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ADDIS ABABA INSTITUTE OF TECHNOLOGY SCHOOL OF CHEMICAL AND BIO-ENGINEERING

Treatment and Recovery of Chrome from Electroplating Wastewater

(By Chemical Precipitation)

(At Homicho Ammunition Engineering Industry)

By

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A thesis submitted to Addis Ababa University AAiT School of Chemical and Bio Engineering in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemical Engineering (Environmental Engineering)

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Treatment and recovery of chrome from electroplating wastewater by chemical precipitation

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

As members of Examining Board of the Final M.Sc. thesis open defense, we certify that we have read and evaluated the thesis prepared by Kidanu G/Selassie entitled "treatment and recovery of chrome from electroplating wastewater by chemical precipitation" and recommended that it can be accepted as fulfilling the thesis requirements for the Degree of Master of Science in Chemical Engineering (Environmental Engineering).

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Abstract

The thesis work entitled "Chromium treatment and recovery" was undertaken to investigate the reduction process of hexavalent chromium from electroplating wastewater by chemical precipitation in order to achieve the maximum trivalent chromium concentration. Sodium bisulphite is one of the widely used coagulants in waste water treatment process and has good reducing ability. Because of its reducing capacity, sodium bisulphite is applied to reduce hexavalent chromium from electroplating wastewater. The study has been conducted in four phases. In phase one reduction of hexavalent chromium, phase two determination of hexavalent chromium, phase three precipitation of chromium sulphate followed by oxidation of the sludge of Chromium (III) hydroxide. Phase one study was carried out to analyze the reduction process of the toxic soluble hexavalent chromium by using the concept of design experiment to justify the number of affecting factors and levels during the laboratory work followed by the synthetic waste sample preparation at Homicho Ammunition Engineering Industry in Ambo.

Different experiments were considered like classical method of analysis to quantify and qualify the wastewater sample, atomic absorption spectrophotometric technique was utilized to determine the amount of total chromium, and finally colorimetric method to determine the amount of hexavalent chromium with a suitable complexing agent to engulf the ionic hexavalent Chromium. The total numbers of experiments were fifty four (54), the first twenty seven (27) run was analyzed by labeling the distributed parameters in each beaker of the solution and the number of factors with their levels were indicated. For the purpose of optimization of the selected parameters experiments were replicated, then at the second round of the experiment run number 44 was the optimized one. In order to perform these activities, the concentration of the stock solution was 100 mg/L, and 50 ml of volume was taken to each 500 ml beaker volume with concentration of 10 mg/L. With this amount phase two was conducted, to solidify the solution containing chromium sulphate $Cr_2 (SO_4)_3$ generated from the redox reaction. . The required reduction time to reach equilibrium, the effectiveness of pH value for Cr (VI) reduction and the required amount of sodium bisulphite to complete reduction were investigated. The redox reaction was completed within 40 minutes, at pH of 2 and 50 mg/L of hexavalent chromium was reacted with 200 mg/L of sodium bisulphite in deionized water.

Sodium hydroxide was used to precipitate the solution after the reaction of the precipitating agent and hexavalent chromium. In Final phase oxidation of Chromium (III) hydroxide to hexavalent chromium was carried out;

Key words: Cr (VI) reduction, Sodium bisulphite, wastewater treatment

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ABBREVIATIONS AND ACRONYMS

AAU	Addis Ababa University
ACS	American Chemical Society
ASTM	American Society of Testing and Materials
CAS	Chemical Abstracts Service
DPRK	Democratic peoples of Republic Korea
ECP	Electrochemical precipitation
EEPA	Ethiopian Environmental Protection Authority
FDRE	Federal Democratic Republic of Ethiopia
HAEI	Homicho Ammunition and Chemical Engineering Industry
HSDB	Hazardous Substances Data Bank
IARC	International Agency For Research on Cancer
IDLH	Immediately Dangerous to Life and Health
MCL	Maximum Contaminant Level
NAS	National Academy of Sciences
NEQS	National Environmental Quality Standards
NIOSH	National Institute for Occupational Safety and Health
Pm	Pico meter
ppm	parts per million
RAO	Remedial Action Objective
rpm	Revolution Per Minute
TDS	Total dissolved solids
TS	Total solids
TSS	Total suspended solids
USEPA	U.S. Environmental Protection Agency
UNEP	United Nations Environmental Program
WHO	World Health Organization
mS/cm	mill Siemens per centimeter
FAAS	Flame Atomic Absorption Spectrophotometer
m.a.s.l	meter above sea level

1. Introduction

1.1 Background

Metal plating encompasses a broad range of processes that are performed on manufactured parts to decorate objects, for corrosion inhibition, to improve solder ability, to harden, to improve wearability, to reduce friction and to alter conductivity of the surface of the article, thus lending its properties not possessed in its "unfinished state" (Murphy, 1996; USEPA, 1995). Industrial wastewater often contains considerable amounts of heavy metals that would endanger public health and the environment if discharged without adequate treatment.

Plating facilities have a variety of possible release mechanisms and the potential to impact multiple environmental media (soil, air, surface water, and groundwater). Due to environmental toxicity of Chromium, mainly hexavalent Chromium is crucial to limit its further discharge into the environment (Cervantes et al., 2001).

Technology of Chromium wastewater neutralization is, in most cases, based on detoxification of waste, which is done by reducing hexavalent Chromium to trivalent Chromium and then, using ferrous sulfate or calcium hydroxide, insoluble Chromium(+3) hydroxide is precipitated. At the same time other metal hydroxides are precipitated and their amount strictly depends on the cations concentration in the wastewater. Dewatered sludge is stored at landfills in specially prepared graves.

Chromium is a steely-gray, lustrous, hard metal that takes a high polish and has a high melting point. It is odorless, tasteless, and malleable metal. Chromium is important metal due to its high corrosion resistance and hardness. It is used extensively in manufacturing of stainless steel. Although trivalent Chromium is required in trace amounts for sugar and lipid metabolism in humans, however its deficiency causes diseases. Hexavalent Chromium is a toxic and a carcinogen metal pollutant that tremendously affects the environment. Hence its environmental cleanup is highly essential.

In Ethiopia, the generation of industrial waste, including hazardous waste, is increasing rapidly as a result of industrialization, urbanization, and the implementation of a new economic policy.

While the Ethiopian economy grew by 1.9% in the period 1980 to 1990 in real terms the toxic load generated per unit of industrial output increased by 1.8% which is higher as compared to the Sub-Saharan Africa average of 1.3 (UNIDO, 2001).

Homicho Ammunition Engineering Industry (HAEI) has been practicing Chrome plating fully since 2005. This has enabled the products (objects) to prevent corrosion, to obtain a hard surface or to have attractive finish, to have good wear resistance, so that they will stay long enough for years in their storage and usage areas. But the wastes generated from the Chromium industry have not ever been treated and creates a great dilemma to the factory decision makers and the society of the industry. The wastes are stored in three plastic barrels and in one stainless steel container to be treated; this indicates that there is a chance of leakage to the environment; which can contaminate the soil and the nearby streams.

1.2 Statement of the Problem

The increasing level of heavy metals in the environment represents a serious threat to human health, living resources and ecological systems (Sastre. et al., 2002). Although there are many sources of heavy metals, some industrial sectors are at present contribute the most to environmental pollution with those toxic metals. Among such industrial sectors, the metal finishing industry and metal plating industry are important ones. These contaminants must be removed from wastewaters before discharge as they are considered persistent, bio-accumulative and toxic substances. The Chrome plating wastewater is highly toxic in nature because of the presence of metals such as Chromium, Copper, Lead, and Iron.

Spent cleaning and plating solutions are the main source of hazardous wastes for the environment in metal finishing industries. Spent plating solutions contain high concentrations of heavy metal impurities, when discarded. In HAEI, Chrome electroplating industry generates waste effluents in large amount, around 3500 liter Chrome aliquots which is highly concentrated and has been stored, amounting to around 300 Liter/year. These wastes are collected and stored in heavy polyethylene plastic barrels and stainless steel containers since 2005without any treatment. Poor storage or improper disposal of these hazardous wastes may cause irreparable environmental damages in the long-term. Besides this, it can cause a great health and psychological impact, to the section workers and the community of the industry including the surrounding environment.

1.3 Objectives

1.3.1 General Objective

The general objective of the study is to treat and recover Chrome from electroplating wastewater.

1.3.2 Specific Objectives

- Determination the waste composition (Cr(VI), SO_4^{2-}, Fe and Cr^{3+})
- Identification of treatment and recovery methods.
- Optimization of process parameters.

1.4 Significance of the Study

The study has great significance in terms of assuring the environmental protection program, which is part of the mean time activities of resolving the climate change challenges. The solution to remediate the environment is neutralization of the toxic chrome metal effluent from electroplating wastewater, In comparison to conventional methods reduction followed by precipitation is simple and widely used in chrome wastewater treatment due to the higher concentration of chrome, simplicity and efficiency in reducing hexavalent chromium. The study will be used as a reference material for anyone who is interested to carry out further study.

1.5 Scope of the study

The scope of this study is to investigate the possibility of reducing the toxic, soluble hexavalent chromium. There will be three major steps to get reduced hexavalent chromium and one final step to recover the sludge produced. Reduction of hexavalent chromium treatment of Chrome containing electroplating wastewater by chemical reduction followed by chemical precipitation. Among the major ions present in the Chromium plating waste like: Sulfate, Iron, Lead, Trivalent Chromium and Hexavalent Chromium. But mainly concerned on the determination of total chrome, Hexavalent Chromium and Trivalent Chromium. The optimum conditions were investigated, like pH, reduction time and dose of reducing agent.

Generally, this study will help those industries which generate Chromium waste to minimize the cost of their wastewater treatments and to recover the insoluble trivalent Chromium to hexavalent Chromium i.e. Chrome sludge treatment.

2. Literature Review

2.1 Introduction

Chromium is a transition metal present in group VI-B of the periodic table. Elemental Chromium is very stable, but it is not usually found pure in nature. Chromium exists in nine valence states ranging from +6 to -2, but Cr(III) and the toxic Cr(VI) are considered by far the most significant due to their stability in the natural environment (Krishna and Philip, 2005), with Cr(III) predominating. Chromium contamination of the environment is of concern because of the mobility and toxicity of Cr(VI). Trivalent and hexavalent Chromium differ widely in physicochemical properties and biological reactivity. While Cr(VI) species and dichromate are extremely water soluble and mobile in the environment, Cr(III) species are much less soluble and comparatively immobile (Viamajala et al., 2004). Moreover, Cr(VI) is recognized to be highly toxic, carcinogenic, mutagenic and teratogenic for mammals including humans (Flores et al., 1999), whereas Cr(III) is an essential trace element necessary for glucose, lipid and amino acid metabolism as well as a popular dietary supplement (Viamajala et al., 2004). Studies have revealed that C r(VI) is approximately 100 times more toxic (Beszedits, 1988) and 1000 times more mutagenic than Cr(III) (Lonfronth et al., 1978).

2.2 Electroplating

2.2.1 Process Description

Electroplating is the process of applying a metallic coating to an article by passing an electric current through an electrolyte in contact with the article, thereby forming a surface having properties or dimensions different from those of the article. Essentially any electrically conductive surface can be electroplated. Special techniques, such as coating with metallic loaded paints or silver-reduced spray, can be used to make nonconductive surfaces, such as plastic, electrically conductive for electroplating. The metals and alloy substrates electroplated on a commercial scale are Chromium, cadmium, cobalt, copper, gold, indium, iron, lead, nickel, platinum group metals, silver, tin, zinc, brass, bronze and many gold alloys. Electroplated materials are generally used for a specific property or function, although there may be some overlap, e.g. a material may be electroplated for decorative use as well as for corrosion resistance (Mandich, 1999).

The essential components of an electroplating process are an electrode to be plated (the cathode or substrate), a second electrode to complete the circuit (the anode), an electrolyte containing the metal ions to be deposited, and a direct current power source. The electrodes are immersed in the electrolyte with the anode connected to the positive leg of the power supply and the cathode to the negative leg. As the current is increased from zero, a point is reached where metal plating begins to occur on the cathode. The plating tank is either made of or lined with totally inert materials to protect the tank. Anodes can be either soluble or insoluble, with most electroplating baths using one or the other type. The majority of power supplies are solid state silicon rectifiers, which may have a variety of modifications, such as steeples controls, constant current and constant voltage. Plate thickness is dependent on the cathode efficiency of a particular plating solution, the current density, and the amount of plating time. The following section describes the electroplating process. Following the description of Chromium plating, information is provided on process parameters for other types of electroplating.

2.2.2 Chromium Electroplating

Chromium plating and anodizing operations include hard Chromium electroplating of metals, decorative Chromium electroplating of metals and chromic acid anodizing. Each of these categories of the Chromium electroplating industry is described below.

2.2.2.1. Hard Chromium Electroplating

In hard plating, a relatively thick layer of Chromium is deposited directly on the base metal (usually steel) to provide a surface with wear resistance, a low coefficient of friction, hardness, and corrosion resistance, or to build up surfaces that have been eroded by use. Hard plating is used for items such as hydraulic cylinders and rods, industrial rolls, zinc die castings, plastic molds, engine components, and marine hardware (Horner, 1994).

The process for hard Chromium electroplating consists of pretreatment, alkaline cleaning, acid dipping, chromic acid anodizing, and Chromium electroplating. The pretreatment step may include polishing, grinding, and degreasing (Figure 1). Degreasing consists of either dipping the part in organic solvents, such as trichloroethylene or perchloroethylene, or using the vapors from organic solvents to remove surface grease. Alkaline cleaning is used to dislodge surface soil with inorganic cleaning solutions, such as sodium carbonate, sodium phosphate, or sodium

hydroxide. Acid dipping, which is optional, is used to remove tarnish or oxide films formed in the alkaline cleaning step and to neutralize the alkaline film. Acid dip solutions typically contain 10 to 30 percent hydrochloric or sulfuric acid. Chromic acid anodic treatment, which also is optional, cleans the metal surface and enhances the adhesion of Chromium in the electroplating step. The final step in the process is the electroplating operation itself.

The plating tanks typically are equipped with some type of heat exchanger. Mechanical agitators or compressed air supplied through pipes on the tank bottom provide uniformity of bath temperature and composition. Chromium electroplating requires constant control of the plating bath temperature, current density, plating time, and bath composition. Hexavalent Chromium plating baths are the most widely used baths to deposit Chromium on metal. Hexavalent Chromium baths are composed of (chromic acid = 150 - 180 g/L), sulfuric acid (H_2SO_4 = 1.4 – 2.1 g/L), and water (Lindsay, 1999). The chromic acid is the source of the hexavalent Chromium that reacts and deposits on the metal and is emitted to the atmosphere. The sulfuric acid in the bath catalyzes the Chromium deposition reactions. The evolution of hydrogen gas from chemical reactions at the cathode consumes 80 to 90% of the power supplied to the plating bath, leaving the remaining 10 to 20% for the deposition reaction. When the hydrogen gas evolves, it causes misting at the surface of the plating bath, which results in the loss of chromic acid to the atmosphere.

2.3 Major Uses of Chromium

Hexavalent Chromium is considerably more toxic than trivalent Chromium, the form most commonly found naturally (ATSDR, 1993). Cr (VI) is generally produced by industrial processes. Chromium and its salts are used in the Chrome plating, leather tanning industry, the manufacture of catalysts, pigments and paints, fungicides, the ceramic and glass industry and in photography, and for Chrome alloy and Chromium metal production and corrosion control. Occupational sources of Chromium exposure may occur in the following industries: Chrome plating, leather tanning, pigments and paints.

An early use of Chromium compounds was as pigments, particularly Chrome yellow. Basic chromic sulfate was used in tanning hides, as the reaction of Chromium with collagen raises the hydrothermal stability of the leather and renders it resistant to bacterial attack. The most

important use of Chromium, namely as an alloying element, developed gradually during the nineteenth century and led to the introduction of Chromium steels.

Chromium is currently used in such widely diversified products as stainless tool and alloy steels, heat and corrosion resistant materials, special purpose alloys, alloy cast iron, pigments, metal plating, leather tanning, chemicals, and refractory materials for metallurgical furnaces. It is used in the metallurgical industry to enhance such properties as hardenability (response to quenching), creep (unit stress that will produce plastic deformation at a specified rate and temperature), strength and impact strength and resistance to corrosion, oxidation, wear and galling; its major use is in the production of stainless steel. Chromium pigments represent the largest use of Chromium in the chemical industry (Papp, 1983).

The steel industry is the major consumer of Chromium. In 2007, estimated consumption of Chromium in the United States by end use was 78% in stainless and heat resisting steel, 13.8% for other steel uses, 3.7% in super alloys, and 4.5% in other alloys (Papp, 2009). Alloys of stainless steel and Chromium typically contain between 11.5% and 30% Chromium (ATSDR, 2000). Hexavalent Chromium compounds are widely used as corrosion inhibitors, in the manufacture of pigments, in metal finishing and Chrome plating, in stainless steel production, in leather tanning, and in wood preservatives (Costa, 1997 and ATSDR, 2000). In 1996, about 52% of all Chromium compounds used in the U.S. chemical industry were used in production of wood preservatives; the rest were used in leather tanning (13%), metals finishing (13%), pigments (12%), refractories (linings for high temperature industrial furnaces) (3%), and other uses (7%)(Papp, 2009). The use of hexavalent Chromium compounds in wood preservatives increased dramatically from the late 1970s to the early 2000s; however, this use is expected to decrease because of a voluntary phase out of all residential uses of wood treated with chromate copper arsenate that went into effect December 31, 2003 (Brooks, 2009). Hexavalent Chromium compounds are also used in textile dyeing processes, printing inks, drilling mud, pyrotechnics, water treatment, and chemical synthesis.

Calcium chromate is used primarily as a corrosion inhibitor and as a depolarizer in batteries (IARC, 1973, 1990). Chromium trioxide is used primarily in Chrome plating and other metal finishing (particularly in the production of automobiles and military aircraft), in production of wood preservatives, as a corrosion inhibitor, and in the production of organic chemicals and

catalysts. Lead chromate has been used in paints and printing inks and as a colorant in vinyl, rubber, and paper. Potassium chromate is used in production of dyes and in textile dyeing processes. Potassium dichromate has largely been replaced by sodium dichromate in many applications; however, it is still used in photomechanical processes and production of pigments and wood preservatives. Sodium chromate is used as a corrosion inhibitor and in textile dyeing processes, inks, paints, leather tanning, wood preservatives, drilling mud, cutting oils, water treatment, and production of other Chromium compounds. Sodium dichromate is the primary base material for the production of Chromium compounds and is used as a corrosion inhibitor, in metal treatments, in drilling mud, and in the production of dyes, wood preservatives, synthetic organic chemicals, and catalysts.

2.4 Toxicity of Chromium

Non-occupational exposure to the metal occurs via the ingestion of Chromium containing food and water, whereas occupational exposure occurs via inhalation (Podersen, 1982). Workers in the chromate industry have been exposed to estimated Chromium levels of 10-50μgm^{-3} for trivalent Chromium and 5-1000 μgm^{-3} for hexavalent Chromium (Salnikowet al., 2008). Humans and animals localize Chromium in the lung, liver, kidney, spleen, adrenals, plasma, bone marrow, and red blood cells. Hexavalent Chromium is transported into cells via the sulfate transport mechanisms, taking advantage of the similarity of sulfate and chromate with respect to their structure and charge. Once developed, Chrome sensitivity can be persistent. In such cases, contact with chromate dyed textiles or wearing of chromate tanned leather shoes can cause or exacerbate contact dermatitis. Chronic inhalation of hexavalent Chromium compounds increases risk of lung cancer. Soluble compounds like chromic acid are much weaker carcinogens (Salnikow et al., 2008).

The primary sources of hexavalent Chromium in the atmosphere are chromate chemicals used as rust inhibitors in cooling towers and emitted as mists, particulate matter emitted during manufacture and use of metal chromates, and chromic acid mist from the plating industry (ATSDR, 1993). Hexavalent Chromium in air eventually reacts with dust particles or other pollutants to form trivalent Chromium (NAS, 1974); however, the exact nature of such atmospheric reactions has not been studied extensively. Both hexavalent and trivalent

Chromium are removed from air by atmospheric fallout and precipitation (Fishbein, 1981). The atmospheric half-life for the physical removal mechanism is dependent on the particle size and particle density. Chromium particles of small aerodynamic diameter (< 10 μm) will remain airborne for a long period (USEPA, 1984).

Hexavalent Chromium may exist in aquatic media as water soluble complex anions and may persist in water. Hexavalent Chromium is a strong oxidizing agent and may react with organic matter or other reducing agents to form trivalent Chromium. The trivalent Chromium will eventually be precipitated as $Cr_2O_3 \cdot xH_2O$. Therefore, in surface water rich in organic content, hexavalent Chromium will exhibit a much shorter lifetime (Callahan et al., 1979).

Any hexavalent Chromium in soil is expected to be reduced to trivalent Chromium by organic matter. The primary processes by which the converted trivalent Chromium is lost from soil are aerial transport through aerosol formation and surface water transport through runoff (USEPA, 1984). Very little Chromium is leached from soil because it is present as insoluble $Cr_2O_3 \cdot xH_2O$ (Fishbein, 1981).

The bio-concentration factor (BCF) for hexavalent Chromium in fish muscle appears to be < 1.0, but values of 125 and 192 were obtained for oyster and blue mussel, respectively (USEPA, 1980).

Table 1.1: CAS numbers and aqueous solubility of selected hexavalent Chromium compounds

Compound	CAS No.	Water solubility
Ammonium chromate ($(NH_4)_2CrO_4$)	7788-98-9	40.5 g/100 mL at 30 ^{0}C
Calcium chromate ($CaCrO_4$)	13765-19-0	2.23 g/100 mL at 20 ^{0}C
Chromic acid (CrO_3)	1333-82-0	61.7 g/100 mL at 0 ^{0}C
Potassium chromate (K_2CrO_4)	7789-50-6	62.9 g/100 mL at 20 ^{0}C
Potassium dichromate ($K_2Cr_2O_7$)	7789-50-9	4.9 g/100 mL at 0 ^{0}C
Sodium chromate (Na_2CrO_4)	7775-11-3	87.3 g/100 mL at 30 ^{0}C
Sodium dichromate dehydrate	7789-12-0	230 g/100 mL at 0 ^{0}C

Sources: Weast, 1980; Hartford

2.5 Hexavalent Chromium Cr (VI) Wastewater Treatment Techniques

Various methods to reduce Chromium from the wastewater stream include physical and chemical methods such as chemical reduction, precipitation, ion exchange, filtration, electrochemical treatment, adsorption, membrane technologies and evaporation recovery (Nyer, 1992, Camargo et al., 2003).

2.5.1 Reduction of Hexavalent Chromium

Hexavalent Chromium-bearing wastewaters are produced in chromium electroplating, chromium conversion coatings, etching with chromic acid and in metal finishing operations carried out on chromium as a basis material. Many common plating solutions contain hexavalent chromium concentration between 10 to 500 mg/L; however concentrations of over 100,000 mg/L can be encountered. Hexavalent chromium may be present in the form of chromic acid, chromate or dichromate in acid solution. To remove chromium from wastewater streams, highly toxic hexavalent chromium (Cr^{+6}) must be reduced to trivalent chromium (Cr^{+3}) which can then be removed from the waste water stream by hydroxide precipitation. Strong reducing agents used in this chemical treatment process include, sodium bisulfite, sodium met bisulfite, sodium hydrosulfite and ferrous sulfite. Sodium bisulfite is the most economic reducing agent used to reduce hexavalent chromium to trivalent chromium for large flow applications. The reaction takes place at a very low pH (around 2.0 for complete reduction). The reduction rate decreases with increasing pH and is extremely slow for pH level 6(Sacramento, 1986).

2.5.2 Chemical Precipitation

The most widely used process for removal of heavy metals from wastewater solution is that of chemical precipitation; approximately 7% of the electroplating facilities employ precipitation treatment (Patterson et al., 1975), using either hydroxide, carbonate, or sulfide treatment, or some combination of these treatments to treat their wastewaters. The most commonly used precipitation is hydroxide precipitation treatment due to its relative simplicity, low cost of precipitant (lime), and ease of automatic pH control (Sorget al., 1979). The solubility of the various metal hydroxides are minimized or pH in the range of 8.0-11.0. Dean et al (1972), point

out that Iron, Manganese, Copper, Zinc, Nickel, and Cobalt result in almost complete removal by hydroxide precipitation with almost no special modification required.

However, precipitation of mercury, cadmium, and lead may be slow and incomplete. When Chromium is present, reduction of the solution with sodium meta-bisulfite, ferrous sulfate, or metallic iron prior to lime treatment is necessary. To reduce hexavalent Chromium to the trivalent form, Chrome bearing streams are generally segregated and treated separately. Employing hydroxide precipitation at elevated pH provides conditions where the metal hydroxides have low solubility and precipitate out upon settling, typically over time periods of 2-4 hours. Lanouette (1977) point out that when two or more heavy metals are found in the same wastewater stream, the optimum pH or precipitation of each cation may be different. The question then becomes whether it is possible and practically precipitates one or more of the metals separately at the source at one pH and treat the remaining stream(s) at another pH. It must also be determined if one pH condition can provide satisfactory although not optimum, removal of the metals present in the wastewater was not effective.

Chemical precipitation of heavy metals may be accomplished by either batch or continuous systems. For small flow rates (less than 50,000 gallons per day), simpler and less expensive batch systems are more feasible. Another application of the batch system is where the waste characteristics may be variable and require modification of treatment from time to time. A continuous treatment system is applicable when wastewater characteristics are uniform or when flow rates are large. Although all the heavy metal wastewater treatment techniques can be employed to remove heavy metals, they have their inherent advantages and limitations. Heavy metals removal from aqueous solutions has been traditionally carried out by chemical precipitation for its simplicity process and inexpensive capital cost. However, chemical precipitation is usually adapted to treat high concentration wastewater containing heavy metal ions and it is ineffective when metal ion concentration is low. And chemical precipitation is not economical and can produce large amount of sludge to be treated with great difficulties.

2.5.2.1. Hydroxide Precipitation

Arumgam (1976) studied hydroxide precipitation or recovery of Chromium from spent tan liquor. This precipitation process was cheapest for the removal and recovery of Chromium. The

optimum pH for maximum removal with lime is 6.6; removal of Chromium exceeded 98% at that pH. The precipitated Chromium hydroxide is separated by settling, filtered, and redissolved in sulfuric acid to form Chromium sulfate which can be recycled for further tanning. The use of lime was more economical than the use of other alkalis (NaOH, Na_2CO_3, and NH_4OH).

Rabosky and Altares (1983) presented a case history of wastewater treatment for a small Chrome plating shop. Caustic soda was used to adjust the wastewater pH to 9.5-10.0 to precipitate the metals as metal hydroxides. For the copper wastewaters, the precipitation was carried out at pH 10.5 using NaOH.

Sheffield (1981) investigated lime precipitation for removal of copper, iron, nickel, Chromium, and lead. These metals from electroplating shops could be successfully removed by precipitating with a hydroxide (such as lime) or soda ash with addition of sulfate or sulfide for the enhancement in removing the copper/iron complexes.

Peters and Ku (1984) studied batch precipitation of zinc, and nickel by both hydroxide and sulfide precipitation for various pH conditions, reaction times, and type and concentration of complexing agents. The metal hydroxide precipitates tend to be colloidal and amorphous in nature, causing the resulting sludge to be voluminous. The presence of complexing agents severely inhibited metal hydroxide precipitation. Generally, a higher pH condition enhances the nucleation rate and enhances the resulting particle size distribution. In the absence of chelating agents, extremely low residual zinc and cadmium concentrations (Zn<0.5 mg/L), (Cd < 0.3 mg/L) were obtained.

Hydroxide precipitation of heavy metals is well suited for automatic pH control and has been shown to be an effective treatment technique in industry. As an example of the effective nature of hydroxide precipitation removal efficiencies exceeded 98% for Cd^{+2}, Cr^{+3}, and Pb^{+2} using spiked well waters and river waters (Sorget al., 1979). Limitations associated with the use of hydroxide treatment include: hydroxide precipitates tend to resoluble if the solution pH is changed, hexavalent Chromium is not removed by hydroxide precipitation, and removal of metals hydroxide precipitation of mixed metal wastes may not be effective because the minimum solubility for different metals occur at different pH conditions.

2.5.2.2. Lime Coagulation

The precipitation of metal hydroxide is dependent upon the concentration of the metal ion in solution and the pH of the solution. The following equation indicates the interdependency of pH, metal concentration and metal solubility; as pH increases the solubility of the metal hydroxide decreases.

2.5.2.3.Carbonate Precipitation

Patterson et al (1977) studied the feasibility of carbonate precipitation or heavy metals removal. Carbonate precipitation has several advantages over conventional hydroxide precipitation: Optimum carbonate precipitation treatment occurs at lower pH conditions than those for optimum hydroxide treatment and metal carbonate precipitates are reported to be denser than the hydroxide precipitate causing improved solids separation.

Sodium bicarbonate can also be used to precipitate the heavy metals out of solution (Barber et al., 1978). Such treatments have the dual advantage of precipitating the metal carbonate holding pH within a narrow range at nearly optimum levels. Although sodium bicarbonate is not as efficient in removing metal solution as other bases, it has the advantage of neutralizing excess acidity and this helps to meet wastewater discharge standards. The sodium bicarbonate acts as a buffer to maintain alkalinity near the optimum pH level. Some metals, such as zinc, do not readily precipitate regardless of the amount of carbonate added. However, by mixing soda ash, sodium bicarbonate, and lime, it is possible to precipitate zinc as hydroxide while using the carbonates to stabilize pH. Sodium bicarbonate treatment has the additional advantage of easy handling, simple application, ability to function in continuous flow operation, and moderate cost.

2.5.3 Ion Exchange

Among the physicochemical methods developed for Chromium removal from wastewater, ion exchange is becoming a popular method that has received much attention in recent years (Lin and Kiang, 2003). Ion exchange is a unit process by which ions of a given species are displaced from an insoluble exchange material by ions of a different species in solution. The Chromium containing electrolyte enters one end of the column under pressure, passes through a resin bed,

and the Chromium is removed from the solution. When the resin capacity is exhausted, the column is back washed to remove trapped solids and then regenerated. Commonly used matrices for ion exchange are synthetic organic ion exchange resins.

The disadvantage of an ion exchange method for Chromium removal is that ion exchange resins are very selective (Sapariet al., 1996). A resin must be chosen that selectively removes the metal contaminant of concern. Further ion exchange equipment can be expensive and there can be incomplete removal; the matrix gets easily fouled by organics and other solids in the wastewater. Moreover ion exchange is non-selective and is highly sensitive to pH of solution.

2.5.4 Electrochemical Precipitation (ECP)

This method utilizes an electrical potential to maximize the removal of heavy metals up to parts per million (ppm) levels from water. (Kongsricharoern and polprasert, 1995) investigated the hexavalent Chromium removals from electroplating wastewater using the ECP process. Using this process, hexavalent Chromium concentration could be reduced from 3,860 mg/L to less than 0.2mg/. Although the process is cost effective its efficiency is affected by low pH and the presence of other salts (ions). The process requires addition of other chemicals, which finally leads to the generation of a high water content sludge, the disposal of which is cost intensive.

2.6 Chromium Regulations

Chromium behavior is fascinating chemistry, and its complexity leads to regulatory problems. Decisions about allowable limits in soils, drinking water, wastewater sludge, and permissible strategies for remediation of land polluted with industrial Chromium have been and must be made. Decisions that affect a multitude of people, local environments raise political and technical controversies.

Presence of Chromium especially hexavalent Chromium more than the standard limit in the water bodies causes many adverse effects to human beings, animals, plants, etc. Hence stringent regulations have been imposed by various organizations. According to the World Health Organizations (WHO, 1993) drinking water guidelines, the maximum allowable limit for hexavalent Chromium and total Chromium (including Cr^{+3}, Cr^{+6} and other forms) are 0.05 and

2mg/L, respectively (Gupta and Rastogi, 2009). According to Safe Drinking Water Act, maximum contaminant level (MCL) is 0.1mg/L (total Chromium). Specific color additives may contain Chromium at levels no greater than 50 mg/L. Chromium may be used in feed for animals provided; it contains Chromium at levels below 2.75% of the total by weight.

2.7 Waste Water Sludge

Regulatory limits for sludge contaminants and rules for the land application and treatment of sludge were mandated under the Clean Water Act (USEPA, 1994). The pollutants initially selected for environmental profile development for land application of sewage sludge included 13 inorganic elements (Chromium, Arsenic, Cadmium, Cobalt, Copper, Fluoride, Iron, Lead, Mercury, Molybdenum, Nickel, Selenium, and Zinc).

The pollutants selected were subjected to risk assessment and were subsequently regulated at the lower concentration of either the 99^{th} percentile concentration determined from the national sewage sludge survey or the risk based concentration as determined from various toxicity tests (USEPA, 1995). USEPA based the commutative pollutant loading rate for Chromium on as assessment of the potential for plant injury (measured as retardation in the growth of a young plant) from Chromium in sewage sludge that is applied to land.

2.8 Wastewater Discharge Standards of Ethiopia

Environmental pollution derived from domestic and industrial activities is the main threat to the surface and groundwater qualities in Ethiopia. The wastewater from domestic and industrial sources in the country is discharged into nearby water bodies and open land without any form of treatment. However, the survival of the ecosystem depends on the ability to manage wastes in an environmentally sound manner. This can only be achieved through establishment and enforcement of appropriate standards and guidelines set to ensure that one does not destroy the environment (EEPA, 2003).

These standards are being introduced to be used throughout the country subject to amendment as more information on the state of pollution is made available. The regional states can establish more stringent standards taking into consideration particular ecological conditions in their localities provided that these present standards are used as the minimum.

Table 2.2: Guideline for metal working, plating and finishing limit values for discharges to water

Parameter	Limit Value
Temperature	40 °C
pH	5.5 – 9.5
Suspended Solids	25 mg/L
Chromium (as Cr(VI))	0.1 mg/L
Chromium (as total Cr)	1 mg/L
Copper (as Cu)	2 mg/L
Lead (as Pb)	0.5 mg/L
Mercury (as Hg)	0.01 mg/L
Nickel (as Ni)	1 mg/L
Silver (as Ag)	1 mg/L
Zinc (as Zn)	1 mg/L
Total Metals	15 mg/L
Trichloroethane	0.1 mg/L
Trichloroethylene	0.1 mg/L

Source: EEPA (2003)

2.9. Bioremediation of Hexavalent Chromium

Bioremediation works by utilizing the relatively recent discovery that some microorganisms have adapted to survive in harsh environments, and are able to naturally transform or degrade a variety of contaminants into less hazardous forms. These include heavy metals (Costley and Wallis, 2001), radionuclide and hydrocarbons of which the majorities are described as biodegradable (Prince et al., 2002).

Discovery of microorganisms capable of reducing hexavalent Chromium to trivalent Chromium have significant potential in development of in situ or on-site bioremediation strategies. In 1977, the first reported bacterial strains, Pseudomonas, were isolated from chromate (CrO_4^{2-}) contaminated sewage sludge by Russian scientists N.A. Romanenko and V.Korenkov. Since 1977, several other CrO_4^{2-} reducing strains have been reported, including other strains such as

B. cereus, B.subtilis, E.coli, Achromobacter Eurydice, microorganisms (Lovley, 1994). A number of bacteria in other genera, viz. bacillus spp., E.coli and a few unidentified strains have also been shown to reduce hexavalent Chromium (Camargo et al., 2003). But, for high concentration heavy metals they are not effective.

While several biological processes have been proposed to manage mixtures of heavy metal contaminants, many of these approaches are only marginally cost-effective for some pollutants, and are often limited by slow rates of reaction and the accumulation of transformation products of equal or even greater toxicity (NAS, 1994). Thus, there is a need to explore alternatives for the remediation of numerous sites contaminated with mixtures of such common priority pollutants.

2.10 General Full Factorial Design

In statistics, a full factorial experiment is an experiment whose design consists of two or more factors, each with discrete possible values or "levels", and whose experimental units take on all possible combinations of these levels across all such factors. A full factorial design may also be called a fully crossed design. Such an experiment allows the investigator to study the effect of each factor on the response variable, as well as the effects of interactions between factors on the response variable. A factorial experiment can be analyzed using ANOVA or regression analysis. It is relatively easy to estimate the main effect for a factor. To compute the main effect of a factor "A", subtract the average response of all experimental runs for which A was at its low (or first) level from the average response of all experimental runs for which A was at its high (or second) level. Other useful exploratory analysis tools for factorial experiments include main effects plots, interaction plots, and a normal probability plot of the estimated effects. When the factors are continuous, two-level factorial designs assume that the effects are linear. If a quadratic effect is expected for a factor, a more complicated experiment should be used, such as a central composite design. Optimization of factors that could have quadratic effects is the primary goal of response surface methodology.

2.11 Factors Affecting Hexavalent Chromium Reduction

Experiments were conducted to study the effect of Reduction time on the Reduction of Chromium against various doses of Reducing agent viz.; Sodium bisulphite. For Sodium

bisulphite it was seen that for a dose varying from 180 to 540 mg/1, the change in %Reduction was rapid in first 30min, and then it tapers towards the end. Therefore 30min was regarded as the Optimum Reduction period for comparison between various doses of Sodium bisulphite, it can be seen that the Reduction of 94.00% can be obtained corresponding to a dose of 180mg/1.When the dose was increased to 180 and 540 mg/l, % Reduction of only 96.32 and 97.47 % respectively were obtained. This shows that %Reduction depends upon the concentration of chromium remaining in the solution. Moreover the Reduction process of Sodium bisulphite completes within 45min.merely increasing the dose beyond a certain limit is of no use. Hence it is better to go for pH adjustment. So the pH was adjusted and its effect on % Reduction was observed, which increased from 96.32 and 97.47 %. Corresponding to pH value from 5 to 2 respectively. (R.S.Karale, October-December 2007).

2.12 Chromium Speciation

Speciation is an analytical process consists of identification and quantification of various forms of a given element present in analysed samples. It requires a multi-step approach, including sampling, sample storage, sample pre-treatment and instrumental analysis. In sampling and sample storage care should be taken in order to samples remain unaffected. Filtration, acidification and extraction are common pre-treatment procedures of environmental samples. A method leading to reliable chromium speciation may be field sampling combined with the immediate Cr (III) and Cr (VI) speciation.

There are many analytical techniques used for speciation of Cr (III) and Cr (VI) either in the off-line or on-line methods. In the off-line methods, separation and pre-concentration of a particular chromium species are carried out before the sample insertion in to the detection instrument. The sample pre-treatment technique includes colour complex formation, soluble membrane filter techniques, chromatographic methods, co-precipitation, ion- exchange, solvent extraction and so on. In the on-line methods, the separation system is coupled with the detection system. (i.e. separation, identification and quantification of chromium are carried out in a one-step analytical process). Among the main separation-speciation techniques are: flow-injection analysis (FIA) and high performance liquid chromatography (HPLC). In a single- line flow-injection only one chromium form is determined directly; whereas the concentration of the other is calculated from the difference between the total chromium contents and that of the measured

one. HPLC is a convenient technique for simultaneous determination of both Cr (III) and Cr (VI) species.

In its most stable form (Cr (III)), chromium can be detected by AAS, by gravimetric Analysis with a number of substances (such as hydrolysis of potassium cyanate to form the insoluble hydroxide. Cr (VI) can also be detected by AAS and also by titration with standard $Na_2S_2O_3$ with I_2.If the solutions to be tested were concentrated enough (above 0.01M), then analysis by titration or gravimetric techniques could be considered. AAS for chromium speciation cannot be considered as this will only determine total Cr (any oxidation state). In water samples, the maximum permitted level is 50μg dm-3 for Cr (VI). As this is far below 0.01M, only one of two methods can be considered. The quicker and easier method will be the complexation of Cr (VI) with 1, 5 - Diphenyl carbazide and the determination of its concentration photo metrically. The carbazide will form a very strongly coloured complex Cr (VI) will absorb best at 540nm.

The molar absorptivity with the complex is 40000 dm^3 g-1 cm-1 at 540nm. Cr (VI) is an element, which will form octahedral complexes with ligands. In this experiment, the ligand is 1, 5- diphenyl carbazide (DPC). By constructing a molecular model of the ligand and positioning it around a suitable 6-branched element, the following structure is proposed as indicated by Fig. 2.2 below. Notice that three of the DPC ligands can be joined to the central Cr. This complex is extremely stable. A second structure has also been proposed. (Shown in Fig. 2.3) with the Cr being 'sandwiched' between the demoralized rings on the primary benzene rings. The second structure is as a result of the use of x-ray diffraction techniques (Addis, M. (2006)).

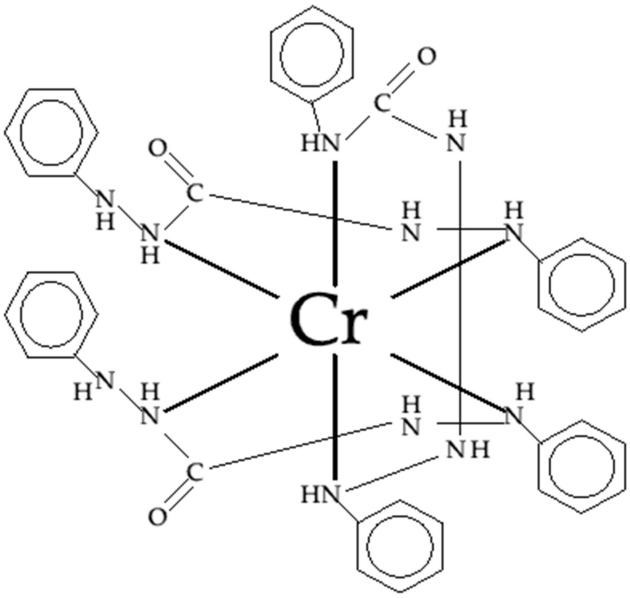

Figure 2.2 Complexation Model

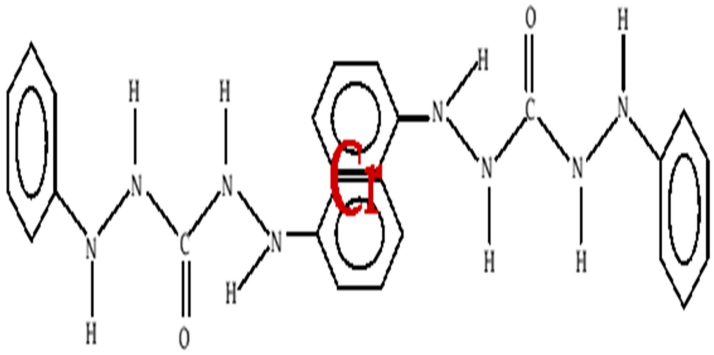

Figure 2.3 X – Ray Diffraction of the Dipc-Cr Complex

3. Materials and Methods

3.1 Experimental Materials and Chemicals

The major raw material used for the reduction of hexavalent chromium during the experimental works was sodium bisulphite. Analytical grade reagent was used for chromium solution; ACS reagent grade concentrated sulfuric acid and 0.1M of NaOH was used to adjusted pH values of samples. In all experimental work, distilled water, Standard buffer solution for pH meter calibration, chromic acid and equipment's such as pH meter/ pH paper, Atomic Absorption Spectrometry (AAS), 250ml Stopper Conical flask, 1000 ml volume of flask, what man number 42 filter paper , Furnace, Digital Weighing Balance, Glass Beakers, Measuring Cylinders ,Burettes & Pipettes are useful. Chrome metal analysis was done, at Homicho Ammunition Engineering Industry and at Defence University College of Engineering, mechanical unit operation and instrumental analysis lab. Real waste water a sample for the reduction of hexavalent chromium was obtained from Homicho Ammunition Engineering Industry (HAEI) located western of Addis Ababa.

3.2. Experimental Methods

3.2.1. Preparation of sodium bisulphite solution

The analytical grade sodium bisulphite is prepared in to three different types of concentration strengths label as 200, 400 and 600 mg/ L. Each of the given concentrations is prepared by weighing using digital balance and dissolved in distilled water of 1000 ml volumetric flask by shaking well.

3.2.2. Preparation of Synthetic Hexavalent Chromium Sample

The potassium dichromate solution ($K_2Cr_2O_7$) is used as source of hexavalent chromium. A stock solution of potassium dichromate of concentration 100 mg/l is prepared in 1000 ml demineralized water in a standard volumetric flask. The solution is diluted to obtain standard solutions containing 10 mg/l of Cr (VI). Initial pH of the synthetic sample is determined by using pH meter.

3.3.Determination of Total Chromium

3.3.1 Preparation of Standard Solutions for Atomic Absorption Spectrometry

From Standard stock solutions that contain 1000 ppm of Chromium, 10 ppm was taken and diluted to 100 ml. Then four working standard solutions (0.5, 1, 2 and 4 ppm) were prepared in 50 mL volumetric flasks. The blank solution and the standard solutions were analyzed with Flame Atomic Absorption Spectrophotometer and a linear calibration curve was obtained.

3.4. Experimental Design

The following conditions are experimental design for hexavalent chromium by sodium bisulphite for all varying conditions (dose of reducing agent, reduction time and pH) with constant stirring rate of 150 rpm. The data is annexed at the appendix.

Table 3.2.Experimental data for response variable reduced Cr (VI), mg/L

Std.	Run No.	Dosage of $NaHSO_3$, mg/L	Reduction Rate, min.	pH	Cr(VI), mg/L
1	44	200.00	40.00	2.00	0.1
2	9	200.00	40.00	2.00	1.5
3	36	400.00	40.00	2.00	1.4
4	23	400.00	40.00	2.00	1.4
5	4	600.00	40.00	2.00	2.0
6	15	200.00	40.00	2.00	2.0
7	50	200.00	60.00	2.00	1.1
8	30	400.00	60.00	2.00	0.2
9	34	400.00	60.00	2.00	0.7
10	52	600.00	60.00	2.00	1.1
11	1	600.00	60.00	2.00	2.0
12	3	200.00	60.00	2.00	0.3
13	48	200.00	80.00	2.00	2.0
14	6	400.00	80.00	2.00	1.5
15	46	400.00	80.00	2.00	1.9
16	8	600.00	80.00	2.00	0.7
17	42	600.00	80.00	2.00	2.0
18	12	200.00	80.00	2.00	0.7
19	22	200.00	40.00	4.00	1.3
20	16	400.00	40.00	4.00	1.0
21	14	400.00	40.00	4.00	1.9
22	27	600.00	40.00	4.00	1.4
23	20	600.00	40.00	4.00	0.6
24	54	200.00	40.00	4.00	1.2
25	49	200.00	60.00	4.00	1.1
26	28	400.00	60.00	4.00	1.8

27	35	400.00	60.00	4.00	0.7
28	25	400.00	60.00	4.00	1.2
29	41	600.00	60.00	4.00	1.6
30	5	600.00	80.00	4.00	0.4
31	29	200.00	80.00	4.00	1.9
32	21	200.00	80.00	4.00	1.9
33	17	400.00	80.00	4.00	0.5
34	39	400.00	80.00	4.00	0.6
35	18	600.00	80.00	4.00	1.3
36	11	600.00	80.00	4.00	1.2
37	26	200.00	40.00	6.00	1.7
38	53	200.00	40.00	6.00	1.8
39	45	400.00	40.00	6.00	1.9
40	33	400.00	40.00	6.00	1.3
41	24	600.00	40.00	6.00	1.8
42	43	600.00	40.00	6.00	0.8
43	13	200.00	60.00	6.00	0.4
44	51	200.00	60.00	6.00	1.9
45	31	400.00	60.00	6.00	1.4
46	7	400.00	60.00	6.00	0.9
47	38	600.00	60.00	6.00	1.4
48	47	200.00	60.00	6.00	0.4
49	19	200.00	80.00	6.00	1.9
50	32	200.00	80.00	6.00	0.3
51	40	200.00	80.00	6.00	1.1
52	2	400.00	80.00	6.00	1.8
53	10	600.00	80.00	6.00	0.9
54	37	600.00	80.00	6.00	0.2

3.5. Batch Reduction Experiment of Hexavalent Chromium by Sodium Bisulfide

From the most common reducing agents **Sodium bisulfite was** available and using the knowledge of design of experiment (DoE) i.e. full factorial design to set the optimum parameters (conditions) is applied. These are $2(3^3)$, three factors (dose of reducing agent, reduction time and pH) and three levels of the factors (does (mg/l) = 200,400 and 600; reduction time (minutes) = 40, 60 and 80 and pH= 2, 4 and 6) with two replicates and response or yield is reduced Hexavalent Chromium Cr (VI). Experiment is conducted to determine the optimum condition of hexavalent Chromium reduction using jar test method. The diluted solution contained 10 mg/ l and each beaker contained 500 ml of synthetic samples of fifty four (54) runs. First, **Sodium bisulfite** of various doses from 200mg/l, 400 mg/l and 600mg/l was added to each beaker in increments to determine the optimum dosage of **Sodium bisulfite**, optimum pH, and reduction time. The above chemical reaction is facilitated by the addition of sulfuric acid with respect to the volume and concentration of the synthetic solution.

Reduction with **Sodium bisulfite** is appropriately used in the experiment, because **Sodium bisulfite** is readily available in Homicho Ammunition Engineering Industry (HAEI); this indicates that availability of **Sodium bisulfite as a** reducing agent had been a key factor when selecting a reducing agent for aqueous hexavalent Chromium Cr (VI). The prepared synthetic sample was agitated at speed of 150 rpm, and six 500 ml volume of beakers were tested at a given reduction rate using Jar test apparatus. The concentrated synthetic sample was diluted to 100 mg/L i.e. using minimum amount or well diluted reducing agent. In my observation the pH adjustment was using strong base of 0.1 N NaOH and 0.3 N of H_2SO_4.

3.6. Determination of Hexavalent Chromium

3.6.1. Preparation of Standard Solutions for Spectrophotometric Analysis

An analytical grade of 0.25 g of 1,5-DipHenyl carbazide (DPC), a common complexing agent of Chromium (VI) for spectrophotometric analysis was taken and dissolved with 95% ethanol and diluted to 100 ml with distilled. Then a freshly prepared 1 ml of 1, 5-DPC was added to each sample and aged until a pink color is developed. For the Preparation of Chromium stock solution (500mg Cr+6/L), an analytical grade of 141.1 gm of K2Cr2O7 was taken and dissolved with deionized water and to prepare (5 mg Cr+6/L) 1 ml of the stock solution is dissolved in 100 ml of distilled water. A series of six standards containing concentration of 0.1, 0.2, 0.3, 0.4, 1, 2 µgm/ml were taken and acidified with 0.2 N of 5 ml of sulfuric acid. Then freshly prepared 1 ml of 1, 5-DPC was added to each standard and a pink was immediately developed. A blank and the standard solutions were analyzed with UV-Vis spectrophotometer with 1 cm quartz cell was used and the absorbance measurements was performed in the range of 400-800 nm. The absorption maxima were observed at 544.03 nm as shown in the following figure.After calibrating the instrument, all the prepared samples were diluted to the required concentration by fivefold dilution procedure i.e. the original concentration solution of the synthetic sample is 10 ppm.

3.7.Precipitation of the Reduced Chrome

After complete reduction of hexavalent Chromium the precipitating agent viz, combination of calcium hydroxide and sodium hydroxide is added to each sample separately of 40mg/l dosage. In order to mix the solution, samples were taken to jar apparatus and samples were mixed for 40 minutes with speed of 120 rpm. The precipitate formed was allowed to settle overnight. Supernatant was separated and analyzed for Chromium using UV/Vis spectrophotometer in the following schematic experiment in fig. 3.1.

3.8.Oxidation of the Reduced Chrome (Cr- Sludge)

Recovery of chrome from the Cr- sludge was tested using the acid-soluble method. The dissolution of the sludge in acids was often incomplete, resulting in a low chromium recovery. In order to improve the leaching rate of chromium from Cr-sludge,H_2SO_4 and its mixture with HCL and HNO_3 were tested. Oxidation of chrome from Cr-sludge was operated with 500 ml beakers in a shaking water bath at 32 ^oC. Each of the beakers held 10 g wet sludge and 5% H_2SO_4 solution was used as a solvent. Three Cr-sludge loads, i.e. 9.90, 13.0 and 23.87 g/l were

settled by adding H_2SO_4 solution to the beakers and oxidation time 25, 35 and 45 min. were tested according to the Cr-sludge loads, respectively. After the reactions, chromium content in the supernatant was tested.

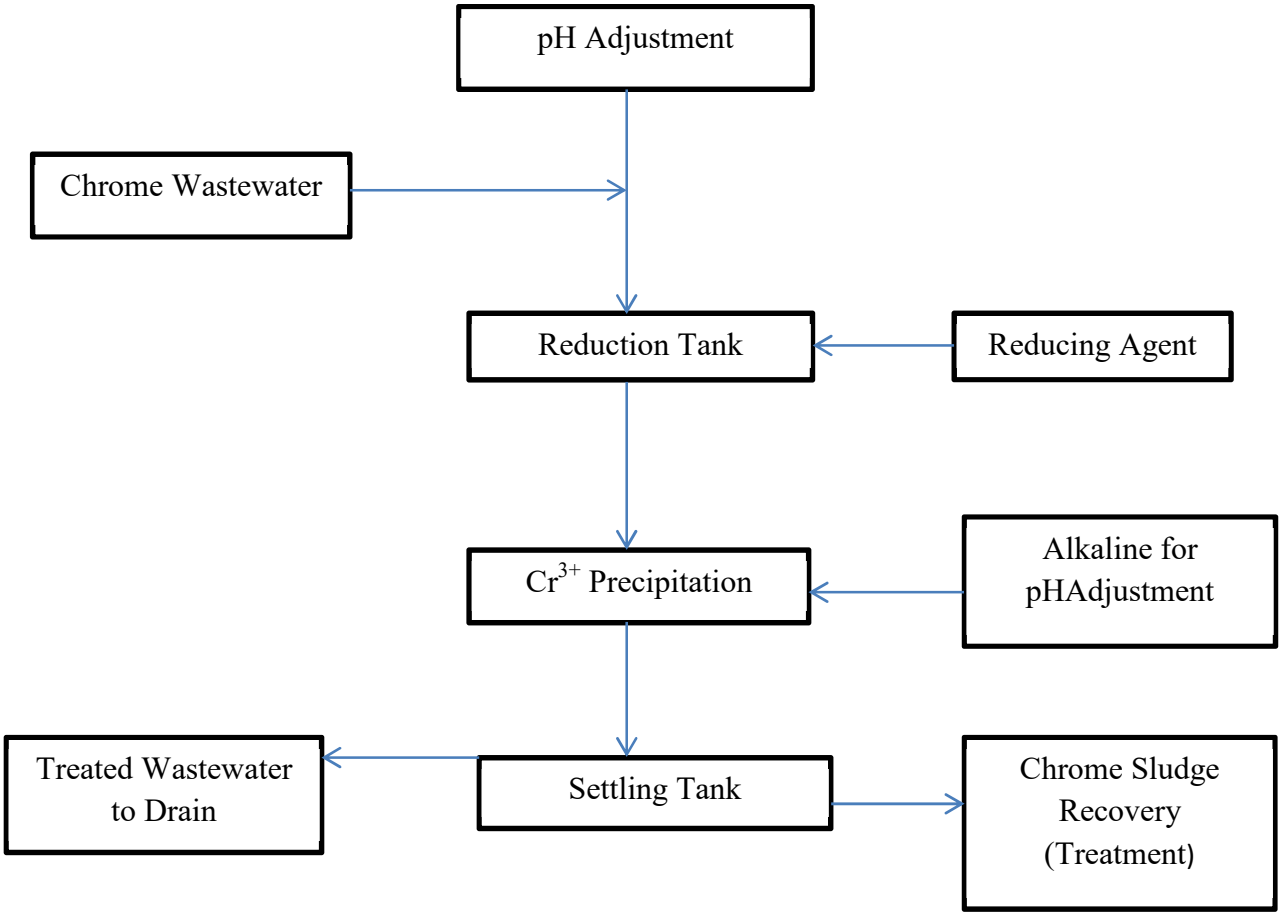

Figure 3.1 Schematic treatment of chromium containing wastewater

Figure 3.2 Jar test apparatus.

4.0 Results and Discussion

The Chemical reduction process on hexavalent chromium Cr (VI) by Sodium bisulfite was done. The result was obtained by the concept of design experiment (DoE), analysis of variance (ANOVA). There are three factors with three levels and replicated two times, these all initiated to discuss the effects of each selected parameters and which levels of the factors were optimized. The main concerned effects are pH, reduction rate and dose of reducing agent.

4.1 Effect of pH on concentration of Cr (VI)

pH effect on reduction of hexavalent chromium Cr (VI) was conducted between pH solution of ranges 2 to 6. This range was chosen because of the evidences that the lower the value of pH the fastest will be the reaction. From the observed data represented by the graph below indicates as the pH decreases the conc. of Cr (VI) is decreased.

Table 4.1 At Constant Dose of reducing agent effect of pH on conc. of reduced Cr (VI)

pH	Conc. of reduced Cr (VI), mg/L		
2	0.1	0.2	0.3
4	0.2	0.3	0.4
6	0.3	0.5	0.6

The Fit linearity of R^2 =0.986, this value is almost near to one i.e. data analysis was easily understandable to determine the optimum parameter of the graph.

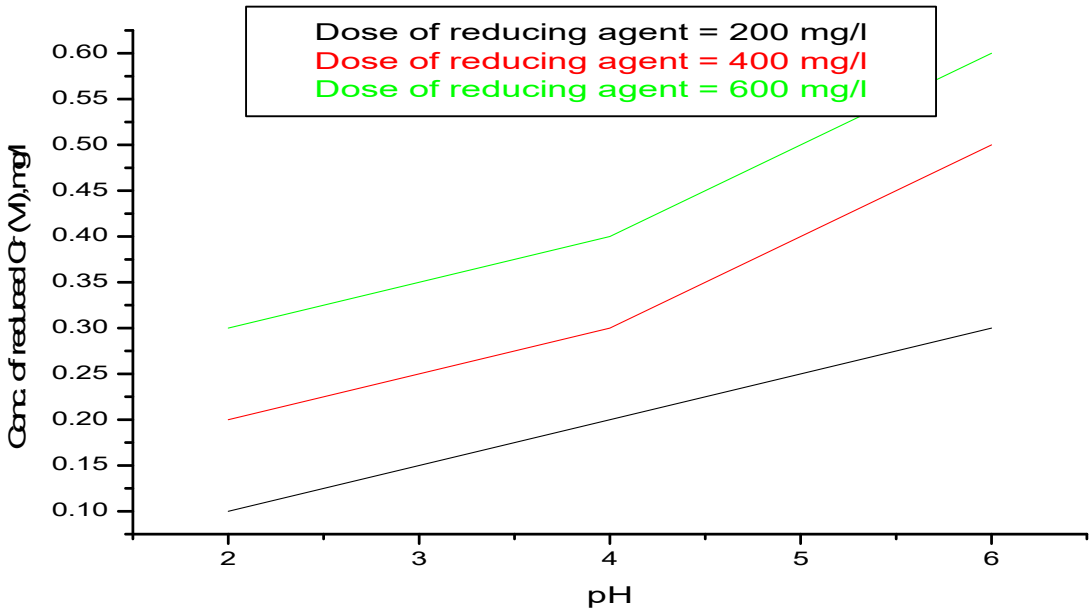

Figure 4.1 Effect of pH Vs. Conc. of reduced Cr (VI) at Constant dose of reducing agent

4.2 Effect of Dose of reducing agent on Cr (VI) Concentration

The effect of the dose of reducing agent of hexavalent chromium Cr (VI) was observed by varying its amount from 200 – 600 mg/L of sodium bisulphite. The reduction reaction highly depends on the strength of the reducing agent and the mixing speed of the jar test apparatus. The preferable dose amount (concentration) was 200 mg/L, because as the dose amount increases the amount of sludge also increased. For comparison of the dose's sludge generated at each three levels were varied depending on their amount. To elaborate the impacts of doses, graphically it is represented from the experiment.

Table 4.2 at constant reduction time effect of dose of reducing agent on conc. of Cr (VI)

Dose ,mg/L	Conc. 0f reduced Cr(VI), mg/L		
200	0.1	0.3	0.4
400	0.2	0.5	0.6
600	0.7	0.9	1.1

The Fit linearity of R^2 =0.94034, this value is not fit appropriately, but the data analysis was easily understandable to determine the optimum parameter from the graph.

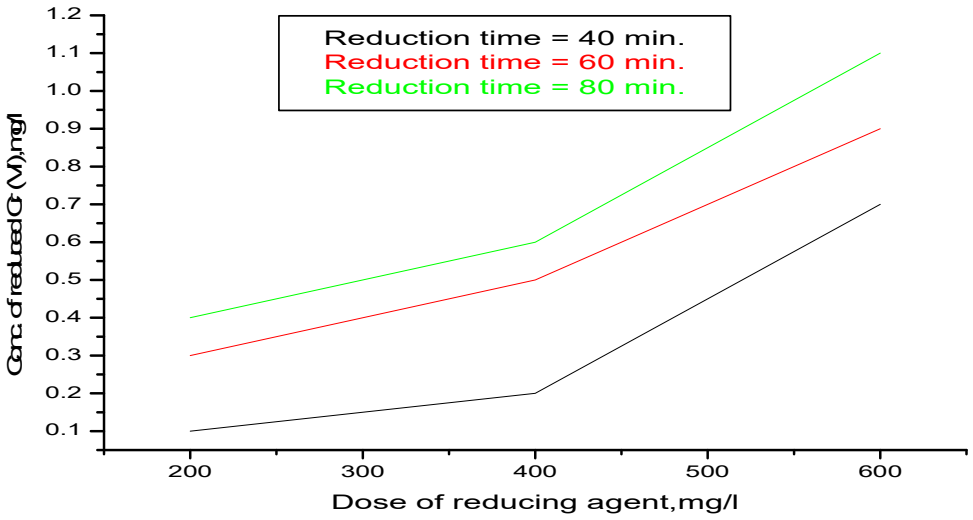

Figure 4.2. Effect of reducing agent Vs. conc. of reduced Cr (VI) at constant reduction time

4.3 Effect of Reduction time on Cr (VI) Concentration

To examine the effect of reduction time on Cr (VI) concentration. Fig.4.3 elaborates the relationship between pH and reduction time, i.e. rate depend on pH value. Minimum concentration of Cr (VI) is observed at 40 minutes, reaction is very fast when the pH is decreased. Controlled pH and rate could be directly proportional; at pH 2 conversions was high. The other parameters that are constraint to the reaction between reducing agent and the synthetic sample should be considered. Such as stirrer speed, man power error and so on.

Table4.3. At constant pH effect of reduction time on conc. of Cr (VI)

reduction time,min.	Conc. of Cr(VI), mg/L		
40	0.1	0.3	0.5
60	0.2	0.3	0.5
80	0.2	0.4	0.5

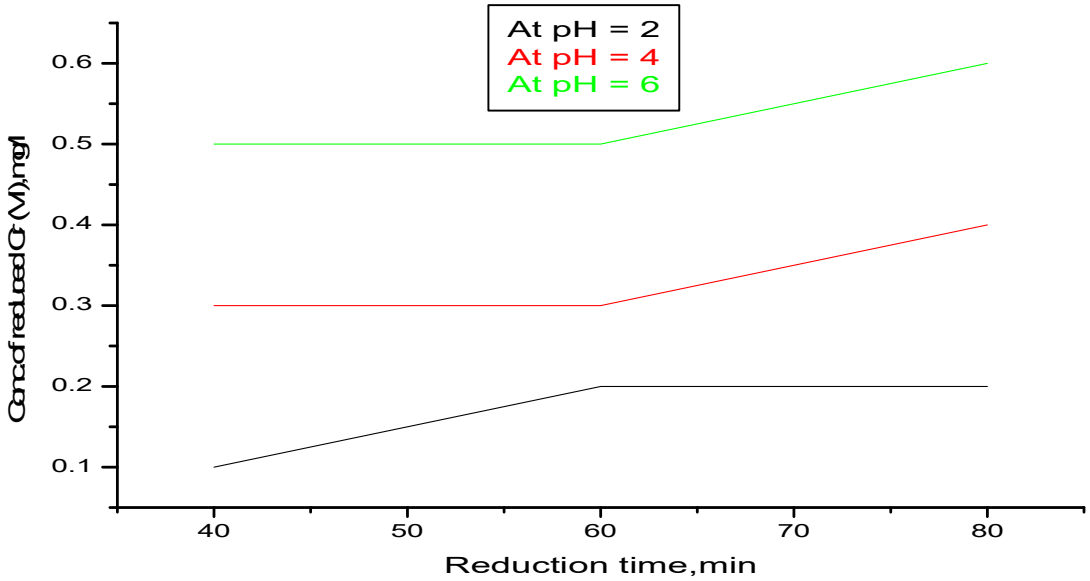

Figure 4.3 Effects of Reduction Rate Vs. Conc. of reduced Cr (VI) at constant pH

The Fit linearity of R^2 =0.952, this value is showed that near to one i.e. data analysis was easily understandable to determine the optimum parameter of the graph.

4.5 Data analysis using Design expert 6.0.8 software

Three basic factors were selected for design expert to determine the total experiment runs. Initially three factors and three levels were selected to give a total experimental runs of 27 with a factorial design of 3^3synthetic waste of Cr (VI). The result was replicated two times to improve reliability of the data and that resulted to perform 54 experiments.

A planning matrix was set up to take account of the factors that could influence with responses, such as dose of reducing agent, reduction rate and pH at different levels. Table 4.4 shows the

factors and levels chosen for the planning matrix. Table 4.4 shown below the combinations of three levels of planning factors. The experiment was performed in batch process under constant stirring rate of 150 rpm.

Table 4.4 Factors and Levels for Cr (VI) reduction

Factors	**Level**	**Level value**
Dose of reducing Agent	1	200
	2	400
	3	600
pH	1	2
	2	4
	3	6
Reduction time	1	40 min
	2	60 min
	3	80 min

The objective of applying a factorial design analysis was to identify the most significant factors affecting the reduction of hexavalent chromium after the precipitation process of batch experiments. Table 4.5 showed: The Analysis of variance (ANOVA) - Influence of the factors studied in the reduction of hexavalent chromium.

Table 4.5 ANOVA Analysis

Source	Sum of Squares	DF	Mean Square	F-Value	Prob>F	
Model	**2.247E+010**	**7**	**3.210E+009**	**48.46**	**< 0.0001**	significant
A	3.275E+009	1	3.275E+009	49.45	<0.0001	
B	2.352E+009	1	2.352E+009	35.51	<0.0001	
C	1.495E+010	1	1.495E+010	225.65	<0.0001	
AB	2.847E+005	1	2.847E+005	4.299E-003	0.9480	
AC	8.555E+008	1	8.555E+008	12.92	0.0008	
BC	6.237E+008	1	6.237E+008	9.42	0.0036	
ABC	4.151E+008	1	4.151E+008	6.27	0.0159	
Residual	3.047E+009	46	6.623E+008			
Lack of fit	2.732E+009	19	1.438E+008	12.33	<0.0001	significant
Pure error	3.149E+008	27	1.166E+007			
Cor total	2.551E+010	53				

The Model F-value of 48.46 implies the model is **significant**. There is only a0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are **significant**. In this case A, B, C, AC, BC, ABC 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.

A= Dose of Reducing Agent, B= Reduction Time, C= pH

The Model generated for the Reduction of Hexavalent Chromium was significant that ANOVA analysis shown in the Table 4.5 proves that the results discussed above at a confidence level of 95%. As shown from Table 4.5 values of P less than 0.05 indicate model terms are significant. Results showed that the effect of the main factors i.e. Dose of reducing agent (factor A), Reduction Time (factor B) and pH (factor C) are of major importance for the reduction of Cr (VI) and the interactions effect AC (dose of reducing agent *pH), BC(rduction time *pH) had a siginificancance value on the reduction of Cr (VI), while the interaction effect of AB (dose of

reducing agent * redcution time) was insignificant model terms for chrome reduction,because the p value is greater than F value as showed from the ANOVA.

For the reduction chrome was also affected by the combination of three factors ABC (dose of reducing agent *reduction time *pH) these all speed up the reduction process. As shown from the ANOVA results, the three separate factors had equal contributions for the reduction of chrome. Because three of them were highly interelated during the oxidation reduction process, so they were the dominant factors that affect chrome reduction. Note that the highest coefficients are related to the factors that most influence the reduction process.

Conc. of reduced Cr(VI) = +3.14576E+005-261.83236 * Dose of reducing Agent-1943.53611 * Reduction Time-39085.49306 * pH+2.57398* Dose of reducing Agent* Reduction Time +53.12760* Dose of reducing Agent * pH+382.12396*Reduction Time * pH-0.63669 * Dose of reducing Agent * Reduction Time * pH

As shown in Figure 4.4 below, the agreement between the experimental (actual) data and the predicted values was good. This indicates that, there is a linearity relationship between the reduction process and the three factors are considered.

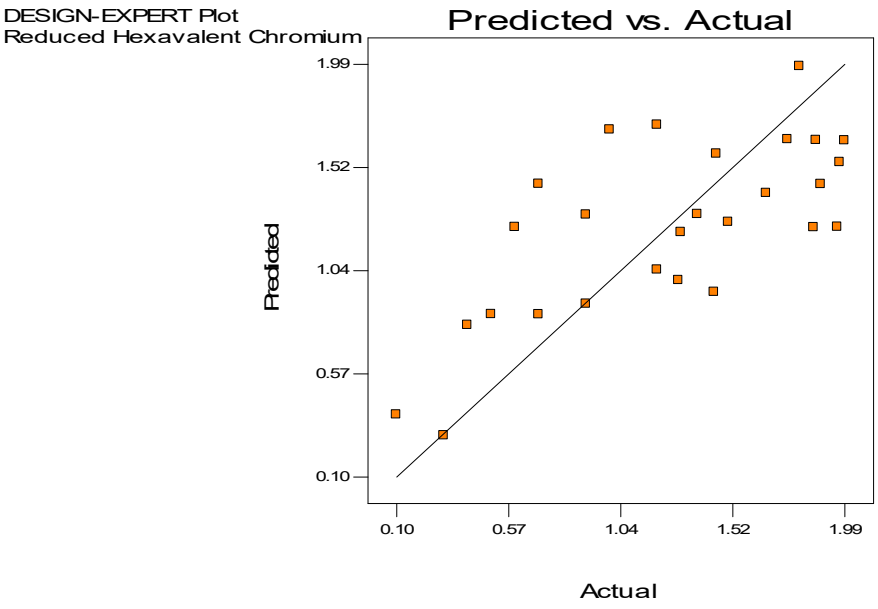

Figure 4.4 Predicted Vs Actual Analysis of Cr(VI) Concentration

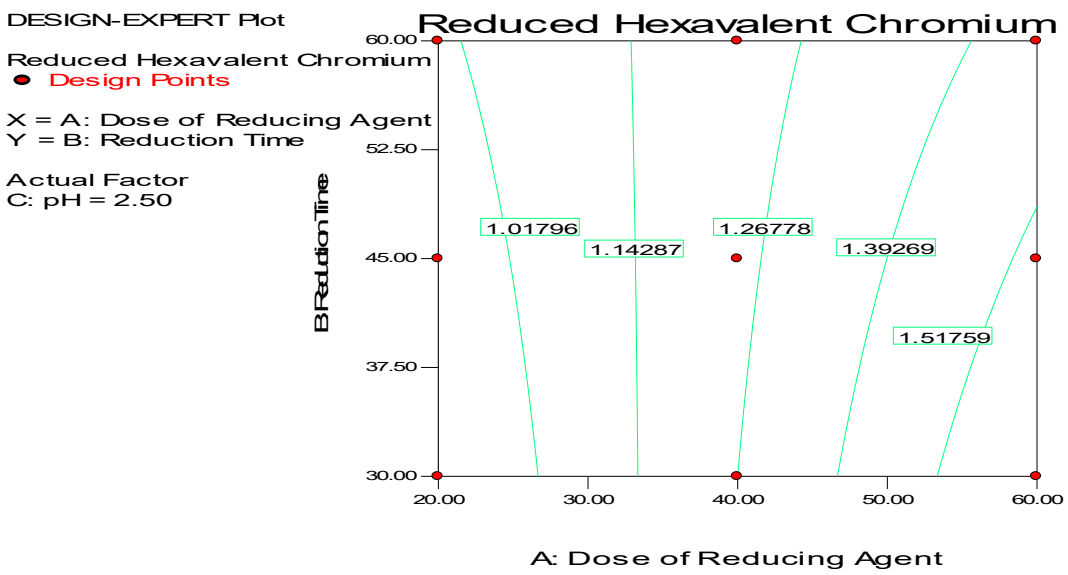

Figure 4.5 Contour plots for the interaction of reduction time and dose of reducing agent on Cr (VI) conc.

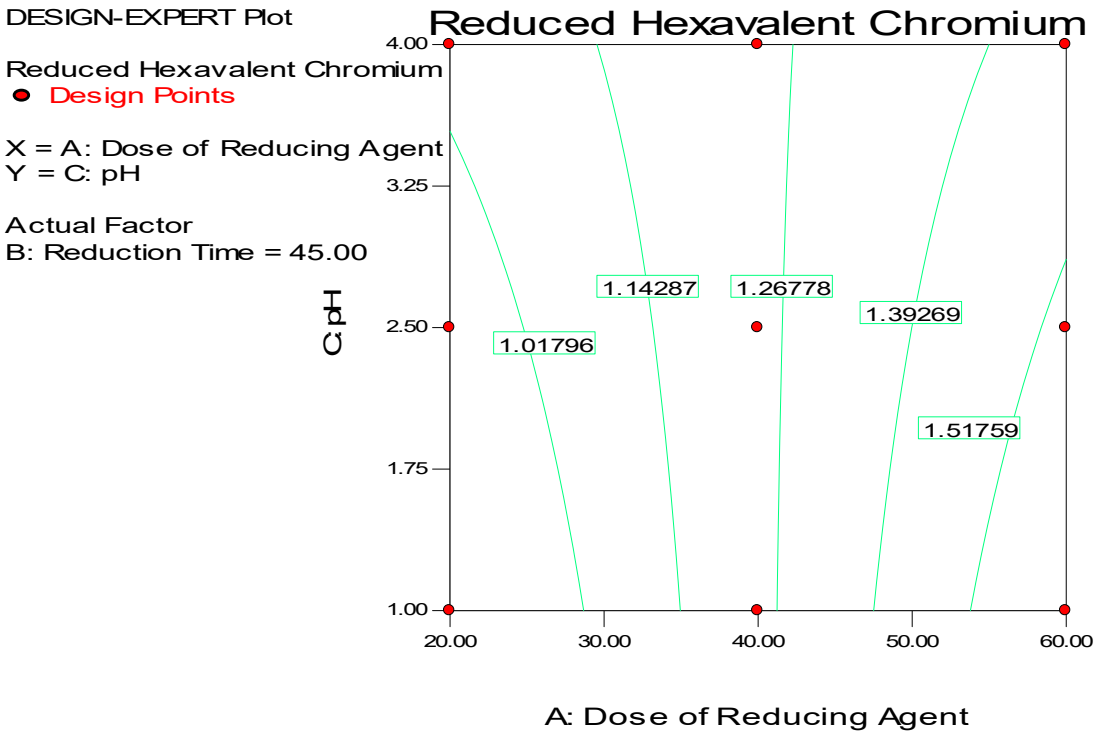

Figure 4.6 Contour plots for the interaction of pH and dose of reducing agent on reduced Cr (VI) conc.

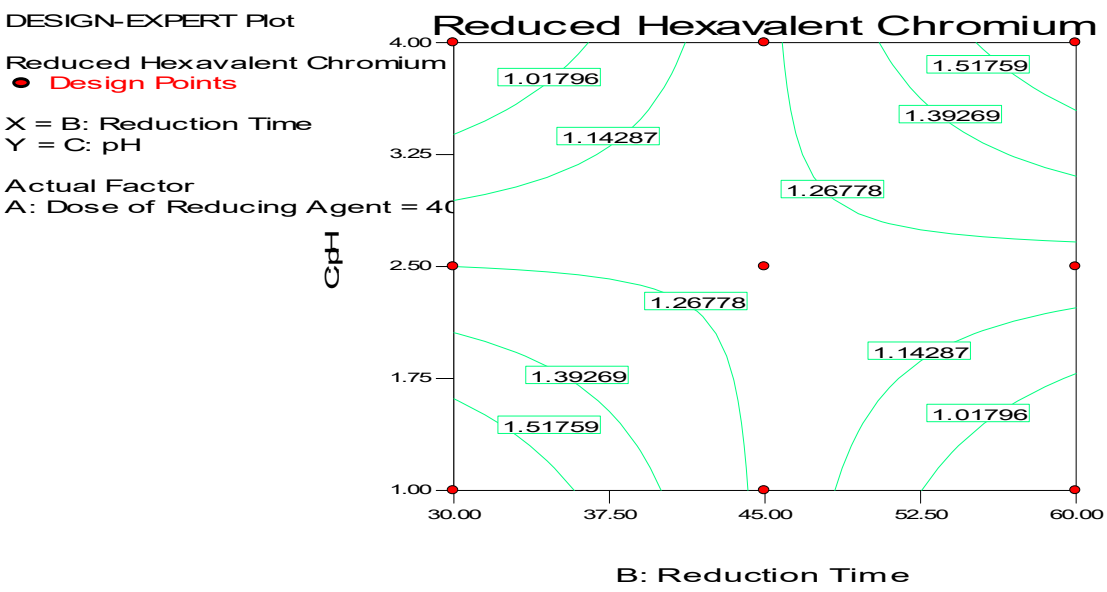

Figure 4.7 Contour plots for the interaction of pH and reduction time on Cr (III) conc.

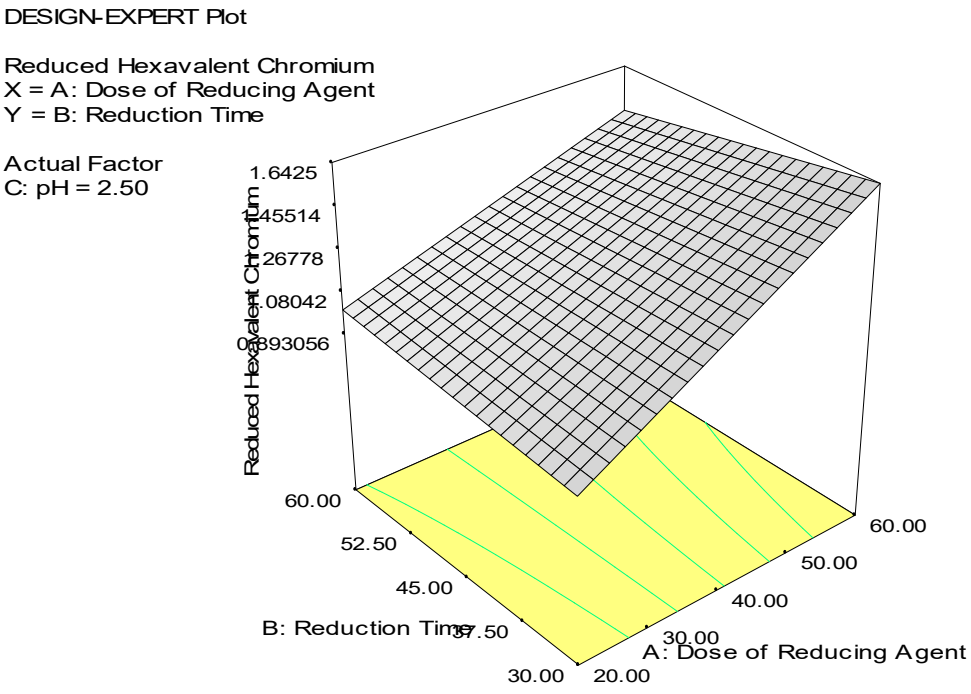

Figure 4.8 3D surface plots for the interaction of reduction time and dose of reducing agent on reduced Cr (III) conc.

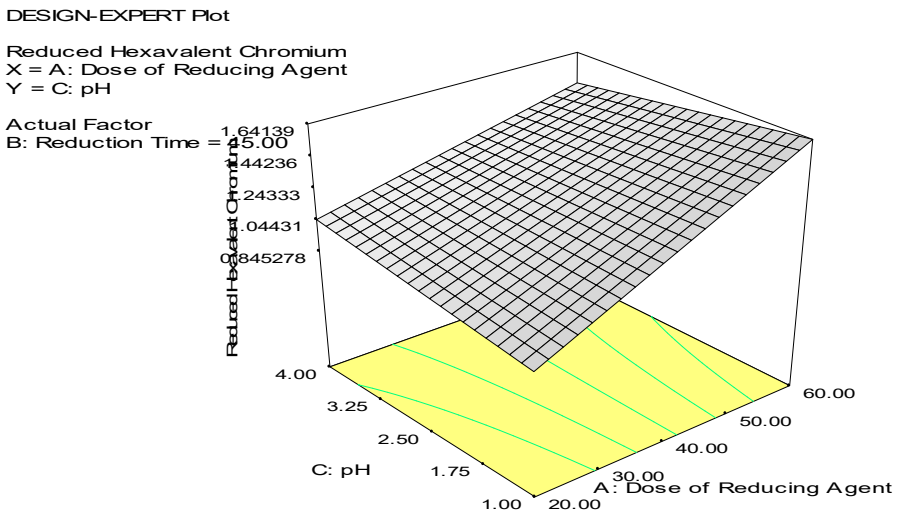

Figure 4.9 3D surface plots for the interaction of pH and dose of reducing agent on reduced Cr (VI) conc.

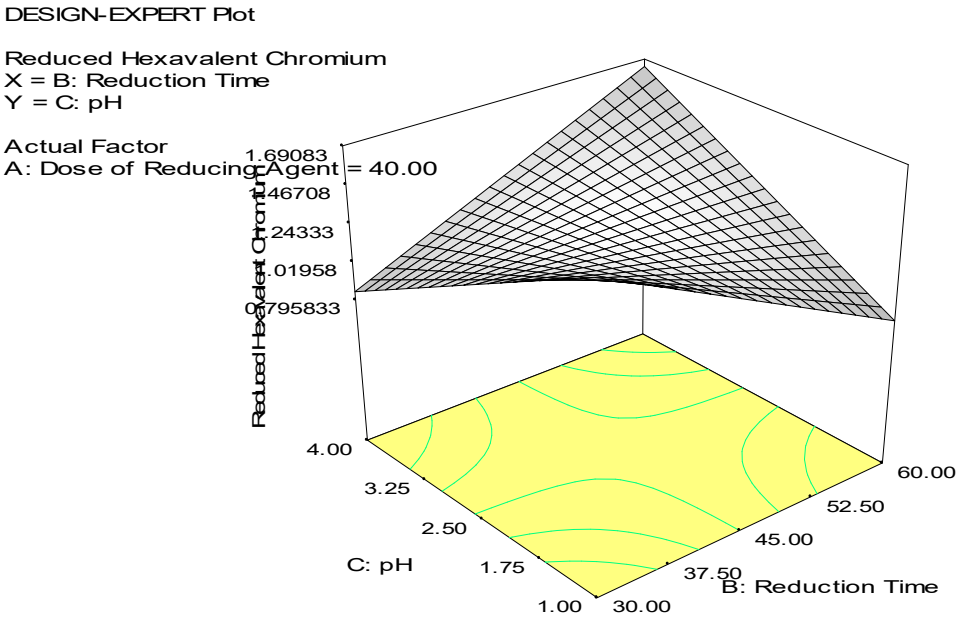

Figure 4.10 3D surface plots for the interaction of pH and reduction time on reduced Cr (VI) conc.

5. Conclusion and Recommendations

5.1 Conclusion

The goal of the study was to treat and recover chrome from electroplating wastewater. The experimental work efforts to collect available chemicals, equipment, data and other necessary materials to propose improvement options available to optimize the factors that affect the treatment process. Based on the study findings the following conclusions were drawn:

The quality of the reducing agent was the major concern for the chemical analysis in terms of the treated wastewater quality, safety, availability and cost effectiveness (environment cost). All the activities that are performed in the experimental analysis were followed with scientific procedures and guidelines. In collaboration to these all the selected process parameters were examined.

From the observed data, pH of the sample and dosage of sodium bisulphite has a strong effect on the reduction rate of hexavalent chromium. The pH value of 2 and contact time of 40 mins with dosage of sodium bisulphite as 200 mg/L were found optimum operational parameters for the reduction of hexavalent chromium.

The process followed by reduction was precipitation, to solidify the remained sludge after complete reduction of hexavalent the precipitating agents were the combination of calcium hydroxide and sodium hydroxide was added to the optimized sample beaker of the reduced hexavalent chrome. To mix the solution, sample were agitated using jar test apparatus for 10 mins with the speed of 80 rpm as in the first step. Second step was samples were analyzed for a mixing time 35 mins with the speed of 40 rpm. Final step was analyzing the optimum operation parameters of precipitation, 80 mg/L of the combined precipitants for 10 mg/L of sludge concentration.

Recovery was also considered to oxidize the sludge remained from the last two processes of treatment of hexavalent chromium. The amount of supernatant separated from the settled chrome was digested by 30 % H_2O_2 after the dissolution of the sludge.

5.2 Recommendations

In order to resolve the Challenges with chrome electroplating wastewater extra studies are required such as:

- Increasing number of factors and levels
- Comparing the reductant and precipitants
- The current electroplating industries are old operation system that are not digitalized and not environment friend. To resolve this process and to control the emission of toxic gases the electroplating process must be shifted to hot deep galvanization.

5.3 Future Work

The remaining work will be applying the thesis work to the ground; more of the implementation of the treatment plant had started. Design part, equipment selection, cost are considered.

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Appendices

Appendix A

Results obtained from AAS, UV/VIs and volumetric analysis of Chrome waste

Run no.	Concentration of Cr(VI)	Absorbance
1	2.0	0.7365
2	1.8	0.6344
3	0.3	0.2588
4	2.0	0.6432
5	0.4	0.2787
6	1.5	0.5590
7	0.9	0.3892
8	0.7	0.3579
9	1.5	0.5685
10	0.9	0.4129
11	1.2	0.4794
12	0.7	0.3413
13	0.1	0.8121
14	1.9	0.6455
15	2.0	0.6853
16	1.0	0.4233
17	0.5	0.3058
18	1.3	0.4974
19	2.0	0.7534
20	0.6	0.3179
21	2.0	0.7542
22	1.3	0.5101
23	1.4	0.5492

24	1.8	0.6562
25	1.2	0.4708
26	1.7	0.6282
27	1.4	0.5490
28	1.8	0.6342
29	1.9	0.6344
30	0.2	0.2318
31	1.4	0.4174
32	0.3	0.3063
33	1.3	0.3920
34	0.7	0.2836
35	0.7	0.3579
36	1.4	0.4036
37	0.2	0.3915
38	1.4	0.5665
39	0.6	0.3362
40	1.1	0.4099
41	1.6	0.6132
42	2.1	0.7978
43	0.8	0.3915
44	0.1	0.2898
45	2.0	0.6196
46	1.9	0.7436
47	0.4	0.2868
48	2.0	0.7890
49	1.1	0.4236
50	1.1	0.4205
51	1.9	0.6455
52	1.1	0.4596
53	1.8	0.7293
54	1.2	0.4436

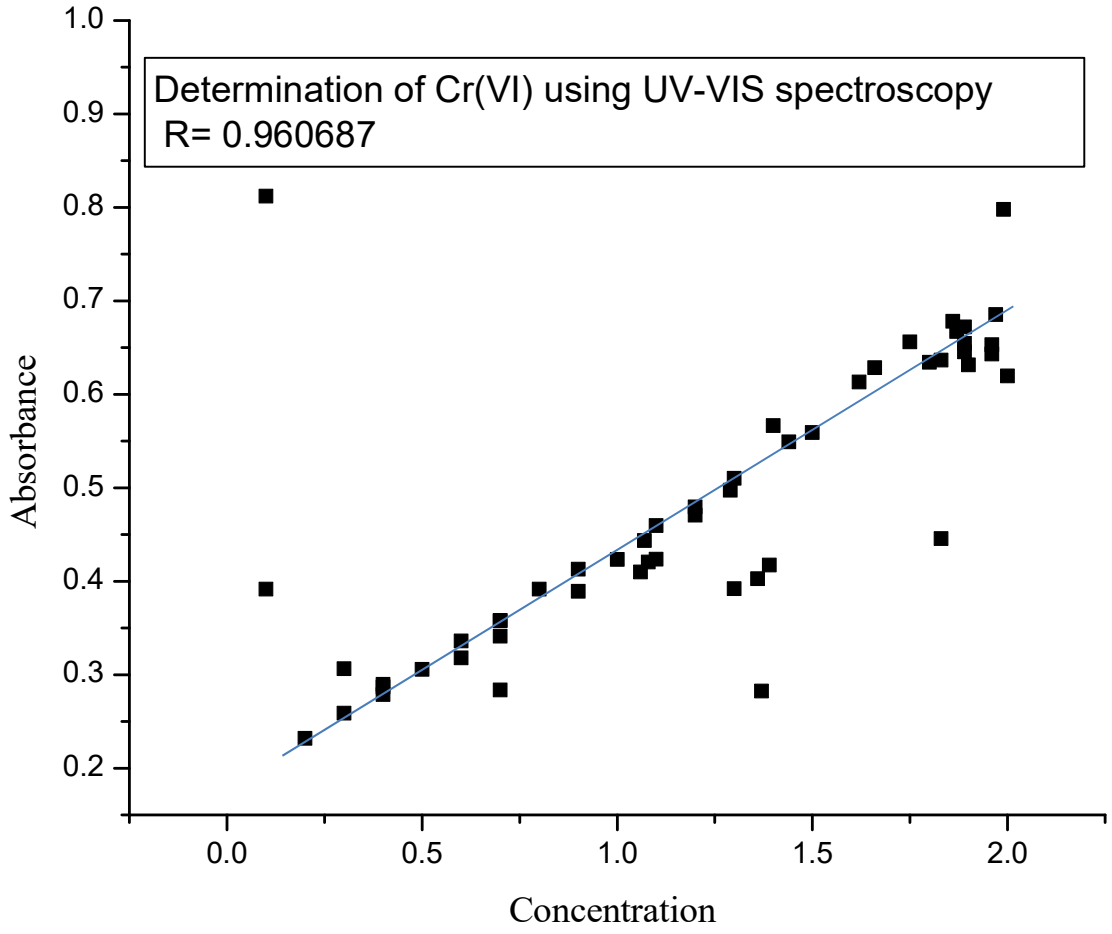
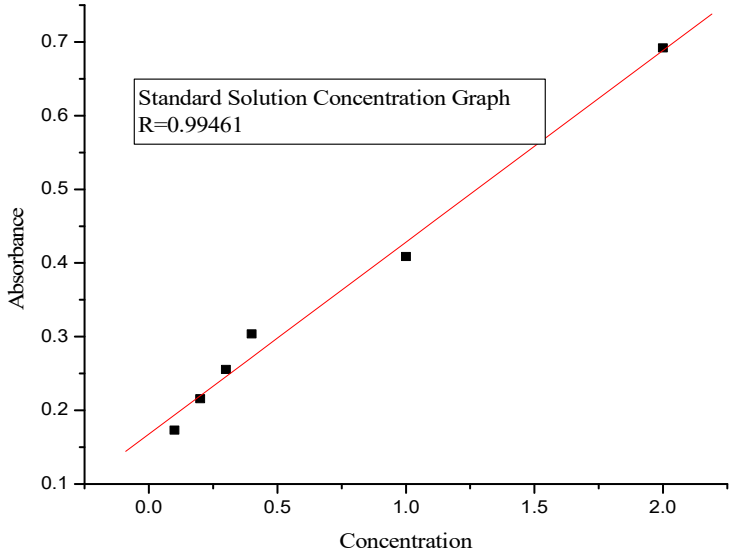

Determination of Cr(VI) using UV-VIS spectroscopy
R= 0.960687
Absorbance
Concentration
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.0
0.5
1.0
1.5
2.0

Table 3.3.Standard concentration (mg/l) & Absorbance

No.	Concentration(mg/l)	Absorbance
1	0.1	0.1730
2	0.2	0.2157
3	0.3	0.2555
4	0.4	0.3037
5	1	0.4088
6	2	0.6918



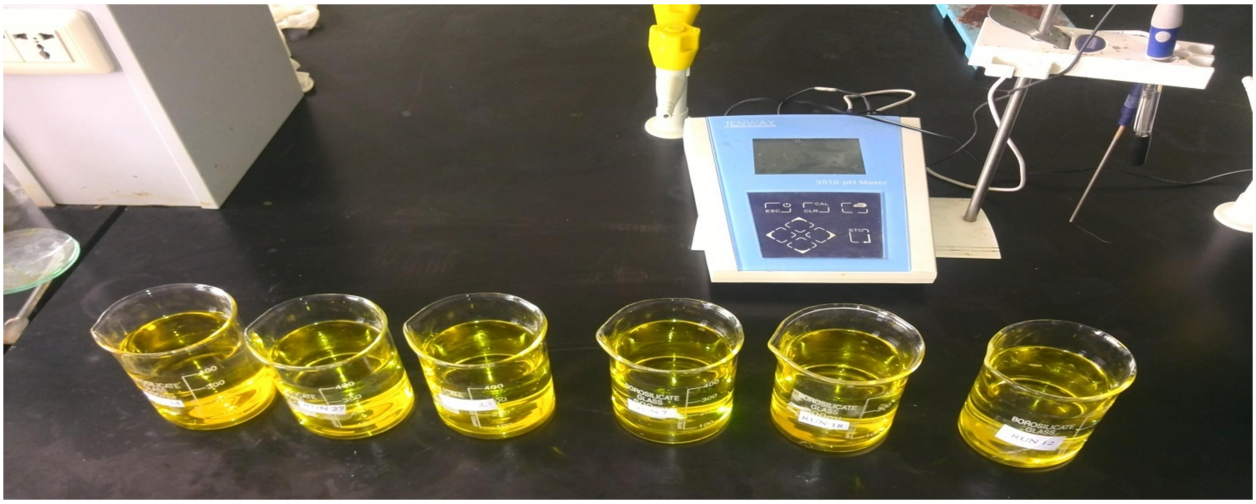
Standard calibration curve for synthetic Chrome

The concentration of synthetic wastewater parameters

No.	Components	Concentration (mg/l)
1	Chromic Acid (CrO_3)	165000
2	Trivalent Chromium(Cr_2O_3)	9000
3	Sulfuric Acid (H_2SO_4)	1600
4	Iron (Fe)	7000

Appendix B

The Detail Photographs for Synthetic Chrome Preparation and Reduction Process.




flocculator | SW6 |
time
05
speed
150
RUN 7
RUN 18
RUN 12
RUN 27


2016/4/16


2016/4/16

Appendix C

Formulas and stoichiometric equations of the entire work

$$K_{sp} = \frac{[M^{n+}][OH^-]^n}{[M(OH)_n]} \quad \text{---------- (2.1)}$$

Where: K_{sp}-solubility product constant

$[M^{+n}]$- Concentration of metal ions (n = valence of the metal ion)

$[OH^-]$ - Concentration of hydroxide

$$Cr^{+6}\ (mg/L) = \frac{(V*l-V1)*3.33}{G} * 1000 \text{ ---------- (3.1)}$$

Where: V-quantity of Mohr's salt solution added to sample, mL

l-correction ratio between solution of Mohr's salt and $KMnO_4$

V_1- quantity of 0.1N $KMnO_4$ solution spent for the titration of the rest Mohr's salt, mL

3.33- titer of 0.1N $KMnO_4$ against CrO_3, mg/L

1000-Coefficient for reduction to the content of CrO_3 in a liter of the electrolyte

G-quantity of sample taken for the analysis, mL

$$Cr^{+3}\ (mg/L) = \frac{[(V*l-V1)-(V*l-V2)]*2.53}{G} * 1000 \text{ ---------- (3.2)}$$

Where: V_1- quantity of 0.1N $KMnO_4$ solution spent for the titration CrO_3, mL

G-Volume of sample taken for analysis, mL

V-Volume of Mohr's salt added, mL

V_2-volume of 0.1N $KMnO_4$ solution spent for the titration of Cr_2O_3, mL

$$2H_2CrO_4 + 3NaHSO_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3NaHSO_4 + 5H_2O \text{ ----------Eq. (3.3)}$$

$$6NaOH + Cr_2(SO_4)_3 \rightarrow 2Cr(OH)_3 \downarrow + 3Na_2SO_4 \text{ ---------- Eq. (3.4)}$$