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Faculty of Graduate Studies

Investigating the Possibility of Trivalent Chromium Oxidation to Hexavalent Chromium of Tanning Wastewater

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Dedication

To my mother and father. The words are silent in front of their bounty.

To the one who taught me how to live life with passion and supports me in every moment of grief or joy, who told me don't accept the imposed reality, and don't accept less than what I deserve. My dear husband "Mamoun".

To the little boy who enjoyed tearing papers and playing with the keyboard and waited for my arrival from university for a long time. My son "Odai".

To my dear daughter "Diala" that God gave me her laughter to comfort my heart.

To my sisters, brothers, and everyone who sincerely wish good things to me.

To the land that was created for peace and has never seen peace, "Palestine", to everyone believes that there is something worth living on it.

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل عنوان

Investigating the Possibility of Trivalent Chromium Oxidation to Hexavalent Chromium of Tanning Wastewater

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Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degrees or qualifications.

Student's Name: **اسم الطالب:** بيان غازي علي بشارات

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Date: **التاريخ:** 17/8/2021

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List of Abbreviations

Abbreviation	Meaning
$AICI_3$	Aluminum Chloride
Al_2O_3	Aluminum Oxide
NH_3	Ammonia
APDC	Ammonium Pyrrolidine Dithiocarbamate
$(NH_4)_2SO_4$	Ammonium Sulfate
Az	Arizona State
AAS	Atomic Absorption Spectrophotometry
BSE	Back Scattered Electron
B_{2f}	Black Soil Sample after Chromium Adsorption
℃	Celsius Degree
$CHCI_3$	Chloroform
CrO_4^{2-}	Chromate
$Cr\ (OH)_3$	Chromium Hydroxide
$Cr(NO_3)_3$	Chromium Nitrate
Cr_2O_3	Chromium Oxide
$Cr_2(So_4)_3$	Chromium Sulfate
DNA	Deoxyribonucleic Acid
$(Cr_2O_7)^{2-}$	Dichromate
DPPA	Differential Pulse Polarographic Analysis
EAAS	Electrothermal Atomic Absorption Spectrometry
EDX	Energy Dispersive X-ray
ESEM-FEG	Environmental-Cell Scanning Electron Microscope with Field Emission Gun
EP	Extraction Procedure
$FeCl_3$	Ferric chloride
W_2	Final Weight
FIA/uv/vis	Flow Injection Analysis-Ultraviolet/Visible Spectroscopy
B_{2i}	Fresh Black Soil Sample
B_{1i}	Fresh Red Soil Sample
GMSF	Goldwater Materials Science Facility
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
Cr^{6+}, Cr (VI)	Hexavalent chromium
HPLC	High Pressure Liquid Chromatography
hr	Hour
HCI	Hydrochloric Acid
HF	Hydrofluoric Acid

$HCrO^{4-}$	Hydrogen chromate
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectrometry
W_1	Initial Weight
LD_{50}	Lethal Dose 50%
LOI	Loss of Ignition
MnO_4	Manganese Oxide
MIBK	Methyl isobutyl Ketone
µg/L	Micro gram per liter
NAA	Neutron Activation Analysis
HNO_3	Nitric Acid
PWA	Palestinian Water Authority
PVD	Physical Vapor Deposition
PIXE	Proton-Induced X-ray Emission Spectrometry
B_{1f}	Red Soil Sample after Chromium Adsorption
SEM	Scanning Electron Microscopy
SEI	Secondary Electron Images
Na_2CO_3	Sodium Carbonate
$Na_6(PO_3)_6$	Sodium hexa meta phosphate
NaOH	Sodium Hydroxide
Na_2O_2	Sodium Peroxide
Cr^{3+}, Cr (III)	Trivalent chromium
UV	Ultraviolet
XRD	X-ray Diffraction
XRF	X-ray fluorescence

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Abstract

Leather tanning is one of the most important Palestinian industries that depend on the use of chemical compounds. The most important hazardous substance is chromium, due to the possibility of converting trivalent chromium to toxic Hexavalent chromium, which negatively affects the environment.

There is a controversy over this transformation process; therefore, this research aims to study the possibility of oxidation the trivalent chromium to hexavalent chromium in the soil under natural conditions. The research was divided into three parts by using red and black soil and chromium sulfate solutions with different concentrations; 5306, 2653 and 1061 ppm.

The first part was done to analyze the original and chromium-saturated soil samples using X-ray Fluorescence (XRF) and X-ray Diffraction (XRD) techniques to examine the concentrations of the chemical components especially total chromium and elements or oxides that affect the adsorption

process of chromium onto the soil, such as manganese oxide, ferrous, and sulfur. XRF results have shown a high concentration of total chromium in both soils. Then the name of soil was known by the USDA soil triangle based on the particles size presented by the percentage of sand, clay, and silt in a soil sample that was calculated by hydrometer analysis.

The second part was prepared chromium sulfate solutions of different concentrations that were exposed to two types of soil; red (silty clay) and black (silty loam). Effluent water was tested for the concentration of chromium as an indication of the adsorption capacity of the soil. Results have shown that black soil has a higher ability to adsorb chromium than red soil. The maximum adsorption capacity (qt) of black soil for chromium sulfate solutions as a function of time is found to vary with initial concentration. For an initial concentration of 5306, 2563, 1061 ppm, adsorption capacity was found to be 14.2, 7, 2.8 mg/g respectively. While for red soil, maximum adsorption capacity was found to be 12.1, 6.6, 2.7 mg/g respectively.

The third part was examined the presence of hexavalent chromium in water. Results have shown that theCr^{6+} concentrations were increased in red soil. While in black soil, the Cr^{6+} concentrations were decreased, but the results haven't a clear trend, the concentration was flocculated. Its depends on several parameter as pH, chemical elements in soil and presence of other compounds from nature or industry effluents. To support findings of this research, it is recommended that effect of pH on adsorption capacity should be tested on same type of soils.

Chapter One

Introduction

1.1 General Introduction

Tanning wastewater is characterized by one of the highest toxicity intensities per unit of effluent; including high concentrations of organic compounds, dissolved solids, and heavy metals like chrome (Affiang et al., 2018). Heavy metals affect human health, plant and animal life, as well as the quality of the limited water resources. When it is released into the environment, it may percolate through the soil and contaminate the groundwater. For instance, Cr^{3+} can undergo oxidation into hazardous Cr^{6+}(WHO, 2016).

Chromium is one of the most recognized pollutants in leather industry. Tanning process using chromium compounds for processing of hides. In this process about 60% - 70% of chromium reacts with the hides. In other words, about 30%- 40% of the chromium amount remains in the solid and liquid wastes (especially spent tanning solutions). The wastewater of tanning process is usually discharged, without proper treatment, into the sewerage system causing serious environmental impact(Abdulla et al., 2010).

In nature, chromium occurs in two major states Cr(VI) and Cr(III). Even when the tanning wastewater has chromium only in trivalent form, since the tanning process does not generate chromium (VI), some countries fixed

regulatory limits for the two species. This criterion appears from the assumption that the oxidation would be produced during storage and sometimes through the tanning process. Although chromium (III) oxidation to chromium (VI) occurs under specific environmental conditions, special attention is devoted to this transformation because chromium (VI) causes adverse effects for the human health, where Cr (VI) induced acute and chronic toxicity, neurotoxicity, dermatotoxicity, genotoxicity, carcinogenicity, immunotoxicity. Cr (III) has relatively low toxicity, when soluble Cr (III) is added to soil, manganese oxides present in the soil may cause oxidation to Cr (VI). When not oxidized to Cr (VI) form, Cr (III) may remain immobilized in the soil (Abdulla et al., 2010).

1.2 Statement of the Problem

In the West Bank, more than 15 tanneries discharge their wastewater contaminated with heavy metals into sewer system or to environment without treatment. Most of these tanneries are located in Hebron. Until now, wastewater treatment plants in Palestine cannot receive wastewater from leather plants due to the high amount of chemicals including heavy metals in wastewater that cannot be easily treated (Al-Jabari et al., 2017a).

In Hebron tanneries, recycling Cr is currently based on the precipitation of Cr using alkaline material (lime). After separating the precipitated solids, sulphuric acid is added to dissolve Cr for its reuse. Sulphuric acid is a banned chemical in Palestine due to security measures; the existing

techniques are used for precipitating the Cr. Thereafter, the precipitate is sent to an "Israeli" company. Large waste disposal charges are being paid by the companies. This affects the economic development (Al-Jabari et al., 2017a).

For Nablus tannery, all effluents from all production process are mixed in open pool, they precipitate chrome by add ferric chloride ($FeCl_3$) with dose 75 mg/L and let it precipitates for 24 hours, where sludge is heavily chromium contaminated. Nablus tannery is not allowed to send sludge to Zahrat Al-Fingan (Al-Jabari et al., 2017a), workers in that tannery said that they dispose it to the surrounding area, and supernatant is sent by tanks to open environment. Therefore, there is a need to track how soil adsorb chromium and study the evolution of chromium in different soil types, one from near area to Nablus tannery and another different one from another far area which is soil from Tammon town, Tubas.

1.3 Significance of Work

The idea of the project goes back to the controversy about the danger of wastewater resulting from leather tanning in terms of chrome in particular.

This study aims to know the extent of the oxidation of non-toxic Cr(III) to toxic Cr(VI) in the tanning wastewater that used in Palestinian tanneries when add it to the soil by studying the effect of two variable parameters on chromium adsorption onto soil: soil type and chromium solution concentration. After obtaining the results, chromium negative impact on

the environment is evaluated, and whether this effect is reduced through soil adsorption. Then, leather tanning can be considered a non-hazardous industry, and this encourages its continuity and supports it economically.

1.4 Research Objective

The main goal of this study is: first to investigate the possibility of oxidizing Cr^{3+} present in the tanning effluents to Cr^{6+}; second, measuring the ability of two soil types to absorb chromium from aqueous solutions of different concentrations.

1.5 Research Questions

- Does Cr^{3+} convert to Cr^{6+} on different surface soil type?
- To what extent can local soil effectively adsorb and store chromium?
- How surface soil type and composition affect the adsorption capacity?

Chapter Two

Literature Review

2.1 Chromium Element

Chromium is a transition metal; it has an atomic number of 24 and mass number of 51.9961. Its oxidation states range between $-\mathbf{2}$ and +6, but only the +3 and +6 states are the most stable ones under environmental conditions. These two oxidation states have different toxicity and mobility. Cr^{6+} is carcinogen and mobile, whereas Cr^{3+} is none toxic and immobile (Pass et al., 1974).

A soluble $Cr^{3+}$is used in the leather tanning industry that penetrates the hide and forms cross-links between the collagen fibers to give leather its durable finish. Although $Cr^{3+}$is predominant in tanning solutions, the presence of Cr^{6+} raised critical questions about the thermodynamic stability of Cr^{3+}. However, in natural systems, manganese oxides can oxidize $Cr^{3+}$to Cr^{6+}(Bartlett, 1991).

2.2 Chemistry of Cr (III)

Trivalent Cr, Cr (III), species are generally considered to be nonlabile because ligand displacement is slow (hours to days at room temperature) compared to most other metal ions (10^{-9}- 10^{-3}sec at room temperature) (Cotton and Wilkinson, 1980). Many Cr(III) complex species that are stable in

solution can be separated due to this kinetic inertness. As other trivalent metal ions, namely, Fe(III) and Al(III), the hydrated Cr(III) ion, $Cr(OH_2)_6^{3+}$, has a tendency to hydrolyze and this step is often accompanied by polymerization. Hydrolysis involves the conversion of a bound water molecule to the hydroxide ion and results in the release of a proton. Equilibrium measurements have identified the existence of the following species in solution:

$Cr(OH)^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3$, $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$ and $Cr_4(OH)_6^{6+}$. (Smith and Martell, 1976)

2.3 Chemistry of Cr (VI)

Because hexavalent Cr is a strong oxidant, Cr(VI) varies with pH values, i.e pH dependent. Therefore, it is considered as soluble oxygenated species that are regulated by the equilibria below(Nieboer and Jusys, 1988).

$$H_2CrO_4 \Leftrightarrow H^+ + HCrO_4^- \log (K_{a1}) = 0.6 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.1)$$

$$HCrO_4^- \Leftrightarrow H^+ + CrO_4^{2-} \log (K_{a2}) = -5.9 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.2)$$

Because the pH of environmental matrices only fluctuates from 3 to 10, $HCrO_4^-$ and CrO_4^{2-} are the dominant species. In addition, at concentrations of Cr(VI) greater than 0.01 M (molar), dimerization of the chromate ion occurs, yielding the dichromate ion.

$$Cr_2O_7^{2-} + H_2O \Leftrightarrow 2HCrO_4^- \log (K) = -2.2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.3)$$

when the chromate concentrations are below 0.01 M the existence of

dichromate is not expected to be significant, especially at physiological pH values of 7 to 8 (Subramanian et al., 2014).

2.4 Oxidation of Cr(III) to Cr(VI)

Oxidation of Cr(III) to Cr(VI) represents a significant environmental hazard because a relatively nontoxic species is transformed into a more toxic one. Manganese oxides are the only naturally occurring oxidant of Cr(III) and oxidation of Cr(III), in the presence of MnO_2, was first observed by (Bartlett and James. 1979). They noted that Cr(VI) was present in the effluents of most soils reacted with Cr(III). Even the manganese oxide with the highest zero point charge and the most crystalline structure, pyrolusite, is an effective oxidant of Cr(III) (Earyand Rai, 1987; Saleh et al., 1989). Adsorption of Cr(III) by Mn oxides is possibly the first step in its oxidation by Mn. In soils, manganese oxides typically accumulate on the surface of clay and iron oxides at relatively high redox potentials.It was noted by (McKenzie, 1977) that Mn minerals tend to have large surface areas and high negative charge at all but extremely acidic pH. These properties are associated with high adsorptive capacities, particularly for heavy metals. Cr(III) can be oxidized to Cr(VI) in the presence of Mn^{4+} where Mn^{4+}acts as the oxidizing agent and is reduced to Mn^{2+}, as shown by the equation:

$$2Cr^{3+} + 3MnO_2 + 2H_2O \Leftrightarrow 2CrO_4^{2-} + 3Mn^{2+} + 4H^{+} \ldots (2.4)$$

2.4.1 Oxidation of Cr^{3+} to Cr^{6+} Under various Conditions

Cr^{3+} can be oxidized to Cr^{6+} under the following conditions

- Presence of Oxygen: The unreduced chromium in the basic chromium sulfate is one of the sources of Cr^{6+}. Oxidation of Cr^{3+} to Cr^{6+} by oxygen in air during the processes carried out at higher pH in leather manufacturing process.
- Moderate high temperature: Cr^{3+} could be oxidized by oxygen at high temperature of 200–300 ℃. (Apteet al., 2006), burning of tanning sludge showed evidence of enhancement of Cr^{6+} concentration.
- Dissolution in Water: $Cr(OH)_3$ and MnO_2 suspension in water, $Cr(OH)_3$ slowly converted to dissolved Cr^{6+}.

2.5 Classification of Tanning Wastewater as Non-Hazardous versus Hazardous Waste.

Based on Article 1 of the Environmental law (1999), hazardous substance defined as: “Hazardous Substance: Any substance or compound, which because of its hazardous characteristics poses a danger on the environment as toxic, radioactive, biologically infectious, explosive or flammable substances”(Elhamouz, 2011).

Tanning of a 1000 kg of leather resulted a 600 to 700 kg of solid waste and 40–50 m^3 of wastewater. Because of the included compounds, primarily heavy metals, processed leather waste has a significant environmental impact due to the primary consequences and risks: changes in landscape

and aesthetic discomfort, air pollution, surface water pollution, and changes in soil fertility, it is recommended to manage it effectively by recycling and recovery or storage in compliance landfills. As a result, tannery waste must be handled and kept properly to avoid leakage, odor issues, and air emissions (Rosu et al., 2015).

In the tannery process, generally, tanning agents are used trivalent chromium (III) compounds. But, some leather products may contain traces of hexavalent chromium, which is considered a hazardous substance, and it may appear as a contaminant in the following situations: after UV exposure (at over 80°C) the fat-liquoring acids is possibly to lead to the oxidation of Cr(III); the formation of Cr(VI) may result in the process of the storage of fat liquored leather at 35% humidity. Also, in shoe production, the use of alkaline glues may contribute to the formation of Cr(VI) (Kolomaznik et al., 2008).Cr(VI) may be formed in the leather by Cr(III) oxidation. The European Commission considered there was an unacceptable risk to human health in case of Cr(VI) presence in the leather goods and articles containing parts of leather that comes into contact with the skin (Regulation 301, 2014).Cr(VI) usually exists in the form of $H_2Cr_2O_7$ and its salts and in the form of $(Cr_2O_7)^{2-}$. Both anions $(CrO_4)^{2-}$and $(Cr_2O_7)^{2-}$are water soluble and their formation are pH dependent. Above pH 7 predominates Cr(III) and below pH 6 predominates Cr(VI) (Fery, 2004). In the European legislation, it must be noted that the leather waste, containing chromium salts isn’t framed as hazardous waste; only the codes marked with an

asterisk (*) are considered as a hazardous waste (EC Decision, 2000, Government Decision, 2002).

Palestinian standards comply with international standards. Various international systems are available for waste classifications and hazardous waste listing. These include: Basel convention for the control of trans-boundary movement of hazardous waste and their disposal, European waste catalogue and hazardous waste list, and EPA-Hazardous Waste Listings in USA.Article 11 of the Palestinian Environmental Law No.(7) 1999. The "Palestinian National Strategy for Solid Waste Management in the Palestinian Territory 2010-2014" (NHWMP) constitutes the framework for all decisions, programs, and plans aiming at developing the solid waste sector in the West Bank and Gaza Strip. It aims to preparing and publishing a list of categories of hazardous waste. International development agencies have motivated activities and funded projects (Al-Jabari, 2014).

Leather industry is believed by community and by some officials to be as one of a producer of hazardous waste (in its solid waste containing residues of chromium). However, such waste is not hazardous since the usedCr^{3+} in leather tanning is not toxic and thus non-hazardous, although still considered to be a pollutant (Al-Jabari, 2014).

2.6 Toxicity of Cr

Cr (VI) is more toxic and soluble whereas Cr (III) is relatively nontoxic and insoluble.

Chromate is toxic because it is a strong oxidizing agent, corrosive, and a

potential carcinogen (National Research Council, 1974). The chromate ion is a class human carcinogen by inhalation and an acute irritant to living cells, and of all the metal carcinogens Cr exhibits properties most nearly consistent with a mutagenic initiation model (Subramanian et al., 2014).

Systemic toxicity may occur in both the oxidation states, mainly because of increased absorption of Cr through broken skin that results in renal chromate toxicosis, liver failure, and eventually death (Lippmann, 2000). Acute exposure of rats to Cr (VI) by various routes of administration affected mainly the liver and kidneys (USEPA, 1980). Soluble salts of chromates are also highly toxic when administered parenterally, with an LD_{50} of 10-50 mg/kg, compared to LD_{50}values of 200-350 and 1500 mg/kg obtained from dermal or oral exposure, respectively. Conversely, oral administration of Cr (III) compounds is relatively nontoxic. Other effects of Cr (VI) poisoning include gastric distress, olfactory impairment, nosebleeds, liver damage, and yellowing of the tongue and teeth (Subramanian et al., 2014).

The Cr (VI) ion is readily taken up into eukaryotic cells by anion-carrying proteins, where it is reduced to Cr (III) by a number of cytoplasmic reducing agents. The reduction of Cr (VI) to Cr (III) causes the generation of oxygen radicals in cells that can produce DNA damage. Additionally, the Cr (III) formed can become adducted to the DNA. Recent studies have shown that Cr (VI) is very potent in forming DNA protein cross links. This complex typically involves the binding of Cr (III) to the phosphate backbone of DNA and cross-linking to a protein (Lippmann, 2000). This

cross-linking may lead to increased mutagenicity and is probably more significant in determining the mutagenicity of Cr than the oxidative DNA damage produced by oxygen (Lippmann, 2000).

2.7 Chromium Cycle in Soil and Water

The starting point for the Cr cycle is $Cr^{6+}$and in most soil conditions, reduction reactions are more preferred. In soil solution, chromate formation is pH dependent and dominated by $HCrO^{4-}$ or $CrO_4{}^{2-}$through adsorption/precipitation reactions, absorption by plants, or leaching from the subsurface layers, Chromium may be extracted from the soil. Some of theCr^{6+} are also reduced by carbon to Cr^{3+}also there is electron donors as Fe^{2+}or S^{2-}.This process, called dechromification, which reduced Cr^{6+} toCr^{3+}.(Subramanian et al., 2014).

Reduced $Cr^{3+}$is bound by ligands such as citrate in soil solution that deliver $Cr^{3+}$to MnO_2surfaces where both the organic ligand and $Cr^{3+}$are oxidized.

The organic ligand is often recycled because Mn^{3+}created by reverse dismutation accepts electrons from the Cr^{3+}in preference to those from the organic ligand and thus oxidizes only Cr. When organic ligands are in extreme concentrations, they appear to induce reverse dismutation ofMnO_2 by linking the Mn^{3+}, and this Mn^{3+} organic complex can prevent or decrease the formation of Cr^{6+}. (Subramanian et al., 2014).

2.8 Chromium Behavior in Soil

The contamination of chromium in soil and groundwater due to tannery waste has been investigated. Surface soil and water samples were obtained from several locations near tanneries, and then analyzed for total Cr. The concentration of soil chromium was reduced due to leaching and chromium in groundwater was increased. Results showed that the soil near tannery industries is polluted, but there is no determination of the existence of Cr (Rangasamy et al., 2015).

Bartlett analyzed soil and water that contain Cr naturally or from any contamination source not especially from tannery wastes. The cycling of chromium in soils and in waters are between and reduction of Cr^{6+}, but there are gaps in oxidation of Cr^{3+}understanding factors controlling oxidation-reduction processes. If solubleCr^{3+} is added to soil, it will oxidize by manganese oxides toCr^{6+}.(Bartlett, 1991).

The oxidation of $Cr^{3+}$to $Cr^{6+}$was examined under three different conditions: (1) Cr_2O_3 was heated in the presence of oxygen; (2)Cr $(OH)_3$ and MnO_2 mixtures were suspended at different pH values in aerobic or anoxic aqueous media, and (3) Cr $(OH)_3$-MnO_2 mixtures interacted in wet aerobic conditions (Apte et al., 2006).

Results indicate that Cr^{3+}in Cr_2O_3 could be converted to Cr^{6+}at a temperature range of 200–300°C, with conversion rates of up to 50% in 12 h. Cr $(OH)_3$was slowly converted to dissolved Cr^{6+} in the presence of MnO_2 , both in aerobic and anoxic conditions, with conversion rates of up

to 1% in 60 days. In moist aerobic conditions with rates up to 0.05% in 90 days. Chromium oxidation also occurred in sludge samples, especially under aerobic conditions up to 17% conversion in 30 days (Apte et al., 2006).

The reduction kinetics ofCr^{6+} in soils and its correlation with soil properties was studied by (Xiao et al., 2012). The reduction of Cr^{6+}in soils was positively related to organic matter content, dissolved organic matter content, Fe^{2+}content and clay fraction, but negatively correlated with Mn content. In natural soils, the reduction process of$Cr^{6+}$is not regulated by a single soil property, but by the combined effects of dissolved organic matter,Fe^{2+}, pH, and distribution of soil particle size (Xiao et al., 2012).

2.9 Chemistry of Soil Cr

The concentration of Cr in soil equals to (the amount present in the parent material from which the soil was formed plus the amounts added through wind, water, and human activities minus the amounts removed through leaching, surface runoff, volatilization, and phyto uptake).

Cary, 1982; Bartlett and James, 1988; Fendorf 1995; Proctor et al., 1997 reviews factors influence the transformations between Cr(VI) and Cr(III) in soils.

2.9.1 Solid-Phase Speciation of Cr in Industrial Contaminated Soils

Up to the researcher’s knowledge, few studies to date have examined the

fractionation of total Cr in industrial contaminated soils. Of the clay loam, loam, and sandy clay loam soils collected from a heavy metal contaminated site, (Wasay et al., 1998) studied the fractionation of total Cr only in the clay loam soil. (Fiedler et al.,1994), propose and used these quential extraction scheme and found that of the total 832 mg/kg of total Cr, only 486.9 mg/ kg (58.5%) was bounded to the organic soil fraction.

(Phillips and Chapple., 1995) used the sequential extraction scheme of (Tessier et al., 1979) to fractionate total Cr along with other metals from a soil collected from a former industrial site. Chromium concentrations in all soil fractions were low, and approximately 80% of the total Cr were associated with organic and oxide fractions with negligible concentrations detected in the exchangeable and carbonate fractions.

In another study by (Maiz et al., 1997), soil samples collected from a polluted mine works, steel factory and highway emissions were sequentially extracted to find the partitioning of total Cr and other metal fractions. A short three step sequential extraction scheme was compared with other modified extraction scheme (Tessier et al., 1979) and (Ure et al., 1993). However, total Cr was found to be predominantly partitioned in the residual fraction of the soils using all three extraction schemes.

In all the aforementioned studies, Cr fractionation was investigated simultaneously with several other metals and the concentration of Cr present in the soils was not very high. In addition, no attempt was made to distinguish between Cr(III) and Cr(VI).

2.10 Solubility of Cr(III) and Cr(VI)

Solubility and availability of Cr(III) in soil solution are critical for the oxidation of Cr(III) to Cr(VI) in soils. At soil pH value of greater than 5.5, the solubility of Cr(III) decreases due to its precipitation as $Cr(OH)_3$. Complexation of Cr(III) with some of the low molecular weight organic acids such as citrate and gallic acid increases its solubility and mobility even at higher pH, there by facilitating its oxidation.

Bartlett and James(1983) compared the oxidizing tendencies of four forms of Cr(III) added to a field moist soil incubated for 15 day. The four forms were freshly precipitated $Cr(OH)_3$, Cr citrate, aged $Cr(OH)_3$, and aged $Cr(OH)_3$with citrate. The maximum Cr(VI) levels observed decreased in the order freshly precipitated $Cr(OH)_3$> Cr citrate > aged $Cr(OH)_3$in citrate > aged$Cr(OH)_3$ (Bartlettand James, 1983).

The oxidation of Cr(III) in tannery waste amended to three soil types was studied by Milacic and Stupar (1995). Their fractionation study showed that after 5 months, 1.1% of the total Cr added was oxidized in clay, 0.45% in sand, and only 0.03% in peat soil. The degree of Cr(III) oxidation was found to be proportional to the concentration of manganese (IV) oxides and water-soluble Cr(III) in the soils. They also observed a decrease in the concentration of water soluble Cr and Cr(VI) on continuance of the

experiment because Cr was redistributed to more sparingly soluble fractions (Milacic and Stupar, 1995).

2.11 Partitioning and Mobility of Cr

The solid phase speciation studies clearly indicate that at low concentrations of total Cr either in natural or contaminated soils, most of the total Cr is partitioned in the residual fraction. In highly organic soils a significant portion of total cris partitioned in the organic fraction and equally partitioned either in the Fe oxide or residual fractions. The concentration of Cr in the water soluble and exchangeable fractions is very low and indicates low mobility of Cr from these soils(Subramanian et al., 2014).

Although in highly contaminated soils Cr is partitioned predominantly in the organic and Fe oxide fractions, a significant amount of Cr existed in water soluble and exchangeable fractions. The determination of exchangeable Cr(III) is necessary because if soil pH conditions are favorable, and in the presence of MnO_2, this fraction could become available for oxidation to toxic Cr (VI). (Milacic and Stupar., 1995) used 1 M NH_4Cl for the exchangeable fraction and 0.015 M $K_2HPO_4$for the water-soluble fraction of Cr in soils. However, information on the labile and exchangeable pools of Cr(VI) in contaminated soils is lacking, and such information may be useful in understanding the desorption chemistry of Cr(VI) and is essential for the development of a suitable remediation strategy for contaminated soils.

2.12 Adsorption and Desorption of Cr(III) Onto Soil Particles

Cr(III) has been shown to be sorbed strongly onto soil minerals, to be bound to soil organic matter, and to form mineral precipitates (Bartlett and Kimble 1976; Cary et.al, 1977; Rai et.al, 1987, 1989; Bartlett and James, 1988; Palmer and Wittbrodt, 1991). Sorption of Cr(III) decreases when other inorganic cations or dissolved organic ligands are present in solution.

Fendorf et al., (1994) and Fendorf and Sparks., (1994) have studied the mechanism of Cr(III) sorption on silica using extended absorption fine structure spectroscopy and found that Cr(III) formed a monodentate surface complex on silica. Arnfalk et al., (1996) studied Cr(III), and Cr(VI) retention on 14 different types of minerals and soil materials considering both pH dependency and other soil physicochemical parameters. The results verified the importance of geochemical parameters of soils such as organic content, type of clay mineral, presence of complexing ions, and redox potential for controlling metal uptake. Montmorillonite (in bentonite and smectite) showed the highest retention of Cr(III) among all minerals and soil materials, whereas illite and kaolinite showed lower retention than the soils. The clay mineral montmorillonite showed highest retention because it had the highest surface activity (Kashef, 1986).

The difficulty in displacing Cr from smectite (caly mineral) indicates that the Cr is bonded specifically because if Cr was held through outer sphere complexes, the smallest hydroxy polymers would be readily displaced by Ca^{2+}(Dubbin and Goh, 1995). Drljaca et al.(1992) found that, while the

montmorillonite was still wet, the adsorbed Cr could be easily exchanged with other cations but, upon drying, Cr becomes virtually nonexchangeable. These authors suggested that as the inter layer region collapsed due to loss of water, Cr came into close contact with the siloxane surface, allowing inner sphere complexes to form. Cr(III) is held strongly, likely through covalent bonds, and its displacement is extremely difficult through simple exchange reactions. However, the potential for Cr(III) to be oxidized to the more toxic Cr(VI) form is of some concern because of the instability of bonding under strong oxidizing conditions.

Both adsorption and precipitation reactions and both specific and nonspecific reactions are possible for the retention of Cr(III) in soils. However, organically complexed Cr (III) could be available in soil solution even at high soil pH for oxidation to toxic Cr (VI) in soils.

Cr (VI) is immobilized in soils and mechanisms of Cr (VI) immobilization are $CaCrO_4$ precipitation and recrystallization with Fe hydroxides (Shi et al., 2020).

2.13 Soil texture

Soil texture can be determined by using quantitative methods such as the hydrometer method based on Stokes' law. Soil texture focuses on the particles that are less than two millimeters in diameter which include sand, silt, and clay.

Twelve major soil texture classifications as shown in Figure 2.1 are defined by the United States Department of Agriculture (USDA)(United States

Department of Agriculture, 1987). The twelve classifications are sand, loamy sand, sandy loam, loam, silt loam, silt, sandy clay loam, clay loam, silty clay loam, sandy clay, silty clay, and clay. Soil textures are classified by the fractions of each soil separate (sand, silt, and clay) present in a soil. Classifications are typically named for the primary constituent particle size or a combination of the most abundant particles sizes, e.g. "sandy clay" or "silty clay". A fourth term, loam, is used to describe equal properties of sand, silt, and clay in a soil sample, and lends to the naming of even more classifications, e.g. "clay loam" or "silt loam"(Soil Survey Division Staff , 1993).

Determining soil texture is often aided with the use of a soil texture triangle plot. One side of the triangle represents percent sand, the second side represents percent clay, and the third side represents percent silt. If the percentages of sand, clay, and silt in the soil sample are known, then the triangle can be used to determine the soil texture classification.

Chemical and physical properties of a soil are related to texture. Particle size and distribution will affect a soil's capacity for holding water and nutrients. Fine textured soils generally have a higher capacity for water retention, whereas sandy soils contain large pore spaces that allow leaching.

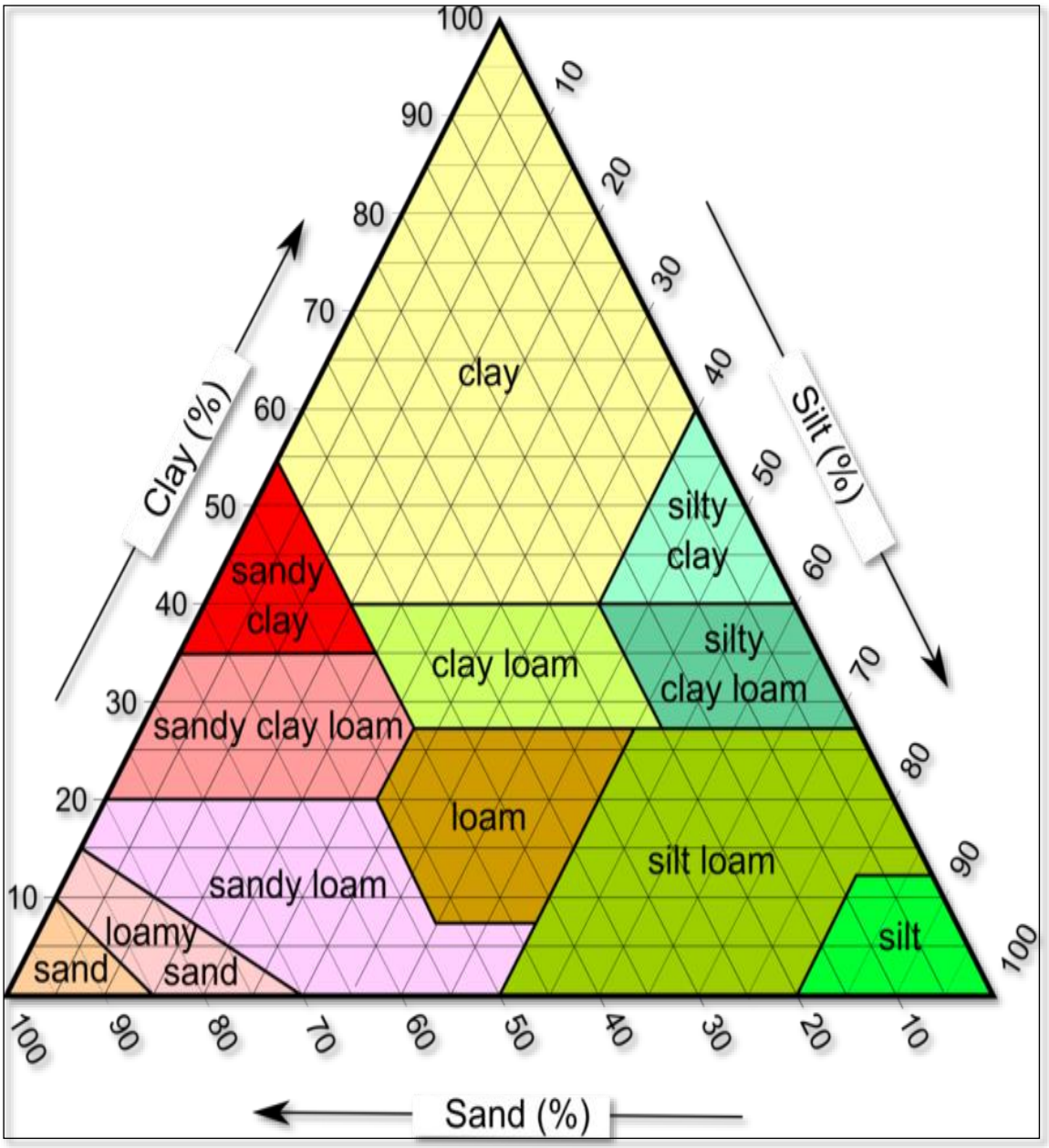

Figure 2.1: Soil texture triangle showing soil textures as determined by the proportion of sand, silt and clay. Source: (United States Department of Agriculture, 1987).

2.14 AnalyticalMethods for Determining Chromium Concentration in Various Sample Matrix.

Table 2.1 shows summery for analytical methods for determining chromium in environmental sample matrices (Services, H, 2002).

Table 2.1: Analytical methods for determining chromium in environmental samples.

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery
Drinking water, surface water, and certain domestic and industrial effluents (dissolved chromium(VI))	Complex chromium(VI) in water with APDC at pH 2.4 and extracted with MIBK	AAS	2.3 µg/L	No data
Drinking water, groundwater and water effluents (chromium(VI))	Buffer solution introduced into ion chromatograph. Derivitized with diphenylcarbazide	Ion chromatography with post-column derivatization and UV-VIS detection	0.3 µg/L	100% at 100 µg/L
Waste water and industrial effluent for chromium(VI) only	Buffered sample mixed with $AICI_3$ and the precipitate separated by centrifugation or filtration	DPPA at pH 10–12	30 µg/L	90% at 0.2 mg/L
Waste water 1986 (chromium(VI))	Derivatization with o-nitrophenylfluorone	UV-VIS spectrometry at 582 nm	Lower than diphenylcarbazone method	No data
Water (total chromium)	Calcium nitrate added to water and chromium is converted to chromium(III) by acidified H_2O_2	GFAAS or ICP/AES	1.0 µg/L (GFAAS) 7.0 µg/L	97–101% at 19–77 µg/L
Water (chromium(III) and chromium (VI))	Solid-phase extraction using anion exchange resins for Cr(VI) adsorption and chelating resins for Cr(III) adsorption	ICP-MS	0.009 µg/L (chromium VI); 0.03 µg/L (chromium III)	86–113%
Industrial wastes, soils, sludges, sediments, and other solid wastes (total chromium)	Digest with nitric acid/hydrogen peroxide	ICP-AES	4.7 µg/L	101% at 3.75 mg/L
Oil wastes, oils, greases, waxes, crude oil (soluble	Dissolve in xylene or methyl isobutyl ketone	AAS or GFAAS	0.05 mg/L	107% at 15 µg/L

chromium)				
Groundwater, domestic and industrial waste (chromium[VI])	Chromium(VI) is coprecipitated with lead sulfate, reduced, and resolubilized in nitric acid	AAS or GFAAS	0.05 mg/L (AAS) 2.3 µg/L (GFAAS)	93–96% at 40 µg/L
Groundwater-EP extract, domestic, and industrial waste (chromium[VI])	Chelation with ammonium pyrrolidine dithiocarbamate and extraction with methyl isobutyl ketone	AAS	No data	96% at 50 µg/L
Water, waste water, and EP extracts (chromium(VI))	Direct	DPPA	10 µg/L	93% at 5 mg/L
Soil, sediment and sludges (chromium(VI))	Acid digestion extraction using hot HNO_3	GFAAS	No data	No data
Sediment (total chromium)	Samples digested with HNO_3 and HF and dried	XRF	No data	No data
Sediment	Acid digestion using 0.5N HCI followed by filtration	AAS	No data	94.88%

In this study the total chromium concentrations were determined by flame atomic absorption spectrophotometry (iCE 3000, wavelength 357.9 nm)at the chemistry department lab in An-Najah University using Analytical Methods for Atomic Absorption Spectroscopy (Perkin Elmer Coorporation, 1996). This method is simple, rapid, and applicable to a large number of environmental samples including, but not limited to, ground water, aqueous samples, extracts, industrial wastes, soils, sledges, sediments, and similar wastes. Analysis for dissolved elements does not require digestion if the sample has been filtered and then acidified. There are many obstacles and difficulties during the study that can be summarized as follows:

1. The chemical analysis of soil elements using the ICP_MS device did not give the required result because it checks the total chromium concentration to a certain limits. In addition, it does not show the result of basic soil components such as silica, which affects the calculations. It's also needs a long time for the examination process.
2. Soil analysis by using XRF and XRD techniques is expensive and time consuming due to the use of external laboratories. It also does not find Na concentration and the LOI of the soil sample, so it must be determined to complete the calculations.

Chapter Three

Methodology

The methodology adopted in this study consists of three stages:

First stage: determine the structural properties of soils by hydrometer analysis to get the particle sizes and use it to know the type of soil, and chemical properties by XRF that find the concentrations of elements oxides and XRD techniques to get the crystallization form.

Second stage: determination the ability of two different soil types to uptake total chromium from different chromium sulfate solutions ($Cr_2(SO_4)_3$) concentration with time. This includes the possibility of the formation of Cr^{6+} in two different soils types with time as a result of chromium oxidation. Also, study the adsorption kinetics for chromium solutions in soil.

Third stage: study the formation ofCr^{6+} from different initial Cr^{3+} liquid solutions of different concentrations without soil.

3.1 Experimental Setup and Design of Experiments

To reach the main goal of this study, laboratory work was done to examine soil samples, prepare chromium sulfate solutions, and conduct the necessary tests for water and soil samples as detailed in the subsequent parts.

3.1.1 Soil Textural Analysis

The percentage of clay, silt and sand were calculated by Hydrometer Analysis test to know the particle size and predict the soil name, then use the result to calculate permeability and porosity.This method has a detection limit of 2.0 % for sand, silt, and clay.

Hydrometer Analysis Test

This method was used to estimate the distribution of soil particle sizes from 0.075 mm sieve to 0.001 mm. This analysis is based on Stoke's law governing the rate of sedimentation of particles suspended in water.

Equipments: Hydrometer (ASTM H-152), 1000 mL cylinder hydrometer jar, mixer, dispersion agent (Sodium hexa meta phosphate, $Na_6(PO_3)_6$), and Thermometer.

Procedure:

Control jar was prepared by adding 125 mL of 4% Sodium hexa meta phosphate solution with distilled water to produce 1000 mL. The hydrometer was then inserted and adjusted tozero. Then 50 gm of soil (passing sieve No.200)were mixed with 125 mL of 4% Sodium hexa meta phosphate solution and were allowed to stand for 12 hours. Themixture was then transferred to a dispersion cup and water was added until two-third full, the solution was transferred to the sedimentation cylinder and water was added to 1000 mL. The cylinder was capped with rubber stopper and was agitated for 1 minute.

Sedimentation and control cylinder were put beside each other and stopwatch (cumulative time t=0) was started. Hydrometer readings were taken at cumulative time t=0.25, 0.5, 1 and 2 minutes, then the hydrometer was placed in the control jar. Readings were continued at 5, 15, 30 and 60 minutes then at 2, 4, 8, 24 and 48 hours.

The following equations were used to find the soil's structural properties:Das, B. (2002)

$$Rcp = R + Ft - Fz \quad \text{.....} \quad (3.1)$$

where,

R: Hydrometer reading.

Fz: Zero correction, if the zero reading in hydrometer (in control cylinder) is below the water meniscus, its (+), if above its (-) and if at the meniscus its zero.

Ft: Temperature correction which approximated as

$$Ft = -4.85 + 0.25\,T \quad \text{.....} \quad (3.2)$$

For (T between 15-28 °C)

$$Percent\ Finer = \frac{a*Rcp*100}{Ws} \quad \text{.....} \quad (3.3)$$

where,

Ws= dry weight of soil used for hydrometer analysis.

a= correction for specific gravity given by

$$\mathbf{Gs} = \left(\frac{\text{Wtofdrysoil}}{\text{Wtofequalvolumeofwater}}\right) \text{.....} \quad \text{.....} \quad (3.4)$$

$$\boldsymbol{a} = \frac{(\mathbf{1.65} * \boldsymbol{Gs})}{(\boldsymbol{Gs} - \mathbf{1})(\mathbf{2.65})} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.5)$$

$$Rcl = R + Fm \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.6)$$

Rcl: corrected hydrometer reading for determination of effective length.

Fm: Difference between the upper level of meniscus and water level of control cylinder.

Effective length (L (cm)) corresponding to Rcl given in Table 3.1 then determine A from Table 3.2 at different temperatures and Gs, where A is varying with Gs.

Table 3.1: Effective length corresponding to hydrometer reading.

Source: https://www.labguider.com/hydrometer-analysis/

Hydrometer reading	L (cm)	Hydrometer reading	L (cm)	Hydrometer reading	L (cm)	Hydrometer reading	L (cm)
0	16.3	13	14.2	26	12	39	9.9
1	16.1	14	14	27	11.9	40	9.7
2	16	15	13.8	28	11.7	41	9.6
3	15.8	16	13.7	29	11.5	42	9.4
4	15.6	17	13.5	30	11.4	43	9.2
5	15.5	18	13.6	31	11.2	44	9.1
6	15.3	19	13.2	32	11.1	45	839
7	15.2	20	13	33	1.09	46	8.8
8	15	21	12.9	34	10.7	47	8.6
9	14.8	22	12.7	35	10.6	48	8.4
10	14.7	23	12.5	36	10.4	49	8.3
11	14.5	24	12.4	37	10.2	50	8.1
12	14.3	25	12.2	38	10.1	51	7.9

Table 3.2: Variation of A with Gs at different temperatures

Gs	Temperature(°C)						
	17	18	19	20	21	22	23
2.5	0.0149	0.0147	0.0145	0.0143	0.0141	0.0140	0.0138
2.55	0.0146	0.0144	0.0143	0.0141	0.0139	0.0137	0.0136
2.6	0.0144	0.0142	0.0140	0.0139	0.0137	0.0135	0.0134
2.65	0.0142	0.0140	0.0138	0.0137	0.0135	0.0133	0.0132
2.7	0.0142	0.0138	0.0136	0.0134	0.0133	0.0131	0.0130
2.75	0.0138	0.0136	0.0136	.0133	0.0131	0.0129	0.0128
2.8	0.0136	0.0134	0.0134	0.0131	0.0129	0.0128	0.0126
Gs	Temperature(°C)						
	24	25	26	27	28	29	30
2.5	0.0137	0.0135	0.0133	0.0132	0.0130	0.0129	0.0128
2.55	0.0134	0.0133	0.0131	0.0130	0.0128	0.0127	0.0126
2.6	0.0132	0.0131	0.0129	0.0128	0.0126	0.0125	0.0124
2.65	0.0130	0.0129	0.0127	0.0126	0.0124	0.0123	0.0122
2.7	0.0128	0.0127	0.0125	0.0124	0.0123	.0121	0.0120
2.75	.0126	0.0125	0.0124	0.0122	0.0121	0.0120	0.0118
2.8	0.0125	0.0123	0.0122	0.0120	0.0119	0.0118	0.0117

Source: https://www.labguider.com/hydrometer-analysis/

$$D = A\sqrt{\left(\frac{L}{t}\right)} \quad \text{……..……... (3.7)}$$

where,

D: diameter of particle (mm)

L: Effective length (cm)

t: Time (min)

Plot a grain-size distribution graph on semi-log graph paper with percent finer on the natural scale and D on log scale.

Equations for porosity and void ratio calculations

$$\gamma d = \frac{(Gs*\gamma w)}{(1+e)} \text{……..…. (3.8)}$$

$$e=((Gs *\gamma_w)/(\gamma_d))-\gamma_d \text{ ……..……..….(3.9)}$$

where,

γ_d = Dry unit weight (kN/m^3)

γ_w = Unit weight of water (kN/m^3)

e= void ratio

$$\boldsymbol{Porosity}\ (\eta) = \frac{\boldsymbol{e}}{(\boldsymbol{1+e})} \text{……...……..(3.10)}$$

3.1.2 Soil Sample Preparation

3.1.2.1 Soil Samples for XRF

Two original soil samples were prepared, the first one was red soil and the second one was black, each soil type was ground manually to a fine powder using alumina mortar and pestle to get 5 gm for each. Part of the soil that adsorbed chrome was taken and dried in the oven at a temperature of 40-60 ℃ for one hour, then ground to get another 5 gm from red and black soil.

3.1.2.2 Epoxy

Monomer and initiator were mixed with ratio 2:1 for 5 minutes, some soil that was dried in the oven were put in a special plastic cup, then the mixture was poured over soil and was dried with cool air for 15 minutes to get out the air bubble, after that the sample were dried overnight.

Grinding and polishing were done for both soil samples. Grinding was done by using grinding paper with 320,600 and 1200 P respectively.

However, the polishing was done by using 0.1 μm Al_2O_3 and 0.04 μm Al_2O_3.

3.1.2.3 Sodium Element Analysis in Soil Samples

The Flame Photometric method was used in sample preparation as follow: Fresh and treated samples from both red and black soil were grounded, and then burned in the oven at a temperature of 500℃ for one hour. Nitric acid and water were added to the soil then filtered and diluted to get asolution for the test with Flame Photometer apparatus.

3.1.2.4 Loss of Ignition (LOI) Test

Fresh and treated samples from both red and black soil were grounded. Four empty crucibles were put in the oven at 1000℃ for 1 hour, then cooled before weight to record theinitial weight (W_1). Soil samples were put in crucibles and reheat at 1000 ^oC for 1 hour and cooled in desiccator, finally weight the crucibles and record (W_2). Then the LOI was calculated as:

$$LOI = \frac{W1-W2}{W1} * 100 \quad \text{..... (3.11)}$$

3.1.2.5 Instrumental Analysis of Soil Samples

Two types of soils were analyzed before and after contaminated with chromium sulfate solution. The techniques used were: (1) X-ray powder diffraction for phase composition; (2) X-ray fluorescence (XRF) for their elemental composition; (3) scanning electron microscopy (SEM) complemented with energy dispersive X-ray spectrometry (EDX) for

imaging of grain morphology and elemental microanalysis. Samples were prepared adequately for each instrumental technique. Sample preparation, type of machine, analytical procedure, and measurement conditions are described below.

1. X-ray powder diffraction (XRD): A small portion of each soil sample was ground manually to a fine powder using alumina mortar and pestle, transferred to a plastic vial and labeled. A small amount of this powder is spread on a sample holder made of a silicon slice. This silicon slide is cut off axis to avoid parasite XRD diffraction peaks. The soil powder samples were analyzed using a Malvern PA NalyticalAerisdiffracto meter with a copper target.It is operated at a voltage of 40kV and a current of 15mA. The measurements were carried out for a 2 theta range of 5-65º, with a continuous scan and a step size of 0.0109º. The raw binary file was then processed and interpreted using Jade10 software available in the XRD lab at Arizona State University (ASU) Goldwater Materials Science Facility (GMSF), Tempe, Arizona (AZ), USA.
2. X-ray fluorescence (XRF): The same aforementioned powdered sample was used for XRF. Analyses were done using a Bruker S2 Pumamachine. This machine has a silver cathode (target) to generate X-ray and is used in energy dispersive mode (EDX) with energy resolution of 0.139 keV. However, it has a limitation on light elements (< Na) analysis. Spectral results are converted to normalized elemental wt. % and light elements are included in the sum. As elemental

compositions of ceramics, rock, minerals and soils are conventionally reported as oxide percentages, the elemental concentrations of the samples are recalculated to express them as oxides. This machine is available at ASU's Goldwater Materials Science Facility (GMSF), Tempe, AZ, USA.

3. Scanning electron microscopy (SEM) complemented with energy dispersive X-ray spectrometry (EDX): Two samples (B_{1i} and B_{1f}) that were embedded in epoxy resin, ground, polished well were observed with a FEI XL-30 Environmental-Cell Scanning Electron Microscope with Field Emission Gun (ESEM-FEG) at LeRoy Eyring Center for Solid State Science, Arizona State University. This microscope offers high resolution secondary electron imaging. As the samples are non-conductive both were coated with a thin film of gold using sputtering (physical vapor deposition or PVD). It is also equipped with secondary electrons as well a back scattered electron (BSE) detector and X-ray energy dispersive detector (EDX) for imaging in BSE mode and for elemental analysis, respectively, when needed. This scope has a spacious vacuum chamber for large specimens and also a large stage to hold multiple samples. Samples were observed using an accelerating voltage of 30kV at a working distance of 10-11mm. The secondary electron images (SEI) of the surface features of the samples presented here were obtained at a varying magnification as low as 36 x and up to 3500 x. Point and area quantitative microanalyses were conducted on different locations (grains), as needed, by switching to EDX mode.

The following equations were needed to determine oxides percentage in soil samples to get the results presented in Table (4.8), see Appendix A.

$$\text{Oxidewt} = (\text{Atomic wt} * \text{element atom}) + (\text{oxygen atom} * \text{Atomic wt ofoxygen}) \quad (3.12)$$

$$\text{Mole of Element} = \frac{\text{Wt.\% Normalized}}{\text{Atomic wt}} \quad (3.13)$$

$$\text{Mole of Oxide} = \frac{\text{Mole of Element}}{\text{Oxygen atom in oxide formula}} \quad (3.14)$$

$$\text{Wt. \% Oxide} = \frac{\text{Mole of Oxide}}{\text{Oxide wt}} \quad (3.15)$$

$$\text{Normalized Oxide} = \left(\frac{\text{Wt.\% Oxide}}{\sum \text{Wt.\% Oxide}}\right) * 100 \quad (3.16)$$

$$\text{Oxide Wt\%} = \text{Normalized Oxide} - (1 - \text{LOI}) \quad (3.17)$$

3.1.3 Soil type Ability to Adsorb Chromium.

In this stage two types of soils and three concentrations of chromium sulfate solutions were used for each soil type.

Chromium sulfate solution of concentration 5306 ppm was prepared by adding 10 gm of chromium sulfate to 0.5 L of water. For the 2653 ppm concentration, 5 gm of chromium sulfate was added to 0.5 L. Same concentration was prepared by adding 10 gm to 1L. Finally, 2 gm were added to 0.5L to have 1061 ppm. A170 gm of red soil from Bait Leed, Tulkarm and 170gm of black soil from Tammon, Tubas were put in conical flask which was 0.5L volume. This was done with 6 flasks, 3 for red soil and another 3 for black soil. Also 170 gm of redsoil were added to flask of

1L volume. 0.5L solutions for each concentration were put in soil type, 3 different concentrations for red and another 3 for black. Finally, the prepared 2653 ppm solution in 1L was added to red soil in flask of 1L volume. All flasks were opened to the atmosphere as shown in Figure (3.3). A 20 ml samples from each flask were taken each time for sampling. Initial pH values were recorded for each sample and found to be 4.13.

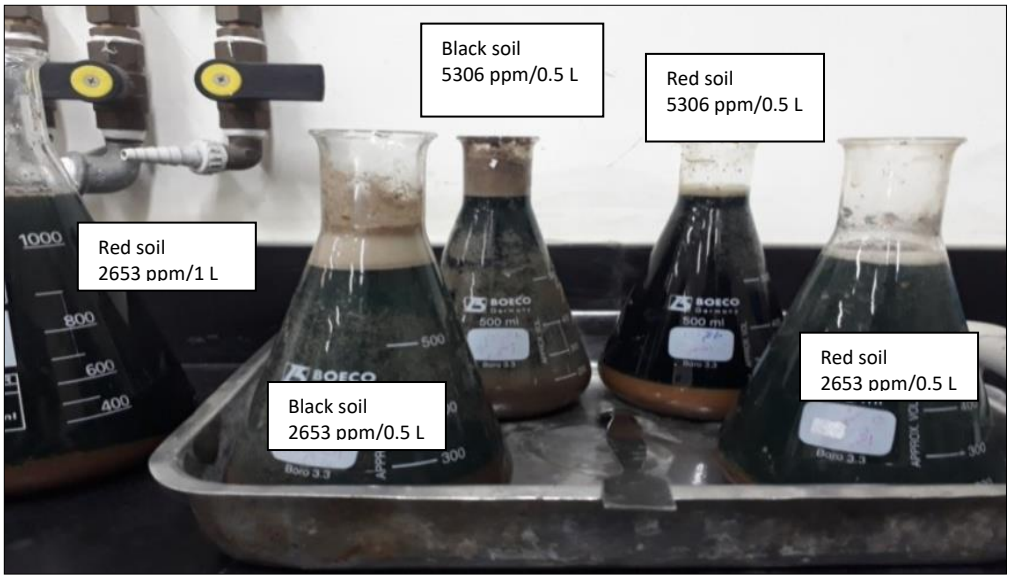

Figure 3.3: Chromium sulfate solution with different concentration in different soils.

3.1.3.1 Sample Preparation and Method of Total Chromium Test

Each Sample taken from flasks was diluted three times with a dilution ratio; 1:100, 2:100 and 3: 100. Standard chromium sulfate solutions were prepared with concentrations; 5, 10, 20, 30, 40 and 50 ppm.

Total chromium concentrations were tested by Flame Atomic Absorption Spectrometer, iCE 3000, wavelength 357.9 nm) in post graduate research laboratory at the Faculty of Science. This was followed by diluting samples to get the required concentration. The chromium concentrations for three diluted samples from each sample were drawn vs. dilution factor; intercept

from trend line represents the total chromium concentration for the sample. This method was repeated for all samples to get the final curve which shows the chromium concentration with time. See Appendix B

3.1.3.2 Hexavalent Chromium Concentrations Test Method

Hexavalent chromium concentrations were tested by 1, 5 Diphenyl carbohydrazide method using a single dry powder formulation called Chroma Ver 3 Chromium Reagent. The colored and turbid sample was diluted to have a clear sample, 10 ml of sample were put in cell to zero DR 900 Colorimeter, then the powder was pillowed in cell and re put the cell in colorimeter to press time which is 5 min. Results obtained are Cr^{6+} (mg/L)

3.1.4 Oxidation of Cr^{3+} from Different Concentrations and Volume with Time but without Soils.

Chromium sulfate solutions were prepared with concentrations 5306, 2653 and 1061 ppm. Each concentration was put in beakers with different volumes which were 100, 250 and 500 ml as shown in Figure 3.11 without soil.

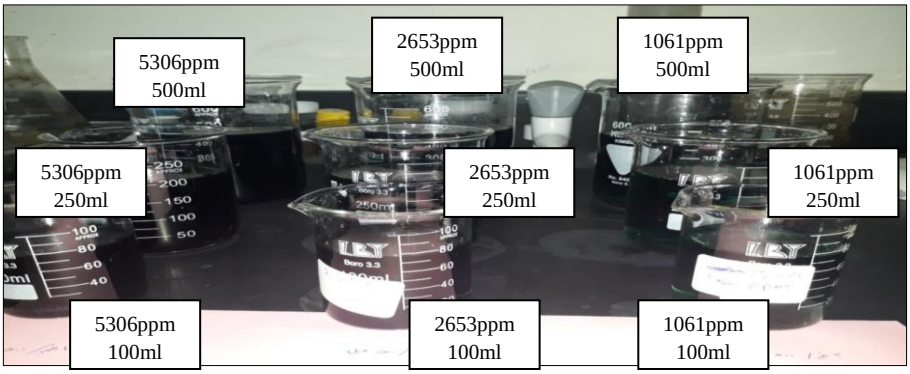

Figure 3.4: Chromium sulfate solutions with different concentration in different volumes without soils.

Samples were taken each time from all beakers, then hexavalent chromium concentrations were tested by 1, 5 Diphenylcarbohydrazide Method as mentioned in previous section.

Chapter Four

Results and Discussions

4.1 Results of Hydrometer Analysis

Soil analysis using a hydrometer is carried out to find the diameter of fine soil particles. Sieve analysis is a method that is used to determine the grain size distribution of soils that are greater than 0.075 mm in diameter. It is usually performed for sand and gravel. The percentage of the fine particles passes sieves were recorded and hence the particle size distribution is recorded. Gravel percent determined in laboratory which is the particles more than 2 mm diameter and still in 2 mm sieve. Then from the Tables 4.1 and 4.2, seek for clay which diameter less than 0.002 mm, the percentage of clay in the sample is represented by % finer. The diameter of sand particle is (2-0.05) mm and the percentage represented by % finer greater than 0.05 minus % clay that calculated before. Finally, the silt particles (0.05-0.002) mm are equal to 100 minus the sum of sand and clay percentages minus the percentage of gravel components.

By using percentages of soil components on the soil triangle, the intercept area represents the name of soil.

Red soil: Wt of soil= 50 gm, T= 25 °C, Fm=+1, Fz=+3

Table 4.1 shows the hydrometer analysis results for red soil.

Table 4.1: Hydrometer reading for red soil

Time (min)	Reading	Rcp	% finer	Rcl	depth L (cm)	A	D (mm)
0.25	50	48.4	94.52	51	7.9	0.0125	0.0703
0.5	49	47.4	92.56	50	8.1	0.0125	0.0503
1	47	45.4	88.66	48	8.4	0.0125	0.0362
2	46	44.4	86.71	47	8.6	0.0125	0.0259
4	44	42.4	82.8	45	8.9	0.0125	0.0186
8	42	40.4	78.89	43	9.2	0.0125	0.0134
15	40	38.4	74.99	41	9.6	0.0125	0.01
30	37	35.4	69.13	38	10.1	0.0125	0.0073
60	34	32.4	63.27	35	10.6	0.0125	0.0053
120	32	30.4	59.37	33	10.9	0.0125	0.0038
240	30	28.4	55.46	31	11.2	0.0125	0.0027
480	28	26.4	51.55	29	11.5	0.0125	0.0019
1440	27	25.4	49.6	28	11.7	0.0125	0.0011

Table 4.2: Information to determine the specific gravity of red soil, and some properties.

Wt of flask+soil+water,W_2(g)	684.66
Wt of flask+water,W_1(g)	669.3
Wt of dry soil,W_3(g)	24.1
Wt of equal volume of water,W_4(g)	8.74
Gs @ T=18 ℃= W_3/W_4	2.757437
A	1.0006
Gs @ T= 20℃= $(W_3/W_4)*a$	2.759092
Dry unit weight (kN/m^3)	17.5
Unit weight of water (kN/m^3)	9.81
Void ratio (e)	0.54
Porosity (n)	0.35
Permeability (k) (m/s)	$1.02*10^{-6}$

Table 4.3 shows the USDA classification of soil particle size.

Table 4.3: The USDA classification of soil particle size. Source: United States Department of Agriculture. (1987).

Type	Diameter (mm)
Sand	2 - 0.05
Silt	0.05 – 0.002
Clay	< 0.002

Calculations for Red soil sample:

From laboratory work, gravel % =4.45%

From Table 4.1

Clay (D <0.002) which here D= 0.0019 mm, then

% clay= % finer (passing) = 51.55 %,

Particles which have diameter (0.05) =92.56%

But the silt equal this percent – percent of clay

% silt= 92.56-51.55=40.95,

% sand=(100-(51.55+40.95)-4.45)= 3.05%. All these component percentage are used in Figure 2.1 to find the clay's type. For the Red soil, Figure 4.1 shows its texture class.

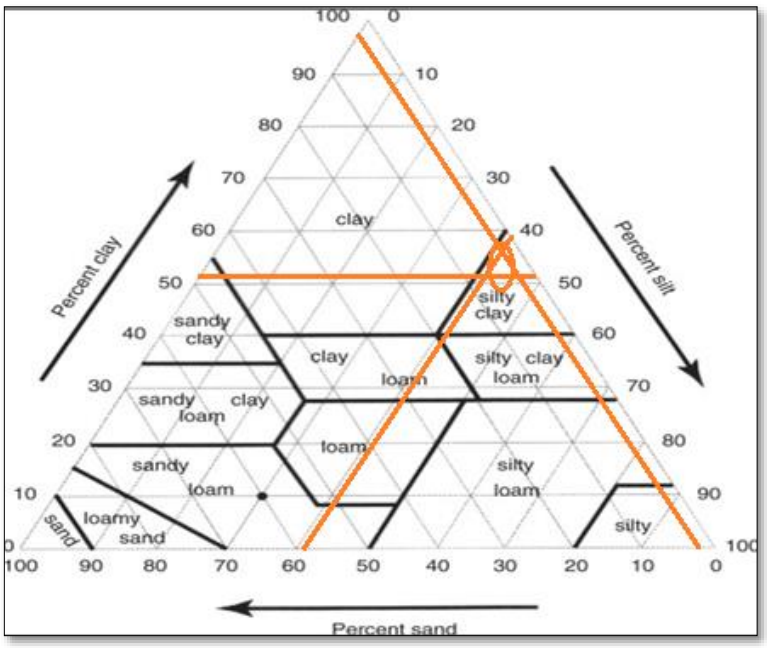

Figure 4.1: Red soil name from textural triangle as a function of soil components percentage

Black soil: Wt of soil= 50 gm, T= 25 °C, Fm=+1, Fz=+3

Table 4.4 shows the hydrometer analysis results for black soil.

Table 4.4: Hydrometer Reading for black soil.

Time (min)	Hydrometer Reading R	Rcp	% finer	Rcl	Effective depth L (cm)	A	D (mm)
0.25	45	43.4	86.02	46	8.8	0.0127	0.0753
0.5	43	41.4	82.06	44	9.1	0.0127	0.0542
1	40	38.4	76.11	41	9.6	0.0127	0.0393
2	34	32.4	64.22	35	10.6	0.0127	0.0292
4	29	27.4	54.31	30	11.4	0.0127	0.0214
8	25	23.4	46.38	26	12	0.0127	0.0155
15	23	21.4	42.42	24	12.4	0.0127	0.0115
30	20	18.4	36.47	21	12.9	0.0127	0.0083
60	18	16.4	32.51	19	13.2	0.0127	0.006
120	14	12.4	24.58	15	13.8	0.0127	0.0043
240	12	10.4	20.61	13	14.2	0.0127	0.0031
480	10	8.4	16.65	11	14.5	0.0127	0.0022
1440	9	7.4	14.67	10	14.7	0.0127	0.0013

Table 4.5: Information to determine the specific gravity of black soil and some properties.

Wt of flask+soil+water,W_2(g)	684.64
Wt of flask+water,W_1(g)	669.3
Wt of dry soil,W_3(g)	24.4
Wt of equal volume of water,W_4(g)	9.06
Gs @ T1=18℃,= W_3/W_4	2.693157
A	1.0006
Gs @ T=20 ℃,= $(W_3/W_4)*a$	2.694773
Dry unit weight (kN/m^3)	16
Unit weight of water (kN/m^3)	9.81
Void ratio (e)	0.65
Porosity (n)	0.39
Permeability (k) (m/s)	$7.19*10^{-6}$

Calculations for Black soil sample:

From laboratory work, gravel % =2%

From Table 4.4

Clay (D <0.002) which here D= 0.0022 mm, then

% clay= % finer (passing) = 16.65 %,

Particles which have diameter (0.05) =82.06% but the silt equal this percent – percent of clay

% silt= 82.06-16.65=65.35%,

% sand= (100-(16.65+65.35)-2) = 16% Using these percentages, then the name of soil can be read from the USDA textural triangle plotted for 12 basic texture classes as function of components percentage, then it can be seen that is Silty Loam as shown in Figure 4.2

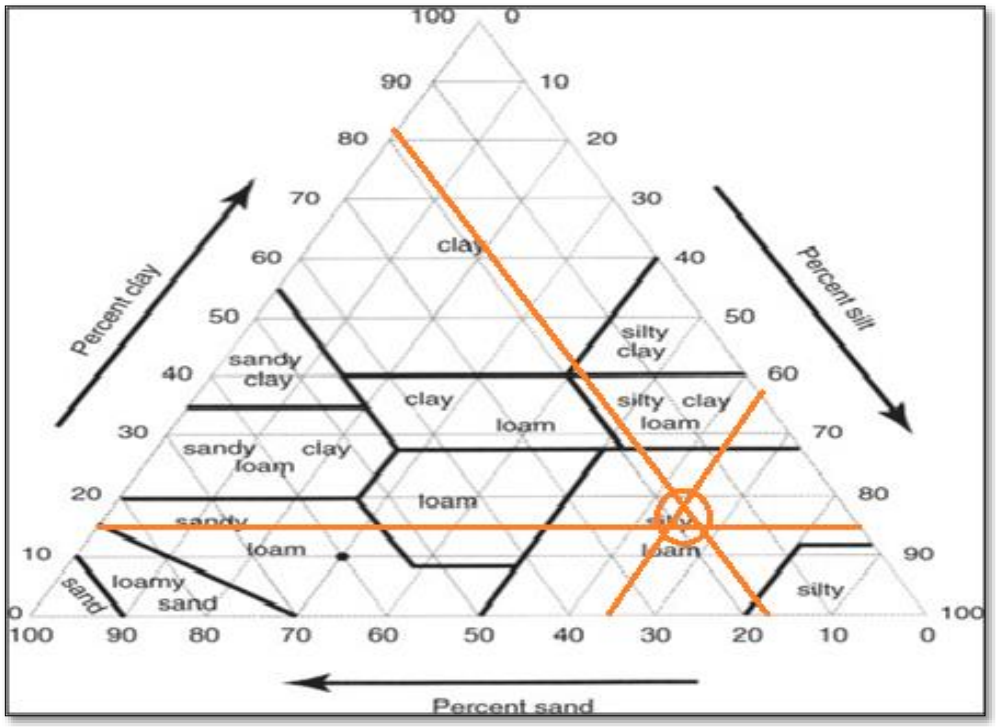

Figure 4.2: Black soil name from textural triangle as a function of soil components percentage.

Comparing the Red & Black soils samples, it was found that the porosity, void ratio and permeability of the black soil were higher than that for the red soil. However, the particle size for the black soil is higher than that of the red soil, because the predominant component in the red one is clay while in the black one is silt.

4.2 XRF Oxide Data and Summery of Calculations.

Since XRF technique does not find Na concentration and the LOI of the soil sample, so it must be determined to complete the calculations to get results in Table 4.8.

Loss of ignition and sodium concentration of the soil samples are shown in Table 4.6 and Table 4.7 respectively.

Table 4.6: Loss of ignition for soil samples.

Soil sample	W_1(gm)	W_2(gm)	W_1-W_2
B_{1i}	24.04	23.81	0.23
B_{1f}	24.78	24.56	0.22
B_{2i}	23.54	23.36	0.18
B_{2f}	24.35	24.17	0.18

Table 4.7: Sodium concentration in soil samples.

Soil sample	ppm
B_{1i}	4.5
B_{1f}	47
B_{2i}	16.8
B_{2f}	85

Table 4.8 represents the Wt% of elements oxides and traces in initial original red and black soil (B_{1i} and B_{2i}) , final chromium- saturated red and black soil (B_{1f} and B_{2f}). The results in **Table 4.8**was determined by using equations (**3.12-3.17**).

For more details of XRF results see **Appendix C**

Table 4.8: Summery of XRF oxide data and calculations

Oxide	B1i	B1f	Delta M	Total Loss	Total Gain	Balance	B2i	B2f	Delta M	Total Loss	Total Gain	Balance
Formula	Wt%	Wt%		%	%	%	Wt%	Wt%		%	%	%
SiO2	35.5729	33.073	-2.500	-9.309	10.305	0.996	46.583	43.742	-2.841	-3.632	3.633	0.001
TiO2	1.6358	1.359	-0.277				1.45	1.358	-0.092			
Al2O3	14.415	13.369	-1.046				11.184	11.585	0.401			
Fe2O3	17.5031	12.52	-4.983				9.72	9.275	-0.445			
MnO	0.23915	0.208	-0.031				0.215	0.21	-0.005			
MgO	1.6208	1.385	-0.236				2.736	2.714	-0.022			
CaO	3.9844	4.929	0.945				7.051	7.086	0.035			
Na2O	0.0002	0.002	0.002				0.001	0.005	0.004			
K2O	0.864	0.778	-0.086				1.952	1.816	-0.136			
P2O5	0.4912	0.491	0.000				0.475	0.515	0.040			
Cr2O3	0.0503	2.825	2.775				0.027	1.62	1.593			
SO3	0.22281	6.807	6.584				0.238	1.798	1.560			
Trace	0.39834	0.248	-0.150				0.369	0.278	-0.091			
Total	**77**	**78**					**81.990**	**81.87**				
LOI	**23**	**22**					**18.000**	**18**				
Trace (ppm)												
Br	25	13					22	0				
Cl	2459	1700					4205	2529				
Nb	235	0					133	0				
Ni	681	460					0	0				
Pb	56	0					0	0				
Rb	498	285					190	169				
Sc	13	19					170	135				
Sr	509	296					646	585				
Zn	1052	658					431	390				
Zr	2819	1640					2023	1900				
V	671	632					370	392				
Y	258	161					108	125				
Sum	9276	5864					8298	6225				

When Wt% change of each element and calculated the mass balance for the B_{1f} and B_{2f} (soils after treatment with chromium sulfate solution), in the results of B_{2f} the total wt% in fresh and chromium saturated samples are equal. However, there is 1% extra gain in B_{1f}, which should not be there if there is no substantial amounts of other ions in solution. Therefore, the possible reason is human error in LOI calculation when reading weight of sample, although it's repeated two times. Also, calcium is inexplicably high

in that sample comparing with other sample although the same solution was used.

In B_{1f} the concentration of total Cr increasing with adorable amount, this increase is accompanied by a decrease in the amount of iron. The concentration ofCr^{6+}increasing due to the amount of Fe and Mn elements.

4.3 XRD Data Analysis

Soils phase identifications were carried out using Jade 10 software at Arizona State University(ASU) for four samples (initial fresh red soil(B_{1i}), final chromium saturated red soil ($B_{1f)}$,initial fresh black soil(B_{2i}), final chromium saturated black soil(B_{2f})) and are shown in Figures 4.3 to 4.6. The major phases in each sample can be pinpointed using its main reflection (diffraction) line with the highest intensities for each. This is a qualitative phase analysis but can be taken as semi-quantitative analysis. The plots show that, the clay component (one or more of the clay minerals like kaolinite, illite, montmorillonite); quartz (SiO_2) is a major inert component; calcite ($CaCO_3$) is present initially in both samples and still present after treatment; another component is the feldspar, which is inert too. As a product, we can see gypsum ($CaSO_4.2H_2O$) in both clays after treatment.

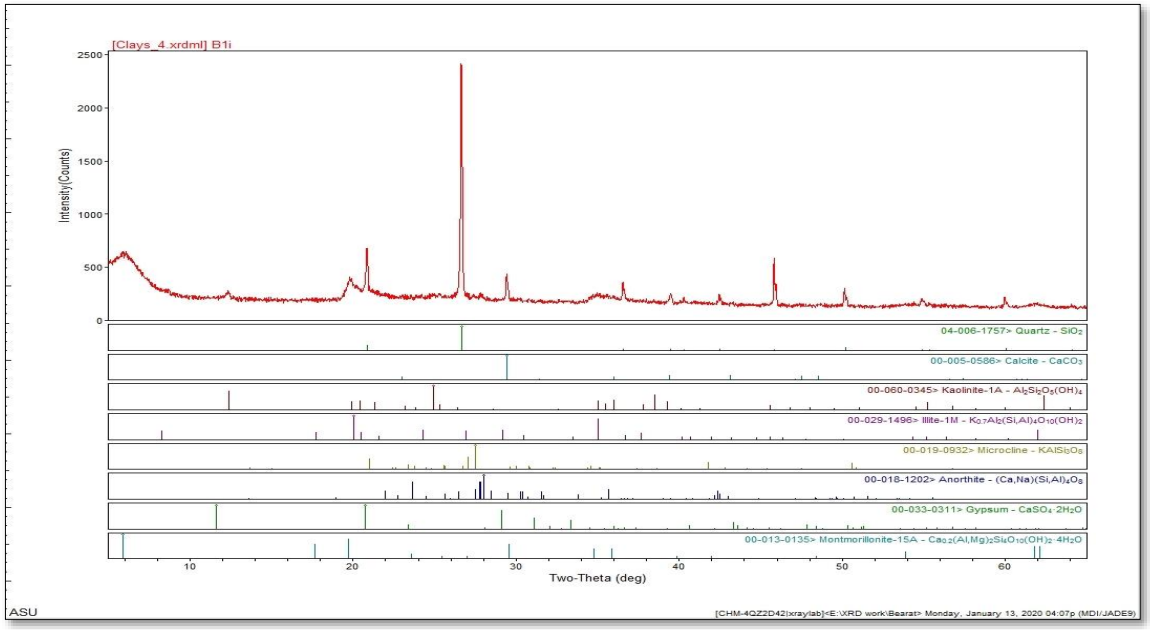

Figure 4.3: Phase identification for soil sample (B_{1i}) from XRD data.

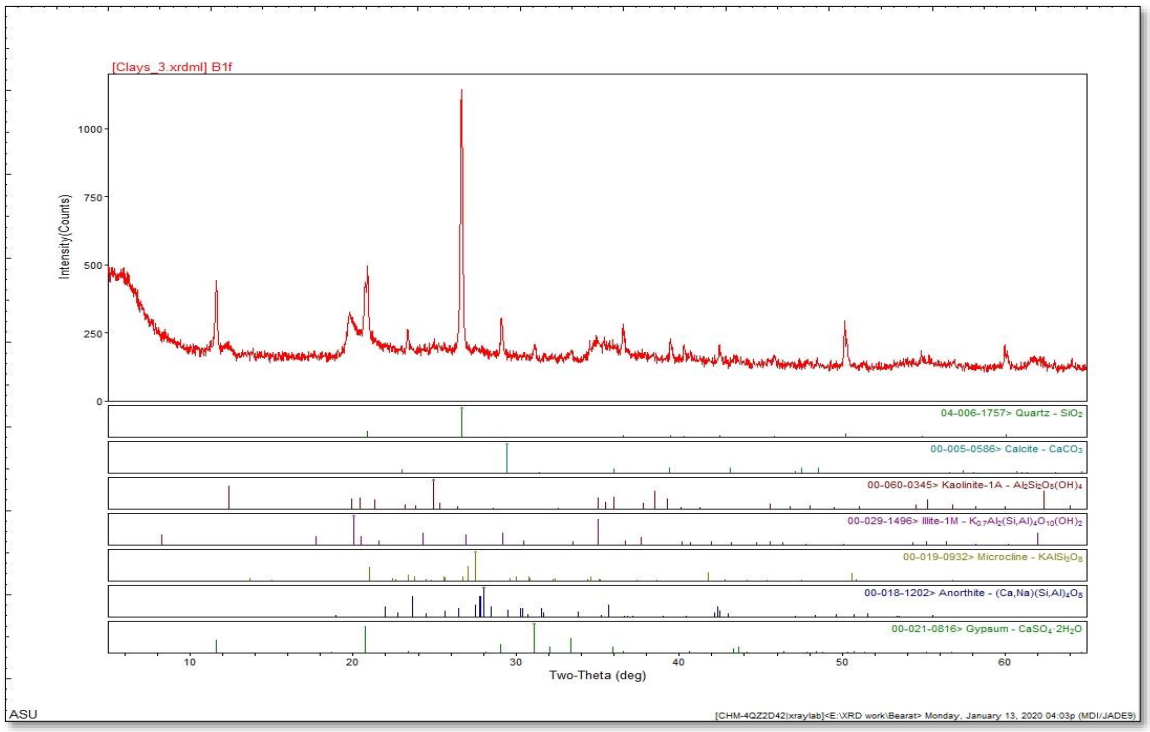

Figure 4.4: Phase identification for soil sample (B_{1f}) from XRD data.

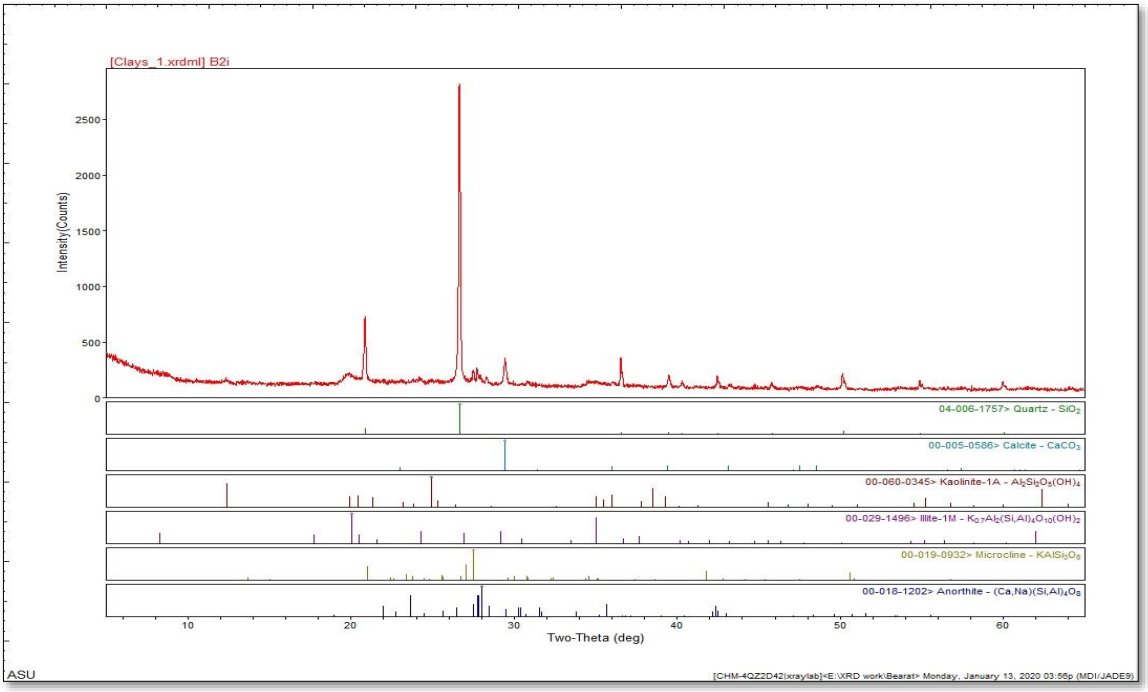

Figure 4.5: Phase identification for soil sample (B_{2i}) from XRD data.

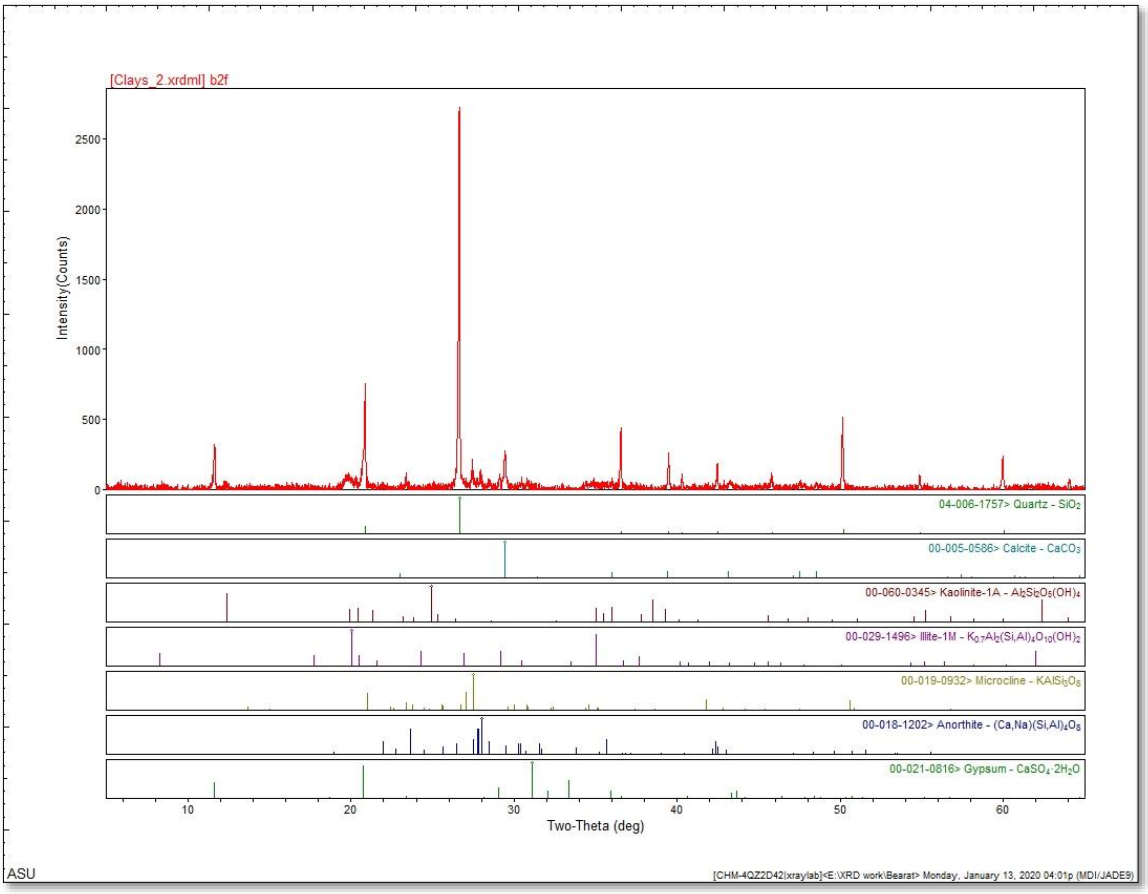

Figure 4.6: Phase identification for soil sample (B_{2f}) from XRD data.

4.4 Soil Type Ability to Adsorb Chromium

Figures 4.7 to 4.10 show samples were taken at various times. Chromium concentration of several samples were observed at various times and are shown in Figures 4.7 to 4.10. In the figures, R and B stand for Red and Black soil samples. The volume of initial solution is 0.5 L and the volume of each sample is 20 ml.

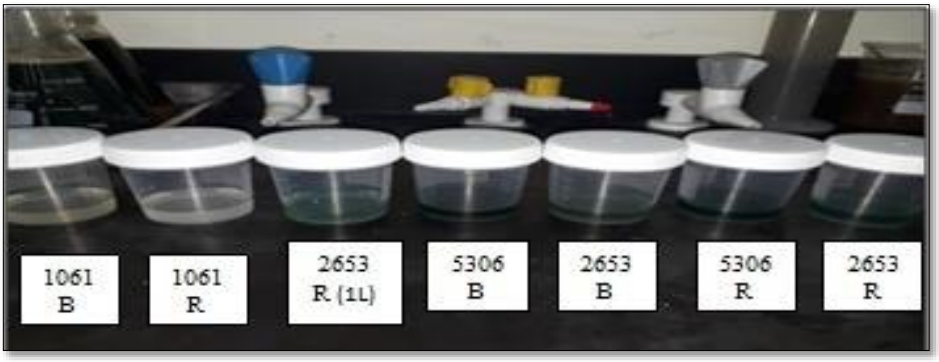

Figure 4.7: Samples from chromium sulfate solutions after 48 hours.

Figure 4.8: Samples from chromium sulfate solutions after 168 hours.

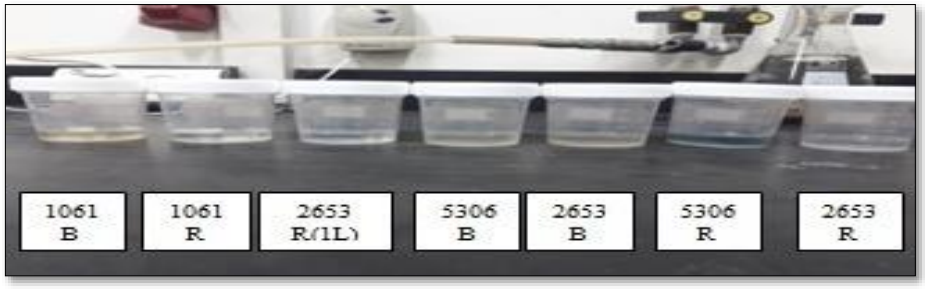

Figure 4.9: Samples from chromium sulfate solutions after 357 hours.

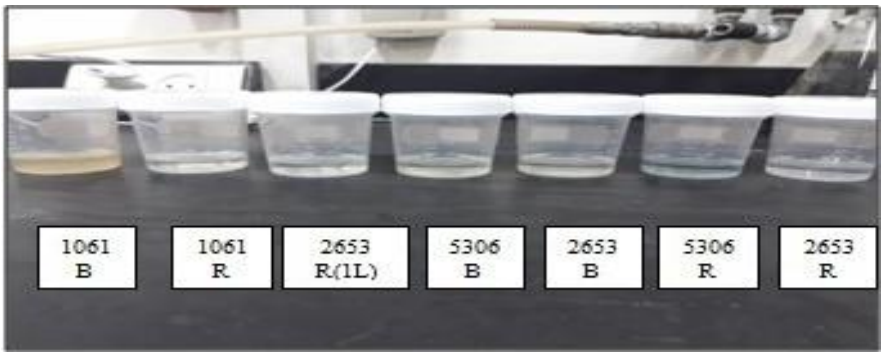

Figure 4.10: Samples from chromium sulfate solutions after 504 hours.

As time elapse, the intensity of the sample's color decreases due to the adsorption of chromium on the soil samples.

Figure 4.11shows a quantitative reduction of total chromium with time when it was soaked into a 170 g of the red and black soils (separately). The initial total chromium concentration (in 0.5l volume) is 5306 ppm and the change of total chromium concentration with time is shown. The total concentration drops to around zero after around 900 hours.

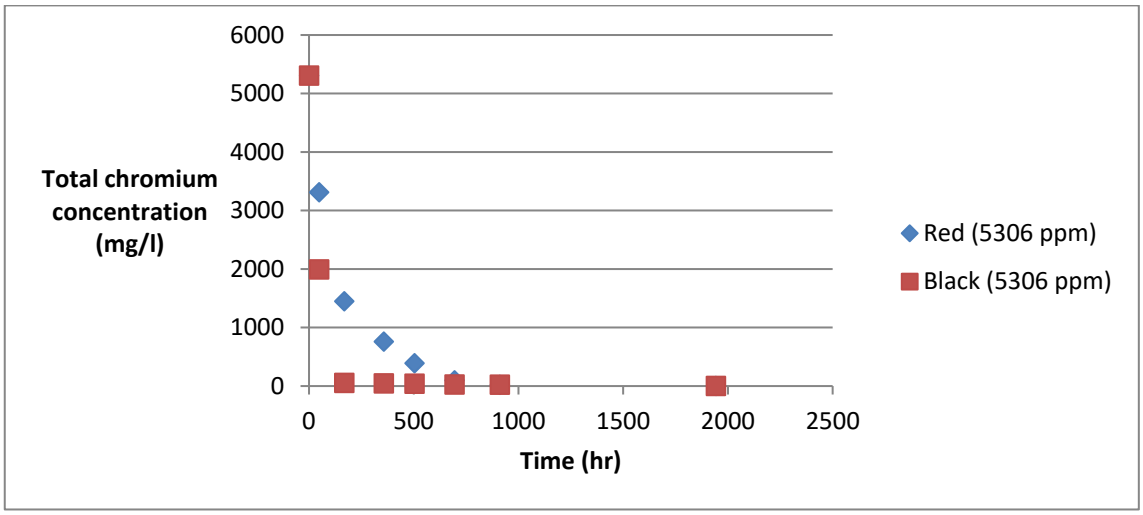

Figure 4.11: Total chromium concentrations for red and black soil with initial total chromium concentration equal to 5306 ppm and 0.5 L volume.

For red soil the total chromium concentrations were decreased gradually in comparison to the sharp decrease of the concentration in the Black sample.

When comparing the two soil types, the initial uptake amount for red and black soils are1994 mg /l, 3312 mg /l, respectively, and the remaining concentrations in red and black soil are0.74 mg /l, 0.52 mg /l, respectively. So, the black soil is better in adsorption of total chromium than red soil.

Figure 4.12 represents the total chromium concentrations with different times for red and black soil and initial total chromium concentration equal to 2653 ppm.

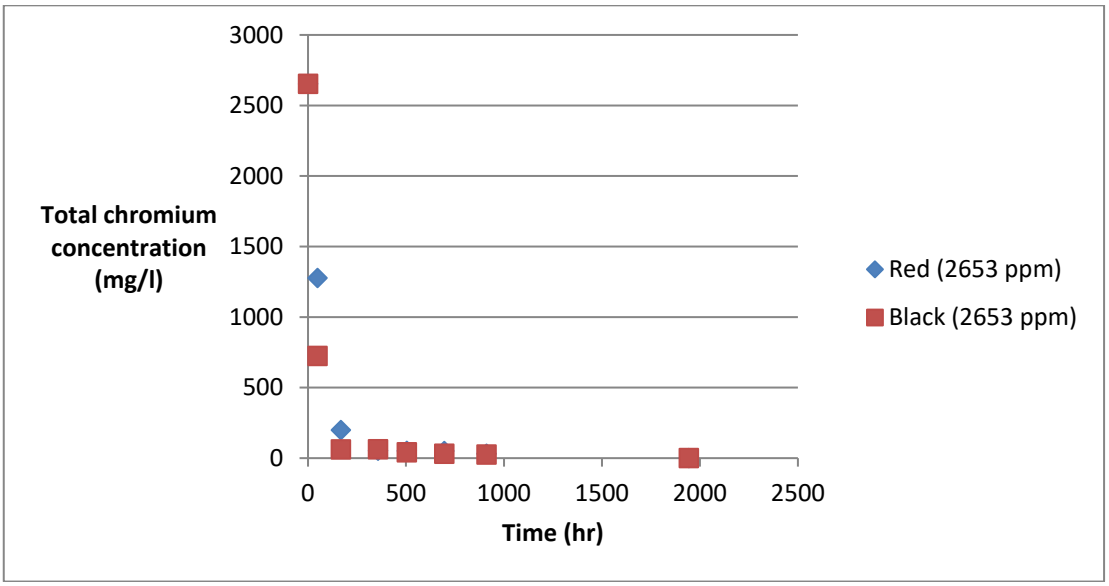

Figure 4.12: Total chromium concentrations for red and black soil with initial total chromium concentration equal to 2653 ppm and 0.5 L volume.

Results shown in Figure 4.12 for a 0.5 l chromium concentration of 2653 ppm added to 170 g soil (Red and Black soil separately). For red soil the total chromium concentrations were decreased gradually in comparison to the sharp decrease of the concentration in the Black sample.

When comparing the two soil types, the initial uptake amount in red and black soils is 1376 mg /l, 1929 mg /l, respectively, and the remaining

concentrations in red and black soil are 0.92 mg /l and 0.65 mg /l, respectively. So, the black soil is better in total chromium adsorption than red soil.

Figure 4.13 represents the total chromium concentrations with different times for red and black soil and initial total chromium concentration equal to 1061 ppm.

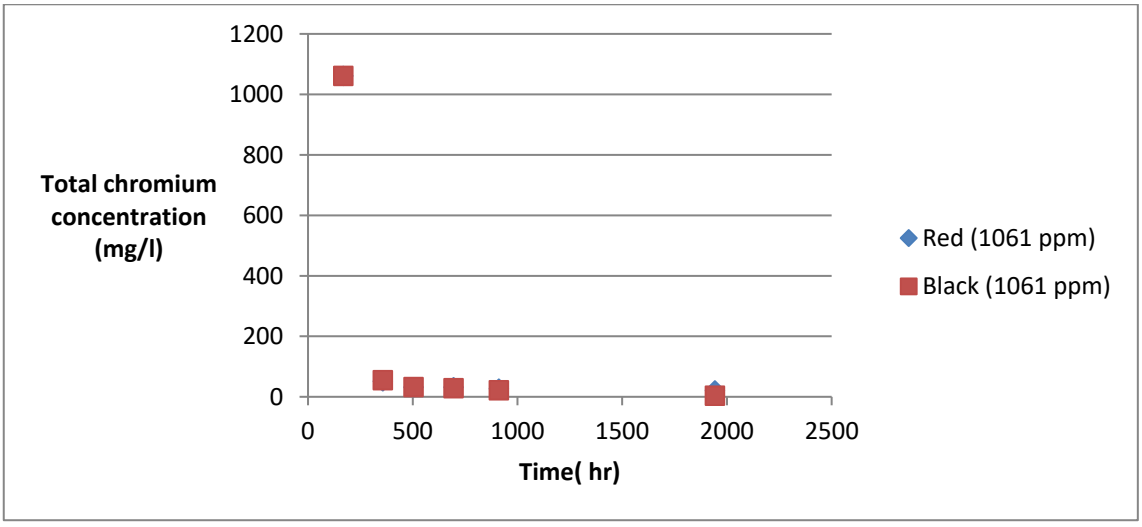

Figure 4.13: Total chromium concentrations for red and black soil with initial total chromium concentration equal to 1061 ppm and 0.5 L volume.

Results shown in Figure 4.13 for a 0.5 l chromium concentration of 1061 ppm added to 170 g soil (Red and Black soil separately). For both red and black soil the total chromium concentrations were decreased sharply.

When comparing the two soil types, the initial uptake amount in red and black soils is 1009.6 mg /l, 1006 mg /l, respectively, and the remaining concentrations in red and black soil is 21 mg /l, 3.7 mg /l, respectively. So, the black soil is better in total chromium adsorption than red soil.

Figure 4.14 represents the total chromium concentrations with different times for red soil and initial total chromium concentration equal to 2653 ppm, volume equal 1 L where weight of soil 170 gm.

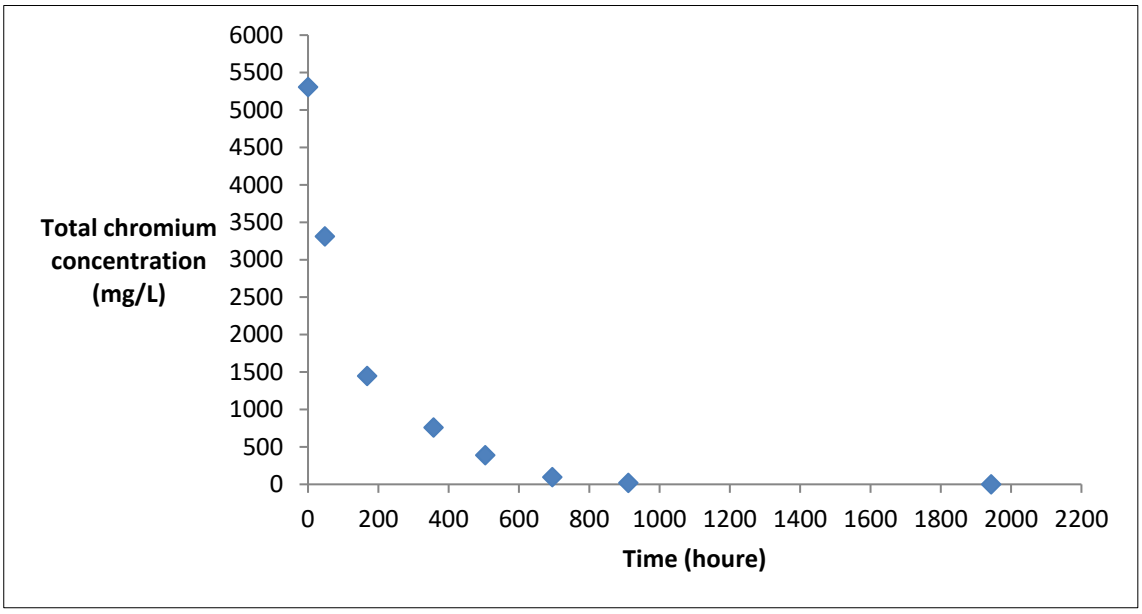

Figure 4.14: Total chromium concentrations for red soil with initial total chromium concentration equal to 2653 ppm and 1 L volume.

Figure 4.15 shows the total chromium concentrations in 1L volume were decreased gradually. While in 0.5 L the total chromium concentrations were decreased in two steps not gradually.

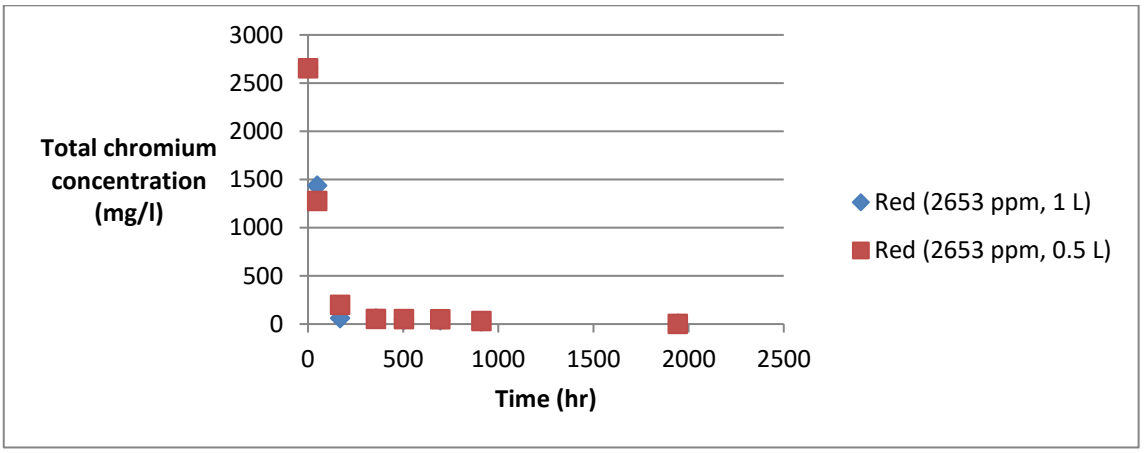

Figure 4.15: Total chromium concentrations for red soil with initial total chromium concentration equal to 2653 ppm and 1, 0.5 L volume.

When comparing the 0.5L and 1L of total chromium concentration equal to 2653ppm and same soil type, the initial uptake amount in 0.5L and 1L are1376 mg / l, 1216 mg / l, respectively, and the remaining concentrations are0.92 mg / l, 2.4 mg / l, respectively. So, the less volume of same soil and concentration is better in total chromium uptake than high one. By comparing between 0.5 L and 1L and same amount of soil, when the volume is 0.5L then the soil was saturated with total chromium faster.

The effect of initial chromium concentration on the adsorption capacity for Red and Black soil samples is shown in Figures 4.16 and 4.17 respectively. At higher initial chromium concentration, the concentration decrease is lower than that of lower initial chromium concentration.

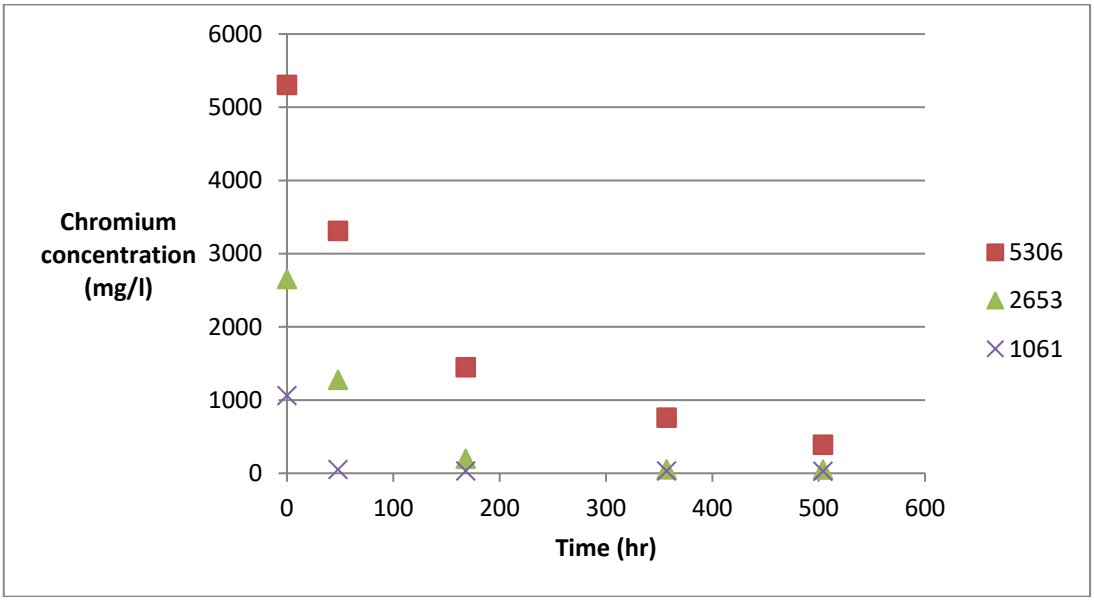

Figure 4.16: Chromium concentrations for red soil with initial total chromium concentration equal to 5306, 2653 and 1061 ppm.

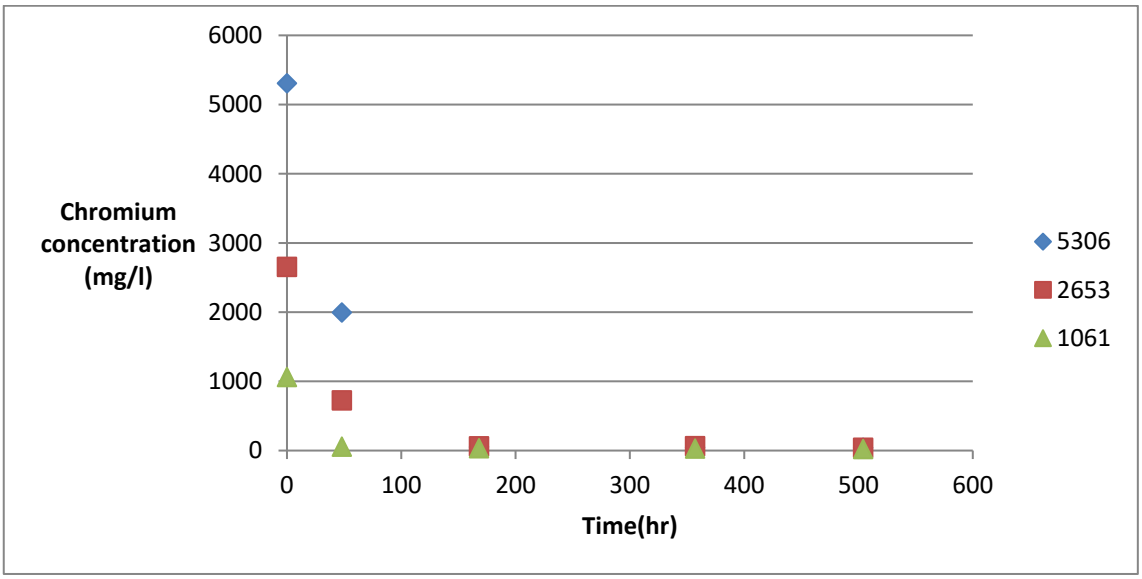

Figure 4.17: Chromium concentrations for black soil with initial total chromium concentration equal to 5306, 2653 and 1061 ppm.

For the solutions with initial concentration equal to 5306 and 2653 ppm of total chromium, in red soil, the total Cr concentrations were decreased gradually. While in black were decreased faster. The black soil is better in total chromium adsorption than red soil. When the initial concentration equal to 1061 ppm, in both soils, the total Cr concentrations were decreased in two steps, but the black soil is better in total chromium adsorption than red soil.

Hexavalent chromium concentrations were tested by 1, 5 Diphenylcarbohydrazide method for all water samples that taken from different soil, total chromium concentration and time.

Figures 4.18 and 4.19 represent some samples afterCr^{6+} test, the darkness of the purple color represent the concentration strength.

Figure 4.18: Samples with high concentrations of hexavalent chromium.

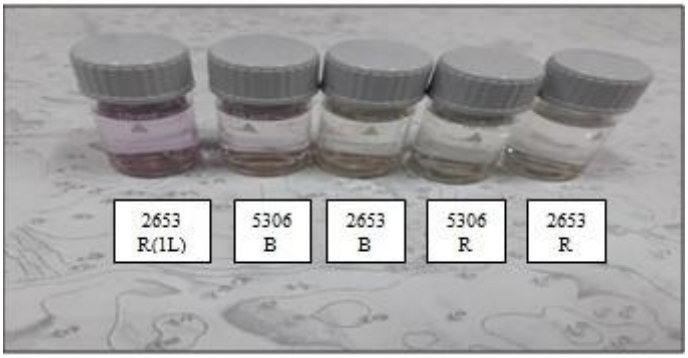

Figure 4.19: Samples with less concentrations of hexavalent chromium

Figure 4.20 represents the Cr^{6+}concentrations with different times for red and black soil samples at an initial total chromium concentration of 5306 ppm.

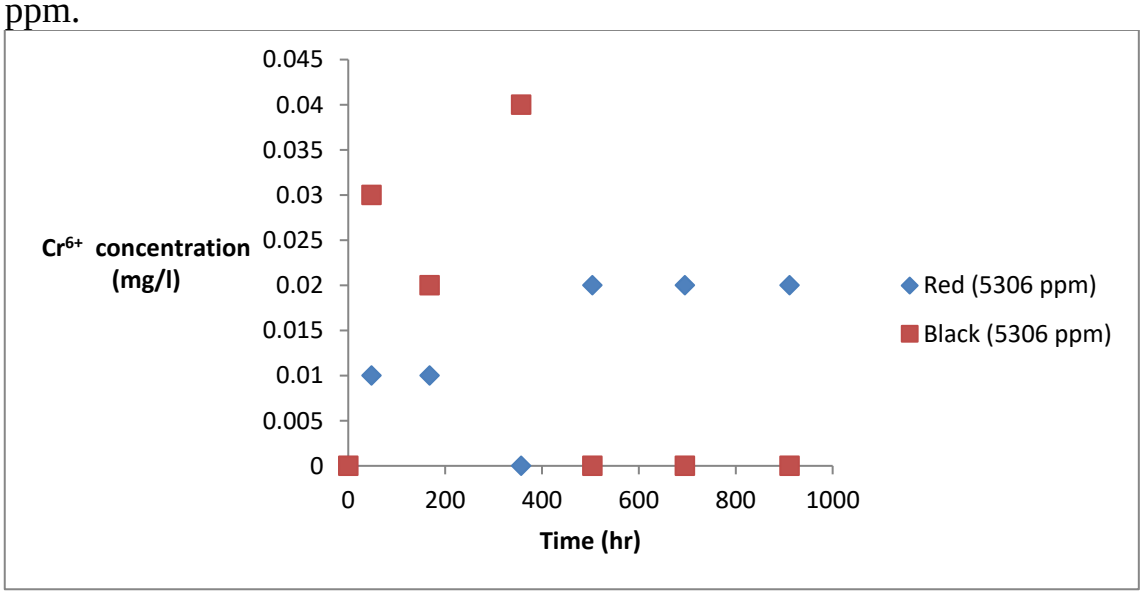

Figure 4.20: Hexavalent chromium concentrations for red and black soil samples with initial total chromium concentration of 5306 ppm and 0.5 L volume.

As shown in Figure 4.20 the Cr^{6+}concentrations fluctuate with time. The change behavior of the Cr^{6+} concentration of the red and black soil samples are not same and can be related to the quantity of manganese oxide in the sample. This evident from the XRF test results which show that red soil sample contains more manganese oxide than the black soil sample. Cr^{3+} has the tendency to be adsorbed by the manganese oxide. In soils, manganese oxides (MnO) typically accumulate on the surface of the clay. Hence, Cr^{3+}can be oxidized to Cr^{6+} as shown by equation 4.1:(Subramanian et al., 2014).

$$2Cr^{3+} + 3MnO_2 + 2H_2O \Leftrightarrow 2CrO^{2-}_4 + 3Mn^{2+} + 4H \quad \text{.....(4.1)}$$

Therefore, due to the higher manganese oxide concentration in the red soil sample, the more tendency of Cr^{3+} to be oxidized to Cr^{6+} in the red soil sample than the black soil sample as shown in Figure 4.20.

Figure 4.21 represents theCr^{6+} concentrations with different times for red soil and initial total chromium concentration equal to 2653 ppm.

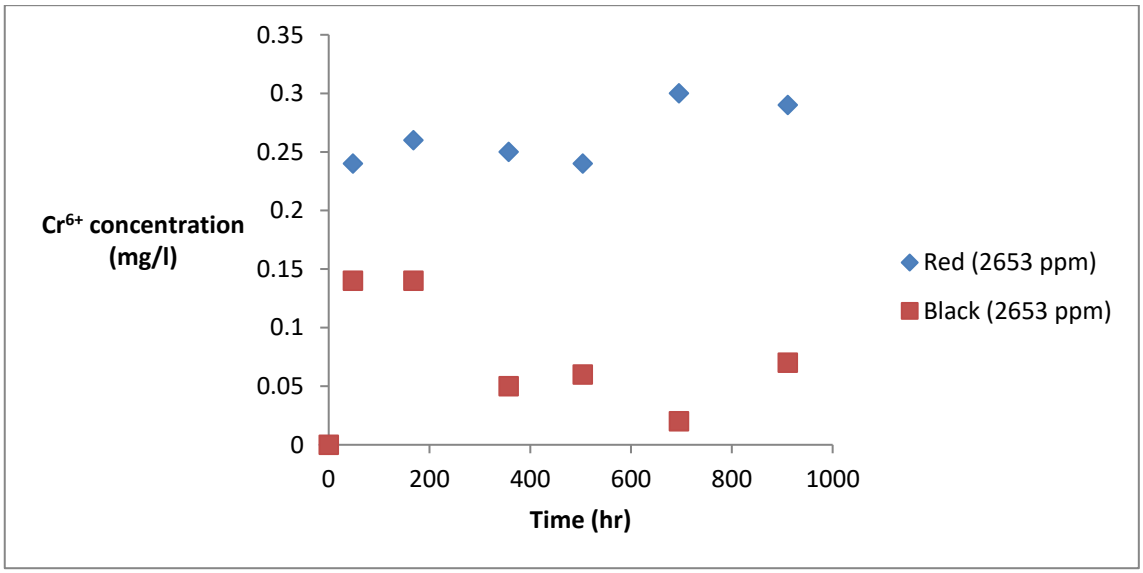

Figure 4.21: Hexavalent chromium concentrations for red and black soil with initial total chromium concentration equal to 2653 ppm and 0.5 l volume.

Figure 4.22 represents theCr^{6+}concentrations with different times for red soil and initial total chromium concentration equal to 2653 ppm, volume equal 1 L where weight of soil 170 gm.

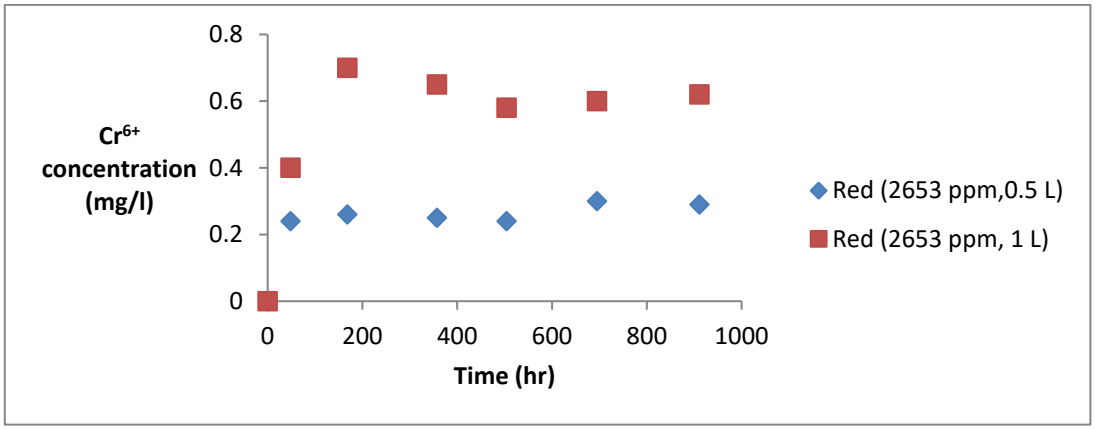

Figure 4.22: Hexavalent chromium concentrations for red soil with initial total chromium concentration equal to 2653 ppm and 1, 0.5 L volume.

As shown in Figure 4.22the larger the volume of the solution, the more oxidation of Cr^{3+} toCr^{6+} due the more adsorption of Cr^{3+} on the manganese oxide. The equilibrium concentration of Cr^{6+} is higher than the allowable level 0.1 mg/L stated by PWA.

In soil, the process of converting Cr^{3+} toCr^{6+} is a complex process that relies on many variables, such as pH, soil content, and soil components that play a role in reactions of oxidation and reduction. The values of the concentration of $Cr^{6+}$are fluctuating, and no clear relationship has been achieved. This could be explained by the method of Redox response and dechromification(Subramanian et al., 2014) and the presence of ferrous and sulfides in the soil samples.

Manganese and iron oxides that settle on the surface of the soil have a wide surface area, a high adsorption potential for heavy metals and a negative

charge under acidic conditions can led to the oxidation of Cr^{3+} toCr^{6+}. Therefore, it is very essential to test the effect of pH on the oxidation of Cr^{3+} to Cr^{6+} in future work.

Ferrous and Sulfide as electron doner can reduced some of Cr^{6+} toCr^{3+}, called this dechromification (Subramanian et al., 2014). This can be a simple explanation of the fluctuation of the $Cr^{6+}$with time.

In red soil, Manganese, Ferrous and Sulfide oxides concentrations are higher than in black soil as obtained from XRF data but due to also higher concentration of manganese oxide, the tendency of oxidizing Cr^{3+} to Cr^{6+} is higher than the reduction of Cr^{6+} to Cr^{3+}, therefore, the concentration of Cr^{6+} is higher Additionally, from the red soil structure, the lower permeability, porosity and void ratio resulted in more Cr^{3+} in the red soil than the black soil and hence more oxidation to Cr^{6+}.

BecauseCr^{6+} is anionic, it's attracted to positively charged surfaces. Therefore, binding of chromium to soil depends on soil mineralogy (Subramanian et al., 2014). So, this binding reduces the Cr^{6+}concentration in water that were tested.

4.5 Oxidation ofCr^{3+} from Different Concentrations and Volume (Total Amount) with Time without Soils.

After chromium sulfate solutions with concentrations 5306, 2653 and 1061 ppm were put in beakers with different volumes which were 100, 250 and 500 ml as shown previously in Figure 3.11 without soil.

Samples were taken each time from all beakers, Then, hexavalent chromium concentrations were tested by 1, 5 Diphenylcarbohydrazide Method.

Table 4.9, 4.10 and 4.11 represent the Cr^{6+}concentration over time.

Table 4.9: Hexavalent chromium concentration (mg/l) for the 1061 ppm of total chromium without soil.

Concentration in ppm after	Volume of solution =volume of beaker		
	100 mL	250 mL	500 mL
7 days (168 hr)	1	1.1	1.4
11 days (264 hr)	1.5	2	2
18 days (432 hr)	2	2.5	2.5

Table 4.10: Hexavalent chromium concentration (mg/l) for the 2653 ppm of total chromium without soil.

concentration in ppm after	Volume of solution =volume of beaker		
	100 mL	250 mL	500 mL
7 days (168 hr)	1	0.8	0.9
11 days (264 hr)	1.5	2	2
18 days (432 hr)	2	2.5	2.5

Table 4.11: Hexavalent chromium concentration (mg/l) for the 5306 ppm of total chromium without soil.

concentration in ppm after	Volume of solution =volume of beaker		
	100 mL	250 mL	500 mL
7 days (168 hr)	0.3	0.6	0.7
11 days (264 hr)	1.5	1.5	1.5
18 days (432 hr)	1.5	1.5	2

As shown in tables 4.9, 4.10 and 4.11, when the volume of the same total chromium concentration was increased, theCr^{6+} concentration was slightly increased. Also, over times the concentration of $Cr^{6+}$was increased. With a solution of chromium sulfate at initial pH = 4.13, which isCr^{3+}, when

placing the solution in beakers of different sizes, the opening of the beaker increase with increasing volume, therefore the chromium solution was exposed to more oxygen concentration. Then $Cr^{3+}$is oxidized toCr^{6+}. As the concentration of Cr^{3+}increases, the oxidation increases and the Cr^{6+}increases.

When comparing the formation of Cr^{6+}between the presence of the soil and its absence in the same volume (500 ml), it was shown that the general trend ofCr^{6+}formation increased over time without soil more than the presence of it. This is due to the effect of soil composition of manganese oxide, ferrous and sulfides. Due to the low concentration, more accurate experimental testing of Cr^{6+} is needed.

4.6 Adsorption Kinetic Models for Removal of Chromium onto Soil.

It is well known that the mass transfer coefficient towards particle surface increases with increasing bulk motion. Therefore, increasing the mass transfer coefficient decreases the characteristic time needed to approach equilibrium. This means that when wastewater peculates through soil (i.e., with the mechanism of flow through porous media), the contamination of soil will be larger than for the case with stagnant wastewater (as the case of this study). This is because the flow of the wastewater past the soil particles increases the mass transfer coefficient. It is obvious that mass transfer coefficient in forced convection is larger than that for stagnant particle (natural convection) (Al-Jabari et al., 2017b).

Experimental data of the chromium solution concentration were tested by the adsorption kinetic models using pseudo first order and second order rate equations, given in equations (4.5) and (4.6), presented in linear forms. (Jean Simonina, 2016).

The amount of adsorption (mg/g) at time t is calculated using the following equations:

$$(q_t) = \frac{(Co - Ct) * V}{w} \quad \text{..... (4.2)}$$

$$(q_e) = \frac{(Co - Ce) * V}{w} \quad \text{.....(4.3)}$$

$$\% \text{ adsorption} = \frac{(Co - Ca)}{w} * 100 \quad \text{.....(4.4)}$$

where,

C_0: initial concentration of solution (mg/l).

C_e: concentration at equilbrium (mg/l).

C_a: concentration after adsorption (mg/l).

W: mass of adsorbent (g).

V: volume of solution (L).

Pseudo first order:

$$\text{Log } (q_e - q_t) = \text{Log } (q_e) - \frac{k_1}{2.303} t \quad \text{.....(4.5)}$$

Where, $q_e$is the intercept and k_1 is slope (min^{-1}).

Pseudo second order:

$$= \frac{1}{k_{12}{q_e}^2} + \frac{1}{q_e} t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.6) \frac{t}{q_t}$$

Where, $q_e$is the slope and k_2 is intercept (g mg^{-1} min^{-1}).

Figures 4.23-4.25show the adsorption capacity (q_t) as a function of time for chromium solution with initial concentrations equal to 1061, 2653, 5306 ppm respectively in different soil types.

Initially, the adsorption capacity is slightly higher in black soil (Silty Loam) than in red soil sample and increases with increasing of chromium concentration in solution for the same solution volume (0.5 L).

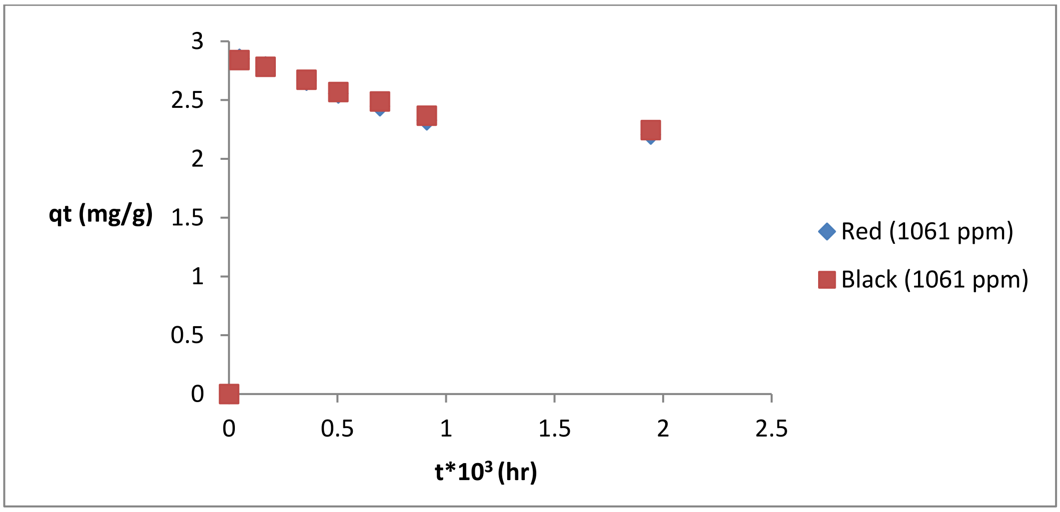

Figure 4.23: Adsorption capacity (qt) as a function of time for chromium solution with initial concentration equal to 1061 ppm in different soil types.

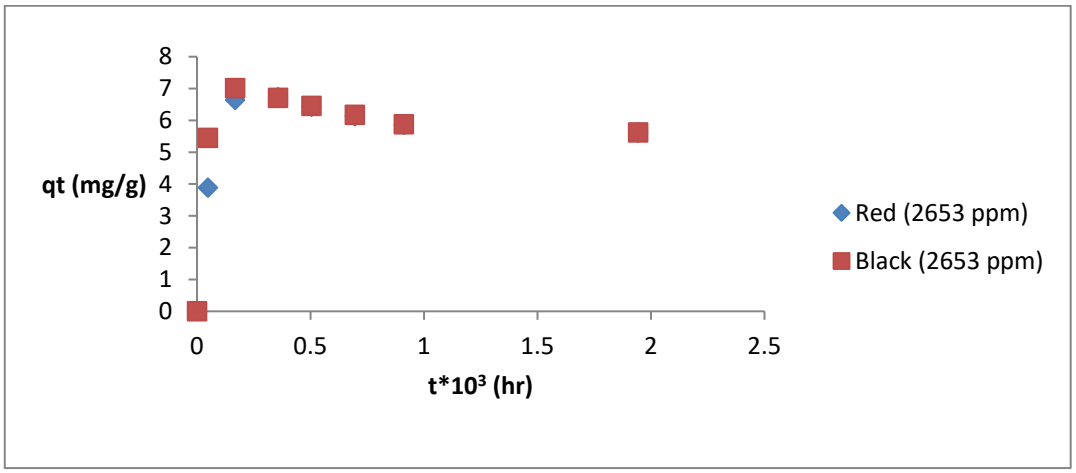

Figure 4.24: Adsorption capacity (qt) as a function of time for chromium solution with initial concentration equal to 2653 ppm in different soil types.

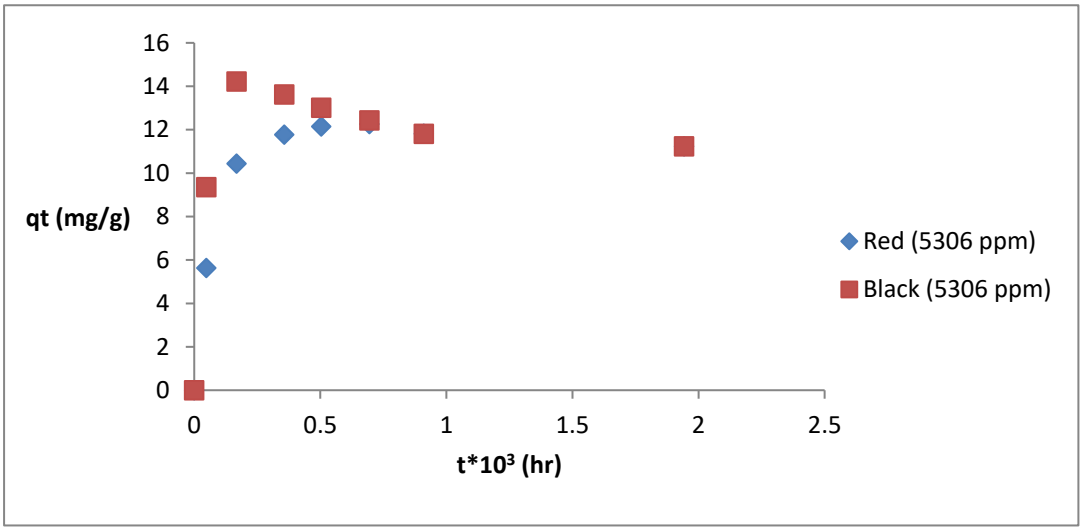

Figure 4.25: Adsorption capacity (qt) as a function of time for chromium solution with **initial concentration equal to 5306 ppm in different soil types.**

With the second order model, the plot of t/ q_t versus time is linear, with a positive slope of $\frac{1}{q_e}$. The resulting lines for the second order model areplotted in **Figures 4.26-4.28**. From data analyses that have done, the pseudo second order model gives better fitting than the first order model i.e., higher R^2 values.

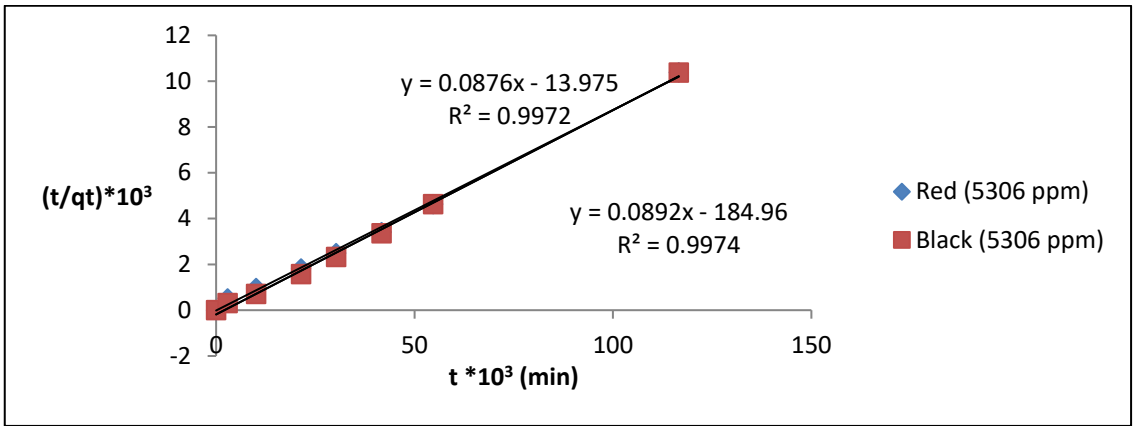

Figure 4.26: Second order kinetic model for the adsorption of total chromium onto soil particles for initial concentration equal to 5306 ppm in different soil.

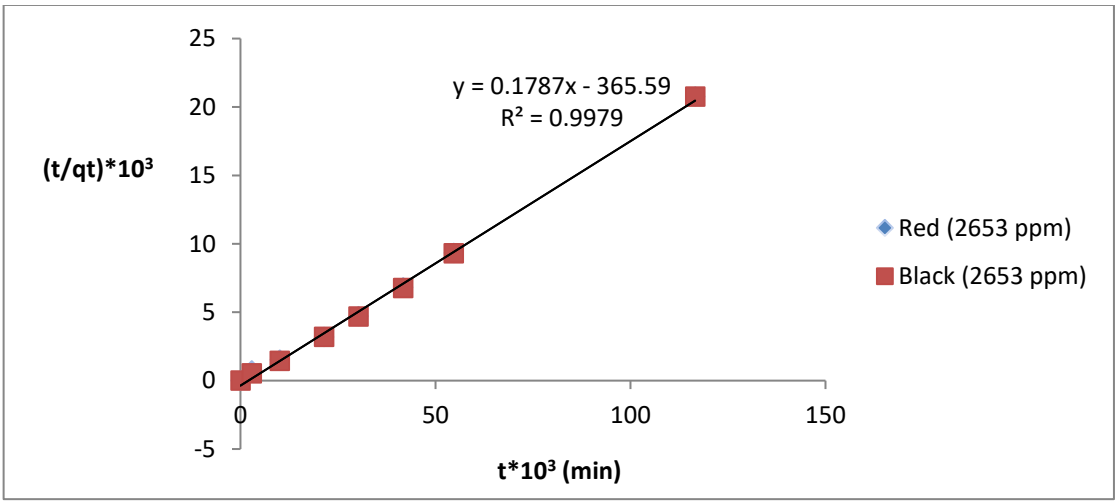

Figure 4.27: Second order kinetic model for the adsorption of total chromium onto soil particles for initial concentration equal to 2653 ppm in different soil.

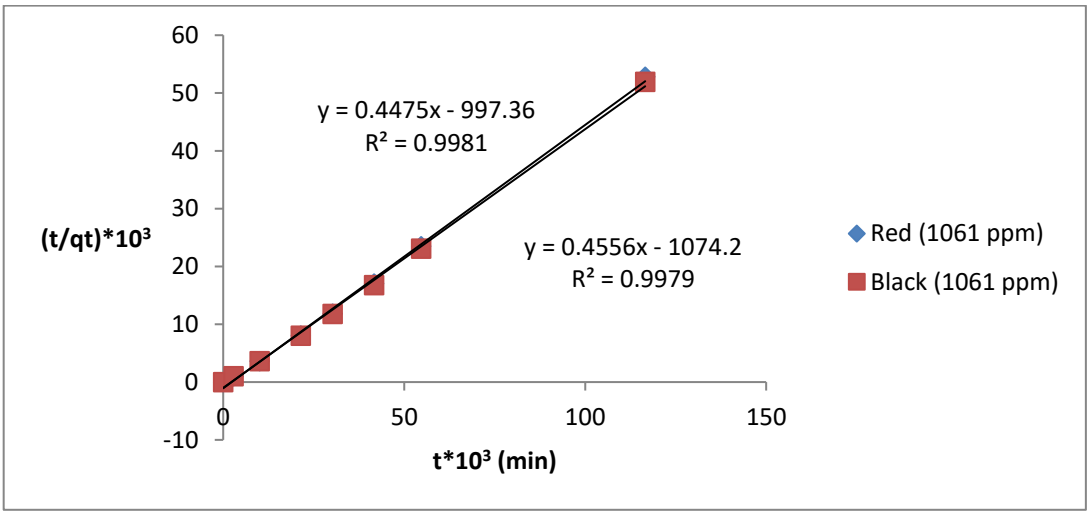

Figure 4.28: Second order kinetic model for the adsorption of total chromium onto soil particles for initial concentration equal to 1061 ppm in different soil.

Table 4.12 shows fitting parameters with pseudo second order model for adsorption of total chromium from different concentrations (5306, 2653 and 1061 ppm) onto different soil types (silty clay and silty loam).

Table 4.12: Fitting parameters with pseudo second order model for different concentrations onto different soils.

Initial chromium concentration (mg/l)	Red soil (Silty clay)			Black soil (Silty loam)		
	q_e(mg/g)	K_2(g mg^{-1} min^{-1})	R^2	q_e(mg/g)	K_2(g mg^{-1} min^{-1})	R^2
5306	11.49	0.00054	0.997	11.24	$4.28*10^{-5}$	0.997
2653	5.62	$8.66*10^{-5}$	0.997	5.62	$8.66*10^{-5}$	0.997
1061	2.24	0.00019	.0998	2.19	0.00019	0.997

As shown in table 4.12, The R^2 value for all concentrations in both soil types are equal. The high chromium concentration whichis 5306 ppm in Red soil has the higher q_e than the same concentration in black soil which is faster in chromium adsorption. However, the values are close. But, for the rest concentrations in both soil, the values are similar.

Chapter Five

Conclusions and Recommendations

5.1 Conclusions

From this work, the following conclusions can be drawn:

A Silty clay red soil and a Silty Loam black soil were analyzed and used successfully to adsorb chromium from Chromium sulfide solution. It was found that these soils can adsorb total chromium from solutions successfully. The adsorption process fitting shows pseudo second order behavior.

For the solutions with initial concentration equal to 5306 and 2653 ppm of total chromium, volume equal 0.5 L and weight of both soil is 170 gm. In red soil, the total Cr concentrations were decreased gradually. While in black were decreased but in two steps. The black soil is better in total chromium adsorption than red soil, when the initial concentration equal to 1061 ppm, in both soils, the total Cr concentrations were decreased in two steps, but the black soil is better in total chromium adsorption than red soil.

There is a possibility of formationCr^{6+} from chromium sulfate solutions in different soil types. The Cr^{6+}concentrations were increased in red soil, while in black soil the concentrations were decreased for the chromium sulfate solutions with concentrations 5306 and 2653 ppm of total Cr. In red soil the concentration of Fe and Mn element are more than in black soil.

When comparing the formation ofCr^{6+} between the presence of the soil and its absence in the same volume, it was shown that the Cr^{6+}formation increased over time without soil more than the presence of it.

When the volume of the same total chromium concentration was increased, the Cr^{6+}concentration was increased. Also, over times the concentration of $Cr^{6+}$was increased. So, the presence ofCr^{6+} depends on several parameters that play role on possibility of negative effect of it, such as soil component, presence of H_2S, the flow speed, and the concentration of solution where it may mix with rain water or with solutions from another leather industry process.

5.2 Recommendations

As recommendation for future work, the followings are suggested:

1. It is necessary to run the experiment with more types of soil like clay, sandy clay and loam for the same research method and to examine the effect of soil properties and their components especially clay on total chromium adsorption and the formation of Cr^{6+}.
2. Leather Tanning industry is not hazardous since the usedCr^{3+} which is not toxic and thus non-hazardous, although still considered to be polluting due to the formation of Cr^{6+}.But, this process depends on many parameters mainly pH. This leads to study other factors such as the effect of pH on soil adsorption of total Cr, soil dose with/without

stirring, and mix chromium solution with solution from lime or pickling step.

3. Study the Kinetic models for chromium adsorption on to soil in more details with different parameters.

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Appendices

Appendix A: Determination of oxides percentages from XRF data for soil.

Table A1: XRF result and oxides percentage in fresh red soil sample(B_{1i})

Element	Wt. % Normalized	Atom. Wt.	Oxide	Ox.Form.Wt	# Mol. Elem	# Mol. Ox.	Wt. % Ox	Normalized Oxide	Oxide Wt%
Si	38.72	28.086	SiO2	60.086	1.379	1.379	82.836	46.199	35.573
Ti	2.283	47.867	TiO2	79.867	0.048	0.048	3.809	2.124	1.636
Al	17.766	26.982	Al2O3	101.964	0.658	0.329	33.569	18.722	14.416
Fe	28.507	55.845	Fe2O3	159.69	0.510	0.255	40.758	22.731	17.503
Mn	0.4313	54.938	MnO	70.938	0.008	0.008	0.557	0.311	0.239
Mg	2.276	24.305	MgO	40.305	0.094	0.094	3.774	2.105	1.621
Ca	6.631	40.078	CaO	56.078	0.165	0.165	9.278	5.175	3.984
Na	0.0005	22.99	Na2O	61.98	0.000	0.000	0.001	0.000	0.000
K	1.672	39.098	K2O	94.196	0.043	0.021	2.014	1.123	0.865
P	0.4992	30.974	P2O5	141.948	0.016	0.008	1.144	0.638	0.491
Cr	0.0802	51.996	Cr2O3	151.992	0.002	0.001	0.117	0.065	0.050
S	0.2078	32.066	SO3	80.066	0.006	0.006	0.519	0.289	0.223
Trace	0.9276						0.928	0.517	0.398
Total	100.0016						179.304	100.000	77.000
LOI	22								0.230

Trace (ppm)	
Br	25
Cl	2459
Nb	235
Ni	681
Pb	56
Rb	498
Sc	13
Sr	509
Zn	1052
Zr	2819
V	671
Y	258
Sum	9276

Table A2: XRF result and oxides percentage in red soil sample after treated with 2653 ppm chromium solution (B_{1f})

Element	% Normaliz	Atom. Wt.	Oxide	Ox.Form.Wt	# Mol. Elem	# Mol. Ox.	Wt. % Ox	Normalized Oxide	Oxide Wt%
Si	36.464	28.086	SiO2	60.086	1.298	1.298	78.010	42.402	33.074
Ti	1.923	47.9	TiO2	79.9	0.040	0.040	3.208	1.744	1.360
Al	16.689	26.9815	Al2O3	101.963	0.619	0.309	31.534	17.140	13.369
Fe	20.655	55.847	Fe2O3	159.694	0.370	0.185	29.531	16.052	12.520
Mn	0.3803	54.838	MnO	70.838	0.007	0.007	0.491	0.267	0.208
Mg	1.97	24.305	MgO	40.305	0.081	0.081	3.267	1.776	1.385
Ca	8.309	40.08	CaO	56.08	0.207	0.207	11.626	6.319	4.929
Na	0.0047	23	Na2O	62	0.000	0.000	0.006	0.003	0.003
K	1.523	39	K2O	94	0.039	0.020	1.835	0.998	0.778
P	0.5058	31	P2O5	142	0.016	0.008	1.158	0.630	0.491
Cr	4.56	51.996	Cr2O3	151.992	0.088	0.044	6.665	3.623	2.826
S	6.431	32.066	SO3	80.066	0.201	0.201	16.058	8.728	6.808
Trace	0.5864						0.586	0.319	0.249
Total	100.0012						183.976	100.000	78.000
LOI	20								0.220

Trace (ppm)	
Br	13
Cl	1700
Nb	0
Ni	460
Pb	0
Rb	285
Sc	19
Sr	296
Zn	658
Zr	1640
V	632
Y	161
Sum	5864

Table A3: XRF result and oxides percentage in fresh black soil sample(B_{2i})

Element	% Normaliz	Atom. Wt.	Oxide	Ox.Form.Wt	# Mol. Elem	# Mol. Ox.	Wt. % Ox	Normalized Oxide	Oxide Wt%
Si	48.903	28.086	SiO2	60.086	1.741	1.741	104.621	56.809	46.583
Ti	1.952	47.9	TiO2	79.9	0.041	0.041	3.256	1.768	1.450
Al	13.293	26.9815	Al2O3	101.963	0.493	0.246	25.117	13.639	11.184
Fe	15.268	55.847	Fe2O3	159.694	0.273	0.137	21.829	11.853	9.720
Mn	0.374	54.838	MnO	70.838	0.007	0.007	0.483	0.262	0.215
Mg	3.705	24.305	MgO	40.305	0.152	0.152	6.144	3.336	2.736
Ca	11.317	40.08	CaO	56.08	0.282	0.282	15.835	8.598	7.051
Na	0.0017	23	Na2O	62	0.000	0.000	0.002	0.001	0.001
K	3.637	39	K2O	94	0.093	0.047	4.383	2.380	1.952
P	0.4661	31	P2O5	142	0.015	0.008	1.068	0.580	0.475
Cr	0.041	51.996	Cr2O3	151.992	0.001	0.000	0.060	0.033	0.027
S	0.214	32.066	SO3	80.066	0.007	0.007	0.534	0.290	0.238
Trace	0.8298						0.830	0.451	0.369
Total	100.0016						184.162	100.000	82.000
LOI	18								18.000

Trace (ppm)	
Br	22
Cl	4205
Nb	133
Ni	0
Pb	0
Rb	190
Sc	170
Sr	646
Zn	431
Zr	2023
V	370
Y	108
Sum	8298

Table A4: XRF result and oxides percentage in black soil sample after treated with 2653 ppm chromium solution (B_{2f})

Element	t. % Normalize	Atom. Wt.	Oxide	Ox.Form.Wt	# Mol. Elem	# Mol. Ox.	Wt. % Ox	Normalized Oxide	Oxide Wt%
Si	45.865	28.086	SiO2	60.086	1.633	1.633	98.122	53.343	43.742
Ti	1.826	47.9	TiO2	79.9	0.038	0.038	3.046	1.656	1.358
Al	13.754	26.9815	Al2O3	101.963	0.510	0.255	25.988	14.128	11.585
Fe	14.552	55.847	Fe2O3	159.694	0.261	0.130	20.806	11.311	9.275
Mn	0.3642	54.838	MnO	70.838	0.007	0.007	0.470	0.256	0.210
Mg	3.671	24.305	MgO	40.305	0.151	0.151	6.088	3.310	2.714
Ca	11.36	40.08	CaO	56.08	0.283	0.283	15.895	8.641	7.086
Na	0.0085	23	Na2O	62	0.000	0.000	0.011	0.006	0.005
K	3.381	39	K2O	94	0.087	0.043	4.075	2.215	1.816
P	0.5042	31	P2O5	142	0.016	0.008	1.155	0.628	0.515
Cr	2.486	51.996	Cr2O3	151.992	0.048	0.024	3.633	1.975	1.620
S	1.615	32.066	SO3	80.066	0.050	0.050	4.033	2.192	1.798
Trace	0.6225						0.623	0.338	0.278
Total	100.009						183.944	100.000	82.000
LOI	18								18

Trace (ppm)	
Br	0
Cl	2529
Nb	0
Ni	0
Pb	0
Rb	169
Sc	135
Sr	585
Zn	390
Zr	1900
V	392
Y	125
Sum	6225

Appendix B: Determination total chromium concentrations.

Table B1: Total chromium concentration in samples that were taken from different solutions in different soils, these results from chromium concentration after dilution the sample with different dilution factors.

Cr concentratiom (ppm)	Soi color	date	15-Sep	17-Sep	22-Sep	30-Sep	06-Oct	14-Oct	23-Oct	05-Dec
		houre	0	48	168	357	504	695	911	1943
2653 ppm	Red (0.5 L)	Cr+6	0	0.24	0.26	0.25	0.24	0.3	0.29	
		Total Cr	2653	1277	198.7	53.37	51.25	50.05	31	0.923
		houre	0	48	168	357	504	695	911	1943
2653 ppm	Black (0.5 L)	Cr+6	0	0.14	0.14	0.05	0.06	0.02	0.07	
		Total Cr	2653	724	61.58	62.67	40.93	30.78	25.41	0.654
2653 ppm	Red (1 L)	Cr+6	0	0.4	0.7	0.65	0.58	0.6	0.62	
		Total Cr	2653	1437	61.65	56.69	46.23	40	27.23	2.46
1061 ppm	Red (0.5 L)	Cr+6	0	0.18	0.11	0.09	0.12	0.13		
		Total Cr	1061	51.31	31.52	31.43	26.81	21		
1061 ppm	Black (0.5 L)	Cr+6	0	0.08	0.13	0.17	0.22	0.27		
		Total Cr	1061	55.05	32.43	28.46	21.5349	3.7785		
5306 ppm	Red (0.5 L)	Cr+6	0	0.01	0.01	0	0.02	0.02	0.02	
		Total Cr	5306	3312	1448	758.9	390.4	97.32	20.7	0.747
5306 ppm	Black (0.5 L)	Cr+6	0	0.03	0.02	0.04	0	0	0	
		Total Cr	5306	1994	52.02	44.43	39.43	25.3	23.51	0.525

Table B2: Flame Atomic Adsorption Results (Total chromium concentrations)

SAMPLE ID	RESULT TYPE	SIGNAL	Rsd	CONC.	CORRECTED CC
		Abs	%	mg/L	mg/L
Blank	Mean	0.000163518	44.0491219	0	
Blank	Resample 1 of 3	8.67E-05			
Blank	Resample 2 of 3	0.000229592			
Blank	Resample 3 of 3	0.000174227			
Standard 1	Mean	0.068228841	0.190839425	5	
Standard 1	Resample 1 of 3	0.068130612			
Standard 1	Resample 2 of 3	0.068179384			
Standard 1	Resample 3 of 3	0.068376534			
Standard 2	Mean	0.106423147	0.287478089	10	
Standard 2	Resample 1 of 3	0.106076039			
Standard 2	Resample 2 of 3	0.106539793			
Standard 2	Resample 3 of 3	0.106653608			
Standard 3	Mean	0.193490297	0.031469427	20	
Standard 3	Resample 1 of 3	0.193488538			
Standard 3	Resample 2 of 3	0.193552047			
Standard 3	Resample 3 of 3	0.193430305			
Standard 4	Mean	0.277584165	0.371641189	30	
Standard 4	Resample 1 of 3	0.276395887			
Standard 4	Resample 2 of 3	0.278106123			
Standard 4	Resample 3 of 3	0.278250515			
Standard 5	Mean	0.385458708	0.394445956	40	
Standard 5	Resample 1 of 3	0.386870414			
Standard 5	Resample 2 of 3	0.385656714			
Standard 5	Resample 3 of 3	0.383848965			
Standard 6	Mean	0.443073392	0.468028009	50	
Standard 6	Resample 1 of 3	0.440680414			
Standard 6	Resample 2 of 3	0.444195926			
Standard 6	Resample 3 of 3	0.444343865			

Sample ID 1	Mean	0.116684698	0.126111865	11.0791302	11.0791302
Sample ID 1	Resample 1 of 3	0.116797961			
Sample ID 1	Resample 2 of 3	0.116518371			
Sample ID 1	Resample 3 of 3	0.116737753			
Sample ID 2	Mean	0.265789211	0.404075772	28.5088749	28.5088749
Sample ID 2	Resample 1 of 3	0.267023712			
Sample ID 2	Resample 2 of 3	0.265069693			
Sample ID 2	Resample 3 of 3	0.265274227			
Sample ID 3	Mean	0.364578843	0.411249697	38.3504601	38.3504601
Sample ID 3	Resample 1 of 3	0.36292991			
Sample ID 3	Resample 2 of 3	0.364946455			
Sample ID 3	Resample 3 of 3	0.365860194			
Sample ID 4	Mean	0.058982104	1.16129673	4.32074547	4.32074547
Sample ID 4	Resample 1 of 3	0.058890723			
Sample ID 4	Resample 2 of 3	0.059708163			
Sample ID 4	Resample 3 of 3	0.058347423			
Sample ID 5	Mean	0.116653085	0.362746179	11.0757027	11.0757027
Sample ID 5	Resample 1 of 3	0.116837114			
Sample ID 5	Resample 2 of 3	0.116169073			
Sample ID 5	Resample 3 of 3	0.11695306			
Sample ID 6	Mean	0.187666744	0.560020506	19.2622643	19.2622643
Sample ID 6	Resample 1 of 3	0.187651515			
Sample ID 6	Resample 2 of 3	0.186623469			
Sample ID 6	Resample 3 of 3	0.188725248			
Sample ID 7	Mean	0.031208355	0.244290158	2.28051782	2.28051782
Sample ID 7	Resample 1 of 3	0.0311567			
Sample ID 7	Resample 2 of 3	0.031295918			
Sample ID 7	Resample 3 of 3	0.031172449			
Sample ID 8	Mean	0.062171001	0.751615345	4.55499792	4.55499792
Sample ID 8	Resample 1 of 3	0.062050514			
Sample ID 8	Resample 2 of 3	0.061775759			
Sample ID 8	Resample 3 of 3	0.062686734			
Sample ID 9	Mean	0.090827167	0.299958616	7.48646593	7.48646593
Sample ID 9	Resample 1 of 3	0.09053608			
Sample ID 9	Resample 2 of 3	0.09086939			
Sample ID 9	Resample 3 of 3	0.091076039			
Sample ID 10	Mean	0.012128691	0.84176147	0.878947794	0.878947794
Sample ID 10	Resample 1 of 3	0.012051021			
Sample ID 10	Resample 2 of 3	0.012090722			
Sample ID 10	Resample 3 of 3	0.01224433			
Sample ID 11	Mean	0.020803554	0.963541448	1.51619327	1.51619327
Sample ID 11	Resample 1 of 3	0.020623233			
Sample ID 11	Resample 2 of 3	0.020768041			
Sample ID 11	Resample 3 of 3	0.021019388			
Sample ID 12	Mean	0.031598229	0.8016873	2.30915761	2.30915761
Sample ID 12	Resample 1 of 3	0.031527553			
Sample ID 12	Resample 2 of 3	0.031387754			
Sample ID 12	Resample 3 of 3	0.03187938			
Sample ID 13	Mean	0.005228743	0.49666211	0.372085631	0.372085631
Sample ID 13	Resample 1 of 3	0.005235714			
Sample ID 13	Resample 2 of 3	0.0052			
Sample ID 13	Resample 3 of 3	0.005250515			
Sample ID 14	Mean	0.007590178	0.807243824	0.545553863	0.545553863
Sample ID 14	Resample 1 of 3	0.007551546			
Sample ID 14	Resample 2 of 3	0.007558163			
Sample ID 14	Resample 3 of 3	0.007660825			
Sample ID 15	Mean	0.008485721	1.15328848	0.61133945	0.61133945
Sample ID 15	Resample 1 of 3	0.008440817			
Sample ID 15	Resample 2 of 3	0.008418367			
Sample ID 15	Resample 3 of 3	0.00859798			
Sample ID 16	Mean	0.307313502	0.294032663	33.1225166	33.1225166
Sample ID 16	Resample 1 of 3	0.30716908			
Sample ID 16	Resample 2 of 3	0.308280617			
Sample ID 16	Resample 3 of 3	0.306490809			
Sample ID 17	Mean	0.188040361	0.856175005	19.3080044	19.3080044
Sample ID 17	Resample 1 of 3	0.186797976			
Sample ID 17	Resample 2 of 3	0.187463924			
Sample ID 17	Resample 3 of 3	0.189859182			
Sample ID 18	Mean	0.375543416	0.027434103	39.2544518	39.2544518
Sample ID 18	Resample 1 of 3	0.375561237			
Sample ID 18	Resample 2 of 3	0.37543264			
Sample ID 18	Resample 3 of 3	0.375636369			
Sample ID 19	Mean	0.004846939	0.241929039	0.344038725	0.344038725
Sample ID 19	Resample 1 of 3	0.004836082			
Sample ID 19	Resample 2 of 3	0.004859375			
Sample ID 19	Resample 3 of 3	0.004845361			
Sample ID 20	Mean	0.004731872	0.768757105	0.335586041	0.335586041
Sample ID 20	Resample 1 of 3	0.00473299			
Sample ID 20	Resample 2 of 3	0.004767677			
Sample ID 20	Resample 3 of 3	0.004694949			

Sample ID 21	Mean	0.004278441	0.822347045	0.302277505	0.302277505
Sample ID 21	Resample 1 of 3	0.004317172			
Sample ID 21	Resample 2 of 3	0.004248454			
Sample ID 21	Resample 3 of 3	0.004269697			
Sample ID 22	Mean	0.004528339	1.34979153	0.320634753	0.320634753
Sample ID 22	Resample 1 of 3	0.004578351			
Sample ID 22	Resample 2 of 3	0.004460204			
Sample ID 22	Resample 3 of 3	0.004546464			
Sample ID 23	Mean	0.004393287	1.45655847	0.310713947	0.310713947
Sample ID 23	Resample 1 of 3	0.004339175			
Sample ID 23	Resample 2 of 3	0.004376768			
Sample ID 23	Resample 3 of 3	0.004463918			
Sample ID 24	Mean	0.004574616	0.714246154	0.324034184	0.324034184
Sample ID 24	Resample 1 of 3	0.004537113			
Sample ID 24	Resample 2 of 3	0.004596939			
Sample ID 24	Resample 3 of 3	0.004589796			
Sample ID 25	Mean	0.004690655	1.80658782	0.332558274	0.332558274
Sample ID 25	Resample 1 of 3	0.004787755			
Sample ID 25	Resample 2 of 3	0.004631632			
Sample ID 25	Resample 3 of 3	0.004652577			
Sample ID 26	Mean	0.00484395	1.05528843	0.343819141	0.343819141
Sample ID 26	Resample 1 of 3	0.004788889			
Sample ID 26	Resample 2 of 3	0.004853061			
Sample ID 26	Resample 3 of 3	0.004889899			
Sample ID 27	Mean	0.004805449	1.33915901	0.340990901	0.340990901
Sample ID 27	Resample 1 of 3	0.004742857			
Sample ID 27	Resample 2 of 3	0.004802062			
Sample ID 27	Resample 3 of 3	0.004871428			
Sample ID 28	Mean	0.004915286	1.98362672	0.349059433	0.349059433
Sample ID 28	Resample 1 of 3	0.005027835			
Sample ID 28	Resample 2 of 3	0.004856566			
Sample ID 28	Resample 3 of 3	0.004861458			
Sample ID 29	Mean	0.004959184	1.40400934	0.352284074	0.352284074
Sample ID 29	Resample 1 of 3	0.005036735			
Sample ID 29	Resample 2 of 3	0.004938776			
Sample ID 29	Resample 3 of 3	0.004902041			
Sample ID 30	Mean	0.00496323	0.958487868	0.352581352	0.352581352
Sample ID 30	Resample 1 of 3	0.004928866			
Sample ID 30	Resample 2 of 3	0.005017526			
Sample ID 30	Resample 3 of 3	0.004943299			
Sample ID 31	Mean	0.004959092	0.761129379	0.352277368	0.352277368
Sample ID 31	Resample 1 of 3	0.004973196			
Sample ID 31	Resample 2 of 3	0.004916327			
Sample ID 31	Resample 3 of 3	0.004987755			
Sample ID 32	Mean	0.104704693	0.749773264	9.66807747	9.66807747
Sample ID 32	Resample 1 of 3	0.104061224			
Sample ID 32	Resample 2 of 3	0.104473472			
Sample ID 32	Resample 3 of 3	0.105579384			
Sample ID 33	Mean	0.216200337	0.35081616	22.5612259	22.5612259
Sample ID 33	Resample 1 of 3	0.216494903			
Sample ID 33	Resample 2 of 3	0.215338781			
Sample ID 33	Resample 3 of 3	0.216767341			
Sample ID 34	Mean	0.005786268	2.36425948	0.413040727	0.413040727
Sample ID 34	Resample 1 of 3	0.005913266			
Sample ID 34	Resample 2 of 3	0.005804124			
Sample ID 34	Resample 3 of 3	0.005641414			
Sample ID 35	Mean	0.005865873	0.242215887	0.41888842	0.41888842
Sample ID 35	Resample 1 of 3	0.005864286			
Sample ID 35	Resample 2 of 3	0.005880808			
Sample ID 35	Resample 3 of 3	0.005852525			
Sample ID 36	Mean	0.005370503	1.42058897	0.382499099	0.382499099
Sample ID 36	Resample 1 of 3	0.005283673			
Sample ID 36	Resample 2 of 3	0.005426804			
Sample ID 36	Resample 3 of 3	0.005401031			
Sample ID 37	Mean	0.005557143	1.03415918	0.396209449	0.396209449
Sample ID 37	Resample 1 of 3	0.005579592			
Sample ID 37	Resample 2 of 3	0.005491837			
Sample ID 37	Resample 3 of 3	0.0056			
Sample ID 38	Mean	0.005877929	0.965135515	0.419774026	0.419774026
Sample ID 38	Resample 1 of 3	0.005844898			
Sample ID 38	Resample 2 of 3	0.005943434			
Sample ID 38	Resample 3 of 3	0.005845455			
Sample ID 39	Mean	0.005156504	2.33103848	0.366779	0.366779
Sample ID 39	Resample 1 of 3	0.005287879			
Sample ID 39	Resample 2 of 3	0.005129592			
Sample ID 39	Resample 3 of 3	0.005052041			
Sample ID 40	Mean	0.005646236	0.480048925	0.402754128	0.402754128
Sample ID 40	Resample 1 of 3	0.005672727			
Sample ID 40	Resample 2 of 3	0.005618557			
Sample ID 40	Resample 3 of 3	0.005647423			

Sample ID 41	Mean	0.005913777	0.263389826	0.422407389	0.422407389
Sample ID 41	Resample 1 of 3	0.005895876			
Sample ID 41	Resample 2 of 3	0.005924243			
Sample ID 41	Resample 3 of 3	0.005921212			
Sample ID 42	Mean	0.00548928	0.748396218	0.391224384	0.391224384
Sample ID 42	Resample 1 of 3	0.005530612			
Sample ID 42	Resample 2 of 3	0.005488776			
Sample ID 42	Resample 3 of 3	0.005448454			
Sample ID 43	Mean	0.005646393	1.14898157	0.402765661	0.402765661
Sample ID 43	Resample 1 of 3	0.005571717			
Sample ID 43	Resample 2 of 3	0.005688889			
Sample ID 43	Resample 3 of 3	0.005678571			
Sample ID 44	Mean	0.005547454	0.67795676	0.395497739	0.395497739
Sample ID 44	Resample 1 of 3	0.005523711			
Sample ID 44	Resample 2 of 3	0.005527835			
Sample ID 44	Resample 3 of 3	0.005590816			
Sample ID 45	Mean	0.005825036	0.707403898	0.415888608	0.415888608
Sample ID 45	Resample 1 of 3	0.005857143			
Sample ID 45	Resample 2 of 3	0.005839394			
Sample ID 45	Resample 3 of 3	0.005778572			
Sample ID 46	Mean	0.006024819	1.36001837	0.430564433	0.430564433
Sample ID 46	Resample 1 of 3	0.006027835			
Sample ID 46	Resample 2 of 3	0.005941414			
Sample ID 46	Resample 3 of 3	0.006105208			
Sample ID 47	Mean	0.019377302	0.229375288	1.41142237	1.41142237
Sample ID 47	Resample 1 of 3	0.019426804			
Sample ID 47	Resample 2 of 3	0.019364286			
Sample ID 47	Resample 3 of 3	0.019340817			
Sample ID 48	Mean	0.036528561	0.350099891	2.67133403	2.67133403
Sample ID 48	Resample 1 of 3	0.036382653			
Sample ID 48	Resample 2 of 3	0.036621213			
Sample ID 48	Resample 3 of 3	0.036581818			
Sample ID 49	Mean	0.054668881	0.049373101	4.003901	4.003901
Sample ID 49	Resample 1 of 3	0.054689691			
Sample ID 49	Resample 2 of 3	0.054638382			
Sample ID 49	Resample 3 of 3	0.054678571			
Sample ID 50	Mean	0.005862099	1.47599494	0.418611169	0.418611169
Sample ID 50	Resample 1 of 3	0.005929897			
Sample ID 50	Resample 2 of 3	0.005891752			
Sample ID 50	Resample 3 of 3	0.005764646			
Sample ID 51	Mean	0.005979806	1.12161314	0.427257806	0.427257806
Sample ID 51	Resample 1 of 3	0.006048454			
Sample ID 51	Resample 2 of 3	0.005976531			
Sample ID 51	Resample 3 of 3	0.005914433			
Sample ID 52	Mean	0.00601984	1.71364748	0.430198669	0.430198669
Sample ID 52	Resample 1 of 3	0.006012371			
Sample ID 52	Resample 2 of 3	0.005920619			
Sample ID 52	Resample 3 of 3	0.00612653			
Sample ID 53	Mean	0.005660086	1.17032433	0.403771549	0.403771549
Sample ID 53	Resample 1 of 3	0.005736082			
Sample ID 53	Resample 2 of 3	0.005614583			
Sample ID 53	Resample 3 of 3	0.005629592			
Sample ID 54	Mean	0.005523596	1.61733782	0.393745154	0.393745154
Sample ID 54	Resample 1 of 3	0.00562449			
Sample ID 54	Resample 2 of 3	0.005491753			
Sample ID 54	Resample 3 of 3	0.005454545			
Sample ID 55	Mean	0.005764186	2.05688834	0.411418647	0.411418647
Sample ID 55	Resample 1 of 3	0.005631313			
Sample ID 55	Resample 2 of 3	0.005802062			
Sample ID 55	Resample 3 of 3	0.005859184			
Sample ID 56	Mean	0.005532303	2.52052021	0.394384742	0.394384742
Sample ID 56	Resample 1 of 3	0.005658586			
Sample ID 56	Resample 2 of 3	0.00555567			
Sample ID 56	Resample 3 of 3	0.005382653			
Sample ID 57	Mean	0.005776759	0.949791312	0.412342191	0.412342191
Sample ID 57	Resample 1 of 3	0.005763265			
Sample ID 57	Resample 2 of 3	0.005729897			
Sample ID 57	Resample 3 of 3	0.005837114			
Sample ID 58	Mean	0.005924967	0.223416612	0.423229367	0.423229367
Sample ID 58	Resample 1 of 3	0.005916326			
Sample ID 58	Resample 2 of 3	0.005940206			
Sample ID 58	Resample 3 of 3	0.005918367			
Sample ID 59	Mean	0.00562314	1.06688821	0.401057541	0.401057541
Sample ID 59	Resample 1 of 3	0.005554639			
Sample ID 59	Resample 2 of 3	0.005666327			
Sample ID 59	Resample 3 of 3	0.005648454			
Sample ID 60	Mean	0.005849754	1.17036223	0.417704374	0.417704374
Sample ID 60	Resample 1 of 3	0.0058			
Sample ID 60	Resample 2 of 3	0.005821429			
Sample ID 60	Resample 3 of 3	0.005927835			

Sample ID 61	Mean	0.005986054	0.82852149	0.427716821	0.427716821
Sample ID 61	Resample 1 of 3	0.006033673			
Sample ID 61	Resample 2 of 3	0.005989796			
Sample ID 61	Resample 3 of 3	0.005934694			
Sample ID 62	Mean	0.005800571	0.658671021	0.414091438	0.414091438
Sample ID 62	Resample 1 of 3	0.005809278			
Sample ID 62	Resample 2 of 3	0.005758763			
Sample ID 62	Resample 3 of 3	0.005833673			
Sample ID 63	Mean	0.005945718	0.298965186	0.424753785	0.424753785
Sample ID 63	Resample 1 of 3	0.005930612			
Sample ID 63	Resample 2 of 3	0.005965306			
Sample ID 63	Resample 3 of 3	0.005941237			
Sample ID 64	Mean	0.005940097	1.04661572	0.424340874	0.424340874
Sample ID 64	Resample 1 of 3	0.005922449			
Sample ID 64	Resample 2 of 3	0.00588866			
Sample ID 64	Resample 3 of 3	0.006009184			
Sample ID 65	Mean	0.005869479	0.817604542	0.419153303	0.419153303
Sample ID 65	Resample 1 of 3	0.005860204			
Sample ID 65	Resample 2 of 3	0.005921429			
Sample ID 65	Resample 3 of 3	0.005826804			
Sample ID 66	Mean	0.005933565	0.48666656	0.423860967	0.423860967
Sample ID 66	Resample 1 of 3	0.005932653			
Sample ID 66	Resample 2 of 3	0.005962886			
Sample ID 66	Resample 3 of 3	0.005905155			
Sample ID 67	Mean	0.005945188	0.994969487	0.424714863	0.424714863
Sample ID 67	Resample 1 of 3	0.005879382			
Sample ID 67	Resample 2 of 3	0.005962245			
Sample ID 67	Resample 3 of 3	0.005993939			
Sample ID 68	Mean	0.005938453	1.12403905	0.424220055	0.424220055
Sample ID 68	Resample 1 of 3	0.00589495			
Sample ID 68	Resample 2 of 3	0.006015306			
Sample ID 68	Resample 3 of 3	0.005905102			
Sample ID 69	Mean	0.005782804	2.02712774	0.412786275	0.412786275
Sample ID 69	Resample 1 of 3	0.005774227			
Sample ID 69	Resample 2 of 3	0.005670103			
Sample ID 69	Resample 3 of 3	0.005904082			
Sample ID 70	Mean	0.005749432	1.63398826	0.410334796	0.410334796
Sample ID 70	Resample 1 of 3	0.00585567			
Sample ID 70	Resample 2 of 3	0.005715306			
Sample ID 70	Resample 3 of 3	0.00567732			
Sample ID 71	Mean	0.005920275	1.2744416	0.422884703	0.422884703
Sample ID 71	Resample 1 of 3	0.005860825			
Sample ID 71	Resample 2 of 3	0.005894845			
Sample ID 71	Resample 3 of 3	0.006005154			
Sample ID 72	Mean	0.005985437	0.5353508	0.427671462	0.427671462
Sample ID 72	Resample 1 of 3	0.006012371			
Sample ID 72	Resample 2 of 3	0.005993939			
Sample ID 72	Resample 3 of 3	0.00595			
Sample ID 73	Mean	0.005790676	0.40606156	0.413364589	0.413364589
Sample ID 73	Resample 1 of 3	0.005768687			
Sample ID 73	Resample 2 of 3	0.005815464			
Sample ID 73	Resample 3 of 3	0.005787879			
Sample ID 74	Mean	0.005782266	0.993784308	0.412746757	0.412746757
Sample ID 74	Resample 1 of 3	0.005720619			
Sample ID 74	Resample 2 of 3	0.005834343			
Sample ID 74	Resample 3 of 3	0.005791837			
Sample ID 75	Mean	0.00665771	4.57344866	0.477055877	0.477055877
Sample ID 75	Resample 1 of 3	0.006827551			
Sample ID 75	Resample 2 of 3	0.006839394			
Sample ID 75	Resample 3 of 3	0.006306185			
Sample ID 76	Mean	0.007306013	12.1319113	0.524679482	0.524679482
Sample ID 76	Resample 1 of 3	0.0076875			
Sample ID 76	Resample 2 of 3	0.007937755			
Sample ID 76	Resample 3 of 3	0.006292784			
Sample ID 77	Mean	0.005784354	1.02276433	0.41290012	0.41290012
Sample ID 77	Resample 1 of 3	0.005802041			
Sample ID 77	Resample 2 of 3	0.005832653			
Sample ID 77	Resample 3 of 3	0.005718367			
Sample ID 78	Mean	0.005834508	0.468239963	0.416584402	0.416584402
Sample ID 78	Resample 1 of 3	0.005848453			
Sample ID 78	Resample 2 of 3	0.00580303			
Sample ID 78	Resample 3 of 3	0.005852041			
Sample ID 79	Mean	0.005823349	2.17598844	0.41576463	0.41576463
Sample ID 79	Resample 1 of 3	0.005927551			
Sample ID 79	Resample 2 of 3	0.005860204			
Sample ID 79	Resample 3 of 3	0.005682291			
Sample ID 80	Mean	0.005802168	0.81823045	0.41420874	0.41420874
Sample ID 80	Resample 1 of 3	0.005750505			
Sample ID 80	Resample 2 of 3	0.005843877			
Sample ID 80	Resample 3 of 3	0.005812121			

Sample ID 81	Mean	0.00586707	0.753604531	0.418976367	0.418976367
Sample ID 81	Resample 1 of 3	0.005818557			
Sample ID 81	Resample 2 of 3	0.005877551			
Sample ID 81	Resample 3 of 3	0.005905102			
Sample ID 82	Mean	0.005842469	0.422159344	0.417169213	0.417169213
Sample ID 82	Resample 1 of 3	0.005814142			
Sample ID 82	Resample 2 of 3	0.005854082			
Sample ID 82	Resample 3 of 3	0.005859184			
Sample ID 83	Mean	0.006027807	0.811720729	0.430783927	0.430783927
Sample ID 83	Resample 1 of 3	0.005991753			
Sample ID 83	Resample 2 of 3	0.006083505			
Sample ID 83	Resample 3 of 3	0.006008163			
Sample ID 84	Mean	0.006000035	1.3382014	0.428743809	0.428743809
Sample ID 84	Resample 1 of 3	0.006089796			
Sample ID 84	Resample 2 of 3	0.005935051			
Sample ID 84	Resample 3 of 3	0.005975258			
Sample ID 85	Mean	0.005794484	0.27580753	0.413644254	0.413644254
Sample ID 85	Resample 1 of 3	0.005794792			
Sample ID 85	Resample 2 of 3	0.00577835			
Sample ID 85	Resample 3 of 3	0.005810309			
Sample ID 86	Mean	0.0057728	2.00538731	0.41205138	0.41205138
Sample ID 86	Resample 1 of 3	0.005644898			
Sample ID 86	Resample 2 of 3	0.005803093			
Sample ID 86	Resample 3 of 3	0.005870408			
Sample ID 87	Mean	0.005921295	0.323330462	0.422959685	0.422959685
Sample ID 87	Resample 1 of 3	0.005941237			
Sample ID 87	Resample 2 of 3	0.005903061			
Sample ID 87	Resample 3 of 3	0.005919588			
Sample ID 88	Mean	0.006035031	1.11382198	0.431314588	0.431314588
Sample ID 88	Resample 1 of 3	0.006111111			
Sample ID 88	Resample 2 of 3	0.006010309			
Sample ID 88	Resample 3 of 3	0.005983674			
Sample ID 89	Mean	0.006183505	1.88838327	0.442221314	0.442221314
Sample ID 89	Resample 1 of 3	0.006286598			
Sample ID 89	Resample 2 of 3	0.006056701			
Sample ID 89	Resample 3 of 3	0.006207217			
Sample ID 90	Mean	0.006178328	0.658067107	0.441841006	0.441841006
Sample ID 90	Resample 1 of 3	0.006153608			
Sample ID 90	Resample 2 of 3	0.006225253			
Sample ID 90	Resample 3 of 3	0.006156122			
Sample ID 91	Mean	0.006243616	0.354631424	0.446637005	0.446637005
Sample ID 91	Resample 1 of 3	0.006218182			
Sample ID 91	Resample 2 of 3	0.006254082			
Sample ID 91	Resample 3 of 3	0.006258586			
Sample ID 92	Mean	0.006126799	0.470139682	0.438055724	0.438055724
Sample ID 92	Resample 1 of 3	0.006117172			
Sample ID 92	Resample 2 of 3	0.00610404			
Sample ID 92	Resample 3 of 3	0.006159184			
Sample ID 93	Mean	0.005997816	1.30297625	0.428580791	0.428580791
Sample ID 93	Resample 1 of 3	0.005935714			
Sample ID 93	Resample 2 of 3	0.005972165			
Sample ID 93	Resample 3 of 3	0.006085567			
Sample ID 94	Mean	0.005780154	0.66141057	0.412591606	0.412591606
Sample ID 94	Resample 1 of 3	0.005817172			
Sample ID 94	Resample 2 of 3	0.005740816			
Sample ID 94	Resample 3 of 3	0.005782474			
Sample ID 95	Mean	0.006097739	1.04511368	0.435921043	0.435921043
Sample ID 95	Resample 1 of 3	0.006164646			
Sample ID 95	Resample 2 of 3	0.006037755			
Sample ID 95	Resample 3 of 3	0.006090816			
Sample ID 96	Mean	0.006339214	1.97023666	0.453659505	0.453659505
Sample ID 96	Resample 1 of 3	0.006247423			
Sample ID 96	Resample 2 of 3	0.006288776			
Sample ID 96	Resample 3 of 3	0.006481443			
Sample ID 97	Mean	0.006354672	1.04607618	0.454795063	0.454795063
Sample ID 97	Resample 1 of 3	0.006342857			
Sample ID 97	Resample 2 of 3	0.006426263			
Sample ID 97	Resample 3 of 3	0.006294898			
Sample ID 98	Mean	0.006276601	1.14188766	0.449059993	0.449059993
Sample ID 98	Resample 1 of 3	0.006314433			
Sample ID 98	Resample 2 of 3	0.00619394			
Sample ID 98	Resample 3 of 3	0.006321428			
Sample ID 99	Mean	0.006655235	1.01765978	0.476874083	0.476874083
Sample ID 99	Resample 1 of 3	0.00672653			
Sample ID 99	Resample 2 of 3	0.006591753			
Sample ID 99	Resample 3 of 3	0.006647423			
Sample ID 100	Mean	0.0065052	0.552144647	0.465852618	0.465852618
Sample ID 100	Resample 1 of 3	0.0065			
Sample ID 100	Resample 2 of 3	0.006543434			
Sample ID 100	Resample 3 of 3	0.006472165			

Table B3: Total chromium concentration from diluted sample for 5306 ppm solution in red soil.

# of sample from soil	# of dilluted sample	Dillution factor	Total Cr (mg/l)		
2	16	1	33.1225	3312.25	3312.25
9	1	1	11.0791	1107.91	1100
	2	2	28.5089	1425.445	
	3	3	38.3505	1278.35	
16	4	1	4.3207	432.07	332.6
	5	2	11.0757	553.785	
	6	3	19.2623	642.0767	
23	7	1	2.2805	228.05	213.6
	8	2	4.555	227.75	
	9	3	7.4865	249.55	
30	10	1	0.8789	87.89	91.14
	11	2	1.5162	75.81	
	12	3	2.3092	76.97333	
37	13	1	0.3721	37.21	45.12
	14	2	0.5456	27.28	
	15	3	0.6113	20.37667	

Table B4: Total chromium concentration from diluted sample for 5306 ppm solution in black soil.

# of sample from soil	# of dilluted sample	Dillution factor	Total Cr (mg/l)		
4	17	1	19.308	1930.8	1898
	18	2	39.2545	1962.725	
11	19	1	0.344	34.4	52.02
	20	2	0.3356	16.78	
18	21	1	0.3023	30.23	44.43
	22	2	0.3206	16.03	
25	23	1	0.3107	31.07	39.43
	24	2	0.324	16.2	
	25	3	0.3326	11.08667	
32	26	1	0.3438	34.38	43.76
	27	2	0.341	17.05	
	28	3	0.3491	11.63667	
39	29	1	0.3523	35.23	45.02
	30	2	0.3526	17.63	
	31	3	0.3523	11.74333	

Table B5: Total chromium concentration from diluted sample for 2653 ppm solution in red soil.

# of sample from soil	# of dilluted sample	Dillution factor	Total Cr (mg/l)		
1				1277	1277
8	47	1	1.4114	141.14	143.7
	48	2	2.6713	133.565	
	49	3	4.0039	133.4633	
15	50	1	0.4186	41.86	53.37
	51	2	0.4273	21.365	
	52	3	0.4302	14.34	
22	53	1	0.4038	40.38	51.25
	54	2	0.3937	19.685	
	55	3	0.4114	13.71333	
29	56	1	0.3944	39.44	50.05
	57	2	0.4123	20.615	
	58	3	0.4232	14.10667	
36	59	1	0.4011	40.11	50.9
	60	2	0.4177	20.885	
	61	3	0.4277	14.25667	

Table B6: Total chromium concentration from diluted sample for 2653 ppm solution in black soil.

# of sample from soil	# of dilluted sample	Dillution factor	Total Cr (mg/l)		
3				724	724
10	62	1	0.4141	41.41	61.58
	63	2	0.4248	21.24	
17	64	1	0.4243	42.43	63.9
	65	2	0.4192	20.96	
24	66	1	0.4239	42.39	63.54
	67	2	0.4247	21.235	
31	68	1	0.4242	42.42	54.32
	69	2	0.4128	20.64	
	70	3	0.4103	13.67667	
38	71	1	0.4229	42.29	54.32
	72	2	0.4277	21.385	
	73	3	0.4134	13.78	

Table B7: Total chromium concentration from diluted sample for 1061 ppm solution in red soil.

# of sample from soil	# of dilluted sample	Dillution factor	Total Cr (mg/l)		
6	74	1	0.4127	41.27	51.31
	75	2	0.4771	23.855	
	76	3	0.5247	17.49	
13	77	1	0.4129	41.29	52.75
	78	2	0.4166	20.83	
	79	3	0.4158	13.86	
20	80	1	0.4142	41.42	52.8
		2	0.4165	20.825	
	81	3	0.419	13.96667	
27	82	1	0.4172	41.72	53.28
	83	2	0.4308	21.54	
	84	3	0.4287	14.29	
34	85	1	0.4136	41.36	52.61
	86	2	0.4121	20.605	
	87	3	0.423	14.1	

Table B8: Total chromium concentration from diluted sample for 1061 ppm solution in black soil.

# of sample from soil	# of dilluted sample	Dillution factor	Total Cr (mg/l)		
7	88	1	0.4313	43.13	55.05
	89	2	0.4422	22.11	
	90	3	0.4418	14.72667	
14	91	1	0.4466	44.66	57.15
	92	2	0.4281	21.405	
	93	3	0.4286	14.28667	
21	94	1	0.4126	41.26	52.19
	95	2	0.4359	21.795	
	96	3	0.4537	15.12333	
28	97	1	0.4548	45.48	57.52
	98	2	0.4491	22.455	
	99	3	0.4769	15.89667	
35	100	1	0.4559	45.59	45.59

Appendix C: XRF reports for soil samples.

Table C1: XRF results for fresh red soil (B_{1i})

Sample Information

Sample ID	B1i
Runtime	00:08:31
Experiment name	SMART-Elements
Application	SMART-Elements
Measurement Started	1/24/2020 10:33 AM
R/R0	13

Compound Overview

Compound	Line Name	Concentration	Stat Error(%)
Manganese	Mn KA1	4313 PPM	0.00181
Vanadium	V KA1	671 PPM	0.00035
Titanium	Ti KA1	2.283 %	0.00561
Iron	Fe KA1	28.507 %	0.0157
Yttrium	Y KA1	258 PPM	0.00010
Nickel	Ni KA1	681 PPM	0.00049
Bromine	Br KA1	25 PPM	0.00002
Strontium	Sr KA1	509 PPM	0.00019
Lead	Pb LA1	56 PPM	0.00005
Chlorine	Cl KA1	2459 PPM	0.00153
Rubidium	Rb KA1	498 PPM	0.00019
Potassium	K KA1	1.672 %	0.00517
Phosphorus	P KA1	4992 PPM	0.00303
Chromium	Cr KA1	802 PPM	0.00050
Scandium	Sc KA1	13 PPM	0.00001
Sulfur	S KA1	2078 PPM	0.00173
Zirconium	Zr KA1	2819 PPM	0.00061
Niobium	Nb KA1	235 PPM	0.00009
Aluminum	Al KA1	17.766 %	0.0511
Calcium	Ca KA1	6.631 %	0.0103
Zinc	Zn KA1	1052 PPM	0.00070
Silicon	Si KA1	38.720 %	0.0437
Magnesium	Mg KA1	2.276 %	0.0269

Table C2: XRF results for chromium saturated red soil (B_{1f})

Sample Information

Sample ID	B1f
Runtime	00:09:21
Experiment name	SMART-Elements
Application	SMART-Elements
Measurement Started	1/24/2020 10:17 AM
R/R0	9

Compound Overview

Compound	Line Name	Concentration	Stat Error(%)
Manganese	Mn KA1	3803 PPM	0.00119
Vanadium	V KA1	632 PPM	0.00034
Titanium	Ti KA1	1.923 %	0.00498
Iron	Fe KA1	20.655 %	0.0129
Yttrium	Y KA1	161 PPM	0.00006
Nickel	Ni KA1	460 PPM	0.00034
Bromine	Br KA1	13 PPM	0.00001
Strontium	Sr KA1	296 PPM	0.00011
Chlorine	Cl KA1	1700 PPM	0.00108
Rubidium	Rb KA1	285 PPM	0.00011
Potassium	K KA1	1.523 %	0.00477
Phosphorus	P KA1	5058 PPM	0.00283
Chromium	Cr KA1	4.560 %	0.00607
Scandium	Sc KA1	19 PPM	0.00001
Sulfur	S KA1	6.431 %	0.0116
Zirconium	Zr KA1	1640 PPM	0.00037
Aluminum	Al KA1	16.689 %	0.0453
Calcium	Ca KA1	8.309 %	0.0111
Zinc	Zn KA1	658 PPM	0.00046
Silicon	Si KA1	36.464 %	0.0391
Arsenic	As KA1	44 PPM	0.00004
Magnesium	Mg KA1	1.970 %	0.0220

Table C3: XRF results for fresh black soil (B_{2i})

Sample Information

Sample ID	B2i
Runtime	00:08:47
Experiment name	SMART-Elements
Application	SMART-Elements
Measurement Started	1/24/2020 10:25 AM
R/R0	5

Compound Overview

Compound	Line Name	Concentration	Stat Error(%)
Manganese	Mn KA1	3740 PPM	0.00153
Vanadium	V KA1	370 PPM	0.00020
Titanium	Ti KA1	1.952 %	0.00493
Iron	Fe KA1	15.268 %	0.0100
Yttrium	Y KA1	108 PPM	0.00004
Bromine	Br KA1	22 PPM	0.00002
Strontium	Sr KA1	646 PPM	0.00019
Chlorine	Cl KA1	4205 PPM	0.00193
Rubidium	Rb KA1	190 PPM	0.00007
Potassium	K KA1	3.637 %	0.00761
Phosphorus	P KA1	4661 PPM	0.00258
Chromium	Cr KA1	410 PPM	0.00026
Scandium	Sc KA1	170 PPM	0.00006
Sulfur	S KA1	2140 PPM	0.00156
Zirconium	Zr KA1	2023 PPM	0.00040
Niobium	Nb KA1	133 PPM	0.00005
Aluminum	Al KA1	13.293 %	0.0371
Calcium	Ca KA1	11.317 %	0.0127
Zinc	Zn KA1	431 PPM	0.00032
Silicon	Si KA1	48.903 %	0.0414
Magnesium	Mg KA1	3.705 %	0.0311

Table C4: XRF results for chromium saturated black soil (B_{2f})

Sample Information

Sample ID	B2f
Runtime	00:09:20
Experiment name	SMART-Elements
Application	SMART-Elements
Measurement Started	1/28/2020 5:07 PM
R/R0	5

Compound Overview

Compound	Line Name	Concentration	Stat Error(%)
Manganese	Mn KA1	3642 PPM	0.00128
Vanadium	V KA1	392 PPM	0.00023
Titanium	Ti KA1	1.826 %	0.00492
Iron	Fe KA1	14.552 %	0.0104
Yttrium	Y KA1	125 PPM	0.00005
Strontium	Sr KA1	585 PPM	0.00018
Chlorine	Cl KA1	2529 PPM	0.00139
Rubidium	Rb KA1	169 PPM	0.00007
Potassium	K KA1	3.381 %	0.00756
Phosphorus	P KA1	5042 PPM	0.00288
Chromium	Cr KA1	2.486 %	0.00443
Scandium	Sc KA1	135 PPM	0.00005
Sulfur	S KA1	1.615 %	0.00556
Zirconium	Zr KA1	1900 PPM	0.00039
Aluminum	Al KA1	13.754 %	0.0390
Calcium	Ca KA1	11.360 %	0.0131
Zinc	Zn KA1	390 PPM	0.00031
Silicon	Si KA1	45.865 %	0.0416
Magnesium	Mg KA1	3.671 %	0.0317

جامعة النجاح الوطنية

كلية الدراسات العليا

إمكانية أكسدة الكروم ثلاثي التكافؤ إلى كروم سداسي التكافؤ في مياه الدباغة

إعداد

بيان بشارات

إشراف

أ.د. عامر الهموز

د. عبد الرحيم أبو الصفا

قدمت هذه الأطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في هندسة المياه والبيئة بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.

2021

إمكانية أكسدة الكروم ثلاثي التكافؤ إلى كروم سداسي التكافؤ في مياه الدباغة

إعداد

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إشراف

أ.د. عامر الهموز

د. عبد الرحيم أبو الصفا

الملخص

دباغة الجلود من أهم الصناعات الفلسطينية التي تعتمد على استخدام الكيماويات، وأهم مادة هي الكروم بسبب إمكانية تحويل الكروم ثلاثي التكافؤ إلى سداسي التكافؤ الأكثر سمّية مما يؤثر سلبًا على البيئة.

هناك جدل حول عملية التحول؛ لذلك يهدف هذا البحث إلى دراسة إمكانية تأكسد الكروم ثلاثي التكافؤ إلى الكروم سداسي التكافؤ في التربة في ظل الظروف الطبيعية.

تم تقسيم البحث إلى ثلاثة أجزاء باستخدام نوعين من التربة الحمراء والسوداء ومحلول كبريتات الكروم بتراكيز 5306،2653،1061 جزء في المليون. تم عمل الجزء الأول لتحليل التربة الأصلية والمشبعة بالكروم باستخدام تقنيات الأشعة السينية لفحص تركيز المكونات الكيميائية وخاصة الكروم الكلي والعناصر أو الأكاسيد التي تؤثر على عملية امتصاص الكروم على التربة ، مثل أكسيد المنغنيز، الحديد والكبريت. أظهرت النتائج تركيزًا عاليًا للكروم الكلي في التربة. تم معرفة اسم التربة بواسطة مثلث التربة بناءً على حجم الجسيمات من خلال النسبة المئوية للرمل والطين والطمي في عينة التربة التي تم حسابها عن طريق تحليل مقياس كثافة السوائل.

الجزء الثاني تم تحضير محاليل الكروم بتراكيز مختلفة من الكروم والتي تعرضت لنوعين من التربة، الأحمر (الطين) والأسود (الطمي). تم اختبار تركيز الكروم الكلي في المياه كمؤشر على قدرة امتصاص التربة للكروم. أظهرت النتائج أن التربة السوداء لديها قدرة أعلى على امتصاص الكروم الكلي من الطين الأحمر عند نفس التركيز. كانت السعة القصوى للامتصاص مع مرور

الوقت في التربة السوداء لمحلول الكروم بتركيز أولي 5306،2653،1061 جزء في المليون يساوي 1402 ، 7 ، 208 مغم / غم بالترتيب.

أما بالنسبة للتربة الحمراء فقد وجد أن أقصى قدرةعلى الامتصاص كانت1012 ،606 ، 207 مجم / جم على التوالي. الجزء الثالث تم فحص وجود الكروم سداسي التكافؤ. أظهرت النتائج زيادة تركيزه في التربة الحمراء. بينما في التربة السوداء انخفض التركيز ولكن النتائج لم يكن لها اتجاه واضح حيث كان التركيز متذبذبا لذلك فأن الكروم السداسي لا يلعب دورا ملحوظا بالتأثير السلبي على البيئة تبعا لعامل واحد ولا يمكن الجزم بعد بمدى تأثيره الا بدراسة عدة عوامل مجتمعة . يمكن استكمال منهجية البحث نفسها بدراسة عوامل أخرى مثل تأثير الأس الهيدروجيني واستخدام المزيد من التربة ذات الخصائص والجرعات المختلفة.