ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING DEPARTMENT

ENVIRONMENTAL ENGINEERING STREAM

REMOVAL OF CHROMIUM FROM TANNERY WASTEWATER USING MODIFIED FISH SCALES AS ADSORBENT

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A thesis submitted to the School of Graduate Studies of Addis Ababa University in partial fulfillment of the Degree of Master of Science in Environmental Engineering

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Declaration

I, the undersigned, declare that this thesis entitled “Removal of Chromium from Tannery Wastewater using Modified Fish Scale as Adsorbent” is my original work under School of Chemical and Bio Engineering, AAiT, 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.

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

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ABSTRACT

Industrialization activities have brought many troublesome changes in the environment due to the disposal of huge amount of liquid and solid wastes. However, the presence of a heavy metal such as chromium in the industrial wastewater is a potential hazard to aquatic, animal, and human. Biosorption of heavy metal is an effective technology for the treatment of industrial wastewater because of its low cost and high metal binding capacity. This research study has been focused on the removal of specific metal ion chromium (III) using modified fish scales as sorbents. The collected sample (raw FS) was washed, crushed, chemically modified, and sieved to a range of particle size(125-200µm) and the biosorbent was characterized by FTIR spectroscopy and XRD analysis. A batch adsorption experiment was conducted using model pollutant of tannery wastewater. The adsorption efficiency of MFS was evaluated as the function of adsorbent dosage, pH and contact time and effects of those variables on biosorption efficiency were analyzed. The residual Cr(III) concentrations after biosorption were analyzed using AAS. The results illustrated that the maximum removal efficiency of Cr (III) ion by MFS is 99.7518 % at adsorbent dosage 0.8g, pH of the solution 5 and contact time 90 min, initial concentration 150mg/l chromium ion. The adsorption isotherms data fitted well with Langmuir isotherm model with R^2*= 0.9998,* q_{max}*= 18.3486mg/g, and* R_L*= 0.00007325. Also, adsorption kinetics model was analyzed (pseudo-first-order and pseudo-second-order) for the description of adsorption of Cr (III) using MFS and Pseudo-Second-order model (*R^2*=1) fitted well for adsorption kinetics.*

***KEYWORDS**: Cr(III) biosorption, modified fish scales, Tanning industry, adsorption isotherm, and kinetics model*

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LIST OF ACRONYMS

AAS	Atomic Adsorption Spectrophotometry.
BCS	Basic Chromium Sulfate
Cr (III)	Chromium (III)
Cr (VI)	Chromium (VI)
EEPA	Ethiopian Environmental Protection Authority
ETP	Effluent Treatment Plant
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
SS	Suspended Solids
TDS	Total Dissolved Solids
DAF	Dissolved Air Flotation
ED	Electro-Dialysis
RO	Reverse Osmosis
IUPAC	International Union of Pure and Applied Chemistry
$Cr_2 (SO_4)_3$	Chromium sulfate
HCl	Hydrochloric acid
Na (OH)	Sodium Hydroxide
$Ca (OH)_2$	Calcium Hydroxide
H_2SO_4	Sulfuric Acid
MFS	Modified Fish scale
USEPA	United State Environmental Protection Agency
WHO	World Health Organization
S	Sulfide

1. INTRODUCTION

1.1.Background

Increasing population, industrial, agricultural and commercial activities have brought many troublesome changes in the environment due to the disposal of huge amount of liquid and solid wastes. Industrialization has introduced heavy metal contamination problem into the environment over the past few decades. With an increasing generation of heavy metals from technological activates, many aquatic environments face metal concentrations that exceed water quality criteria designed to protect the environment, animals, and humans (Thaku, 2013).

Unlike other pollutants, heavy metals are nondegradable and persist in nature for a long period of time, accumulate in plants and animals, thus becoming toxic to living organisms (Parmar, 2013). It is interesting that some of these elements are actually required by plants and animals at low concentrations and hence are known as trace metals. These trace metals are of interest both as limiting nutrients and as toxicants in the environment. Despite being a nutrient metal, each of it has a permissible limit (Cd, Hg, Ag, Pb, Sn, Zn, Cu, Ni, and Cr) beyond which, they are notably toxic and some are even hazardous (Etorki, 2014). According to prescribed by WHO, 1993 and ISI, 1991 the permissible limit of chromium in drinking water is 0.05mg/l.

The Industrial wastewater streams containing heavy metals (Chromium, Cadmium, zinc, lead, copper, nickel, and mercury) originate from different metal plating, mining process, smelting, battery manufacture, pesticides, pigment, tanneries, petroleum refining and photographic industries, etc. One such heavy metal, chromium which is used extensively in metal processing, leather processing, chromate production, stainless steel welding and chrome pigment production industries. (Yun Wu, 2008).

Leather processing has emerged as an important economic activity in Ethiopia and the industry is considered to be a major source of pollution because it uses huge quantities of water and chemicals to convert raw skin into leather. Tanning industry wastes pose serious of environmental impact on water, and characteristically contain a complex mixture of both organic and inorganic pollutants. Trivalent chromium present in very high concentrations (Ahmed, 2016). Chromium (III) is used in the leather industry as basic chromium sulfate for the tanning process, which may be converted into chromium (VI) when it is discharged into the environment. Conventional chrome tanning methods give an uptake of only 40 –70% of the materials used for tanning, resulting in wastage of materials as well as ecological concerns (Isam, 2014). Nearly 40% of the total chromium used in leather processing are present in the sludge, disposal of which onto land and water bodies has led to increased chromium levels reaching as high. In the chrome tanning process, chromium in the sectional stream is as high as 1500 – 3000 mg L^{-1} when compared to the environmental regulatory norms (Mannucci et al., 2010). The discharge of Cr^{6+} to surface water is required to be regulated to < 0.05 ppm as per USEPA standards, whereas, total Cr (Cr^{3+} or other forms) to < 2 ppm.

It is essential to recover and recycle chromium from effluents before being released, by adopting appropriate methods like modifications in tanning processes to optimize uptake of chromium by hides/skins, thereby limit chromium content in effluent discharge. Treatment facilities incorporate numerous processes which in combination achieve the desired water quality objectives. In wastewater treatment, various methods are utilized for chromium removal. These include reduction followed by chemical precipitation, ion exchange, electrochemical precipitation, adsorption, solvent extraction, membrane separation, and reverse osmosis (Owlad, 2008). Adsorption is by far more versatile and effective method for removing any contaminants like heavy metal ions, especially, if combined with appropriate regeneration steps. Adsorption has emerged out as an effective, economical and eco-friendly treatment technique. It is a process potent enough to fulfill water reuse obligations and high effluent standards in the industries (Kaya, 2014).

1.2.Statement of the Problem

The accumulation of heavy metal contaminants in the environment has become a concern due to health risks. The exposure to heavy metal contamination has been found to cause kidney damage, liver damage, anemia in low doses and in high concentrations heavy metals can be carcinogenic and teratogenic. Chromium compound is widely used in a number of industries such as a tannery, textile, and chemical, printing dye ink manufacturing. From all this process chromium can escape into the environment through the effluents. Tannery industry is one of the highly polluting industries and plays an important role with respect to environmental pollution due to the high ranked disposal of large volumes of solutions of tanning baths. In Ethiopia, there are more than 20 tanning industries of which 90% of them directly discharge wastewater into nearby surface water or onto open land without treatment. They are the particularly large contribution of chromium pollution (Ketema, 2009).

Chromium can exist in several oxidation states from Cr (0) metallic form to Cr (VI) form. Hexavalent chromium is 100 to 1000 times more toxic compared to common trivalent chromium. Hexavalent Chromium is classified as a primary contaminant because of its mobility in soil and groundwater and it is reported that harmful effects on organisms including humans. Within living cells, chromium compounds can induce cancer and mutation. Hence, several conventional treatment methods have been suggested for removal of metal (chromium) that includes chemical precipitation, reverse osmosis and ion exchange etc. These methods are economical expensive and inefficient for removal from diluted solutions containing dissolved metals. To overcome the disadvantages, it has been reported that biosorbents are having high uptake capacity of chromium from wastewater with effectiveness and low cost. In this investigation, an attempt has been made for the removal of chromium from tannery wastewater using modified fish scales as biosorbents.

1.3.Objectives

1.3.1. General Objective

The main objective of this study is a removal of chromium from tannery wastewater using chemically modified fish scales as adsorbents: batch adsorption process.

1.3.2. Specific Objectives

The specific objectives: -

- Characterization of the adsorbent (fish scales).
- Study of the effects of process parameters i.e., adsorbent dosage, the pH of the solution, and contact time on the chromium adsorption process.
- Modification of fish scales and evaluation of its adsorbent efficiency.
- To determine the adsorption isotherm and kinetics models of chromium (III) ion removal using the MFS as an adsorbent.

1.4.Significance of the Study

Treating the tannery effluent contaminated with heavy metals within the industrial premises before being discharged into ETP is an efficient way to remove heavy metals rather than treating high volumes of wastewater in a common ETP. The significance of this study is intended to develop an environmentally friendly, low-cost adsorption technique for the reduction or removal of chromium (III) from the spent chrome tannery liquor in order to meet effluent discharge standards of the government regulations to make environmentally safe. Also, the major limitations associated with the heavy metal treatment process such as membrane process, precipitation, and clarification, activated carbon process are high cost, productivity decreases with time, requires an excessive amount of chemicals, not effective in case of wastewater containing very low concentration metal ion. But in comparison to conventional methods the low-cost adsorption process has greater significance; low-cost available sorbents, the absence of toxic sludge generation, metal recovery and most importantly effective, economical and eco-friendly treatment technique. Therefore, comparison with conventional methods, adsorption process for the heavy metal/chromium removal has significant values. Also, the raw material used as an adsorbent in this study is normally disposed to the environment in the available area of our country, because considered as functionless, this increases solid waste in the environment, increase air pollution by creating bad odor, and require landfill process for management of this solid fish scales. So, this research has significant to address the disposed of fish scales to use as adsorbents to reduce solid waste disposal to the environment, beyond use as adsorbents applicable for the realization of sustainable environmental development. So, these studies valued for two things, to meet chromium concentration as per the regulations of EEPA and solid waste reduction.

1.5.Scope of the Study

Adsorption method has proven to be an excellent way to treat effluent tannery industries and cost-effective technique. Different adsorbent materials had been used to remove heavy metals from wastewater. In this study, chemically modified fish scales were characterized and used as a sorbent for adsorption of chromium (III) ions from pollutant of tannery wastewater solution. Amount adsorbent dosage used, contact time and pH effects on removal efficiency of chromium (III) adsorption process were also analyzed. Also, adsorption kinetics and adsorption isotherm were developed for this chromium adsorption.

1.6.Conceptual Framework of the Study

The framework of the study is indicated in Figure 1.1.

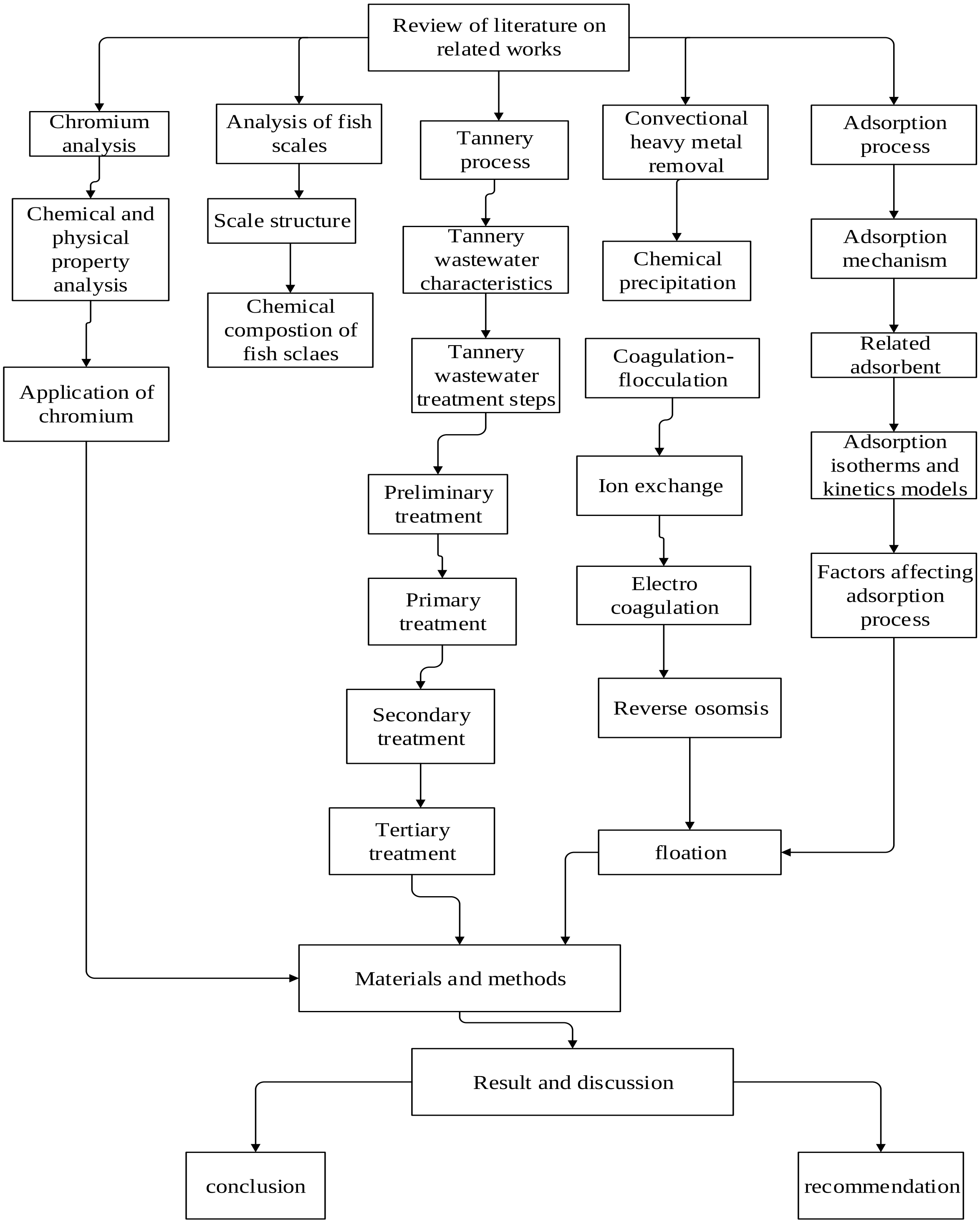


Figure 1.1: Conceptual framework this study

2. LITERATURE REVIEW

Development of rapidly increasing industry and population growth is the utilization of water for various purposes, increases tremendously as a result sources of water are polluted by discharging wastewater from both industry and domestic sectors. When compared to water pollution caused by domestic sector, pollution caused by industry sector contributes more. Still, however, several industrialists try to discharge their effluents into natural river streams and municipal sewers through unauthorized direct discharges. Such a tendency on the part of industries may pollute the entire river water to a grave extent, thereby making its purification almost an impossible task. The industries are, therefore, generally prevented by laws from discharging their untreated effluents.

Various industries produce and discharge wastes containing different heavy metals into the environment such as mining; surface finishing industry; energy and fuel production; electroplating; Leatherworking; and atomic energy installation, etc. Thus, metal as a kind of resource is becoming shortage and also brings about serious environmental pollution, threatening human health and ecosystems (Jianlong Wang, 2009**.** The methods for removing metal ions from aqueous solution mainly consist of physical, chemical and biological technologies which include chemical precipitation, ion exchange, membrane separation, coagulation-flocculation, and adsorption. Adsorption is a well-established and powerful technique for treating the industrial effluents. In comparison with conventional technology methods adsorption process, appeared to be preferable in terms of its efficiency, simplicity of design/operation, and the ease with which it can be applied in its application in the removal of heavy metals in wastewater (Adelagun, 2014).

2.1.Overview of Chromium

Chromium is a naturally occurring element found in rocks, animals, plants, and soil, where it exists in combination with other elements to form various compounds. Chromium is a metallic element with oxidation states ranging from chromium (-II) to chromium (+VI) with the trivalent (III) and hexavalent (VI) are the most predominant. Chromium released into the air, water, and soil can be transported among the various environmental media through various intermediate transport processes. Once in the environment, chromium can be taken up by human and other ecological receptors. Chromium can be found in air, soil, and water after releasing from industries. Chromium is most of deposited into the soil and water and can change from one form to another in water and soil, depending on the conditions present (Portier, 2012).

2.1.1. Chemical Properties of Chromium

Chromium is a fairly active metal. It does not react with water but reacts with most acids. It combines with oxygen at room temperature to form chromium oxide (Cr_2O_3). Chromium oxide forms a thin layer on the surface of the metal, protecting it from further corrosion or rusting. The solubility of chromium compounds varies, depending primarily on the oxidation state.

Trivalent chromium compounds, with the exception of acetate, hexahydrate of chloride, and nitrate salts, are generally insoluble in water. The zinc and lead salts of chromic acid are practically insoluble in cold water. The hexavalent chromium compounds are reduced to the trivalent form in the presence of oxidizable organic matter (Portier, 2012).

2.1.2. Sources of Chromium.

Chromium emission sources can be either direct or indirect. The direct category primarily includes sources that either produce chromium or consume chromium or a chromium compound to manufacture a product. The source categories within the direct category are described in table 2.1. From the table concluded leather tanning process is the maximum source of chromium when compared to other sources of chromium. Several directions are suggested on way to increase uptake of chromium on to the skin surface and how to remove from effluent. So, based on this description this document finding to the solution to make tannery effluent environmental safe.

Table 2.1: Sources of chromium. [sources, (Sunil H, 2014)]

Chromium chemicals	17-18%
Chromium plating	70%
Steel production	12-28%
Leather tanning	90%
Chromite ore refining	60%
Refractory production	3%
Ferrochromium production	71%

2.1.3. Application of Chromium

Chromium is the sixth most abundant element in the earth’s crust and has been numerous applications in the chemical industry, pigments, wood preservation, leather tanning, electroplating, ceramics, and manufacturing of various alloys. The metallurgical, refractory, and chemical industries are the fundamental users of chromium. In the metallurgical industry, chromium is used to produce stainless steel, alloy cast iron, and other miscellaneous materials. In the refractory industry, chromium is used as linings for high-temperature industrial furnaces. In the chemical industry, both chromium (III) and chromium (VI) are used primarily in pigments.

Around 85% of leathers made worldwide are by chrome tanning system and has been used as the primary tanning for many types of leather over 100 years. In early, the tanning Cr (III) was produced from Cr (VI) in the form of dichromate, by reduction of chrome on the tanning bath using sugars at low pH. Later on, basic chromium sulfate (BCS) was introduced as a product, to be readily used for tanning. In these processes, trivalent chromium, the most common oxidation state, is used, often in the form of Cr (III) sulfide. Commercially, BCS is prepared by the direct reduction of sodium dichromate with a sugar-sulfuric acid mixture or sulfur dioxide, which is shown in the following equations below.

$$4Na_2Cr_2O_7 + 12H_2SO_4 + C_6H_{12}O_6 \longrightarrow 8Cr(OH)SO_4 + 4Na_2SO_4 + 14H_2O + 6CO_2 \qquad 2.1$$

$$8Na_2Cr_2O_7 + 24H_2SO_4 + C_{12}H_{22}O_{11} \longrightarrow 16Cr(OH)SO_4 + 8Na_2SO_4 + 27H_2O + 12CO_2 \qquad 2.2$$

$$Na_2Cr_2O_7 + 3SO_2 + H_2O \longrightarrow 2Cr(OH)SO_4 + Na_2SO_4 \qquad 2.3$$

2.1.4. Advantages and Disadvantages of Chrome Tanning

Advantages:

- High hydrothermal stability
- Good strength characteristics that are most flexible
- Good affinity and compatibility with dyes, retaining materials, fat liquors and finishing materials

Disadvantages:

Recent reports suggest that at higher levels and under certain ligand environments, chromium (III) also in toxic. The problem is aggravated by the fact that the currently practiced chrome tanning procedures result in an uptake of only 60-70 % of the chromium offered to the leather and hence a substantial amount of chrome is discharged into the effluent (Esmaeili, 2005).

It has also been shown that there is a possibility for the formation of chromium (VI) during the various processing conditions. It is well established that hexavalent chromium is carcinogenic and can cause damage to skin, respiratory tract, kidney etc. Many chrome management measures like addition adjuncts improving the uptake of chromium, reusing/recycling the chrome liquor and recovery and reuse of chromium salts have been attempted. As of now, there is no safe disposal method available for used chrome tanned leather products, which is a major concern.

2.1.5. Aqueous Chemistry of Chromium Related to Tanning

Chromium is in the VI B group of periodic tables and the electronic configuration of chromium is $1s^2$; $2s^2$; $2p^6$; $3s^2$; $3p^6$; $3d^5$; $4s^1$. The chromium having six unpaired electrons in 3d and 4s orbitals gives rise to variable valence (oxidation number), the most common being Cr^{3+} and Cr^{6+}. Chrome tanning involves a reaction between collagen and trivalent chromium salts (Cr^{3+} salt) by coordination of carboxylic groups of collagens with chromium. In the solution of trivalent chromium salt like $CrCl_3$ exists a complex ion in the form of $[Cr\ (H_2O)_6]^{3+}3Cl^-$. The reactions occurred may be as follows:

Self-Hydrolysis

Anhydrous chromium sulfate or chloride, when dissolved in water, get hydrated. Each chromium ion can take up a maximum of six molecules of water; but, this condition does not normally obtain. Invariably, some sulfate also is present inside the complex. Even in a 1% solution of chromium sulfate as much as 50% sulfate is reported to be complexly held.

Olation of Chrome Salt

The phenomenon is important for understanding the relationship between metal ions in aqueous solution and metal oxides. One application where olation is important is leather tanning using chromium (III) sulfate. Basic chromium salt having a hydroxyl group coordinated with chromium can form olated polynuclear complex. The hydroxyl group present in coordinate chrome complex may form an additional coordinated bond with another chromium atoms thus linking two chromium (III) atoms through OH bridges which is generally called the “Ol” bridge. Thus, a very stable type of “Ol” linkage occurs between a pair of chromium (III) atoms as shown in the figure below. Increasing basicity means increasing hydroxyl content and since greater hydroxyl content favors the formation of linear structure of polynuclear olated chrome complex.

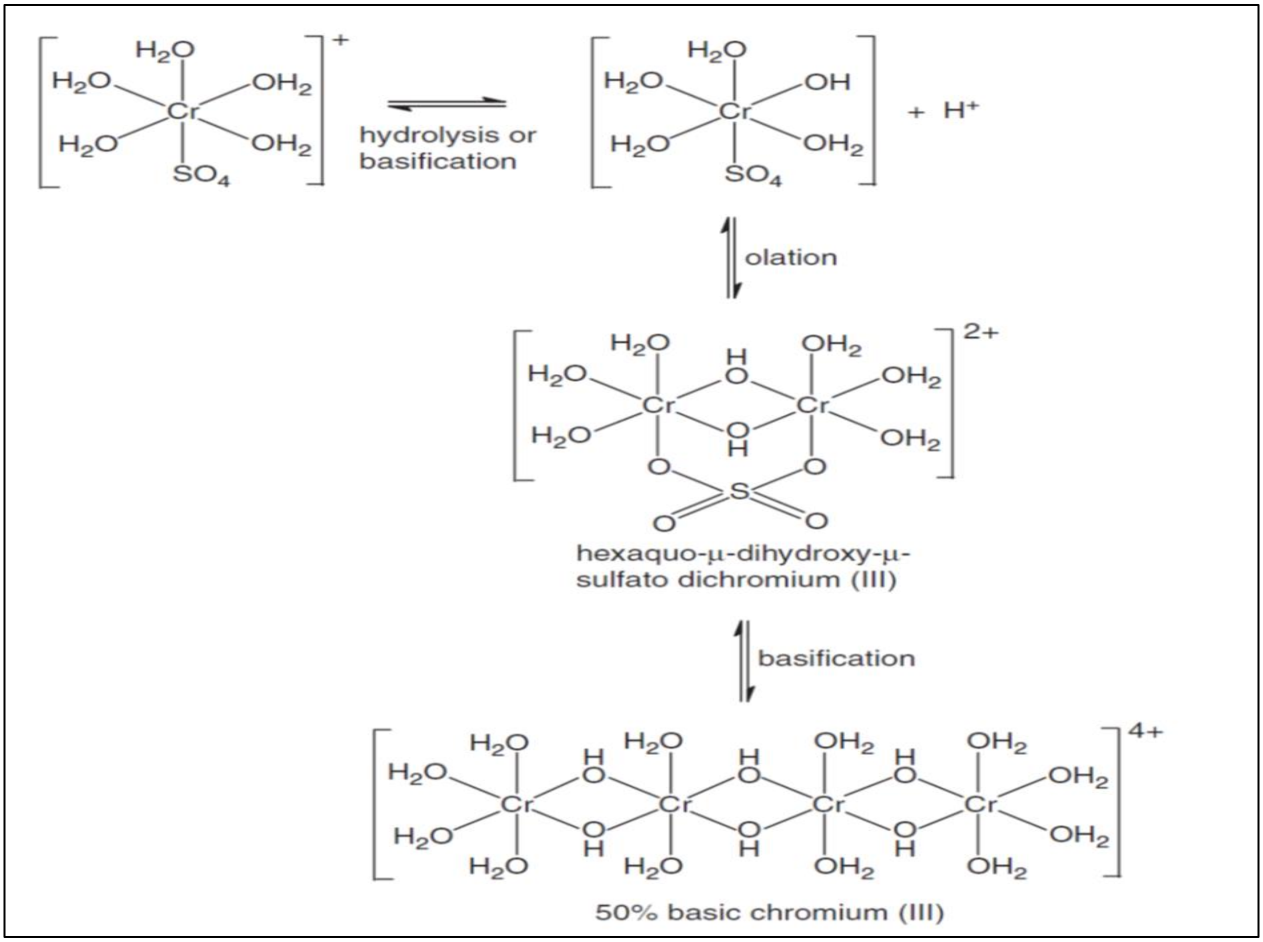


Figure 2.1: Olation process basic chromium salt

2.2.Overview of the Fish Scales

Nature has increasingly served as a source of inspiration for engineers and scientists over the last few decades. Among the natural materials of interest, the highly-mineralized materials including bones, teeth, have received substantial attention due to their special combination of properties and composition. Materials with lower mineral content like fish scales are now receiving attention as well due to their combination of flexibility, specific strength and toughness (Gil-Duran, 2015).

Fish Scales are the skeletal elements that cover and protect the skin of fishes and which is lightweight flexible dermal armor and they characteristically overlap; besides protection. Fish scales vary enormously in size, shape, structure, and extent ranging from strong and rigid armor plates and has an orthogonal plywood structure of stratified lamellae, 1–2μm in thickness consisting of closely packed 70- to 80-nm-diameter collagen fibers. X-ray diffraction, energydispersive X-ray analysis, and infrared spectroscopy indicate that the mineral phase in the scale is calcium-deficient hydroxyapatite containing a small amount of sodium and magnesium ions as well as carbonate anions in phosphate sites of the apatite lattice. (Toshiyuki Ikoma, 2003).

Scale structure

According to (Gil-Duran, 2015) analysis, two main regions are evident and denoted as the exposed and unexposed areas. The exposed area is the part of the scale that is fully exposed, while the unexposed region indicates the portion that is covered by neighboring scales. The scales overlap each other such that most of the scale is covered by another scale, which provides greater protection of the dermis by increasing the total thickness of scales on top of it.

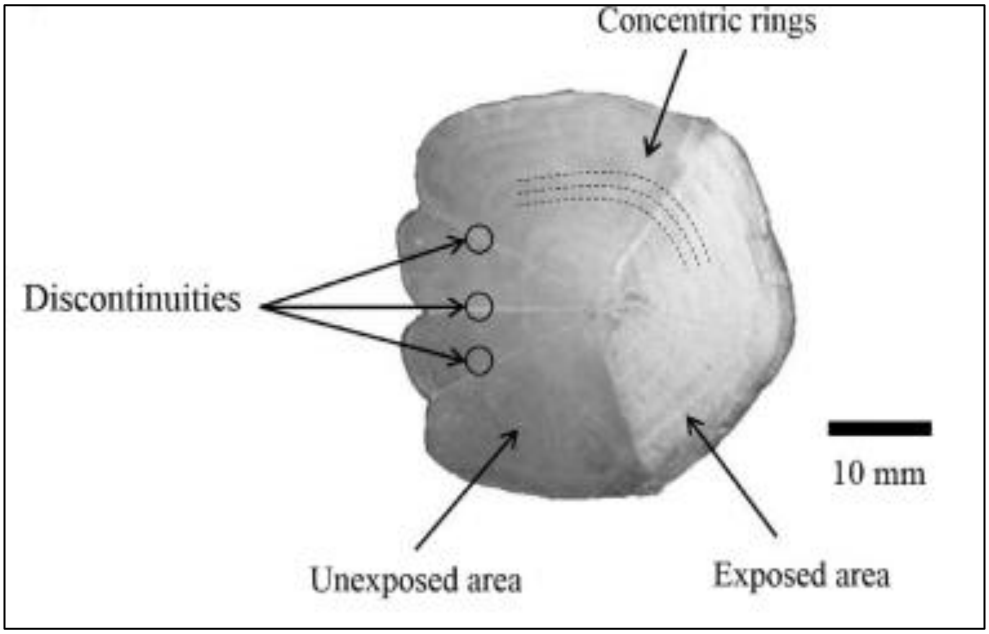


Figure 2.2: Fish Scale structure

Mechanical behavior

According to (Murcia, 2017) investigation**,** summarizes findings of the mechanical properties as a function of body position (head, mid-length, and tail) for specimens oriented in the longitudinal direction of the fish (0^o). There were statistical differences in Young's modulus of scales among the regions evaluated. While the elastic modulus of scales from the head region was significantly greater than that from the middle and tail, there was no significant difference in modulus between scales from the middle and tail.

Chemical composition fish scales

Recently, (N. Othman, 2016) reported, XRF analysis was used to analyze the chemical composition in fish scales before and after chemical pretreatment washing with nitric acid. The result demonstrates calcium oxide, CaO as the highest chemical compound in biosorbent. The presence of CaO is important as it confirms the high potential and efficiency of fish scales in adsorbing heavy metals.

Table 2.2: Chemical composition and concentration of treated fish scales, (N. Othman, 2016)

Formula	Concentration(untreated)	Concentration(treated)
Original(g)	7	7
Added (g)	3	3
CO_2	0.1%	0.1%
CaO	52.4%	63.8%
P_2O_5	28.6%	32.4%
FeO	9.75%	-
MgO	3.25%	0.24%
Al_2O_3	2.04%	-
PbO	1.76%	-
SO_3	1.51%	2.64%
SrO	0.2%	0.17%
SiO_2	0.16%	0.24%
Na_2O	0.15%	-

2.3.Leather Industry and Environmental Issues

The leather industry has gained a negative image in the society not only because of pollution causing potency but also of its dirty nature. The fact that leather industry is one of the most polluting industries, which in turn are more polluting than others. With respect to pollution potential, over 80% of the organic pollution is generated in beam house, of which 10% is derived from soak liquor, 60% from unhairing and liming, 15% from de-liming and bating, remaining 15% from the rest of the tanning process. The leather industry consumes large quantities of water, about 40-50 L/kg of hiding processed which poses environmental problems (Dixit, 2015).

Implementation of effluent treatment technologies, water management, waste minimization, recovery and reuse of chemicals in the tanneries are very important for stable growth in the leather industry, in the present context of stringent environmental regulations on one hand and increased public awareness on the other. The management of chromium-bearing effluents from tanneries is still a serious problem regardless of the implementation of several advanced processing techniques and treatment systems. While the tanning industry has been in existence for long, the problem of environmental pollution received serious consideration only in recent years. The environment is under increasing threat due to solid and liquid wastes emanating from the leather industry. These are inevitable byproducts of a leather manufacturing process that cause significant pollution unless treated prior to discharge (Lofrano, 2013).

2.4.Overview of Tannery Effluent Treatment

Acids, chromium salts, solvents, sulfides, dyes, and many others compounds which are used in the transformation of raw or semi-pickled skins into commercial goods, are not completely fixed by skins and remain in the effluent. Tannery effluent treatment is a multi-stage process to purify wastewater before it is discharged into the body of natural water, to the land, or it is reused. Three stages of treatment are usually required in order to meet the stringent discharge norms applicable in many countries for safe disposal of tannery effluent to the environment. They are primary, secondary and tertiary stage treatments. Such three stages of treatment are required because of the complex characteristics of tannery effluent. Primary treatment involves screening, equalization, chemical treatment and primary sedimentation. It is mainly employed to remove suspended solids, chromium, oil and grease, and sulfides in some cases. Secondary treatment usually involves a biological process for removal of non-conservative type organic matter (COD/BOD), sulfide, and TKN/NH4-N in some cases. Tertiary treatment is essential for removing refractory organic compounds imparting color and inorganic salts and they are considered as conservative pollutants (Dotro, 2012).

2.4.1. Process in Tanning Industry

In considering the character of tannery effluents, it is convenient to start with the processes involved in a typical tanning sequence such as the production of full chrome leather from wet salted hides. Beam house Processes (Soaking, unhairing, liming, deliming, and bating, with intermediate washes).

In beam house process animal skins are steeped in a solution of alkali solution that breaks down the structure of the hair at its weakest point or the root and send to liming to complete removal of hair and to alter the properties of the skin using a solution of alkali and sulfide and skin structure is further treated with enzymes and further unwanted material in deliming and bating (Lofrano, 2013).

Since the beam house handles the hides in their raw and dirtiest state and involves most of the cleaning up process, this work gives rise to an overwhelming proportion of the total polluting load generated in the tannery. Some estimates put the proportion at more than 80% of the total, this being associated with perhaps 20 to 25% of the total water discharged. The waters are of high pH and contain high in suspended solids, including dirt, lime, and organic matter from the hair, hide and dung. These substances confer a very high Oxygen Demand but, being of animal origin, are basically amenable to biological breakdown.

Tanning operation, in the tanning operation the skin is treated with substances chromium salts, vegetable substances, aldehydes, oils (Mohammed, 2015). During tanning, the skin structure is stabilized in its open form by replacing some of the collagen with complexions of chromium. Depending on the compounds used, the color and texture of the leather changes. When leather has been tanned it is able too much more flexible than an untreated dead skin. Fairly small volumes of liquors of low pH are generated, containing the chromium which is not taken up by the leather. These liquors contain some protein and are high in neutral salts, mainly sodium sulfate and chloride (Lofrano, 2013).

Post-tanning wet processes (fat liquoring, retanning and dyeing). In the post-tanning operations, the tanned semi-finished leathers are dyed to give a color determined by the fashion demand and fat liquored to impart the degree of softness needed in the final leather and retanned to impart the filling, grain tightening and improve the uniformity in substance.

Finishing; finishing includes all operations performed on the hide after fat liquoring and includes enhancement of color resistance to stains and abrasions, smoothing stretching the skin, drying, conditioning, staking, dry milling, buffing and plating. Finishing operations generate little liquid effluent apart from that used in spray booths to scrub the exhaust air. Problems may be caused if this liquor contains dissolved or condensed organics, or pigment or dye residues containing toxic metals such as cadmium, lead or copper (Lofrano, 2013).

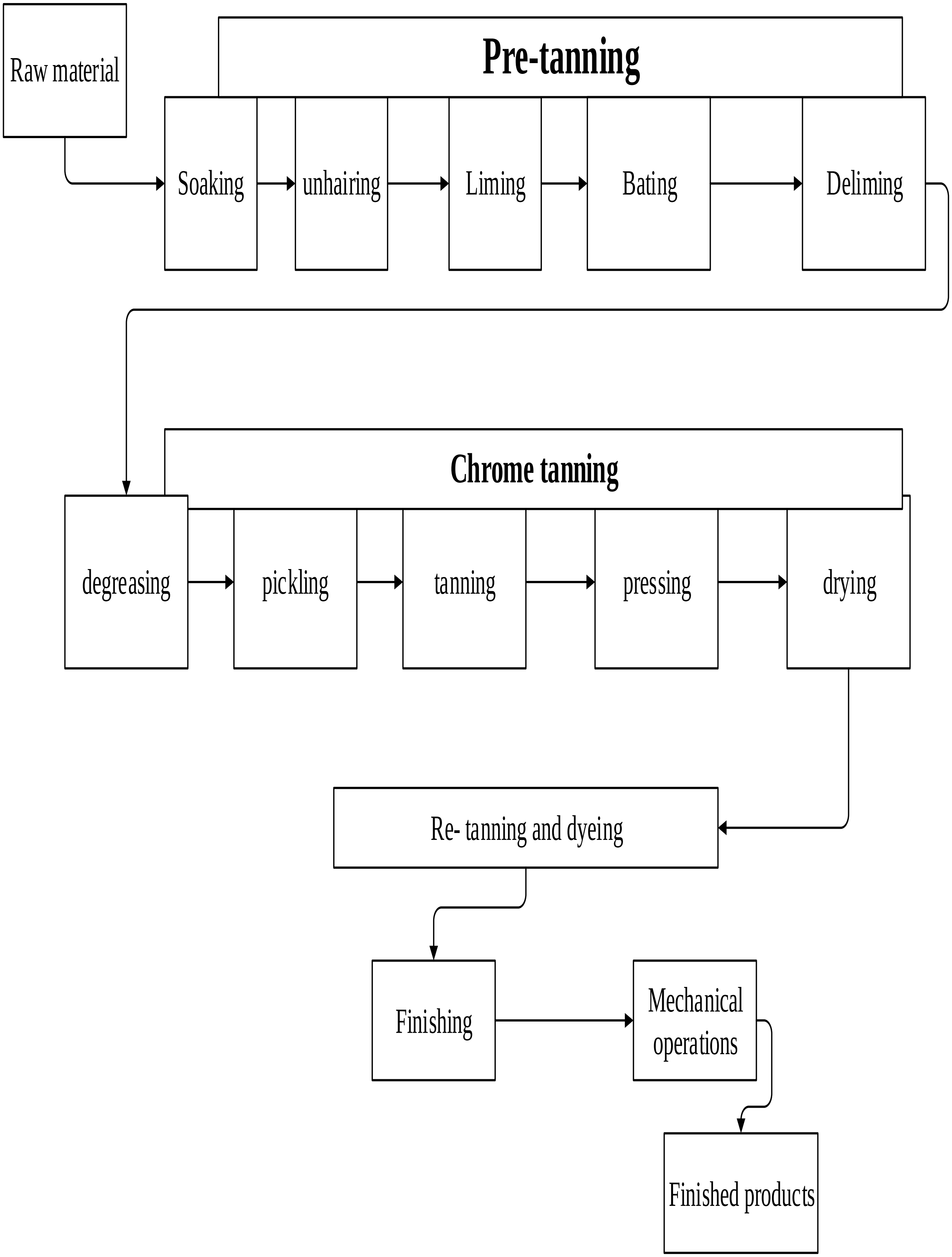


Figure 2.3: Typical process flow diagram of tanning industry.

2.4.2. Discharge of Tannery Effluents – Legislative Requirements

The liquid effluent produced by leather making operations must be disposed of at approximately the same rate at which it is generated. Direct discharge into a watercourse frequently raises many problems, scientific, legal and aesthetic. Under most circumstances, however, such a discharge would only be accepted after the effluent had been subjected to a high degree of purification that is pre-treatment. The discharge standards of tannery effluents as per Ethiopian Environmental Protection Authority (EEPA) are listed in Table 2.3.

Table 2.3: Effluent standards as per EEPA, all are in mg/l expect pH

Parameter	**Discharge standard**
pH	6 – 9
BOD 5 days at 20^{o}C (Total)	200 or 90%
COD (Total)	500
Sulfide (as S)	1
Total Solids (TS)	-
Total Dissolved Solids (TDS)	2100
Suspended Solids (SS)	50
Chlorides as Cl	1000
Chromium (as Cr-VI)	0.1
Chromium (as Total Cr)	2

2.4.3. Characterization of Tanning effluent

The characteristics of tannery wastewater vary considerably from tannery to tannery depending upon the chemicals used for a specific process, the size of the tannery, amount of water used and types of final product produced by tanneries. Tannery wastewater is characterized mainly by measurements of Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Suspended Solids (SS), Total Dissolved Solids (TDS) and chromium and sulfides etc. In general, tannery wastewaters are basic, have a dark brown color and have a high content of organic substances that vary according to the chemical use.

Table 2.4: Characteristics of tannery wastewater.

Parameters	**Soaking**	**Liming**	**De-liming**	**Pickling**	**Vegetable Tanning**	**Chrome Tanning**	**Dyeing and Fat liquors**	**Composite (including Washing)**
pH	7.5-8.0	10.0-12.8	7.0-9.0	2.0-3.0	4.0-7.0	2.5-4.0	3.5-4.5	7.0-9.0
BOD (5 days @20^{0}C)	1100-2500	5000-10000	1000-3000	400-700	6000-18000	350-800	1000-2000	1000-3000
COD	3000-55000	1000-25000	2500-7000	1000-3000	15000-40000	1000-2500	2500-7000	2500-8000
Total solids	35000-55000	30000-50000	4000-10000	35000-70000	25000-60000	30000-60000	4000-10000	15000-25000
Dissolved solids	32000-48000	24000-30000	2500-6000	34000-67000	21000-50000	29000-57500	3400-9000	13000-21000
Suspended solids	3000-7000	6000-200000	1500-4000	1000-3000	4000-10000	1000-2500	600-1000	2000-4000
Chlorides	15000-30000	4000-8000	1000-2000	2000-30000	1000-2500	15000-25000	500-1000	6000-9500
Total Chromium	-	-	-	-	-	2000-5000	-	100-250

Except for pH all values are in (mg/l), source: (Isam, 2016)

2.5.Tannery Wastewater Treatment Process

The processes and technologies used to remove contaminants from water and to improve and protect water quality are similar all around the world. The choice of which treatment to use from the great variety of available processes depends on the characteristics of the water, the types of water quality problems likely to be present, and the costs of different treatments. Wastewater treatment, however, can also be organized or categorized by the nature of the treatment process operation being used it may be physical, chemical or biological.

Tannery wastewater treatment is necessary due to the wide range of toxic effects on the environment caused by untreated tannery effluents and sludge. There are situations in which an individual tannery applies all the below-described wastewater treatment steps on the site. In other situations, an individual tannery may apply on-site only pre-treatment or a partial pre-treatment or no treatment at all, sending the effluent to a centralized effluent treatment plant (Yusif et al., 2016).

2.5.1. Preliminary Treatment

Pre-treatment units installed in individual tanneries. Their role is to remove large particles, sand/grit, and grease, but also to significantly reduce the content of chrome and sulfide before the effluent is discharged into the collection network.

2.5.1.1.Mechanical Treatment

Usually, the first treatment of the raw effluent is the mechanical treatment that includes screening to remove coarse material. Up to 30-40% of gross suspended solids in the raw waste stream can be removed by properly designed screens. Mechanical treatment may also include skimming of fats, grease, oils and gravity settling. After a mechanical treatment, physicochemical treatment is usually carried out which involves the chrome precipitation and sulfide.

Screening is one of mechanical treatment usually the first unit operation at wastewater treatment plants. A screen is a device with openings, general of uniform size that is used to retain solids found in the effluent wastewater to the treatment plant or in combined wastewater- collection systems. The principal role of screening is to remove coarse materials from the flow stream that could damage subsequent process equipment, reduce overall treatment process reliability and effectiveness. The screening units include racks, coarse screens, and fine screens.

2.5.2. Primary Treatment

The objective primary treatment is the removal of settling able organic and inorganic solids by sedimentation, and the removal of materials that will float or scum by skimming. Approximately 25-50% of the incoming biochemical oxygen demand (BOD_5), 50-70% of total suspended solids (SS), and 65% of the oil and grease are removed during primary treatment (Kral., 2011). The function of Primary treatment is: to eliminate the coarse material normally present in the raw wastewater that could clog/block pumps, pipes and possibly sewer lines; to mix and balance well different tannery streams and thus produce homogenized raw material that can be treated in a consistent manner; to adjust pH and eliminate toxic substances and avoid shock loads that can negatively affect the rather sensitive biological treatment; to significantly decrease the BOD/COD load and thus simplify the biological treatment phase and reduce its cost.

2.5.3. Equalization and Homogenization

In this process the main objective is a homogenization of the effluent quantity and quality; and sulfide elimination, mostly by catalytic oxidation. It is very important to keep all particulate matters in suspension that is to avoid settling of solids. This is process will be achieved by using mixing-cum-aeration devices such as diffused-air systems, the most preferred, and fixed or floating aerators. In practice, to play it safe, the volume of the equalization tank corresponds to the total daily effluent discharge. The inlet and the outlet of the equalization tank should be as far away from each other as possible to allow proper mixing and no short-circuiting.

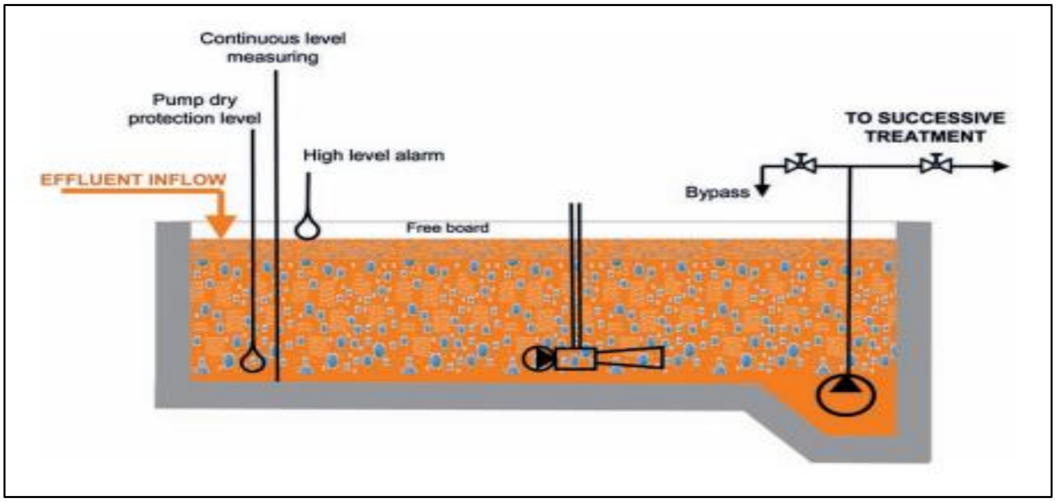


Figure 2.4: Schematic view of an equalization and homogenization tank.

2.5.4. Chemical Treatment (Coagulation and Flocculation)

In wastewater treatment operations, the processes of coagulation and flocculation are employed to separate suspended solids from water. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge (zeta potential) of the colloids. As a result, the particles collide to form larger particle flocs. The most frequently used coagulants in tannery effluent treatment are: alum: industrial aluminum sulfate $Al_2(SO_4)_3 \cdot 18H_2O$; iron sulfate: industrial $FeSO_4 \cdot 7H_2O$; iron chloride: industrial $FeCl_3 \cdot 6H_2O$ (Crittenden et al., 2012). Flocculation is the action of polymers to form bridges between flocs and bind particles into large agglomerates. In this process, it is essential that the flocculating agent is added by slow and gentle mixing to allow for contact between the small flocs and to agglomerate them into larger particles. Once suspended particles are flocculated into larger particles, they can usually be removed from the liquid by sedimentation, filtration, straining or floatation.

2.5.5. Settling (Primary Sedimentation)

The main objective at this stage is the removal of suspended solids, however, various constituents such as fats, waxes, floating non-fatty materials, etc. grease, not already removed in the screening and equalization, are also separated here. Primary settling tanks clarifiers are either circular more commonly used or rectangular with continuous grease scum removal at the top and sludge removal at the bottom.

2.5.6. Biological Treatment

Biological processes are also employed as a secondary treatment option after primary treatment to remove the major portion of dissolved organics and nutrients from tannery effluent. The major types of biological processes include aerobic, anaerobic and combine biological method which can be suitably adopted in various phases of tannery effluent treatment (Yusif et al., 2016).

In the biological treatment process, various microorganisms are capable of reducing the content of pollutants significantly by utilizing them as energy and nutrient source in the presence or absence of oxygen. Treatment of wastes with bacteria involves the stabilization of waste by decomposing them into harmless inorganic solids either by the aerobic or anaerobic process (Rajasimman, 2011).

2.5.6.1.Aerobic Treatment

The principle of the aerobic biodegradation is a significant aspect of biological treatment. This is the process where oxygen is needed by degradable organisms in their degradation at two metabolic sites, at the initial attack of the substrate and at the end of the respiratory chain Yusif et al., 2016). Oxygenase and peroxidases could be produced by the Bacteria and fungi which could help with the pollutant oxidization and get benefits from observing the energy, carbon and nutrient elements released during this process. There are two types of relationships between the microorganism and organic pollutants; that is the microorganisms use organic pollutant as source of carbon and energy, and the microorganisms use a growth substrate as carbon and energy source, while another organic compound in the organic substrate which could not provide carbon and energy resource is also degraded co-metabolism. Biodegradation of tannery wastewater using activated sludge process has been reported by many research workers. Various parameters of importance relating to the growth of microorganisms and substrate utilization on which the operation of the reactor is based include mean cell residence time, Mixed Liquor Volatile Microorganism (MLVSS) concentration, hydraulic detention time, food to microorganism (F: M) ratio and the dissolved oxygen the reactor. Aerobic microorganisms use organic carbon in the effluent and convert it to biomass and carbon dioxide (Dey, 2008).

2.5.6.2.Anaerobic Treatment

The treatment of tannery effluent anaerobically is a process in which microorganisms break down biodegradable material in the absence of oxygen. Anaerobic treatment of wastewater converts the organic pollutants into a small amount of sludge and a large amount of biogas, methane and carbon dioxide. The principle of the anaerobic treatment is the insoluble organic pollutant breaks down the insoluble substances, making them available for other bacteria, the acidogenic bacteria convert the sugars and amino acid into carbon dioxide, hydrogen and carbon dioxide and finally the methanogens convert the acetic acid into hydrogen, carbon dioxide and methane (Yusif et al., 2016). The anaerobic process is a very attractive solution for the treatment of highly loaded wastewaters, due to low sludge production and energy consumption; nevertheless, its application to tannery wastewater shows several drawbacks due to the complexity of the chemical composition (Mannucci, 2010). The anaerobic biological membrane process includes fluidized bed reactor, anaerobic rotating biological contactor, anaerobic filter reactor.

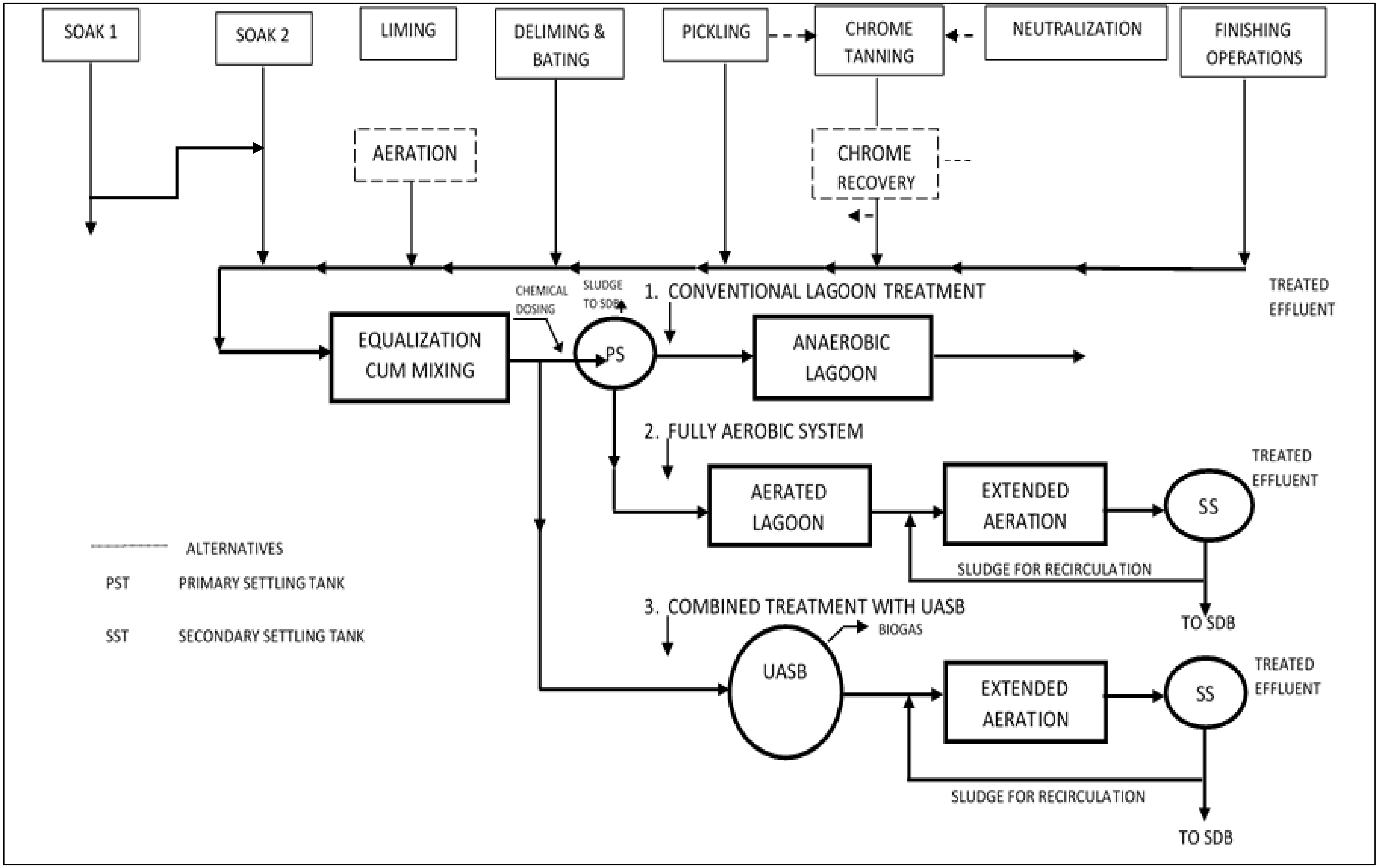


Figure 2. 5: Flow diagram of tannery wastewater treatment process

2.6.Conventional Heavy Metal Removal Methods

Metal removal processes are carefully considered not only toxic heavy metal removal in environmental aspects. Those metals considered environmentally hazardous, or which are of technological importance, strategic significance or economic value must be removed or recovered from their source using appropriate treatment systems. Treatments such as physicochemical, ion exchange; chemical precipitation; reverse osmosis; floatation; coagulation and flocculation and adsorption can be employed to remove heavy metals [chromium (Cr)] from contaminated wastewater (Etorki, 2014).

1. Chemical precipitation

Chemical precipitation is a widely used process for removal of heavy metals from different solution. The mechanism of this process is based on to produce insoluble metal precipitation by reacting dissolved metals in the solution and precipitant. In the precipitation process, very fine particles are generated and chemical precipitants, coagulants, and flocculation processes are used to increase their particle size to remove them as sludge. The most commonly used precipitation technique is hydroxide treatment due to its relative simplicity, low cost of precipitant, and ease of automatic pH control. Sulfide precipitation has also been used for the treatment of metal-containing wastewater and effective process for the treatment of toxic heavy metals ions (Fenglian Fu, 2011). Generally, precipitation has been widely used for its simplicity, but has drawbacks: it usually results in a net increase in the total dissolved solids in the wastewater being treated, and a large amount of sludge requiring treatment, which, in turn, may contain toxic compounds that may be difficult to treat.

2. Coagulation and flocculation

Coagulation process is the destabilization of colloids by neutralizing the forces that keep them apart and reduces the net surface charge of the colloidal particles to stabilize by electrostatic repulsion process. Flocculation process continually increases the particle size to discrete particles through additional collisions and interaction with inorganic polymers formed by organic polymers added. Production of sludge, use chemicals and transfer of toxic compounds into solid phase are main drawbacks of the process. The objective of the coagulation depends on the source of water and the nature of the suspended, colloidal, and dissolved organic constituents (Crittenden, 2012).

3. Ion exchange

Ion exchange can attract soluble ions from the liquid phase to the solid phase, which is the most widely used method in water treatment industry (Gunatilake, 2015). However, it requires pretreatment process to reduce suspended solids concentration in solution to prevent fouling or channeling. Ion exchange resins, either synthetic or natural solid resin, has the specific ability to exchange its cation with the metals in the wastewater. The most common cation exchangers are strongly acidic resins with sulfonic groups (-SO_3H) and weakly acids resins with carboxylic acid groups (-COOH). Ion exchange resins have also been frequently used for the removal of chromium ions from aqueous solutions (Ahmad, 2014). As the solution containing heavy metal passes through the cations column, metal ions are exchanged for the hydrogen ions on the resin with the following ion-exchange process:

$$nR - SO_3H + M^{n+} \longrightarrow (R - SO_3^-)_n M^{n+} + nH^+$$

$$nR - COOH + M^{n+} \longrightarrow (R - COO^-)_n M^{n+} + nH^+$$

4. Electrocoagulation

Electrocoagulation (EC) is a treatment process of applying an electrical current to treat and flocculate contaminants without having to add coagulations (Adhoum, 2004). Electro-coagulation technique uses a direct current source between metal electrodes immersed in polluted water. The electrical current causes the dissolution of metal plates including iron or aluminum into wastewater. Electrocoagulation consists of pairs of metal sheets called electrodes that are arranged in pairs of two; anodes and cathodes and using the principles of electrochemistry, the cathode is oxidized (loses electrons), while the water is reduced (gains electrons), thereby making the wastewater better treated. When the cathode electrode makes contact with the wastewater, the metal is emitted into the apparatus.

5. Reverse osmosis

Reverse Osmosis (RO) process uses a semi-permeable membrane, allowing the fluid that is being purified to pass through it while rejecting the contaminants and the techniques able to remove a wide range of dissolved species from water and an increasingly popular wastewater treatment option in chemical and environmental engineering (Fenglian Fu, 2011).

The process requires high-quality feed for efficient operation, thus wastewater must be treated to remove solids prior to RO treatment. The major drawback of RO is the high-power consumption due to the pumping pressures, and the restoration of the membranes, partial removal of certain ions and apart from the expense, membranes are also unable to resist certain types of chemicals and pH values and are prone to deterioration in the presence of microorganisms. Using appropriate RO systems to remove heavy metals have been investigated, but these have yet to be widely applied.

6. Flotation

Flotation has nowadays found extensive use in wastewater treatment and employed to separate heavy metal from a liquid phase using bubble attachment. Dissolved air flotation (DAF), ion flotation, and precipitation flotation are main flotation process for the removal of metal ions from solution. Ion flotation has been shown that a promising method for the removal of heavy metal ions from wastewaters (Fenglian Fu, 2011).

DAF is to allow micro-bubbles of air to attach to the suspended particles in the water, developing agglomerates with lower density than water, causing the flocs to rise through the water and accumulating at the surface where they can be removed as sludge. Precipitate floatation process is another alternative of flotation method, based on the formation of a precipitate and subsequent removal by attachment to air bubbles. Depending on the concentration of the metal solution, the precipitation may proceed via metal hydroxide formation or as a salt with a specific anion like sulfide, carbonate, etc.

7. Electrodialysis

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 characteristic. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cation toward the cathode, crossing the anion exchange and cation-exchange membranes. A noticeable disadvantage is membranes replacement and the corrosion process. Its advantage for the treatment of highly concentrated wastewater loaded with heavy metals to recovery undesirable impurities from water. In the electrodialysis process, ionic components of a solution are separated through the use of semipermeable ion-selective membranes (Wang, 2009).

2.7.Adsorption

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 and where one or more components adsorbate is attracted and bonded to the surface of a solid adsorbent with which they are in contact (Cecen, 2012). In this manner, the components of either gaseous or liquid solutions can be separated from each other and in principle, adsorption can occur at any solid-fluid interface. In adsorption, molecules diffuse from the bulk of the fluid to the surface of the solid adsorbent forming a distinct adsorbed phase. The driving force for adsorption is the reduction in interfacial (surface) tension between the fluid and the solid adsorbent as a result adsorption of the adsorbate on the surface of the solid. Separation by adsorption depends on one component being more readily adsorbed than another (Richardosn,2002)**.**

Adsorption is commonly used in the treatment of industrial wastewaters containing organic compounds not easily biodegraded during secondary, biological treatment or toxic and well-established and powerful technique for treating domestic and industrial effluents. Adsorption finds applications in tertiary wastewater treatment as a polishing step before final discharge.

2.8.Types of Adsorbents

Biosorption of heavy metals from aqueous solutions is a relatively new process that has been confirmed a very promising process in the removal of heavy metal contaminants (K. Vijayaraghavan, 2015). The major advantages of biosorption are its effectiveness in reducing the heavy metal ions and the use of inexpensive biosorbent. Biosorption processes are particularly suitable to treat dilute heavy metal wastewater. Typical biosorbents can be derived from different inexpensive, non-living plant material such as potato peels, sawdust, seed shells, coffee husks, orange peel (white inner skin), orange peel (outer skin), modified wool, dry redwood leaves, moss, and citrus peels have been widely investigated in the different chemical modification of surface area as potential sorbents for heavy metals (Fenglian Fu, 2011). The researchers use sorbents from agricultural waste, biosorbents, industrial wastes, using different steps to increase the removal efficiency like chemical modification, thermal activation, and activated carbon. Finally, they concluded that different value of removal efficiencies (U. Rafique, 2013; Monser, 2001; Garg, 2003; Singanan, 2013; Albadarin, 2012; Morris, 2012; Martin, 2017; S. Arris, 2016; Ozturk, 2012; Adamczuk, 2016).

2.8.1. Physical Properties of the Adsorbent

The most important property of adsorbent which determines its usage is the pore structure and the specific surface area (Mohamed, 2011). The total number of pores, their shape, and size determine the adsorption capacity and even the dynamic adsorption rate of the adsorbent. The factors in the properties of an adsorbent number of pores, size, and shape have a vital role in the removal efficiency. Accordingly, researchers use different chemical and thermal methods to modified physical properties of the adsorbent for considering the surface area, pore structure, and size of adsorbent to overall removal efficiency of those material used as an adsorbent.

The range of pore sizes which is defined according to the International Union of Pure and Applied Chemistry (IUPAC) is shown in table 2.7.

Table 2.5: IUPAC classifications of pore sizes

Pores	**Pore width (W; nm)**
Ultra-micropores	W<0.7
Super-micropores	0.7<W<2
Micropores	W<0.2
Mesopores	2-50
Macropores	W>50

2.8.2. Previous Study using Fish Scales and Related Adsorbent

Activated Carbon has been the most used adsorbent, nevertheless, it is relatively expensive. Therefore, searching for low-cost and easily available adsorbents to remove heavy metal ions have become the main research focus. To date, hundreds of studies on the use of low-cost adsorbents have been published. Agricultural wastes, industrial by-products and wastes and natural substances have been studied as adsorbents for the heavy metal wastewater treatment. In the last few decades, alternative sorbents for the treatment of chromium (Cr) contamination have been investigated using biosorption as adsorbents. (N. Othman, 2016), carried out batch adsorption using waste fish scales as a cost-effective adsorbent in removing Zinc and Ferum ion in wastewater. (Darge, 2013), investigate batch adsorption process, treatment of industrial wastewater by using banana peels and fish scales. (Marrakchi, 2016), analysis the mesoporous carbonaceous material from fish scales as low-cost adsorbent for reactive orange 16 adsorptions. (Balaska, 2012), purifying aqueous solutions containing heavy and toxic metals such as chromium has been investigated using polymer assisted ultrafiltration. This research study when consider beyond above cited journals different which is focused on removal of chromium (III) ion from tannery wastewater because most tanning industry in Ethiopia is direct discharge to the environment which is above permissible limit according to Ethiopian Environmental Protection Authority. So, in comparison of those studies, the study added positive impact on sustainable environmental development in considering pollution from tannery wastewater.

2.9.Adsorption Mechanism

The complexity of the adsorbent structure implies that there are many ways for the metal to be captured by the cell. The adsorption process of the adsorbate molecules from the bulk liquid phase into the adsorbent surface is presumed to involve: mass transfer of the adsorbate molecules across the external boundary layer towards the solid particle; adsorbate molecules transport from the particle surface into the active sites by diffusion within the pore-filled liquid and migrate along the solid surface of the pore; Solute molecules adsorption on the active sites on the interior surfaces of the pores.

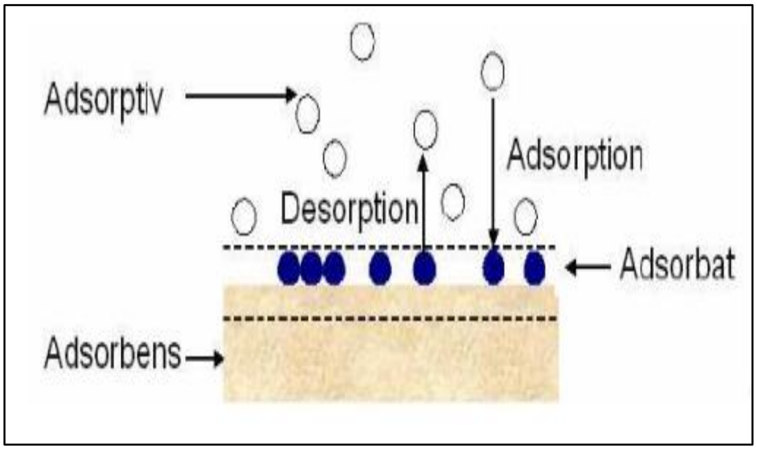


Figure 2. 6: Mechanism of adsorption process

Physical adsorption: When the force of attraction existing between adsorbate and adsorbent are weak the type is Van der Waals forces of attraction; the process is Physical adsorption. Adsorbates are said to undergo physical adsorption if the forces of attraction include only physical forces that exclude covalent bonding with the surface and columbic attraction of unlike charges.

Physical adsorption takes place with the formation of a multilayer of adsorbate on the adsorbent. In physical adsorption process, there is no electron exchange between adsorbent and adsorbate and it's a reversible process (Cecen, 2012).

Chemical adsorption occurs when the adsorbate reacts with the surface of adsorbent to form a covalent bond or an ionic bond. In chemisorption, the attraction between adsorbent and adsorbate approaches that of a covalent or electrostatic chemical bond between atoms, with shorter bond length and higher bond energy. Adsorbates bound by chemisorption to a surface generally cannot accumulate at more than one molecular layer because of the specificity of the bond between adsorbate and surface. Chemical adsorption results from the chemical link between adsorbent and adsorbate molecule, therefore it is specific as well as irreversible and chemical as well as electronic properties of adsorbent are changed. (Thaku, 2013).

2.10. Adsorption Equilibrium Models

Adsorption will continue until equilibrium will be established between the substance in solution and the same substance in the adsorbed state. At equilibrium, a relationship exists between the concentration of the species in solution and the concentration of the same species in the adsorbed state i.e., the amount of species adsorbed per unit mass of adsorbent. The equilibrium position in a considered system depends on the strength of the adsorbate/adsorbent interactions and is significantly affected by the properties of the adsorbate and adsorbent but also by properties of the aqueous solution, such as temperature, pH value, and occurrence of competing for adsorbates. Upon contacting an amount of adsorbent with a wastewater containing absorbable substance adsorption will take place (Albadarin, 2012).

Equilibrium isotherm model equations such as Langmuir and Freundlich 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). 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.

$$\mathrm{q_{eq}} = \mathrm{f}\left(\mathrm{C_{eq}}, \mathrm{T}\right) ----------------------2.1$$

Where C_{eq} 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.

2.10.1. Langmuir Adsorption Isotherm

Langmuir adsorption isotherms are widely used to describe the relationship between the amount of adsorbate adsorbed onto the adsorbent and its equilibrium concentration in aqueous solution an 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:

$$q_e = \frac{q_{max}K_LC_e}{1+K_LC_e} ---------------------- 2.2$$

Where q_e 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 C_e, C_e is concentration of metal ions in solution at equilibrium and K_L is a Langmuir constant.

The linear form is

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_Lq_{max}} -------------------- 2.3$$

The value of q_{max} and K_L computed from slope and intercept of the Langmuir plot of C_e/q_e versus C_e. 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, 2012).

$$R_L = \frac{1}{1++K_LC_o} -------------------- 2.4$$

Where C_o 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 $R_L = 0$.

2.10.2. 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

$$q_e = K_f C_e^{\frac{1}{n}} ---------------------- 2.5$$

Where C_e = the equilibrium concentration of adsorbate (mg/L) , q_e = 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 n are indicators of adsorption capacity and adsorption intensity respectively. The linear form is:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \; ------------- 2.6$$

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.

2.11. Adsorption Kinetics Models

The prediction of adsorption rate gives important information for designing batch adsorption systems. Predicting the rate at which biosorption occurs for a given system is another important factor in biosorption system design, since adsorbate residence time and the reactor dimensions should be in accordance with the systems kinetics. In spite of the importance of biosorption equilibrium studies, that determine the efficiency of the process, kinetic models were used to elucidate the mechanism of biosorption together with its rate controlling steps.

Furthermore, data on the kinetics of heavy metal uptake are necessary to select the best conditions for full-scale biosorption process. The kinetics of adsorption was studied by using first order, and second order models. These models take into account the adsorbed quantities that will enable us in determining the reactor volume.

2.11.1. Pseudo-first-order Kinetic Model

The pseudo first order rate equation is:

$$\frac{\mathrm{dq}}{\mathrm{dt}} = \mathrm{k_1(q_e - q_t)} ------------------2.7$$

Where k$_1$ is the rate constant for the pseudo-first-order kinetic equation and q$_e$ and q$_t$ are amounts of solute adsorbed per unit adsorbent at equilibrium and at time t, respectively (Agnieszka Adamczuk, Dorota Kołodyn´ ska, 2016).

The linear form of equation 2.6 expressed in the form of:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t ------------ 2.8$$

2.11.2. Pseudo-second-order Kinetic Model

The pseudo-second-order rate equation is:

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

Where k$_2$ is the rate constant for the pseudo-second-order kinetic equation and q$_e$ and q$_t$ are the amounts of solute adsorbed per unit adsorbent at equilibrium and at time t, respectively (Albadarin, Chirangano et a., 2012).

The linear form expressed as in the form of:

$$\frac{\mathrm{t}}{\mathrm{q_t}} = \frac{1}{\mathrm{k_2 q_e^2}} + \frac{\mathrm{t}}{\mathrm{q_e}} \quad ----- -- -- ---- --- -- 2.9$$

2.12. Factors Affecting Adsorption Process

2.12.1. Effect of 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 a the amount of adsorbents and keeping the other parameters constant. According to (Joshi, 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 (III) ion in solution has been decreased drastically with the increase in the sorbent dosage.

2.12.2. Effect of Contact Time or Residence Time

Contact time is one of the effective factors in batch adsorption process. On increasing the time, the initial concentration reduces, that is removal efficiency increased with an increase in contact time before equilibrium is reached. The amount adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under the operating conditions. The longer the time the more complete the adsorption will be (Emoruwa & Agbozu , 2014).

2.12.3. Effect of Initial Metal Ion Concentration

Initial concentration is one of the effective factors on adsorption efficiency. It is generally agreed that the adsorption capacity increases as the initial metal ion concentration in the solution increase, whereas the metal removal percentage efficiency decreases by increasing the metal ion initial concentration. As a rule, increasing the initial metal concentration results in an increase in the adsorption capacity because it provides a driving force to overcome mass transfer resistance between the sorbent and sorption medium (Emoruwa & Agbozu , 2014). The removal efficiency of the ions by the sorbent initially increases with increasing the initial ion concentration. At lower ion concentration in the solution, the ions would interact with the binding sites and thus facilitated almost 100% adsorption whereas, at higher concentrations, more ions are left un-adsorbed in the solution due to the saturation of the binding sites (Abbas et al., 2014).

2.12.4. Effect of pH

For biosorption of heavy metal ions, pH is one of the most important environmental factors. The pH value of solution strongly influenced not only the site of dissociation of the biomass surface but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic or inorganic ligands, redox reactions, precipitation, the specification and the biosorption availability of the heavy metals (Wang, 2009). In a certain pH range, most metal adsorption increases with increasing pH up to a certain value and then decreases with further increases in pH, that is not linear relationships (Ahmaruzzaman, M., 2011). According to the analysis of (Singanan & Peters, 2013), the removal Cr (III) ions in the aqueous solution is low at low pH values and gradually increased with pH of the solution.

2.12.5. Effect of Surface Area of Adsorbent

The extent of adsorption is generally considered to be proportional to the specific surface area. Specific surface area is that proportion of the total surface area which is available for adsorption. The more finely divided and more porous adsorbents would be expected to yield more adsorption per unit weight of the adsorbent. The surface can be characterized either as external when it involves bulges or cavities with a width greater than depth or internal when it involves pores and cavities that have a depth greater than the width (Cecen, 2012).

2.12.6. Effect of Porosity Adsorbent

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, mesopores are pores of a width between 2 and 50 nm, and Macropores are pores of a width greater than 50 nm. A further classification involves ultra-micropores, which are pores of a width less than 0.7 nm. The specific surface area of Macropores adsorbents is very small. Therefore, adsorption on this surface is usually neglected. In the case of mesopores, the adsorbent surface area has a distinct physical meaning. Mono- and multilayer adsorption takes place successively on the surface of mesopores, and adsorption proceeds according to the mechanism of capillary adsorbate condensation. Specific surface area, pore volume, and pore size distribution are basic parameters characterizing mesopores. Mesopores and Macropores play an essential role in the transport of adsorbate molecules through the micropores. The sizes of micropores are usually comparable to those of adsorbate molecules. Consequently, adsorption in micropores is essentially a pore-filling process. Therefore, the volume is the main controlling parameter for adsorption in micropores. Considering also that most of the total surface area is found in the micropores and the contribution of Macropores to the total surface area is very low, the contribution of micropores to adsorption would be expected to be higher (Cecen, 2012).

3. MATERIALS AND METHODS

3.1.Materials

3.1.1. Chemicals and Apparatus Equipment

All the chemicals used were analytical grade. Basic chromium sulfate ($Cr_2 (SO_4)_3$), hydrochloric acid (HCl), sodium hydroxide (Na (OH)), calcium hydroxide (CA $(OH)_2$, and sulfuric acid (H_2SO_4) were purchased from chemical plc. market, Addis Ababa. Basic chromium sulfate used as a preparation of model stock solution which represents tannery wastewater containing chromium (III) ion. Hydrochloric acid (HCl), Sodium Hydroxide (Na (OH)), Calcium Hydroxide (CA $(OH)_2$ and Sulfuric acid (H_2SO_4) solution, which is used for modifying the raw fish scale and to control pH of the solution.

In this experiment, the apparatus and equipment were used to set up the batch tests and analyze the samples. Different size beaker, volumetric flasks, graduated cylinder, centrifuge plastic tube, pipettes, plastic and glass bottles, plastic bag and magnetic stirrer are used during batch tests. Main equipment, Oven used for drying adsorbent and material used and Fourier transform infrared (FTIR) spectra were recorded using (Perkin Elmer, Spectrum 65FT-IR spectrophotometer) to analyze the functional groups present in the fish scale. X-ray Diffraction used to identify crystalline or amorphous properties of the raw fish scales and solution pH was adjusted using pH meter. The orbital shaker for mixing of the sample in the solution and graphite Atomic Adsorption Spectrophotometry (AAS) was used to analyze the final Chromium (III) concentration in pollutant solution.

3.2. Methods

3.2.1. Raw Fish Scales Collection and Preparation

The fish scales were collected from Sable restaurant which is located Arat kilo beyond ministry of education, Addis Ababa city using plastic bags. To reduce the difference available between raw fish scale for considering the efficiency of the adsorption process, the fish scales were collected from those market, transporting from Arbaminch. The raw fish scale submitted to the laboratory room of School Chemical and Bio-Engineering, Addis Ababa Institute of technology. The collected raw fish scale was soaked in water for 24 hours and washed repeatedly with running water to remove adhering dust and soluble impurities from their surface for purification purpose.

The washed fish scales were allowed to dry in sunlight for two days. After sunlight drying, the scales were kept in an oven at 65^{o}C till the fish scales become constant weight and crispy. The dried scales were converted into fine powder, to make for a required size by grinding in a mechanical grinder. The powder was then sieved through octagon sieve to obtain biosorbents with homogeneous known particle size. The fraction 125 to 200µm were separated for use in sorption experiment and preserved in plastic containers for further use as biosorbent.

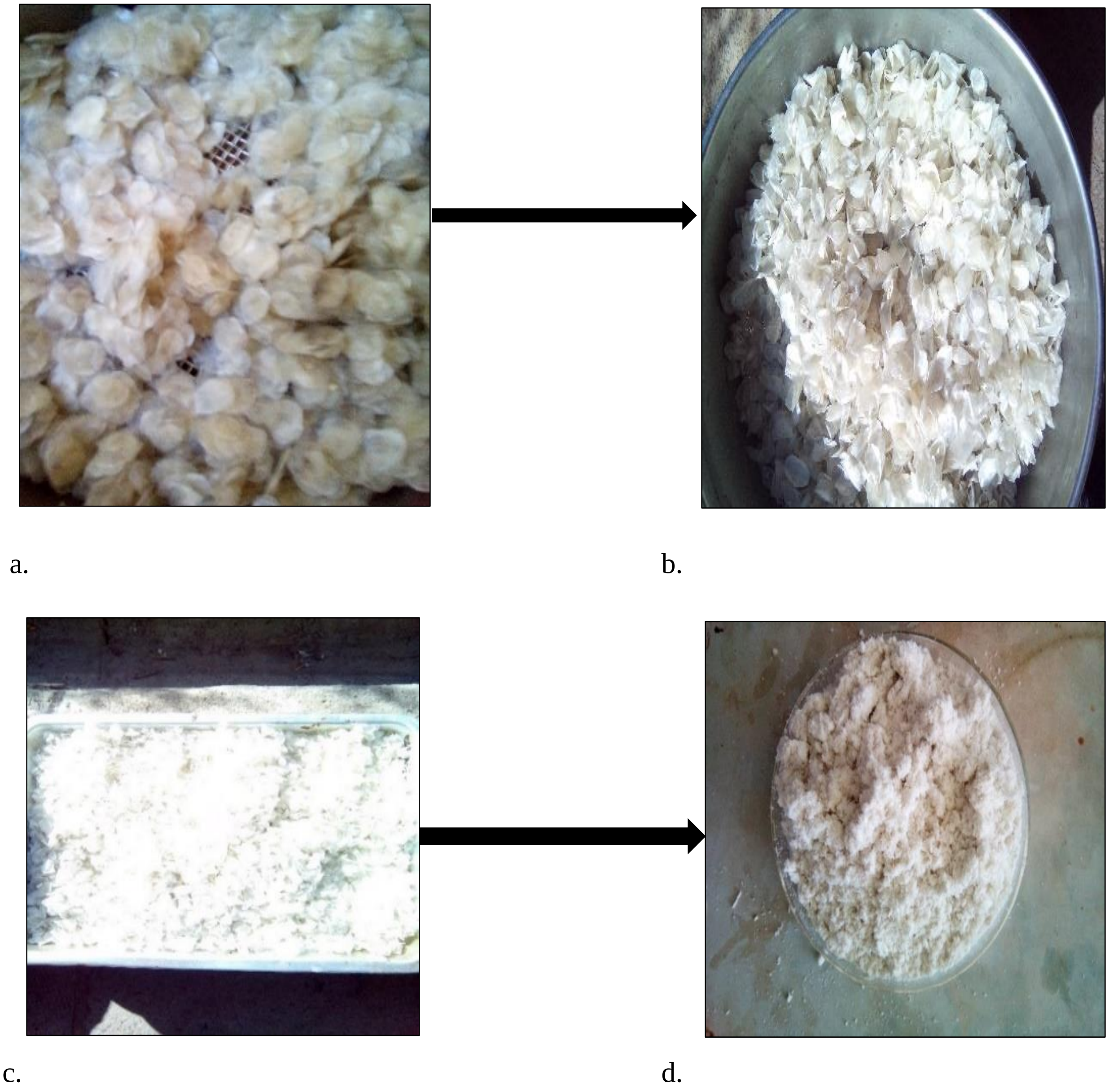


Figure 3.1: Raw material preparation, (a). Raw fish scales, (b). Dried fish scales, (c). Oven dried fish scale, and (d). Fish scale powdered(adsorbent).

3.2.2. Chemical Solution Preparation

Pretreatment/ modification methods using different kinds of chemicals were developed by different researchers such as base solution, mineral and organic acid solutions (Darge & Mane, 2013). This chemical modification is used for raw adsorbent purification and increases surface area/ pore. This study has used the solution of sulfuric acid, sodium hydroxide, hydrochloric acid, and calcium hydroxide applied for modification of fish scale having 0.1M in 150ml. The way to prepare 0.1M in 150ml is described in appendix J.

3.2.3. Chemically Modification of Fish Scales

(a). (b).

(c). (d).

Figure 3.2: Chemical modification of fish scale, (a). Fish scales before modification, (b). Modification process, (c). Washing process for pH neutralization, (d). Fish scale after modification.

The crushed fish scales (size 125-200µm) were chemically treated for surface area modification to improve the efficiency of chromium (III) ion uptake and to remove adhering dust and soluble impurities from their surface for purification purpose those not removed during tab water washing. Chemically modified fish scales, 10gm of the sample prepared according to size were soaked in 150ml of 0.1M H_2SO_4; Ca $(OH)_2$; NaOH and HCl of concentrated for 2.5 hours in a rotary shaker at 100rpm at room temperature. After the time, the mixture was decantation and filtration process using filter paper via vacuum filter pump equipment. The chemically pretreated fish scales were washed repeatedly using distilled water until neutral pH solution was attained. After that, the dosage was dried at room temperature for 2-2.5hr and finally the dosage of fish scale dried in an oven at 80^{o}C till constant mass. Dried pretreated samples were ground in a mortar and sieved to optimized of 150µm prior to their testing for Cr (III) biosorption.

3.2.4. Characterization of Biosorbent (Fish Scales)

The functional groups are the potential sites for adsorption and the uptake of metal depends on various factors such as the abundance of sites, their accessibility, chemical state and attraction between the adsorption site and metal. FT-IR spectroscopy was used to identify the functional groups in the fish scales biosorbent. FTIR spectra of the biosorbent before, after chemically modification and after biosorption of Cr (III) loaded were recorded in the range 4000-400 cm-1 using spectrum 65FT-IR (Perkin Elmer) KBr pellets. X-ray diffraction spectra were recorded, using a step size of 10^o, step time of 1s and 2θ range of 10^o to 70^o. The samples powder, particles retained in the sieve with 150µm were used in this characterization analysis. Using the equation below which is Bragg's law:

$$n \curlywedge = 2dsin\theta ----------------------3.1$$

For moisture content determination, aluminum foil was dried in an oven at 65^{o}C for 1 hour and placed in desiccators to cool, and weight of foil, W_1 was determined. To analysis weight differences about 40g of fish scale was weighed in dry aluminum foil, W_2 and dried at 65^{o}C until constant weight was obtained, then the final dried sample was weighed, W_3 again. The moisture content was determined using equation 3.1.

$$\text{moisture content } (\%) = \frac{W_2 - W_3}{W_2 - W_1} * 100 ---------3.2$$

3.3.Batch Adsorption Process

3.3.1. Preparation of Synthetic Wastewater

Synthetic solution (1000mg/l) of chromium (III) was prepared by dissolving basic chromium sulfate ($Cr_2 (SO_4)_3$) in deionized water as a model pollutant wastewater from tannery industry. For adsorption experiment, 150 mg/l was prepared from stock solution by dilution to obtain the standard solutions.

Figure 3.3: Synthetic solution of Basic Chromium Sulfate

3.3.2. Batch Adsorption Experiment Setup

The experiments were carried out in the batch mode adsorption process to analyze removal capabilities of modified fish scales at room temperature. Using the 250ml stopper conical flask containing 100ml of model pollutant solution batch adsorption studies were carried out at the desired pH value, contact time and adsorbent dosage. The pH of the solution was monitored by adding 0.1M of HCl and NaOH solution. Amount of modified fish scales was added to each flask containing model pollutant of wastewater and agitated intermittently by mechanical shaking at speed of 200rpm for a contact time from 30 min to maximum time 150min at room temperature.

After adsorption process, separation of the sorbent and solutions was carried out by filtration process using ninety-millimeter diameter filter paper via vacuum filtration unit and the filtrate was stored in sample cans for determining the metal ion concentration of chromium, to analysis removal percentage chromium (III) ion, to develop adsorption kinetics model and to analyze adsorption isotherm. The experiment was carried out at different sorbent of dosage (0.4, 0.8, 1g), pH (3, 5, 8) and contact time (30, 90, and 150min) to analysis effect of one factor on adsorption efficiency when other factor constants.

Figure 3.4: pH adjusted test solution

3.3.2.1.Effect of Contact Time

For the determination of the rate of chromium biosorption by adsorbent from 100ml at 150mg/l in a conical 250ml flask, the solution was analyzed for residual chromium at different time intervals (30, 90, and 150 min). The pH and the adsorbent dosage were kept constant, but, which varied according to the contact time varied, and the process was done under constant shaking speed, 200rpm, and at room temperature.

3.3.2.2.Effect of Adsorbent Dosage

The effect of adsorbent dosage on t e adsorption of chromium was studied at different dosages ranging from 0.4 to 1g with chromium concentrations of 150mg/l in pollutant solution. The contact time and the pH were kept constant, which is varied according to the variation of adsorbent dosage added to model wastewater pollutant and adsorption is process was done at constant shaking speed 200rpm, at room temperature.

3.3.2.3.Effect of pH

To determine the effect of pH on the adsorption of chromium from pollutant solutions (100ml) of concentration 150mg/l in conical flasks 250ml were adjusted to desired pH (3, 5, and 8) values and mixed with constant amount of adsorbent, which is varied with pH varied and agitated at a preset equilibrium time with constant agitated speed 200rpm of adsorption process.

3.4. Determination of the Percentage Removal and Adsorption Capacity

3.4.1. Determination of the Percentage Removal of Chromium (III) ions

Adsorption studies were carried out at room temperature and constant agitation speed for a known initial concentration of the chromium (III) solution. The supernatant liquid was filtered and the concentrations of Cr (III) ions left in the pollutant wastewater were determined using atomic adsorption spectrophotometer. The adsorption efficiency values which is recorded by atomic adsorption spectrophotometer were described the ability of modified fish scales to adsorb chromium ion from tannery wastewater. The adsorption efficiency (%) was calculated using the following expressions:

$$\text{adsorption efficiency } (\%) = \frac{(C_o - C_e)}{C_o} * 100\% - - - - - - - - - - - 3.3$$

Where, C_o and C_e are the concentrations of Cr (III) at the initial and at the final of the adsorption process at a time (t), respectively.

3.4.2. Determination of the Adsorption Capacity Adsorbent

The equilibrium adsorption capacity of adsorbent (q_e) was found in by using the values of adsorption capacity of adsorbent at a particular time (q_t) for initial Cr (III) concentrations. When q_t value became constant after a certain period of time, a constant value of q_t was termed as equilibrium sorption capacity which is point maximum ability of fish scales to adsorb chromium ions. The amount of chromium (III) ions adsorbed per gram of biosorbent was calculated using the following expressions:

$$q_e = \frac{(C_o - C_e)V}{M} ---------------------- 3.4$$

Where, q_e is the amount of Cr (III) sorbed per gram of adsorbent, C_o and C_e are the initial and equilibrium or final concentrations of Cr (III) (mg/L) respectively, V is the volume of solution (L), and m is the mass of adsorbent (g).

3.5.Adsorption Isotherms

Adsorption isotherm is defined as a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium, and it shows the distribution of an adsorbable solute between the liquid and solid phases at various equilibriums. It is also helpful in model prediction for analysis and design of an adsorption process.

3.5.1. Langmuir Isotherm

The Langmuir isotherm is valid for monolayer adsorption with a homogeneous distribution of sorption sites and sorption energies without interactions between the sorbed molecules. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant (separation factor).

The Langmuir isotherm is represented by the equation: -

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} ---------------------- 3.5$$

Where: q_e is the amount of the metal adsorbed at equilibrium per amount of the adsorbent (mg/g), q_o is the saturation monolayer adsorption capacity (mg/g), and b is the equilibrium adsorption constant (l/mg).

3.5.2. Freundlich Isotherm

The Freundlich model can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. Freundlich isotherm is commonly expressed as follows:

$$q_e = K_f C_e^{\frac{1}{n}} - 3.6$$

Where, q_e is equilibrium loading in mg/g; C_{eq} equilibrium concentration in mg/l, K_f Freundlich constant in mg/g, and n, Freundlich exponent.

3.6.Design of the Experiment

Design of experiments (DOE) is defined as a statistical technique or approach that is used for the design and the analysis of experiments. Design Expert is a piece of software designed to help with the design and interpretation of multi-factor experiments. The use of DOE is required in designing experiments in order to draw valid and accurate conclusions about any set of experiments. Data analysis was carried out by DESIGN EXPERT version 7.0. Software (general factorial design) to evaluate the effects of the process variables on efficiency removal.

3.6.1. Factorial Design Methodology

The full factorial design, batch adsorption studies three factors, adsorbent dosage, pH and contact time are considered to study the main effects and interactions on the removal efficiency of chromium from wastewater and adsorption capacity as response variables. The main objective of this study is to investigate the effects and the interactions between the studied factors so that invalid and inaccurate conclusions can be avoided by the process. Results found are also verified by studying and generating the analysis of variance (ANOVA). This statistical approach is used to determine the most chromium removal efficiency from wastewater**.** One way to understand and represent the interactions between the tested factors is through generating their related predictive regression models.

4. RESULT AND DISCUSSION

4.1.Characterization of Fish Scales

4.1.1. Moisture Content of Fish Scales

Drying process was terminated at 24 hr. as the weight of the sample was approximately equal to the weight at 21hr. The reason to terminate after 24hr is due to almost near to same value after three hours in the oven, this indicates not much value is changed in the moisture content. The moisture content of the sample was obtained in Table 4.1 at 24h using equation 3.2.

Table 4.1: Moisture content of fish scales.

Weight of sample(g)	**Drying time (hour)**		
	0	21	24
	20	15.47	15.45
	40	32.83	32.80

From the above table, the moisture content of the fish scale sample with 20, and 40g was 23.9%, and 18.5% respectively. Thus, the average moisture content of the two samples was 21.2%.

4.1.2. Fourier Transform Infrared (FTIR) spectrum Analysis.

The FTIR spectroscopy is an important analytical technique which detects the vibration characteristics of chemical functional groups in a molecule. On the interaction of an infrared light with the matter, chemical bonds will stretch, contract and bend. The adsorbents spectra were measured on spectrum 65FT-IR (Perkin Elmer) in the range of 400- 4000 cm^{-1} using KBr pellets. FT-IR spectra of the adsorbents (raw fish scales, modified fish scale and chromium (III) loaded fish scale) are shown in figure 4.1(a) (b) (c) below respectively. The raw fish scales, the stretching broadband at 3365cm^{-1} corresponds to O-H groups (figure 4.1, a). The region between 3000 and 2800cm^{-1} exhibited medium peak, it indicates the C-H stretching vibrations –CH_3 and -CH_2 functional groups. Distinct strong peaks observed between 1715 and 1630 cm^{-1} characterize carbonyl groups strong stretching. From 1300-1470cm^{-1} there was the deformation stretching of CH, CH_3, and CH_2 functional groups. There also a medium peak at 1030 cm^{-1}, this due to C–O group. There are also spectra recorded adsorption bands of P-O due to PO_4^{3-} groups in 750, and 550cm^{-1}, which are characteristic of the inorganic phase.

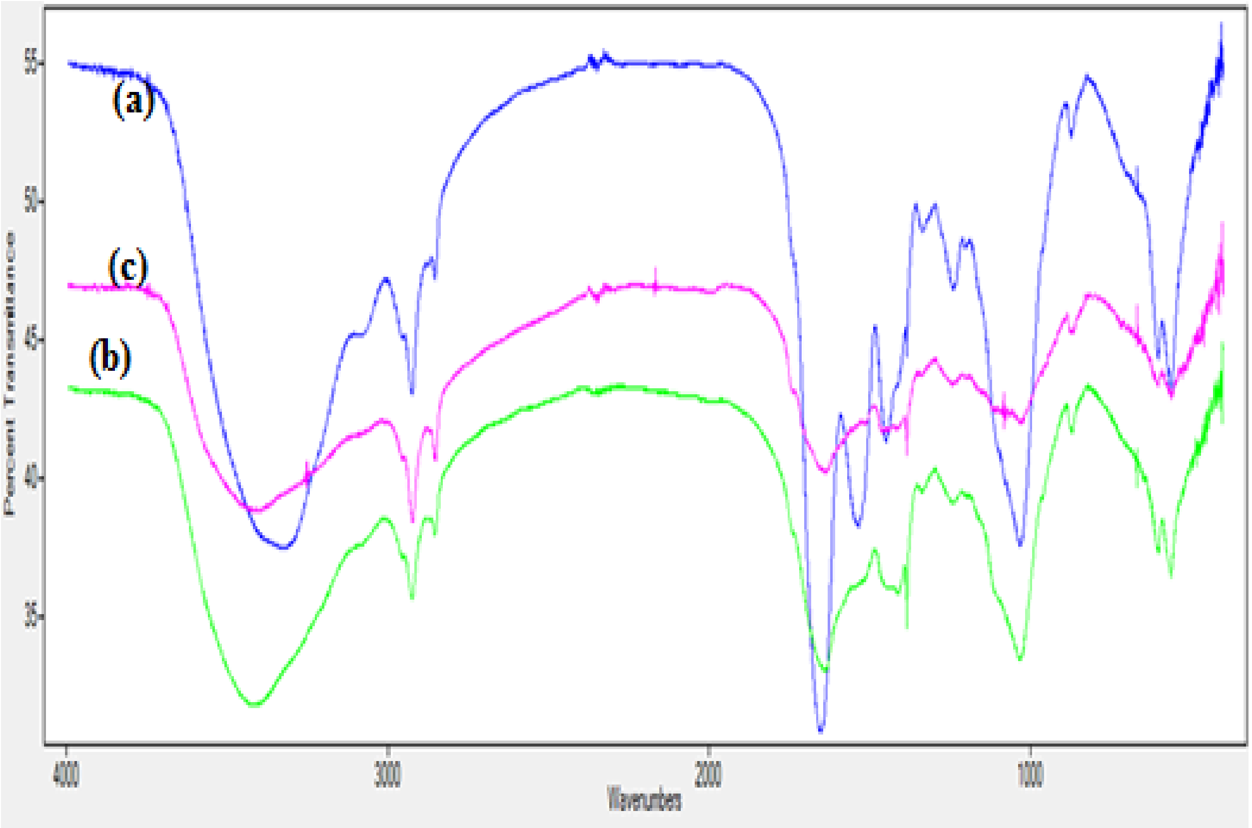


Figure 4.1: FT-IR spectra of fish scale: (a). raw fish scale, (b). modified fish scale, and (c). chromium loaded fish scale.

Changes in intensity and shift in the position of the peaks could be observed in FT-IR spectrum after Cr (III) adsorption on modified fish scales (figure 4.1 c). The shifting of the peak at 1660 to 1655 cm^{-1} indicates that the involvement of C=O/C=C in the adsorption process. The strong peak of raw biosorbent at 1030cm^{-1} (figure 4.1. a) ranging from 1100 to 1020 cm^{-}1 shifted to 1025cm^{-1}(figure 4.1.c). This suggested the involvement of C-O group in the binding of Cr (III). Also, the deformation stretching peak between 1300-1407(figure 4.1.a) was changed and PO_4^{3-} medium peak (figure 4.1.a) is changed to small peak (figure 4.1.c). The result indicates that the hydroxyl and carbonyl groups are the main functional groups on the surface of raw fish scales involved in chromium (III) binding to the modified fish scale. According to the investigation from the figure 4.1(c), main functional groups present on the surface of fish scales were hydroxyl, carbonyl, and phosphate. These observations have good agreement with the previously published FTIR data for fish scales (Prabu K, 2012). From the FT-IR analysis, the possible mechanism of adsorption of chromium (III) ion on the fish scale may be due to physical adsorption, ion exchange, chemical reaction with surface sites, and complexation with functional groups.

4.1.3. X-ray Diffraction (XRD) Analysis.

General X-ray diffraction phase/composition identification will distinguish the major, minor, and trace compounds present in a sample. XRD was conducted on the surfaces of the fish scales. Figure 4.2. Shows the XRD patterns with a 2θ scan from 20˚ to 70˚. The peaks at 2θ of 25.96°, 28.66° 31.66°, 32.05°, 39.71°, 44.22°, and 49.66° correspond to a "d" spacing of 0.3432, 0.3115, 0.2827, 0.2792, 0.2270, and 0.1836nm respectively using the Bragg's law equation 3.1. The broad peaks of the XRD pattern indicate that the scale has low crystallinity which corresponds to an amorphous property. The XRD results are consistent with the results by (Wei, 2011) which have peaked at 2θ of 25.9°, 31.9°, 39.8°, 47.2°, 49.3°, and 53.2° correspond to *d* spacing of 0.343, 0.281, 0.226, 0.193, 0.185, and 0.172 nm, respectively and (Torres et al.,2008)which has peaked at which are 25.8°, 31.8°, 39.6°, 47.2°, 49.3°, and 53.1° corresponding to *d* spacing of 0.345, 0.281, 0.227, 0.192, 0.184, and 0.172 nm respectively.

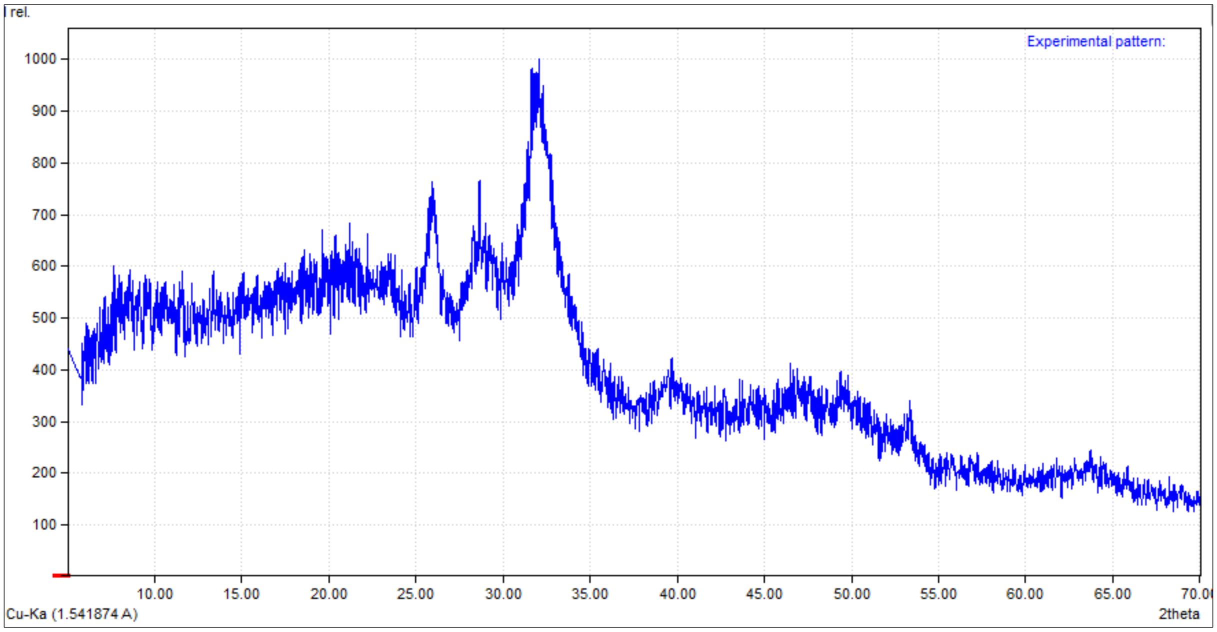


Figure 4.2: X-ray Diffraction patterns of fish scales

4.2.Statistical Analysis of the Experimental Results.

In this study, the process is to analyze the effect of the process parameters adsorbent dosage, pH, and contact time on adsorption of chromium (III) from wastewater which is a model pollutant of tannery industry wastewater. The laboratory experiment was done at a constant initial concentration of pollutant, shaking speed 200rpm, and room temperature.

Those effects of parameters on the efficiency of chromium removal are analyzed using design-expert®7.0. Design summary three levels and three factors. The design model of the experiments is a quadratic polynomial with no block.

Table 4.2: Design summary of factorial design.

Design summary of design expert®7.0.	
Study type	Response surface
Initial design	General factorial design
Design model	Quadratic polynomial
Run	27
Block	No block

4.2.1. Analysis of Variance (ANOVA)

In this study, the experiment results analysis was done using analysis of variance of the quadratic regression model for analysis significant model term. To determine whether or not the quadratic model is significant, it was required to perform analysis of variance (ANOVA). The probability (P-values) values were used as a device to check the significance of each coefficient, which also showed the interaction strength of each parameter. The smaller the P-values are, the bigger the significance of the corresponding coefficient. F- Value is a test for comparing model variance with residual (error) variance. It is calculated by Model Mean Square divided by Residual Mean Square. If the variances are close to the same, the ratio will be close to one and it is less likely that any of the factors have a significant effect on the response. The range and level of parameters variables described in table 4.3: below.

Table 4.3: Variables designed for the adsorption process.

Independent variables	Range and level variables		
	Low	Medium	High
Adsorbent dosage(g) (A)	0.4	0.8	1
pH(B)	3	5	8
Contact time(min)(C)	30	90	150

Accordingly, from table 4.4, ANOVA analysis it was observed that the values “prob >F” less than 0.0500 indicates model terms are significant. In this case, C, B^2, C^2, and AB are significant model terms. Values greater than 0.1000 indicates the model terms are not significant. So, the table indicates that the independent variable pH (B) and contact time (C) were significant terms and that of dosage (A) is least significant. The goodness of fit of the model was checked by the determination coefficient (R^2) as shown in the Table (4.5). The R^2 value provides a measure of how much variability in the observed response values can be explained by the experimental variable and their interaction.

Table 4.4: Analysis of variance (ANOVA) for response surface quadratic model

	Sum of Squares	**DF**	**Mean square**	**F value**	**p-value Prob>F**
Model	114.7	9	12.74	6.85	0.0004 significant
A-Dosage	0.46	1	0.46	0.24	0.6275
B- Ph	12.21	1	12.21	6.49	0.0208
C-Cont. time	27.87	2	27.87	14.81	0.0013
A^2	0.036	1	0.036	0.019	0.8922
B^2	25.14	1	25.14	13.36	0.0020
C^2	35.44	1	35.44	18.84	0.004
AB	10.90	1	10.90	5.79	0.0278
AC	3.81	1	3.81	2.02	0.1731
BC	1.81	1	1.81	0.96	0.3410
Residual	31.99	17	1.88		
Cor Total	146.69	26			
The model F-value of 6.85 implies the model is significant. There is only A 0.04% chance that a “model F-value” this large could to noise Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case, B, C, B^2, C^2, and AB are significant model terms. Values greater than 0.1000 indicate the model terms are not significant					

Table 4.5: Model adequacy measures

Std.Dev	1.37	R-Squared	0.7819
Mean	97.42	Adj R-Squared	0.6665
C.V.	1.40	Pred R-Squred	0.4716
PRESS	76.95	Adeq Precision	8.281

The "Pred R-Squared" of 0.4716 is as close to the "Adj R-Squared" of 0.6665 less than 0.2, the difference as one might expect. "Adeq Precision" measures the signal to disturbance ratio due to random error. A ratio greater than 4 is desirable. Here the ratio of 8.411 indicates an adequate signal. Therefore, this model can be used to navigate or direct the design space.

The regression coefficient and the corresponding 95% Confidence Interval (CI) High and Low were described in table 4.6. If Zero was in the range High and Low 95% Confidence Interval the factors has no effect.

Table 4.6: Regression coefficient and the corresponding 95% CI High and Low

Factor	**Coefficient Estimate**	**DF**	**Standard Error**	**95% CL Low**	**95% Cl High**	**VIF**
intercept	100.59	1	0.76	98.98	102.20	
A-Dosage	0.16	1	0.32	-0.52	0.84	1.04
B-Ph	0.83	1	0.33	0.14	1.52	1.03
C-Contact time	1.26	1	0.33	0.57	1.95	1.02
A^2	-0.088	1	0.64	-1.44	1.27	1.04
B^2	-2.15	1	0.59	-3.39	-0.91	1.01
C^2	-2.43	1	0.56	-3.61	-1.25	1.00
AB	-0.93	1	0.39	-1.74	-0.11	1.02
AC	0.55	1	0.39	-0.27	1.37	1.02
BC	0.39	1	0.39	-0.44	1.22	1.01

From designed experimental data which is **appendix A**, the quadratic polynomial model equation for chromium (III) adsorption using modified fish scale was shown in equation 4.1 and 4.2.

Final equation in terms of coded factors:

Efficiency (%) = 100.59+0.16*A+0.83*B+1.26*C - 0.93*A*B

$+0.55*A*C+0.39*B*C-0.088*A^2$

$-2.15*B^2-2.43*C^2$--4.1.

Where, A= dosage, B= pH, and C= contact time variables.

Final Equation in Terms of Actual Factors

Efficiency (%) = 78.59517+5.95967*Dosage+4.74610*pH + 0.10687*Contact time - 1.23943*Dosage*pH+0.030721*Dosage*contact time

$+2.56923E-003*PH*contacttime-0.98102*Dosage^2-0.3434*pH^2$

$-6.75102E-004*Contact\ time^2$ ---------------------------- 4.2.

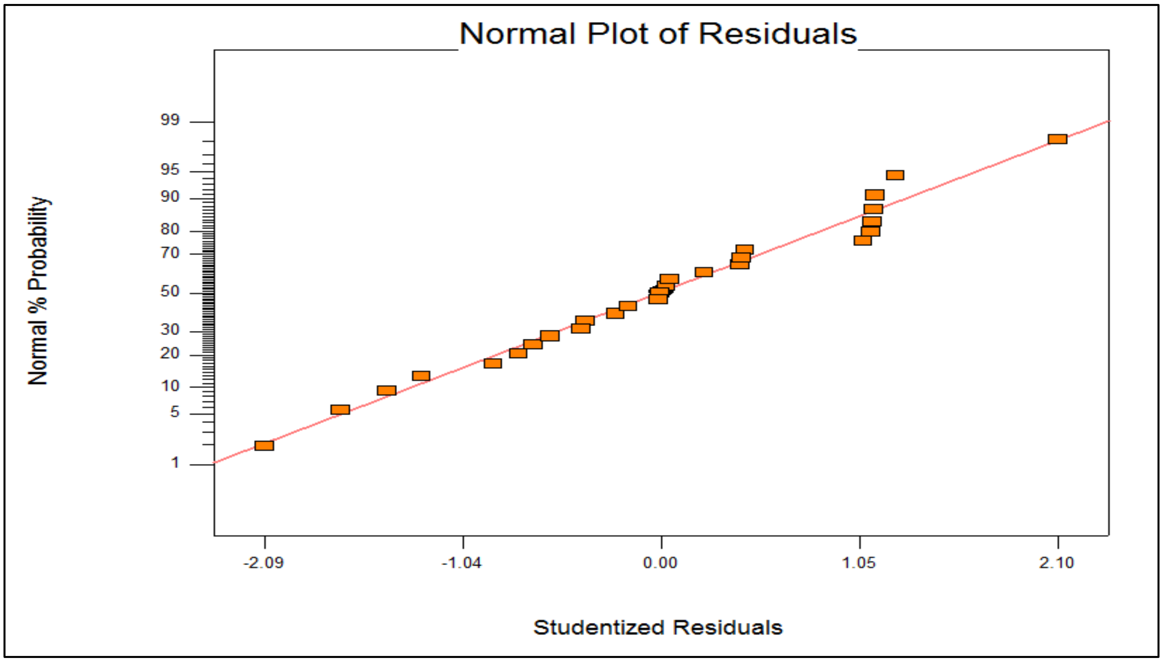


Figure 4.3: Normal plot of residuals

From the figure 4.3., the normal probability plot indicates that the residuals observed value more of following to normal distribution, this indicates the experiment points in the plots fit a straight line this show that the quadratic polynomial model satisfies the assumptions of analysis of variance.

4.3.The individual Effect of Process Variables on Chromium (III) Uptake.

4.3.1. Effect of Biosorbent Dosage on Chromium (III) Uptake.

The effects of adsorbent dosage on the removal of chromium (III) at room temperature was investigated by varying the amount of Sorbent from 0.4g to 1g in a stock solution having Cr (III) ion concentration of 150mg/l.

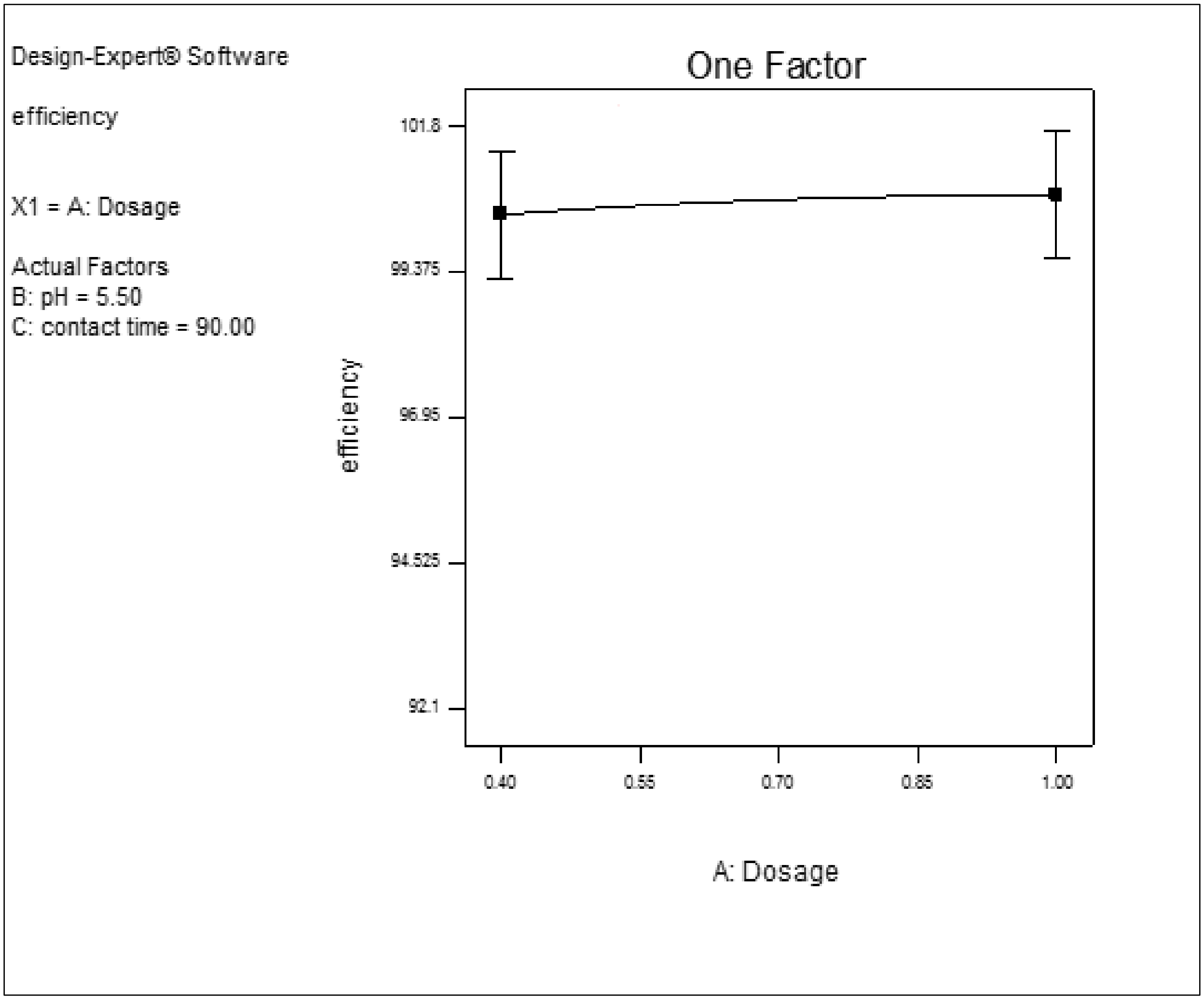


Figure 4.4: Effect of biosorbent dosage on Cr (III) removal efficiency.
(Initial concentration 150mg/l, adsorbent dosage 0.4g to 1g/100ml at constant pH and contact time, room temperature and shaking speed 200rpm).

From figure 4.4 above, it indicates that the removal percentage of chromium ion concentration by using a modified fish scale with a dosage of 0.4 to 0.8, was slowly increasing. Until the adsorbent dosage reaches near to 0.8g the removal percentage chromium (III) ion increased this is due to the availability of more adsorbent sites as well as the enhanced free surface area. This indicates that at the small amount of adsorbent, free to uptake chromium from wastewater which means less interaction of adsorbent with each other. This describes the positive correlation between adsorbent dose and chromium removal, can be related to increasing the adsorbent surface area and availability of more adsorption sites. Beyond 0.8g, the removal percentage of chromium was almost near to constant this is less removal of chromium due to particulate interaction such as agglomeration. Such aggregation leads to a decrease in total surface of the adsorbent, which describes not exposing the surface area to adhere the chromium (III) from tannery wastewater rather occupied by agglomerated matter. This point out that almost near decrease in the percentage of chromium removal with increasing the adsorbent dosage. Further increase in an adsorbent dosage greater than the maximum values obtained does not have significantly improved the percentage of metal removal because the equilibrium between chromium ions and the solid phase was reached (Elabbas et al., 2016).

4.3.2. Effect of pH on Chromium (III) Uptake

The pH of the solution is the most important parameter affecting metal ion adsorption. This is because hydrogen ion competing with the positively charged metal ions on the active sites of the adsorbent (M. Rafatullah, 2009). Figure 4.5 represents the effects of pH on chromium (III) adsorption from pollutant tannery wastewater. The selected pH ranges from 3 to 8 at a constant biosorbent dosage and contact time against the initial concentration 150mg/l with agitation speed 200rpm at room temperature. The figure maximum removal percentage was observed around pH 5.8. Also, result emphasizes that with increase pH of the solution near to neutral, the adsorbed increase and at pH values lower, the adsorption capacities were found to be low due to the competitive adsorption of HO^{3+} ions and chromium ions for the same active adsorption site (Yun Wu, 2008). From pH 5.8 to 6.3 rates of adsorption chromium made constant value beyond this the efficiency of biosorbent is slightly decreased, because, at high pH, tannery wastewater becomes basic, as a result, chromium (III) ion was not adhering into the binding's sites of adsorbents. This slight decrease in adsorption at high pH is due to the formation of soluble hydroxyl complexes. These species are adsorbed at the surface of sorbent by ion exchange mechanism with the functional groups present in sorbent or by hydrogen bonding (M. Rafatullah, 2009). So, the results describe that pH of the solution affects the adsorption efficiency of adsorbent.

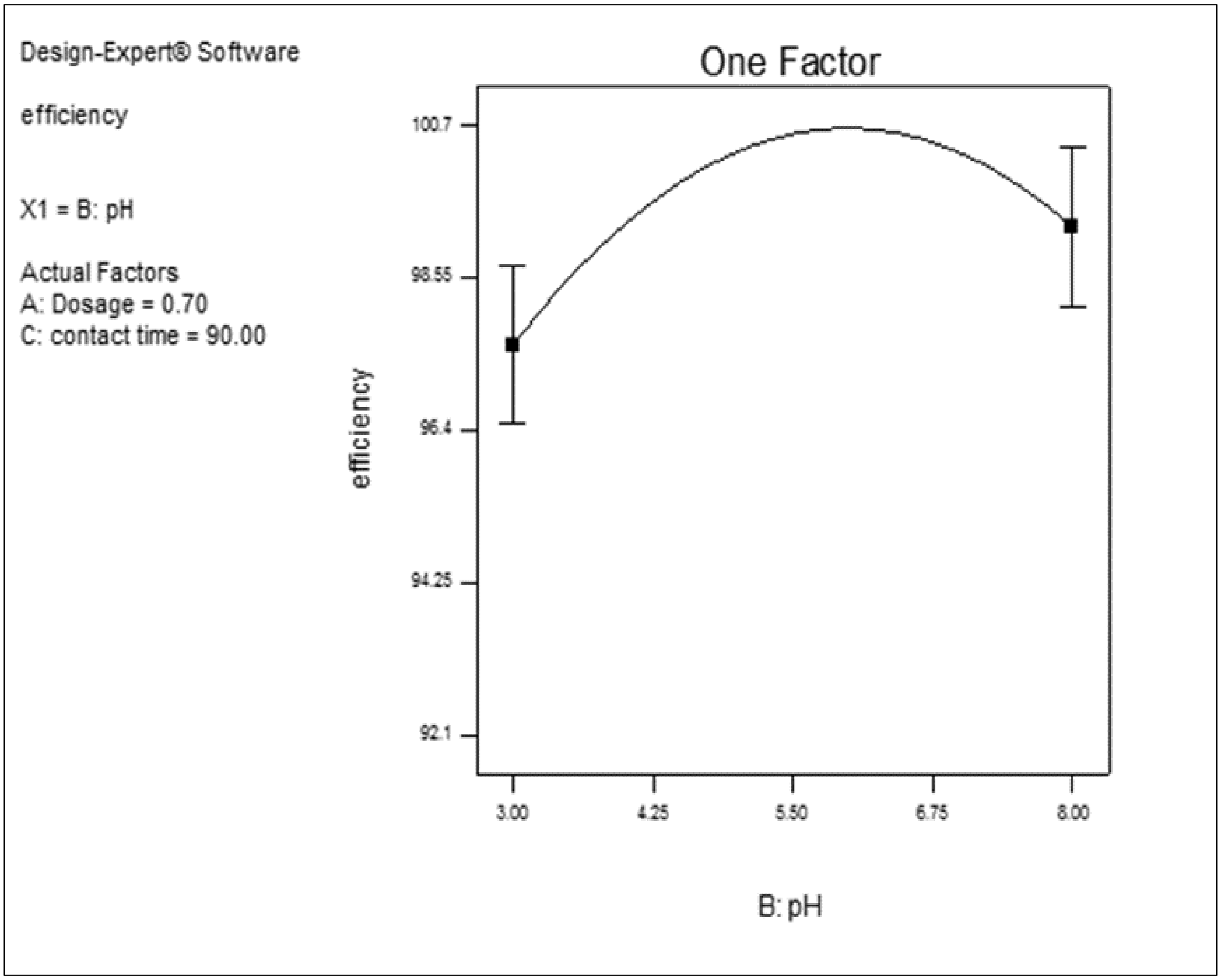


Figure 4.5: Effect of pH on Cr (III) removal efficiency
(Initial concentration 150mg/l, pH= 3, to 8 at dosage and constant time, room temperature and shaking seed= 200rpm)

4.3.3. Effect of Contacting Time on Chromium (III) Uptake

Figure 4.6 represents the effects of contact time on chromium (III) ion adsorption efficiency from pollutant tannery wastewater at the center point using a modified fish scale. The selected contact time was 30min, 90min, and 150min at the constant adsorbent dosage and pH of against initial concentration 150mg/l at room temperature with shaking speed 200rpm. So, from the figure, adsorption capacity sharply increased for the first 80 min, this indicates that chromium (III) ion adsorption efficiency increased with increasing contact time, beyond that slowly increasing with time and attains equilibrium at 110min. Probably due to the availability of larger surface area of the modified fish scale for the adsorption of these ions and prolonged contact between the sorbent surface and the solute chromium (III) solution. After the active sites of the adsorbent get exhausted when equilibrium is attained, the rate of uptake is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the sorbent particles. Lower adsorption efficiency rate in the latter stage of 110min was due to the difficulty encountered by Cr^{3+} ions in occupying the remaining vacant surface sites because of forces between the solute molecules of the solid and bulk solution. This same idea with the conclusion of (M. Rafatullah, 2014) in adsorption characteristic of heavy metal ions onto a low cost biosorbent from aqueous solutions.

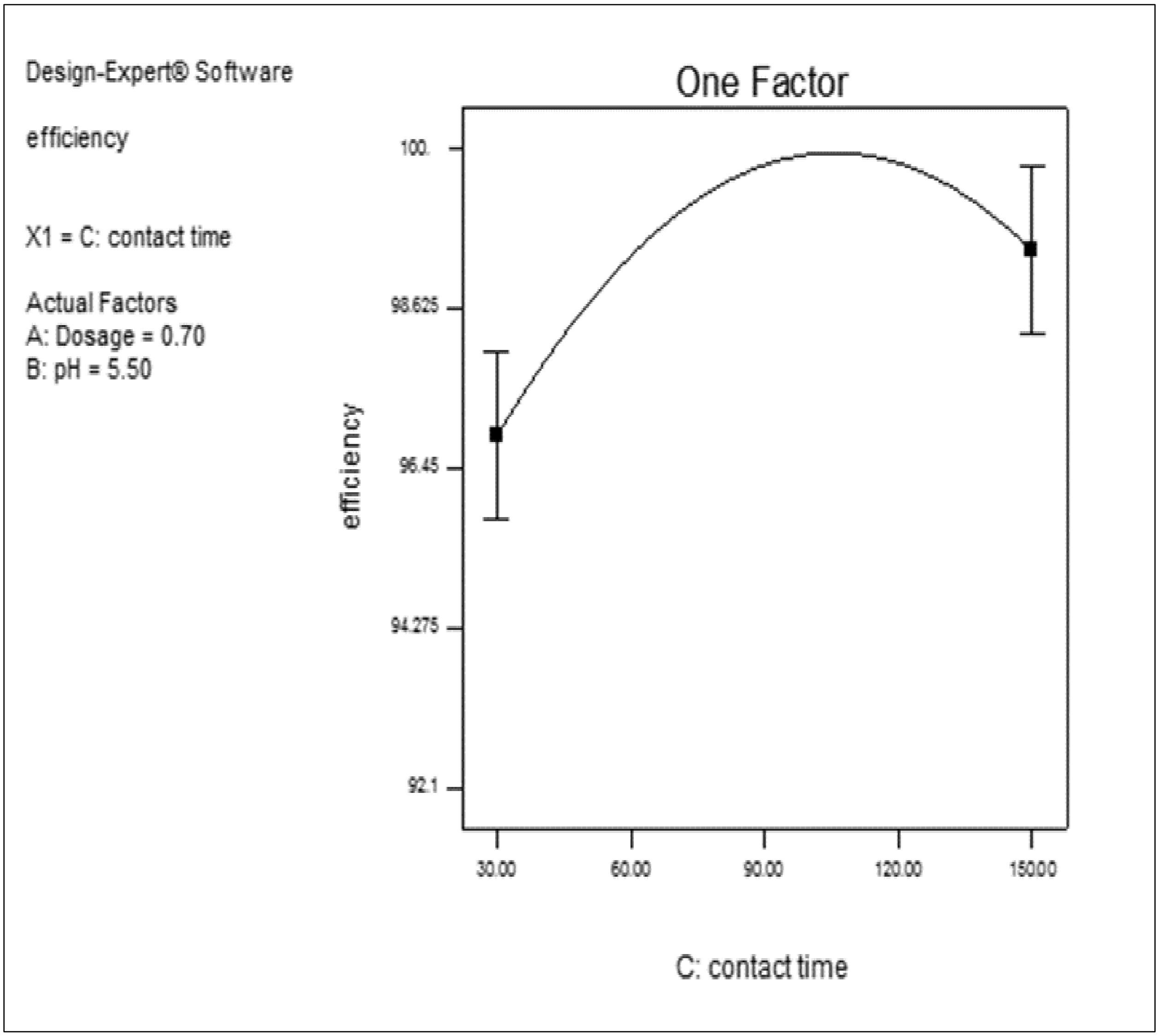


Figure 4.6: Effect of contacting time on Cr (III) removal efficiency

(Initial concentration=150mg/, time from 30min to 150min at constant pH and biosorbent dosage, temperature and shaking speed= 200rpm).

4.4.Interaction Effects of Process Variables on Chromium (III) Uptake

The interaction effect of process variables on chromium (III) ion uptake using design expert was analyzed using contour and 3D plots of three-dimensional views of response surface as a function of two independent variables and other variables at the center point. These plots can be used in understanding both the main and interaction effects the independent variables on the response variable.

4.4.1. The Interaction Effect of Adsorbent Dosage and pH

Contour and 3D plot graph showing predicted the response of chromium (III) ion removal efficiency as a function of adsorbent dosage and pH were shown in figure 4.7. The graph describes that as pH of the solution increases with adsorbent dosage increasing, the percentage of chromium removal efficiency increases. 96.43 % chromium (III) removal was obtained at sorbent dosage 0.4mg/l, and pH 3 at fixed contact time 90 min. But, removal increased up to 99.95 % at sorbent dosage increased to 0.8 mg/l, and pH increased to 5 at contact time at the center time. The increase in removal percentage of chromium due to increase in adsorbent dose, this increases the availability of more surface area (H.Yarkandi & Naeema, 2014). Also, the increase in percentage removal may be due to the complete utilization of all active sites in the adsorbent dosages by lower pH of the solution. Generally, as pH increases at the lower level of adsorbent dosage and as adsorbent increases at the low level of pH gives a positive effect on the chromium removal efficiency.

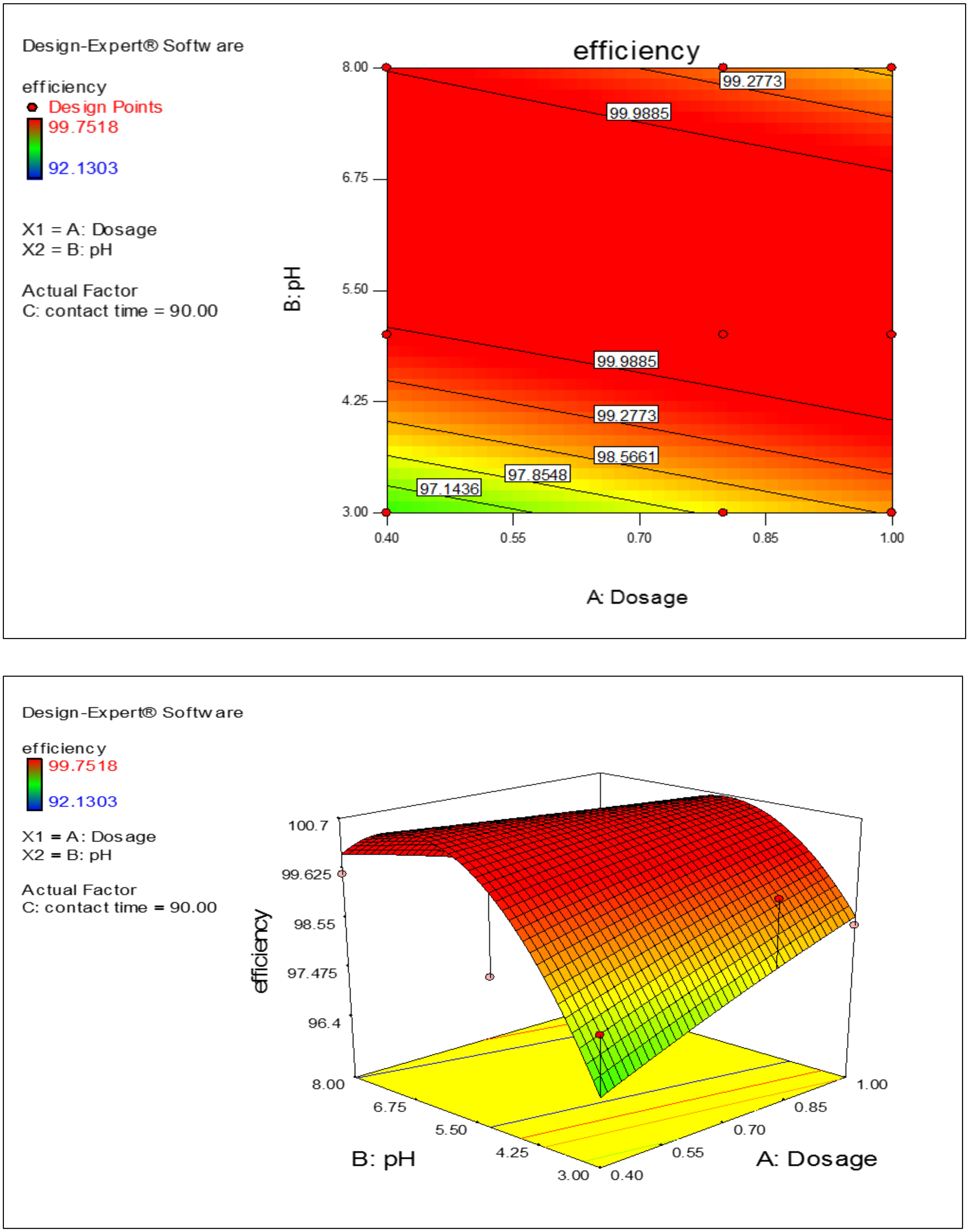
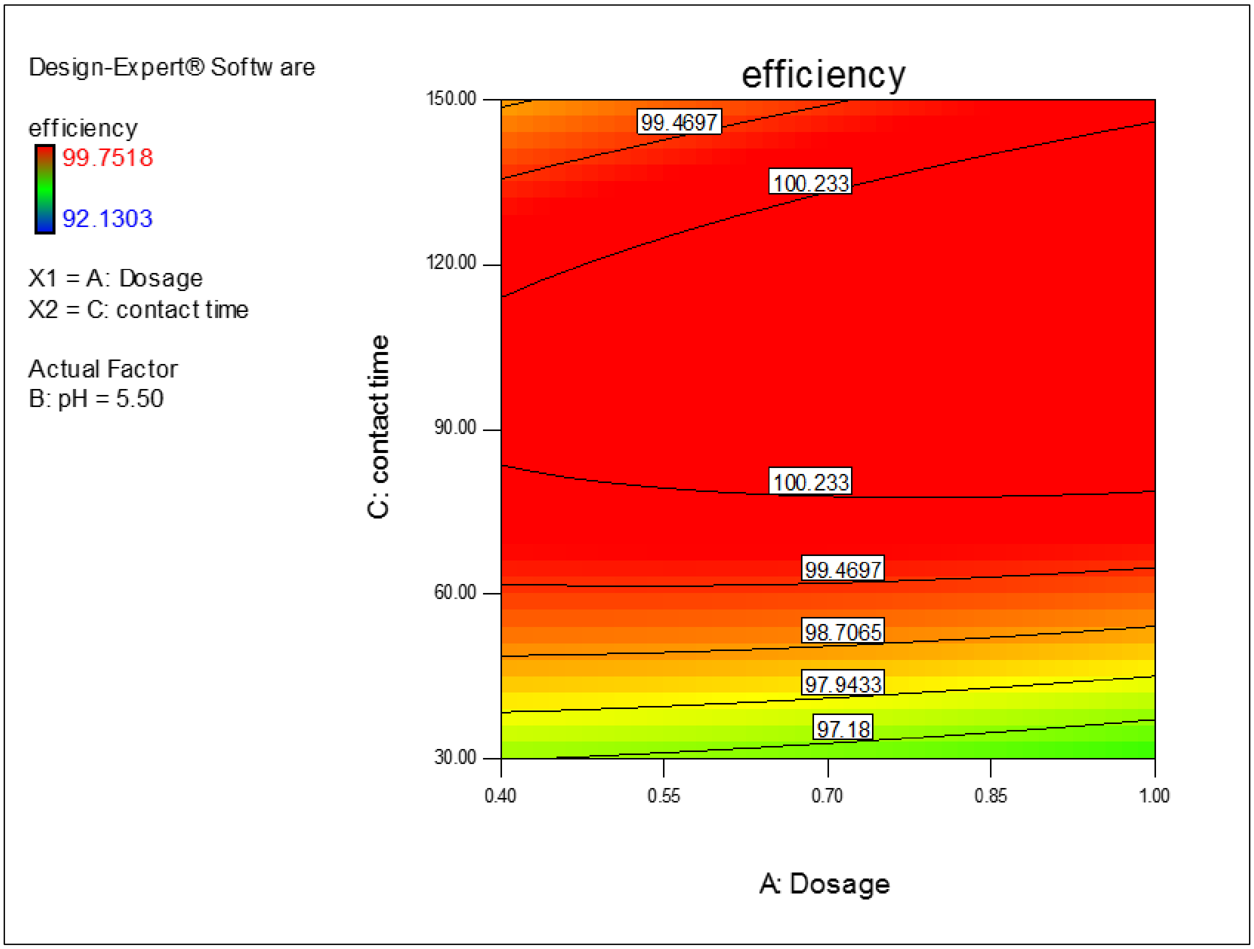


Figure 4.7: Contour and 3D plot of the effect of adsorbent dosage and pH on Cr (III) removal efficiency when the time at the center point.

4.4.2. The Interaction Effect of Adsorbent Dosage and Contact Time

Figure 4.8, contour and 3D respectively, shows the effects of the independent variables and their mutual interaction on the removal efficiency of chromium (III) using modified fish scales. From the surface response and contour plot, at a definite contact time (90 -120) min, the efficiency of chromium removal increased slightly and nearly reach a peak, beyond that removal efficiency decreases. However, upon increasing the dose, beyond 0.8g, there is a gradual decrease in the removal efficiency, this because of sorbent particulate agglomeration this decline active site for adsorption surface area. General, the maximum percentage removal of chromium (III) ion using MFS was obtained at a medium value of dosage and higher contact time(110-120min). The graph shows that the maximum adsorption (99.985%) occurs under dosage value in between 0.7 to 0.8 g, and contact time from 110 to 120 min. From the figures, as contact time increase at lower adsorbent dosage gives positive effects on the efficiency of chromium removal and decreases in efficiency at a higher dose with lower contact time.



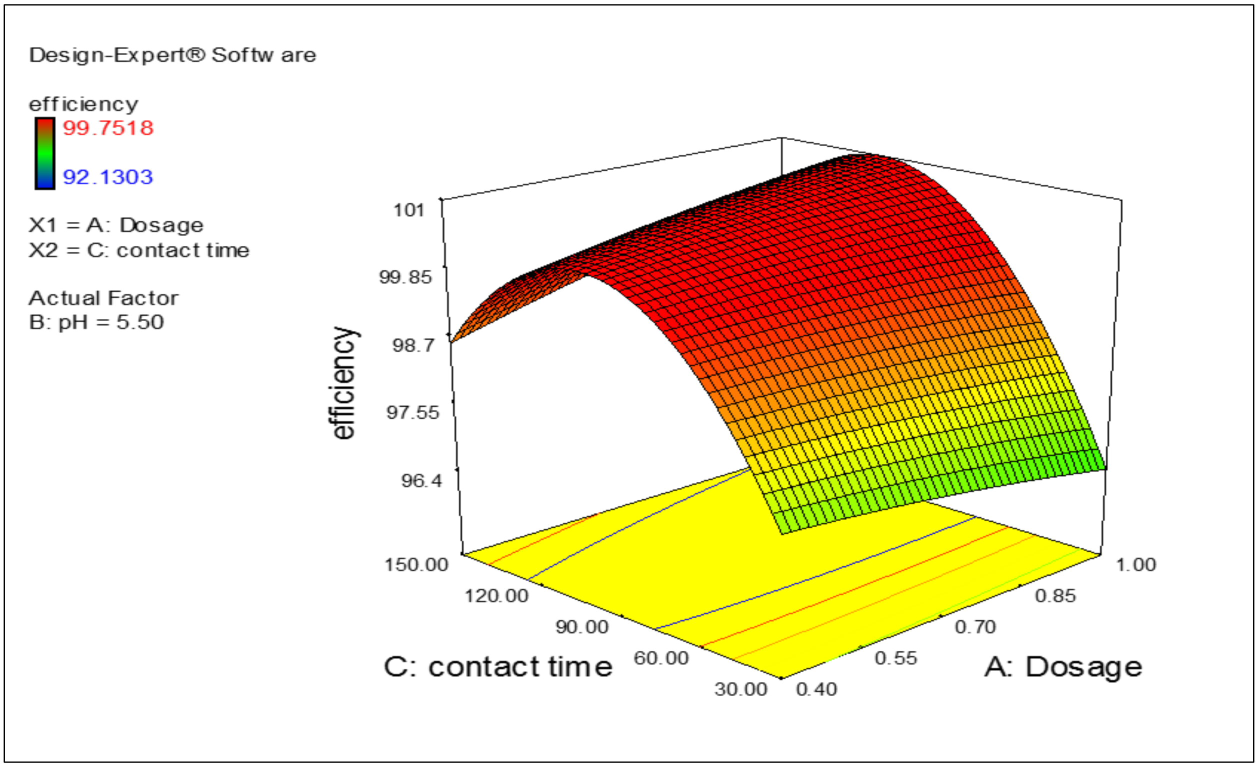


Figure 4.8: Contour and 3D plot of the effect of adsorbent dosage and contact time on Cr (III) removal efficiency when pH at the center point.

4.4.3. The Interaction Effect of pH and Contact Time

Contour and surface response plot showing predicted the response of chromium (III) ion removal efficiency as a function of pH and contact time was shown in figure 4.9. The figures show the effects of the independent variables and their mutual interaction on the removal efficiency of chromium (III) ion using modified fish scales. The graph illustrated that as contact time increased at a lower level of pH and as pH value increases at the low level of contact time made a positive effect on chromium (III) removal efficiency. Also, from figures, as contact time increase to the first 110 min removal efficiency chromium increases, and reach peak value beyond that removal efficiency decreases slowly. Also, as pH value increase 3 to around 5.8 the chromium removal efficiency increases and beyond that, it illustrates decreases in removal efficiency, this indicates pH value of solution strongly affect the site of dissociation of the biomass surface and solution chemistry of the heavy metals. General, when contact time increase at lower of pH and when pH of the solution increases at lower contact time have positive effects on the efficiency of chromium (III) ion removal using MFS.

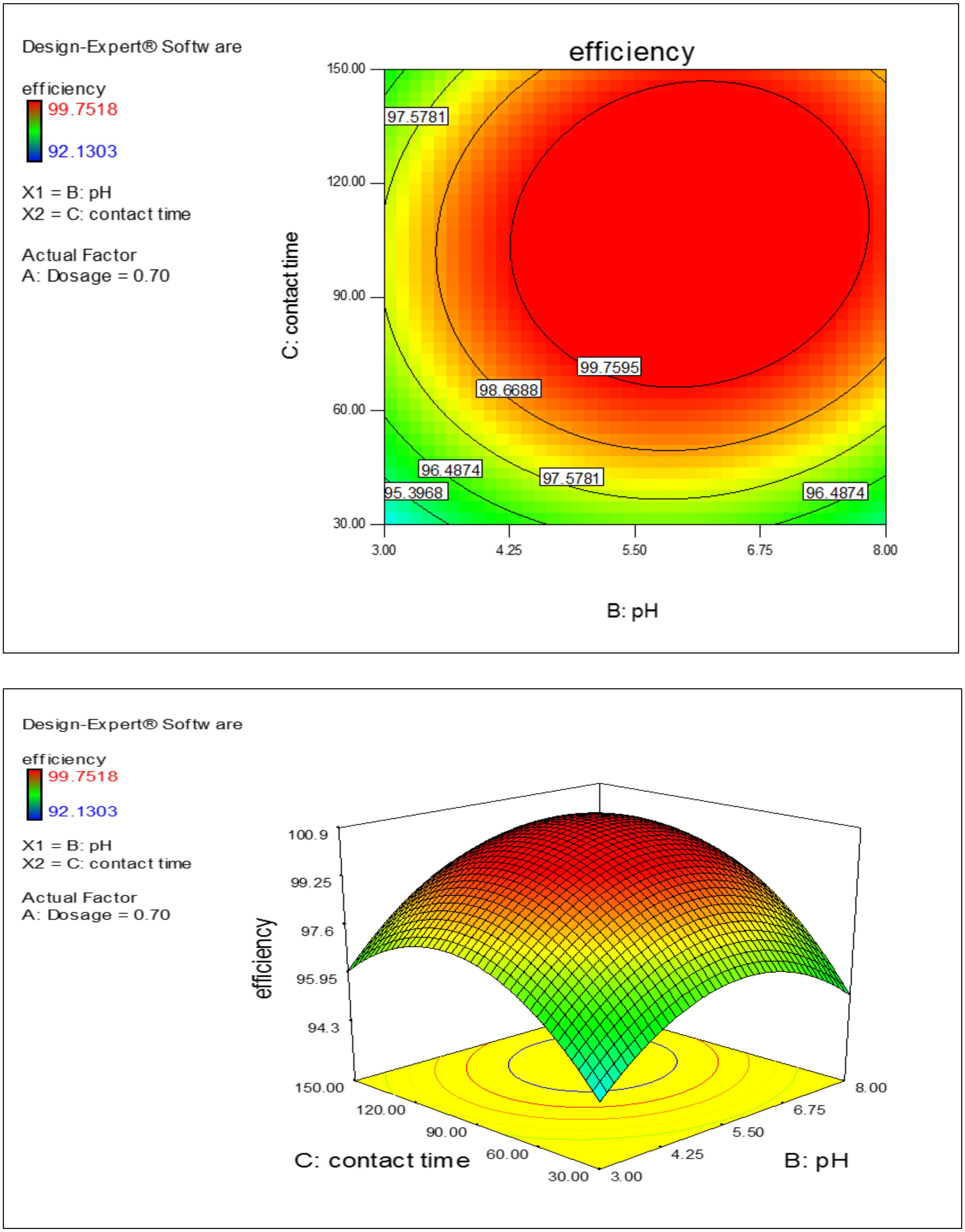


Figure 4.9: Contour and 3D plot of the effect of PH and contact time on Cr (III) removal efficiency when adsorbent dosage at the center point.

4.5.Adsorption Isotherm

Adsorption isotherms show the distribution of a solute between the liquid and solid phases and can be described by several mathematical relationships such as the standard Langmuir and Freundlich models (Sadeek et al., 2015). 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. In this study, the isotherm studies were performed in the solution with the initial concentrations of chromium ion 150 mg/L at pH values (pH = 5), adsorbent dosage 0.8g and contact time 2.5hr with shaking speed 200rpm at room temperature. The biosorption equilibrium uptake capacity for each sample was calculated according to mass balance on the ions expressed in the equation 4.3 below.

$$\mathrm{q_e} = \frac{\mathrm{C_o - C_e}}{\mathrm{M}} * \mathrm{V} - 4.3$$

Where V is the sample volume (L), C_0 is the initial ion concentration (mg/L), C_e is the equilibrium or final ion concentration (mg/L), M is the biomass dry weight (g), and q_e is the biomass biosorption equilibrium ions uptake capacity (mg/g). Langmuir and Freundlich isotherms, the two classical adsorption models, were used to describe the equilibrium between adsorbed ions on the sorbent (q_e, q) and ions in the solution (C_e, q) in this study.

4.5.1. Langmuir Isotherm Model:

The Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases (Dada, 2015). The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. . This describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Based upon these assumptions, Langmuir derived in linear from represented:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad - - - - - - - - - - - - - - - - - 4.4$$

Where, C_e, q_e, q_{max} and K_L representing the equilibrium concentration of chromium (III), adsorption capacity of modified fish scales at equilibrium, the maximum capacity of Modified fish scales and Langmuir constant respectively. The q_{max} and R_L in the Langmuir isotherm can be determined by plotting (C_e/q_e) versus (C_e).

The essential characteristics of Langmuir isotherm can be expressed by the dimensionless constant called equilibrium parameter R_L, equation 4.5:

$$R_L = \frac{1}{1+K_L C_o} ------------------- 4.5$$

Where C_o is the initial concentration of metal ion (mg/l), R_L is dimensionless equilibrium parameter. The characteristics of the R_L value indicate the nature of biosorption: - unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) and irreversible ($R_L = 0$) (Reddi et al., 2017).

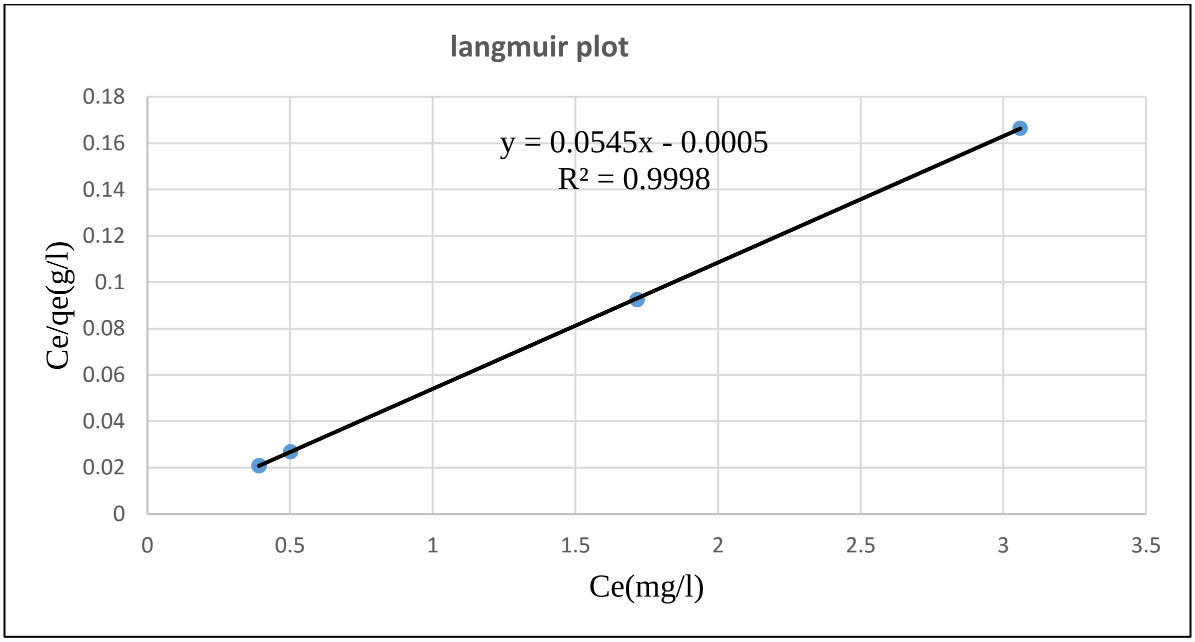


Figure 4.10: Langmuir isotherm model plot for Cr (III) adsorption

(Adsorbent dosage= 0.8g, pH= 5, shaking speed = 200rpm at room temperature and contacting time 2.5hr).

4.5.2. Freundlich isotherm model

The Freundlich isotherm model is describing the adsorption of solutes from an aqueous phase to a solid surface. The Freundlich isotherm model assumes that the uptake of metal ions occurs on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration. The Freundlich isotherm assumes several adsorption energies are involved in the adsorption process.

Freundlich adsorption isotherm is the relationship between the amounts adsorbed per unit mass of adsorbent, q_e, and the concentration of Cr (III) at an equilibrium, C_e. The linear form of the logarithmic equation for Freundlich isotherm is written as equation 4.6 below:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e ---------------------- 4.6$$

Where K_f and n are the Freundlich constants, K_f and n are the indicators of the adsorption capacity and adsorption intensity respectively. In this case, the plot of log C_e vs log q_e was employed to generate the intercept value of K_f and the slope of = 1/ n. Freundlich biosorption models for the removal of chromium (III) on the modified fish scale was illustrated in figure 4.11.

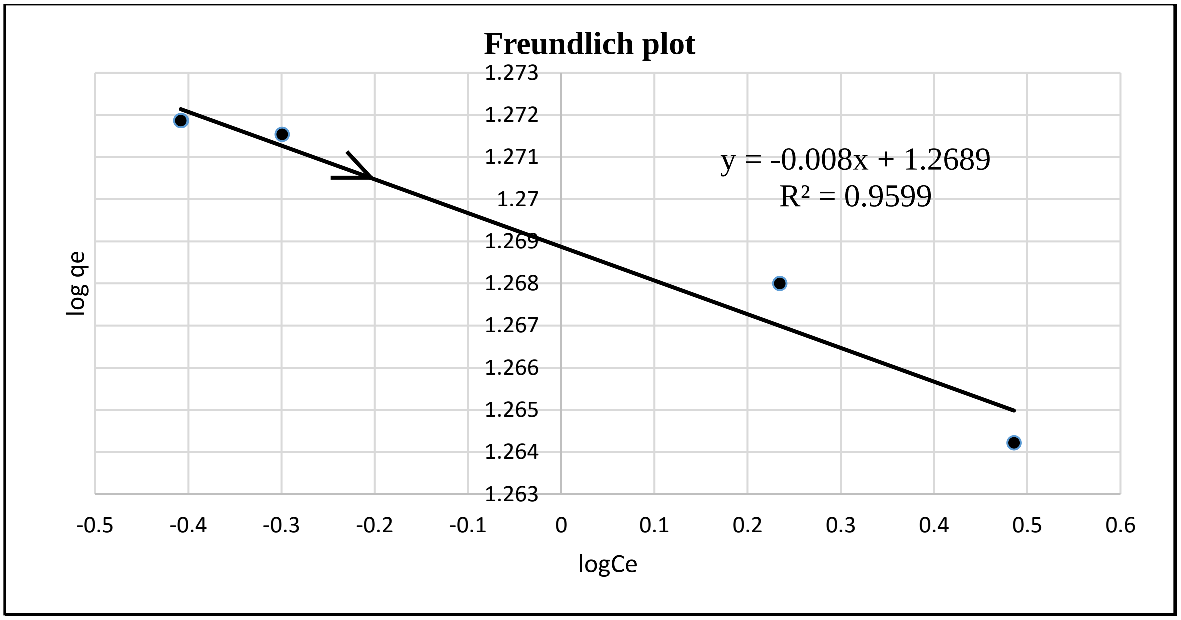


Figure 4.11: Freundlich isotherm model plot for Cr (III) adsorption (Adsorbent dosage= 0.8g, pH= 5, shaking speed = 200rpm at room temperature and contact time 2.5hr)

Table 4.7: The Langmuir and Freundlich isotherm model parameters for the removal of Cr (III) using Modified Fish Scale.

Metal ion	**Langmuir parameters**	**Freundlich parameters**
Cr(III)	q_{max}= 18.3486mg/g	k_f = 14.9107
	K_L= 91.001L/mg	1/n=0.008
	R_L = 0.00007325	
	R^2=0.9998	R^2= 0.9599

The calculated q_{max}, K_L, and correlation coefficients [R^2] for the Langmuir equation and R_L values and K_f, 1/n, and [R^2] for the Freundlich equation at constant temperatures are listed in table 4.7 above. The regression coefficient (R^2) for Langmuir and Freundlich isotherms are made 0.9998, and 0.9599, respectively. Thus, from the result of correlation coefficient R^2 comparison of Langmuir and Freundlich isotherm models, the Langmuir adsorption isotherm is the fit model for chromium (III) ion adsorption onto the modified fish scale sorbent. The Langmuir isotherm (R^2 = 0.9998) fits the experimental data very well, this describes/concluded that homogeneous distribution of active sites onto modified fish scale sorbent surface, since the Langmuir equation assumes that the surface is homogeneous. Form this study, obtain behavior of the adsorbent, Langmuir and Freundlich adsorption isotherms were plotted, and on the basis of the obtained correlation coefficients, it can be concluded that the adsorption of ions studied on prepared adsorbent given to the correlation coefficient higher than 0.9998 follows Langmuir isotherm.

4.6.Adsorption Kinetics Model

Adsorption kinetic models correlate the adsorbate uptake rate with bulk concentration of the adsorbate. The pseudo-second-order equation is the most widely used kinetic models to describe the adsorption of a solute from a liquid solution. The pseudo-second-order equation fitted the adsorption data very well in a large quantity of literature reported (AL-Othman, 2012). Equally large number of works has been reported where the second order kinetic model has been found to be the most suitable one for explaining adsorption of metal ions (Gupta, 2011). A relatively high R^2 value indicated that the model successfully describes the kinetics of metal adsorption. The rate kinetics of Cr (III) adsorption by the modified fish scales adsorbent was analyzed using the pseudo-first-order rate kinetics and pseudo-second-order rate kinetics model. The kinetics of chromium (III) adsorption was studied from the time versus percentage of removal curves (mg/g). The figure 4.12 below describes the relationship time and amount of chromium adsorbed per adsorbent (mg/g) which is used to analyze adsorption kinetics model.

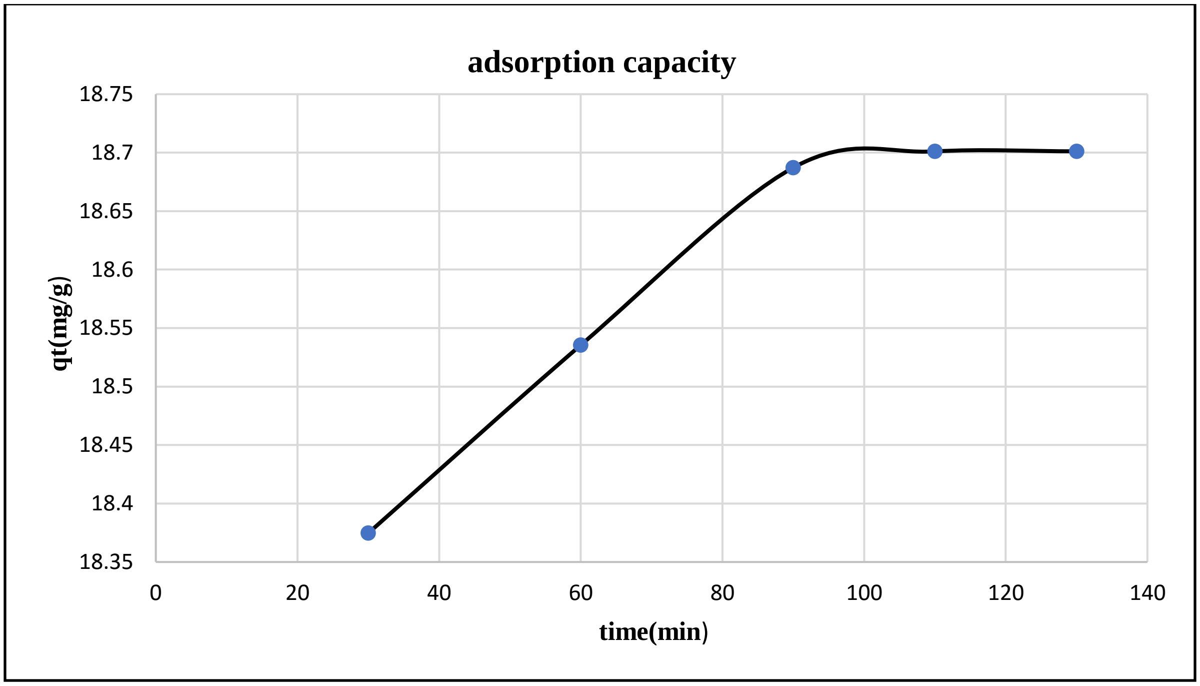


Figure 4.12: Adsorption capacity/uptake of MFS (initial concentration =150mg/l, pH =5, adsorbent dosage= 0.8g, contact time varies from 30 min to 130min).

4.6.1. Pseudo-first-order Kinetic Model

In order to investigate the mechanism of adsorption, the pseudo-first-order equations were used to test experimental data of initial concentrations. The pseudo first order kinetic equation is represented:

$$\frac{\mathrm{dqt}}{\mathrm{dt}} = \mathrm{K}_1(\mathrm{qe} - \mathrm{qt}) ------------------- 4.8$$

Where, q_e and q_t are the adsorption capacities at equilibrium and time t respectively (mg/g) and k_1 is the rate constant of pseudo-first-order adsorption (mn^{-1}). The equation can be rearranged into:

$$\log(q_e - q_t) = log q_e - \left(\frac{K_1}{2.303}\right) t ------------ 4.9$$

The values of log (q_e - q_t) were linearly correlated with t. The plot of log (q_e - q_t) vs. t should give a linear relationship. The first-order rate constant k_1 (1/min) and the equilibrium capacity q_e can be obtained from the slope and intercept, respectively. The observed rate constant for the removal of Cr (III) ions on MFS for this Pseudo-first-order kinetic model was described in table 4.8 below.

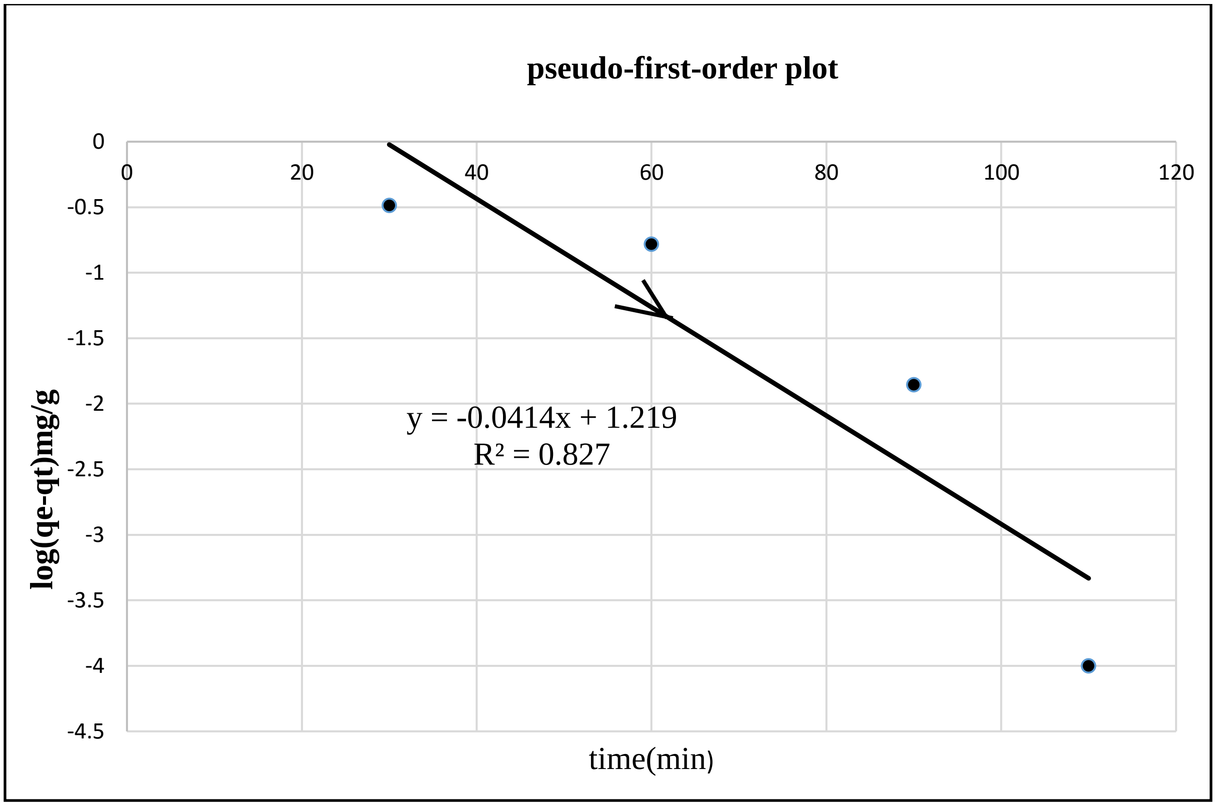


Figure 4.13: Pseudo -first-order kinetic model plot Cr (III) adsorption.
(Adsorbent dosage=0.8g, initial concentration = 150mg/l, pH= 5, shaking speed = 200rpm at room temperature with contact time 30 to 130 min).

4.6.2. Pseudo-second-order Kinetic Model

The pseudo-second-order model is the most widely used model for studying the kinetics of sorption processes (Chowdhury, 2012). In this investigation, pseudo-second-order is used to analyze the kinetic process of chromium (III) ion adsorption onto modified fish scales. The pseudo-second-order adsorption kinetic is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 --------------------4.10$$

For the boundary conditions t=0 to t=t and q_t= 0 and q_t=q_t, the integrated form of above equation will be written in equation 4.11.

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t ----------------------4.11$$

The equation above can be rearranged to obtain linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} -4.12$$

Where q_e and q_t are the sorption capacity at equilibrium and time t (mg/g), respectively, k_2 is the rate constant of the pseudo-second-order sorption (g/mg min). The k_2 and q_e are found from the intercept and slope of t/q_t versus t linear plot such that q_e = 1/slope and k_2 = slope^2/intercept.

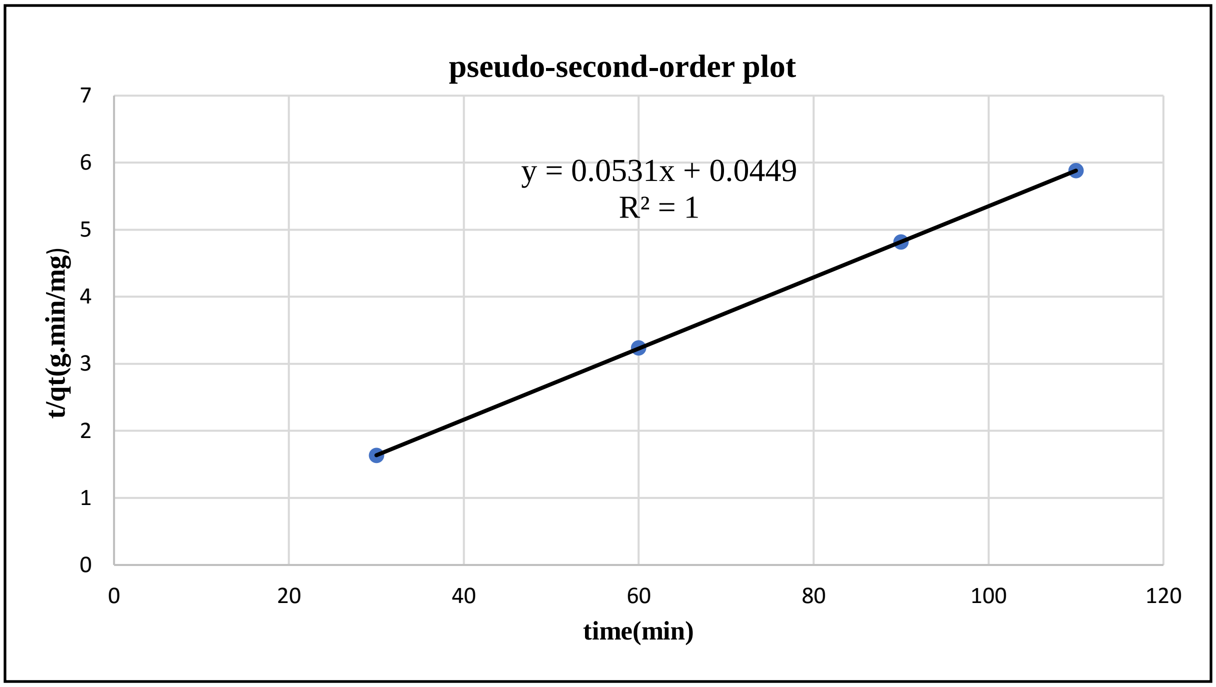


Figure 4.14: Pseudo second-order kinetic model plot Cr (III) adsorption (Adsorbent dosage=0.8g, initial concentration = 150mg/l, pH= 5, shaking speed = 200rpm at room temperature with contact time 30 to 130 min).

The comparison of experimental sorption capacities (q_{exp}) and the Predicted values (q_{cal}, K_1, K_2, and R^2) from pseudo first order, and pseudo-second order are given in Table 4.8.

Table 4.8: Adsorption kinetic model parameters for chromium adsorption.

Initial Cr(III) ion concentration(mg/l)	Pseudo 2nd order kinetic model				Pseudo 1st order kinetic model		
	q_e(mg/g) (cal)	qe(mg/g) (exp)	K_2 (g/mg.min)	R^2	q_e(cal)	K_1(min^{-1})	R^2
150mg/l	18.8323	18.70116	0.0627	1	16.5576	0.0953	0.827

Based on Table 4.8, the results demonstrated that among these models, Pseudo second-order kinetic equations have high R^2 (R^2= 1) values and sorption capacity q_e (mg/g), calculated and experimental value near to same value. So, Pseudo second-order kinetics models were taken as the fit equations for the description of the mechanism of sorption of chromium (III) ion using modified fish scales. Therefore, from the table concluded that the sorption of chromium (III) ions from tannery wastewater onto modified fish scale were found to follow Pseudo second-order kinetics equations.

5. CONCLUSION AND RECOMMENDATION

5.1.Conclusion

Removal of chromium (III) form of tannery wastewater solutions were possible using modified fish scale (adsorbents). Fish Scales is lightweight flexible and skeletal elements that cover and protect the skin of fishes. The batch study for chromium removal by adsorption process using MFS were carried out in batch shake flasks. The modification of fish scale using chemicals [H_2SO_4, HCl, Na(OH), and $Ca(OH)_2$] was carried out for surface area modification to increases the removal efficiency Cr (III) ion from tannery wastewater.

To know the potential of MFS for removing Cr (III) from the tannery wastewater, the experiments was conducted with varying adsorbent dosage, pH, and contact times at constant initial concentration. The result indicates that MFS is having the potential to removal Cr(III) from tannery wastewater. Thus Cr(III) removal using MFS reached 99.7518% at adsorbent dosage 0.8g, pH=5, and contact time ninety-minute, amount 150mg/l of initial solution of wastewater. Also, the adsorption Cr(III) mostly depends on pH and contact time, which are significant factor, it indicates as pH and contact time increases the removal efficiency increases till equilibrium. The FTIR analysis describes that the adsorbent fish scales contain functional groups such as carboxyl, amine and hydroxyl groups. Based on the graph of FTIR spectra, those functional groups participate on chromium binding on to surface of MFS and the X-ray Diffraction analysis indicates that fish scales have properties of an amorphous.

The adsorption kinetics studies indicated at equilibrium in the adsorption of Cr(III) ion was reached in 130min of contact between the MFS and the solution. It was found that the kinetics of the adsorption on modified fish scale followed by pseudo-second-order. The Langmuir and Freundlich theories were used to describe the distribution chromium ion in between the solid and liquid and the Langmuir isotherms showed a better fit to the process (R^2= 0.9998).

Generally, the Modified fish scale is found to be a better biosorbent for the removal of chromium (III) from tannery wastewater. The results prove that MFS have high possibility and efficiency in removing Cr (III) ion in wastewater. It is a capable biosorbent and poses as an environmental friendly adsorbent to society and environment.

5.2.Recommendation.

Based on this study work, the modified fish scale have a high potential to remove chromium ion from tannery wastewater, therefore, the following direction of work is recommended in the modification of fish scales for the removal of chromium (III) ion from tannery effluent.

- In this study BET analysis for biosorbent doesn’t analyzed, so, further research is required to analysis difference between raw and modified fish scale in surface area. Since potential of adsorption is depend surface area of adsorbent, so, it directs potential difference in removal efficiency of chromium from tannery wastewater in between them.
- In this study only the effect of adsorbent dosage, pH, and contact time were analyzed and concluded on the efficiency of chromium (III) ion uptake, but, further research recommended to the concluded effect of initial concentration, temperature and shaker speed of on adsorption efficiency.
- In this study synthetic wastewater was used to evaluate the adsorption test process. However, it’s recommended to use real tannery wastewater for the more perfection of the studies because synthetic wastewater does not contain other interacting material.
- The chromium ion saturated adsorbent is not directed for disposal due to the environmental constraints. So, it is important to propose a method for regeneration and re-use of adsorbent and recovery of Cr (III) to reduce polluted adsorbent to the environment.
- Study adsorption process for other metals which is a tackle for environmental sustainable using fish scale sorbent.

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APPENDIXES

Appendix A: Value form design-expert@7.0.

RUN	Block	Factor 1 A: Dosage(g)	Factor 2 B: pH	Factor 3 C: contact time(min)	Response Efficiency (%)
R1	Block1	0.4	3	30	93.4529
R2	Block1	0.8	3	30	92.1436
R3	Block1	1	3	30	94.9904
R4	Block1	0.4	5	30	96.8722
R5	Block1	0.8	5	30	97.9603
R6	Block1	1	5	30	98.7918
R7	Block1	0.4	8	30	97.4359
R8	Block1	0.8	8	30	94.0102
R9	Block1	1	8	30	92.1303
R10	Block1	0.4	3	90	97.688
R11	Block1	0.8	3	90	99.4254
R12	Block1	1	3	90	98.4185
R13	Block1	0.4	5	90	98.1974
R14	Block1	0.8	5	90	99.7518
R15	Block1	1	5	90	99.1054
R16	Block1	0.4	8	90	99.5204
R17	Block1	0.8	8	90	99.5321
R18	Block1	1	8	90	996787
R19	Block1	0.4	3	150	93.6061
R20	Block1	0.8	3	150	97.0618
R21	Block1	1	3	150	97.6567
R22	Block1	0.4	5	150	99.2705
R23	Block1	0.8	5	150	99.3728
R24	Block1	1	5	150	98.9028
sR25	Block1	0.4	8	150	98.2341
R26	Block1	0.8	8	150	98.3929
R27	Block1	1	8	150	98.6035

Appendix B: Adsorption kinetic model table

time(min)	Chromium(III) %(removal)	initial(mg/l)	final(mg/l)	qt(mg/g)
30	97.9984	150	3.0596	18.3747
60	98.8559	150	1.7162	18.535475
90	99.6654	150	0.5019	18.6872
110	99.739	150	0.3915	18.70106
130	99.7395	150	0.3907	18.70116

Appendix C: Dilution of Cr(III) stock solution preapration

Using stock solution which is 1000mg/l

From the relationship :

mass of stock solution = mass of diluted solution

$C_1V_1 = C_2V_2$, C_1 = 1000mg/l, V_2 = 100ml, to find V_1?

$$V_1 = \frac{C_2 * V_2}{C_1} = V_1 = \frac{150*100}{1000} = 15ml$$

Therefore 15 ml of stock soluiton was taken from prepared and measure by a micropipette.

Appendix D:**Calculation of Basic Chromium sulfate**

To Prepare 1000 mg/L of Cr(III) Stock Solution we have to calculate how much $Cr_2(SO_4)_3$ is required to get concentration of Cr(III) stock solution of 1000mg/L.

Basic chromium sulfate [$Cr(SO_4)_3$] has molecular weight $= 2 * 52 + 32 * 4 + 16 * 12 = 104 + 96 + 192 = 392 \text{g/mol}$

= 104g of Cr(III) in available = 392g of $Cr_2(SO_4)_3$, 1g Cr(III).

Use this relation to write the conversion factor. Start always from the concentration we need to prepare 1000 ppm (mg/L).

$$\frac{1000\text{mgCr(III)}}{\text{l}} * \frac{1\text{gCr(III)}}{1000\text{mgCr(III)}} * \frac{392\text{gCr}_2(\text{SO}_4)_3}{104\text{gCr(III)}} * 1\text{l} = 3.7692\text{g Cr}_2(\text{S0}_4)_3$$

To prepare stock solution dissolve 3.7692g of $Cr_2(SO_4)_3$ in small amount of solvent then complete to total volume 1 Liter.

Appendix E: Oven used for drying and mechanical grinding for size reduction

Appendix F: Graphite atomic adsorption spectrophotometry (AAS) and Sieve

Appendix H: Sample digestion for AAS analysis and digital balance

Appendix I: Synthetic wastewater, and Modified fish scales after Cr(III) loaded

Appendix J: Diluted solution preparation

Sulfuric acid solution preparation

To prepare solution containing 0.1MH_2SO_4 solution in 150ml, molarity relationship,

$$\text{molarity} = \frac{\text{mole of solute}}{\text{volume of solution}}, \text{where, mole} = \frac{\text{given mass}}{\text{molecularweight}}$$

$$\text{molarity} = \frac{\text{given mass}}{\text{molecularweight}} * \frac{1}{\text{volume of solution}}, \text{from this equations:} \frac{\text{given mass}}{\text{volume of solution}} = \text{density}(\rho)$$

$$\text{molarity} = \frac{\text{density}}{\text{molecular weight}} = \frac{\rho}{M_{wt}}$$

$$M = \frac{1.84 * 1000 * 0.98}{98.08} = 18.38M = M_s$$

Molecular weight of H_2SO_4 = 98.08gm/mol

$$M_sV_s = M_1V_1 = V_s = \frac{M_1V_1}{M_s}, M_1 = 0.1M \text{ and } V_1 = 150ml$$

$$V_s = \frac{0.1M * 150ml}{18.38M} = 0.816M$$

Therefore, to prepare 0.1M H_2SO_4 solution in 150ml 0.816m of sulfuric acid required

The same procedure for sodium hydroxide and calcium hydroxide solution preparation.