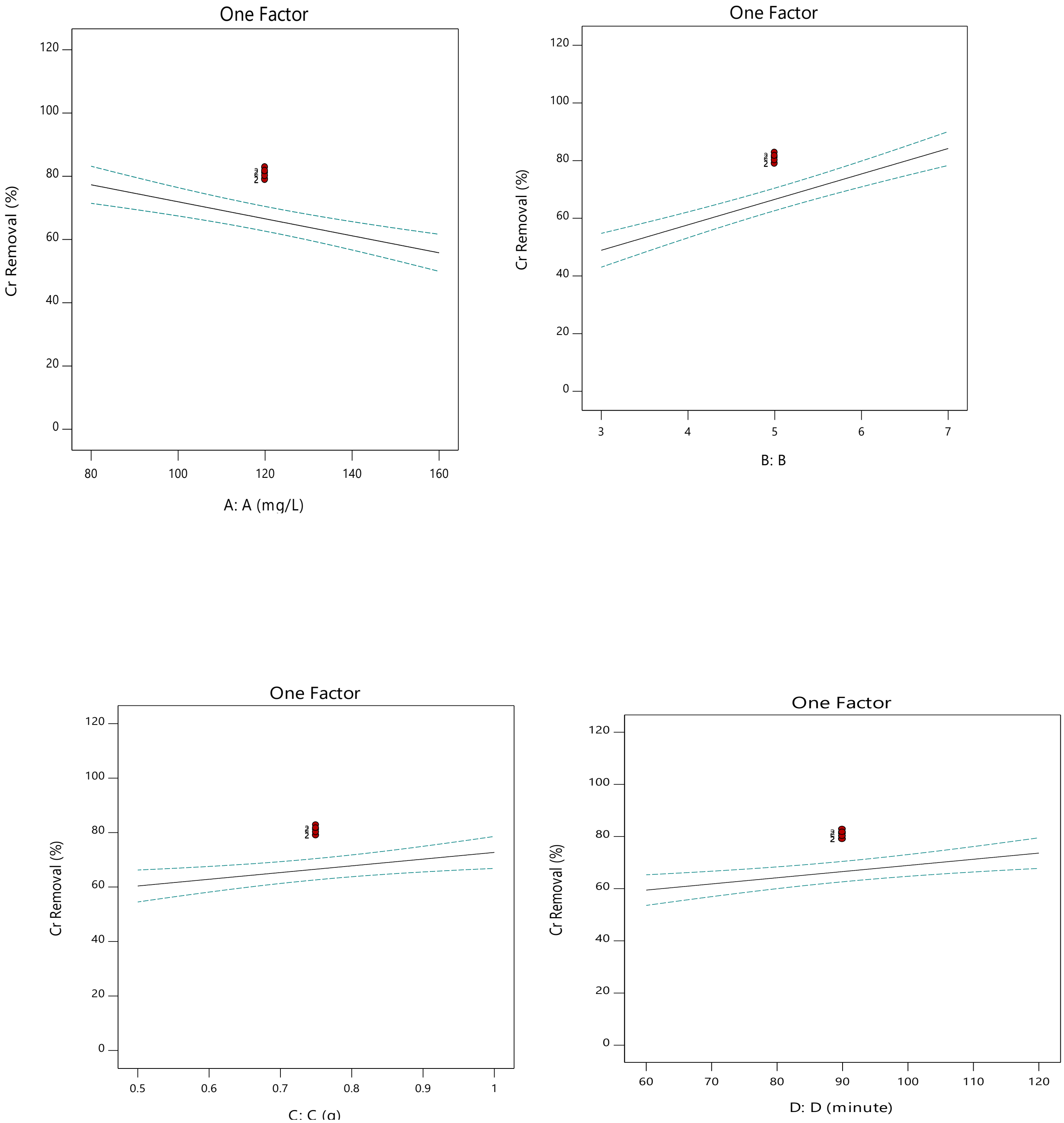
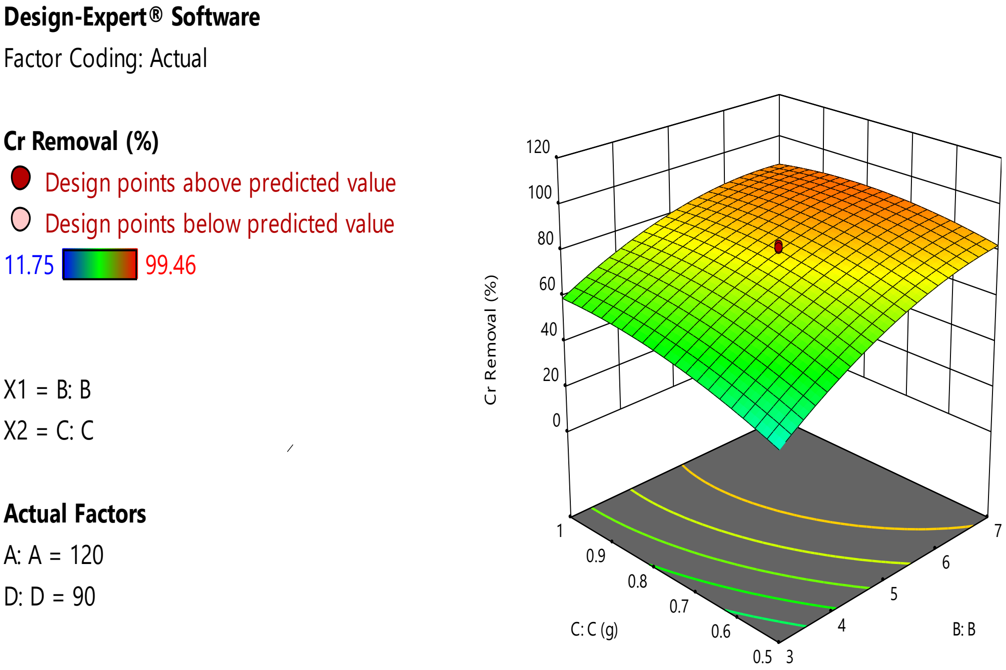


Figure 4. 16: Single factor plots showing individual factor effect on Cr removal

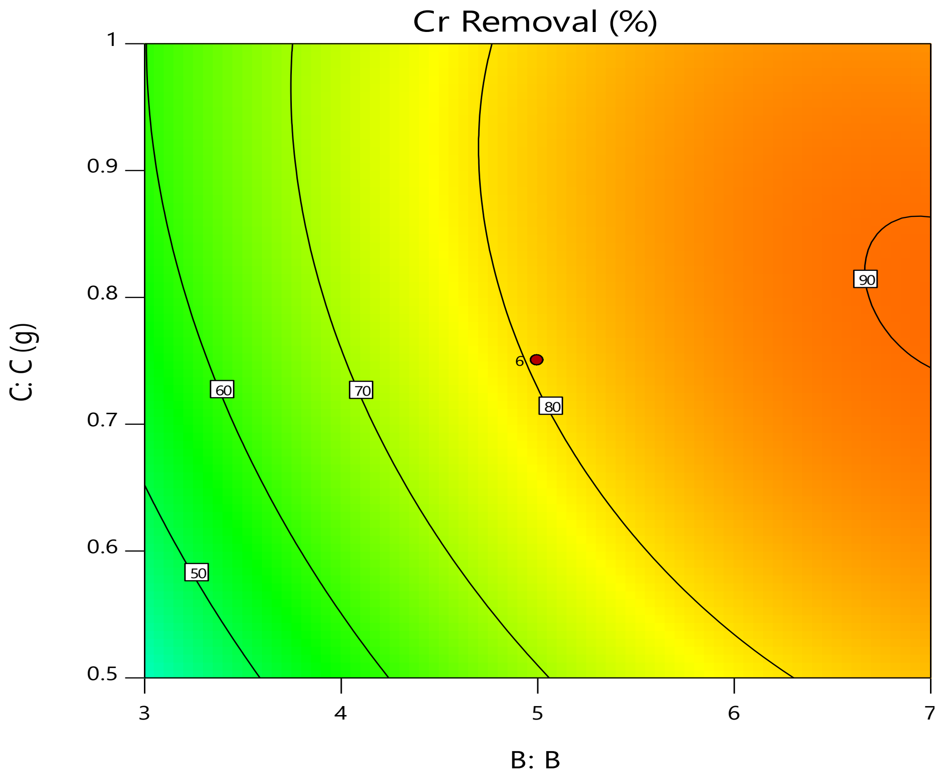
4.3.3.2 The combined effect of solution pH and adsorbent dose

In order to study the interaction effect among different independent variables and their corresponding effect on the response variable, contour plots were drawn. A contour plot is a graphical representation of a three dimensional response surface as a function of two independent variables, maintaining all other variables at fixed medium level. These plots can be helpful in understanding both the main and interaction effects of the independent variables on the response variable. Interaction effect of pH and adsorbent dose (BC) was shown in 3D and contour plot of Figure 4.17 a and b respectively. Removal percentage increases with increasing both pH and dose. 90% chrome removal is achieved at pH 6.68, adsorbent dose of 0.815g and the rest two variables set at their medium level. Figure 4.17 indicates maximum percent removal was obtained at higher value of both pH of the solution and adsorbent dose. The figure also showed the removal of Cr was highly dependent on pH than adsorbent dose. This indicates the percent removal was highly dominated by pH.

.



(a)



(b)

Figure 4. 17:Effect of interaction plot between pH and dose on Cr removal: a (3D response surface plot) and b (counter plot).

4.3.3.3 The combined effect of solution pH and contact time

Interaction effect of pH and contact time (BD) was shown in 3D and contour plot of Figure 4.18 a and b respectively. Removal percentage increases with increasing both pH and time. 92.45% chrome removal is achieved at pH 6.91, 114.8 min time and the rest two variables set at their medium level. Figure 4.17 indicates maximum percent removal was obtained at higher value of both pH of the solution and contact time. The figure also showed the removal of Cr was highly dependent on pH than contact time. This indicates the percent removal was highly dominated by pH. AS shown in the graph below percent removal increases as pH and contact time increases, decrease as pH and contact time decreases.

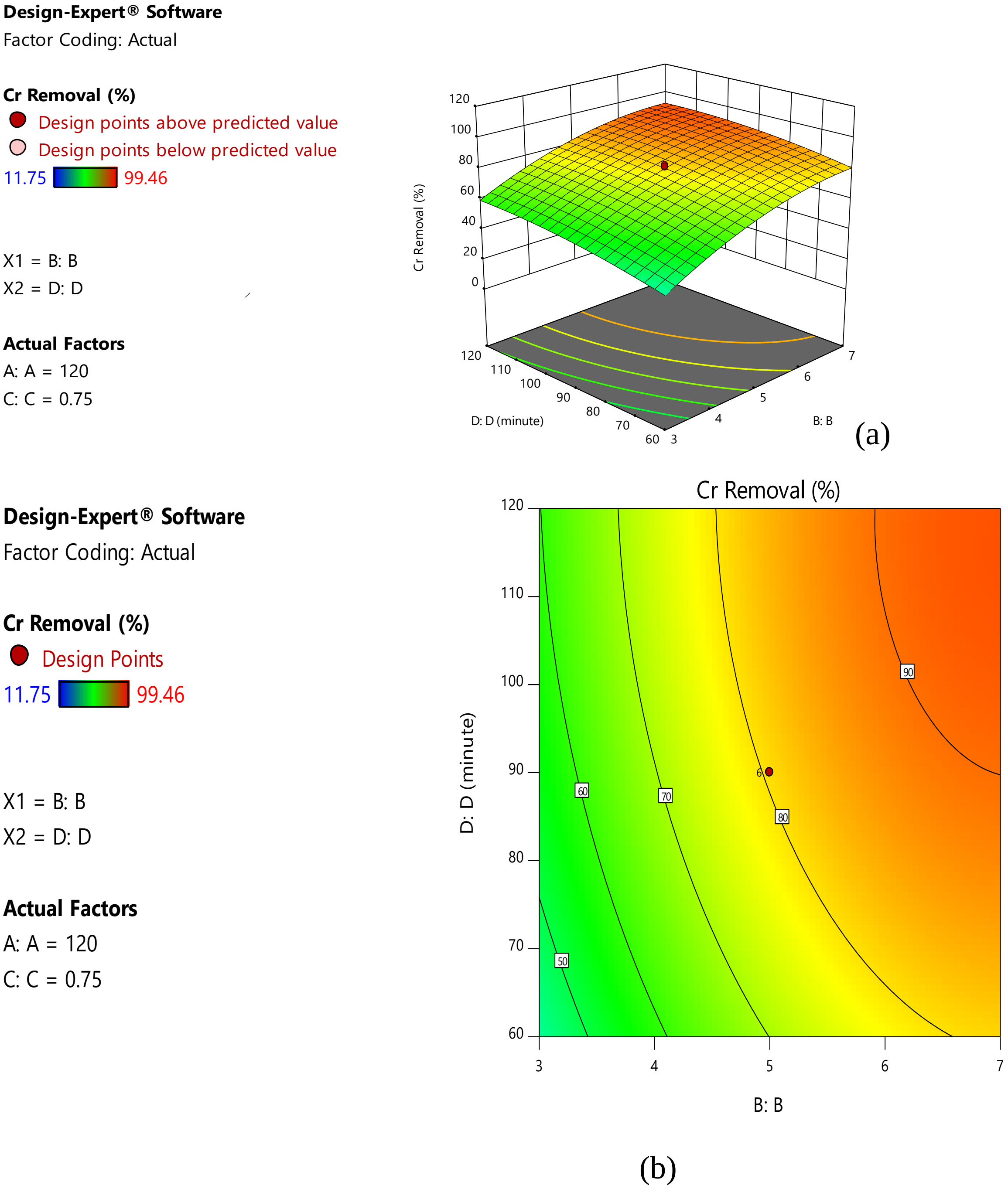


Figure 4. 18:Effect of the interaction between pH and contact time on Cr removal

4.3.4 Optimization of percentage removal of chromium ions

One of the main objectives of RSM is the determination of the optimum settings of the control variables that result in a maximum (or a minimum) response over a certain region of interest(Khuri and Mukhopadhyay, 2010). In the Design Expert software's (DOE) numerical optimization, the possible goals are maximizing, minimize, target, in range and set to an exact value (factors only).

Therefore, in present study, the desired goal for each factor as well as for the response function was selected from the menu. A weight is usually assigned to each goal in order to adjust the shape of the particular desirability function. The goals are then combined to an overall desirability function. Desirability is an objective function. It can normally range from zero to one for any given response. A desirability value of one represents the ideal case while a zero indicates that one or more responses fall outside the desirable limits. The numerical optimization identifies a point that will maximize the desirability function. The possibility of finding the best local maximum can generally be increased by starting from several points in the design space(Amini et al., 2008).

Table 4. 6: working conditions of factors and response for optimization.

Variables	Ultimate goal	Experimental range	
		Lower limit	Upper limit
Initial Cr ion concentration (ppm)	In the range	80	160
pH	Maximum	3	7
Adsorbent dose (g)	In the range	0.5	1
Contact time (min)	In the range	60	120
%Removal of chromium	Maximum	17.75	99.46

4.3.4.1 Validation of Experiments

In order to verify the optimization results, an experiment was performed under predicted conditions by the developed model. The model predicted 99.505 % removal of Cr ion at pH 7, concentration 80 mg/L, adsorbent dose10 g/L and contact time 120 min. The experimental value obtained at these conditions is 99.46 % and is closely in agreement with the result obtained from the model and hence validated the findings of the optimization.

Table 4. 7: Optimum conditions and model validation

Variables	Optimum results
Initial concentration (ppm)	80
pH	7
Adsorbent dose (g/100ml)	1
Contact time (min)	120
%Removal of chromium	99.505
Experimental % removal of Cr	99.46
Desirability	1

5. Conclusions and Recommendation

5.1 Conclusion

In this study the adsorption behavior of Cr ion as total onto the thermally modified eggshell powder from tanning effluent has been investigated based on batch mode of experiments. The low cost eggshell adsorbent makes it better because of it have low moisture content of 0.99% and less than this 0.133% for modified. Due to this the adsorbent stored for long period of time without any preservation. The method that used to prepare thermally modified eggshell resulted in a significant increase in the specific surface area (SSA) of calcinated eggshell. Therefore, thermally modified eggshell was found to be very effective adsorbent for removing chromium ions as total from tanning effluent waste water. Effects of different parameters (such as contact time, initial pH, amount of adsorbents, and initial Cr(III) concentration) were investigated using central composite design expert 11.1.0.1. From the ANOVA result the interaction effect of initial pH vs dose and pH vs contact time were significant. pH was found the most dominant factor. Maximum percentage removal of 99.505% was obtained at optimum working conditions (such as at pH =7, dose=1g, contact time =120 min and 80ppm initial concentration of chromium ion). The equilibrium data obtained at varying initial concentration and at fixed pH =7, dose =0.75g and contact time =120min were well fitted into Langmuir adsorption isotherm. The kinetics of the adsorption was found to be fitted with pseudo second order model.

5.2 Recommendation

The following recommendations was made for future work and application of eggshell.

- In addition to thermal modification, further research can be done to chemically augment the results obtained by modifying the eggshell characteristics with chemicals like acids or bases, as this might increase the number of active binding sites and/or functional groups on the eggshell and thus the adsorption capacity.
- The efficiency of this material should also be investigated for the removal of dyes, TS, TSS, TDS. BOD and COD from tanner wastewater and also the application of the material on wastewater containing all sorts of pollutants.
- Column adsorption can be developed to move laboratory batch adsorption results into practical wastewater treatment containing heavy metal ions.
- The development of the bio sorption processes by eggshell requires further investigation in the direction of modeling, regeneration of bio sorbents material, comparative analysis with ion exchange resins and other conventional removal techniques.
- Various experiments with different experimental parameters like the temperature and agitation speed to increase the adsorptive efficiency.

Reference

Ajala, E. O., Eletta, O. A. A., Ajala, M. A., & Oyeniyi, S. K. (2018). Characterization and Evaluation of Chicken Eggshell for Use As a Bio-Resource, *14*(1), 26–40. Retrieved from www.azojete.com.ng

Aksu, Z., Sag, Y. and Kutsal, T. (1992). The biosorption of copper by C. vulgaris and Z. ramigera. Environmental Technology, 13(6), pp.579-586.

Al-awwal, N. Y., & Ali, U. L. (2015). Proximate Analyses of Different Samples of Egg Shells Obtained from Sokoto Market in Nigeria, (April), 4–7.

Amini, M., Younesi, H., Bahramifar, N., Lorestani, Z., A. A., Ghorbani, F., … Sharifzadeh. (2008). "Application of response surface methodology for optimization of lead biosorption in an aqueous solution by Aspergillus niger." Journal of Hazardous Materials 154(1): 694-702.

Anderson, R. A. (2000). Chromium in the prevention and control of diabetes. Diabetes & amp; Metabol. 26(1): 22–27 Doi:DM-03-2000-26-1-1262-3636-10-10-19-ART67.

Baisakh, P. C., & Patnaik, S. N. (2002). Removal of Hexavalent Chromium from Aqueous Solutions by Adsorption on Coal Char. *Indian Journal of Environmental Health*, *44*, 189–196. https://doi.org/10.1016/j.desal.2009.02.062

Balarak, D., Pirdadeh, F., & Mahdavi, Y. (2015). Biosorption of Acid Red 88 dyes using dried Lemna minor biomass. Journal of Science, Technology & Environment Informatics, 1(2), 81-90.

Barakat, M. (2011). New trends in removing heavy metals from industrial wastewater. Arabian Journal of Chemistry, 4: 361-377.

Barnhart, J. (1997). Chromium chemistry and implications for environmental fate and toxicity. Soil and Sediment Contamination.6(6): 561-568.

Basci, N., Kocadagistan, E., & Kocadagistan, B. (2004). Biosorption of copper (II) from aqueous solutions by wheat shell. Desalination, 164(2), pp.135-140.

Bedemo, A., Chandravanshi, B. S., & Zewge, F. (2016). Removal of trivalent chromium from aqueous solution using aluminum oxide hydroxide. *SpringerPlus*, *5*(1).

https://doi.org/10.1186/s40064-016-2983-x

Bhaumik, R., Mondal, N. K., Das, B., Roy, P., Pal, K. C., Das, C., … Datta, J. K. (2012). Eggshell powder as an adsorbent for removal of fluoride from aqueous solution: Equilibrium, kinetic and thermodynamic studies. *E-Journal of Chemistry*, *9*(3), 1457–1480. https://doi.org/10.1155/2012/790401

Borgwardt, R. H. (1985). Calcination kinetics and surface area of dispersed limestone particles. *AIChE Journal*. https://doi.org/10.1002/aic.690310112

Chang, Y. ., Chang, J. ., Lin, T. ., & Hsu, Y. . (2002). Integrated copper-containing wastewater treatment using xanthate process. Journal of Hazardous Materials, 94(1), pp.89-99.

Chen, G. H. (2004). Electrochemicals technologies in wastewater treatment. Sep. Purif. Technol. 38: 11–41.

Chojnacka, K. (2005). Biosorption of Cr (III) ions by eggshells. Journal of Hazardous Materials, 121(1), pp.167-173.

Cree, D., & Rutter, A. (2015). Sustainable Bio-Inspired Limestone Eggshell Powder for Potential Industrialized Applications. ACS Sustainable Chemistry & Engineering, 3(5), pp.941-949.

Dada, A.O, Olalekan, A. . (2012). Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn 2+ Unto Phosphoric Acid Modified Rice Husk. *IOSR Journal of Applied Chemistry*, *3*(1), 38–45. https://doi.org/10.9790/5736-0313845

Dagmawi, M., & Mekibib, D. (2013). Chromium Removal from Modjo Tannery Wastewater Using Moringa stenopetala Seed Powder as an Adsorbent. Water, Air, & Soil Pollution.224(12): 1-10.

De Souza Macedo, J., da Costa Júnior, N. B., Almeida, L. E., da Silva Vieira, E. F., Cestari, A. R., de Fátima Gimenez, I., Carreño, N. L. V. and Barreto, L. S. (2006). Kinetic and calorimetric study of the adsorption of dyes on mesoporous activated carbon prepared from coconut coir dust. Journal of colloid and interface science.298(2): 515-522.

Der-Jiun, O., Shahid, I., & Maznah, I. (2012). Proximate composition, nutritional attributes and mineral composition of Peperomia pellucida l. (ketumpangan air) grown in Malaysia.

Molecules 17, 11139-11145.

Director, General, Enterprise, O., & Industry. (2012). The leather industry's commitment to the environment,accessedfrom:http://ec.europa.eu/enterprise/sectors/leather/environment/index en.htm on 10 June 2014.

EEPA. (1997a). *Ethiopian Environmental Protection Authority. Annual Report; Addis Ababa, Ethiopia.*

EEPA. (1997b). *Ethiopian Environmental Protection Authority*.

EEPA. (2003). Standards for industrial pollution control in Ethiopia, Part Three: Standards for Industrial effluents. ESIS project - US/ETH/99/ 068/ETHIOPIA, EPA/UNIDO, Addis Ababa, 46p.

El, S., A.G., Lartiges, B. ., & Villiéras, F. (2008). Chemical coagulation of combined sewer overflow: Heavy metal removal and treatment optimization. Water Research, 42(4), pp.951-960.

Favazzi, A. (2003). Study of the impact of the main policies and environment protect ions measures in Africa's leather industry. *Accessed from: Www.Unido.Org/Fileadmin on 3 June 2014.*

Fei, C., Luo, G., Yang, W., & Wang, Y. (2005). Preparation and adsorption ability of polysulfone microcapsules containing modified chitosan gel. Tsinghua Science & Technology, 10(5), pp.535-541.

Fenglian, F., & Qi, W. (2011). "Removal of heavy metal ions from wastewaters: A review." Journal of Environmental Management 92: 407-418.

Ferhan Cecen, O. A. (2012). Acticated Carbon for Water and Wastewater Treatment: Integration of Adsorption and Biological Treatment. Germany: British library cataloguing-in-publication data.

Ferrari, L., J. Kaufmann, F. W. and J. P. (2010). "Interaction of cement model systems with superplasticizers investigated by atomic force microscopy, zeta potential, and adsorption measurements." Journal of colloid and interface science 347(1): 15-24.

Fomkin, A. (2009). Nanoporous Material and Their Adsorption Properties. Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Vol. 45, is-sue 2, 133 149.

Gulipalli, C. S., Prasad, B., & Wasewar, K. L. (2011). Batch study, equilibirum and kinetics of adsorption of selenium using rice husk ash (RHA). J. Eng. Sci. Technol.6: 586-605.

Gunatilake, S. K. (2016). Removal of Cr (III) Ions from Wastewater using Sawdust and Rice Husk Biochar Pyrolyzed at Low Temperature. *International Journal for Innovation Education and Research*, *4*(4), 44–54.

Guru, P. S., & Dash, S. (2013). Amino acid modified eggshell powder (AA-ESP) — A novel bio-solid scaffold for adsorption of some Styrylpyridinium dyes. Journal of Dispersion Science and Technology 34 (8), 1099–1112.

Han X, Wong YS, W. M. T. N. (2007). biosorption and bioreduction of Cr (VI) by a microalgal isolate Chlorella miniata. J Hazared Mater.146 (1-2):65-72.

Hariharan, Varghese, Cherian, D. A. B., Sreenivasan, D. P. V., Paul, & Asmy. (2014). Synthesis and Characterisation of CaCO3 (Calcite) Nano Particles from Cockle Shells Using Chitosan as Precursor. International Journal of Scientific and Research Publications, 4(10), pp.1-5.

Ho, Y.-S. (2006). Review of second-order models for adsorption systems. Journal of hazardous materials.136(3): 681-689.

Iram, S., & Abrar, S. (2015). Biosorption of copper and lead by heavy metal resistant fungal isolates. International Journal of Scientific Research, 5, pp.1-5.

Jiaping, P. . (2012). ‗Decontamination of Heavy Metals: Processes, Mechanisms, and Applications‘ CRC Press, Print ISBN: 978-1-4398- 1667-7.

Joshi, N., Lokeshwarl, & Keshava. (2009). Biosorption of Heavy Metal(Chromium)Using Biomass. Global.

Kasiri, M. B., Aleboyeh, H., & Aleboyeh, A. (2008). Modeling and optimization of heterogeneous photo-fenton process with response surface methodology and artificial neural networks," Environmental Science and Technology, vol. 42, no. 21, pp. 7970– 7975, 2008.

Khuri, A. I., & Mukhopadhyay, S. (2010). "Response surface methodology." Wiley Interdisciplinary Reviews: Computational Statistics 2(2): 128-149.

Kimbrough, D., Y. Cohen, A. Winer, L. C. and C. M. (1999). "A critical review of chromium in the environment." Environmental Science and Technology 29: 1-46.

King, P., Rakesh, N., Beenalahari, S., Kumar, Y. P., & Prasad, V. S. R. K. (2007). Removal of lead from aqueous solution using Syzygium cumini L.: equilibrium and kinetic studies. Journal of Hazardous Materials, 142(1-2), 340-347.

Kobya, M., Demirbas, E., Senturk, E., & Ince, M. (2005). Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. Bioresource Technology, 96(13), pp.1518-1521.

Kotaś, J., & Stasicka, Z. (2000). Chromium occurrence in the environment and methods of its speciation. Environ Pollu. 107: 263–283.

Kumaraswamy, K., Dhananjaneyulu, B.V. Vijetha, P., & Kumar, Y. (2015). Kinetic and equilibrium studies for the removal of chromium using eggshell powder. Research Journal of Pharmaceutical, Biological and Chemical Sciences, 6(1), pp.529-532.

Kurniawan, T. A., G. Y. Chan, W.-H. L. and S. B. (2006). “Physico–chemical treatment techniques for wastewater laden with heavy metals.” Chemical engineering journal 118(1): 83- 98.

Kyzas, G. Z. (2012). Commercial coffee waste as material for adsorption of heavy metals from aqueous solutions. Matrials, 5, 1820-1840.

Lakshmi, U. R., Srivastava, V. C., Mall, I. D., & Lataye, D. H. (2009). Rice husk ash as an effective adsorbent: Evaluation of adsorptive characteristics for Indigo Carmine dye. *Journal of Environmental Management*, *90*(2), 710–720. https://doi.org/10.1016/j.jenvman.2008.01.002

LIDI. (2012). Assessment on the waste water treatment and the solid waste management of Tanneries in Ethiopia. Addis Ababa: Ethiopia.

LIDI. (2013). Ethiopian Leather Industry Development Institute annual report, Addis Ababa: Ethiopia.

Malarkodi, M., R. Krishnasamy, R. K. and T. C. (2007). “Characterization of heavy metal contaminated soils of Coimbatore district in Tamil Nadu.” Journal of Agronomy 6(1): 147-151.

Malik, R., Ramteke, D. S., & Wate, S. R. (2006). Physico-chemical and surface characterization of adsorbent prepared from groundnut shell by ZnCl2activation and its ability to adsorb colour. *Indian Journal of Chemical Technology*, *13*(4), 319–328.

Martinez, S. A., & Rodriguez, M. G. (2007). "Dynamical modeling of the electrochemical process to remove Cr (VI) from wastewaters in a tubular reactor." Journal of Chemical Technology and Biotechnology 82(6): 582-587.

Mashangwa, T. D. (2016). an Investigation Into the Efficacy of Eggshells As a Low Cost Adsorbent for the Removal of Potentially Toxic Inorganic Elements From Aqueous Solutions, (September). Retrieved from http://uir.unisa.ac.za/bitstream/handle/10500/22963/dissertation_mashangwa_td.pdf?sequence=1

Midha, V., & Dey, A. (2008). Biological Treatment of Tannery Wastewater for Sulfide Removal. *Int. J. Chem. Sci*, *6*(2), 472–486. Retrieved from http://www.tsijournals.com/articles/biological-treatment-of-tannery-wastewater-for-sulfide-removal-a-review.pdf

Mishra, S. (2007). Preparation and characterization of Micropous Activated Carbon from Biomass and its Application in the Removal of Chromium (VI) from Aueous phase, (January). Retrieved from http://ethesis.nitrkl.ac.in/4468/1/Ph.D_Thesis_Ramakrishna_Gottipati_507ch001.pdf

Moges, F., Tegegne, A., Dessie, T., & Improving. (2010). Indigenous chicken production and marketing systems in Ethiopia: Characteristics and opportunities for market-oriented development. *IPMS of Ethiopian Farmers Project Working Paper*, (24), 8–45.

Mohadi, R., Anggraini, K., Riyanti, F., & Lesbani, A. (2016). Preparation Calcium Oxide From Chicken Eggshells. *Sriwijaya Journal of Environment*, *1*(2), 32–35. https://doi.org/10.22135/sje.2016.1.2.32-35

Mohan, D., Singh, K. P., & Singh, V. K. (2005). "Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth." Industrial & Engineering Chemistry Research 44(4): 1027-1042.

Mwinyihija, M., A. Meharg, N. S. and K. K. (2005). "Ecological Risk Assessment of the Kenyan tannery industry." J Am Leather Chem Assoc 100(11): 380-395.

Mwinyihija, M., Strachan, N.J.C., Dawson, J., Meharg, A. and Killham, K. (2006). An ecotoxicological approach to assessing the impact of tanning industry effluent on river health. Arch Environ Contam Toxicol. 50: 316–324.

Netzahuatl-Muñoz, A. R., Aranda-García, E., Cristiani-Urbina, M. D. C., Barragán-Huerta, B. E., Villegas-Garrido, T. L., & Cristiani-Urbina, E. (2010). Removal of hexavalent and total chromium from aqueous solutions by Schinus molle Bark. *Fresenius Environmental Bulletin*, *19*(12), 2911–2918.

Nguyen, T. A. H., Ngo, H. H., Guo, W. S., Zhang, J., Liang, S., Yue, Q. Y., … Nguyen, T. V. (2013). Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. *Bioresource Technology*, *148*, 574–585. https://doi.org/10.1016/j.biortech.2013.08.124

Nicholson, R.A., Roth, S.H., Zhang, A., Zheng J., Brookes, J., Skrajny, B. and Benninghton, R. (1998). Inhibition of respiratory and bioenergeticmechanisms by hydrogen sulfide in mammalian brain. J. Toxicol Environ Health, 54: 461–507.

Nimmo, J. (2004). Porosity and pore size distribution. Encyclopedia of Soils in the Environment.3: 295-303.

Ogedengbe, K., & Akinbile, C. (2004). “Impact of industrial pollutants on quality of ground and surface waters at Oluyole Industrial Estate, Ibadan, Nigeria.” J. Technol. Dev 4(2): 139-144.

Papita Das Saha, Apurba Dey, P. M. (2012). Batch removal of chromium (VI) from aqueous solutions using wheat shell as adsorbent: process optimization using response surface methodology. Desalin. Water Treat. 39:95-102.

Qiu, H., Lv, L., Pan, B. –., Zhang, Q. –., Zhang, W. –., & Zhang, Q. –. (2009). Critical review in adsorption kinetic models. Journal of Zhejiang University Science A.10(5): 716-724.

Rao, M.N. Datta, A. K. (1987). *Waste Water treatment, Second ed, Oxford and IBH Publishing Company Pvt. Ltd.*

Reiffenstien, R.J., Hubert, W.C. and Roth, S. H. (1992). Toxicology of Hydrogen Sulphide. Annu Rev Pharmacol Toxicol. 32: 109–134.

Repo, E. (2011). EDTA- and DTPA- Functionalized Silica Gel and Chitosan Adsor-bents for the Removal of Heavy Metals From Aqueous Solutions. Lappeenranta Uni-versity of

Technology.Thesis.

Rohim, R., Ahmad, R., Ibrahim, N., Hamidin, N., & Abidin, C. Z. A. (2014). Characterization of calcium oxide catalyst from eggshell waste. Advances in Environmental Biology 8, 35–39.

Ros, M. and Ganter, A. (1998). Possibilities of reduction of recipient loading of tannery waste Slovenia. Water Sci Tech. 37: 145–152.

Segura-Campos, M., Pérez-Hernández, R., Chel-Guerrero, L., Castellanos-Ruelas, A., Gallegos-Tintoré, S., & Betancur-Ancona, D. (2013). Physicochemical and Functional Properties of Dehydrated Japanese Quail (Coturnix japonica) Egg White. Food and Nutrition Sciences 4, 289-298.

Seyoum, L., Assefa, F., & G.Dalhammar. (2003). Characterization of tannery wastewater and assessment of downstream pollution profiles along Modjo River in Ethiopia. Eth J Biol Sci. 2: 157–168.

Seyoum Leta, Fasil Assefa, Gumaelius. L, and Dalhammar, G. (2004). Biological nitrogen and organic matter removal from tannery wastewater in pilot plant operations in Ethiopia. Appl Microbio Biotechnology. Springer-Verlag .

Shan, S., Ma, A., Hu, Y., Jia, Q., Wang, Y., & Peng, J. (2015). Development of sintering-resistant CaO-based sorbent derived from eggshells and bauxite tailings for cyclic CO2 capture. Environmental Pollution, 208, pp.546-552.

Sharma, Y. (2013). A Guide to the Economic Removal of Metals from Aqueous Solu-tions. Wiley (Scrivener), 31-43.

Sharphouse, J. (1983). *Leather technicians Handbook, leather producer"s Association, Northampton,UK.*

Shrivastava, K., & Gupta, S. K. (2015). Removal of Chromium from Waste Water by Adsorption Method Using Agricultural Waste Materials. *International Journal of Chemical Sciences and Applications*, *6*, 1–5. Retrieved from http://www.bipublication.com

Song, Z., Williams, C.J. and Edyvean, R. J. (2000). Sedimentation of tannery wastewater. Water Res. 34: 2171–2176.

Talouizte, H., Merzouki, M., & Benlemlih, M. (2013). Treatment of real textile wastewater using

SBR technology: Effect of sludge age and operational parameters. Journal of Biotechnology Letters, 4(2), pp.79.

Trivedi, R.K., Goel, P. K. (1984). Chemical and Biological methods of water pollution studies, Environmental Publications, India.

UNEP, I. (1994). Tanneries and the Environment – A Technical Guide, Technical Report (2nd Print) Series No 4, ISBN 92 807 1276 4.

UNIDO. (2011). Introduction to Treatment of Tannery Effluents, UNIDO, Austria: Vennia, Ausria.

Wang, L., Vaccari, D., Li, Y. and Shammas, N. (2005). Chemical Precipitation. In:"Physicochemical Treatment Processes" (L. Wang, Y.-T. Hung, and N. Shammas, Eds.), Vol. 3, pp. 141-197. Humana Press, Totowa, New Jersey.

Wionczyk, B., Apostoluk, W., & Charewicz, W. A. (2006). Solvent extraction of chromium (III) from spent tanning liquors with Aliquat 336. *Hydrometallurgy*, *82*(1–2), 83–92. https://doi.org/10.1016/j.hydromet.2006.03.055

Yadav, O. P., & Boka, T. (2012). Adsorption of Methylene Blue on Carbonized Banana Musa Acuminata Peel. Diss. Haramaya University, 2012.

Zheng, J.C., Liu, H.Q., Feng, H.M., Li, W.W., Lam, M.H.W., Lam, P.K.S. and Yu, H. Q. (2016). Competitive sorption of heavy metals by water hyacinth roots. Environmental Pollution, 67(4), pp.237-243.

APPENDIX A: Photos Taken at different stages of laboratory Works

(A) Collection of eggshell, (B) Removing impurities by distill water, (C) drying, (D)grinding

(E) Sieving, (F) calcination process and (G) Calcinated eggshell powder

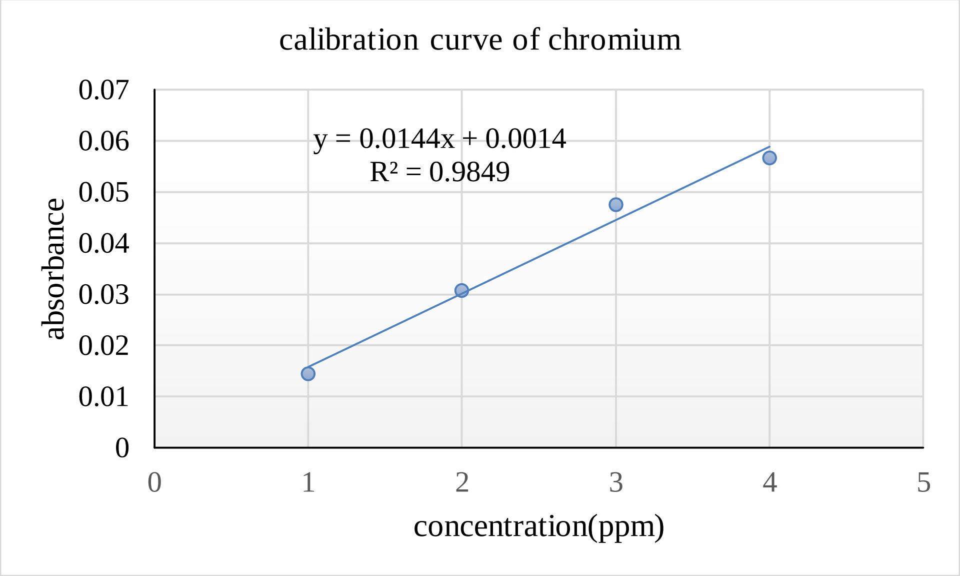
Two evaporation pond chrome line waste water treatment system of ETSC

(A) Composite waste water from chrome line effluent, (B) pH Adjustment, (C) After adjusting the required parameter it was ready to insert into incubator shaker, (D) Shaking at 150 rpm and room temperature, (E) Filtration, (F) Digestion and (G) Cr analysis using AAS

APPENDIX B Fourier Transform Infrared Spectroscopy (FTIR) Correlation Table

Functional Group names	Absorption Ranges (cm^{-1})	Type of vibration causing IR absorption
Alkane	3000 - 2000	H-C-H asymmetric & symmetric stretch
	1500-1440	H- C - H bend
	3100-3000	C=C-H asymmetric stretch
Alkene	1675-1600	C - C=C symmetric stretch
Aromatic Rings	3100-3000	C=C-H asymmetric stretch
	1600-1580	C - C = C symmetric stretch
	1500-1450	C - C = C asymmetric stretch
Phenols & Alcohols	3650-3100	Hydrogen bonded – OH stretch
Carboxylic Acids	3400-2400	Hydrogen bonded – OH stretch
	1730-1650	C= O stretch

APPENDIX C: standard calibration curves of chromium



Appendix D: Experimental design matrix

	Factor 1	Factor 2	Factor 3	Factor 4	Response 1
Run	A:A	B:B	C:C	D:D	Cr Removal
unit	mg/L		g	minute	%
1	160	7	0.5	120	73.31
2	80	3	0.5	60	37.27
3	160	7	0.5	60	61.78
4	40	5	0.75	90	99.03
5	120	9	0.75	90	84.65
6	120	1	0.75	90	11.75
7	200	5	0.75	90	55.45
8	120	5	0.75	90	81.07
9	160	3	1	60	38.21
10	80	3	0.5	120	55.65
11	160	7	1	60	64.05
12	80	7	0.5	120	93.01
13	160	3	0.5	120	33.99
14	120	5	0.75	150	82.85
15	80	3	1	60	57.75
16	80	7	0.5	60	86.21
17	120	5	0.75	90	80.08
18	120	5	1.25	90	75.01
19	120	5	0.75	90	79.05
20	160	3	0.5	60	16.59
21	120	5	0.75	90	78.83
22	120	5	0.75	30	51.67
23	80	7	1	120	99.46
24	120	5	0.25	90	46.45

25	160	7	1	120	76.86
26	80	3	1	120	71.98
27	80	7	1	60	87.42
28	120	5	0.75	90	81.64
29	120	5	0.75	90	82.75
30	160	3	1	120	52.89

Appendix E: Experimental data.

Table E -1: Effect of solution pH on the adsorption of Cr ions using calcinated eggshell.

Co (mg/L)	Adsorbent dose (g)	Contact time (min)	pH	Trial 1	Trial 2	Final average concentration	Adsorption Capacity q_e (mg/g)	%Removal
				Ce_1	Ce_2	C_e (mg/L)		
80	0.75	120	1	55.18	52.86	54.02	3.46	32.47
80	0.75	120	3	27.68	27.84	27.76	6.96	65.3
80	0.75	120	5	10.21	10.37	10.29	9.29	87.13
80	0.75	120	7	1.47	1.25	1.36	10.48	98.3
80	0.75	120	9	7.86	7.95	7.904	9.61	90.12
80	0.75	120	11	13.29	13.27	13.28	8.89	83.4

Table E -2: Effect of adsorbent on the adsorption of Cr ions using calcinated eggshell.

Co (mg/L)	Adsorbent dose (g)	Contact time (min)	pH	Trial 1	Trial 2	Final average concentration	Adsorption Capacity q_e (mg/g)	% Cr Removal
				Ce_1	Ce_2	C_e (mg/L)		
80	0.25	120	7	41.9	42.14	42.02	5.06	47.47
80	0.5	120	7	5.38	5.82	5.6	9.92	93
80	0.75	120	7	1.47	1.43	1.45	10.47	98.18
80	1	120	7	0.35	0.354	0.352	10.62	99.56
80	1.25	120	7	0.36	0.3601	0.36	10.61	99.55
80	1.5	120	7	0.355	0.345	0.35	10.62	99.56

APPENDIX F: pH of Point of zero charge values

pH_i	pH_f	change in pH
2	1.2	-0.8
3	1.35	-1.65
4	1.5	-2.5
5	3.33	-1.67
6	5.15	-0.85
7	7.55	0.55
8	10.5	2.5
9	11.25	2.25
10	12	2

APPENDIX G: Langmuir, Freundlich and Temkin isotherm parameter values.

Co(ppm)	Trial 1	Trial 2	C_{av}	Ln c_e	%R	q_e(mg/g)	Ce/q_e	LogCe	Log q_e
	Ce_1(ppm)	Ce_2(ppm)	Ce(ppm)						
40	0.09	0.11	0.1	-2.3	99.75	5.7	0.017	-1	0.755
80	1.5	1.3	1.4	0.336	98.25	10.48	0.133	0.146	1.02
120	20.64	20.52	20.58	3.02	82.85	14.2	1.45	1.31	1.15
160	33.7	36.02	34.86	3.55	78.21	17.87	1.95	1.54	1.25
200	68.76	69.12	68.94	4.23	65.53	18.72	3.68	1.84	1.27

APPENDIX H: Analysis Result Values for Kinetic Parameters

Time (min)	$Time^{1/2}$	Co(ppm)	Trial 1	Trail 2	C_{av}	%R	qe	qt	qe-qt	Log(qe-qt)	t/q_t
			C_1	C_2	C_t						
15	3.87	80	64.16	67.04	65.6	18	10.48	1.92	8.56	0.93	7.81
30	5.47	80	33.99	34.81	34.4	57.03		6.08	4.4	0.64	4.93
45	6.7	80	30.16	27.88	29.02	63.72		6.8	3.68	0.56	6.61
60	7.74	80	10.34	10.46	10.4	87		9.28	1.2	0.08	6.46
75	8.66	80	8.43	8.51	8.47	89.41		9.533	0.947	-0.023	7.86
90	9.48	80	8.03	7.97	8	90.23		9.6	0.88	-0.055	9.37
105	10.24	80	4.88	4.72	4.8	94.03		10.02	0.46	-0.33	10.47
120	10.95	80	1.37	1.39	1.38	98.27		10.48	-	-	11.45
135	11.61	80	1.38	1.388	1.384	98.27		10.48	-	-	12.88