AN INVESTIGATION ON THE REMOVAL OF IRON AND CHROMIUM FROM STEEL INDUSTRY EFFLUENT BY ADSORPTION PROCESS USING BREWERY SPENT GRAIN

Ergalem Amare Kibret

A Thesis Submitted to the Department of Chemical Engineering

School of Mechanical, Chemical and Materials Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master's in Chemical Engineering (Specialization in Process Engineering)

Office of Graduate Studies

Adama Science and Technology University

July, 2023

Adama, Ethiopia

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Declaration

I hereby declare that this Master Thesis entitled **"an investigation on the removal of iron and chromium from steel industry effluent by adsorption process using brewery spent grain)"** is my original work. That is, it has not been submitted for the award of any academic degree, diploma, or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation.

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Name of the Student Signature Date

Recommendation

We, the advisors of this thesis, hereby certify that we have read the revised version of the thesis entitled **"an investigation on the removal of iron and chromium from steel industry effluent by adsorption process using brewery spent grain)"** prepared under our guidance by Ergalem Amare Kibret submitted in partial fulfillment of the requirements for the degree of Mater's of Science in Chemical Engineering. Therefore, we recommend the submission of the revised version of the thesis to the department following the applicable procedures.

Mulugeta Yilma (PhD)	_____	_____
Advisor	Signature	Date

Approval Page of M.Sc. Thesis

Me, the advisor of the thesis entitled **"an investigation on the removal of iron and chromium from steel industry effluent by adsorption process using brewery spent grain)"** and developed by Ergalem Amare Kibret, hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

Mulugeta Yilma (PhD) _____ _____

Advisor Signature Date

We, the undersigned, members of the Board of Examiners of the thesis by Ergalem Amare Kibret have read and evaluated the thesis entitled **"an investigation on the removal of iron and chromium from steel industry effluent by adsorption process using brewery spent grain)"** and examined the candidate during the open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Chemical Engineering.

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Finally, approval and acceptance of the thesis is contingent upon submission of its final Copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate Council (DGC) and School Graduate Committee (SGC).

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School Dean Signature Date

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Office of Postgraduate Studies, Dean Signature Date

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ACRONYMS AND NOMENCLATURES

AAS	Atomic Absorption Spectroscopy
APHA	American Public Health Association
BSG	Brewery spent Grain
CCM	Continuous casting Machine
Ce	Concentration of the sorbate at equilibrium (mg/L),
Fe_3O_4	Magnetite (Ferrous-ferric Oxide)
FTIR	Fourier-Transform Infrared Spectroscopy
Kf	Freundlich adsorption capacity (mg/g)
kf	Pseudo first order rate constant
KL	Langmuir equilibrium constant (l/mg).
ks	Pseudo second order rate constant
n	Sorption intensity
qe	Amount of sorbate sorbed at equilibrium per unit mass (mg/g),
qm	Monolayer sorption capacity at equilibrium (mg/g)
RMI	Roll and Mill Industry
SEM	Scanning Electron Microscopy
TMT	Mechanical heat treatment
UV	Ultraviolet
WHO	World health organization

Abstract

Presence of excess heavy metals in water leads to various health problems due to their toxicity. In this paper removal of chromium and iron by using brewery spent grain as adsorbent were studied the adsorption study was evaluated as initial concentration, time, dose and pH of both chromium and iron. BSG was treated with 4M sulphuric acid, cellulose of BSG extracted and grinded to have particle size 250-350 µm. Batch adsorption was done using artificial waste water containing synthesized Fe_3O_4 for iron and potassium dichromate for chromium. The batch adsorption result indicates that removal percentage of chromium and iron was 87.94% & 97.85% at pH=2 & pH=6 respectively. And also, adsorption parameters equilibrium isotherm and kinetics were conducted. The sorption of chromium by brewery spent grain is well fitted to both Langmuir and freudlich isotherm model with correlation coefficient of 0.98085 and 0.9832 respectively. In addition, the result of the kinetic model proved that pseudo-second-order provided a good description of the experimental data with a maximum R^2 of 0.990 and 0.999 respectively for Iron and chromium respectively. So it can be concluded that treated brewery spent grain can be best to remove chromium and iron from waste water.

Key Words: *Adsorption, Kinetics, Isotherm, chromium, iron*

1. Introduction

1.1. Background

From different environmental issues, pollution by heavy metals of surface water, ground water and soil in urban areas are the major environmental problems. Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products. The presence of heavy metal ions is of major concern due to their toxicity to many life forms. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, steel industries, tanneries, paint, radiator manufacturing, smelting, alloy industries and storage batteries industries. The most common and harmful heavy metals are mercury, lead, copper, nickel, chromium and zinc. They are stable elements that cannot be metabolized by the body and get passed up in the food chain to human beings. When waste is disposed into the environment, a further long- term hazard is encountered (Ibrahim Olaniyi,2011).

The increasing awareness of the environmental consequences arising from heavy metal contamination of the aquatic environment has led to the demand for the treatment of industrial wastewater before discharge into the aquatic environment (Ibrahim Olaniyi,2011).

Thus, treatment of this polluted liquid is recognized as one of the most burning issues. Many processes for the removal of heavy metals from water and wastewaters have been proposed. Amongst these removal methods, chemical precipitation, coagulation, physical treatment such as ion exchange, membrane separation, and activated carbon adsorption are some of the processes that have been reported to be the most effective (Huang; Wu. M.H.,1975).

Adsorption in comparison with other methods appeared to be preferable in terms of its efficiency and ease with which it can be applied in its application in the removal of heavy metals in wastewater. An adsorbent can be considered as cheap or low-cost if it is abundant in nature, requires little processing and is a byproduct of waste material from waste industry. Plant wastes are inexpensive as they have no or very low economic value (Bailey, 1989). Today, in this regard, biosorption is one of the main components of environmental and bio-resource technology

due to its economical and efficient in removing of very diluted metal concentrations from waste water (Holan & Volesky, 1995).

Most developing nations continuously produce abundant agro-industrial residues such as brewer's spent grain (BSG), which are underexploited (Aliyu & Bala, 2011). Brewers' spent grain (BSG) is the major byproduct of the brewing industry, representing around 85% of the total by-products generated (Mussatto et al., 2006). The brewing industry generates relatively large amounts of byproducts and wastes; spent grain, spent hops and yeast being the most common. However, as most of these are agricultural products, they can be readily recycled and reused (Mussatto et al, 2006).

This research reveals the significance of Cr(VI) and Fe(II) removal from wastewater streams and discusses the adsorption potential of brewery's spent grain (BSG), at different operation conditions such as pH, dose required, initial concentration of metal Cr(VI) and Fe(II) and contact time. In addition, sorption isotherms, sorption kinetics as well as models used to characterize biosorbent sorption have been investigated.

Waste water sample received from STEELY RMI PLC. This Company was established in October 2004 in response to the growing construction sector and the associated huge demand of construction materials in Ethiopia. So the company owners had taken a strategic decision to invest in this sector. As a fast growing economy, the domestic market especially in the construction sector can absorb more production capacity. By using this advantage, the company has been profitable for last nineteen (19) years (steely,2020).

The factory is located east of Addis Ababa in Oromia National Regional State, at Bishoftu town, 45 kilometers away from Addis Ababa. The factory was built on 125,000m^2 with open areas for scraps and finished good storage. Its initial investment was 486millon birr and currently total asset of the company has reached 1.77billion birr(steely,2020).

The factory installed advanced technology like PLC, CCM, TMT, Spectrometer, modern physical test machine etc. to produce quality product at competitive price. The theoretical (ideal) production capacity of first installed factory is 120,000 metric ton of rebar per year. The new factory production capacity is 210,000 metric tons per year. This will raise the production

capacity of the company to 330,000 metric tons per year. Its total power consumption is 30MW. The factory uses local scrap and imported billets as raw material for production.

The company is mainly engaged in manufacturing and selling of steel products. Its main products are: -

- Reinforcement bar of G60 and G75. Its main features are high strength, superior bending properties, better elongation, excellent corrosion and fire resistance. The product size composed of 8, 10, 12,14,16,20, and 24mm diameter.
- Steel wire rod for further industrial process or direct use in the construction sector. Its size is 5.5-12mm dimensions((steely,2020).

1.2. Statement of the problem

Now days, wastewater treatment is serious issue due its adverse impact on environment especially in aquatic life. In steel industry, there are wastes which impact environment and aquatic life negatively. Those wastes include oil and greases (damages aquatic organisms, plant and animals etc..), acids and alkalis, and heavy metals are some of steel industry wastes. Heavy metals (Fe and Cr,) discharges from industries effluent in Ethiopia are above the permissible standards and it is one of the most toxic metals to plants, animals and microorganisms (EPA, 2001). Similarly, wastewater from the steel mill contains a high concentration of heavy metals due to the accumulation of filtered particles from the filtration process of wastewater (sponza D. etal. 2002).

Heavy metals (Fe, & Cr) can damage and alter the functioning of brain, kidney, lungs, liver, cause allergic reactions to body, anemia, damage sperm cell of male reproductive organ, gait disorder, cognitive disorder and postural disability are some of effects of those heavy metals.

The adsorption and precipitation process has been successfully applied to remove the heavy metals. Hence low cost, long lasting, renewal adsorbent is being considered to remove the heavy metals (Hyung.etal.2008). The most investigated bio-materials are the agricultural by products. Maize cob (J.C. Igwe etal.2003), husk, coconut fiber, sunflower stalk (J.C. Igwe .etal.2005), medicago sativa (Alfalfa), cassava waste (J.L. Gardea etal.1998), sawdust (C. Raji etal. 1998) , wild cocoyam (M. Jnr.etal.2004) , sphagnum peat moss (L. Dupond etal. 2003) , banana pith

(K.S. Low etal.1995), sugar-beet pulp (Z. Reddad etal. 2003), sugarcane bagasse (Krishnani etal. 2004), spent grain brewery (Mussatto etal. 2006) &sago waste (Quek ,1998) are few to mention.

1.3. Basic Research Questions

1. Is it possible to convert brewery spent grain waste (HEINIKEN BREWEWRIES BSG) into valuable products particularly as adsorbent?

2. which isotherm and kinetics well fitted for removal of chromium and iron?

3. What are the optimum parameters such as pH, adsorbent dose, contact time, and initial concentration for Fe (II) Cr (VI) removal?

1.4. Objectives of the study

1.4.1 General objective

The aim of this study is an investigation on the removal of iron and chromium from steel industry effluent by adsorption process by using brewery spent grain.

1.4.2. Specific objective

- ✓ To characterize brewery spent grain
- ✓ To characterize steel industrial effluent before and after treatment
- ✓ To investigate the effects of pH, time, dose and initial concentration on adsorption performance of BSG.
- ✓ To study adsorption capacity of BSG.
- ✓ To investigate adsorption isotherm and kinetics.

1.5. Significance of the study

The study is significant in that it will be used as supportive idea to do further detailed researches regarding to environmental impact of waste water in steel industry. Heavy metals from waste water of steel industry must be treated to minimize toxicity, mutanogenecity, carcinogenicity and non- biodegradability. In STEELY RMI plc wastes released from rolling mill, continuous casting machine and furnace. Around **508,868**L water released in 6 months.

The outcome of this study benefits

- ✓ to do further detailed researches regarding to environmental impact of waste water in steel industry.
- ✓ Solid waste management for brewing industries
- ✓ provides cheap treatment methods for industries to treat their wastes before discharge to environment.

1.6. Scope of the study

This thesis focused on the characterization of brewery spent grain an adsorbent for the removal of heavy metals from steel industry waste water. The FTIR were used to characterize the brewery spent grain. The initial and final concentrations of heavy metal, in the filtrate were determined by using UV/VIS spectrophotometer (lambda 950). Furthermore, adsorption studies of various effects such as adsorbent dose, initial nitrate concentration, pH, and contact time on heavy metal removal by brewery spent grain were investigated. In addition, adsorption kinetics, and adsorption isotherm were conducted.

1.7. Thesis Structure

This thesis is organized in five chapters. The first chapter includes introduction about the work, problem of statement, objective of the study and its significance. The second chapter is literature review includes description of heavy metals in environment and their toxicity, methods of heavy metal removal, adsorption isotherm and kinetics were briefed.

The third chapter is about materials methods. Materials used and methods in this thesis are listed. The 4^{th} chapter examines characterization of BSG, kinetics and equilibrium was described. The last chapter concludes the whole works and recommendation for further researches.

2. LITERATURE REVIEW

2.1. General description of heavy metals in environment

Industrialization has introduced the metals contamination problem in the environment over the past decade. The heavy metals being released from steel industries commonly include Fe and Cr. These metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organism causing health problems in animals, plants and human beings (H.L. Needlemana, 2001 and H.Howard, 2002). The understanding of the noxious health impacts of metals on humans lead to the development of stricter environment protection laws and this fact gave encouragement to the studies of metal's removal and recovery by using various techniques. Different techniques are used for the removal of metals from industrial waste waters like: precipitation (Navarro *etal*,2005, S.Y. Bratskaya.*etal*.2009, floatation (C. Aldrich.*etal.*,2000 & J. Rubio.*etal*.1997), Liquid Extraction (Sprynskyy *etal*.2008, Membrane filtration (C. Blocher *etal*.2003), ion exchange (A. Wojtowicz *etal.*,2002), electrochemical processes C. Ahmed Basha *etal.,2008)* and adsorption using synthetic adsorbents like; activated carbon and alumina (] S.D. Faust *etal*.,1987 J.W.Shim, 2001).

Bio-sorption being an eco-friendly technique employs the waste, inactive and dead biomaterials for the removal or recovery of metals. The most investigated bio-materials are the agricultural by products. Maize cob, husk (J.C. Igwe *etal.*,2003 and J.C. Igwe *etal.*, 2005), coconut fiber (J.C. Igwe *etal*.,2005), medicago sativa (Alfalfa) (J.L. Gardea *etal.*,1998), sunflower stalk (S. Gang, S *etal*.,1998), cassava waste (J.L. Gardea *etal.*,1998), sawdust (J.L. Gardea *etal.*,1998) , wild cocoyam (M. Jnr,2004) , peanut skins(.M. Randell *etal*.,1994) , wheat bran (Dupond,& E. Guillon *etal.*,2003), shea butter seed husks (C. Eromosele *etal.*,1994) , sphagnum peat moss (G. Mckay *etal.*,2000), chitosan(W.S. Ngah, & K.H. Liang *etal.*,1999) , banana pith (K.S. Low, C.K. Lee, & A.C. Leo *etal*.,1995), sugar-beet pulp (Z. Reddad *etal*.,2003), sugarcane bagasse (V. Parmala, & X. Men *etal.,2004*), spent grain brewery (Mussatto *etal.*,2006,&sago waste (S.Y. Quek etal.,1998) are few to mention.

2.2. Toxicity and health effect of heavy metals

The presence of heavy metals in the environment is a major concern because of their toxicity to Many life forms. Heavy metals like mercury, lead, cadmium copper, chromium and nickel are toxic even in extremely minute quantities. Since the majority of heavy metals do not degrade in to harmless end products, their concentrations must be reduced to acceptable levels prior to discharge of industrial effluents. Otherwise, they could pose threats to public health and affect the aesthetic quality of potable water. According to the WHO, the metals of most immediate concern are aluminum, chromium manganese, iron, cobalt, nickel, copper, zinc, cadmium, and mercury and lead (Williford, C, 2000)

Table 2.1: - Common Source and Diseases of Heavy Metals (Williford, C,2000)

S.NO	Metal	Major Source	Related Disease
1	Arsenic	Arsenic containing fungicides, pesticides and herbicides, metal smelters.	Cancer, Discoloration of Skin
2	Cadmium	Industries, electroplating, welding. Byproducts from Pb, Zn and Cu, fertilizers, pesticides, cadmium–nickel batteries, nuclear fission.	Bone softening, kidney failure
3	Chromium	Metallurgical industries, cement and asbestos units.	Lung cancer
4	Copper	Iron and steel industry, fertilizes, burning of wood, discharge of mine tailings, disposal of industrial wastes.	Gastrointestinal disease, vomiting
5	Iron	Cast Iron, Wrought Iron, steel, alloys, machine manufacturing.	Hemochromatosis, diabetes
6	Lead	Automobile emissions, lead smelters, burning of coal, lead arsenate pesticides, smoking, mining.	high blood pressure, anaemia
7	Manganese	Dry cell batteries, chemical manufacturing, manufacture of glass, leather and textile industry & fertilizer industries.	Difficulty in walking,irritability, decrease lung functions
8	Mercury	Mining and refining of mercury, organic mercurial, labs using mercury.	neurological and behavioural disorders
9	Nickel	Metallurgical industries using nickel, burning coal, electroplating units using nickel salts.	chronic bronchitis
10	Zinc	Galvanizing processes, brass manufacture, metal plating, and plumbing.	Stomach cramps, nausea and vomiting.

2.3. General description of chromium in environment

Chromium (Cr) is a naturally occurring element present in the earth's crust, with variable oxidation states. The most common oxidation states of chromium are 0, +2, +3 and +6 with +3 being the most stable. But only three oxidation states are found in nature; these are: Cr(0) which occur in metallic form, Cr(III) in chromic compounds and Cr(VI) occurs as soluble chromate(CrO_4^{2-})and dichromate ($Cr_2O_7^{2}$) compounds (Jacobs JA**.;** Testa SM.,2005). Chromium compounds are stable in the trivalent [Cr(III)] form and occur in nature in this state in ores, such as ferrochromite. The hexavalent [Cr(VI)] form is the second-most stable state next to lead (Baig *et al*.,2003). Elemental chromium [Cr (0)] does not occur naturally. Chromium enters into various environmental matrices (air, water, and soil) from a wide variety of natural and anthropogenic sources with the largest release coming from industrial establishments. Industries with the largest contribution to chromium release include metal processing, tannery facilities, chromate production, stainless steel welding, and ferrochrome and chrome pigment production. The increase in the environmental concentrations of chromium has been linked to air and wastewater release of chromium, mainly from metallurgical, refractory, and chemical industries. Chromium released into the environment from anthropogenic activity occurs mainly in the hexavalent form [Cr(VI)] (U.S. Department of Health and Public Health Service,1992). Hexavalent chromium [Cr(VI)] is a toxic industrial pollutant that is classified as human carcinogen by several regulatory and non-regulatory agencies (International Agency for Research Center, 1990). The health hazard associated with exposure to chromium depends on its oxidation state, ranging from the low toxicity of the metal form to the high toxicity of the hexavalent form. All Cr(VI)-containing compounds were once thought to be man-made, with only Cr(III) naturally ubiquitous in air, water, soil and biological materials. Commercially chromium compounds are used in industrial welding, chrome plating, dyes and pigments, leather tanning and wood preservation.

Chromium is also used as anticorrosive in cooking systems and boilers (Velma V. *et al*., 2009). The formation of the different Cr(VI) species depends on the pH and the chromium concentration. The pH effect is shown Figure (1). Hexavalent chromium compounds such as chromate and dichromate behave as strong oxidants at low pH. Cr(VI) has complicated hydrolysis and it can form only neutral and anionic species. According to Figure (1),Cr(VI)

exists primarily as salts of chromic acid (H_2CrO_4), hydrogen chromate ion ($HCrO_4^-$), and chromate ion (CrO_4^{2-}) (Hyder,A.H.M.G.,2013). In the pH range from 1 to 6.5 and chromium concentrations above 1g/L, dichromate ions ($Cr_2O_7^{2-}$) predominate. H_2CrO_4 predominates at pH below 1.0, $HCrO_4^-$ at pH between 1.0 and 6.0, and CrO_4^{2-} at pH above 6.0.

2.3.1 Chemical and physical properties of chromium(VI) compounds

Chromium (VI), also known as hexavalent chromium, is the second most stable oxidation state of chromium. Rarely occurring naturally, most chromium (VI) compounds are manufactured (products or by-products). Chromium (VI) can be reduced to the more stable chromium (III) in the presence of reducing agents (e.g. iron) or oxidizable organic matter (OSHA, 2006). Chromium (VI) compounds are customarily classed as soluble or insoluble in water. Examples of water-soluble chromium (VI) compounds are sodium chromate (873 g/L at 30°C) and potassium chromate (629 g/L at 20°C). Water insoluble chromium (VI) compounds include barium chromate (2.6 mg/L at 20°C), and lead chromate (0.17 mg/L at 20°C) (Lide, 2008). Compounds with solubilities in the middle of this range are not easily classified, and technical-grade compounds, such as the various zinc chromates, can have a wide range of solubilities (International Agency for Research Center, 1990). In the United States of America, the department of Occupational Safety and Health Administration (OSHA) has divided chromium (VI) compounds and mixtures into the following three categories: water-insoluble (solubility < 0.01 g/L), slightly soluble (solubility 0.01 g/L–500 g/L), and, highly water-soluble (solubility = 500 g/L) (OSHA, 2006).

Chromium (VI) compounds are mostly lemon-yellow to orange to dark red in colour. They are typically solid (i.e. crystalline, granular, or powdery) although one compound (chromyl chloride) is a dark red liquid that decomposes into chromate ion and hydrochloric acid in water (OSHA, 2006).

2.3.2 Anthropogenic sources of chromium compounds

Anthropogenic sources involve the man-made activities that are taken in to consideration in the formation of chromium compounds. The level of chromium concentration in anthropogenic

sources is much higher compared to natural sources. Thus chromium contamination in the environment is mainly due to anthropogenic sources. Chromium levels in soil vary according to area and the degree of contamination from anthropogenic chromium sources. Tests on soils have shown chromium concentrations ranging from 1 to 1000 mg/kg, with an average concentration ranging from 14 to about 70 mg/kg (United States Environmental Protection Agency, 1984). Chromium(VI) in soil can be rapidly reduced to chromium(III) by organic matter. As chromium is almost ubiquitous in nature, chromium in the air may originate from wind erosion of shales, clay and many other kinds of soil. In countries where chromite is mined, production processes may constitute a major source of airborne chromium. In Europe, endpoint production of chromium compounds is probably the most important source of chromium in air (WHO, 2000).

Cr(VI) is found in industrial effluents such as metallurgical refractory, chemical, and pigment industry where as tannery, textile, and plating industry effluent exhibits Cr(III) affluence in wastewater. Some other prominent sources of chromium include the chromite-ore processing industry, automobile, paper and pulp, fertilizer, textile, steel, metal finishing, magnetic tapes, leather tanning, wood protection, petroleum refining, brass, electrical and electronic equipment etc.(Hyder**A.** H. M. Golam, 2013). They generate huge quantities of chromium containing effluents which can end up contaminating surface and ground water resources. Other significant man-made sources of chromium include municipal wastes, and sludge generated from the municipal waste. Sewage treatment plants from industrial and residential sources also discharge substantial amounts of chromium in waste stream.

2.3.3 Advantages of chromium compounds

Since its discovery chromium has become a very important industrial metal because of its many applications in ferrous and non-ferrous alloy metal fabrication, and in the chemical industry. Chromium compounds are used in a wide variety of industrial and manufacturing applications including steel alloy fabrications, where they enhance corrosion and heat resistance and in plated product fabrication where they are used for metal decoration or increased wear resistance. They are also used in nonferrous alloy metal fabrication to impart special qualities to the alloys; in production and processing of insoluble salts, as chemical intermediates; in the textile industry for dyeing, silk treating, in the leather industry for tanning to obtain leather of desirable quality; in

the manufacture of green varnishes inks, paints and glazes; as catalyst for halogenations, alkylation and catalytic cracking of hydrocarbons; as fuel and propellant additives; and in ceramics (Sumathi *et al.*,2004).

Table 2.2: Uses and color of different forms of chromium.

Form	Appearance (colour)	Uses
Cr(0)	Metallic grey / silvery	Stainless steel production, Alloy production, etc.
Cr(III)	Green	Alloy manufacturing, brick lining, chrome plating, tanning, and textiles, copying machine toner.
Cr(VI)	Red, orange or yellow	Chrome plating, Leather tanning, textiles and machine toner.

Source:(Agaje Bedemo, 2007)

2.3.4 Toxicity and health effect of chromium compounds

The presence of heavy metals in the environment is a major concern because of their toxicity to many life forms. Heavy metals like mercury, lead, cadmium copper, chromium and nickel are toxic even in extremely minute quantities (Selvaraj *et al.*,2003). Since the majority of heavy metals do not degrade in to harmless end products, their concentrations must be reduced to acceptable levels prior to discharge of industrial effluents. Otherwise, they could pose threats to public health and affect the aesthetic quality of potable water.

According to the WHO, the metals of most immediate concern are aluminum, chromium manganese, iron, cobalt, nickel, copper, zinc, cadmium, and mercury and lead (Baig *et al.*, 2003). Chromium contamination of soil and ground water is one of the significant environmental problems today. Chromium is believed to be the second common inorganic contaminant after lead. The toxicity of chromium does not reside solely with the elemental form but varies greatly among a wide variety of chromium compounds. Oxidation state and solubility are crucial factors in this regard (Hyder **A.** H. M. Golam, 2013). Chromium occurs in the environment primarily in two valence states, the oxidized hexavalent chromium, Cr(VI), and the less oxidized trivalent chromium, Cr(III). Under common environmental conditions of pH, Cr(III) compounds are slightly soluble in water, whereas Cr(VI) compounds are quite soluble. Chromium(III) is

considered to be essential to mammals for glucose, lipid, and protein metabolism and hence is an essential dietary element. On the other hand, Cr(VI) is much more toxic and mobile in ground water than the relatively immobile Cr(III) and possesses mutagenic and carcinogenic activity (Nomanbhay; Palanisamy, 2005).

In humans, Cr(VI) exposure causes marked irritation of the respiratory track and ulceration and perforation of the nasal septum in workers in the chromate producing and using industries (Ageje Bedemo,2007). Ingestion of 1.0 to 5.0g of Cr(VI) as chromate results in severe acute gastrointestinal disorders, hemorrhagic diathesis, convulsions and death may occur following cardiovascular shock. The maximum levels in drinking water are 5 mg/L for trivalent and 0.05 mg/L for hexavalent chromium. But, there is still uncertainty regarding what daily dose of Cr(VI) is considered toxic and what ingestion concentration of Cr(VI) is acceptable (Acar; Malkoc,2004).

2.4. General description of Iron in Environment

Iron is the second most abundant metal in earth crust. It is about 5%. It is found as Fe^{2+} and Fe^{3+} combine with oxygen- and sulphur- containing compounds to form carbonates, oxides, hydroxides & sulphides. Iron is the most commonly found in nature in form of oxides (Elinder *etal*., 1986).

2.4.1. Physico chemical properties of Iron

Table 2.3 physico chemical property of Iron

Property	Value	Reference
Melting point	1535°C	Budavari etal.,1989
Specific gravity	7.86@25°C	

2.4.2. Organoleptic propery of iron

Iron (Fe^{2+}) concentration of 40 µg/liter can be detected by taste in distilled water. In drinking-water supplies, iron(II) salts are unstable & are precipitated as insoluble iron(III) hydroxide, which settles out as a rust-coloured silt. Anaerobic groundwaters may contain iron(II) at concentrations of up to several milligrams per litre without discoloration or turbidity in the

water when directly pumped from a well, although turbidity and colour may develop in piped systems at iron levels above 0.05–0.1 mg/litre. Staining of laundry and plumbing may occur at concentrations above 0.3 mg/litre (ISO 2015).

2.4.3. Uses of Iron

Iron is used as constructional material, *inter alia* for drinking-water pipes. Iron oxides are used as pigments in paints and plastics. Other compounds are used as food colours and for the treatment of iron deficiency in humans. Various iron salts are used as coagulants in water treatment.

2.4.4. Environmental fate of Iron

Aeration of iron-containing layers in the soil can affect the quality of both groundwater and surface water if the groundwater table is lowered or nitrate leaching takes place. Dissolution of iron can occur as a result of oxidation and decrease in pH.

2.5. Methods for Heavy Metal Removal

2.5.1. Conventional methods

This category includes mainly the physical methods for the separation like mechanical screening, hydrodynamics, concentration, and floatation, density factor between soil and water, hydrophobic properties of metals, hydrophilic properties of metal (Smith, 1995).

2.5.2. Coagulation and flocculation

In this process of water purification, water analysis is done prior to steps. Zeta potential is firstly measured between the pollutants and the coagulant agent (Gunatilake, 2015). The process of coagulation reduces the electrostatic repulsion and flocculation increase the particle size. Once the particles size is increased they are removed by filtration.

2.5.3 Biological methods

Since ancient times, biological and natural techniques have always been useful to mankind. For the water purification case, the microorganisms work in the water bodies and form sludge. The activated sludge is used as it decomposes the metals present in the water by aeration and agitation and then the unwanted part is settled and separated out. The bacteria working repeats the cycle again and again depending upon the demand. Biosorption is another method for the

removal of heavy metals from water. Red mud provides a selective adsorption for particular metals (Gupta.*etal*.2001).

2.5.4. Chemical precipitation

As a result of its easy operation, the process of chemical operation is widely used in the process of removing the inorganic impurities from the water containing them. The experimental procedure is quite simple. The sample water is taken and a precipitating agent is added as a result of which the heavy metals present in the water starts to precipitate as their corresponding sulphides, chlorides etc. depending upon their affinity with them. Once the precipitate is formed it starts to settle at the bottom of the sample holder, as more and more of tiny particles starts to come together. Later, the solid impurity is removed by the simple methods of filtration or via filter membrane.

2.5.5. Membrane filtration

Membrane filtration is a widely used method in different sectors for different purposes. It serves to be an easy, effective and quick method. It has a high capacity to remove the heavy metal even in the form of organic, inorganic effluent. The principal of the membrane technology is the relative size between the membrane itself and the substance to be eliminated. The size may vary from the nano size to the reverse osmosis.

The type of membrane used to remove the heavy particles of the size 5-25 nm is the Ultrafiltration (Vigneswaran R, *et al*. 2004]. Depending upon the need they can work within the limits of 90% efficiency. The other types of membrane used are the polymer based Polymer-Supported Ultrafiltration (PSU) (Rether *etal.,* 2003). They require low energy and works as binding the heavy metal to the solvent and making a macromolecular structure. Kinetically it is a very fast and effective reaction. Other similar technique is complexation-filtration.

2.5.6. Electrochemical method

The process of converting electrical energy into chemical energy is known as electrolysis. The setup is not a complicated suitcase. It consists of two metal electrodes, ionic electrolytic, connecting wires, a salt bridge and a source of electricity. It is again an easy yet effective method for the removal of heavy method by the process of coagulation. As the current passes into the

solution the chemical reaction starts to take place and the sample water ions gets attracted to the anodic compartment of the electrochemical cell. As the ions starts to move to the left, the electrons moving also combines to them and electrode stabilization of colloids occurs. As a result, the heavy metal is separated from the water and is accumulated at anode. The removal technique is again simple. The insoluble precipitate is removed by filtration (Shim, H Y *et al*, 2014).

2.5.7. Ion exchange method

Another cost effective, reliant and easy method for the inorganic impurity removal from water is the Ion exchanger. It is used when the foreigner heavy metal is present in low concentration. It consists of a column which is filled with the cationic resin. Resin is an aluminosilicate which has the capacity to exchange the ions passing through it. As the process starts, the impure water is sent through the resin and the cationic heavy metals like nickel, zinc, copper as exchanged by the cationic ions of the resin which can be hydrogen or sodium ions. As they get trap into the exchanger, the water which comes out from the nozzle is free from these heavy metals and then can be forwarded for the further treatments (Dizge e*tal*., 2009 and , Hamdaoui *etal.*, 2009)

Generally, metal ions removal by biosorption process is more advantageous than conventional treatment methods because of the following reasons (Khan *etal*.,2004)

- Low investment and low operational cost
- It requires little processing
- It is abundant in nature
- It is a byproduct or waste material from another industry
- High removal efficiency, reducing residual metals to below 1 ppb in many cases
- Minimization of chemical and/or biological sludge
- No additional nutrients requirement that cause disposal and space problems
- Regeneration of biosorbent and
- Possibility of metal recovery.

2.6. Magnetic Nano Particles (MNPs)

Nowadays, the development witnessed within the nanotechnology area has contributed to the improvement and revolutionizing of various fields. The listing of advantages and applications of

nanotechnology is developing unexpectedly. Substances at the nanoscale, normally called "nanomaterials," have usually grabbed the eye of researchers for hundreds of years. amongst those unique types of nanomaterials, magnetic nanomaterials have been the focal point of considerable interest over the past many years as evidenced by an extraordinary increase in the wide variety of research papers focusing on these materials (Gul et al., 2019).

Nanoparticles (NPs) are small particles that exist in an average size between 1 and 100 nm that distinguish them from their parental bulky materials and lead them to perfect for numerous applications. Among them, magnetic nanoparticles (MNPs), a nanoscale material, with unique magnetic properties were widely used in extraordinary fields inclusive of biomedical, energy, engineering, and environmental applications. The MNPs have become an area of intensive research inside the recent beyond due to their particular and outstanding properties which make their potential application in biomedicine, catalysis, agriculture, and the environment (Ali et al., 2021).

Magnetic nanoparticles (MNPs) have appeared promising execution in toxin evacuation or poisonous quality relief (Mohammed et al., 2017). Many studies have been reported on newly developed magnetic adsorbents, such as magnetic zeolites for removing dyes and synthetic magnetite for removing radioactive elements. Not only can all magnetic adsorbents effectively remove adsorbed water, but also they easily separated from the solution under a magnetic field. Magnetic nanoparticle adsorbents are of great interest because they can be easily separated from water by an external magnetic field, can be used repeatedly, and are of great interest(Lai et al., 2016)**.**

According to (Jiang et al., 2017) report, Magnetic technology has been developed as an alternative to water treatment, especially for adsorption processes. After adsorption of contaminants by using magnetic adsorbent with two characteristics of magnetic adsorption, without using centrifugation and filtration, contaminants can be removed from solution by magnetic separation technology. To this end, Fe_3O_4 has been widely used as a magnetic carrier to prepare novel adsorbents according to its unique magnetic properties.

In spite of the fact that there are numerous unadulterated phases of iron oxide in nature, the foremost prevalent MNPs are the nanoscale zero-valent iron (nZVI), Fe_3O_4 and γ-Fe_2O_3. Among them, magnetite (Fe_3O_4), which could be a ferromagnetic black color iron oxide of both Fe(II)

and Fe(III), has been the foremost broadly considered. Magnetite is the favored sort since of the nearness of the Fe^{2+} state with the potential of acting as an electron giver. (Mohammed et al., 2017).

Over the past decades, magnetic nanoparticles (MNPs, particularly magnetite (Fe_3O_4) have gotten considerable attention for their interesting nano-sized and morphology-dependent physicochemical properties, and for their biocompatibility, magnetic properties, and strong binding affinity and capacity. However, due to high surface free energy Fe_3O_4 MNPs with fewer functional groups are susceptible to air oxidation and undergoes leaching under acidic conditions and prone to aggregation in aqueous solution which reduce the ion removal capacities and restricts the ranges of applications (Peng et al., 2017).

2.6.1. Synthesis of Magnetic Iron Oxide

A large number of researchers studied the synthesis of magnetic iron oxide nanoparticles with versatile compositions and phases. Synthetic routes were selected to manipulate the shape, stability, and dispersion tendencies of iron oxide magnetic nanoparticles. Great quality iron oxide magnetic nanoparticles can be synthesized with the aid of adopting flexible synthetic techniques consisting of thermal decomposition, co-precipitation, micelle formation, hydrothermal, and laser pyrolysis techniques. It turned hard for us to bring together all this literature and we have been attempted to give every synthetic technique by giving a few examples in conjunction with the corresponding formation mechanism (Gul et al., 2019).

2.6.1.1. Co-precipitation Methods

Co-precipitation is perhaps a greater suitable approach to prepare magnetic iron oxide nanoparticles from an aqueous solution containing Fe (II) and Fe (III) by including a base under the anaerobic situations at ambient or high temperatures. However, there are certain factors just like the type of iron salts, Fe(II): Fe(III) ratio, the temperature of the reaction, pH of the medium, volume, and ionic strength of the solution that markedly have an effect on size, shape, and composition of the magnetic iron oxide nanoparticles. In the co-precipitation method, once the synthetic situations are met high quality of the magnetic iron oxide nanoparticles are efficiently produced (Gul et al., 2019).

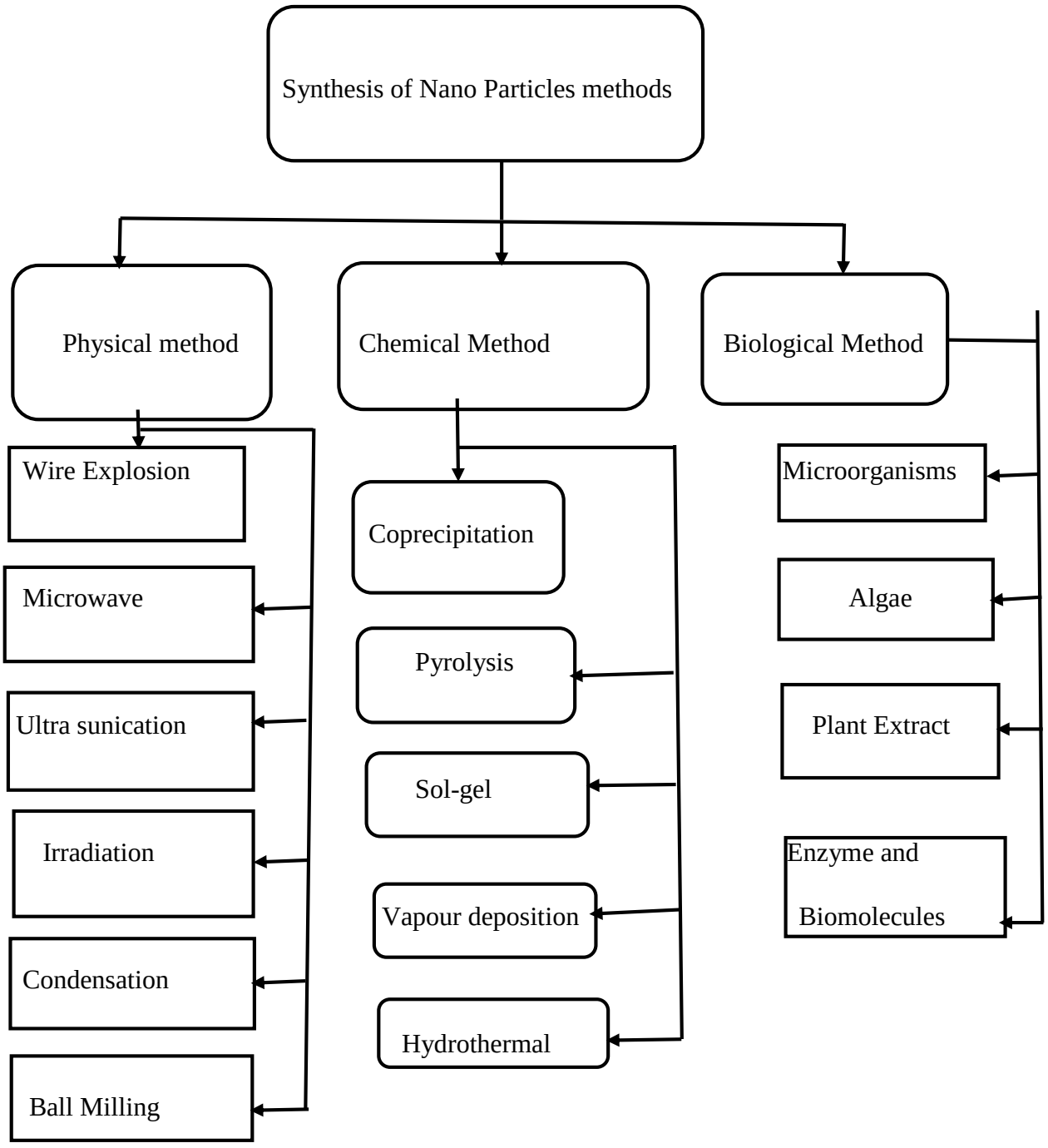


Figure 2. 1: Synthesis methods of Magnetic Nano particles(Gul et al., 2019).

2.7. Biosorption

Biosorption is defined as the capacity of a substrate to retain metallic species, ionic forms and/or ligands from fluids in the molecular structure of the cell wall. The biosorption mechanisms include extracellular and intracellular bonds, as well as complex interactions that depend on the type of metal and the biosorbent structure (Thomas *etal.*,2003)

Biosorption can be defined as the removal of metal or metalloid species, compounds and particulates from solution by biological material. Large quantities of metals can be accumulated by a variety of processes dependent and independent on metabolism. Both living and dead biomass as well as cellular products such as polysaccharides can be used for metal removal. Biosorption utilizes the ability of biological materials to accumulate heavy metals from wastewater by either metabolically mediated or physico-chemical pathways of uptake (Mohan *et al*.,2008)

2.8. Adsorption

Adsorption is a surface phenomenon in which it is characterized by chemical species (adsorbate) from its vapor or liquid solution phase onto or near the surface of solid (adsorbent). The presence of excess surface occurs when the attractive energy of a substance with the solid surface that is adhesive work is higher than that of cohesive energy of the substance (Chiou, 2003). Adsorption is the mass transfer operation of solute (adsorbate) exists in a fluid phase to the surface of solid phase (adsorbent) due to the existent of high molecular interaction between them. It is a process of the interface in which a film of adsorbates is created on the surface of the adsorbents of material. Thus, it is the result of surface energy (Machado et al., 2011). Adsorption is commonly employed as a polishing step to remove organic and inorganic contaminants in water and wastewater treatment. The surface area or active sites, the lack of selectivity, and the adsorption kinetics usually limit the efficiency of conventional adsorbents (Qu et al., 2013). Adsorption is a term used to describe the metal or organic substances in solution attached to a solid adsorbent at low, medium, and high coverage(Al-anber, 2011). Adsorption as a separation process is widely applied in our manufacturing economy and daily life. The adsorption process takes advantage of the ability of a particular solid to preferentially concentrate a particular substance in a solution (gas or liquid) on the surface. Therefore, the required purpose of purification or separation can be achieved by contacting the fluid with such a solid.

Adsorption can be categorized into physical adsorption (physisorption) and chemical adsorption (chemisorption) in nature. Physical adsorption has relatively weak intermolecular forces. It does not allow the sharing or transfer of electrons. Hence always maintains as individuality of interacting species. Even though the process is slow due to the occurrence of diffusion of molecules, the interactions are fully reversible which enables desorption to occur at a similar

temperature. Not only the adsorbed molecules are free to move and cover the entire surface, but also have low heat in the case of physical adsorption (Aly, 1987).

The main characteristic of chemical adsorption is the large interaction potential, which leads to a high heat of adsorption close to the value of the chemical bond. This fact, combined with other spectroscopy, electron spin resonance, and susceptibility measurements, confirms that chemical adsorption involves the transfer of electrons and the formation of true chemical bonds between the adsorbate and the solid surface. Because chemisorption involves chemical bonding, it often occurs at high temperatures and is generally, related to the activation energy. Furthermore, the adsorbed molecules are located in specific locations and therefore cannot freely migrate to the surface. Table 2.6 Comparison of physical and chemical adsorption. Generally, adsorption can occur at any interface. That is either gas-solid interface or liquid-solid interface (Abdalla et al., 2020).

Table 2. 4 The difference between chemical and Physical Adsorption (Abdella et al.,2020)

Parameters	Chemical Adsorption	Physical Adsorption
Force of Attraction	Strong attraction forces or chemical bond such as ionic bonds	Weak inter particle bond as van der waal forces
Temperature	Higher heat of adsorption	Low heat of adsorption
Electron transfer	electron transfer leading to bond formation between sorbate and surface	Not involve electron transfer, although polarization of sorbate may occur.
Adsorption layer	Monolayer only	Monolayer or multilayer
Kinetics Adsorption	Activated, may be slow and irreversible	Rapid, non- activated and fully reversible
Adsorption sites	Site specific, adsorbed molecule are fixed at specific sites	Not site specific, the adsorbed molecules are free to cover the entire surface

The most literature studies showed that adsorption process could considered an efficient treatment method for the removal of emerging compounds from water. It allows reaching good

removal percentage. In addition, a process does not imply by-products formation, which could be more toxic than parent compounds. It is obvious that adsorption process encompassed in an integrated treatment system, which involves many factors, such as available space for the construction of treatment facilities, waste disposal constraints, desired finished water quality, and capital and operating costs. All these factors imply the achievement of the optimal operating conditions for low-cost high efficiencies (Grassi et al., 2012).

2.9. Mechanism of Adsorption

The molecules diffuse into the bulk through the extreme planes of the laminar layer around the solid particles to the turbulent flow as result of the concentration gradient given by the four diffusion mechanisms that tends to be natural. The first is the diffusion of molecular-scale adsorbed water into the liquid film that surrounds the adsorbent molecules in bulk. The second film diffusion is the diffusion of adsorbed water on the surface sites of the adsorbent molecules in a liquid film. On the third, a pore diffusion of intraparticle diffusion of adsorbed water in the interstices of the adsorbent. Lastly, the adsorption of adsorbed water on the inner surface of the adsorbent (Kaushal, 2017).

In the context of adsorption, the main challenge is to select the most promising types of adsorbents, mainly in terms of low cost, high capacity (often expressed as q_{max} values) high adsorption rates, high selectivity, and fast kinetic adsorption mechanisms, especially adsorbents/adsorbates interactions that occur at interfaces. This is an important topic because the adsorption mechanisms involved in the collection of contaminants are what dictate the design of desorption strategies (e.g., the recovery of certain contaminants, such as "precious" metal ions, is also an important parameter for the economics of the process (Crini et al., 2019).

The basic principle of adsorption: The preferred concentration of seeds on the surface of the adsorbed solid operates in two different processes. That is, chromatography, and ion exchange. In fact, adsorption, ion exchange, and chromatography can often be grouped together in engineering textbooks. Chromatography, like most adsorption operations, operates in fixed layer mode. It is designed to intermittently feed the solution to separate, and then pass through the eluate to separate the liquid mixture. The solid material used in ion exchange contains charged groups that interact with the charged ions present in the liquid solution. Looking at adsorption during an exchange process involving virtual seeds reveals the equivalence between adsorption

and ion exchange. In fact, most of the information presented in this book is also applicable to ion exchange(“Chi Tei,” 2019).

2.10. Principles and conditions influencing adsorption in batch systems

According to ((Vernon *etal.*, 1967) several factors have been determined that could affect the outcome of the results in batch adsorption experiments, as described the following principles and conditions:

2.10.1 Nature of the adsorbent

The adsorption process is mainly a surface phenomenon in which adsorption depends on the portion of the total surface area available to the adsorption process. The adsorption capacity is directly proportional to the specific surface area (weber,1972). The physicochemical nature of the surface of carbon is an important factor in the adsorption process, and should be considered in selection or preparation of carbons for specific applications ((Vernon*etal.*, 1967)

2.10.2 Nature of the adsorbate

The adsorption process is mainly affected by the nature of the adsorbate in the sense of its solubility in the solute. The adsorption capacity is inversely proportional to the solubility of an adsorbate in the solute, and this is the Lundelius rule, one of two rules used to predict the effect of a solute’s chemical character on its uptake (Weber, 1972). The greater the solubility, the stronger the solute-solvent bond is and therefore the smaller the extent of adsorption. The molecular size of the adsorbate is of significance too. The molecular size relates to the rate of uptake of solutes from aqueous solution by porous adsorbents so that the smaller the molecular size, the faster the reaction is. However, it must be kept in mind that the adsorption process dependence on molecular size can be generalized only within a particular chemical class. For example, large molecular size of a certain type of a chemical series may be adsorbed more rapidly than smaller ones of another class. Moreover, the rate of uptake dependence on the molecular size is expected only for rapidly agitated batch reactors which are of limited interest in water and wastewater systems. In contrast to the molecular size effects, the variations in the geometry and structure of the molecules have smaller effects on the equilibrium conditions ((Faust,1998).

Ionization also plays a role in the uptake capacity, where many components of water and waste water exist as ionic species. For example, fatty acids, amines, and pesticides have the property of being ionized under appropriate conditions of pH. The ionization of some chemical components and classes is believed to be of significance for the carbon adsorption process due to the fact that activated carbon commonly exists with a net negative charge in water. It has also been observed that as long as the compounds are structurally simple, the uptake capacity decreases for the charged species and increases for the neutral ones. As compounds become more complex, the effect of ionization becomes less important. Thus, the adsorption capacity was on the decrease by the increasing of ionization for many different types of simple organic acids. To conclude, it has been observed that a polar solute will tend to be strongly adsorbed by a polar adsorbent in anon polar solvent (Stafiej *etal.,* 2007).

2.10.3. Solution pH

The pH of the metal ion solution is an important parameter for adsorption of metal ions because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate (Ii et al., 2011). Therefore, pH of solution influences the nature of biomass binding sites and metal solubility; Metal biosorption has frequently been shown to be strongly pH dependent in almost all systems examined, including bacteria, cyanobacteria, algae, and fungi (Holan & Volesky, 1995).

It has been generally reported that in highly acidic medium (pH≈2) the removal of metal ions is almost negligible and it increases by increasing the solution pH up to a certain limit (Abdelghani & Elchaghaby, 2014). This can be explained that decreasing of biosorption levels by lowering pH can be due to competition between protons and metal ions for the capturing same sites (Igwe, 2008). On the other hand, too high pH value can cause precipitation of metal complexes, so it should be avoided during experiments. For different biosorption system of metal ions, the optimal pH is different. (Wang & Chen, 2006)

2.10.4 Effect of temperature

Temperature influence has more effect in a situation where by metal uptake increases within a temperature range of about 20-300C, but decreases with an increase of temperature above a critical value (Sulaiman, 2015). Increase in temperature probably weakens the bond formed

between the metal ions and the adsorption sites on the adsorbent thereby resulting in an increase in the amount of metal ions adsorbed on the adsorbent. At high temperature, adsorption is expected to decrease due to the increased tendency of the metal ion to escape from the surface of the adsorbent to the solution phase, hence there will bound to be weak adsorption interactions between the adsorbent and the adsorbate (Ojedokun & Solomon, 2016).

2.10.5 Initial solute concentration

It is generally agreed that the biosorption capacity increases as the initial metal ion concentration in the solution increases, whereas the metal removal percentage (also called removal efficiency) decreases by increasing the metal ion initial concentration (Abdelghani & Elchaghaby, 2014). As a rule, increasing the initial metal concentration results in an increase in the biosorption capacity because it provides a driving force to overcome mass transfer resistance between the biosorbent and biosorption medium (Pahlavanzadeh et al., 2010).

2.10.6 Biosorbent dosage

The amount of biomass added in the solution during sorption process also affects the specific metal uptake. In principle, with more biosorbent present, the available adsorption sites or functional groups also increase (Mosbah & Sahmoune, 2013). At low biomass dosage, the number of ions adsorbed per unit adsorbent weight is high. Adsorption capacity is reduced when the biomass dosage increases as a result of lower adsorbate to binding site ratio where the ions are distributed onto larger amount of biomass binding sites (Ojedokun & Solomon, 2016).

2.11. Adsorption equilibrium isotherms

Isotherm refers to the relationship between the equilibrium adsorbate concentrations in the liquid-phase and the equilibrium adsorption amount on the solid-phase at a certain temperature. Sorption equilibria deliver fundamental physicochemical data for assessing the relevance of sorption processes as a unit operation. Sorption equilibrium is normally described by an isotherm equation whose parameters express the surface properties and affinity of the sorbent, at a constant temperature and pH. Therefore an accurate mathematical description of the equilibrium isotherm, preferably based on a correct sorption mechanism, is essential to the effective design of sorption systems (Ho et al., 2002). We can model the equilibrium adsorption data by the isotherms, and investigate the adsorption information, such as the adsorption mechanisms, the

maximum adsorption capacity, as well as the properties of adsorbents by the isotherms (J. Wang & Guo, 2020). According to the paper, studied by (Berkessa et al., 2019) adsorption isotherm can be described as a curve that explains the phenomenon governing the retention (release) or mobility of a substance to a solid at constant temperature and pH in an aqueous porous medium or aquatic environment.

Adsorption isotherm gives an idea about relation between the adsorbate and the extent of adsorbate adsorbed on the surface of adsorbent at fixed temperature (Mor et al., 2016). The adsorption equilibrium has continuously been clarified by the isotherm equations such that their parameters demonstrate the surface characteristics and affinity of the adsorbent toward the adsorbate(Ghadiri et al., 2017). The two popular isotherms are Langmuir and Freundlich isotherms which have been used to explain the equilibrium of an adsorption system (Nsami & Mbadcam, 2013).

2.11.1. Langmuir isotherm

Langmuir isotherm decides the adsorption of ions on the surface of the adsorbent on the monolayer and comparable destinations on the surface (Mor et al., 2016). According to Langmuir isotherm, assumptions can be taken based on adsorption that occurs at specific homogeneous sites within the adsorbent (Nsami & Mbadcam, 2013).

2.11.2. The Freundlich adsorption Isotherm

The Freundlich isotherm is an empirical equation employed to describe the heterogeneous system. This empirical model can be applied to non-uniform surface adsorption heat and non-uniform distribution of affinity and multi-layer adsorption. Historically, this was developed for the adsorption of animal charcoal, and indicates that the proportion of adsorbed water in the adsorbent in a given mass of solute is not constant at other solution concentrations. From these perspectives, the amount adsorbed is the sum of the adsorptions of all sites (with their respective binding energies) until the adsorption energy decreases exponentially when the adsorption process is complete, and the stronger binding sites are occupied first(Foo & Hameed, 2010).

At present, Freundlich isotherm is universally applied in varied systems especially for organic syntheses or considerably interactive species on triggered carbon and molecular sieves. The slope ranges between 0 and 1 is a measure of adsorption intensity or surface variousness, turning

better heterogeneous as its value gets closer to zero. Whereas, a value below unity implies a chemisorption process where 1/ n above one is indicative of collaborative adsorption (Ho et al., 2002).

2.12. Adsorption Kinetics studies

Adsorption kinetics reflects the evolution of the adsorption process as a function of time. This is an important parameter to consider when choosing an adsorbent. Fast adsorption is recommended for treatment methods that use adsorption as a purification process. Several models have been developed that describe the diffusion of solutes on the surface of particles and within pores (such as film distribution models, intra-particle diffusion models, out-of-particle diffusion models, and pore diffusion models). In the case of nitrates removal, simplified models such as pseudo-first-order kinetics and pseudo-secondary kinetics were common (Battas et al., 2019).

The adsorption dynamic is one of the foremost imperative issues for understanding both the mechanisms of adsorption and the evaluation of persuasive factors on the reaction rate. Kinetics explains solute take-up rates additionally characterize the residence time of the adsorbate at the solid-liquid interface. Kinetic modeling was used to investigate the adsorption mechanism and potential velocity control processes (Ghadiri et al., 2017)**.**

2.13. Brewers' spent grain

Grain in brewery that have been removed of their sugar content is classified as a byproduct known as spent grain. Brewers' spent grain (BSG) is the most abundant by-product generated from the beer-brewing process, representing ~85% of the total by-products obtained. After the mashing process the insoluble part of the barley grain, the BSG, is in solution with the soluble (liquid) wort. The wort, which will be fermented into beer, is filtered through the BSG, which is a by-product and must be disposed of (Mussuto *etal.*, 2014).

The main constituents of BSG include fibre (30–50% w/w) and protein (19–30% w/w), which are staple nutritional components in the human diet and thus make this material very attractive for improving the nutritional value of foods (Vernon *etal.*, 1967). In addition, several components that are constituents of BSG such as arabinoxylans, proteins in the form of

hydrolysates and phenolic compounds, have gained increasing attention for their potential health benefits (Steiner *etal*.,2015).

2.13.1. Generation of BSG

Barley is the main raw material used for the production of beer. The barley grain can be divided into three main parts: the germ (embryo), endosperm (aleurone and starchy endosperm) and grain coverings. The grain coverings can further be divided into (from inside to outside) the seed coat, the pericarp layers and the husk (Mussuto *etal.,* 2006).

During the brewing process the starchy endosperm of malted barley is subjected to enzymatic degradation, resulting in the liberation of fermentable (maltose and maltotriose) and non-fermentable (dextrins) carbohydrates, soluble proteins, polypeptides and amino acids. The resulting medium (which will be fermented into beer by the action of yeast) is known as wort. The insoluble grain components (comprising mainly the grain coverings) are the BSG (Mussuto *etal.,* 2006).

2.13.2 BSG composition

BSG consists of the seed coat–pericarp–husk layers that covered the original barley grain. Depending on the efficiency of mashing, more or less starchy endosperm and walls of empty aleurone cells may remain. The starch content will be low, and some residues of hops introduced during mashing may be present depending on the brewing regime used (Mussuto *etal.,* 2006).

BSG is a heterogeneous substance, particularly with respect to inter-brewery variation. This is due to a number of factors, such as the cereal variety, time of harvesting, type of hops added, the malting and mashing.

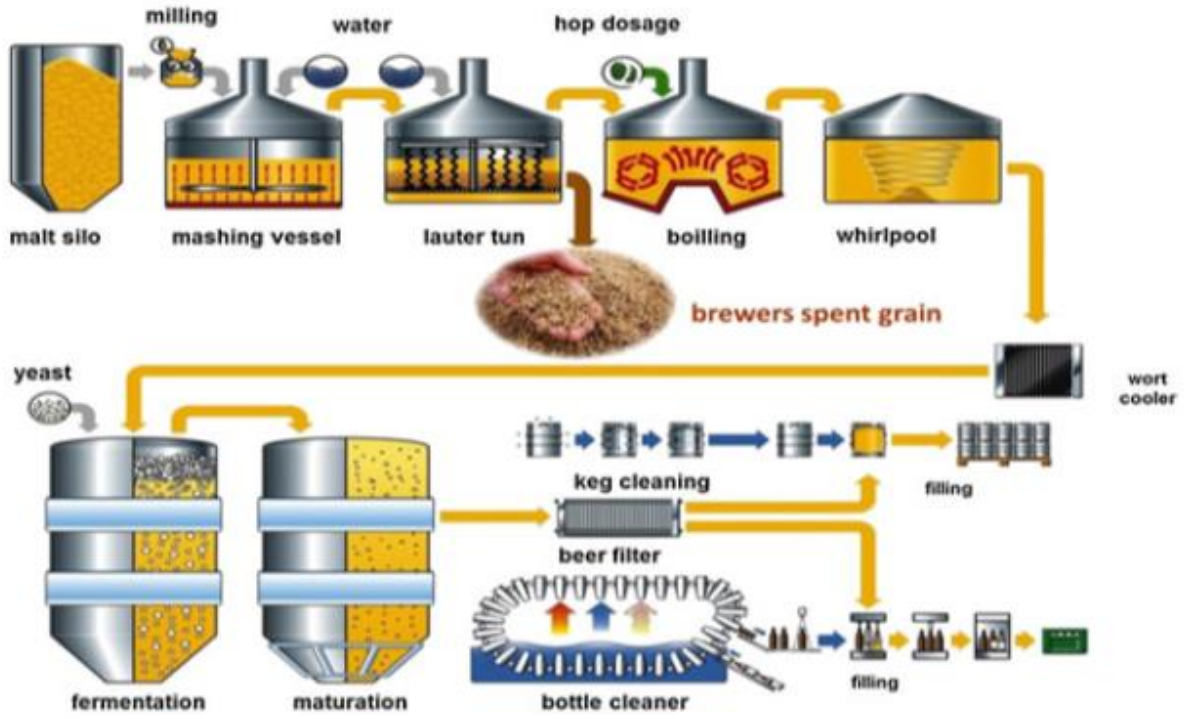


Figure: - 2.2 an overview of the brewing process (Mussuto *etal.*, 2009)

2.14. Brewery Spent Grain as an Adsorbent: Review On Pervious Work

Harmful metal particles have deadly impacts on all shapes of life and these metals particles may enter the nourishment chain when untreated effluents are released into environment. Due to its low cost and easy availability, BSG has been tested as adsorbent for several types of compounds (mussato et al. 2006). BSG is sold as a feed stock supplement and was also reported to improve soil quality & yield of eggplant, to the production of xylitol and alcohol, to remove heavy metals from industrial pollutants, and to be able to increase the porosity & strength of bricks (Mussuto *etal.*, 2009).

Modified spent grain(MSG), uses as adsorbent, with hollow and layered structures containing many functional groups such as carboxyl, hydroxyl and amine that are responsible for the binding of metal ions and since it has a large specific surface area and small size (Qingzhu et al., 2008).

Pretreatment methods using different kinds of modifying agents such as organic compounds (ethylene diamine, formaldehyde, epichlorohydrin, methanol), oxidizing agent (hydrogen

peroxide), mineral and organic acid solutions (hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid, thioglycollic acid) , base solutions (sodium hydroxide, calcium hydroxide, sodium carbonate) etc. (Ngah & Hanafiah, 2008).

Brewery spent grain adsorbent treated with HCl greatly enhanced adsorption of Cr(VI) and Fe(II) ions with removal efficiency of 97% and 77% respectively (Francilio etal.,2021 & Akibiyi etal.,2019). HCl treated brewery spent grain adsorbent has higher adsorption capacity than the untreated spent grain to remove chromium (Francilio etal., 2021).

Table 2.5 Summarized metal ions uptake capacity of chemically treated and untreated brewery spent grain

ADSORBENT	Tittle	Purpose	Reference	Modification material	**Result (%)**
BSG	performance evaluation of Fe (III) adsorption onto brewers' spent grain	To remove Fe(II)	O.C. Izinyon etal.,2021	Treated by NaOH	**77**
				untreated	**66**
	Biosorption of Fe (II) from Aqueous Solution by Brewing Waste	To remove Fe(II)	**Akibiyi etal.,2019**	Trated by H_2SO_4	**98**
				untreated	**93**
	Brewery spent grain:- a potential bio sorbent for the hexavalent chromium	To remove chromium	**Francilio etal.,2021**	HCl treated	97
				Hydrogen peroxide treated	0.5
				Alkaline treated	21
				Petroleum ether treated	0.9
				NaOH treated	22
	Removal of Lead from Aqueous Solutions By Brewer ´ s Spent Grain	To remove Lead	**Isabel etal., 2014**	NaOH treated	**95.45**
				untreated	**88.24**

2.15. Steel production block flow diagram (steely R.M.I manual, 2020)

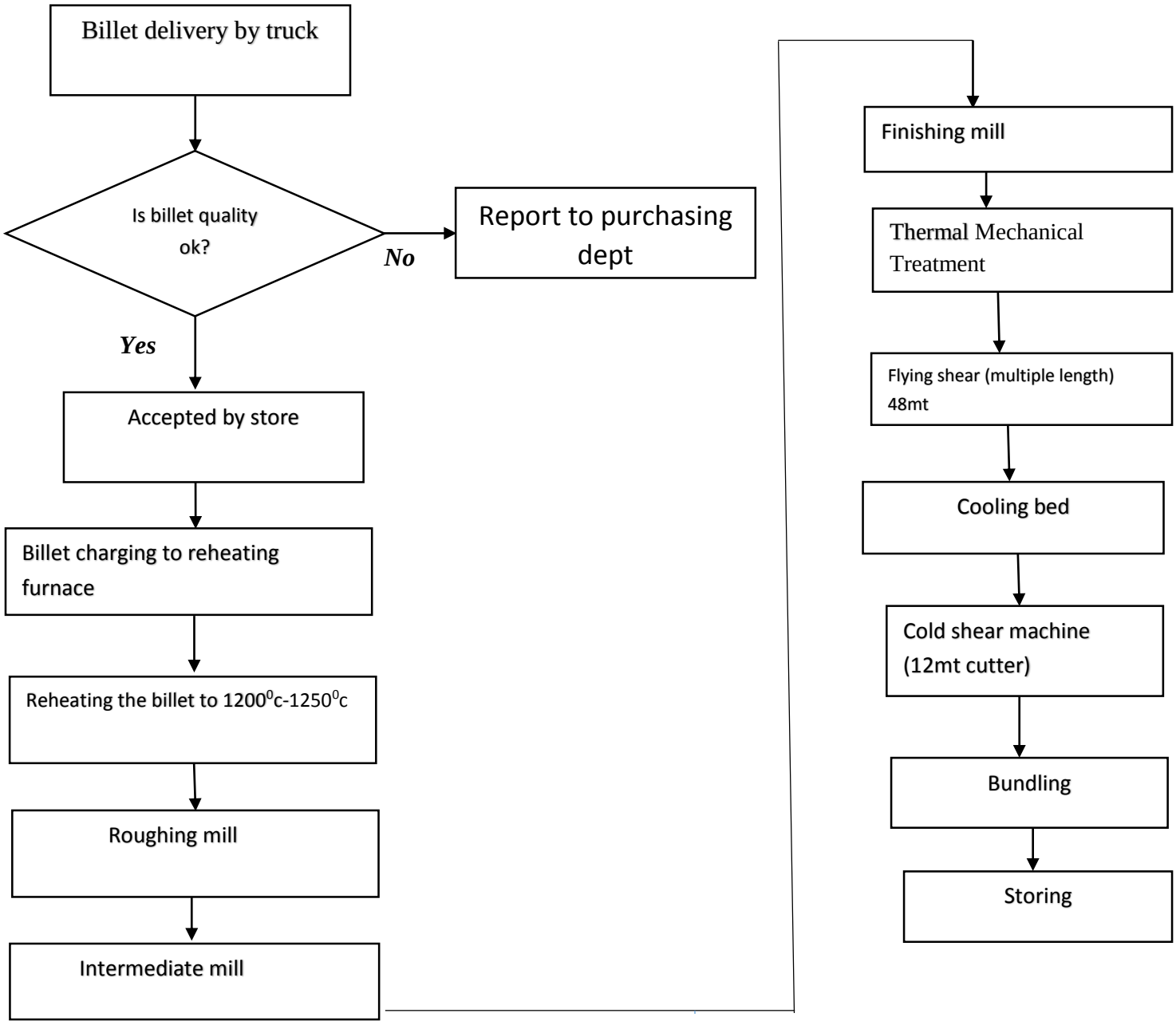


Figure 2.3: - production process of rolling mill

3. MATERIALS AND METHODS

The main raw material in this research was brewery spent grain which was collected from Heineken breweries which found in Addis Ababa. This sample was packed in polyethylene bags and transported to Adama science and technology university chemical engineering department laboratory. and also waste water of steel industry was used (from Steely RMI PLC) which was found in Bishoftu. the Laboratory experiments presented in this chapter were carried out in order to evaluate the adsorption efficiency of the BSG. A series of experiments were conducted to determine the removal efficiency of heavy metal using brewery spent grain as an adsorbent. In addition to the adsorption experiments, material physical characteristics experiments were carried out in order to know the characteristics of the BSG and sulphuric acid treated BSG used in these experiments.

Therefore, the purpose of this section is to mention the chemicals, material, and instruments used and methodology followed to achieve the objectives of the study.

3.1. Equipment and Materials

3.1.1 Chemicals, apparatus and equipment used

All chemicals used in this study were analytical reagent grade and were used without further purification. Concentrated sulphuric acid (4M H_2SO_4) was used to remove some impurities and oxides of metals, 0.1MNaOH and 0.1MHCl were used to adjust the solution pH of the experiments.2.7 g of $FeCl_3.6H_2O$ and 5.56g of $FeSO_4.7H_2O$ were reacted to form Fe_3O_4 product.

In this experiment the apparatus and equipment were required to set up the batch tests and to analyze the samples. Beaker, volumetric flasks, graduated cylinder, funnel, oven, conical flask, ball mill, electronic balance, vacuum filter, filter paper, burette, pipettes, plastic and glass bottles, glass stirrer, and magnetic stirrer are some of the apparatus, various mesh size sieves were used during batch tests. Acid treated sample was dried in hot air oven at 105^oC for 12hrs, and electrical furnace was used to determined ash content and volatile content of the samples. Fourier transform infrared (FTIR) spectra were recorded using (Perkin Elmer, Spectrum 65 FT-IR spectrophotometer) to analyze the functional groups present in the adsorbent. Solution pH was adjusted using pH meter. The orbital shaker for mixing of sample in the solution and computerized atomic concentration analyzer UV-spectrophotometer (Perkin Elmer lambda 950 UV/visible Spectrometer) were used to evaluate the final heavy metals ions concentration.

3.1.2. Materials used for characterization of brewery spent grain

Materials used for raw material characterization of brewery spent grain were Fourier Transforms Infrared Spectroscopy (FTIR) and Scanning Electron microscope (SEM).

3.1.3. Materials used during production of cellulose

Materials used during production of cellulose were: autoclave (Electrical Heated Vertical Steam Sterilizer), thermostatic Incubator shaker, centrifuge and water-bath.

3.2 Methods

3.2.1 Collection and preparation of BSG

Fresh spent grain was obtained from BGI Ethiopia brewery located in Addis Ababa. It was successively washed with distilled water to remove impurities, and then dried at 75°C. Afterward it was treated with sulphuric acid solution of 4M for 4 hours at room temperature to enhance its metal sorption capacity. The excess of alkaline solution was removed by washing spent grains with distilled water until it was completely free from the base in successive washings, according to the procedure described by (Low, et al. 2000). This material was designated as TSG (Treated Spent Grains). Then TSG was dried in an oven at 75^{o}C for 24hrs.

3.2.2 Fourier Transforms Infrared Spectroscopy (FTIR) Analysis of BSG

FTIR analysis was carried out in order to identify the functional group might be involved in binding of metal ions. The FTIR spectrum from 4000-400 cm^{-1} in resolution 4 cm^{-1} recorded. Sample for the FTIR analysis were prepared by weighting the amounts of sample 1 gm. The FTIR pattern is plotted within the FTIR machine by generating the transmittance peaks (%) as the Y-axis versus wavenumber (cm^{-1}) as the X-axis. FTIR analysis was done in Addis Abeba Science and Technology University at Central laboratory.

3.2.3. Scanning Electron microscope (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample. In this study, the morphology of BSG before and after adsorption of iron and chromium ions. BSG before and after adsorption of chromium and

iron ions was conducted using SEM analyzer of model: JCM-6000PLUS Bench Top SEM, JEOL, Japan. The procedure of analysis includes, 30 mg specimen is mounted on a metal stub using a sticky carbon tape, which increases conductivity. The clip holds the sample securely and that the clip was not obscuring any area that you intend to image. The specimen must be electrically grounded to the sample holder to minimize specimen charging. Specimen exchange, evacuation, and automatic adjustment of image carried out to photographing and finally the image saved. SEM analysis was done in Adama science and Technology University, school of Material, chemical and mechanical engineering in material engineering department.

3.2.4. Particle size classification

The dried biomass was grinded and sieved. The particle size classification was done using a sieve system with meshes of different openings' sizes and respective vibrator. The masses of the fraction collected in each sieve were recorded until the particle size reached to 250- 350 μm.

3.2.5. Cellulose content determination

Raw cellulose contents of brewery spent grain were determined by using weendize method, 2 g of BSG sample in 250 ml flask, added 1.25 % of 250 ml sulfuric acid to remove all glycosid. Besides boiled for 30 minutes, filtered and washed with hot water several times. Added 1.25 percent of sodium hydroxide to remove protein by hydrolysis and fats by saponification, then boiled for 30 minutes. Filtered and washed several times with hot water. Finally, residue was dried at 105 ºC for 15 min, cooled and weighed.

$$cellulose\ content = \frac{final\ dried}{total\ initial\ weight\ of\ BSG} \quad \text{.....(3.1)}$$

3.2.6. Determination of moisture content

Moisture content was determined using the standard official methods of analysis of the AOAC (1990). This involved drying to a constant weight at 105 ºC and calculating moisture as the loss in weight of the dried samples. The crucible was thoroughly washed and dried in an oven at 100 ^{0}C for 30 min and allowed to cool inside desiccators. After cooling, they were weighted using a weighing balance and their various weights were recorded as (W_1). Then, 2 g of the finely-ground samples were put into the crucible andweighed to determine (W_2). Thereafter, the sample and crucible were placed inside the oven and dried at 100 ºC

for 4 hr., then cooled and weighed at the same temperature for 30 min until constant weights were obtained to get (W_3). Then, the moisture content of the samples was calculated as the following equation:

$$\frac{\text{(initial weight of filled curricle)}-\text{(final weight of filled crucible)}}{\text{(initial weight of filled crucible)}-\text{(initial weight of empty crucible)}} * 100\% \ldots \ldots\ldots.3.2$$

3.2.7. Determination of dry matter content

Dry matter represents everything contained in a sample except water; this includes protein, fiber, fat, and minerals. In practice, it is the total weight of the sample minus the weight of water, expressed as a percentage. In this study, it was determined by drying the sample in an oven until the sample reached a stable weight. The sample was weighed and about 2 g placed in a dry crucible. The crucible and sample were oven-dried for 24 hr. after that, the crucible and sample were weighed. The percentage of dry matter was calculated and recorded (Nennich and chase, 2007). The formula was as follow: -

$$\%\ dry\ matter = \frac{dry\ weight}{total\ weight} * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.3)$$

3.2.8 Preparation of treated spent grain brewery for adsorption

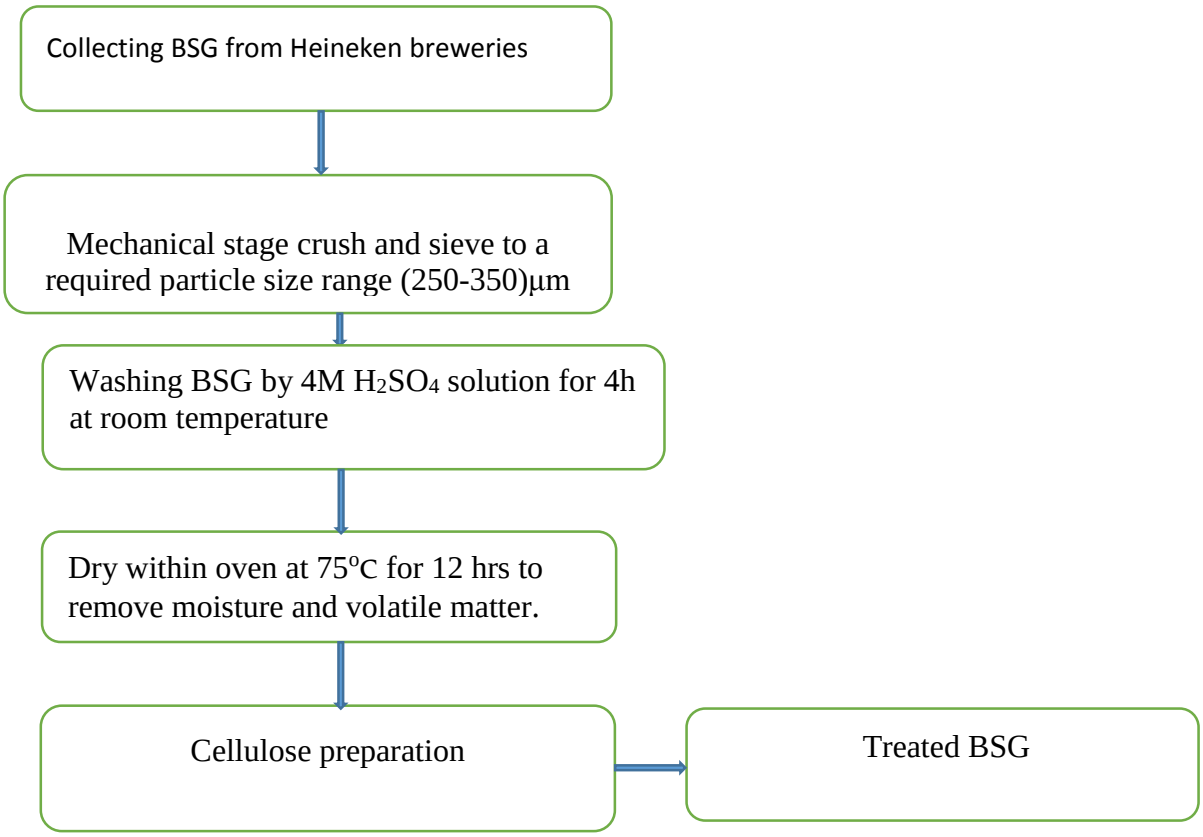


Figure: -3.1 Preparation process of brewery spent grain for adsorption

3.2.8. Fe_3O_4 Synthesis

Magnetic particle of magnetite was synthesized using of method co-precipitation of ferric and ferrous salts. According to (Wubishet et al., 2020) method 2.7 g $FeCl_3 \cdot 6H_2O$ and 5.56 g of $FeSO_4.7H_2O$ were dissolved in 100 ml of 0.3 M HCl. Then the solution of 120 mL of 3 M NaOH over a period of 2 hr under vigorous stirring at 80 ^{O}C was added drop wise from separatory funnel. Precipitation was expected at pH between 10 and 12.

After the system cooled to room temperature, the precipitate separated by permanent magnet, and washed with distilled water until neutral pH. Finally Fe_3O_4 was washed with acetone and dried in oven at 65°C overnight (Hariani et al., 2013).

3.2.9. Sorption experimental setup

Absorption process BSG was prepared to find out the effects and the optimum experimental parameters for each run of 200ML glass flask of known concentration (5, 10 and 15 mg/l) of Cr &(30, 91.5 and 153 mg/l) of Fe which is prepared artificial waste water depending on initial concentration of STEELY R.M.I waste water. The initial and final concentrations of heavy metal, in the filtrate were determined by using atomic absorption spectrophotometer and UV/VIS spectrophotometer (lambda 950).

The desired PH (2-6) was adjusted by adding 0.1M NaOH or 0.1M HCl. After that known amount of adsorbent dosage will have added in a 200ml glass flask. The flasks were shaken at room temperature, at a constant rate, and allowing sufficient time for adsorption equilibrium. The time (0, 30, 105, and 180 minutes) required for reaching equilibrium condition will have estimated by drawing samples at regular interval of time till the equilibrium was reached.

The glass flasks containing adsorption solution was collected at the end of time required for adsorptions. The supernatant liquid was filtered using filter paper, stored and the final concentrations of Fe &Cr ions were determined. The amount of heavy metals adsorbed onto BSG from solution was evaluated and the optimum parameters were then used to analyze the appropriate equilibrium isotherm, and adsorption reaction kinetic rates.

The sorption capacity of metals can be calculated as (Ashraf, Mahmood, & Wajid, 2011):

$$Qe== \frac{Co-Ce}{m} * v \quad \text{.....(3.5)}$$

where; Q_e= adsorption capacity at equilibrium, V = volume of adsorbate solution (ml), m=mass of BSG (g), C_o = initial concentration in mg/L, C_e= concentration at equilibrium (mg/L). The removal percentage (R %) is defined as the ratio of difference in metal concentration before and after adsorption (C_o–C_e) to the initial concentration of the adsorbate in aqueous solution (C_o) shown below:

$$\%R = \frac{Co-Ce}{Co} * 100 \quad \text{.....(3.6)}$$

where; C_o = initial concentration in mg/L, C_e= concentration at equilibrium (mg/L).

3.2.10 Cr(VI) and Fe (II) analysis using UV-visible spectrophotometer

The samples were analyzed to measure concentration of Cr(VI) and Fe (II) by using 84.86mg of Fe (II) which was prepared from 2.7 g of $FeCl_3.6H_2O$ and 5.56g of $FeSO_4.7H_2O$ and 0.211g of potassium dichromate in 1000ml distilled water. Other working solutions were prepared from those stock solutions by serial dilution by serial dilution with distilled water. Then measured using UV spectrophotometer (Perkin Elmer lambda 950 UV-vis Spectrometer) from 240nm-800nm by following the 1,5 DPC method (APHAet al., 1998). UV-visible analysis was done in Addis Abeba science and Technology in Central laboratory.

An absorbance calibration curve was developed by using dilutions of Cr(VI) and Fe(II) concentrations as shown in table 3.1 Fe(II) from 10 to 50 mg/L and from 6 to 14 mg/L for Cr(VI) against blank solution of distilled water, Fe_3O_4 and potassium dichromate. All standard solution was prepared in identically the same fashion. The difference is only their concentrations. The absorbance was measured from 200nm-800nm and the highest absorbance was taken. The calibration curve (appendix I and II) was constructed by plotting absorbance against known concentration.

The absorbance of samples was converted to a Cr(VI)and Fe(II) concentration using the calibration curve equation developed in the equation of (y = mx + b) the value you see for the intercept (b), slope(m), absorbance (y), and concentration (x). slope of the best straight line through the data points in the calibration plot passing through the origin, and y-intercept (b) zero is given by:

$$Slope(m) = \frac{y(adsorbance)}{x(concentration)} \text{----------(3.7)}$$

Table 3.1: Standard solutions and absorbance for calibration curve (for Cr(VI) and Fe(II)

Metal ions			
Cr(VI)		Fe(II)	
Concentration(ppm)	absorbance	Concentration(ppm)	absorbance
0	0	0	0
6	0.7841	10	0.1738
8	1.1284	20	0.307
10	1.3383	30	0.4447
12	1.65139	40	0.5691

3.3. Experimental design for adsorption

Batch experimental study was conducted to know influence of (initial concentration, adsorbent dosage, PH and time) on removal from aqueous solution. Two factor factorial design was used to generate factor combinations effect and obtain optimum adsorption of metal ions by using DOE software version 7.0. Two factor factorial design is an experimental combination design in which data is collected for all possible combination of levels of two factorial interests ((Montgomery; Wiley, 2001).

3.3.1 Description of experimental for factors and response variables

The analysis of two factor factorial design for four variable factors, each with two levels was carried out according to the design showed in Table 3.3 and 3.4.

Table 3.2: Variables and levels considered for the adsorption of Cr(VI)

Metal ions				
Cr(VI)			Fe(II)	
Independent variables	Low Level	High Level	Low Level	High Level
1. Initial concentration (ppm) (A)	5	15	30	153
2. Adsorbent dosage (g) (B)	0.5	2	0.5	2
3. pH (C)	2	6	2	6
4. time (min) (D)	30	180	30	180

3.4 Determination of adsorption isotherm model (Langmuir and Freundlich)

Adsorption of a solute from a solution can be determined basically by the use of two equations described by (Sundstrom et al., 1976), i.e. the Langmuir (1) and Freundlich (2) equations.

3.4.1 Langmuir equilibrium adsorption isotherm

Irving Langmuir (1916) published an isotherm for gases adsorbed on solids, which retained his name.

The Langmuir sorption isotherm (Langmuir, 1916) has been the most widely used adsorption isotherm for the adsorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogenous sites within the sorbent. It is then assumed that once a metal ion occupies a site, no further adsorption can take place at that site.

In this study, physically the Langmuir model represents that adsorption of monolayer Cr(VI) and Fe(II) take place on the homogeneous surface of adsorbents (BSG). The Langmuir model is expressed linearly in Eq. (3.8) as follow

$$\frac{Ce}{qe} = \frac{1}{qmkL} + \frac{Ce}{qm} \text{ ----------(3.8)}$$

Equation (3.8) yields equation (3.9) as follows

$$\frac{1}{qe} = \frac{1}{qmkL} * \frac{1}{Ce} + \frac{1}{qm} \text{ ----------(3.9)}$$

The essential characteristics of the Langmuir isotherm may also be expressed in terms of a dimensionless separation factor of equilibrium (RL) which may be calculated from Eq. (3.10)

$$RL = \frac{1}{1+kL+Co} \text{ ----------(3.10)}$$

The parameter RL is related to the shape of the isotherm according to the following characteristics: RL> 1 represents unfavorable adsorption; RL = 1 corresponds to a linear relationship; 0 <RL< 1 is favorable adsorption and RL = 0 is irreversible.

3.4.2 Freundlich equilibrium adsorption isotherm

The Freundlich isotherm model works based on the assumption that the adsorption of adsorbate occurs in multilayer on heterogeneous adsorbent surfaces since the active sites of adsorbent have heterogeneous surface energy. The model is expressed linearly in Eq. (3.11) as follow that multilayer Cr(VI)and Fe(II) adsorption occurs on heterogeneous surfaces of adsorbents (BSG).

$$qe = K_F Ce^{1/n} \text{ ----------(3.11)}$$

Equation (4) yields equation (3.12) as follows by taking algorithms

$$\log qe = \frac{1}{n}\log(Ce) + \log(KF) \quad \text{----------(3.12)}$$

The isotherm that had R^2 value nearest to 1.0 was selected for modeling of the adsorption of Cr(VI) and Fe(II) onto the adsorbent being considered.

3.5. Determination of adsorption kinetics (First and Second Order)

3.5.1 First order adsorption reaction kinetic model

Recent time, first-order kinetics has been widely used to describe the adsorption of contaminants from wastewater, (Hameed; El-Khaiary, 2008b). Physically the first-order kinetic model expresses that adsorption reaction rate depends on one parameter such as the adsorbate concentration or dosage. The mathematical representation of the first-order kinetic model is as follows in equation (3.13)

$$\frac{dqt}{dt} = K1(qe-q1) \quad \text{----------(3.13)}$$

where qe (mg/g) is the sorption capacity at equilibrium, qt (mg/g) is the sorption capacity at time t (hr), and K1 (hr) is the first-order rate constant for the kinetic model. Integrating Eq. (3.14) withthe boundary conditions of qt -1= 0 at t = 0 and qt = qt at t = t, yields the following equation (HoY. S., 2004):

$$\ln\frac{qe}{qe-qt} = k1\ t \quad \text{----------(3.15)}$$

Equation (3.15) can be rearranged as follows,

$$\log(qe-qt) = -\ \frac{-k1}{2.303}t\ + \log(qe) \quad \text{----------(3.16)}$$

A plot was made following the first-order kinetic model of Eq. (3.16) by using the value of log(qe-qt) (mg/g) in the y- axis and the values of time, t (hr) in the abscissa which has shown later in the results section. The plot was used to determine the first order rate constant (K1), equilibrium adsorption capacity (qe), and regression coefficient (R^2). Conventionally, if the R^2 value is very close to 1.0, the adsorption of Cr(VI) and Fe(II) on to the adsorbent follows the first-order rate equation. Because the linearized first-order model has regression coefficient (R^2) value equal to 1. If R^2 value is not close to 1.0, the adsorption system is assumed not to follow

the first order reaction rate. In this case, higher-order rate equations would be applied and tested for their applicability.

3.5.2 Second order reaction kinetic model

In the second-order kinetic model, the kinetics of the adsorption reaction depends upon the amount of metal ions present on the surface of adsorbent at time t, and the amount of adsorbate species adsorbate at equilibrium. This means that the adsorption reaction rate is directly proportional to the number of active sites on the surface of adsorbent (Ho &McKay, 1998). In other words, physically a second-order kinetic model means that the adsorption reaction rate depends on two parameters such as adsorbate concentration and adsorbent dosage. The equation of the second-order kinetic model can be written as follows which has shown in Eq. (3.17).

$$\frac{dpt}{dt}=K2(po-pt)^2 \quad \text{----------(3.17)}$$

where P0 denote the amount of equilibrium sites available on the adsorbent, Pt denote the amount of active sites occupied on the adsorbent at time t, and k_2 is the second order adsorption rate constant in g.mg-1.h-1 (Ho; McKay, 1998). The value of (qe-qt) as defined previously is directly proportional to the available fraction of active sites (Po–Pt), and substitution in the second order rate Eq. (3.18) yields the following equation:

$$\frac{dqt}{dt}= K_2(qe-qt)^2 \quad \text{----------(3.18)}$$

Equation (3.19) can be rearranged as follows,

$$\frac{dqt}{dt}= K_2(qe-qt)^2 \quad \text{----------(3.19)}$$

The expression in Equation 3.19 can be rearranged as follows:

$$\frac{dqt}{(qe-qt)2}= K_2\ dt \quad \text{----------(3.20)}$$

Integrating Eq. (3.20) with the boundary conditions of qt = 0 at t = 0 and qt = qt at t = t, yields the following equation:

$$\frac{t}{qt} = \frac{1}{qe}t + \frac{1}{k2qe2} \quad \text{----------(3.21)}$$

Where qe (mg/g) is the adsorption capacity at equilibrium, qt (mg/g) is the adsorption capacity at a time t (hr), and K_2 is the second order adsorption rate constant in g.mg-1.h-1. To determine the second-order kinetic model of Eq. (3.21) parameters, the values of t/ qt are plotted against time t, where, the values of t/ qt and t were placed in the vertical axis and abscissa respectively, as it can be shown in the results section. The second order rate constant (K_2), equilibrium adsorption capacity (qe), and regression coefficient (R^2) were calculated from the plot. When the R^2 value is found to be closer to 1.0, then the adsorption onto the adsorbent system is believed to follow the second-order rate equation. The theoretical values of equilibrium adsorption capacity (qe) were found from the first and second order kinetic model were compared with the experimental (qe) values, and deviation of these qe values in percentage units were calculated to suggest whether the adsorption system follows the first-order or second order reaction kinetic model.

4. RESULT AND DISCUSSION

4.1. Characterization of Materials

4.1.1 Fourier transforms infrared spectroscopy (FTIR) analysis of BSG

FTIR was used to determine information on the nature of the bond and to identify functional groups available on the adsorbent surface. BSG can also contain functional groups such as C-H stretching and C-H deformation, O-H deformation and C-O stretching, -CH_3 stretching and C=O stretching carbonyl. All functional groups, wave number, intensity and types of vibrations are listed in table 4.1 below.

Table 4.1 characteristic IR absorption frequencies of BSG functional groups

Functional groups	Types of vibration	Wave number (cm^{-1})	Intensity
-CH_3	Stretching	2975-2950	Strong
C-O(Alcohol)	Stretching	1050	Strong
-OH(Alcohol)	Stretching	3620-3600	Medium
≡ Alkynes	Stretching	3300-3200	Strong
C-H(Alkane)	Stretching	2929	Strong
-CH=CH2 (vinyl)	Bending	3040-3010	Variable
C=C (Alkene)	Stretch	1634	Variable

The spectra of brewery spent grain which was collected from Heineken breweries BSG before adsorption, Chromium loaded, Iron loaded and extracted cellulose were depicted in figure 4.2 below. The broad band peak around 3280 cm^{-1} show a result of C-H stretching alkane. The C-H alkane group's shifts from 3280 to 3279.76 and 3279.08 to 3276.62 from BSG, ex-cellulose, chromium loaded and iron loaded respectively. Decrease in wave number of this peaks attributed to the attachment of chromium and Iron ions to C-H alkane groups. And also the peaks 1032.89, 1031.79, 1030.79 show a result Stretching of C-O alcohol. Wave numbers were decreased from BSG to iron loaded for all peaks.

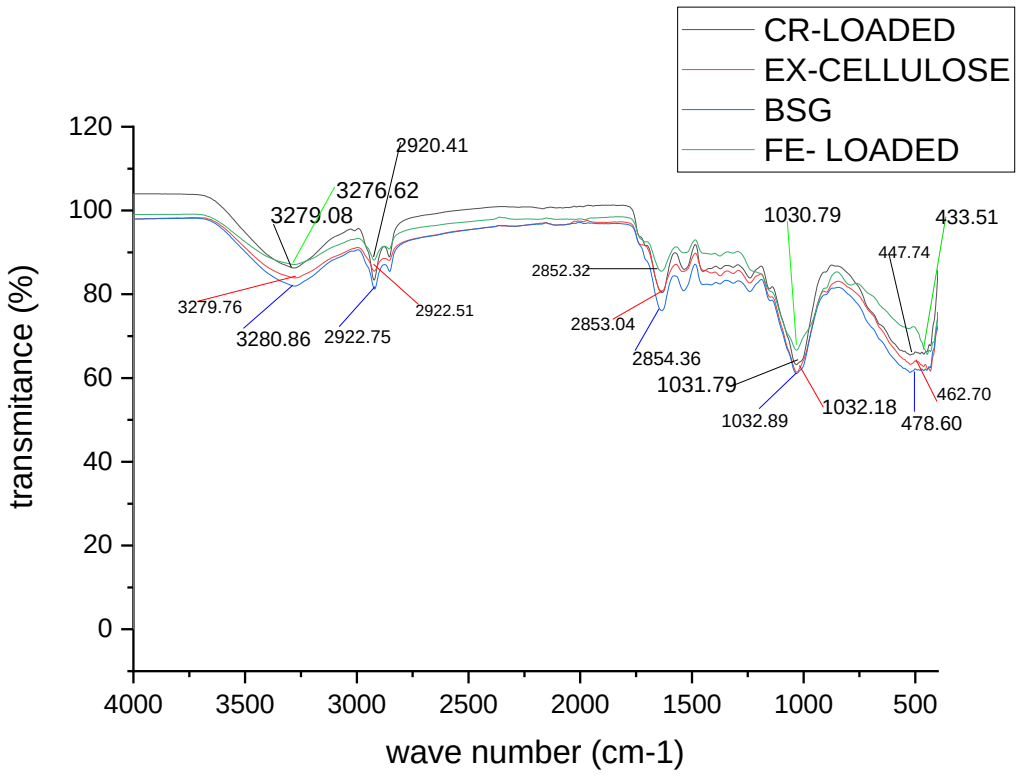
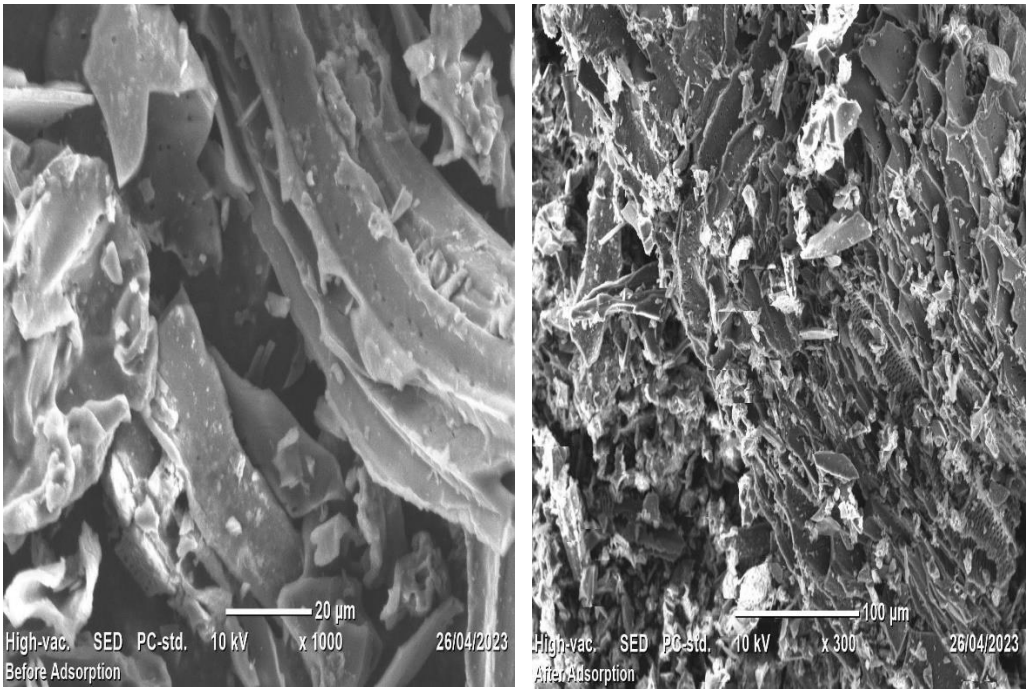


Fig 4.1 FTIR spectra for brewery spent grain before and after adsorption of metal ions

4.1. 2. Scanning Electron Microscope (SEM) Analysis

Scanning Electron Microscope (SEM) examined the morphology nature of BSG before and after adsorption. As seen in figure 4.3(a) the vacant pores of BSG was seen before adsorption. The surface of BSG shows a highly porous structure, which enables a suitable diffusion channel for chromium and iron adsorption. In addition, it consist of smaller particles which had larger surface area to uptake to metal ions (Mussotto,2006). On the other side, as figure 4.3(b) depicted, BSG after adsorption appeared to have improved, smooth and homogenous surfaces. The porous structure of BSG loosed, and the irregular collective surface was observed after adsorption. After adsorption, the SEM images indicate that pores and interstice were occupied by the solute molecules of iron and chromium ions. The external surface of BSG after adsorption is almost flat in the presence of agglomeration and cavities of the adsorbent observed.



a) b)

Figure 4. 2: SEM images of a) BSG before adsorption b) BSG after adsorption

4.2. Design of Experiment Result Analysis

Table 4.2: Chromium (VI) adsorption results at different levels of pH, contact time, dosage and metal initial concentration with constant temperature of 298K and stirring of 200rpm.

Run	Time(min)	dosage	pH	Co(mg/l)	Ce(mg/l)	% Removal	qe (mg/g)
1	30	0.5	2	15	2.406	83.96	5.04
2	105	1.25	4	10	3.208	67.92	1.09
3	180	2	6	15	3.205	78.63	1.18
4	30	0.5	6	5	2.142	57.16	1.14
5	180	0.5	6	15	3.053	79.64	4.78
6	30	2	2	15	2.448	83.68	1.26
7	180	2	2	5	2.528	49.44	0.25
8	**180**	**0.5**	**2**	**15**	**1.808**	**87.94**	5.28
9	180	0.5	2	5	1.685	66.30	1.33
10	180	0.5	6	5	2.89	42.40	0.84
11	30	2	2	5	2.82	43.60	0.22
12	30	0.5	6	15	3.312	77.92	4.68
13	30	2	6	15	3.297	78.02	1.17
14	30	0.5	2	5	1.4142	71.71	1.43
15	180	2	6	5	2.424	51.52	0.26
16	30	2	6	5	2.706	45.88	0.23

Table 4.3: Fe(II) adsorption results at different levels of pH, contact time, dosage and metal initial concentration with constant temperature of 298K and stirring of 200rpm.

Run	Time(min)	dosage	pH	Co(mg/l)	Ce(mg/l)	% Removal	qe (mg/g)
1	30	0.5	6	30	12.47	58.43	7.012
2	30	0.5	2	153	6.05	96.05	58.78
3	105	1.25	4	91.5	4.66	94.91	13.8944
4	180	2	6	153	5.97	96.10	14.703
5	180	2	2	30	10.74	64.20	1.926
6	30	2	6	30	11.74	60.87	1.826
7	30	2	6	153	5.15	96.63	14.785
8	30	0.5	2	30	5.28	82.40	9.888
9	180	0.5	2	30	7.73	74.23	8.908
10	180	2	6	30	15.90	47.00	1.41
11	**30**	**0.5**	**6**	**153**	**3.282**	**97.85**	59.8872
12	180	0.5	6	30	4.33	85.57	10.268
13	180	2	2	153	9.96	93.49	14.304
14	30	2	2	153	10.40	93.20	14.26
15	180	0.5	2	153	2.43	98.41	60.228
16	180	0.5	6	153	7.31	95.22	58.276

Table 4. 4 Analysis of variance influence of the factors studied on Cr(VI) & Fe(II) removal

Metal ions	Source	**Sum of squares**	**DF**	**Mean square**	**F-values**	**Prob>F**	**Significance**
Cr(VI)	Model	0.000	0	0			
	Residual	3804.70	15	253.65	132.41	0.0300	Significant
	Cor Total	3804.70	15				
Fe(II)	Model	0.000	0	0			
	Residual	4481.01	15		298.73	>0.0001	Significant
	Cor Total	4481.01	15				

Values of "Prob > F" less than 0.0500 indicate model terms are significant and Values greater than 0.1000 indicate the model terms are not significant.

4.2.1. Development of regression model of chromium

As shown in table 4.5 below the ANOVA analysis was significant with correlation coefficient values of $R^{2,}$ adj. $R^{2,}$ and pred. R^2 having values of 0.9723, 0.9684 and 0.95431 and 0.94734, 0.94324 and 0.9284 for chromium and iron respectively. And also as shown in figure 4.4 and 4.5 below the regression data close to straight line. It indicates that the result of predicted and experimental data was good and developed model was close to actual data.

Table 4.5 The R^2 values Cr(VI) and Fe(II) adsorption

Cr(VI)				Fe(II)			
Std. Dev.	15.93	R^2	0.9723	Std. Dev.	17.28	R-Squared	0.94734
Mean	66.61	Adj R^2	0.9684	Mean	82.99	Adj R-Squared	0.94324
C.V. %	23.91	Pred R^2	0.95431	C.V. %	20.83	Pred R-Squared	0.9284
PRESS	4328.90	Adeq Precision	43.398	PRESS	5098.40	Adeq Precision	32.438

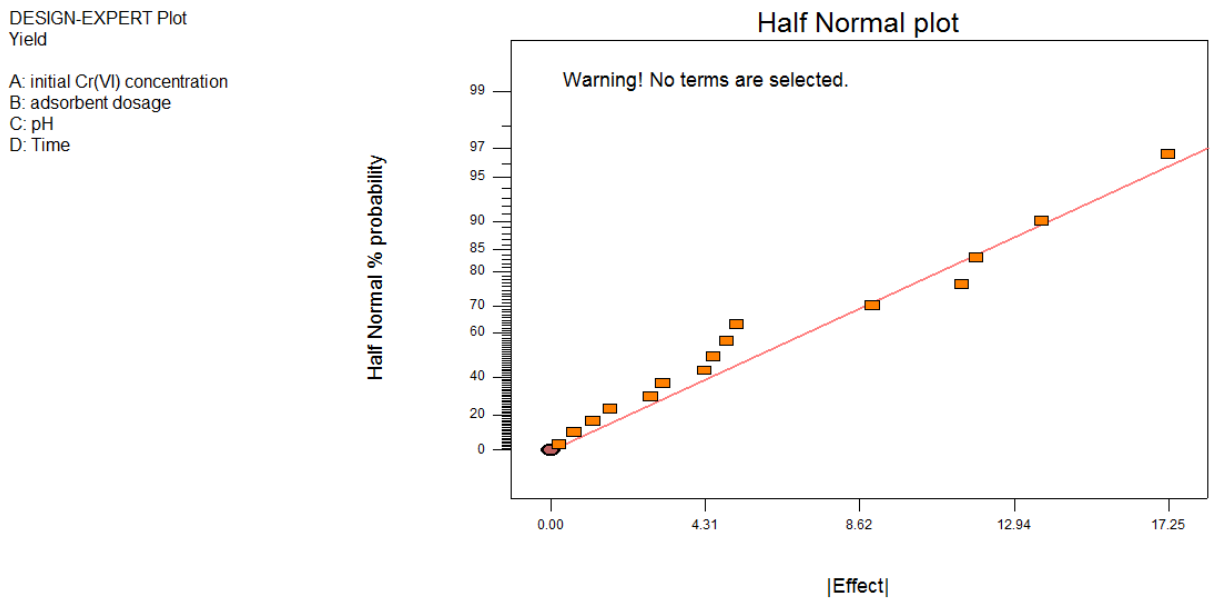


Figure 4.3 predicted vs actual experimental data for Cr (VI)

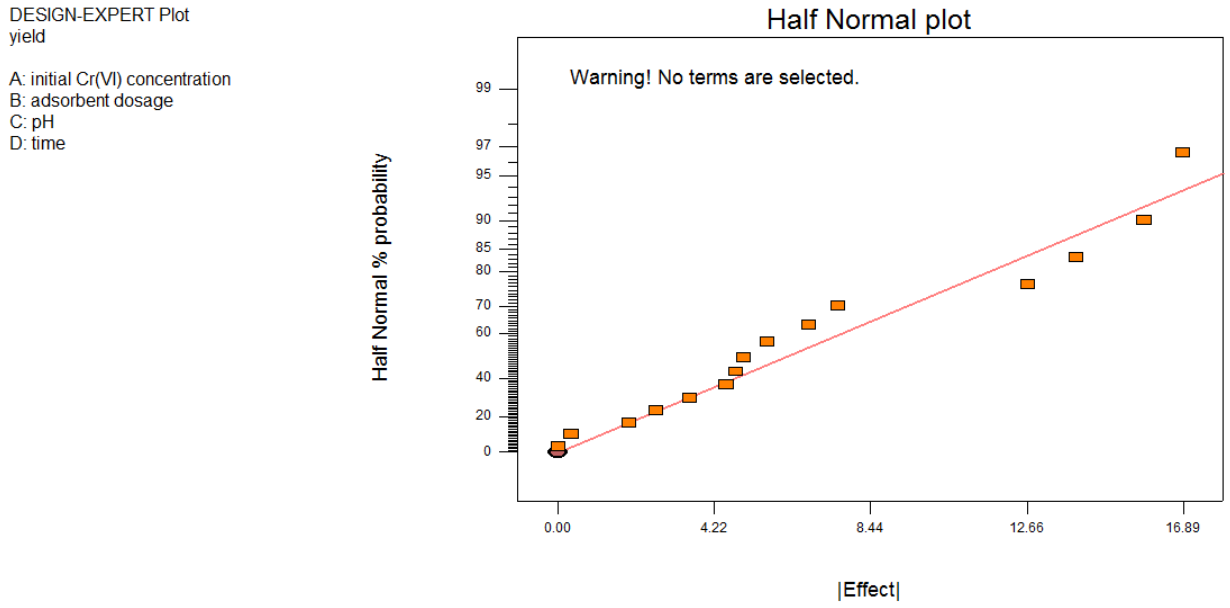


Figure 4.4 predicted vs actual experimental data for Fe (II)

4.3. Equilibrium Isotherm

Adsorption system can be designed with the aid of adsorption isotherms commonly referred to as equilibrium isotherms, which constitute the amount of solute adsorbed per unit weight of sorbent. These isotherms use equilibrium concentration of sorbent at a fixed temperature. To remove the iron and chromium ions from the wastewater, a particular design is optimized in

order to generate proper correlations for experimental data, which is referred to as adsorption isotherm (Batool et al., 2018).

4.3.1. Adsorption Isotherm

The interaction of adsorbate with adsorbent can be identified by studying isotherm, which is a critical to optimizing and designing the desired adsorption system (Zhang et al., 2015). The adsorption isotherm of chromium and iron studied. The equilibrium concentration of chromium ion at constant optimized parameters of 180 min, 0.5 g/200 mL BSG dose and, 2 pH and iron ion at constant optimized parameters of 30 min, 0.5 g/200 mL of BSG dose and, 6 pH at a room temperature were carried out. The adsorption of isotherm data for chromium and iron ion was analyzed by applying two commonly used isotherms, Langmuir and Freundlich Isotherms. Their correlation coefficients and constant were obtained from the slope and intercept of the graph for each equation of the isotherms.

4.3.1.1. Langmuir Isotherm

The adsorption isotherm determines the difference between the amounts of sorption and the solute concentration at equilibrium. The concentration of chromium and iron ions in their respective equilibrium phase at room temperature was studied to obtained maximum adsorption capacity of BSG for iron and chromium ion removal. The maximum adsorption capacity (q_{max}) can be determined from the intercept of Langmuir plots of $C_{e/}qe$ vs C_e. The maximum adsorption capacity (q_{max}) and energy of adsorption (K_L) from Langmuir isotherm model were to be determined 3.96 mg/g and 2.296 L/mg respectively for chromium and 2.674 mg/g and 4.155 L/mg respectively for iron. The values of correlation factor (R^2) gained for Langmuir isotherm equals to 0.98085 and 0.9585 for chromium and iron respectively. Which were slightly higher than the R^2 values of freundlich model for Fe(II). The result shows that the adsorption of Fe(II) on BSG were well fitted to Langmuir model. That means BSG surface are homogenous sorption patches, on which monolayer coverage of Fe(II)ions were formed outer surface of biosorbent.

Table 4.6: isotherm data for the removal of chromium to BSG

C_o(mg/L)	C_e(mg/L)	ln (Ce)	$1/C_e$	q_e (mg/g)	$1/q_e$	Ln(q_e)	C_e/q_e
5	1.414	0.34	0.7	1.43	0.69	0.35	0.98
10	3.208	1.16	0.31	1.09	0.91	0.086	2.94
15	1.808	0.59	0.55	5.28	0.18	1.66	0.34

Table 4.7 isotherm data for the removal of Iron to BSG

C_o(mg/L)	C_e(mg/L)	ln (Ce)	$1/C_e$	q_e (mg/g)	$1/q_e$	Ln(q_e)	C_e/q_e
30	4.33	1.46	0.23	10.26	0.09	-2.40	0.42
91.5	4.66	1.53	0.21	13.89	0.07	-2.65	0.33
153	3.282	1.18	0.30	59.88	0.016	-4.13	0.05

Table 4.8 isotherm parameters for the removal of Iron and chromium to BSG

Heavy metal ions	Langmuir isotherm			Freundlich isotherm		
	R^2	q_{max} (mg/gm)	kL(1/mg)	R^2	Kf (mg/g)	n
Cr(VI)	0.98085	3.96	2.296	0.9832	1.235	5.54
Fe(II)	0.9585	2.674	4.155	0.9099	2.66	3.47

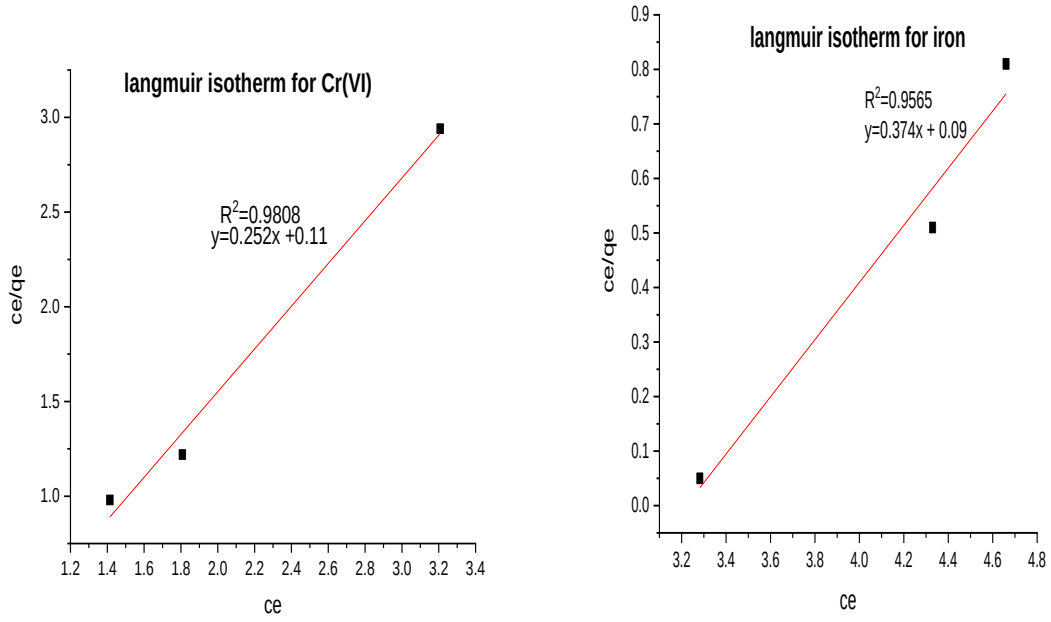


Figure 4.5 Langmuir isotherms for chromium and Iron adsorption by BSG

4.3.1.2. Freundlich Isotherm

It is an empirical equation that can be employed to describe the heterogeneous systems. Freudlich isotherm constant parameter Kf and n were determined by linear regression from the plot of log (qe) vs log (Ce). Kf is the degree of adsorption. When Kf value is low it indicates that minimal adsorption. Whe Kf value is low indicates high sorption ability (oves etal.,2013). For this case Kf value is high (2.66 mg/g) for Fe(II) and low (1.235 mg/g for Cr(II). The magnitude of the exponent 1/n indicates the favorability of the adsorption. 1/n is a heterogeneous factor, which is related to adsorption intensity or surface heterogeneity. The value of $1/n < 1$ which equals to 0.18 for chromium and 0.28 for iron indicates normal adsorption (Keshav et al., 2019). In order to reach a favorable adsorption process, the value of n should be in the range of 1 to 10. Table 4.4 depicts the value of n was 5.54 and 3.47 for chromium and iron respectively, which confirmed favorable adsorption. The value of n is low for Fe(II) and higher for Cr(VI). Suggests that a maximum bisorption for Cr(VI) and least for Fe(II). But all favored to freudlich isotherm. The values of correlation factor (R^2) gained for Freundlich isotherm equals to 0.9832 and 0.9099 for chromium and iron respectively.

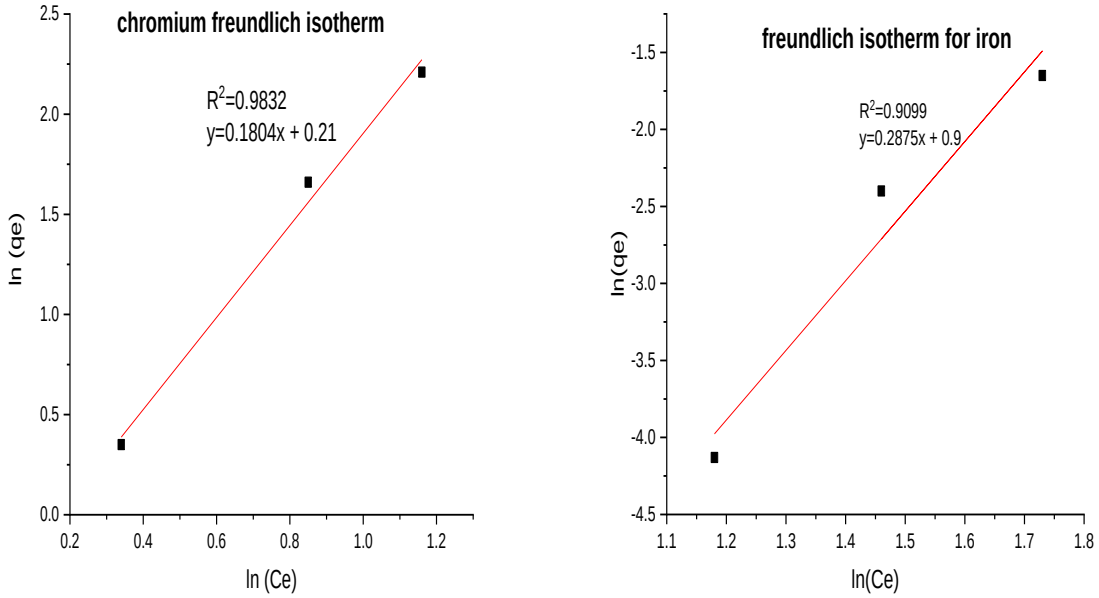


Figure 4.6 freundlich isotherms for chromium and Iron adsorption by BSG

4.4. Adsorption Kinetics

Kinetic experiment was investigated to examine the rate of chromium and iron adsorption on BSG adsorbent and the time required to reach equilibrium. The purpose of studying equilibrium kinetic is to know the adsorbent retention time and provide information about the specified time to reach the maximum capacity of adsorption and the controlling mechanism in the process that includes mass transfer or chemical reactions (Tohfegar et al., 2019). In this study Pseudo-first-order and Pseudo-second-order were analyzed to obtain the best kinetic models for iron and chromium removal. In this study Pseudo-first-order and Pseudo-second-order kinetic models were analyzed to obtain the best kinetic models for chromium and Iron removal. The kinetics study time dependence of iron was investigated from 30 to 180 min at constant room temperature, 153 mg/L initial concentration, pH =6, adsorbent dose = 0.5 g/200 mL and 30 to 240 min at constant room temperature, 15 mg/L initial chromium concentration, pH =2, adsorbent dose = 0.5 g/200 mL.

Comparing the correlation coefficients of both kinetic models, it definitely revealed that the pseudo-second-order model best fit the adsorption kinetic of iron and chromium onto BSG and the adsorption processes were chemisorption. As shown in the figure 4.9 the Pseudo-second-

order rate model show the best agreement with the experimental results, which implies that the whole process was controlled by chemical adsorption is the rate limiting steps of the process. Pseudo-second-order kinetic model predicts that adsorption behavior involves valance forces through sharing of electrons among iron & chromium ions and the BSG. In addition, the experimental adsorption capacity was in agreement with that of calculated adsorption capacity, which proved the model adopted is reasonable. The value of kinetic parameters was summarized in table 4.9.

Table 4. 9 Kinetics model parameters for Pseudo-first-order & Pseudo-second-order

Metal ions	Kinetics	Parameters	Value
Fe(II)	Pseudo-First Order	q_e (mg/g)	1.3
		K_1 (min^{-1})	0.1844
		R^2	0.7535
	Pseudo-Second Order	$q_{e\ calc}$(mg/g)	64.24
		q_e exp(mg/g)	60.224
		q_e^2	4126.77
		K_2 (g/mg.min)	0.18
		R^2	0.999
Cr(VI)	Pseudo-First Order	q_e (mg/g)	0.6
		K_1 (min^{-1})	0.095
		R^2	0.698
	Pseudo-Second Order	$q_{e\ calc}$(mg/g)	5.65
		q_e exp(mg/g)	7.97
		q_e^2	63.52
		K_2 (g/mg.min)	0.004
		R^2	0.990

Table 4.10: Pseudo first and second order kinetics and constant values for Iron

Time (min)	C_o (mg/L)	Ce(mg/L)	q_t (mg/g)	q_e (mg/g)	ln(qe-qt)	t/q_t (g.min/mg)
0	0	0	0	0	0	0
30	153	3.282	59.887	60.224	-1.09	0.500
60	153	3.211	59.915	60.224	-1.174	1.0014
90	153	2.834	60.066	60.224	-1.845	1.498
120	153	2.438	60.224	60.224	-	1.992
180	153	2.438	60.224	60.224	-	2.988

Table 4.11 Pseudo first and second order kinetics and constant values for chromium

Time (min)	C_o (mg/L)	Ce(mg/L)	q_t (mg/g)	q_e (mg/g)	ln(qe-qt)	t/q_t (g.min/mg)
0	0	0	0	0	0	0
30	15	5.287	3.885	5.516	0.489	7.722
60	15	4.201	4.319	5.516	0.179	13.892
90	15	3.828	4.468	5.516	0.0468	20.143
120	15	2.384	5.046	5.516	-0.755	23.781
180	15	1.808	5.276	5.516	-1.427	34.116
210	15	1.208	5.516	5.516	-	38.071
240	15	1.208	5.516	5.516	-	43.509

Pseudo first order kinetics

$$\ln(q_e - q_t) = lnq_e - k_1 t$$

Metal ions	**Intercept**	**slope (k1)**	**$q_{e\ cal}$ (mg/g)**	**K_1**	**R^2**
Fe(II)	0.248	0.1844	1.3	0.1844	0.7535
Cr(VI)	0.519	0.095	0.6	0.095	0.698

Pseudo second order kinetics

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{t}{q_e}$$

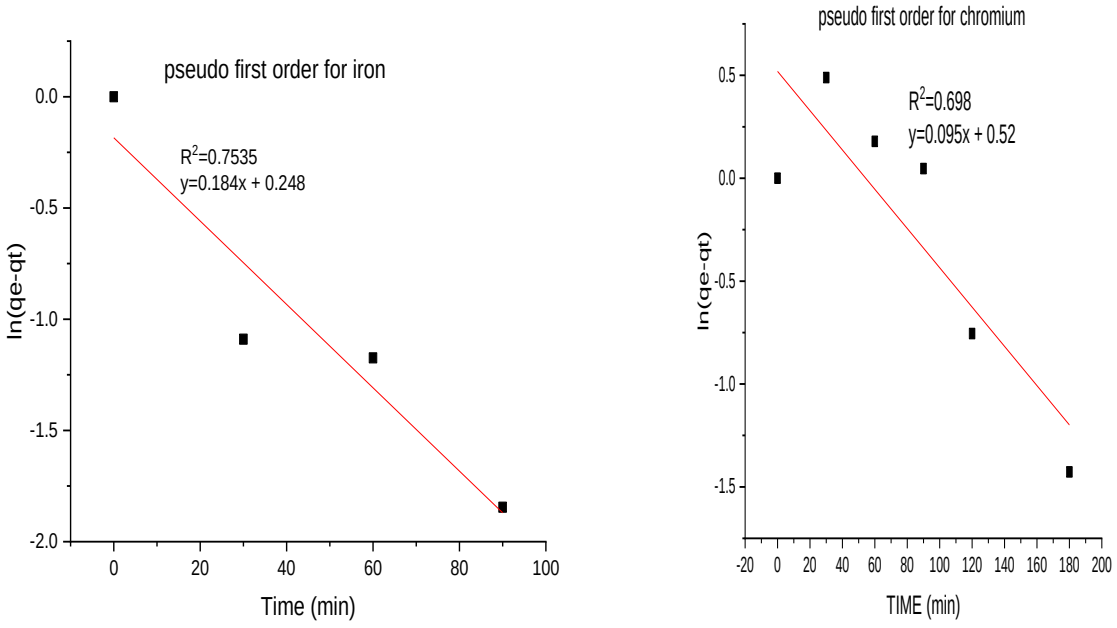


Figure 4.7: Pseudo first order for sorption of iron and chromium ions

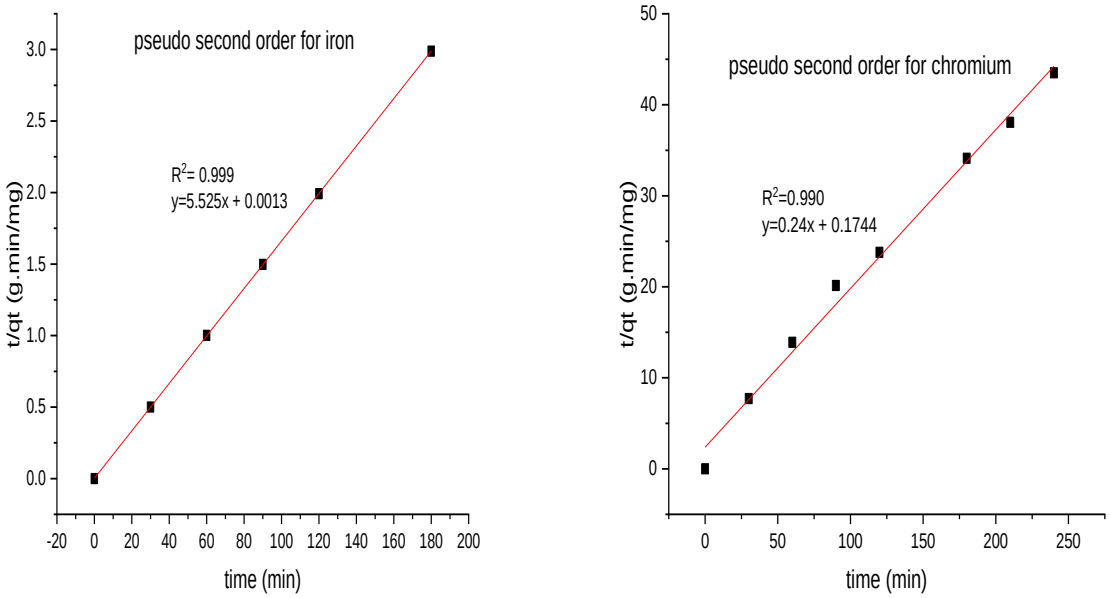


Figure 4.8 Pseudo second orders for sorption of iron and chromium ions

4.5. Concentration of heavy metals in steel industry waste water

In this factory water used for processing discharged in six months. So the first samples were taken after 30 days of discharge, second sample after 90 days of discharge and third sample taken after six months.

Table 4.12 concentration of heavy metals from steel industry waste water

Metal ions	Samples	Values (mg/L)	WHO std(WHO,2011)	Ambient env. Standard for Ethiopia
Fe(II)	1	0.33	5	1
	2	125		
	3	153		
Mn	1	0.06	0.3	0.3
	2	0.24		
	3	0.61		
Cr(VI)	1	5	0.05	0.05
	2	9		
	3	15		
Cu	1	0.24	2	0.05
	2	ND		
	3	ND		
Ni	1	0.27	3	-
	2	ND		
	3	ND		
Pb	1	ND	0.01	0.05
	2	ND		

4.6. Removal efficiency of Brewery spent grain for real waste water

This process is for comparison of experimental results to application in real world. Waste water samples containing chromium and Iron were received from steely R.M.I PLC which was found in Bishoftu town from rolling mill plant. Currently, waste water from this industry was discharged into environment without proper treatment and not met specified standards of WHO and Ethiopian waste water discharge standard.

Tests were conducted were for both metal ions at their optimum points. The samples were taken from three different sites with in a factory.

Table 4.13 metal ions concentration from steel industry waste water

Metal ions (mg/L)	Places			
	1	2	3	Average
Fe(II)	30	153	125	102.6
Cr(VI)	5	9	15	9.6

For sorption of waste water containing Iron, optimum parameters were selected. pH=6, dose= 0.5g, time=30 min and also maximum initial concentration were selected(153mg/L). And also for chromium pH=2, dose= 0.5g, time=180 min and also maximum initial concentration were selected (15 mg/L).

Table 4.14 Optimum points chosen for batch chromium and iron sorption onto BSG

Metal ions	Parameters			Co (mg/L)	Ce(mg/L)	%R(real waste water)	%R(synthetic waste water)
	Contact time(min)	Dose(g)	pH				
Fe(II)	30	0.5	6	153	68.25	55.39	97.85
Cr(VI)	180	0.5	2	15	8.321	44.52	87.94

After adsorption real waste water removal efficiency of Iron was 55.39 and chromium was 44.52. These results were much lower than the removal efficiency of synthetic waste water for both metal ions. This is due to the presence of other metal ions and competing of one another.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Brewery spent grain was chosen for removal of iron and chromium. Sulphuric acid was used to treat BSG to remove impurities. Cellulose was extracted to remove left impurities. This BSG was characterized and utilized for removal of chromium and iron from aqueous solution using batch adsorption techniques. The result indicates that BSG is good adsorbent. Thus removal of iron with BSG reached 97.85% with dose 0.5g and initial concentration 153mg/L in 200mL volume of solution. And also chromium reached 87.94% with dose 0.5g and initial concentration 15mg/L in 200mL volume of solution.

FTIR analysis showed that BSG contains many functional groups mainly alkene, alcohol and $-CH_3$. The development of mathematical model for adsorption of chromium and Iron using statistical design of experiments shows useful tool for prediction and understanding of interaction effects between process variables and two factor factorial design. Isothermal data of metal ions sorption by BSG showed the biosorption process followed both freundlich and Langmuir isotherm models. Data analysis showed maximum biosorption for chromium and least for Iron. The kinetics of biosorption was well represented by pseudo second order.

The real waste water and synthetic waste water adsorption were compared. After adsorption real waste water removal efficiency of Iron was 55.39 and chromium was 44.52. These results were much lower than the removal efficiency of synthetic waste water for both metal ions. This is due to the presence of other metal ions and competing of one another. The studies data presented showed that the adsorbent, BSG is locally available, low cost and can be employed as adsorbent for removal of chromium and Iron for contaminated waste water before discharge into environment.

5.2. Recommendations

In the future the following work should be explored on brewery spent grain for waste water treatment.

- Further research is needed to study economic feasibilities on BSG utilization in the wastewater treatment which has not been done in this work.
- Study the adsorption process using other metals like zinc, lead, arsenic among others.
- Batch adsorption can be carried out by considering other excluded parameters such as various temperature and stirring rpm.
- Adsorption experiments can be carried out by treating raw brewery spent grains with different chemicals such as base (sodium hydroxide, calcium hydroxide, sodium carbonate), organic compounds (ethylenediamine, formaldehyde, epi-chlorohydrin, methanol) and oxidizing agent (hydrogen peroxide), inorganic acids (hydrochloric acid, nitric acid, tartaric acid, citric acid, thioglycollic acid).
- Regeneration of brewery can be carried out after biosorption process. So, regenerated brewery spent grain can be used until it become exhausted.
- In this study waste water was taken only from rolling mill section of steely RMI factory. So further study needed by taking waste water sample melting section.

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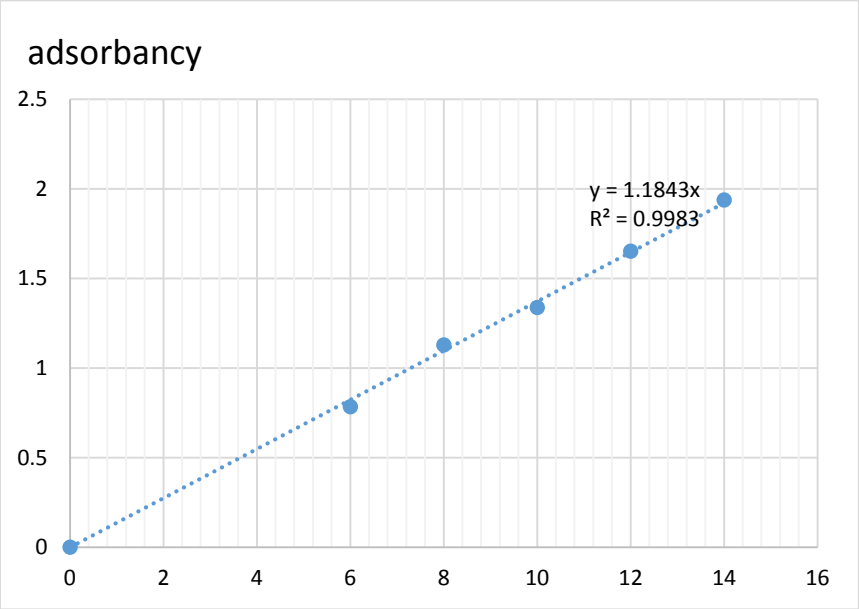
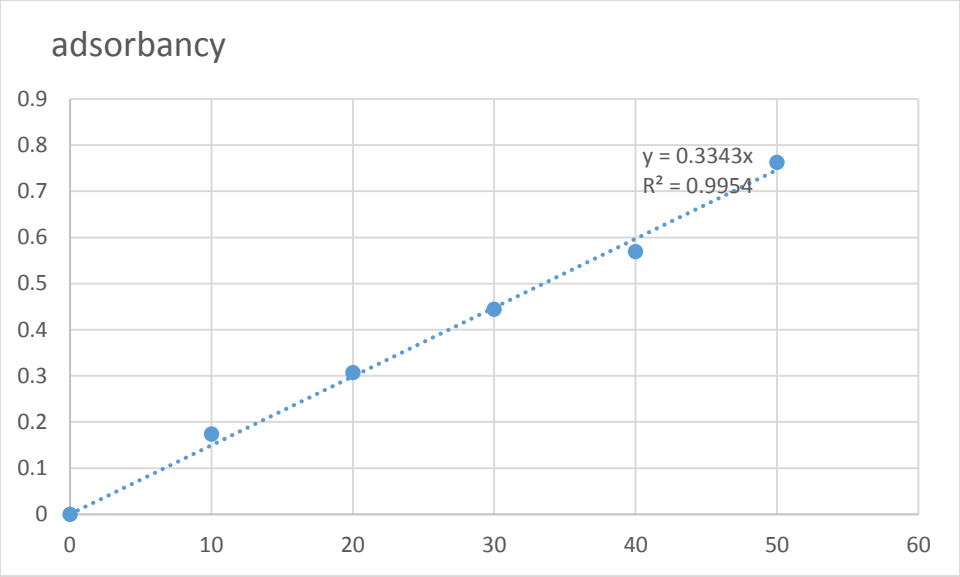
Appendix I Calibration Curve for standard solution (for Cr(VI))



Appendix II Calibration Curve for standard solution (for Fe(II))



Appendix III: Calculation of Removal efficiency and adsorption capacity of chromium(VI)

1. Calculation of chromium(VI) Removal efficiency

According to equation 3.6 the percentage of chromium (VI) removal at a particular time(t) for aqueous solution as follows: -

$$\%R = \frac{Co-Ce}{Co} * 100 \text{----------(3.6)}$$

Example $\%R = \frac{15-2.406}{15}$*100

%R= 83.96

Similar procedure was followed for other calculations.

2. Calculation adsorption capacity of chromium(VI)

   According to equation

qe= $\frac{Co-Ce}{m} * v$----------(3.5)

Example Qe= $\frac{15-2.406}{0.5} * 0.2$

qe = 5.04

Co = initial concentration of Cr(VI) in the solution

Ce = equilibrium concentration of Cr(VI)

V = volume of the solution

m= dry mass of absorbent

Similar procedure was followed for other calculations.

Appendix IV: Calculation of Removal efficiency and adsorption capacity of Fe(II)

1. Calculation of Fe(II) Removal efficiency

According to equation 3.6 the percentage of Fe (II) removal at a particular time(t) for aqueous solution as follows: -

$\%R = \frac{Co-Ce}{Co}$*100----------(3.6)

Example $\%R = \frac{30-12.47}{30}$*100

%R= 58.43

Similar procedure was followed for other calculations.

2. Calculation adsorption capacity of Fe(II)

   According to equation

$$qe = \frac{Co - Ce}{m} * v \text{----------(3.5)}$$

Example $Qe = \frac{30 - 12.47}{0.5} * 0.2$

qe = 7.012

Co = initial concentration of Cr(VI) in the solution

Ce = equilibrium concentration of Cr(VI)

V = volume of the solution

m= dry mass of absorbent

Similar procedure was followed for other calculations.

Appendix V. Calculation of equilibrium isotherm models

1. Langmuir isotherm for chromium

According to figure 4.4 equation of linearized Langmuir isotherm was: -

Y= 0.252x + 0.11

And also according to equation 3.9 Langmuir isotherm was expressed as: -

$$\frac{1}{qe} = \frac{1}{qmkL} * \frac{1}{Ce} + \frac{1}{qm} \text{----------(3.9)}$$

By using both equations

$\frac{1}{qmax}$ =intercept and $\frac{1}{qmaxkL}$ = slope

$\frac{1}{qmax} = 0.252$ and $qmax = \mathbf{3.968}$

$\frac{1}{qmaxkL} = 0.11$ and kL = **2.296**

qm= maximum adsorbent amount of Cr(VI) per BSG = **3.968** mg/g and

kL= Langmuir equilibrium constant = **2.296** L/mg

2. Langmuir isotherm for Iron

According to figure 4.4 equation of linearized Langmuir isotherm was: -

Y= 0.374x + 0.09

And also according to equation 3.9 Langmuir isotherm was expressed as: -

$$\frac{1}{qe} = \frac{1}{qmkL} * \frac{1}{Ce} + \frac{1}{qm}$$ ----------(3.9)

By using both equations

$\frac{1}{qmax}$ =intercept and $\frac{1}{qmaxkL}$ = slope

$\frac{1}{qmax} = 0.252$ and $qmax =$ **2.674**

$\frac{1}{qmaxkL} = 0.09$ and kL = **4.155**

qm= maximum adsorbent amount of Cr(VI) per BSG = **2.674** mg/g and

Appendix VI: Calculation of kinetic model parameters

1. Calculation of 1st order kinetics order parameters for chromium (k1 and qe)

According to figure 4.6 equation of 1st order kinetic model was: -

Y= 0.095x + 0.519

And also according to equation 3.16 Langmuir isotherm was expressed as: -

$\log(qe-qt) = -\frac{-k1}{2.303}t + \log(qe)$ ----------(3.16)

By using both equations

$lnqe$ =intercept and $k1$ = slope

$\boldsymbol{qe = 0.6}$ and $k1 =$ **0.095**

qe= adsorption capacity = **0.6** mg/g and

k1= first order rate constant = **0.095** min^{-1}

2. Calculation of 1st order kinetics order parameters for iron (k1 and qe)

According to figure 4.6 equation of 1st order kinetic model was: -

Y= 0.1844x + 0.248

And also according to equation 3.16 Langmuir isotherm was expressed as: -

$\log(qe-qt) = -\frac{-k1}{2.303}t + \log(qe)$ ----------(3.16)

By using both equations

$lnqe$ =intercept and $k1$ = slope

$qe = 1.3$ and $k1 = 0.1844$

qe= adsorption capacity = **1.3** mg/g and

k1= first order rate constant = **0.095** min^{-1}

3. **Calculation of 2nd order kinetics order parameters for chromium (k2 and qe)**

According to figure 4.67equation of 2nd order kinetic model was: -

Y= 0.1744x + 2.379

And also according to equation 3.21 second order was expressed as: -

$$\frac{t}{qt} = \frac{1}{qe}t + \frac{1}{k2qe2} \quad \text{----------(3.21)}$$

By using both equations

$\frac{1}{k2}$ =slope and $\frac{1}{k2qe2}$ = intercept

$qe = 7.97$ and $k2 = 0.004$

qe= adsorption capacity = **7.97** mg/g and

k2= 2nd order rate constant = **0.004** mg^{-1} min^{-1}

4. **Calculation of 2nd order kinetics order parameters for iron (k2 and qe)**

According to figure 4.67equation of 2nd order kinetic model was: -

Y= 0.165x + 0.025

And also according to equation 3.21 second order was expressed as: -

$$\frac{t}{qt} = \frac{1}{qe}t + \frac{1}{k2qe2} \quad \text{----------(3.21)}$$

By using both equations

$\frac{1}{k2}$ =slope and $\frac{1}{k2qe2}$ = intercept

$qe = 64.24$ and $k2 = 0.18$

qe= adsorption capacity = **7.97** mg/g and

k2= 2nd order rate constant = **0.18** mg^{-1} min^{-1}

Appendix VII: calculation of cellulose content

According to equation 3.1 cellulose content determination can be calculated as: -

$$cellulose\ content = \frac{final\ dried}{total\ initial\ weight\ of\ BSG} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.1)$$

Cellulose content = $\frac{1.24}{2}$

= 0.62

Similar calculation was done for all experiments.

Appendix VIII: Important photos taken during experimental work

a) Steely RMI PLC waste water

b) Prepared solution to adjust PH

C) Adjusting PH

d)Samples prepared for uv test

e) jar test

f) weighing BSG

g) Fe_3O_4 Synthesis

h) synthesized Fe_3O_4

i) weighing synthesized Fe_3O_4

k) stock solution for chromium

l) stock solution for Iron

Appendix: IX: Waste water analysis (for chromium, iron and manganese)

JIJE LAB GLASS Pvt. Limited Company	JIJE Analytical *Testing* Service Laboratory	Doc. No: JATSL/F5.10-3.1	Page 1 of 1	
			Ver. No: 04	Effective Date: July 08, 2017
	Analytical Test Report			
Customer Name:	Ergalem Amare	Test Report No:	204	
Contact Person:	Ergalem Amare	Report Date:	20/07/2022	
Sample Type:	Waste Water	Test Request No:	Not Specified	
Sample Source:	From steel Industry	Tel (Mob):	+251922661326	
Sample Collected By:	Ergalem Amare	Fax:	Not Specified	
Sample Collection Date:	08 /07/22	E-mail:	ergalemamare@yahoo.com	
Sample Receiving Date:	08/07/22	Tested By:	JATSL	
Sample Condition:	Normal	Dates Tested:	08/07/2022 - 19/07/2022	

S/N	Lab No	Customer ID	Results (mg/L)		
			Cr	Fe	Mn
1	J-0730/0807/22	-	0.23	153.00	0.61

S/N	Parameters	Test Methods
1	pH	APHA 4500 H^+ B Potentiometric
2	Metals (Cr, Fe and Mn)	APHA 3111 C. MP-AES Method

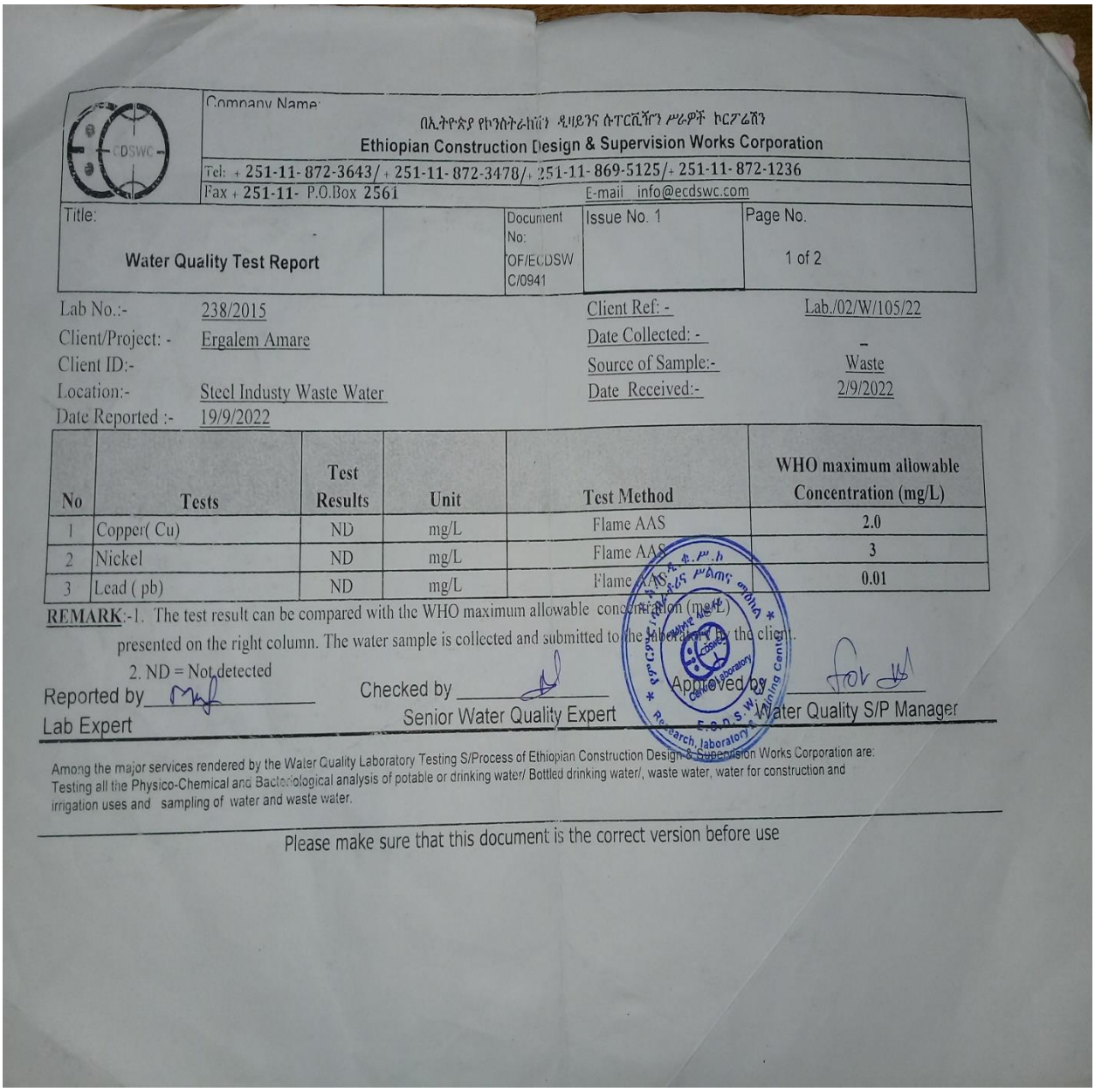
Remark:

1. This test report is only for specific sample(s) which has been tested by JIJE Analytical *Testing* Service Laboratory.

Verified by			*Authorized by*		
Name	**Signature**	**Date**	**Name**	**Signature**	**Date**
Teshome Gezahagne		**20/07/2022**	**Mulugeta Terefe**		**20/07/2022**
Technical Signatory			*Laboratory Manager*		

Tel : +251-37207 01/ 02
Fax : +251-011-372 07 03
P.O. Box: 70077
Email: info@jijelabglass.com
Web site: www.jijelabglass.com
Physical Address: Nifas Silk Lafto Sub City, Woreda 01, Lebu, Foziana Building 6th Floor, Infront of Varnero Real Estate, Addis Ababa, Ethiopia.

Appendix: X: Waste water analysis (for copper, nickel and lead)



Company Name:
በኢትዮጵያ የኮንስትራክሽን ዲዛይንና ሱፐርቪዥን ሥራዎች ኮርፖሬሽን
Ethiopian Construction Design & Supervision Works Corporation
Tel: + 251-11- 872-3643/ + 251-11- 872-3478/ + 251-11- 869-5125/ + 251-11- 872-1236
Fax + 251-11- P.O.Box 2561 E-mail info@ecdswc.com

Title:		Document No:	Issue No. 1	Page No.
Water Quality Test Report		OF/ECDSWC/0941		1 of 2

Lab No.:- 238/2015 Client Ref: - Lab./02/W/105/22
Client/Project: - Ergalem Amare Date Collected: - –
Client ID:- Source of Sample:- Waste
Location:- Steel Industy Waste Water Date Received:- 2/9/2022
Date Reported :- 19/9/2022

No	Tests	Test Results	Unit	Test Method	WHO maximum allowable Concentration (mg/L)
1	Copper(Cu)	ND	mg/L	Flame AAS	2.0
2	Nickel	ND	mg/L	Flame AAS	3
3	Lead (pb)	ND	mg/L	Flame AAS	0.01

REMARK:-1. The test result can be compared with the WHO maximum allowable concentration (mg/L) presented on the right column. The water sample is collected and submitted to the laboratory by the client.
2. ND = Not detected

Reported by Lab Expert
Checked by Senior Water Quality Expert
Approved by for Water Quality S/P Manager

Among the major services rendered by the Water Quality Laboratory Testing S/Process of Ethiopian Construction Design & Supervision Works Corporation are: Testing all the Physico-Chemical and Bacteriological analysis of potable or drinking water/ Bottled drinking water/, waste water, water for construction and irrigation uses and sampling of water and waste water.

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