



ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

(ENVIRONMENTAL ENGINEERING STREAM)

*Removal of Chromium from Painting Industry Wastewater Using
Bioelectrochemical Fuel Cell Technology*

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A thesis is submitted to graduate department of Addis Ababa University
in partial fulfillment of the degree of Master of Science in Chemical
Engineering under Environmental Engineering stream

Advisor: Dr. Shimelis Kebede

July, 2021

Addis Ababa Ethiopia

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This research paper in title of “Removal of Chromium from Painting Industry Wastewater Using Bioelectrochemical Fuel Cell Technology” is submitted to graduate program of Addis Ababa University for partial fulfillment for requirement of degree in Master of Chemical Engineering under Environmental Engineering stream. And approved by:

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Declaration

This research thesis in title Removal of Chromium from Painting Industry Wastewater Using Bioelectrochemical Fuel Cell Technology is my original work and not presented by other person for award of degree or research projects in this University and others and all resource and material used for this research have been acknowledged. And it is undersigned declared by:

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Acronym

AAiT	Addis Ababa Institute of Technology
APHA	American Public Health Association
BBD	Box Behnken Design
BECFC	Bioelectrochemical Fuel Cell
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DM	Dissolved material
NTU	Nephelometric Turbidity Unit
RSM	Response Surface Methodology
SS	Suspended Solid
UV	Ultra Violet
WHO	World Health Organization
X1	1 st factorial or time
X2	2 nd factorial or concentration
X3	3 rd factorial or pH

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Abstract

Chromium is heavy metal that released as waste dominantly from chemical industries and causes chronic and acute health problems on human beings and other living environments. From different industrial sector in Ethiopia Painting industries are developing but their wastewater treatments are not get attention. This was one of the reason to select the sector for the removal of chromium from their wastewater using Bioelectrochemical Fuel Cell Technology (BECFC). The technology is an effective, efficient, and environmental-friendly that remove chromium without using external energy. The methodology can generate electrical energy from wastes that helps it to avoid the cost of energy during treatment. The sub objectives of this research were synthesizing chromium wastewater using APHA methodology, constructing set up of BECFC, enumerating *Bacillus Cereus*. And others were investigating the efficiency of the methodology by varying three parameters at three different operational level, using statistical method of RSM optimizing operation parameters and verified on synthetic wastewater. Also characterizing real wastewater and verifying again optimum operation parameters on real wastewater were sub-objectives of the research. BECFC remove chromium from wastewater when electro-active bacterial like *Bacillus Cereus* metabolize organic waste in anodic chamber and release electrons during the process. Then generated electrons are transferred to the cathodic chamber through the external wire. Then after chromium is reduced, attached on electrode, detached and settle to the bottom of cathodic chamber. To see results of the research, over all above 95% efficiencies of removal of chromium were achieved. The highest efficiency of removal achieved was 99.6% at a concentration of 15 mg/L, pH of 9, and time of treatment 16hrs. The efficiency of optimum operation parameter was 98.1% and current density generated was 17.51mA/m² with an optimum concentration of 9mg/L, pH 7, and optimum time of 17.357hrs. And the efficiency of removal of chromium from real wastewater of (3400mg/L SS, 2164NTU turbidity, 738mg/L COD and 148mgg/L BOD) was 84%. In conclusion, BECFC is a promising technology, but more research in full facilitated laboratories are requested to make the methodology applicable on real wastewater.

Keyword: Bioelectrochemical, Painting Industry, Chromium Removal, Wastewater

Chapter One

Introduction

1.1 Background

Water is a unique material that can available in three states liquid, solid, and gas. It covers 71% of the earth's surface (UNESCO, 2012) even though only 3% of a water body is freshwater, which exposes to pollution due to waste released from city, industry, agriculture, and other sources of waste materials. This waste expose water to be polluted and cause high health problems on humans, animals, and all biotic ecosystems. Water is called wastewater when its chemical and physical properties like color, smell, and chemical composition are changed. The main sources of water pollution are industries that release chemicals contained acid, base, and toxic heavy metals. Some of the heavy metals that released by industries are chromium, lead, copper, iron, mercury, and other transition metals (P.U. et al., 2017). Among heavy metal chromium is targeted metal in this research and the metal released from painting, textile, and leather industries into wastewater stream. Most of heavy metals are toxic and cause chronic or/and acute diseases like cancer, kidney, lunge damage and other.

One of the challenging things in wastewater treatment is removing of heavy metal from wastewater targeted methodologies are required to remove them from wastewater. Chromium is one of the heavy metals used as electroplating, pigments, inks, fungicides, wood preservatives, rubber ceramics, photography, and textiles (Ivase et al., 2020). The two major chromium forms are three balance electrode chromium (Cr^{3+} , $\text{Cr}(\text{OH})^{2+}$ and $\text{Cr}(\text{OH})^{4-}$) and hexavalent chromium ($\text{Cr}(\text{IV})$, $\text{Cr}_2\text{O}_7^{2-}$) which is a toxic form of chromium and more dangerous than $\text{Cr}(\text{III})$. Due to its high valance of oxidation, it can enter easily into the biological system of living things (Y. Wang et al., 2017) then interrupt the normal factions of the organ system. Some health problems related to chromium are corrosion skin, eye irritation, and cancer. The acute organ of toxicity is the kidney, and it results in kidney fell and finally leads to fatal (Wani et al., 2019). Some of the methodologies used for removing chromium from wastewater are adsorption, precipitation, oxidation, reduction, electrochemical evaporation, and ion exchange. Those methodologies have some common drawbacks such as; high energy of operation due to most wastewater treatment use electric energy

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for operation like adsorption, photoelectro-catalytic oxidation, UV-activated oxidation (Junqun. D et al., 2020), and technology like chemical coagulation are not environmentally friend because they use chemicals for treatment and some technologies have less efficiency of treatment (Risk Husk Adsorption 71%, Bio-sorbent 80%, Photo-catalyst 60%) (Shrestha et al., 2021) but these weaknesses can be solved by Bioelectrochemical fuel cell technology.

This research focuses on the removal of chromium from wastewater of painting industries. Dying industries reals toxic heavy metal like chromium in the environment and cause pollution this is there reason to target wastewater of painting industries. To remove chromium from synthetic wastewater and to validate on the actual industry combination of biological and electrochemical technology was used. Microbial community like bacterial have a role in waste removal which produce organic ion from nitrogen, phosphorus, hydrocarbon and other organic wastes. Also microbial facilitate the uptake of plat toxic metal, mobile metal ions by breaking complex ions into simple nutrients (Shahid et al., 2020). And some electro-active bacteria release electron and H^+ ion which used for heavy metal reduction during metabolizing of organic materials (Mathuriya & Yakhmi, 2014). BECFC technology use this electro active bacterial to remove hexavalent chromium from waste water and the technology has advantage of minimization of operational cost, high efficiency, and environmentally-friend.

1.2 Statement of Problem

Water is basic for living organisms and for the regulation of the environmental ecosystem so it has to be clear and useable. But due to different factors like improper disposal of domestic, industries, and other wastewater sources water become polluted. One research done on water supply and water treatment by Global business program show that in Ethiopia different industrial parks are constructing and 11 fully operating industrial parks release 56500m³ per day which and these industrial parks use advanced conventional and zero liquid discharge for their wastewater treatment (Harrendorf, 2020). But these method of wastewater treatment require high operation cost, require high recovery system and have challenge of material and effluent compositions (Ahirrao, 2014) If polluted water is not treated it affects human life and the whole ecosystem of our plant mainly the aquatic environment. To reduce this risk it is better to discover a new and advanced way of wastewater treatment. The main cause of wastewater is heavy metal released from industries like painting industries. Heavy metal like chromium which released into the water body from leather, painting, textile industries and pollute water.

There are different methods which used to remove heavy metal like chromium from wastewater. Removing heavy metal from wastewater by biosorption (Ali Redha, 2020), electro dialysis (Dos Santos et al., 2019), and chemical precipitation for treating electroplating wastewater treatment (Peng et al., 2004) and others. As they show in their literature, the methodologies can remove heavy metal from wastewater but not much effective and environmentally sustainable. This research deals with bioelectrochemical fuel cells how to remove chromium from wastewater of painting industries. Bio electrochemical fuel cell uses electroactive bacterial that digest waste material in anodic chamber and remove chromium by cathodic reduction method. This method is effective and efficient for removal of chromium from wastewater and it has advantage of generate electric energy from wastewater. Another important thing that makes this method selective is that it is environmentally sustainable technology.

1.3 Objectives

1.3.1 General Objective

The general objective of this thesis research was to remove effectively and efficiently chromium from painting industry wastewater using new promising technology of bioelectrochemical fuel cell technology.

1.3.2 Specific Objectives

The specific objectives of this research are derived from the general objective and they help for achievement of main objective. These objectives are;

- To synthesize chromium wastewater which correspond to real wastewater of painting industries at different concentration and pH.
- To multiply cultured *Bacillus ceruse* bacteria which used as biomaterial.
- To construct BECFC reactor-setup that used as working reactor.
- To statistically investigate the performance of BECFC at three different selected operational parameters
- To determine statistically optimum operation parameters toward highest efficiency and verifying on synthetic wastewater
- To characterize real wastewater and verify again the optimum operation parameters on characterized real wastewater

1.4 Significance of the study

There are different methods of removal heavy metal from wastewater. The one which makes Bioelectrochemical technology different from others is that it involves microbial for removing chromium from wastewater without use chemicals for treatment. This technology is new, environmental-friendly, and nullity purpose technology to remove heavy metal without using external energy sources. This technology produces electric energy when an electron transfers from an anode to a cathode.

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The other significances of this research is that it serve as alternative wastewater treatment methodology. That adds value for future development and to apply the methodology to other heavy metal treatments. Bioelectrochemical fuel cell is the best and environmentally friendly technology that uses microbial and electro chemical technology for removing heavy metal from wastewater of industries like painting. Different technologies are developing to remove heavy metals from wastewater, but they are less effective and environmentally not friendly when compared with BECFC. The additional significance of this research is that the research paper can serve as a reference for other researcher when they want to study more on this and related area.

1.5 Scope of the study

The scope of the research was performing laboratory experiment on synthesized chromium wastewater using Bioelectrochemical fuel cell technology by Surface respond statistical method of Box Behnken Design. And investigating optimum operation parameters that verified on synthetic and real wastewater.

Chapter Two

Literature Review

2.1 Industrial Wastewater

Water is basic for all living thing which cover above 70% of body fluid of organism. On earth major part is covered by ocean, sea, ground water, polar ice, rivers, lakes and it covers 71% of our planet earth (UNESCO, 2012) and 97% is salty water (Ranade & Bhandari, 2014). This means only 3% of water is fresh water. Though 3% is not used for domestic purpose large amount are used for agriculture irrigation this cause the scarcity of useable water (bottle water). Due to lack of clean fresh water over millions of people are dying especially in developing countries (Baroni L., et al, 2007).

Wastewater contain polluting material change natural, physical and chemical characteristic of water. The main indicators of wastewater are change in color, get bad Odor and changed in their physical appearances when seen by naked eye (Gomes & Ebrary, 2009). As well when checked their chemical composition it contains toxic heavy metal, minerals organic and inorganic substances. There are a lot of sources which make water pollution and categorized as natural pollution and humans pollution. By nature water polluted due to natural phenomena like volcanic eruptions, pollen gray, flooding and other causes (P.U. et al., 2017). The other source of water pollution are human beings activities, in daily life of activity people pollute water knowingly and unknowingly. The main activity of human being which produce wastewater are industries that release a lot of metric cub of wastewater per day which contain vey toxic heavy metal, acidic, basic and pathogenic materials. Around 0.1% of wastewater is contain organic matter, heavy metal and other inorganic material, microorganism pathogen, Bactria, viruses, protozoa and result mas disasters (Cristina.T, 2020).

Wastewater can be industrial wastewater and municipal wastewater, domestic wastewater (Boutin et al., 2017) and main containment of wastewater are organic wastewater, inorganic wastewater and pathogenic wastes (Slavov, 2017). Water for industries are necessary thing as raw material ingredient, system cooling and for washing. And this water most of it final become wastewater

that released to sewerage or treated and pumped in to municipal sewage disposals. Chemical industries are called water-intensive factors because they use large amount of water and they release high amount of wastewater (Ranade & Bhandari, 2014). Industrial wastes are the major cause of wastewater containing very toxic heavy metals. Some of the major industries that cause water pollution are nuclear reaction plant, dying industry, lather industry and other industries which release toxic heavy metals (Lipponen & Nikiforova, 2017).

2.1.1 Painting Industry Wastewater

Dye industries produce dye or coloring materials which used in other production industries, for painting of buildings, art paintings and other uses in societies. The main constituents of painting are pigment to impact color and opacity, binders which are polymer create matrix to fix pigment in place, extender used to improve adhesion which upgrade film and binder protection, solvent or thinner it decrease viscosity of painting for better use, additives are applicable for modifying the properties of liquid paint or dry film (Aboulhassan et al., 2014). There are different kind of dye those are Azo dye, Triarylmethane dye and Anthraquinone (Benkhaya et al., 2018), (Deepika Malviya, 2018). Painting industries use chromium which help for prevention metal from corrosion (Sabty-Daily et al., 2005). The material which create shiny, brightness, durability, hardness and give good appearance on materials is chromium. Chromium serve as pigment in dye, inks, plastic materials, electroplating on metals, aircrafts and cars (Enviromental Health, 2006).

The main contaminant of wastewater of painting industries are organic matter, high amount of heavy metal, Sulphur reach and great amount of suspend solid. They contained heavy metal like lead, arsenic, cadmium, nickel, mercury, copper, zinc, chromium and other metals (Körbahti & Tanyolaç, 2009). These heavy metal are non-biodegradable and toxic this lead for the accumulation, health problem like cancer. In Ethiopia there are many different company which involved in the production of dye (Woldeamanuale, 2017). Among all of painting factors Nifas Silk painting factory is the oldest and the larges painting factory. Current number of painting industries are among highly growing sector of industries due to the fact of this it is better to focus how to treat heavy metals from wastewater of painting industries. Different research paper are done on treatment of painting industry wastewater. Combination of biological aeration and coagulation flocculation was studied and it was more effective for treating of high BOD and COD

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painting industry wastewater (Aboulhassan et al., 2014). Electrochemical treatments is also used for treating of painting industry wastewater and efficiency is around 80% for treating on turbidity, color and enabling COD (Körbahti & Tanyolaç, 2009).

Table 1: Effluent heavy metal, physical and chemical contend of painting industries

Parameter	Painting industries				
	Zamillic	Nifas Silik	Cadisco	Rainbow	Bright
pH	7.16	6.72	6.77	7.7	6.48
SS	9525	6912.5	1965	22528	8862.5
PO	41.8	15.37	2.265	65.375	44.5
BOD	246	350	47	600	360
COD	3524	1949	425	7662.5	3887.2
Cr	8.25	9.32	1.5	2.95	5.28
Pb	25.84	8.33	0.68	53.4	18.73
Cd	2.47	7.813	1.58	69.22	16.82
Cu	9.22	2.24	2.09	22.47	189.16
Ag	15.23	5.69	6.08	14.72	28.06

Source (Woldeamanuale, 2017) all units are mg/L except pH

2.1.2 Heavy Metal in wastewater

Including chromium there are different heavy metals which are toxic to biotic ecosystem when released into environment without treatment. Table 2 below shows some heavy metals sources, toxic effect and their standard of limit.

Table 2: Source, toxic effect of heavy metal and their minimum standard limitation (mic g/L)

Heavy metal	Main sources	Major toxic effect	WHO	USEPA	Citation
Arsenic	Pesticides, mining, fossil fuel	Bronchitis, bone marrow, skin cancer, depression, pigmentation changes, neurological disorders, muscular weakness, dermatitis, hepatomegaly kidney damage emphysema, weight loss, gastrointestinal disorder itailta disease, bronchitis, hypertension.	10	50	(Atkovska et al., 2018)
Cadmium	Fertilizer, pesticide, plastic welding, mining	Kidney damage, emphysema, weight loss, gastrointestinal disorder, latria disease, bronchitis	3	5	(Atkovska et al., 2018)
Chromium	Steel, electroplating, dye, textile industry, leather industry	Carcinogenic, severe diarrhea, skin rash, respiratory problem, kidney and liver damage, vomiting, weaken immune system and genetic material.	50	100	(Atkovska et al., 2018)

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Copper	Cu cooking pots, mining, electroplating, batteries	Neuroticism, anemia, hyperactive, schizophrenia, psychosis, insomnia, cystic fibrosis, autism, stuttering, inflammation, and dizziness	250	1300	(Zhou et al., 2018)
Lead	Batteries, mining, paint, pigments, explosives	Anemia, malaise, brain damage, anorexia, liver dysfunction, kidney dysfunction, gastrointestinal damage, mental retardation	10	5	(Zhou et al., 2018)
Mercury	Mining, paper, paint industries, batteries	Damage to kidney and nervous system, protoplasm poisoning, dermatitis, corrosive to skin, eyes, muscles	1	2	(Zhou et al., 2018)
Nickel	Paint, batteries storage, electroplating, porcelain enameling	Dermatitis, lung cancer, chronic bronchitis, pulmonary fibrosis, rapid respiration, headache, dizziness	200	134	(Azizi et al., 2016)
Zinc	Mining, refineries, brass manufacturing plumping	Gastrointestinal distress. Metal-fume fever	5000	5000	(Azizi et al., 2016)

Notice: WHO is abbreviation for world health organization and USEPA is US environmental protection agency

2.2 Heavy Metal Removing Technology

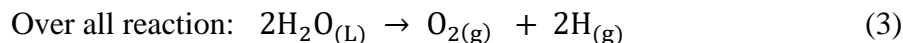
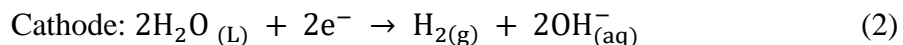
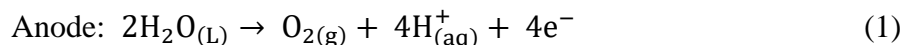
There are different methods which are used for removing of heavy metal from wastewater. The major and most common methods are adsorption, precipitation, electrochemical and other methodologies. Let see few of them;

2.2.1 Electro Coagulation

This technology use coagulant chemicals which help the process of coagulation of waste material or heavy metals. This method is versatile and has easy process these make it preferable and selective for heavy metal removing. Most common heavy metal which removed by this method are zinc, nickel, cobalt, copper, manganese and chromium. In the process of treatment coagulate chemical create condition for the formation of precipitation of solid waste and removed after it segmented, flocculated coagulated and filtration (Pokhrel, 2017). Electro coagulation is electrochemical method which involve the scarification of anodes due to oxidation and which make metal ion to dissolved and there is situation which create precipitation and floc which help for removing at cathode due to formation of $H_{2(g)}$ and OH^- . This technology has advantage of easy for operation, amount of sludge effluent is low and it affected by pH change due to it has the buffering ability (Pokhrel, 2017). Even though it has advantages it has drawback too, electrode used can easily corrode, through time cathodic efficiency is decreased due to formation of oxide layer and it require high energy consumption.

2.2.2 Electro Flotation

This method of wastewater treatment use electrochemical electrolysis of water which help for removing of suspended material by bubble created. Electro flotation is most applicable in wastewater of high conducting material it help to cost saving which spent for power consumption. The method can be used in small and intermediate treatment of non-water mixing fin particle (Mohtashami, 2018). Reaction involved in the process is as following;



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At anode there is metal scarification which help for removing of waste by acting as coagulant. Electro flotation is used in industrial wastewater treatment which generate fine bubbles which is more efficient (Daneshvar et al., 2007).

2.2.3 Electrodialysis

Electrodialysis is method of wastewater treatment which use membrane for separation of large size particle from small. These method more clear which can be reused and electrolyte stream discharged. Electrodialysis can be used desalination of brackish waters, desalting of whey and stabilization of win, metal removing and recovery (Gurreri et al., 2020). In electro dialysis there is ion exchange which occur in membrane module which contain anion and cation exchanger.

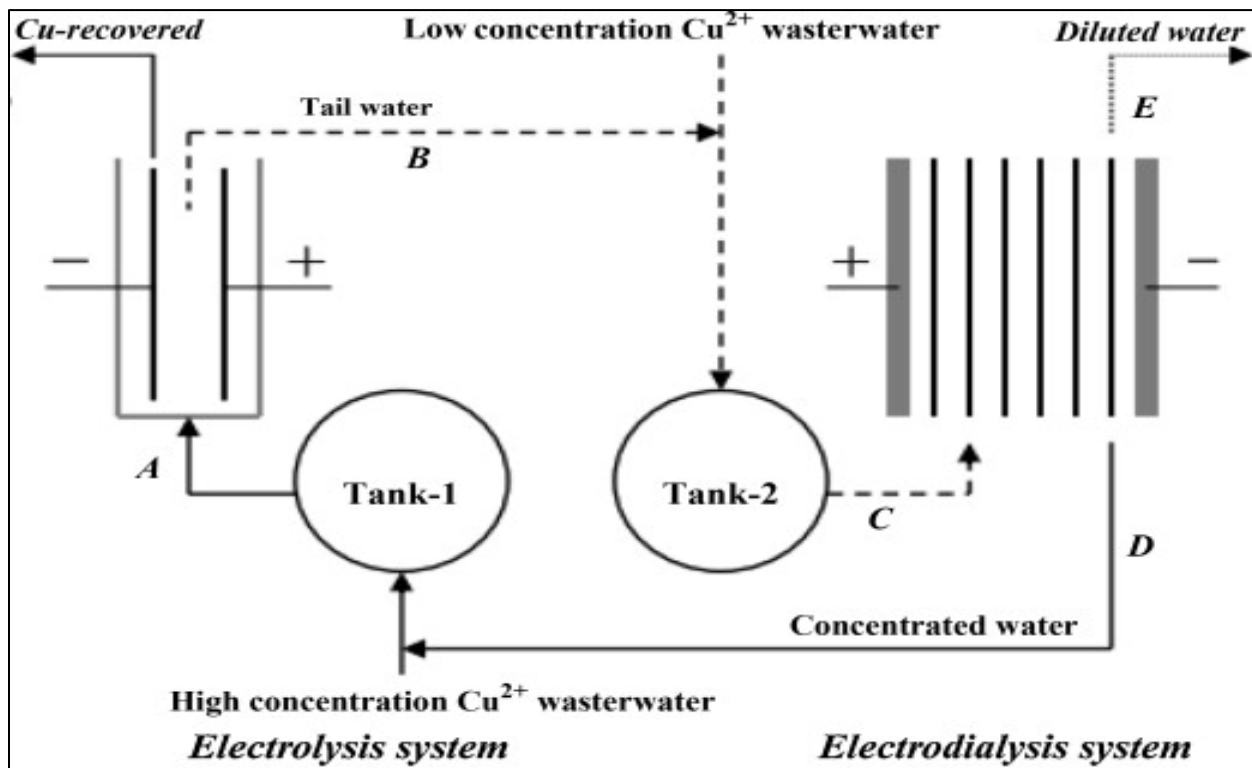


Figure 1: Heavy metal removing using Electro Dialysis (Gurreri et al., 2020).

2.2.4 Oxidation Process

There are different technology for removing of toxic metal from wastewater like chemical precipitation, membrane separation, adsorption and other. Adsorption use pores material for adsorbing and chemical precipitation use chemical for formation of complex reaction with heavy metal and create instable precipitate. Adsorption and chemical precipitation has their own drawback, in adsorption process it is not easy to generate adsorbents, whereas chemical precipitation has the limitation of high cost of chemical used. Other method used for removing of heavy metal is membrane separation which use membrane that can prevent from passing of large material like heavy metal. These membrane base technology has limitation of easily plugged of membrane by impurities (Du et al., 2020a). Oxidation process is better than the listed above method due to oxidation ability like electrochemical oxidation (Z. Zhao et al., 2018), fenton (L. Zhang et al., 2019), photocatalytic (Yang et al., 2019) and other oxidation technology. The oxidation process based on OH^- and other radical to break bond of heavy metal complexes and free ion of metal removed by precipitation.

2.2.4.1 Fenton

These oxidation technology can be divided into homogeneous and heterogeneous reaction. Homogeneous oxidation (Clarizia et al., 2017) use Fe^{2+} and hydrogen peroxide which used environmental friendly for removing of wastes. Fenton oxidation use OH^- for distraction of heavy metal complex and prevent connection with organic ligands (Aramyan, 2017). Homogenous fenton is called traditional form and OH^- -created convert heavy metal to high oxidation state Cr(III) to Cr(VI) which then react with ligands for distraction. Homogenous fenton has advantage of no energy input needed, high efficiency, simple and flexible and it has also disadvantage of strict on pH, large Fe^{2+} needed, high amount of sludge containing iron generated (J. Zhang et al., 2018).

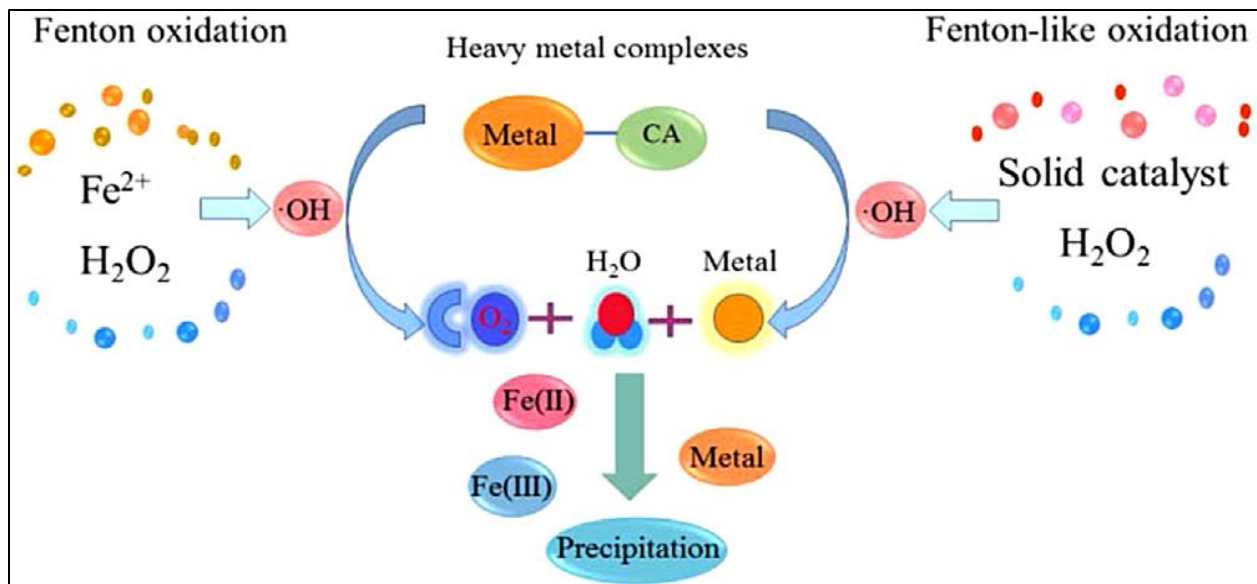
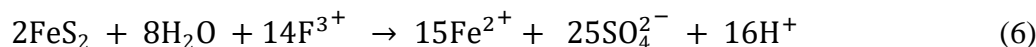
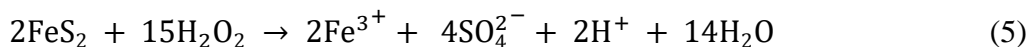
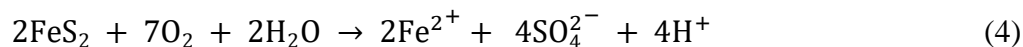


Figure 2: Heavy metal complex decomposition by Fenton oxidation (Du et al., 2020a).

Heterogeneous Fenton (Thomas et al., 2021) which is new technology employing solid catalysts for reducing dissolved metal ion with variety range of pH. Pyrite is oxidized for facilitating cycle between Fe²⁺ and Fe³⁺



Fenton heterogeneous oxidation has limitation of small amount of water treatment (J. Zhang et al., 2018).

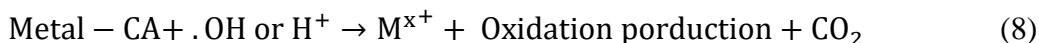
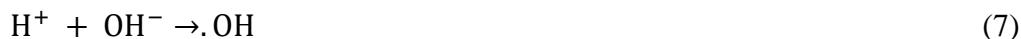
2.2.4.2 Electrochemical Oxidation

This method is the most common and can be used with other oxidation processes and reactions occurring at anodic and cathodic sides (C. Wang et al., 2019). Heavy metal is oxidized at the anode and removed directly or by generating OH⁻. The main processes involved are electron movement to the anode surface, OH⁻ is liable which generates high physios orbels at the anode and powerful OH⁻ distract complex of heavy metal and free metal stored at cathode. Anodic oxidation has advantage of high distraction efficiency of heavy metal, versatility and flexibility (Bi et al., 2017).

Removal of Chromium from Painting Industry Wastewater Using Bioelectrochemical Fuel Cell

Whereas high operational cost and less low organic ligand treatment efficiency is its drawback. The other kind of electrochemical oxidation treatment method is electrochemical Fenton oxidation which include generation of Fe^{2+} and generation of hydrogen peroxide this create strong oxidation state in process of treatment. This combination method has advantage of generation of peroxide avoid difficulties occurred during transportation and storage, high efficiency of treatment due to occurrence of Fe^{2+} , avoid the creation of sludge and other pollutant and not need other oxidation and redaction cost for operation. Its main limitation is rate of aeration must optimized before operation, matter of current density and solution pH must also optimized. Photochemical oxidation is also type of electrochemical oxidation which use photo catalysts. Heavy metal complex is degrade when excited photon and surface electron react (Cho et al., 2006). The most used photo catalyst is TiO_2 and the mechanism of removing heavy metal is by adsorption(Gurreri et al., 2020).

Reaction occurred is;



Advantage of TiO_2 photocatalyst is mineralization of organic waste, adsorption of metal on photocatalytic the limitation of TiO_2 based photocatalyst is it need pay attention on oxidation since anode require prevention of photo damage.(Do et al., 2020).

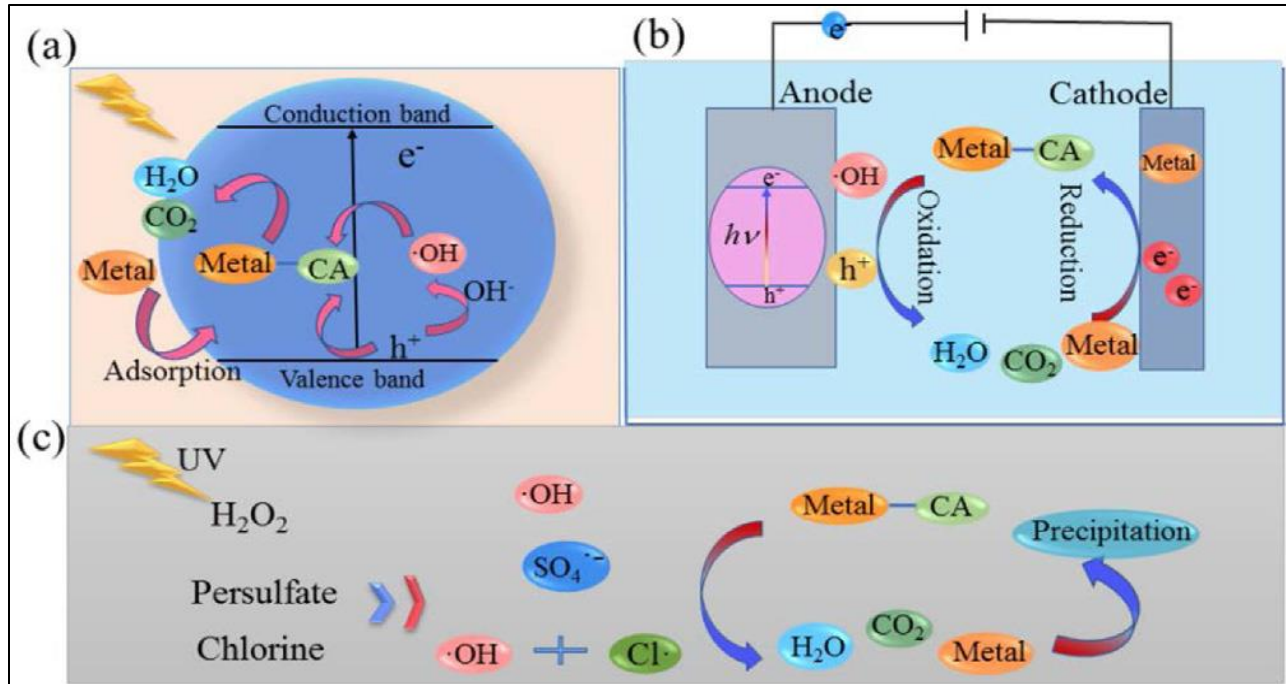


Figure 3: Illustration for a, photocatalytic oxidation b, Photoelectro catalytic oxidation c, UV activated oxidation (Do et al., 2020).

2.2.4. 3 Ozone Oxidation

Ozone based oxidation is not much affect environment during treatment and form waste which can be degrade biological and amount of toxicification is low. In heavy metal removing ozone play role of reacting with metal to create trigger mechanism (Guan et al., 2018). In process of ozone oxidation $\cdot OH$ oxidize toxic contaminant in to CO_2 and water. The technology is popular and promising form oxidation process in which no sludge waste can be generated. For more efficiency ozone is used in combination of H_2O_2 , UV and catalyst (J. Wang & Chen, 2020). There main advantage of ozonation is its efficiency of treatment and no sludge producing but it has also drawback which is its selective behavior and solubility problem of O_3 with water. Also it has high cost of operation for the production of ozone due to high consumption of energy (Agustina et al., 2006).

2.3 Chromium Removing Technology from Wastewater

Chromium is one of transition metal and it has variety of oxidation states. This metal is used in different industries for different function in elector plating industry it used for smoothing, giving brightness and cleanness of metal plate. It is also used in painting industries as prevention of corrosion and painting of metal. The other use of chromium are in chemical industries in pesticide, insecticide, inks, textile and other insect and microbial preservatives (A.L. Singh, 2008). The valance oxidation of chromium can range from zero up to six but the most available oxidation state are Cr (III) and Cr (VI). These two oxidation statutes are act as strong acid Cr(III) and strong base Cr(VI) (Asfaw et al., 2017). Chromium which has three valance electrons is less toxic than that of hexavalent chromium. Hexavalent chromium (CrO_4^{2-}) is very toxic and cause health problem which can inter into living cell easily. In cell it result reeducation of enzymatic activity and create condition for formation of reactive oxygen species which lead to damage of cellular proteins, lipids and DNA (Mitra et al., 2017). Other health problems caused by chromium is cancer, kidney and gastric damage, and irritation of skin and eyes, and when it stored to much in human body it cause fatal (Mitra et al., 2017).

Many industries release chromium specially Cr(VI) from their factories into water as wastes, Some of these industries are dye, tannery, paints and textile factories. When chromium released into rivers it inhaled by aquatic life and animals some time also direct by human being. This toxify aquatic living thing and through food chain it put in danger other living things and human beings. Through food chain after toxic Cr(VI) tope level or human being it case different health problem toxicity body system, case cancer, lead to kidney fall, skin damage and other more . These is why heavy metal like chromium removing need special target to remove from wastewater.

As stated by WHO maximum limit of chromium in potable water is 0.05mg/L if the limit exide this it cause health problem(Mehra & Juneja, 2003). There are different method which used for removal of chromium from wastewater. These are liquid-liquid extraction, reduction of chromium by precipitation, adsorption, solid phase extraction, biomass, nanotechnology, plant micro fuel call and other (Mitra et al., 2017). Their detail is listed in table 3 blow. From these methods plant micro fuel cell is new recent technology and which use microbial and plat for removing and reduction of chromium from wastewater. In this method bio electrochemical is applied for removing of chromium whereas plats are used for initiating the process. Chromium can be removed by plant

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uptake (Kassaye et al., 2017), direct chromium reducing and adsorption but in plant micro fuel cell chromium removing occurred at cathodic reduction. As chromium reduced at cathode pH of solution is increase which help for settlement of Cr compound. The Reaction is; Reaction:

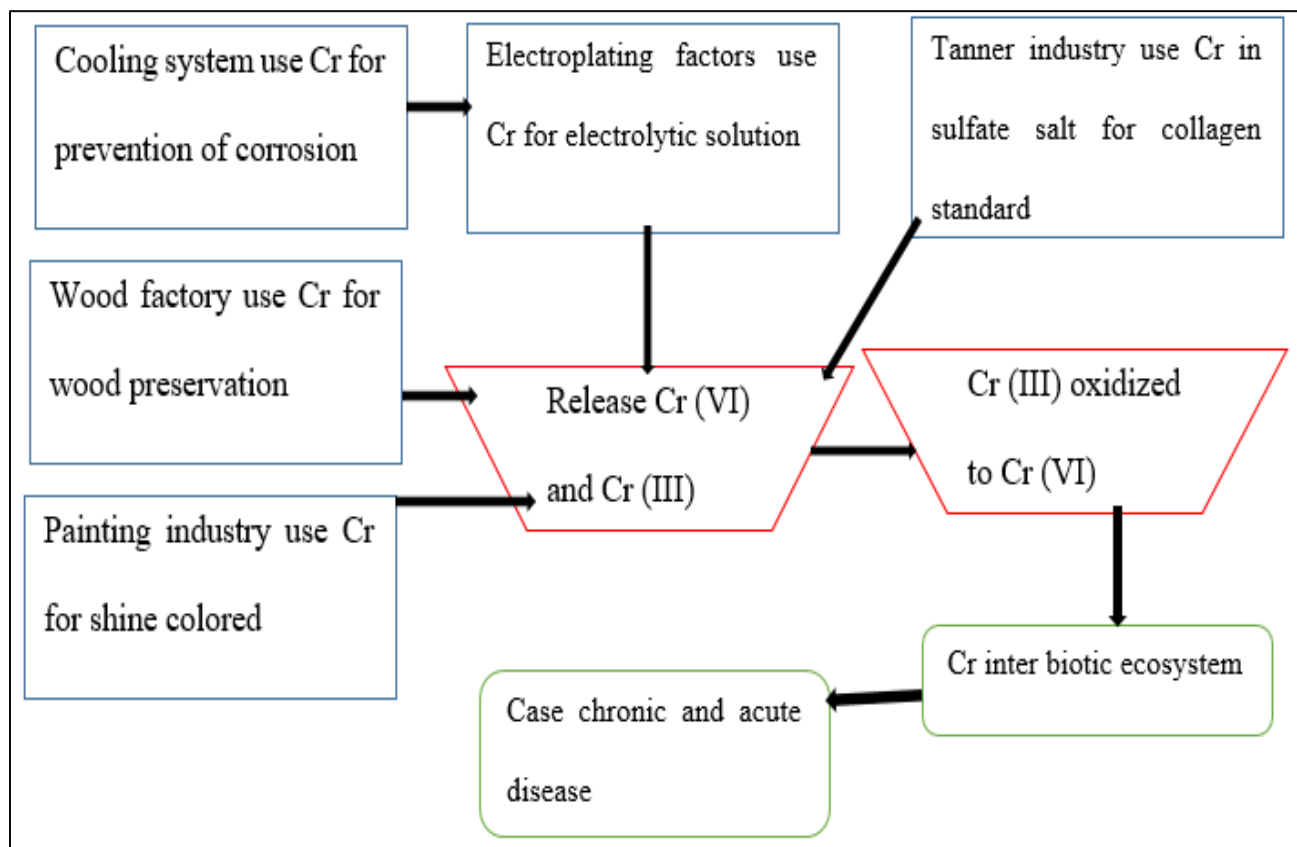
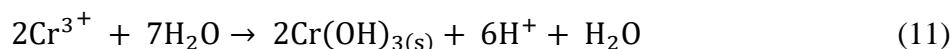
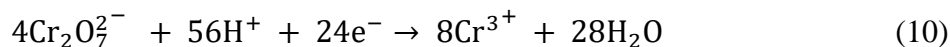


Figure 4: Different source of Cr releasing industries and their final destination (Mitra et al., 2017)

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Table 3 : Different technology for removing of chromium form wastewater

No.	Technology	Treatment	Explanation	Reference
1	Liquid-liquid extraction	Physical	It use amine based extraction, in dichloromethane tetra butyl ammonium at acidic condition used.	(Kalidhasan et al., 2010)
2	Reduction of Cr(VI) to Cr(III) by bisulphate & precipitation using lime/alkali	Chemical	Recovery of precipitated Cr(III) using sulfuric acid. Much sludge produced and the process is costly.	(Verma, 2020)
3	Adsorption	Physical	Popularly used, it use peroxide-modified TiO ₂ , zeolite, chitosan and activated carbon enriched with nitrogen also magnetic lignin composite	(Dula et al., 2014)
4	Solid phase extraction	Physical	Inorganic adsorbent like silica and alumina or organic cellulose, graphite,	(Ścigalski & Kosobucki, 2020)
5	Polymer-based chelating ion exchange	Physicochemical	In acidic condition used for removing Cr(VI) an ionic condition with amine is used.	(Berber, 2020)
6	Adsorption by biopolymers	Physical	It used containing cellulose, chitosan, chitin, lignocellulose	(Dula et al., 2014)
7	Adsorption by hybrid clay material	Physical	Natural organic clay like red clay, acidic activated kaolinite, sodium montmorillonite and EDTA	(Dula et al., 2014)

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8	Polycrystalline hematite	Physicochemical	Physical adsorbate by iron also reduce Cr(VI) to Cr(III)	
9	Biosorbant	Biological	After fungi is die it used for adsorption of Cr(VI), to reduce Cr(VI) to Cr(III) chlorella miniata algae is used.	(Ghosh & Mitra, 2018)
10	Nanotechnology	Bio Physicochemical	Chemical, physical and biological method used. Zero-Valant iron nanopartic is common used. Challenging is it dispose material away treated water.	(Mitra et al., 2017)

(source: Mitra et al., 2017)

2.4 Bio Fuel Cell Technology

Electrochemical full cell has double uses one is treating wastewater and the other is generating electric in the process (Munoz-Cupa et al., 2021). The generation of electric emerging is due to the action of electroactive bacteria. Oxygen free anode is immerse into the water which content biofilm of bacteria growth. Wastewater (Miran.W, et al., 2018) are used as substrate for the growth of electro active bacterial. In microbial full cell bacterial metabolize organic wastes (G. Wang et al., 2008), sulfamethoxazole (Miran.W, et al., 2018) and germs are also eliminated in the process. When bacteria metabolize wastes they release electron in to the surrounding where electron transferred by directly, by mediators or by nanowires (Environ et al., 2012). In order to full the circulation of current reaction have to occur in both at cathode and anode. In small scale or in laboratory potassium hexacyanidoferra (III) is mostly used as last electron recover. If the hazard potential due to the gases formed can be reduced by skillful operation, an operation without a membrane is also possible and NaOCl formation takes place directly in the undivided reactor (Brankovic & Stevanovic, n.d.2013).

In industries wastewater contained different elements or waste material among this metal is the one which cause great pollution in the environmental. Most of metals are heavy metals which released from the factory by linkage of process or from solution of washing like and treatment. There are different kind of treatment mechanism those are biological, chemical and biological are used for removing of metal. The mechanism of treatment can be chemical precipitation, coagulation-flocculation, adsorption, membrane filtration and electrochemical treatment technologies (Fu & Wang, 2011).

Bio fuel cell have multiple purpose which can treat wastewater as well it generate electric city during the processes due to the action of electron generation and movement in the cathode and anodic reaction. It is promising new technology and it is cost feasible with environmental friendly way of treating water by generating energy. In anode of MFC microbial or bacteria are used to generated electrons and proton during metabolizing of wastewaters and on cathode electron generated are transferred by external circuit (Ankur & Shipra, 2018).

2.4.1 Working Principle of Bio Fuel Cell

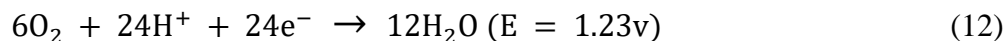
In these method electro active bacterial are anaerobically metabolize organic waste material and release electron in the process. This type of electro active microbial have ability to integrate with electron surface treat conduct charge and they are act as electron donors or acceptor (Sophia & Romero, 2018). Two reaction is occurred one is at anode and these is where biofilm produce electro and generated electron transferred to the other side called cathode then in processes electric produced due to the transferred of electron (Mathuriya & Yakhmi, 2014). Once electron generated at anode electro active bacteria transfer the electron by direct contact, conducting wire or redox mediators or electron shuttle microbes sometime use combination of transferring methods (Raouf MS & Raheim ARM, 2016). Organic matter is oxidized at anode and paired with the reduction of oxygen at cathode, some element or compounds like nitrate, permanganate, persulfate, dye molecules and heavy metals are used for the improve or electron accept at cathode (Raouf MS & Raheim ARM, 2016).

At cathode reduction deposit of electron are formed on surface of cathodic material used the deposited particle are removed by different mechanism (Song et al., 2019). Way of removal on the cathode reduction are chemical precipitation and electrochemical reduction, bio cathodes mechanism can be metal removed by bio reduction, bioaccumulation, bio sorption, bio mineralization (Colantonio, 2016). Metal recovery or removal can be performed by single or double chambered MFC (Saravanan & Karthikeyan, 2018). Anodic chamber contend organic matter and electron release microbe whereas cathodic chamber is where removal or metal occurred. Removed metal can be iron, cadmium, zinc, cobalt, copper, silver, chromium and other heavy transition metal.

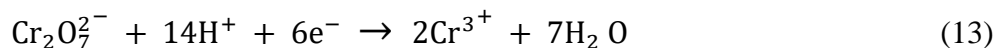
2.4.2 Bioelectrochemical Fuel Cell for Chromium Removing

The two way of fuel cell preparation for removing of heavy metal which mean double and single chamber bio electro chemical fuel cell can effectively remove metals (Saravanan & Karthikeyan, 2018). In which cathodic chamber is where reduction occurred and the anodic chamber is where microbial degrade organic waste and release carbon and electron from waste matter (Mathuriya & Yakhmi, 2014). Produced electron at anodic chamber are moved in to the cathodic chamber through external circuit.

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For chromium reduction toxic Cr (VI) used as electron acceptor and the reaction look like;



Using bio electro chemical fuel cell removing of chromium was achieved by reduction of Cr(VI) in to Cr(III) which deposit on cathodic surface with 1600mW/m² power density and complete remove of Cr(VI) influent concentration of 100mg/L in six day and six hour (Wang et al. 2008). When graphite used as cathode 92.8% of Cr(VI) is removed in 10hrs. With 108mW/m² power density (Zhao et al. 2009).

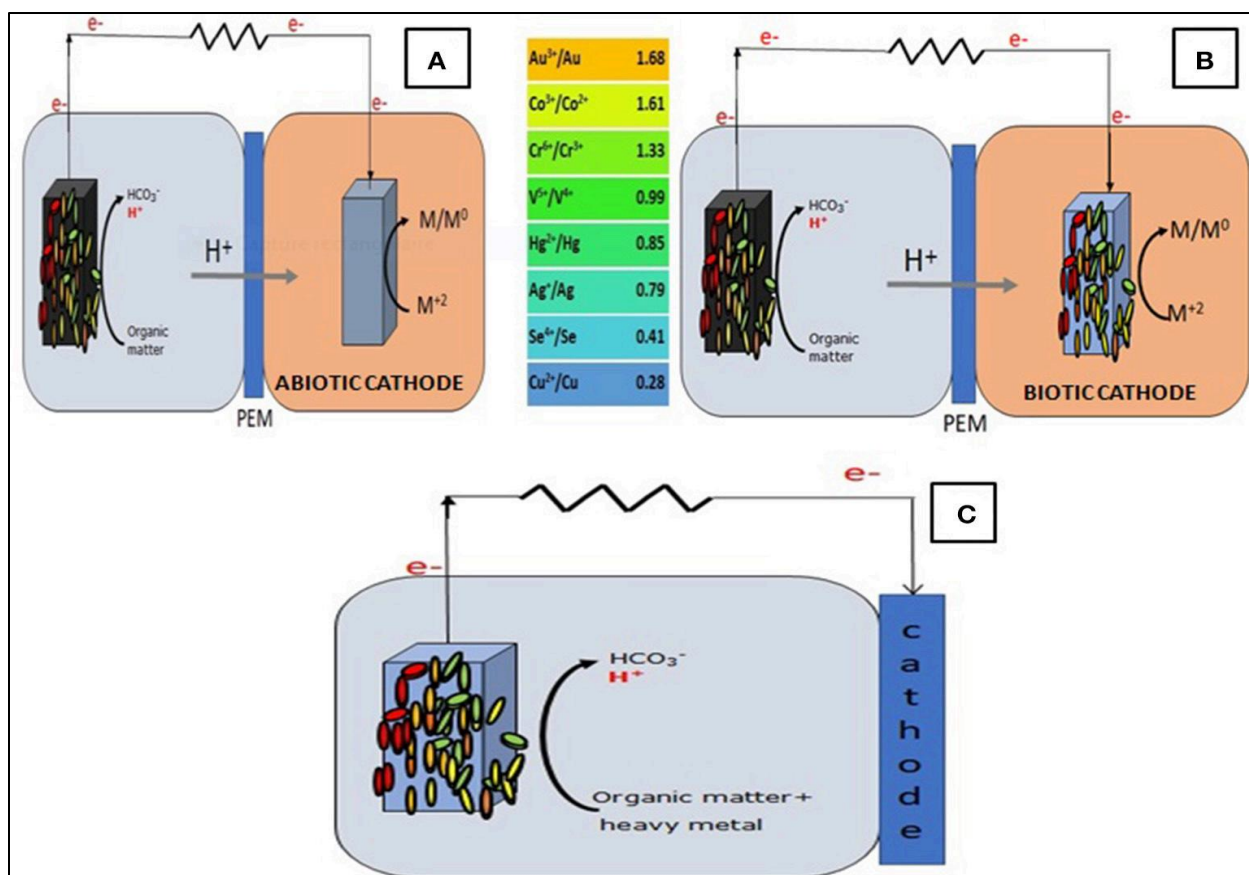


Figure 5 : Abiotic, biotic and air double chamber MFC principle for removal of heavy metals (Ezziat et al., 2019).

Double Chamber

Chromium found in different valance state, one is very toxic Cr(VI) which have to be reduced in to Cr(III) less toxic state using bioelectrochemical mechanism. Which happen by anodic and cathodic reaction. Double chamber has separate chamber of anode and cathodic chamber by membrane. This type of chamber has easy to investigate effects of factors by control other less effect parameters. Using graphite plate electrodes maximum of 150mW/m^2 power density is produced at rate of redaction $0.67\text{g/m}^3/\text{h}$ in Cr(VI) amount of 200mg/L by using of less cost salt bridge than expensive membrane Nafion (Ezziat et al., 2019). The removing mechanism is in cathodic chamber where reduction and deposition is occurred. Also removing can occurred by precipitation and reduction of Cr(VI) to Cr(III) these mechanism is done in abiotic cathode chamber (Colantonio, 2016). Whereas in biotic cathode chamber removing done by bioaccumulation, bioreduction, bio sorption and bio mineralization (M. S. Wu et al., 2017).

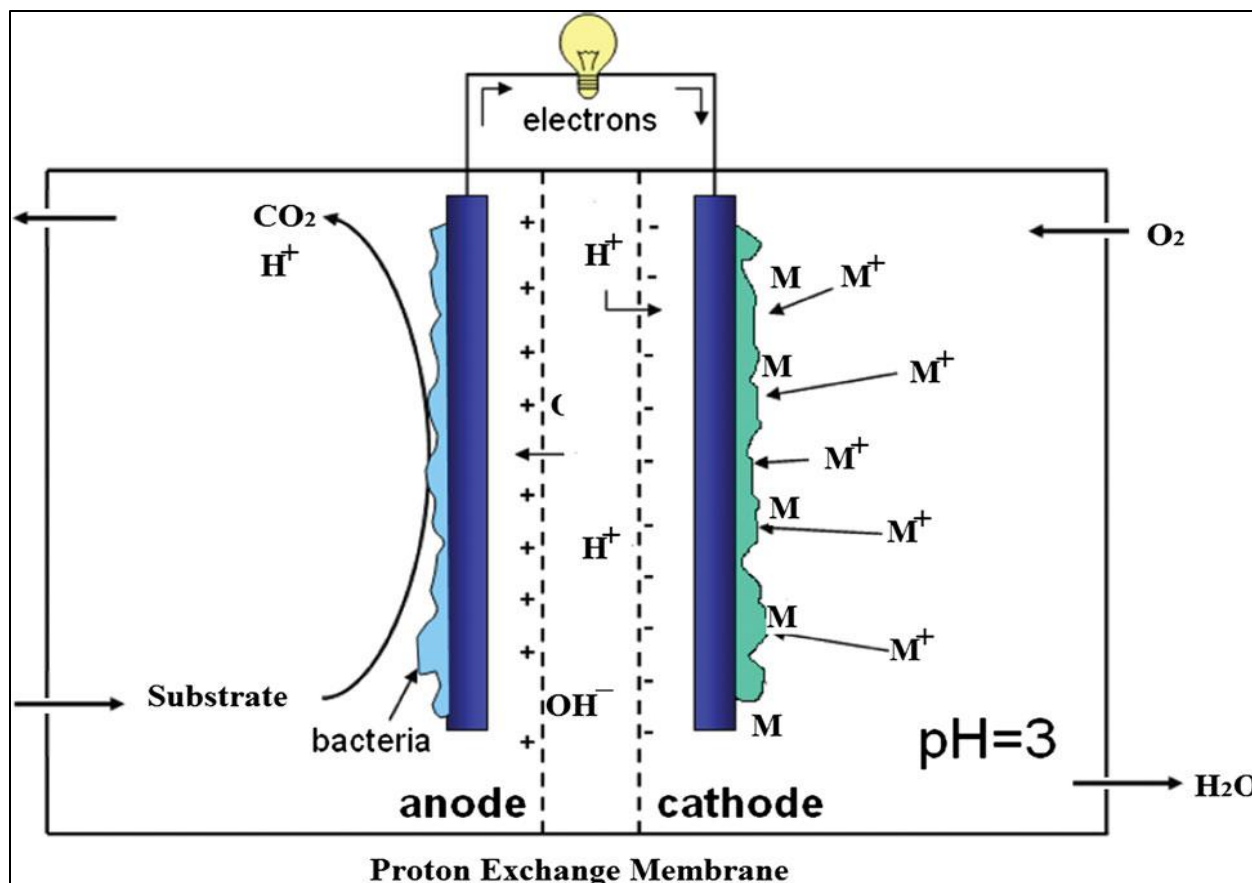


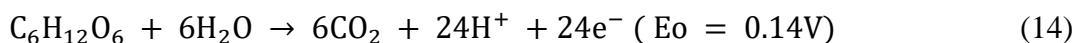
Figure 6 : Heavy metal removing by MFC where produced electron and proton at anode pass to cathode by external circuit and proton pass through membrane (Mathuriya & Yakhmi, 2014)

2.5 Factor Affecting the Performance of BECFC

There are different factors which affect the performance of BECFC in the process of metal removal as well as in the generation electric (Mustakeem, 2015). These factors has great role on the efficiency of removal of chromium from wastewater and factors are; concentration, pH, terminal electro accepter, anodic chamber, configuration, type of permeable electron membrane, electron material and time it take for treatment (Mustakeem, 2015). Among this factors time of treatment, concentration of heavy metal (Cr) and pH has major effects.

2.5.1 Anodic Materials

Anodic material selection is improve for microbial and to improve the interaction of surface of electrode and current collection. Materia to be anode it have to be stable, highly conductive, biocompatible and able to create a large surface area. Carbon based material are preferred as anode those are graphite rods, graphite plates, graphite felt, carbon cloth, carbon brush, carbon paper and other carbon based material are used (Beretta et al., 2020). At anode chamber oxidation reaction occurred when glucose is used as electron source or substrate the following reaction occurred (Bagchi & Behera, 2020).



2.5.2 Cathode Materials

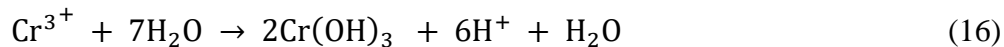
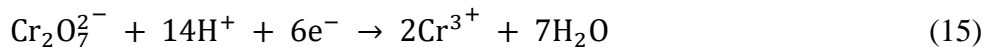
Cathode is where electron are transferred though external circuit. Some characteristics of cathodic material used for BECFC are mechanically strong, high conductive, possesses catalytic properties (Mustakeem, 2015). Cathode can be abiotic (either aerobic or anaerobic) and bio cathodes from all kind of cathodic material platinum is used mostly (Chandrasekhar et al., 2021). Cathodic electron accepter is one of factor which affect performance of BECFC. Oxygen is most common electron accepter due to ready availability, high oxidation potential and advantage of producing clear water as oxygen reduced (Logan and Regan, 2006).

There are three cathodic chamber type those are cathodic with biotic, abiotic cathode and in air cathodes (Badessa et al., 2020). Abiotic cathodic is which not involve microorganism for removing of heavy metals this type of cathode involves catalyst like platinum for oxygen reduction. But this catalyst through long time cause posing and stability of operation decrease. To overcome these

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drawbacks of abiotic cathode there is new type of cathode which is biotic cathode. Which involve microbes for facilitating of metal reduction or removing. The importance of bio cathode are; cost of catalyst reduction, avoid poisoning caused by Pt and sulfur (Mekuto et al., 2020). The drawback of biotic cathode is that it stabilize after 8 day of operation and its power density and coulombic efficient is higher 430W/m³ and 59.6% while abiotic is 257W/m³ and 15.6% (Ezziat et al., 2019). The common biofuel cell is double chamber with separate anaerobic anode and cathode to avoid contamination of anode which contained microbial. But in practical world both metal and organic matter co-exist together in the same wastewater (H. Wang & Ren, 2014). To avoid this some recent research focused on single chamber micro fuel which contain both organic matter and contaminate. In different studies as amount of metal found in wastewater increase amount of power produced is increased but some time it rivers when high concentration of metal inhibit microbes like 10g/L of Cr(VI) (Ezziat et al., 2019).

In the cathodic chamber heavy metal like chromium is reduced in to its low oxidation state and became less toxic and deposit on surface of cathode. Reaction occurred when pH is in range of 6.5 and 10 are (H. Wang & Ren, 2014);



2.5.3 Treatment Time

Wastewater treatment time which called retention or residence time is the time that influent wastewater stay in treatment reactor. Which has formula of;

$$HRT(h) = \frac{\text{hydraulic volume}(L)}{\text{permeate flow}(\frac{L}{h})} \quad (1)$$

Where HRT is hydraulic retention time in hours L is liter and h is hour. As HRT increase bacteria for acclimate the reactor in biotic wastewater treatment reactor. In MFC power density generated is decrease as HRT increase above optimum under batch but in continues reactor power generate increase for 8 to 13 days (Munoz-Cupa et al., 2021). In wetland for treatment of wastewater rate of inflation is reduced in low sand content though highest growth rate is obtained under small HRT (below one days) (Sirianuntapiboon et al., 2006, P1).

2.5.4 Substrate Concentration

Microorganism degrade organic material of waste water, whereas inorganic compound COD of wastewater has role on efficiency of MFC. For more amount electron production from organic waste they have to be digested well by microbial (Krieg et al., 2017). The composition of wastewater has their own effect on the amount of electron generated that mean non-fermentable organic compound like glucose is more suitable than fermentable substrate like brewery material (Munoz-Cupa et al., 2021, P13). The dissolved rate of heavy metal decrease as suspended solid and concentration of heavy metal in waste wastewater increase. This decrease the rate of removal and redaction of heavy metal (Ida & Eva, 2021, P8).

2.5.5 Effects of pH

pH value determine the acidity and basicity of wastewater and this value has effect on treatment of wastewater and generation of electric power. The rate of proton exchange in between anode and cathodic chamber of fuel cell has some effects on performance of treatment. One of the reason is as much H^+ accumulate in anode make the chamber acidic and inhibit the growth of microorganism and the second case is alkalinity of cathodic chamber is occurred due to more reaction of H^+ in chamber with excess oxygen and it decrease electric generation due to reduction of O_2 potential in abscisic condition (Samsudeen et al., 2015).

2.6 Role of Microorganism in Chromium Removing from Wastewater

Microorganism which used in method of bioelectrochemical fuel cell for chromium removal is electro active microbial mostly they are bacteria. Organic compound can be digester and oxidized and their electrons are transferred to anodic electrode the mechanism is electric gens. Different electric gens are on the moment were discovered and most of them are protobacteria and firm cutes (Cao et al., 2019). They play different role in nature of metal circulation distribution which can be by assimilation, dissimilation and bioremediation of metal.

The role of microorganism in chromium removal are; bio sorption, remove by anaerobic and aerobic bacteria, uptake by bacteria, by oxidation reduction due to electron release in process of metabolism (H. Wang & Ren, 2014). Very toxic form of $Cr(VI)$ is reduced into less toxic form of chromium valance three by microbial in their process of metabolism. This occurred when

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bacterial generate energy from metal and metalloid proton donation or accepting. The table below shows summary of some microbial use for wastewater treatment.

Table 4: Use of microorganism in wastewater treatment of micro fuel cell

Microorganism	wastewater treatment
<i>Pseudomonas aeruginosa</i>	Synthetic
<i>Geobacter, shewanella</i>	Brewery
Proteobacteria, Bacteroidetes	Biorefinery
<i>Shewanella oneidensis</i>	Landfill
<i>Geobacter sulfurreducens</i>	Leachate
Mixed culture anaerobic sludge	Paper mill, Azo dye, spent caustic, municipal
Mixed culture dairy wastewater	Agro-food, industry, kitchen

Source (Munoz-Cupa et al., 2021, P9)

Bacillus Cereus

Bacillus cereus is type of electro-active bacteria which find in different environment like fruit, soil and vegetable. They are rod shaped gram-positive facultative anaerobic bacteria and they cause food related health problem and on the other hand they have benefits in decomposition of wastes (Waffa et al., 2016 P1). Those microbial are endospore forming bacteria that live in range of environmental temperature which range 5 to 50⁰C (Guinebretière et al., 2008) (Kabite et al., 2012). In wastewater treatment *B.cereus* remove 50.68% COD and 44.07% BOD within seven days while wastewater pH is in range of 6.7 to 8.54 (Gawai et al., 2017). And this microbial remove 66% of NH₄⁺-N and 61% of NO₃⁻-N from domestic wastewater (Rout et al., 2018). Anti-methanogenic and electroactive properties of *Bacillus cereus* power generation from wastewater using MFC increase (Islam et al., 2017).

2. 7 Summary of Literature Review

In the literature review about Industrial wastewater, dying industry wastewater, wastewater treatment technologies and heavy metal removing, chromium removing technology and bio fuel cell technology for removal of heavy metal are revised and. To see some of revised technologies their strength and draw back, Electro coagulation which has advantage of easy for operation, amount of sludge effluent is low and it can't affected by pH change because it has the buffering ability and its drawbacks are, electrode used can easily corrode, through time cathodic efficiency is decreased due to formation of oxide layer and it require high energy consumption (Pokhrel, 2017). Other technology is oxidation process from this type Fenton is the one, homogenizes Fenton has advantage of no energy input needed, high efficiency, simple and flexible and it has also disadvantage of strict on pH, large Fe^{2+} needed, high amount of sludge containing iron generated (Du et al., 2020). Anodic oxidation is other form of electrochemical oxidation method and it has advantage of high distraction efficiency of heavy metal, versatility and flexibility (Bi et al., 2017). Whereas high operational cost and less low organic ligand treatment efficiency is its drawback (Bi et al., 2017). The other type of electrochemical oxidation for treatment of heavy meal like chromium from wastewater is photo catalyst oxidation technology. And advantage of TiO_2 based photo catalyst are mineralization of organic waste, adsorption of metal on photocatalytic. The limitation of TiO_2 based photo catalyst is it need pay attention on oxidation since anode require prevention of photo damage.(Do et al., 2020). Other more technologies are revised in tables in this chapter and bioelectrochemical fuel cell has more advantages than that of revised.

Bioelectrochemical fuel cell is new promising and futuristic technology which has multiple purpose which can generate electric city from wastes during treating wastewater. Generated electric reduce cost of energy of operation which is the main drawback of other technologies and it is environmentally friendly since it not use chemicals catalysts in process of treatment. The two way of fuel cell preparation for removing of heavy metal which are double and single chamber bio electro chemical fuel cell can effectively remove metals. In which cathodic chamber is where the reduction occurred and contain removable toxic heavy metal and the anodic chamber is where microbial reduce the size of material (organic waste) which are digested the material and serve as carbon and release electron from waste matter (Mathuriya & Yakhmi, 2014). Using bioelectro chemical fuel cell removing of chromium was achieved by reduction of $Cr(VI)$ in to $Cr(III)$ which

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deposit on cathodic surface with 1600mW/m^2 power density and complete remove of Cr(VI) influent concentration of 100mg/L in six day and six hour (Wang et al. 2008). When graphite used as cathode 92.8% of Cr(VI) is removed in 10hrs. With 108mW/m^2 power density (Zhao et al. 2009). In this research using Bioelectrochemical fuel cell how much the methodology is efficient was studied at three different point of three selective affecting parameters (time, pH and concertation of chromium).

Chapter Three

Materials and Methods

3.1 Materials

For construction and operation of Bioelectrochemical fuel cell different materials and chemicals were used. Most of the chemicals and materials are purchased from local market and measuring instruments are used from AAiT environmental, bio and analytical laboratory. Materials are; Graphite rod electrodes (1cm diameter 10cm length), 470ohms resistor, 1mm cemeter copper wire, American product gasket maker, 1.7cm diameter PVC tube. And chemicals are; laboratory standard Potassium Dichromate (99.5%, $K_2Cr_2O_7$, Nice chemical PLC.), 0.1N HCl , 0.1N NaOH, 99% Dextrose anhydrous (glucose $C_6O_6H_{12}$, Neolab life science co., Effective laboratory supplier), Agar powedr (Labtech chemicals supplier), Nutrient broth (HiMedia laboratories PLC.) and Potasium chloride (KCl, 99.5%, TMMEDIA supplier) their stock forms were used for preparation requested solution. These listed materials are common used material and chemicals in the research but other chemicals, materials and measuring instruments were specified in respective of methods.

3.2 Methods

3.2.1 Multiplying Bacillus Ceruse

There are different electro active bacteria can be used as bio material for micro fuel cell. Some of them are bacillus ceruse, bacillus karlensis, bacillus subnils, micrococcus luteus, micrococcus varians, enlerabacrer intermedius and rarumellla terrea. Among those bacillus cereus (X. Wu et al., 2018) was preferred since it has best efficiency of chromium removing and it find in food, vegetables, and soil, which make it easy for separation and culturing. For this research Bacillus ceruse was taken from Ethiopia Institute of Bio-Diversity and multiplied in AAiT bio laboratory. The transportation of the BC was in sterilized specimen container in ice. The transportation based prevention the damage and loss of the specimen, avoiding health related problem if the microbial spilt and spray on human body and minimize delay of microbial (Wilson, 1996).

Media used for enumerating bacillus cereus is nutrient agar and broth, the main ingredients of the media are peptic digest of animal tissue, sodium chloride, beef and yeast extract, adjusting pH in

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between 7 to 7.5 at room temperature. Media was prepared by adding 28gms of nutrient agar in 100ml distilled water, then the solution heated and stirred for well dissolution. Nutrient media was sterilized in autoclave at 15psi and 121°C for 15 minutes, then cool down to 30°C. Using Aseptic technique the sample of microbial was cultured on sterilized petri dish. After 24hrs Pure cultured *Bacillus Cereus* checked and multiplied in nutrient broth. The multiplication was done in six test tube by adding one colony of cultured microbial into the tubes and shaken at 10000rpm for 2 minutes and placed in shaking incubator at 30°C for 24 hours (Yu et al., 2020). Then at 4°C *Bacillus cereus* was stored in the refrigerator until it was used for Bioelectrochemical fuel cell. Microbial used for *Bacillus cereus* for BECFC was enumerated to know how much cell number was effectively remove chromium from wastewater. Method used for enumeration was Viable count of quantification of colony formation (CFU/ml of sample). To do this 8 consecutive dilution of sample was prepared and the number of colonies were counted using hemocytometer (Arana et al., 2013, P2).

$$\frac{\text{CFU}}{\text{ml}} = \frac{\text{colonies average}}{\text{volume ml}} \times \text{Dilution factor} \quad (2)$$

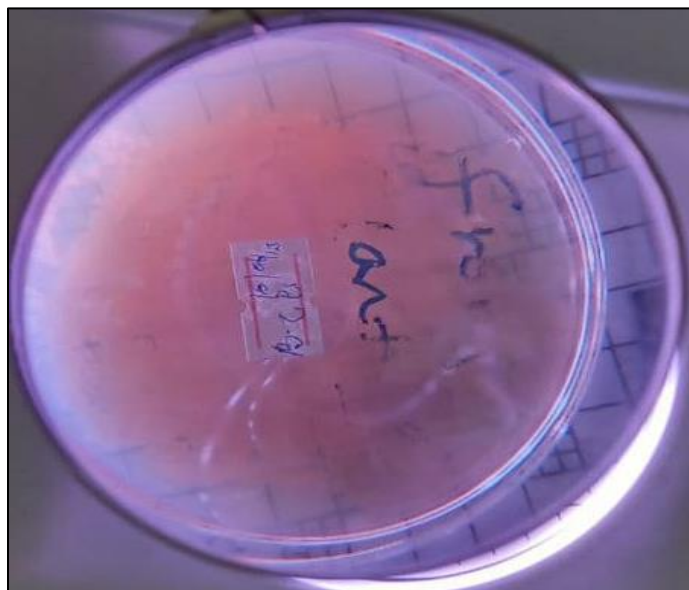


Figure 7: Pink orange colored pure *Bacillus cereus* in petri dish view by magnifying glass.

3.2.2 Synthesizing Chromium Wastewater

Synthetic wastewater containing chromium was prepared using distilled water and potassium dichromate based on real dyeing industry wastewater. 1g/L of Cr(VI) synthetic solution was prepared by dissolving 2.83g analytical grade $K_2Cr_2O_7$ in 1000 ml of distilled water based on American Public Health Association (APHA) method (APHA, 1992). The stock solution was further diluted with distilled water to desired concentration of test solution (Zhao et al., 2012). For varying pH of solutions 0.1 N HCl and NaOH were used depending on the basicity or acidity of the sample solution (Badessa et al., 2020). Dilution of other 3 solutions from stock solution 1mg/L Cr (VI) were done using equation:

$$C_1V_1 = C_2V_2 \quad (3)$$

Where: C_1 and C_2 stands for concentration one and two respectively, V_1 , V_2 represent volume one and volume two respectively.

Glucose which used as carbon source for *Bacillus Cereus* was dissolve in distilled water (7g/L) and autoclaved in autoclave (new model electric heated vertical steam sterilizer) for disinfection of the solution at 120°C and 15Psi for 15minuts. Then synthesized chromium added into cathode chamber as electrolysis and final electron whereas Glucose solution was added into anodic chambers acceptor which used as carbon source for *Bacillus cereus* and electron and H^+ released during microbial metabolizing.



Figure 8: Different concentration of Cr(VI) solution

3.2.3 Reactor Set-up and Operation

The set-up of the reactors were H-shaped double chamber fuel cell reactor which shown in figure 8 blow. Individual reactor consist of pair of 600ml plastic bottle which used as cathodic and anodic chamber and filled by solution up to 500ml. Two chamber of the reactor was connected by tube (PVC, 7cm length and 1.7cm diameter) which contend salt bridge made of 7.5gm KCl and 3gm agar, the salt bridge used as source of ions and preserve neutrality of both chamber electrolyte. Rode shaped graphite (length 10cm, diameter 1cm) were used as cathode and anode electrode. 25cm length copper wires were served as external wire for electron transfer from anodic chamber into cathode chamber and 470ohms resistor (proto supplier) (Brunetti.G et al., 2017) was used in-between for balancing of current flow. The selection of resistor mainly based on amount of power generated from the system. When resistor amount is to small it can't function well for regulation of current follow and in revers when resistor amount is to high it block the system to function properly it resist current follow. Considering this and availability of material in market 470ohms was selected as appropriate (Mitra.S et al., 2017). Anodic chambers were anaerobic and filled with autoclaved 500ml Dextrose solution ($7\text{g/LC}_6\text{H}_{12}\text{O}_6$, Effective Laboratory supplies PLC.), that served as source of carbon for microbial and electrolyte (Najafpour, 2015). Cathodic chamber were aerobic and filled with 500ml synthesized chromium wastewater solution that served as cathodic electrolyte and Chromium is final electron acceptor. After set-up was finished gasket maker (Black RTV Silicone, American standard) was squeezed around connecting tube to prevent linkage of electrolyte from chambers. At the last, respective electrolyte solution were filled the chambers and 1mL (900,000CFU of microbial) of cultured *Bacillus Cereus* was pipetted into anodic chamber and covered well by its coverage and gasket maker was squeezed around hole of wire inter the chamber to block iterance of air. The system were operated at constant temperature 30°C in water bath by varying time from 8 hours up to 24 hours with 8hours interval(Thermostat, Wise team supplier). And after Cr(VI) reduced and settled down at the bottom of chamber it can easily remove from the system and used for other process of recovering the metal. Recovering of the metal was out of the scope of the research but it can be recovered by purifying impurities from the metal (Kanagaraj et al., 2008).



Figure 9: Full set up of Bio Electrochemical Fuel Cell used for Cr treatment

Labels on the reactor represent; A stand for resistor, B copper wire, C synthetic waste water, D plastic bottle, E cathode electrode, F carbon source solution with microbial, G salt bridge and H anode electrode.

3.2.4 Experimental Design

From different Experimental designs in this research Surface Response Methodology (RSM) of Box Behnken Design (BBD) was used with three selected operational parameters. RSM is used to analyze the interaction effects between parameters. Other roles are appropriate in problem-solving for engineering optimizing and developing (Mäkelä, 2018). It is a popular method used for optimization in different experimental designs and processes. RSM implements different designs as Box-Behnken design (BBD), fully factorial design (FFD), and central composite design (CCD) (Yolmeh & Jafari, 2017). Box-Behnken design (BBD) is a second-order response design that is more precise and time-saving to apply than other RSM. BBD is easy to get large experimental trials within few runs. Independent variables and response of the experiment was related by second-order polynomial equation.

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Two equation written blow indicate equation 4 general second-order equation of BBD, and equation 5 is equation used in BBD to calculate number of runs.

$$Y = B_0 + \sum_{i=1}^3 B_i X_i + \sum_{i=1}^3 B_{ii} X_i^2 + \sum_{i < j}^3 B_{ij} X_i X_j + \varepsilon \quad (4)$$

$$N = K^2 + K + C_p \quad (5)$$

Where B_0 is constant, B_1, B_2, B_3 are coefficients and X_1, X_2, X_3 are selective parameters. And Equn.3, N stands for the number of runs, K selective factors, and C_p is the central replication point (3) (Kassahun et al., 2017). In this research, each selected parameter has three identified testing areas. And based on the equation of Box Benken Design for three central replication number of runs are fifteen. Design-Expert version 11 was used for linear regression and analysis of variance, experimental result model of equation, quality of fit were done by using R^2 , adjusted R^2 , predicted R^2 and coefficient of variance (Gebregziabher et al., 2021). Selected three important parameters were time labs, concentration of chromium in the solution and pH, for each parameter three different levels were identified based on previous related works (C. Zhao et al., 2012). Targeted point of treatment were concentration at 5, 10 and 15 mg/Lt, time at 8, 16 and 24 hours and pH 5, 7 and 9.

Table 5: Selected testing points of parameters

Factors	Levels		
	Low point	Mid-point	High point
Time in hours (X1)	8	16	24
Concertation in g/L (X2)	5	10	20
pH (X3)	5	7	9

The above three parameters were selected based of their high effect (which referred in literature part) on the removal or wastewater and based on the real wastewater characteristics. Most real wastewater of Ethiopian painting industries has variety of concentration and pH (Woldeamanuale, 2017) so it was important in this research to target both parameters. Whereas time has effect on

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microbial growth and efficiency of chromium removal, the effect these parameters were checked during preliminary laboratory work and they has great effect relative to other affecting parameters.

After each run data were recorded using UV spectrophotometry (Double beam PC 8 scanning Auto cell UVD-3200, LABOMED,INC) to read amount of chromium removed. The step of spectrophotometer operation were; first blanking de-ionized water, set wave length at 450nm then after calibrating the instrument different chromium absorbance were recorded (Berihun, 2017). Beer equation were used to calculate concertation of chromium from Absorbance.

$$A = CLe \quad (6)$$

Where C is concentration of chromium in solution, e is molar absorptivity of chromium derived from calibration curve ($2.0700 \times 10^4 \text{L/mol.cm}$) and L is path length of light travel (1cm). (Suvardhan et al., 2005). Efficiency of treatment can be determined by equation;

$$\text{Efficiency of Cr removal} = \frac{C_0 - C_f}{C_0} \quad (7)$$

Where Cr is chromium, C_0 and C_f indicate before and after removal of concentration of chromium.

3.2.5 Determination of Optimum Operation parameters and Verification on synthetic wastewater

The best optimum operation parameters were estimated using BBD of Surface response methodology and verified on synthetic wastewater. For three factors and three level of operational parameters the specification criteria of optimization was taken referring real wastewater of painting industries and previous research works. Selected specified operation parameters were; specifying time of treatment in range of the lowest and highest time (8 - 24 hours), this because of that the time range taken in the research was economical feasible and it is possible to take in range. The other specifications were concentration and pH of treatment, the concentration and pH of real wastewater of sample taken painting industries (Nifas Silk PF.) wastewater is (8.75mg/L and 6.95 respectively) due to this the estimation of optimum operation parameters of both concentration of chromium and pH were targeted at practical wastewater characteristic. After optimum operation parameters were determined using statistical software tool of Design-expert, optimum operation parameters were verified twice in laboratory on chromium contained synthetic wastewater and the average result of verifications were used as result of verification.



Before treatment



After treatment

Figure 10: Removal of Chromium from wastewater before and after treatment (Cr (VI) was reduced, attached to cathode electrode, detached and settle down).

3.2.6 Characterizing Real Wastewater and Verification of Optimum

Operation Parameters on Real wastewater

Actual wastewater of painting industry was collected from Nifas Silk painting industry and characterized in AAiT Environmental laboratory. The common characterizations performed and technique and instrument used for measuring were; color, turbidity (measured using 2100N turbidimeter) and total suspended solid, COD (HI 839800 COD reactor, Nanocolor 400D) , pH (3505 pH meter), chromium contain (spectrophotometer), conductivity (DT9205A digital multimeter), BOD and density (density bottle method) (Xiang et al., 2016). Both COD and BOD are common determinant of organic characteristic of wastewaters. BOD measure biochemical oxygen demand that mean if high amount oxygen is demanded BOD is high and microbial needs high amount of oxygen to decompose organic matter which mostly measured after 5 days (APHA 5210 B method). COD is chemical oxygen demand and it takes few hours unlike BOD tests. The test of COD (APHA 5220 D method) need some chemical standards (0.25N $K_2Cr_2O_7$ as oxidizer, 50% H_2SO_4 for acidic condition, silver sulfate as catalyst and mercury sulfate for eliminate chloride interferences). Some common ratio between COD and BOD which help for prediction of BOD by testing COD independently are for food process wastewater 2:1 and textile and dying industries COD: BOD is 5:1 APHA standard (Bod, n.d.). The ratio indicate the property of wastewater which mean if the ratio is high it indicate more inorganic material are available in the wastewater. And the ratio is used to estimate one of them and to predict the other. To get the two result in short hours COD is measured and BOD is calculated based on their ration and during the shortage of chemical for testing of COD, BOD is measured and COD is estimated based on the ratio. Also the ratio is important to check how much the result recorded is fitted with the standards ratio and to take corrective action if missed from the ratio (Attigobe et al., 2009).

Nifas Silk painting industry wastewter was selected because the factory is the oldest and the largest painting industry in the country and release relatively high amount of chromium (9mg/L) than other painting industries (Woldeamanuale, 2017). Sample of wastewater was randomly taken from the factory effluent stream. Process of determining (Colorimetric method 7196) concentration of chromium in industry wastewater involves some reagent. To determine amount of chromium wastewater of painting industry, 10ml of sample wastewater was measured and diluted 10 time to avoid effect of other ion and turbidity of real wastewater (Soares et al., 2015) then 0.005% 4-

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aminoantipyrine and 0.5ml of 0,1% of 1-naphthol was added in to the sample at oxidizing acidic media, after solution was formed at 450nm wave length solution contend was measured by spectrophotometers (Suvadhan et al., 2005) and to gat chromium concentration of the sample dilution factor was multiplied with obtained result. And it was treated in laboratory at verified optimum operation parameters using BECFC. The importance of verification of real wastewater was to determine the effectiveness of the methodology on actual wastewater.

Chapter Four

Result and Discussion

4.1 Laboratory Result

Based on the methodology of the research different laboratory experiments were performed. Microbial (*Bacillus Cereus*) which used as bio material for generation of electron from organic materials was brought from Ethiopian Bio Diversity institute and its purity was checked by culturing on petri dish and After 24 hours the result show that pure pink orange bacillus cereus grew on petri dish. referred elsewhere(Liu et al., 2020) and on controlled petri dish no external microbe growth was found which show no contamination of microbial. During multiplication of BC from six test tubes three of test tube were found pure and in the rest of three test tubes some impurities settled were investigated which may occurred during transferring of microbial from cultured petri dish in to test tube. Then the three pure test tubes were used for experiment investigation of chromium removing using BECFC. And 900,000 colony forming unit of BC were enumerated in 1mL of microbial sample which used for one reactor referred elsewhere (Campinas & Alimentos, 2012, P3). This indicate that 900,000CFU of *Bacillus cereus* were added into 500mL of anodic solution to generate the electron and hydrogen ions. During preparation of synthetic wastewater with different pH and concentrations, yellowish-colored solution was formed for low concentration and the color becomes orange-reddish when the concentration of the solution is more than 200mg/L (Verger et al., 2018). As stock solution 1g/L of chromium was prepared and used for preparation of other needed solution and it was effective.

After the necessary reagents, material, and measuring instruments were prepared over months of laboratory works were performed until targeted results were obtained. Among the laboratory investigation checking the effect of high concentrated chromium wastewater were performed. The results of the trial show that the efficiency of Bioelectrochemical fuel cell decreased as the concentration of chromium in the solution increase more than 80mg/Lt also referred on (Tandukar et al., 2009). The other trial test was checking the effect of time on treatment. And results show that most of the treatments were achieved within one day. As the time of treatment increases, more than 24 hours salt bridge which serves as the membrane starts to link solution from cathodic

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chamber to anodic chamber and Vis verse which affects treated efficiency. Based on the result it was preferred to make time variations by 8 hours for 24 hours, referred elsewhere (C. Zhao et al., 2012).

The third laboratory trial was investigating the best amount of *Bacillus cereus* which add into glucose solution. From different amount of trial one mill liter of *Bacillus cereus* sample solution was preferred based on efficiency and cost-effectiveness.

Table 6: Experimental runs According to BBD and Result of the Removal

Run	Factors			Response	
	X1	X2	X3	Predicted Value	Actual Value
1	16	5	5	0.9887	0.988692
2	16	10	7	0.9802	0.980203
3	16	5	9	0.9588	0.958826
4	16	15	9	0.9957	0.995655
5	24	15	7	0.9754	0.975386
6	8	10	9	0.9548	0.954807
7	8	10	5	0.9561	0.956072
8	24	10	9	0.9696	0.969604
9	8	15	7	0.9449	0.944879
10	16	15	5	0.9725	0.972464
11	24	5	7	0.9517	0.951729
12	8	5	7	0.9498	0.949754
13	24	10	5	0.9753	0.975257
14	16	10	7	0.9812	0.98121
15	16	15	7	0.9822	0.982238

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As summary, three different concentration of synthetic chromium solution were prepared and treated by varying pH and time of treatment. As shown in table 6 from all laboratory runs of removal of chromium from wastewater above 95% efficient were achieved. Among all synthetic wastewater was treated best efficiency was 99.6% at pH 9 and time 16hours for 15mg/L chromium concentration in solution and the less efficient was 94.5% at concentration of 15mg/L, pH 7 at 8 hours of treatment. From the operational parameters we can see the effect of time in the higher and lower efficient of removal of chromium has great effects. The time has such effect because of that it has effect on the growth of microbial (has lag phase of 4 hours in these experiment) and has effect on reduction of chromium as time increase more chromium was reduced. To see the effect of other parameters concentration run3 (95.6%) and run4 (99.6%) in these two runs the two parameters remain constant and only the concentration of chromium is changed 5 to 15 mg/L and has efficiency difference of 4%. This indicate that as concentration increase the efficiency of removal is increasing this is due to the availability of enough chromium ion as final electron acceptor (Beretta et al., 2019, P7). The effect of pH can be shown more correlating with the variation of concentration because they has great interaction effect for instant; run1 (98.9%) and run3 (95.6%) both runs has constant time (16 hrs.) and constant concentration (5mg/L) but they have pH of 5 and 9 respectively. More chromium is reduced at low pH with 5mg/L but when we see run4 (99.6%) and run10 (97.2%) they have high concentration constant 15mg/L and pH of 9 and 5 respectively. Here more chromium was reduced at high pH value since the concentration is high. This show that pH has direct interaction effect with concentration this is due to fact that Cr(VI) is base and Cr(III) is acidic and the optimum pH redaction of heavy metal is 5 to 7(Beretta et al., 2019, P8). And high concentrated Cr(VI) reduced to more Cr(III) which mean more acid is produced and pH is reduced from pH 9 to pH 7 and the same scenario is applied for low concentration which show no more pH change occurred due to low Cr(III) is produced from low Cr(VI) (Ngoc-Dan Cao et al., 2021). The maximum efficiency was obtained in 16 hour and the result decrease in 24 hours run 4 and run 5 show. This cause is related with the reverse oxidizing of incomplete dissolution of Cr(OH)₃ into hexavalent chromium (Apte et al., 2005, P1). And also due to crack of salt bridge through time and not more much serve as preamble member which has effect of result of reading.

4.2 Data Analysis

4.2.1 Analysis of Variance (ANOVA)

Table 7: ANOVA table for Quadratic model, significant and non-significant validation

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.0034	9	0.0004	673.18	< 0.0001	Significant
A-time	0.0006	1	0.0006	995.67	< 0.0001	
B-con	0.0002	1	0.0002	349.59	< 0.0001	
C-pH	0.0000	1	0.0000	41.65	0.0013	
AB	0.0002	1	0.0002	366.98	< 0.0001	
AC	4.814E-06	1	4.814E-06	8.68	0.0320	
BC	0.0007	1	0.0007	1268.99	< 0.0001	
A ²	0.0015	1	0.0015	2764.51	< 0.0001	
B ²	0.0001	1	0.0001	194.35	< 0.0001	
C ²	0.0000	1	0.0000	63.78	0.0005	
Residual	2.773E-06	5	5.546E-07			
Lack of Fit	7.022E-07	3	2.341E-07	0.2261	0.8726	not significant
Pure Error	2.071E-06	2	1.035E-06			

Sum of squares is Type III – Partial and table 6 show that the Model F-value of 673.18 and p-value is very small that implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, BC, A², B², C² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. To camper the significance of factors time is highly significant parameters relative to others with F-value of 995.67 and from interaction effect the interaction effect between concentration and pH is

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highest with F-value of 1268.99. The reason that time is highly significant is because of that the first 4 hours no significant treatment was shown but within 8 hours gap of treatment there were high significant difference of results. Time has effect of the growth phase of microbial and on the reduction of chromium. And the interaction effect of pH and concentration was high may be due to the cause that during laboratory works 5mg/L concentration is well treated under low pH and in reverse high concentration of chromium was removed best under basic condition also referred (C. Zhao et al., 2012) this show that the two parameters has direct effect relation. The Lack of Fit F-value of 0.23 implies the Lack of Fit is not significant relative to the pure error. There is 87.26% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good and we want the model to fit. These show that model equation can help predict value.

4.2.2 Model of Fitness

Table 8 of summary of fit equation show that quadratic equation is well fit for that of all specification due to lowest p-value, no lack of fit, adjusted and predicted R^2 value is closed well. Therefore, based on BBD of Surface response method Quadratic equation is adequate for representation of experimental model for predict value

Table 8: Summary of fit of equation

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	0.3948	0.0036	0.0184	-0.5214	
2FI	0.3000	0.0037	0.1249	-1.1149	
Quadratic	< 0.0001	0.8726	0.9977	0.9953	Suggested
Cubic	0.8726		0.9957		Aliased

As shown in table 9 mean of 15 runs of chromium removal efficiency is 0.9691 which show on average the Bioelectrochemical fuel cell technology can treat 96.91% of synthetic wastewater for range of concentration in between, 5 and 15, pH in 5 and 9 and time of treatment 8 up to 24 hours. The standard of variance is very low mean that the variation of teste result is small and it indicate the error of the experiment is small. Predicted R^2 of 0.9953 is in reasonable agreement with the Adjusted R^2 of 0.9977; which imply the difference between the two R^2 is less than 0.2. Adequate

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Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. As shown from table 9 the ratio of 83.017 indicates an adequate signal. This model can be used to navigate the design space.

Table 9: Statistical fit of data

Std. Dev.	0.0007	R ²	0.9992
Mean	0.9691	Adjusted R ²	0.9977
C.V. %	0.0768	Predicted R ²	0.9953
		Adeq Precision	83.0172

4.2.3 Regression Model Equation

Actual equation of laboratory runs in term of factors is;

$$E = 1.00920 + 0.009924t - 0.006831c - 0.02385p + 0.000178tc - 0.000069tp + 0.001326cp - 0.000318t^2 - 0.000216c^2 + 0.000774P^2 \quad (5)$$

Where; E is efficiency of methodology for chromium removal from wastewater, t is time taken for treatment, c is concentration of chromium in wastewater and p is pH of wastewater. Equation (5) in terms of actual factors can be used to make predictions about the response for given levels of each factors. Here, the levels should be specified in the original units for each factors. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space. Fitness of this equation can be more justified using diagnostic plot blow (figure 11-14). The graphs show that the actual and predicted values are close to each other within limited boundary.

4.2.4 Diagnostic Plots

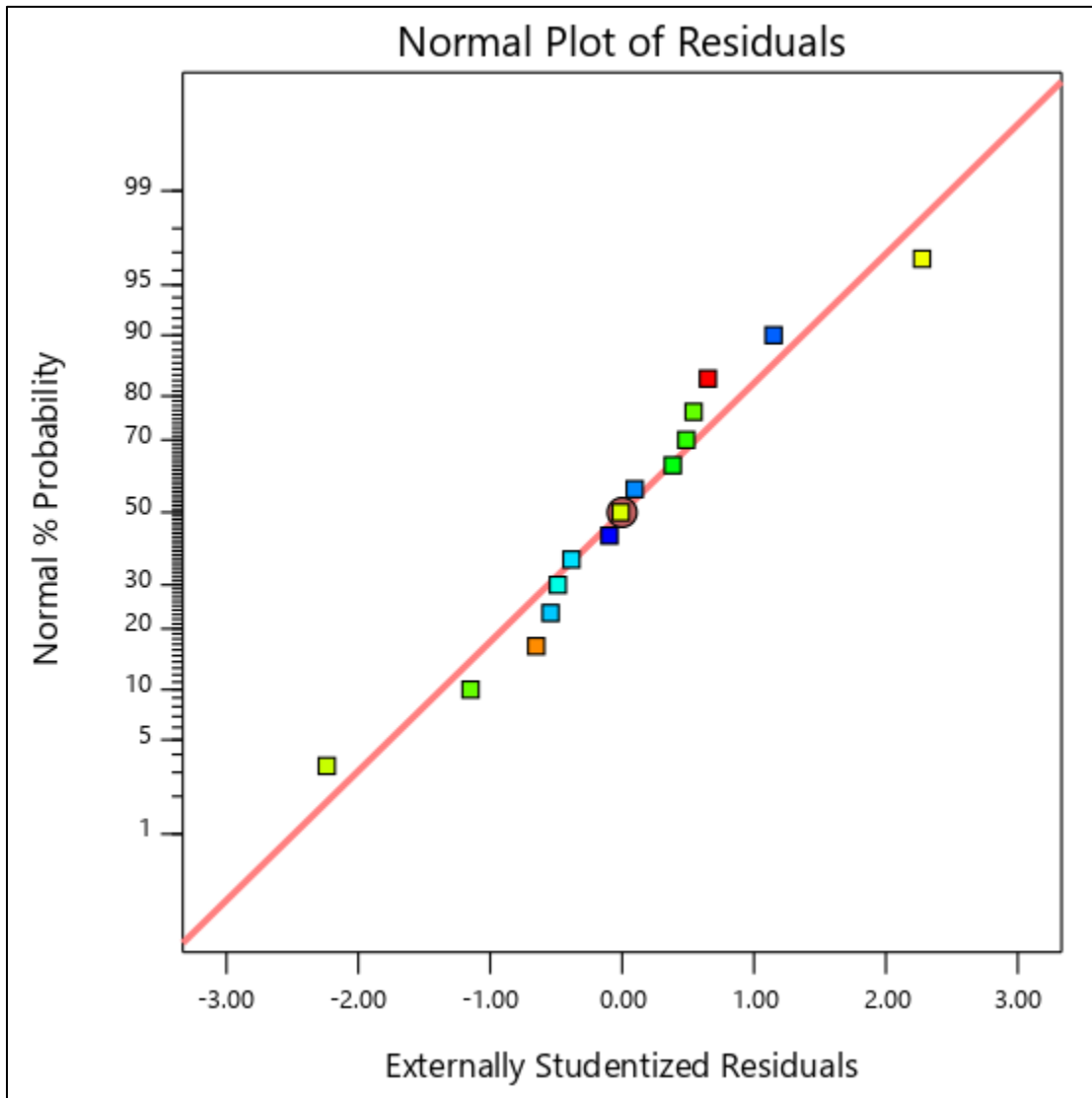


Figure 11: Normal probability vs. residuals graph

The above graph show that linear graph plot of normal present probability graph verses external standardized graph and from the graph almost all the point lay on the straight diagonal line except some residual point. Studentized residuals obtained by dividing residual by standard deviation estimation. The graph indicate that no high leverage data which found outlier and affect the fit of model equation.

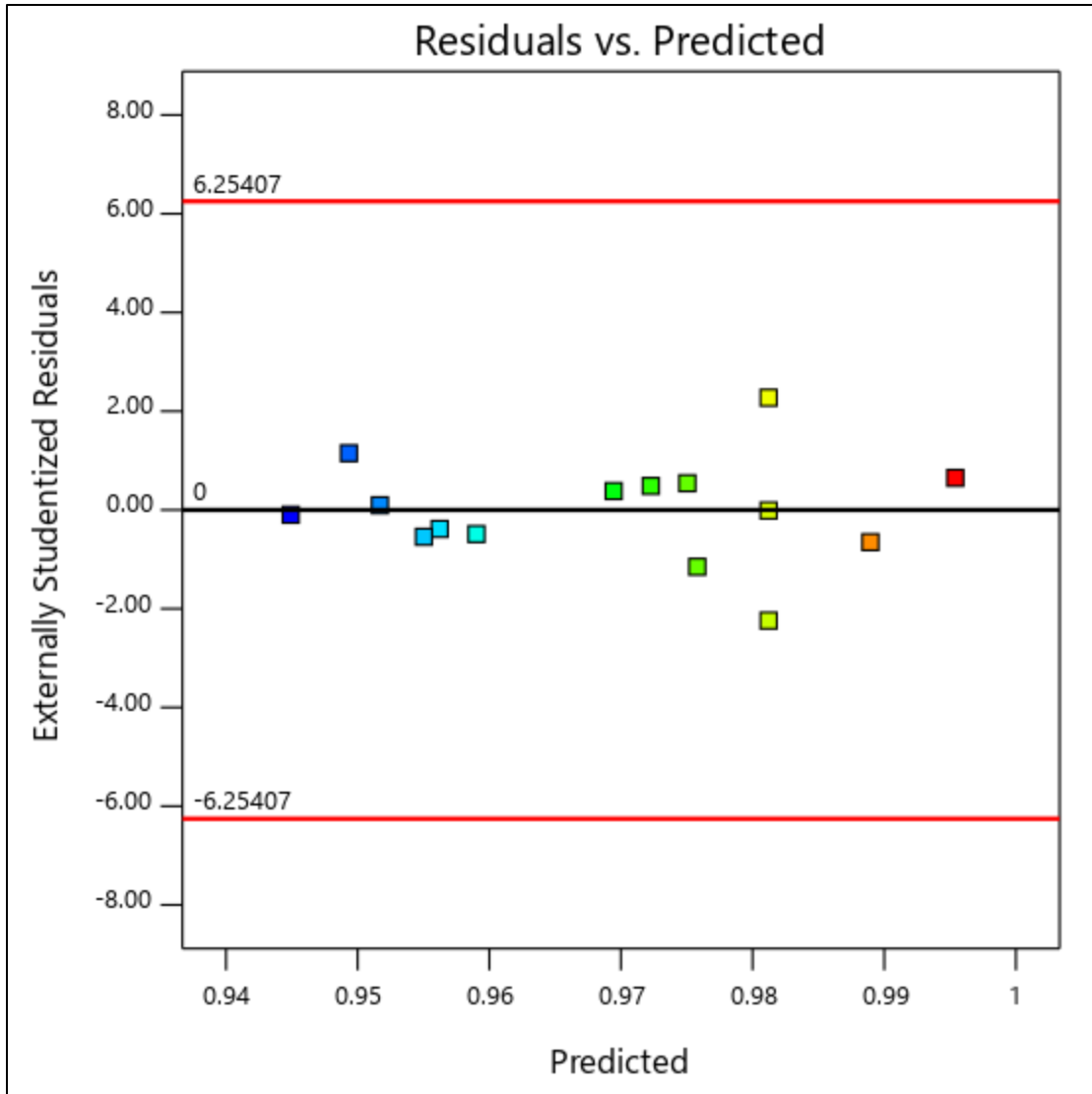


Figure 12: Residuals vs. predicted graph

This graph shows the graphical relation of residual and predicted value. As seen from the graph, most of the points are around the horizontal center line, and no points exist outside of the top and bottom limit of the line, which implies that the graph is acceptable and the predicted and external studentized residual fit the model equation.

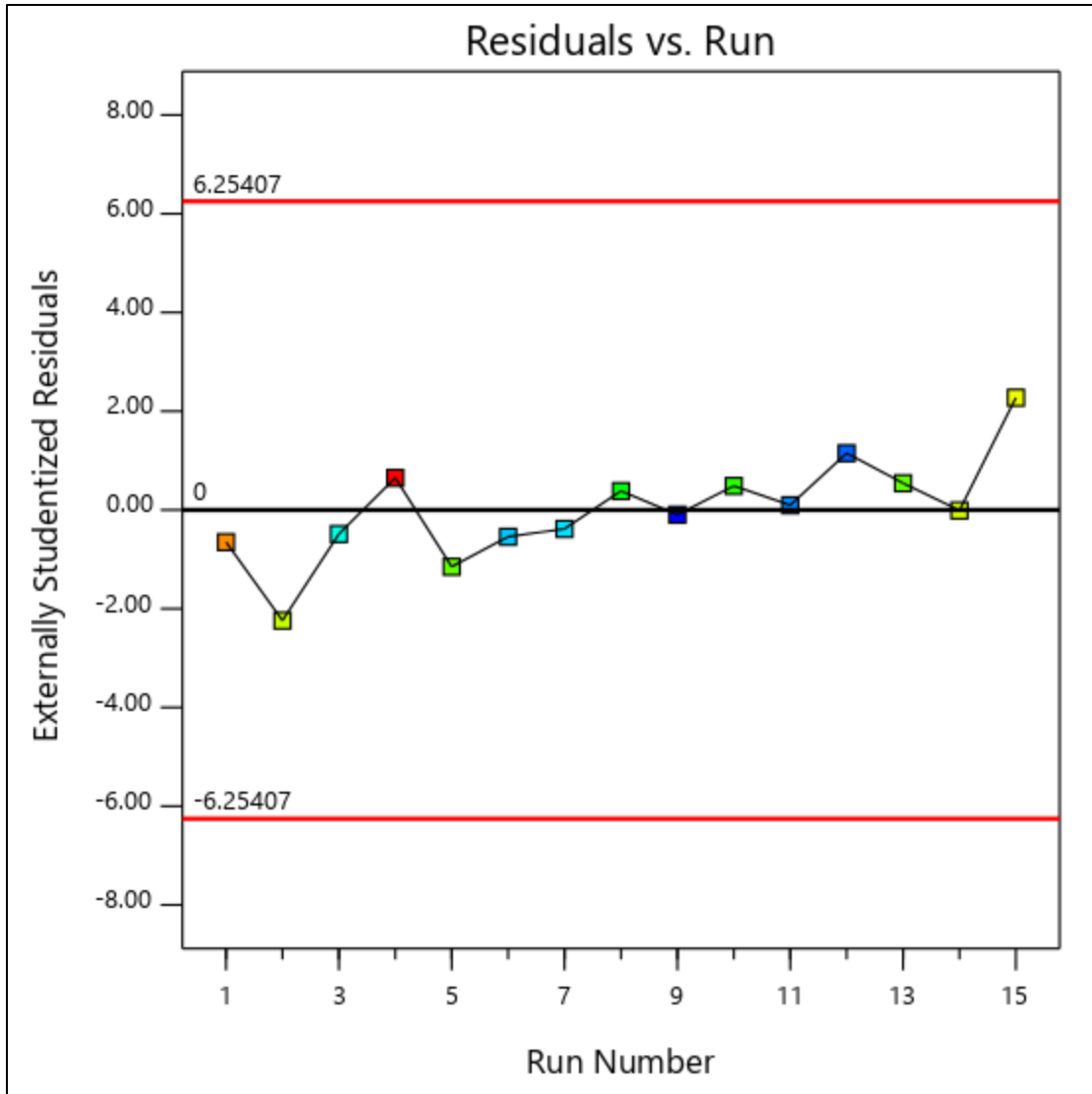


Figure 13: Residual vs. run graph

The graph indicate that none of residual vs. run values are out of two boundary line. Which mean it is acceptable that residual not affect run treatment values. The two boulder lines of graph are drown at 6.25407 and -6.23407 of external residuals whereas the values of residual verses run are at the center line connected by zigzag line on the boundary line and no outline found.

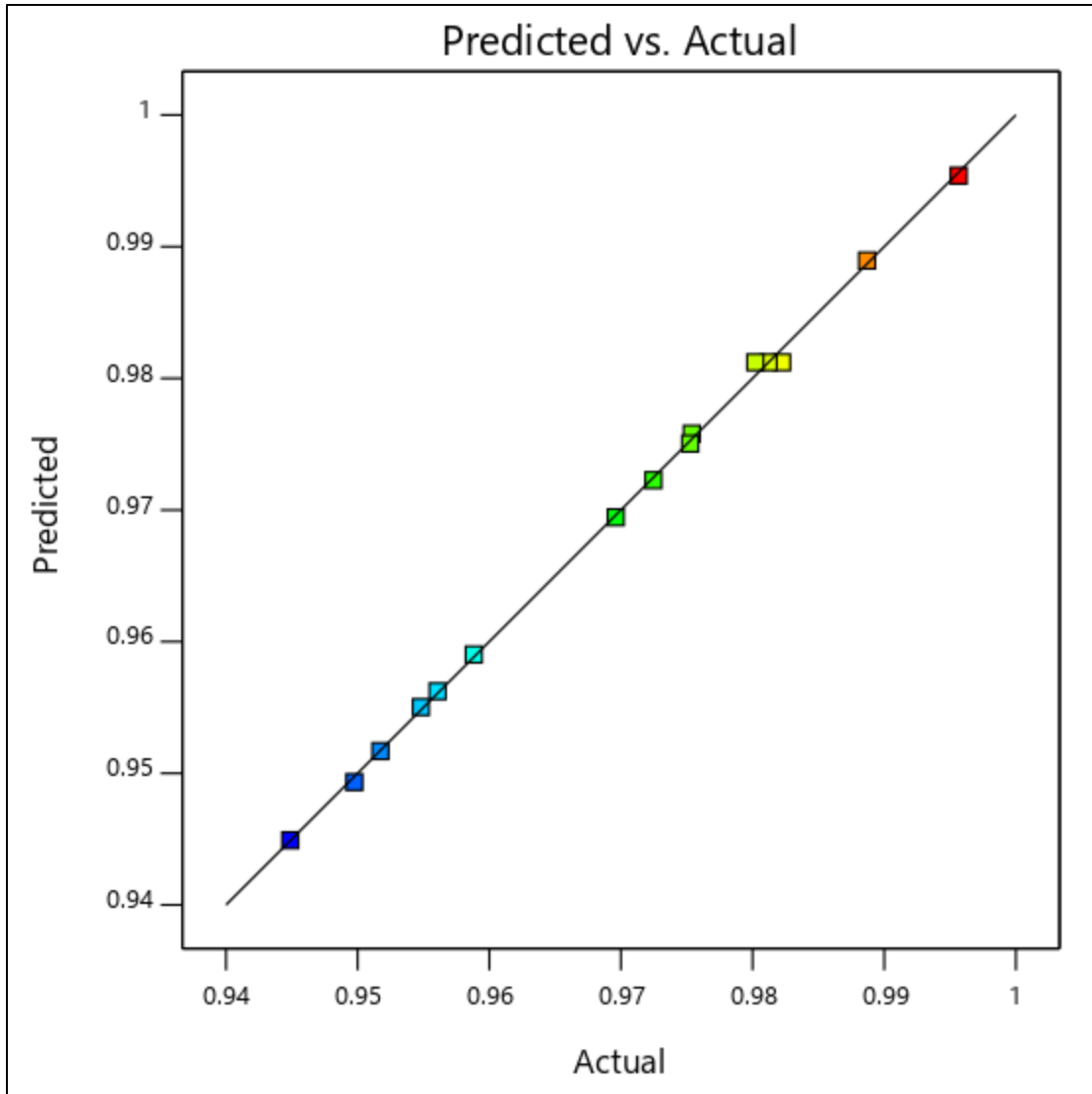


Figure 14: prediction vs. actual graph

Figure 14 show that predicted and actual value are fit each other, that is why all point of predicted vs actual graph point lay of linear diagonal line. The predicted value indicate the predication of statistical tool base on the initial impute value of works and actual is the actual laboratory work efficiency values of chromium removal. The graph also shows that predicted and actual is lineally lay on diagonal line which mean the result of laboratory work is acceptably fit with prediction. And justify that the model equation can be used for the predication of next efficient of treatment value.

4.2.5 Linear and Interaction Effect of Operational Parameters on Removal

Efficiency

The research was done by varying three factors (time of treatment, concentration of chromium in solution and pH of synthetic solution). Their effects are analyzed using surface response methodology of Box Behnken Design and the interaction effects are illustrated using 3D diagrams blow. As general the observation of laboratory works show that the effect of time on treatment is positive until 19 hours but above that as time rise microbe in anodic chamber start to dead and salt brig not much permeable for prevention of liquid pass from one chamber to the other chamber and the leakage case improper for treatment which lead to reduction of removal efficiency. And the second factor (concentration) has also positive effect on efficiency of treatment within selected range of concentration of the research but as it over concentrated (Tandukar et al., 2009) it has negative effect on the efficiency of treatment, because as heavy metal over concentrated the movement of electron and reduction is reduced due to cathodic electrode is covered by more reduced ions (Bagchi & Behera, 2020). Whereas, pH effect was separately explained, acidic condition is good for treating of lower concentrated (5gm/L) solution and the basic condition is good for high concertation (9gm/L). Whereas the anodic chamber containing microbial has constant pH of 7.

As shown in table 7 the interaction of time with concentration, concentration with pH and pH with time are significant. More illustration of interaction effects of parameters were shown using 3D diagram blow by keeping one factor constant and demonstration the interaction effect of the rest two factors on the diagram. Figure 15 elaborate that the effect of concentration and time on efficiency of chromium removal at pH 7. In time range of 15 and 19 hours and with increasing of concentration efficiency of wastewater treatment are increasing. Whereas 3D diagrammatic representation of figure 16 show that interaction effect of concentration and pH on efficiency of treatment. In acidic condition good for low concentration and with increasing of concentration of given range treatment efficiencies are increasing in higher pH. Finally figure 17 illustrate that the effect of time and pH on efficiency of removal of chromium. The graph display that around 15 up to 20 hours and pH of 6 up to 8.5 the efficiency of removal of chromium from wastewater are increasing. As whole the interaction effect of selected parameters on treatment of the wastewater were high and for better efficient of treatment optimization is important.

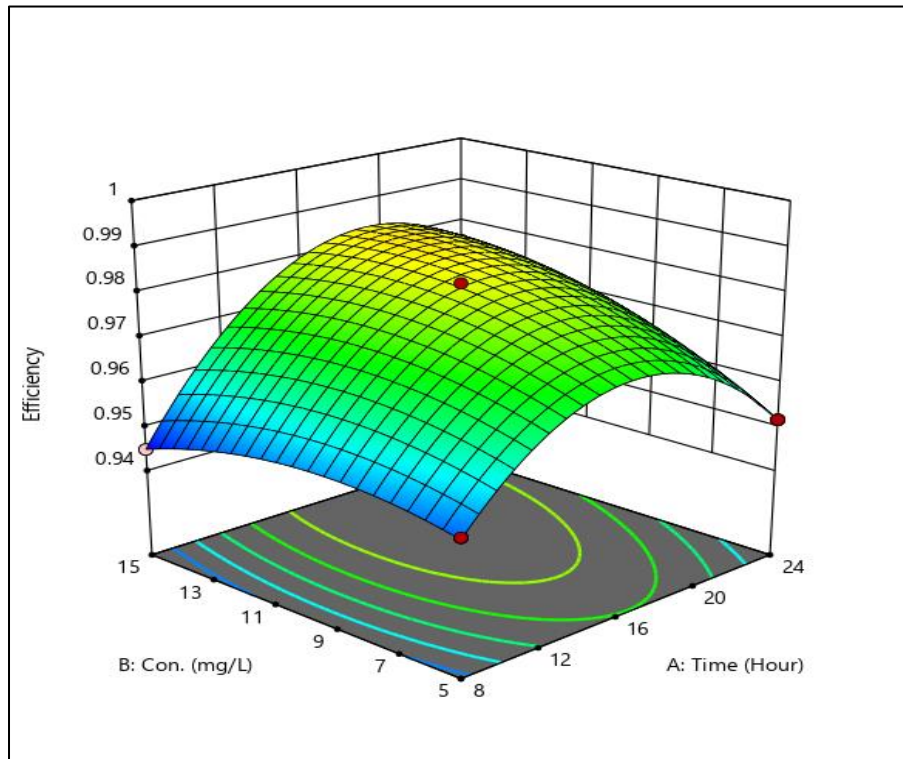


Figure 15: Interaction Effect of time and concentration on efficiency of treatment

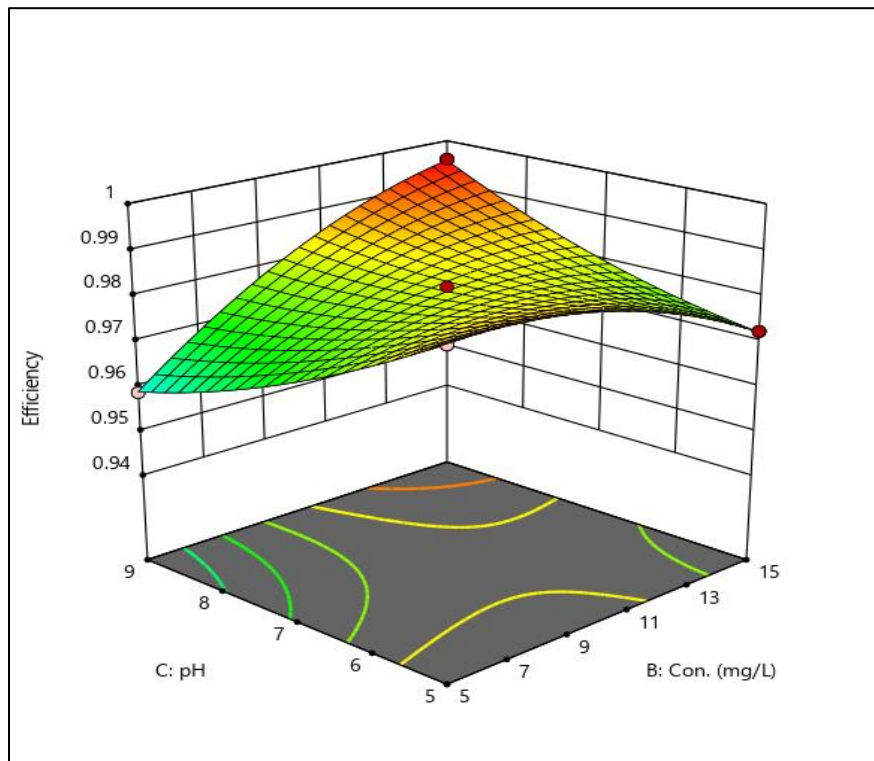


Figure 16: Interaction effect of pH and concentration on efficiency of treatment

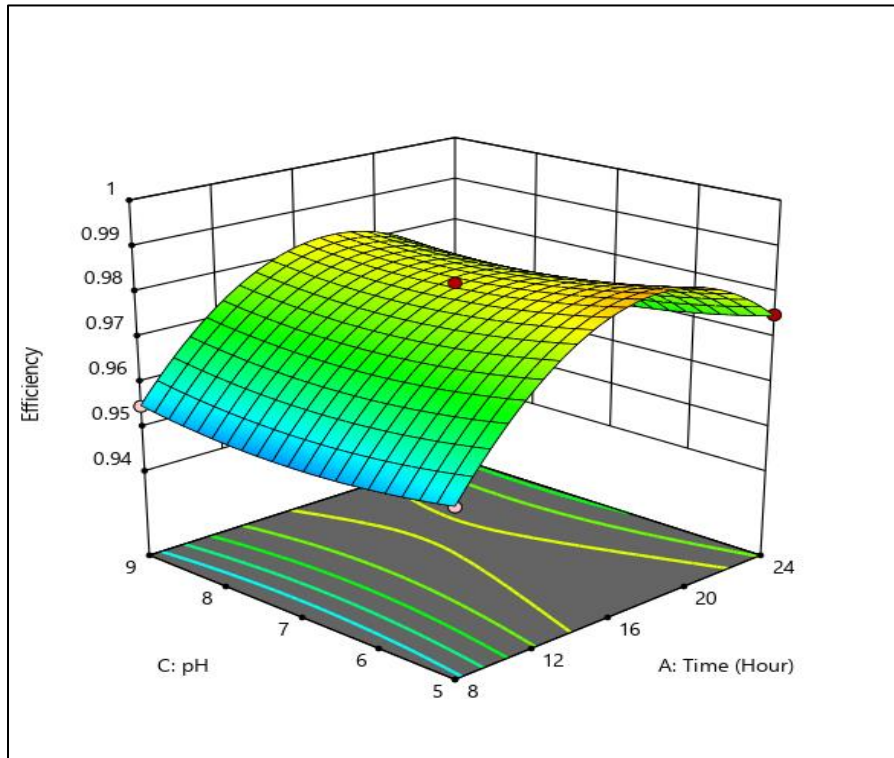


Figure 17: 3D interaction effect of pH and time on efficiency of treatment

4.3 Optimization and verification of Operation parameters

In table 9 optimization criteria were specified and the base for criteria were real wastewater of painting industries characteristics shown in table 1. Synthetic wastewater at concentration and pH of real wastewater were prepared and verify the optimum operation parameters. After two different tests of verification were taken (efficiency 0.975 and 0.95) with average efficiency of 0.966 and error of estimation 0.02 which is acceptable error and the verification of optimum operation parameters were valid. For optimum operation parameters electric current generated was measured using digital multi-meter. From 5 result recorded at different time the average of current value of optimum operation was 0.76mA and voltage of 0.34V. For 6cm diameter and 20cm height cylindrical reactor chamber current density generated was 17.51mA/m². The result prove that the BECFC has function of treating wastewater (removing chromium) and generate electrical energy.

Table 10: Optimization criteria

Specified	Goal	Lower Limit	Upper Limit
A:Time	is in range	8	24
B:Con.	is target = 9	5	15
C:pH	is target = 7	5	9
Efficiency	Maximize	0.944879	0.995655

As shown from table 9 optimization criteria were specified based on real wastewater and from over 100 combination optimum operation parameters, the 0.965 desirability and 0.981 efficiency was selected based on statistical method of surface response methodology of BBD with optimum time 17.357hours , 9mg/L concentration and pH of 7. The concentration and pH value of optimum operation parameters were approximately the same to real wastewater Nifas Silk painting wastewater (8.75mg/L and pH of 6.95).

4.4 Characterization of Actual Wastewater and Verification of Optimum Operation Parameters on Real Wastewater

Table 11 shows the physical, organic and chemical properties of Nifas Silk painting factory wastewater. The result show the wastewater was turbid and has high suspended solid and intermediate COD and BOD relative to other painting industrial wastewater. And in this research with these characteristic the wastewater was treated using BECFC for removal of chromium contained.

Table 11: Real wastewater characteristics

Parameter	Turbidity	COD	BOD	pH	Cr	Conductivity	Density	SS	Color
Unit	NTU	Mg/L	Mg/L	pH	Mg/L	mA/L	Mg/L	Mg/L	Appearance
Amount	2164	738	148	6.95	8.75	0.014	1002.6	3400	Dark blue

With such property Bioelectrochemical method was applied for removal of chromium and the efficiency was less than that of synthetic wastewater treatment efficiency. The reason is due to the existence of different ions like iron, suspended solid, phosphors, high amount of COD and BOD, lead cadmium, copper, silver (Woldeamanuale, 2017) and other inorganic and organic ion and other sludge of wastewater. Metals and anions form wastewater make complexes with chromium ion and reduce the efficiency of reduction of Cr(VI) (Asha Lata Singh, 2016). But the result of validation of the methodology on actual wastewater of painting industry is acceptable even though, due to different external factor efficiency reduced to 0.84 this treatment method combine with the other methodology can increase the efficiency more and as it is 84% efficient of treatment is not too small.

Chapter Five

Conclusion and Recommendation

5.1 Conclusion

The research aims to remove chromium from synthetic wastewater and to verify the methodology on real wastewater of painting industries, using Bioelectrochemical Fuel cell technology. And the results of research laboratory and statistical analysis show that the main aim of the research were achieved. To see the summary results of research from the laboratory experiments, maximum efficiency was 0.996 which was achieved at a concentration of 15mg/L, pH 9, and time 16 hours. And data were analyzed using the surface response methodology of Box-Behnken Design and as shown in table 7 all factorial parameters and their interactions have significant effects on removal of chromium from wastewater and lack of fattiness is not significant which indicate the results are totally acceptable. And the quadratic equation fits well the mode equation of laboratory data and all analysis graphs show laboratory research results are within the range bonder line. Optimum operation parameters were; time 17.357, concentration 9mg/L and pH of 7, and efficiency of optimum was 0.981 and current density generated was 17.51mA/m². Whereas, verification efficiency was 0.966 for synthetic wastewater and 0.84 for the validation of real wastewater of Nefas Silk painting industry which has characteristic of SS (3400mg/L), turbidity (2164NTU), COD (738mg/L) and BOD of 148mg/L. Due to different factors which affect the treatment technology of Bioelectrochemical fuel cell efficiency of real wastewater becomes lower than synthetic wastewater treatment efficiency. In summary, this treatment method is an effective, efficient, and environmental-friendly technology, but it is new and it needs more research to make the technology applicable.

5.2 Recommendation

To do this research, multiple articles and journals were reviewed to investigate other chromium-removal technologies. And it was found that the Bioelectrochemical fuel cell method of heavy metal treatment technology is effective, efficient, and environmentally friendly than reviewed. But the technology is laboratory-scale, and it needs more development to make it applicable in real heavy metal removal from wastewater. For anyone who wants to do more research on this area in the future, I have some recommendations. It is suggest to find more advanced laboratory centers for doing more research on the topic. In Ethiopia as a whole, there is no well-advanced setup of fuel cell technologies so it is better to find advanced laboratory from out of country. The second recommendation is to anyone who wants to do more study on the area how the methodology works interrelatedly with other technologies. It is recommend to study how the technology work with organic waste treatment technologies. The third recommendation to investigate how the methodology apply real wastewater treatment. To apply this method on real application one chamber fuel cell is recommended due to the case that the wastewaters are huge and intermixed each other, even though it is difficult to control factors in a single chamber method. In general, more researches are required to make this promising technology to be applicable on real wastewater treatment.

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