

**TECHNOLOGICAL VIABILITY OF COFFEE HUSK ASH, SOIL  
RICH IN KAOLINITE-FERRINATRITE AND KAOLINITE-  
GEOHITE FOR THE ADSORPTIVE REMOVAL OF  
CHROMIUM (VI) FROM INDUSTRIAL WASTEWATER**

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Submitted in fulfilment of the requirements  
for the degree of Doctor of Philosophy in Engineering

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December, 2017

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## DECLARATION

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## ABSTRACT

Most industries in developing countries discharge a high amount of untreated wastewater, containing toxic chemicals, into nearby water bodies. Heavy metals and chemicals above permissible levels can be emitted to the environment as wastewater effluents from industries such as leather, electroplating, tanning, metal, fertilizer, and other industries. When these are discharged into the environment, they significantly pollute the quality of the water bodies and the environment, thereby substantially affecting river and human health. The safe and effective purification of polluted water containing heavy metals is always a challenge in many parts of the world, because cost-effective treatments are not readily available. Various methods are used for removing heavy metals, such as irradiation, chemical precipitation, ion exchange, adsorption, biological and chemical treatment. However, the adsorption technique is the best option due to easy to operate, simple, cheap, efficient, and suitable for the environment. The adsorption method is a suitable technique for developing countries like Ethiopia, where the advanced wastewater treatment technologies for high amount of toxic industrial wastewater are unaffordable. Locally-available adsorbent materials reasonably meet the criteria that have been established for the wastewater treatment process, due to their natural availability as adsorbents, their high natural porosity, their very low price, easy design, operation and maintenance, as well as their suitability for pollutant adsorption. The applicability of low-cost, locally-available adsorbent materials for the adsorptive removal of heavy metals from industrial wastewater is important.

This study investigated the technological viability of low-cost materials, such as coffee husk ash, soil that is rich in kaolinite (40.4%) and ferrinatriite (59.6%), and soil that is rich in kaolinite (29.4%) and goethite (70.6%), for the adsorptive removal of chromium from industrial wastewater. The physical properties and elemental composition of the three adsorbents (soil rich in kaolinite-ferrinatriite, coffee husk ash and kaolinite-goethite) were characterized. The experiments were conducted under batch adsorption set-ups to assess the effect of different parameters and their optimum removal efficiency. The optimum adsorption of Cr(VI) on the three adsorbents used were observed at 40 minutes and two pH values and their doses of adsorbent, shaker speed, and initial Cr (VI) ion concentration were different in the batch

adsorption experiments. The adsorption of Cr(VI) followed pseudo second-order kinetics, with a coefficient of determination  $r^2 > 0.99$  for the three-adsorbent media. Results of the adsorption isotherm show that Freundlich adsorption isotherm model better described Cr(VI) adsorption into soil rich in kaolinite-ferrinatriite (SRKF), soil rich in kaolinite-goethite (SRKG) and coffee husk ash (CHA) with coefficients of determination;  $r^2 > 0.93$ . The adsorption capacity of the adsorbent followed the decreasing order  $CHA > SRKF > SRKG$ . The findings on the adsorption characteristics of batch system from this work suggests that soil rich in kaolinite-ferrinatriite, coffee husk ash and soil rich in kaolinite-goethite could represent an interesting low-cost naturally available adsorbent material that could be used for the chromium (VI) removal from wastewater. The empirical data and models developed in the study were used to establish theoretical design analysis of adsorptive treatment plant for industry emits such wastewater. However, further investigations will be required for the practical application of these locally-available adsorbent materials for the removal of chromium from wastewater.

**Keywords:** *Adsorption; batch; chromium (VI); coffee husk ash; heavy metal removal; isotherm kinetics; low-cost adsorbents; pollution; removal; soil rich in kaolinite-ferrinatriite; soil rich in kaolinite-goethite; wastewater treatment.*

## **ACKNOWLEDGMENTS**

In Jesus' Name, I thank GOD for giving me the patience and strength to complete this research, after several months of hard work in the laboratory. I thank God for giving me this great opportunity to work under the supervision of Prof. Tilahun Seyoum Workneh, Prof. Christina Trois and Dr. Fekadu Fufa Feyessa for accepting me as their student and for their scientific guidance and valuable discussions. Their constructive criticism and optimism have always been a great source of inspiration for me and their confidence in me has been very stimulating. Their concern for, as well as their support in my personal matters, is very much appreciated.

I am deeply grateful to my beloved wife, Abebech Kasahun, who continuously encouraged and prayed to God about me and our children (Kal, Kidist and Mintesinot) over all these years. I thank my parents and family (mother, father, sisters, and a brother) who have always prayed for me. I would also like to thank all those, especially Dr. Tsion Tesfaye Kidane and Getachew Neme Tolesa, who encouraged me and assisted me with the completion of this Thesis.

I also thank the Ministry of Education of Ethiopia, the Federal Democratic Republic Government and the Jimma University Institute of Technology, for their financial support, as well as the University of KwaZulu-Natal for the facilitation of my studies.

## DEDICATION

**To:**

*My beloved wife, Abebech Kasahun and our kids (Kal, Kidist and Mintu)*

*My Dear Mother W/ro Worke Debebe and father Ato Asmelash Samuel*

## PREFACE

This Thesis begins with the introduction. Chapter Two is the literature review on the challenges of wastewater discharge and the techniques for treatment discussed that are important for this study. The following chapters (Chapter Three, Four, Five and Six) cover the analysis of the efficiency of the chromium (VI) ion adsorption, using three adsorbents, namely soil rich in kaolinite-ferrinatriite, soil rich in kaolinite-goethite and coffee husk ash in a batch adsorptive experiment. Finally, Chapter Seven and Eight discuss the theoretical design process, conclude with the results of this study, and give perspectives for the further study.

The work reported in this Thesis, together with the two manuscripts accepted, one under review as well as one recently submitted, and four papers, were presented at the International Conference for evaluation for the degree of Doctorate in Philosophy (PhD) in Engineering at the University of KwaZulu-Natal (UKZN), College of Agriculture, Engineering and Science, School of Engineering, Pietermaritzburg, South Africa. The manuscript and the material presented in this Thesis describe a serious scientific investigation into the suitability of coffee husk ash, soil rich in kaolinite (40.4%)-ferrinatriite (59.6%) and soil rich in kaolinite (29.4%)-goethite (70.6%) in relation to industrial wastewater treatment. In the less-developed world, where highly sophisticated purification treatment plants are not affordable, due to this the conversion of conventional adsorbents to locally-available, easy-to-use and low-cost soil and coffee media would significantly improve the performance of industrial wastewater treatment units.

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## LIST OF CONTRIBUTIONS

### A. The following research papers are in journals:

1. Z.A. Samuel, T.S. Workneh, C. Trois and F.F. Feyessa (2017), Removal of Cr(VI) from contaminated water using soil rich in kaolinite-ferrinatriite, coffee husk ash and soil rich in kaolinite-goethite: Characteristic, isotherm, and kinetic study. *Desalination and Water Treatment Journal* (accepted and in press, doi:10.5004/dwt.2018.21785, DWT 21785)
2. Z.A. Samuel, T.S. Workneh, C. Trois and F.F. Feyessa (2017), Technical viability of coffee husk ash for adsorptive removal of Cr (VI) from industrial wastewater discharge, *Journal of Central South University* (accepted, with a manuscript ID, JCSU-1710-1100)
3. Z.A. Samuel, T.S. Workneh, C. Trois and F.F. Feyessa (2017), Applicability of soil rich in kaolinite-ferrinatriite for adsorptive removal of Cr (VI) from contaminated water, *Global Nest Journal* (under review, with a manuscript ID, gnest\_02218)
4. Z.A. Samuel, T.S. Workneh, C. Trois, F.F. Feyessa (2017), Practical applicability of Chromium (VI) removal from contaminated water by using soil rich in kaolinite-goethite: Kinetic and equilibrium studies, *Heliyon*, (submitted)

### B. The following research paper presentations/ papers in international conference proceedings:

1. Z.A. Samuel, T.S. Workneh, C. Trois and F.F. Feyessa (2016), Challenges of wastewater discharge and techniques for treatment: a review, *Sixth International Conference on Industrial Engineering and Operations Management (IEOM)*, Kuala Lumpur, Malaysia, March 8 – 10, 2016; pp 63-64, info@ieomsociety.net;www.ieomsociety.org/ieom2016/
2. Z.A. Samuel, T.S. Workneh, C. Trois and F.F. Feyessa (2017), Technical viability of kaolinite-goethite soil for chromium (VI) removal from contaminated water, *Seventh International Conference on Industrial Engineering and Operations Management (IEOM)*, Rabat, Morocco, April 11-13, 2017; pp 60, info@ieomsociety.org; www.ieomsociety.org/ieom2017/

3. Z.A. Samuel, T.S. Workneh, C. Trois and F.F. Feyessa (2017), Technical viability of coffee husk ash for adsorptive removal of Cr (VI) from industrial wastewater discharge. The 8th Annual Research Conference, Strengthening University-Community Linkage: A National Framework for Research and Technology Transfer, Jimma University, Jimma, Ethiopia, April 27-28, 2017.
4. Z.A. Samuel, T.S. Workneh, C. Trois and F.F. Feyessa (2017). Applicability of soil rich in kaolinite-ferrinatriite for adsorptive removal of Cr (VI) from contaminated water. The role of water technology innovation in the blue economy 4<sup>th</sup> Water Research Conference Waterloo, Ontario, Canada, September 10-13, 2017.

# 1. INTRODUCTION

Agricultural Development Led Industrializations (ADLI) is the basic road map for Ethiopian development (GTP-MoFED, 2010; FDRE-CRGE, 2011). Thus far, industrial development is being realized in the leather industry and other agriculturally-based processing industries, such as beverages and food, textiles and the sugar industry. During the future implementation of the Growth and Transformation Plan important strategies (GTP-MoFED, 2010; FDRE-CRGE, 2011) will be enacted to promote environmentally-sustainable, agriculturally-based processing industries. Others industries, such as the chemical, textile, leather, cement, pharmacological and metal industries, are also rapidly growing. Continued population growth and rapid industrialization are found to be the cause of wastewater discharge into the environment, affecting the environment, human health and compromising the life of future generations (Lin et al., 2018).

In the capital city, Addis Ababa, an estimated annual volume of 49 million m<sup>3</sup> total wastewater is discharged, of which about 4 million m<sup>3</sup> is industrial wastewater, with only 4% of the wastewater being treated and re-used (Qadir et al., 2010; van Rooijen et al., 2010; Krishna, 2011). The techniques that are currently being implemented in Ethiopia are conventional treatment methods. However, these conventional treatment processes require large investments, making their application unaffordable for developing countries, like Ethiopia (Mandal, 2014). The liquid waste discharged from industries contains heavy metals that are toxic to living organisms (Barakat, 2011; Panda et al., 2017), necessitating the search for the development of appropriate and applicable wastewater treatment technologies (Deepali and Gangwar, 2010). The present challenge is how to effectively treat increasing volumes of industrial wastewater before it is released into the water bodies or environment, and by so doing, how to prevent the associated environmental and health problems. Unfortunately, like other developing countries, Ethiopia cannot afford to use advanced treatment technologies to deal with toxic industrial wastewater, therefore, it is crucial to explore low-cost locally available materials. Bearing this in mind, the following adsorbent materials, namely, soil rich in kaolinite-ferrinatriite, coffee husk ash and kaolinite-goethite, were investigated for the adsorptive removal of hexavalent chromium (Cr (VI)) ions from industrial discharge.

The following research questions were investigated:

- (a) Is it possible to prepare and characterized three adsorbents locally found in Ethiopia?

- (b) Could evaluate the suitability of three adsorbents for adsorptive removal of Cr (VI) from wastewater?
- (c) Will the adsorbent media be practically applicable for the effective treatment of industrial wastewater under a batch adsorption technique?
- (d) Can it be concluded that adsorption efficiencies of the soil rich in kaolinite-ferrinatriite, coffee husk ash and soil rich in kaolinite-goethite media vary under batch adsorption setups?

The main aim of this research was to assess the technological viability and efficiency of adsorbents such as soil rich in kaolinite-ferrinatriite, coffee husk ash and soil rich in kaolinite-goethite for the adsorptive removal of chromium (VI) from industrial wastewater under batch adsorptive experimental design. Firstly, the adsorbents media (*i.e.* soil rich in kaolinite-ferrinatriite, coffee husk ash and soil rich in kaolinite-goethite) were characterised and the chemical, SEM, TEM, electrical conductivity, cation exchange capacity, total nitrogen, organic carbon, organic matter and pH were analysed. The adsorptive experiment investigated were the effects of the shaker speed, the duration of contact time, the amount of the adsorbent, the pH, the initial concentration of ions and other effects, and the optimum values of these parameters were reported. Finally, the development of a low-cost (soil rich in kaolinite-ferrinatriite, coffee husk ash and soil rich in kaolinite-goethite) adsorptive technology for sustainable wastewater treatment were recommended.

The research methodology involved collecting soil rich in kaolinite-ferrinatriite, kaolinite-goethite and coffee husks from the site and analysing their physicochemical properties. A series of batch by batch analyses were conducted for the adsorption experiment to determine the adsorptive removal capacity and isotherm of Cr(VI) ions characterization from an aqueous solution and actual industrial wastewater. The SRKF, CHA and SRKG were used for the experiments. The experimental result was determined using the UV-Visible spectrophotometer at 540 nm. The statistical data were analysed by using OriginPro-8 software.

The outline of this thesis/dissertation contains the Chapter One and Chapter Two that is relevant to the low cost, locally-available adsorbents in the treatment of wastewater that contains toxic heavy

metals, like chromium and others. This is presented in the Chapter Two. This chapter gives a detailed analysis of the current status of wastewater treatment technologies and the volume of wastewater discharge into the environment, as well as an outline of the requirements for further research. The next four chapters (Chapter Three, Four, Five and Six) appear in the form of four manuscripts, each containing an abstract, an introduction, the experimental procedure, the materials, and methods results as well as discussion, conclusion and references. Finally, the theoretical design and conclusions as well as recommendation of the research study appear in Chapter Seven and Eight.

## 2. CHALLENGES OF WASTEWATER DISCHARGE AND TECHNIQUES FOR TREATMENT: A REVIEW

### 2.1 Abstract

The aim of this study was to assess the efficiency and the practical applicability of locally abundant low-cost adsorbents for the adsorptive removal of heavy metals from industrial wastewater. Most industries, in less developing countries, such as the electroplating, textile, fertilizer, battery, leather, and other industries, discharge huge volumes of untreated wastewater into the local water bodies. The industrial wastewater may contain toxic chemicals above the threshold level, which, when released into the environment, particularly into the aqueous environment, significantly degrade the quality of the water, thereby affecting the sustainability of river health and, subsequently, human health. There are several techniques for removing toxic chemicals such as ion exchange, membrane filtration, adsorption, irradiation, chemical and biological treatments. However, the adsorption method is believed to be the best option because it is cost-effective, simple, and easy to operate, and is efficient and environmental friendly. Accordingly, this method is a preferable option for developing countries like Ethiopia, where advanced treatment technologies for high volumes of toxic industrial wastewater are unaffordable. This review of literature deals with wastewater composition and the applicability of low-cost adsorption techniques for the removal of heavy metals. The current status of the challenges surrounding wastewater generation and discharge are also discussed.

**Keywords:** *Adsorption; Chromium (VI); Heavy metal removal; Low-cost adsorbents; Wastewater treatment*

### 2.2 Introduction

The sustainability of the environment has become a critical global issue (Dişli, 2010) and the protection of fresh water bodies from various contaminants has become a major challenge facing the planet (Chaturvedi and Sahu, 2014; Panda et al., 2017). According to five various indicators, such as environmental impact, use, capacity, access and resources, national values for the water poverty index figure indicated that Ethiopia is the third lowest country in of the world (Lawrence

et al., 2002). Among the major causes of environmental pollution is the discharge of untreated industrial wastewater containing toxic chemicals such as heavy metals (Kulkarni and Kaware, 2014; Park et al., 2010). The direct industrial wastewater discharge into rivers is a communal practice, particularly in less developed countries like Ethiopia, where no stringent environmental regulations have been enacted according similar reporting of (Asfaw, 2007; Belay and Sahile, 2013; Mekuyie, 2014; Padanilly et al., 2008; Tong, 2012; Wosnie and Wondie, 2014; Zinabu, 2011; Kan et al., 2017). The release of toxic chemicals from industrial wastewater into the environment degrades water quality and is hazardous for human beings, as well as, other living organisms such as aquatic life (Ahluwalia and Goyal, 2007; Lin et al., 2018).

Toxic chemicals in the industrial wastewater is a main concern for the environment, because it is rich in copper (Cu), chromium (Cr), cadmium (Cd), zinc (Zn), nickel (Ni), arsenic (As), lead (Pb), and mercury (Hg) (Bhattacharyya and Gupta, 2008; Naiya et al., 2009; Panda et al., 2017; Zwain et al., 2014). Population growth, an increase in development and the expansion of investment in the industrial sector have contributed to the rising demand for industrial products. This expansion and development of various types of industries can result in generating huge volumes of wastewater along with complex toxic chemical compositions which demand advanced technological treatment techniques (Corcoran, 2010; Keng et al., 2013; Zwain et al., 2014). Subsequently, most industries in developing countries produce huge volumes of raw wastewater effluent in rivers and streams, causing environmental and health damage to the local population.

As a result of industrialization and urbanization, the volume of wastewater generated from the Ethiopian industrial sector has increased rapidly. From 1980 to 1990, the toxic load discharged per unit of industrial output increased by 1.8, which was about 1.3 times higher than sub-Saharan African countries such as Swaziland, Seychelles, and others (Sato et al., 2013; Tegegn, 2014; UNIDO, 2001). The investment inflow for establishing industries in Ethiopia is increasing; for example, the contribution to the Gross Domestic Product (GDP) from industry is expected to increase to 19.1% at the end of the Growth and Transformation Plan (GTP) 2014/15, from 8.1% in 2004/05 (FDRE-CRGE, 2011; GTP-MoFED, 2010). In order, to prevent increasing environmental and health related problems, Ethiopia faces the challenge of effectively treating the industrial

wastewater discharge. As with other developing countries, Ethiopia cannot afford to use advanced technologies for the treatment.

## **2.3 Wastewater**

Wastewater comprises water generated from homes, public and private institutions, rural areas, urban areas, farms, industries, and others point and non-point sources (Majeed et al., 2014). Billions of gallons of liquid waste from agricultural, industrial, domestic, and commercial sources are discharged into fresh surface water bodies every day (Renge et al., 2012). Worldwide, between 300 to 400 million tons of liquid and hazardous waste are discharged from industries annually to living organisms in nearby river bodies (Palaniappan, 2010; Pizano et al., 2010; UNEP, 2010). Similarly, approximately two million tons of liquid wastewater is released each day from non-point sources, like agricultural areas, and from point sources, like industries, to surface water bodies across the globe (Corcoran, 2010). The release of untreated wastewater to the surrounding area can lead to the pollution of rivers and streams. Industrial wastewater contains harmful suspended and dissolved matter, like heavy metals, and inorganic matters, which when released untreated greatly affects the environment and causes serious health problems to living organisms. According to available evidence, including the World Health Organization (WHO), (El-Gendy et al., 2011; Isah and Lawal, 2012; Muiruri et al., 2013; Shahmohammadi-Kalalagh et al., 2011; Sonde and Odoemelam, 2012; WHO, 1984), heavy metals and toxic chemicals that are of immediate concern are Pb, Hg, Cd, Cr, Zn, Cu and Fe. The industrialization drive of most developing countries, like Ethiopia, has attracted foreign investments, it has led to the heavy pollution of water bodies because of the discharge of untreated industrial waste. This pollution has been of great concern to Governments and other stakeholders, and therefore, exploring low-cost and effective treatment techniques is the focus of many researchers and scientists across the globe.

### **2.3.1 Heavy metals pollution**

Heavy metals are poisonous chemicals that have specific gravity more than 5 g.cm<sup>-3</sup> and consistence  $\geq 5$  and five times greater than specific gravity of water at 4<sup>0</sup>C (Abas et al., 2013). In

addition, the atomic number and atomic weight of heavy metals is high (Al-Farraj et al., 2013; Srivastava, 1995). In a global context, the major problem of surface water pollution is heavy metal discharge from industrial activities (Alfarra et al., 2014; Narain et al., 2011; Pawar et al., 2014).

Table 2.1 Pollution of water with heavy metals in some African countries

| Country      | Source         | Heavy metal concentration in mg.L <sup>-1</sup> |        |     |        |       |      |      |        | References        |
|--------------|----------------|---|--------|-----|--------|-------|------|------|--------|-------------------|
|              |                | Pb  | Cd     | Hg  | Cu     | Co    | Zn   | Cr   | Ni     |                   |
| Cameroon     | River sediment | 20.3  | 2.8    |     | 42.8   |       | 28.8 | 94.7 | 2.680  | Ekengele (2008)   |
| Ethiopia     | River          | 0.069   | 0.0076 |     |        | 0.067 |      | 0.09 |        | Mersha (2008)     |
| Ghana        | River          | 0.075   | 0.0410 |     |        |       | 2.45 |      |        | Fianko (2007)     |
| Nigeria      | Water          | 0.046   | 0.0044 |     | 0.0033 | 0.018 | 0.14 |      | 0.0031 | Mombeshora (1998) |
| South Africa | Water          | 16.30   | 72.000 |     | 42.600 |       | 27.6 |      |        | Fatoki (2001)     |
| Tanzania     | Lake           | 54.60   | 7.0000 | 2.8 | 26.100 |       | 83.7 | 12.9 |        | Kishe (2003)      |
| Uganda       | Lake           | 1.440   | 0.0200 |     |        | 0.160 |      | 0.02 | 0.1300 | Muwanga (2006)    |
| Zimbabwe     | Water          | 1.020   | 0.1200 |     |        |       |      | 2.48 | 2.3700 | Meck (2006)       |

The development of the industrial sector on the African continent is the primary cause of heavy metals being released into water, air, and soil in all countries, including Ethiopia (Table 2.1). Industries, such as electroplating, chemical, textile, leather, fertilizer, tanneries, batteries, paper, pesticides, and others, are the point sources of heavy metals (Pehlivan, 2008). Industries release their wastewater containing various harmful heavy metals into the environment, without treatment (Fasinu and Orisakwe, 2013). These harmful toxic chemicals include elements such as Ur, Se, Zn, Ag, Au, Ni, Cd, Cu, Cr, Pb and others (Ahalya et al., 2003). The presence of these harmful heavy metals, even at low concentrations, affects the health of humans and other living organisms (Duruibe et al., 2007; Srivastava, 1995). The fact that these toxic elements are highly soluble in water and not easily degradable by soil makes their presence in water bodies more alarming (Kurniawan et al., 2006b).



Figure 2.1 Wastewater discharge from HAFDE tannery into river (Ethiopia)

### **2.3.2 Health effects of heavy metals**

Excess amount of heavy metals in the surrounding affect the health of organisms (Table 2.2). The toxic heavy metals are gradually stored in the body of an organism (Renge et al., 2012). The storage of these chemicals in the body of an organism is greater than their release, which may occur gradually. As these heavy metals, cannot break down easily, the negative effects are worsened by the ecosystem of the environment (Abas et al., 2013). For example, Cd can be accumulated in the human body for up to 30 years, without being destroyed or becoming soluble like organic matter (Mohod and Dhote, 2013). According to the study conducted by Biney and Ameyibor (1992), untreated industrial wastewater, containing toxic elements Cd, Hg, Cr, Cu, Zn, Pb and Fe, that is released to fresh water bodies can also be stored in the bodies of aquatic organisms, for example, in the Pink Shrimp. Therefore, the need to treat wastewater is of great importance, in order to safeguard the environment and reduce associated health problems. According to the WHO reports and other studies (El-Gendy et al., 2011; Isah and Lawal, 2012; Muiruri et al., 2013; Sahni, 2011; Shahmohammadi-Kalalagh et al., 2011; Sonde and Odoemelam, 2012; WHO, 1984), heavy metals i.e. Cr, Cu, Pb, Cd, Hg, Zn and Fe are the greatest concern with regards to human health. Most products such as pharmaceutical products and dental products, some drugs, and Unani drugs, cosmetic products like shampoos, lipsticks, hair colors and others contain heavy metals (Bocca et al., 2014; Sahni, 2011).

The metals are transferred from these products and the environment to humans and other living organisms, by means of the food chain or food web and by coming into contact with the skin. In the food chain process, heavy metals are absorbed into the body of the organism through eating food that have high amount of heavy metals, or by drinking water, through inhalation, through the skin, as well as contact with the eyes and the other sense organs (Yadanaparthi et al., 2009). Small amounts of these elements, beyond allowable limits, have serious effects and are unsuitable for living organisms because of their high-energy particle output (Ali et al., 2013; Arora et al., 2008; Ghiloufi et al., 2014; Kara, 2005; Memon and Schröder, 2009). This causes the wellbeing of living organisms to be compromised (Ghiloufi et al., 2014; Pawar et al., 2014), and they are easily exposed to different diseases and associated problems such as carcinogens, schizophrenic like behavior, lung fibrosis, liver disease, high blood pressure, mental disorders, kidney damage, headaches, intestinal problems and others (Renge et al., 2012).



Figure 2.2 Effects of wastewater discharge from HAFDE industry affect living organisms and environment.

Table 2.2 Standard, source, and health effect of heavy metals

| HM | Permissible limits (mg.L <sup>-1</sup> ) |      |       |      |       | Major Industries Source   | Health Effects  | References              |
|----|--|------|-------|------|-------|---|---|-------------------------|
|    | Ethiopia                                 | WHO  | USEPA | EU   | MCL   |   |   |                         |
| Pb | 0.05                                     | 0.01 | 0.015 | 0.01 | 0.006 | Steel works, Pulp and paper, Fertilizer, Automobile, Organic chemicals, Batteries and paints. | Disease of kidneys, high blood pressure, headache and vomiting, muscles and joint weakness, cirrhosis of liver, anemia, mental retardation, degeneration of motor neurons, suspected carcinogen, schizophrenic like behavior. | Tajrishy (2012)         |
| Cu | 2  | 2    | 1.3   | 2    | 0.25  | Pharmaceuticals, Steel, Pesticide, Insecticides, Fungicides.                                  | Insomnia, liver damage, heart problem, long term exposure cause, stomachache, mental disorder, irritation of nose, eyes, mouth, nausea, vomiting.   | Akkaya and Güzel (2013) |
| Cr | 0.1                                      | 0.05 | 0.1   | 0.05 | 0.05  | Textile, Steel, Pulp and paper, Petroleum refining, Tanning, Power plants.                    | Carcinogenic, respiratory problem, producing lung tumors, kidney and liver damage, headache, weakened immune systems, alteration of genetic material, pulmonary fibrosis.   | FAO (2011)              |

| HM | Permissible limits (mg.L <sup>-1</sup> ) |       |       |      |      | Major Industries Source  | Health Effects  | References                 |
|----|--|-------|-------|------|------|--|---|----------------------------|
|    | Ethiopia                                 | WHO   | USEPA | EU   | MCL  |  |   |                            |
| Ni | 1  | 0.02  | 0.1   | 0.02 | 0.2  | Electroplating, Steel works, Organic chemicals, Fertilizers, Zinc base casting and storage battery industries. | Cancer of lungs, chest pain, dermatitis, chronic asthma, rapid respiration, nausea, coughing, headache, dizziness, myocarditis, pulmonary fibrosis. | Mungray et al. (2012)      |
| Zn | 1  | 3     | 5     |      | 0.8  | Fertilizer, Organic chemical, Pulp and paper, Steel works.   | Lethargy, restlessness, depression, neurological signs and increased thirst, cause short term illness.  | Fu and Wang (2011a)        |
| Cd | 0.5                                      | 0.003 | 0.005 | 0.01 | 0.01 | Organic chemical, Petroleum refining, Steel works, Fertilizer, Aircraft plating and finishing, Fertilizer.     | Human carcinogen, dyspnea, mental disorder, kidney damage, causes lung fibrosis.  | Boparai et al. (2011)      |
| As | 0.25                                     | 0.01  | 0.01  | 0.01 | 0.05 | Steel works, Organic chemicals, Alkalis, Chlorine, Fertilize, Petroleum refining.                              | Visceral cancers, gastrointestinal effects, producing liver tumors, skin manifestations.  | Babel and Kurniawan (2003) |

Note: WHO: World Health Organization; USEPA: United States Environmental Protection Agency; EU: European Union and MCL: Maximum Contaminant Level

Table 2.3 Various treatment methods/technologies for wastewater treatment

| Category | Methods/Technologies       | Advantages   | Disadvantages   | References  |
|----------|----------------------------|--|---|---|
| Physical | Ion- exchange process      | High removal potential for heavy metals  | Expensive for solid waste discharge;<br>It is not applied on large scale; | Rao et al. (2010);<br>Pal and Banat (2014)                            |
|          | Membrane filtration        | Easy removal of toxic elements   | High cost for disposal and complex process;                               | Zwain et al. (2014)   |
|          | Coagulation/ Flocculation  | Economically feasible  | Formation of large particles and production of sludge is high;            | Fu and Wang (2011);<br>Kurniawan et al. (2006b)                       |
|          | Adsorption                 | Simplicity and flexibility of design and operation, cheap and insensitivity to toxic pollutants; | Adsorbents requires regeneration;   | Ahmaruzza man (2011);<br>Fufa et al. (2014);<br>Mohanty et al. (2006) |
|          | Irradiation                | Successful in laboratory standards;  | It wants high $O_2$ ;   | Ahmaruzza man (2011)  |
|          | Electrokinetic coagulation | Cost-effective;  | Has huge sludge discharge;  | Abas et al. (2013)  |
| Chemical | Electrochemical treatment  | Rapid process for some metals; small sludge produced   | Expensive treatment technology;   | Kurniawan et al. (2006b)  |
|          | Photochemical              | Not solid water discharge;   | Product generation;   | Ahmaruzza man (2009)  |
|          | Oxidation                  | Remove toxic contaminants by rapid process;  | Cost of energy is expensive;  | Ahmaruzza man (2011)  |

|             |                    |                                      |  |                          |
|-------------|--------------------|--------------------------------------|--|--------------------------|
|             | Ozonation          | Use for gaseous condition;           | Immediately exposed, short half-life;                          | Ahmaruzza man (2011)     |
| Biologic al | Biological process | Effective for removal of few metals; | It's ongoing for commercializati on, requires large land area. | Wang and Shamm as (2009) |

### 2.3.3 Technologies for heavy metal removal

Heavy metals are the cause of various disorders and diseases, as they can be easily stored in the body of a living organism, without breaking down. Therefore, it is important to remove toxic heavy metals from polluted water, using conventional techniques. There are several conventional techniques for the removal of toxic heavy metals, containing the following: ion exchange processes, membrane filtration, adsorption, electrochemical treatment, photochemical oxidation, and ozonation and biological processes (CROSTAT, 2012). These technologies have been widely applied for some time and can be classified into three groups, namely, physical, biological and chemical treatment techniques (Abas et al., 2013). However, these heavy metal removal technologies have their own disadvantages, for example, they are expensive, due to initial and operational costs, they are less efficient, carry high disposal costs, consist of complex processes and require large land areas (Ahmaruzzaman, 2011).

Table 2.3 illustrates the ion-exchange process, electronic coagulation, irradiation, as well as chemical and biological techniques that are used for the removal of toxic heavy metals. The data shows that these techniques are not widely used because they are less feasible for small-scale industries, as well as having high expenses (Ghiloufi et al., 2014). They also produce a harmful sludge and have been found to be not ecologically-friendly mainly because the technology requires high energy for operation (Abas et al., 2013). In addition, these technologies are reported to be and difficult to control (Alfarra et al., 2014; Chaturvedi and Sahu, 2014b; Habuda-Stanić et al., 2014; Zwain et al., 2014b), and do not totally remove the toxic heavy metals from the contaminated water (Ahalya et al., 2003; Wang and Chen, 2009). In contrast, due to it being inexpensive, environmentally friendly, and efficient, the adsorption technique has been chosen as a method of wastewater treatment with a special interest in the removal of toxic heavy metals from contaminant

rivers (Li et al., 2007). The adsorption technique is also found to be easy and simple to operate, effective and efficient in removing toxic heavy metals (Hua and Li 2014; Tajrishy 2012).

Generally, in developed countries, toxic heavy elements that are discharged from different industrial areas, along with polluted liquid waste, have been successfully removed by high resolution and costly treatment methods (Abas et al., 2013). However, in developing countries the application of such advanced technologies for wastewater treatment is technically complex and expensive (Yadanaparthi et al., 2009). This is attributed to the fact that handling wastewater requires technically skilled manpower and sufficient funds, as the process is so costly. Therefore, the adsorption method has the potential to treat wastewater and remove heavy metals using low-cost locally available materials (Renge et al., 2012).

#### **2.3.4 Adsorption technique**

Adsorption technique is a mass transfer process of adsorbate to adsorbent materials (Babel and Kurniawan, 2003). For example, toxic heavy metals like Cu, Pb, As, Cd, Cr, and Ni can transfer to different available materials/ adsorbents like industrial byproducts, natural abundant materials, and agricultural waste materials (Ahluwalia and Goyal, 2007; Aksu and Tezer, 2005; Gupta et al., 2011; IWRG701, 2009). The adsorption of toxic chemicals from polluted water allows for the attachment of toxic chemical ions to the adsorbents (Gupta, 2009). This method of treatment is found to be effective, easy to operate, cheap, and sustainable (Kapanji, 2009), versatile (Abas et al., 2013; Fufa et al., 2014; Tran et al., 1999), and most eco-friendly (Chang et al., 2012; Saraswat and Rai, 2010). Adsorption has many merits; for example, it is easy to operate, it generates only small quantities of sludge and it is cheap (Mohanty et al., 2006). The low-cost adsorptive adsorbents are easily available in the form of natural materials (Abas et al., 2013). In addition, it is a globally acceptable process for green chemistry endeavors (Bhattacharyya and Gupta, 2008). However, this method has some constraints, such as requiring the modification of pH due to the dangerous suspension of adsorbents (Fufa et al., 2014; Li et al., 2012). Therefore, in developing countries like Ethiopia, the development and the introduction of low-cost adsorption technology from locally-available materials is crucial for a sustainable and appropriate wastewater treatment system, which is also environmentally friendly.

### 2.3.5 Low-cost adsorbents

Low-cost adsorbents are naturally-available materials or adsorbents, and are defined as waste products from agriculture, industries and domestic use. These materials are thus, less expensive (Renge et al., 2012), affordable (Lim and Aris, 2014), environmentally friendly as well as abundant (Kirbiyik 2012; Kurniawan et al., 2006b; Lim and Aris, 2014) and cheap (Carvalho et al., 2011; Kurniawan et al., 2006a). They have high treatment efficiency for the removal of toxic chemicals (Tajrishy, 2012). These cheap adsorbents are simply gathered from agricultural waste, industrial by-products, clay soil, food waste and seafood (Bailey et al., 1999; Jain et al., 2013). Hence, they are economically affordable and widely/abundantly available (Kaushal, 2013; Li et al., 2007). For example, the cost of bagasse fly ash adsorbent is available at US\$0.002 kg<sup>-1</sup>, including the cost of transport to the adsorption processing site and the energy used. The final, total cost of this bagasse fly ash is around 0.009 US dollars per kilogram (Srivastava et al., 1995).

Some low-cost adsorptive materials serve as a scavenger of contaminants by absorbing anions and cations. For example, clay is an environmentally-suitable material for wastewater treatment containing heavy metals (Bhattacharyya and Gupta, 2008; Öncel ,2008; Sarı et al., 2007) and it is an excellent adsorbent material, and also 20 times cheaper than activated carbon at the current market price (Kaushal and Upadhyay, 2014).

Table 2.4 Low-cost adsorbent materials

| Adsorbents          | Price (US\$kg <sup>-1</sup> ) | References                 |
|---------------------|-------------------------------|----------------------------|
| Bagasse fly ash     | 0.009                         | Srivastava et al (1995)    |
| Waste metal sludge  | 0.004-0.005                   | Bhatnagar (2008)           |
| Blast furnace waste | 0.038                         | Srivastava et al (1995)    |
| Blast furnace slag  | 0.04                          | Atun (2003)                |
| Clay                | 0.04-0.12                     | Babel and Kurniawan (2003) |

### 2.3.5.1 Type of low-cost materials

There are various types of adsorbents, such as natural (soil and/or ore) materials, industrial by-products (waste), agricultural waste (products), which can be used to remove unwanted toxic metals from polluted water bodies, such as rivers, streams, lakes and others.

#### 2.3.5.1.1 Natural materials

The heavy metal adsorption capacity of natural materials, like clay, is either better, or equivalent to, other low-cost adsorbents, and they act as scavengers to remove Cu, Pb, Cd, Zn, Cr, As, Co and Fe from wastewater (Bhattacharyya and Gupta, 2008).

Table 2.5 Removal efficiency ( $\text{mg.g}^{-1}$ ) by natural materials like clay

| Adsorbent            | Cu <sup>2+</sup> | Pb <sup>2+</sup> | Cd <sup>2+</sup> | Zn <sup>2+</sup> | Cr <sup>6+</sup> | References                 |
|----------------------|------------------|------------------|------------------|------------------|------------------|----------------------------|
| Illit                | -                | 4.29             | -                | -                | -                | Babel and Kurniawan (2003) |
| Bentonite            | -                | -                | 11.4             | 4.54             | -                | RMSSO (2011)               |
|                      | -                | -                | -                | -                | 0.57             | Khan and Khan (1995)       |
|                      | -                | 20               | -                | -                | -                | Naseem and Tahir (2001)    |
| Kaolinite            | -                | -                | -                | -                | 1.25             | Babel and Kurniawan (2003) |
|                      | -                | 0.12             | 0.32             | -                | -                | Babel and Kurniawan (2003) |
| Fly ash-wollastonite | 1.18             | -                | -                | -                | -                | RMSSO (2011)               |
| Montmorillonite      | -                | 0.68             | 0.72             | -                | -                | Babel and Kurniawan (2003) |
|                      | -                | -                | 4.78             | 4.98             | -                | Babel and Kurniawan (2003) |

#### 2.3.5.1.2 Industrial wastes

Coffee husk is one of the byproducts of industrial waste. The removal of Pb<sup>2+</sup>, Cr<sup>6+</sup>, Hg<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> has been studied. Coffee husk adsorption efficiency was shown to be 7.5, 6.96, 5.57 and 6.85  $\text{mg.g}^{-1}$  for Pb<sup>2+</sup>, Cr<sup>6+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup>, respectively. Bagasse fly ash is also other industrial

byproducts produced from the sugar processing industries displaying good sorptive abilities. In 2003, the uses of bagasse fly ash to remove  $\text{Cr}^{+6}$ ,  $\text{Cd}^{+2}$ ,  $\text{Zn}^{+2}$  and  $\text{Pb}^{+2}$  from wastewater were investigated (Goswami, 2000; Gupta, 2003). The adsorption capacity of bagasse fly ash was found

Table 2.6 Removal efficiency ( $\text{mg.g}^{-1}$ ) of heavy metals by industrial waste products

| Adsorbent          | Heavy metals     |                  |                  |                  |                  |                  |                  | References  |
|--------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|---|
|                    | $\text{Pb}^{2+}$ | $\text{Cu}^{2+}$ | $\text{Cr}^{6+}$ | $\text{Ni}^{2+}$ | $\text{Hg}^{2+}$ | $\text{Zn}^{2+}$ | $\text{Cd}^{2+}$ |   |
| Lignin             | 1865             | 22.87            | -                | -                | -                | 73               | 25.4             | Srivastava (1994);<br>Wu et al. (2008)  |
| Waste slurry       | 1030             | 20.97            | 640              | -                | 560              | -                | 15.73            | Lee (2001);<br>Srivastava (1989)  |
| Coffee husk        | 7.5              | -                | 6.96             | -                | -                | 5.57             | 6.85             | Oliveira (2008)   |
| Tea industry waste | 65               | 11.29            | 455              | 5                | -                | 11               | 11.29            | Ahluwalia and Goyal (2005);<br>Amarasinghe and Williams (2007);<br>Çay (2004)       |
| Blast furnace slag | 40               | 133.3            | 7.5              | -                | -                | 103.3            | 38               | Dimitrova (1996);<br>Gupta et al. (1998);<br>Srivastava (1997)                      |
| Red mud            | -                | 106.44           | 75               | 160              | -                | -                | 66.67            | Apak (1998);<br>Gupta (2001);<br>Zouboulis and Kydros (1993)                        |
| Sugar beet pulp    | 43.5             | 30.9             | 17.2             | 12               | -                | 35.6             | 46.1             | Ogedengbe and Akinbile (2004);<br>Pehlivan et al. (2006);<br>Pehlivan et al. (2008) |
| Bagasse fly ash    | 285-566          | -                | 4.25             | -                | -                | 13.21            | 1.24-2           | Goswami and Das (2000);<br>Gupta (2003)   |

to be 13.21, 285.00-566.00, 4.25, and 1.24 mg.g<sup>-1</sup> for Zn<sup>+2</sup>, Pb<sup>+2</sup>, Cr<sup>+6</sup> and Cd<sup>+2</sup>, respectively, and it followed both the Freundlich and Langmuir isotherm adsorption models. These all show that an adsorption media can be available locally, technically applicable and economically feasible.

### 2.3.5.1.3 Agricultural waste

Cotton seed hulls are an example of agricultural waste or by-product. The removal efficiency of heavy metals with a cotton seed hull has indicated to be 97.6, 98.8, 96.7 and 96.6% for Cr<sup>6+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup>, respectively.

Table 2.7 Removal efficiency in percent of heavy metals by agricultural waste

| Adsorbent              | Removal efficiency in % of heavy metals |                  |                  |                  |                  |                  | References                    |
|------------------------|---|------------------|------------------|------------------|------------------|------------------|-------------------------------|
|                        | Cr <sup>6+</sup>                        | Ni <sup>2+</sup> | Cu <sup>2+</sup> | Zn <sup>2+</sup> | Cd <sup>2+</sup> | Pb <sup>2+</sup> |                               |
| Rice husk biomass      | 98.9                                    | -                | -                | -                | 98.0             | 99.4             | Daifullah et al. (2003)       |
| Raw sugarcane bagasse  | 88.0-100.0                              | -                | -                | -                | -                | -                | APHA (2005)                   |
| Untreated tree sawdust | -                                       | 91.0             | 86.0             | 75.7             | -                | -                | APHA (2005)                   |
| Cotton seed hulls      | 97.6                                    | 96.7             | 98.8             | 96.6             | -                | -                | Marshall and Champagne (1995) |
| Soybean hulls          | 98.1                                    | 95.6             | 99.7             | 96.4             | -                | -                | Marshall and Champagne (1995) |
| Coconut husk           | > 80.0                                  | -                | -                | -                | -                | -                | Tan et al. (1993)             |
| Sago waste             | -                                       | -                | > 75.0           | -                | -                | > 95.0           | APHA (2005)                   |

## 2.4 Current Status of Wastewater Treatment

An estimated amount of 300 to 400 million tons of toxic sludge, heavy metals and toxic chemicals are discharged to rivers and streams every year from industrial sectors around the world (Pizano et al., 2010). While significant growth has been made in many industrialized countries to minimize the raw discharge of chemicals into water bodies, more than 70% of industrial waste is still discharged to water bodies in less developed countries (Corcoran, 2010). In Ethiopia, 90-96% (Getachew, 2006) of industrial toxic substance often alter receiving waters characteristics like acidity, salinity, or turbidity, leading to affected environments and greater occurrences of diseases (Alemayehu, 2014). Heavy metal discharge from various industries such as oil, steel and mining

wastewater combined with contaminants affect surrounding species and environment (Alemayehu, 2014). Moreover, the concentration of Cu, Cr, and Cd is higher in wastewater and effluent discharge from textile and tannery industries. These industries discharge wastewater to the water bodies, which finally percolates through the soil and contaminates the subsurface water. These toxic metallic components were reported to have an effect on living organisms because they cannot dissolve completely (Malarkodi, 2007).

In North America 84.968 km<sup>3</sup> wastewater is generated per year, out of which 72% of the wastewater is treated, while the rest is discharged, without treatment. Four percent of the treated wastewater is used for various activities, like irrigation of agricultural land (Sato et al., 2013; Solley, 1998). In 2000 in Latin America, Argentina re-used 87.5%, and the Dominican Republic and Nicaragua re-used 14% of treated wastewater for agricultural irrigation or/and urban environments management. 34.5% and 1.0% of treated wastewater were used for agricultural irrigation and for watering urban environments in Brazil and El-Salvador during 1996 and 2010, respectively.

In Europe, information about wastewater is available only from six countries (United Kingdom, Spain, Portugal, Italy, Germany and France). The Republic of Macedonia generated the highest percentage with 100% treated wastewater, while the lower 5 % was recovered in Serbia during 2010 and 2011, respectively. Spain used about 11% of the treated wastewater, while the United Kingdom about 4% of treated wastewater during 2007 and 2008, respectively (Sato et al., 2013).

In the Russian Federation and independent states, in different years and in various countries such as Armenia, Azerbaijan, Belarus, Kazakhstan, Kyrgyzstan, Latvia, Tajakistan, Turkmenistan, Ukraine and Uzbekistan the volume of wastewater generated and a treated was 16.826 km<sup>3</sup>.year<sup>-1</sup> and 5.759 km<sup>3</sup>.year<sup>-1</sup>, respectively. This shows only 34% of wastewater is treated per year due to the lack of sufficient and affordable wastewater treatment plants in the region. In North Africa and the Middle East the available data for 16 countries estimate that the volume of wastewater generated is 20.668 km<sup>3</sup>.year<sup>-1</sup>, only 10.693 km<sup>3</sup>.year<sup>-1</sup> (52%) is treated. From this treated wastewater, 3.083 kilo meter cubic (km<sup>3</sup>) per year (29%) are used for irrigation.

The wastewater which is generated treated and used in sub-Saharan African countries, such as Ethiopia, Ghana, Senegal, Seychelles, South Africa and Swaziland is  $3.617 \text{ km}^3 \cdot \text{year}^{-1}$ , treated  $3.2469 \text{ km}^3 \cdot \text{year}^{-1}$  and only around 1% from the total treated wastewater in various years by the six countries. Asian countries (*i.e.* India, Japan, Mongolia, Nepal, Pakistan and Vietnam) discharge  $49.209 \text{ km}^3$  wastewater of which only  $19.657 \text{ km}^3$  (40%) is treated for reuse due to the absence of sufficient and affordable treatment facilities as well as lack of skilled manpower in the field of wastewater treatment technology (Chakraborty and Mukhopadhyay, 2014; Dore and Nagpal, 2006; Sato et al., 2013).

Generally, wastewater is treated and used for various purposes and differs in quality and quantity from country to country. It depends on the financial capacity and availability of professional manpower in the respective country. For example, available data shows that an average amount of around 70% of wastewater treated is generated as follows: 8% of low-income (developing) countries, 28% of lower-middle-income countries and 38% of upper-middle-income (developed) countries, (Sato et al., 2013). This information shows the finding low-cost adsorption treatment technologies.

The unsafe discharge of heavy metals into surface water carries serious health risks. For example, Cu has several health effects such as arthritis/rheumatoid arthritis, mental disorders, anemia, insomnia, liver damage and heart problems. The effects of Cr include carcinogens, respiratory problems, haemolysis, acute renal failure, skin rashes, pulmonary fibrosis and lung tumours. Cd may also affect bone marrow; produce carcinogenic, cause lung fibrosis, dyspnoea, kidney damage, bronchitis, gastrointestinal disorders and cancer (Ahmaruzzaman, 2011; Alluri et al., 2007). The unsafe release of contaminants has significant health hazards and the deterioration of environments like water bodies is becoming critical and more complex. Therefore, it is important to screen locally-abundant adsorptive materials (adsorbents) for wastewater treatment not only in less developed countries like Ethiopia, but also in developed countries.

Table 2.8 Wastewater generation, treatment and use in the world

| Continent     | Country     | Wastewater Generated                |  | Wastewater Treated                  |  | Wastewater Used                     |  | References                |
|---------------|-------------|-------------------------------------|--|-------------------------------------|--|-------------------------------------|--|---------------------------|
|               |             | Reporting year annual <sup>-1</sup> | Amount (km <sup>3</sup> year <sup>-1</sup> ) | Reporting year annual <sup>-1</sup> | Amount (km <sup>3</sup> year <sup>-1</sup> ) | Reporting year annual <sup>-1</sup> | Amount (km <sup>3</sup> year <sup>-1</sup> ) |                           |
| North America | Canada      | 2006                                | 5.395  | 2006                                | 4.477  | -                                   | NA   | Sato et al. (2013)        |
|               | U. S. A     | 1995                                | 79.57  | 1995                                | 56.64  | 2002                                | 2.345  | Solley (1998)             |
| Latin America | Argentina   | 1997                                | 3.530  | 2000                                | 0.104  | 2000                                | 0.091  | Sato et al. (2013)        |
|               | Brazil      | 1996                                | 2.567  | 1996                                | 0.885  | 2008                                | 0.117  | Jiménez and Asano (2008a) |
|               | Colombia    | 2010                                | 2.395  | 2010                                | 0.597  | -                                   | NA   | Sato et al. (2013)        |
|               | Costa Rica  | 2000                                | 0.086  | 2000                                | 0.005  | -                                   | NA   | FAO (2011)                |
|               | Cuba        | 1994                                | 0.502  | 1994                                | 0.109  | -                                   | NA   | Sato et al. (2013)        |
|               | D. Republic | 2011                                | 0.427  | 2000                                | 0.131  | 2000                                | 0.019  | Pérez and ontas (2012)    |
|               | Ecuador     | 1999                                | 0.631  | 1999                                | 0.158  |                                     | NA   | FAO (2011)                |
|               | El Salvador | 2010                                | 0.097  | 2010                                | 0.001  | -                                   | NA   | Deras (2012)              |
|               | Nicaragua   | 1996                                | 0.067  | 2000                                | 0.007  | 2000                                | 0.001  | Sato et al. (2013)        |
|               | Peru        | 2012                                | 0.786  | 2012                                | 0.275  | 2000                                | 0.019  | Tong (2012)               |
|               | Croatia     | 2011                                | 0.343  | 2011                                | 0.267  | -                                   | NA   | CROSTAT (2012)            |
|               | France      | 2004                                | 7.910  | 2004                                | 6.654  | 2004                                | 0.411  | FIE (2012)                |
| Germany       | 2007        | 6.172                               | 2007   | 5.213                               | 2000   | 0.042                               | EUROSTAT (2012)                              |                           |

| Continent                                 | Country      | Wastewater Generated                |  | Wastewater Treated                  |  | Wastewater Used                     |  | References         |
|---|--------------|-------------------------------------|--|-------------------------------------|--|-------------------------------------|--|--------------------|
|   |              | Reporting year annual <sup>-1</sup> | Amount (km <sup>3</sup> year <sup>-1</sup> ) | Reporting year annual <sup>-1</sup> | Amount (km <sup>3</sup> year <sup>-1</sup> ) | Reporting year annual <sup>-1</sup> | Amount (km <sup>3</sup> year <sup>-1</sup> ) |                    |
| Europe                                    | Italy        | 2007                                | 3.926  | 2007                                | 3.902  | 2000                                | 0.233  | AQUAREC (2006)     |
|   | Monaco       | 2009                                | 0.008  | 2009                                | 0.006  | -                                   | NA   | PMDFEU (2009)      |
|   | Montenegro   | 2009                                | 0.066  | 2009                                | 0.015  | -                                   | NA   | MONSTAT (2010)     |
|   | Portugal     | 2009                                | 0.577  | 2009                                | 0.561  | 2000                                | 0.001  | NIWP (2010)        |
|   | R. Macedonea | 2010                                | 0.020  | 2010                                | 0.02   | -                                   | NA   | RMSSO (2011)       |
|   | Serbia       | 2011                                | 3.499  | 2011                                | 0.189  | -                                   | NA   | SORS (2012)        |
|   | Slovenia     | 2010                                | 0.173  | 2010                                | 0.146  | -                                   | NA   | SORS (2012)        |
|   | Spain        | 2007                                | 5.204  | 2007                                | 4.570  | 2007                                | 0.487  | NASI (2012)        |
|   | U. Kingdom   | 2002                                | 4.019  | 2008                                | 3.806  | 2008                                | 0.164  | Sato et al. (2013) |
| Russian Federation and independent states | Armenia      | 2011                                | 0.750  | 2011                                | 0.115  | 2006                                | 0.0001                                       | NSSRA (2012)       |
|   | Azerbaijan   | 2005                                | 0.659  | 2005                                | 0.161  | 2005                                | 0.161  | Sato et al. (2013) |
|   | Belarus      | 2010                                | 0.990  | 2010                                | 0.676  | -                                   | NA   | NSCRB (2011)       |
|   | Kazakhstan   | 1993                                | 1.833  | 1993                                | 0.274  | 2000                                | 0.274  | Sato et al. (2013) |
|   | Kyrgyzstan   | 2006                                | 0.701  | 2006                                | 0.148  | 2000                                | 0.0001                                       | UNECE (2009)       |
|   | Latvia       | 2009                                | 0.282  | 2009                                | 0.128  | 2000                                | 0.012  | CSBL (2011)        |
|   | Tajikistan   | 2008                                | 0.092  | 2008                                | 0.089  | -                                   | NA   | Sato et al. (2013) |

| Continent                    | Country       | Wastewater Generated                |  | Wastewater Treated                  |  | Wastewater Used                     |  | References         |
|------------------------------|---------------|-------------------------------------|--|-------------------------------------|--|-------------------------------------|--|--------------------|
|                              |               | Reporting year annual <sup>-1</sup> | Amount (km <sup>3</sup> year <sup>-1</sup> ) | Reporting year annual <sup>-1</sup> | Amount (km <sup>3</sup> year <sup>-1</sup> ) | Reporting year annual <sup>-1</sup> | Amount (km <sup>3</sup> year <sup>-1</sup> ) |                    |
| Middle East and North Africa | Turkmenistan  | 2010                                | 1.275  | 2004                                | 0.336  | 2004                                | 0.336  | Sato et al. (2013) |
|                              | Ukraine       | 2011                                | 8.044  | 2011                                | 1.763  | -                                   | NA   | SUSU (2012)        |
|                              | Uzbekistan    | 2001                                | 2.200  | 2001                                | 2.069  | 1994                                | 0.205  | UNECE (2001)       |
|                              | Algeria       | 2010                                | 0.730  | 2010                                | 0.150  | -                                   | NA   | Sato et al. (2013) |
|                              | Bahrain       | 2010                                | 0.084  | 2005                                | 0.062  | 2005                                | 0.016  | Sato et al. (2013) |
|                              | Egypt         | 2011                                | 8.500  | 2011                                | 4.800  | 2010                                | 0.700  | Sato et al. (2013) |
|                              | Iran          | 2010                                | 3.548  | 2010                                | 0.821  | 2010                                | 0.328  | Tajrishy (2012)    |
|                              | Iraq          | 2012                                | 0.580  | 2012                                | 0.580  | -                                   | NA   | Aziz (2012)        |
|                              | Israel        | 2007                                | 0.500  | 2007                                | 0.450  | 2004                                | 0.262  | Sato et al. (2013) |
|                              | Libya         | 1999                                | 0.546  | 1999                                | 0.040  | 2000                                | 0.040  | Sato et al. (2013) |
|                              | Morocco       | 2010                                | 0.700  | 2010                                | 0.124  | 2008                                | 0.070  | Sato et al. (2013) |
|                              | Oman          | 2000                                | 0.090  | 2006                                | 0.037  | 2006                                | 0.037  | Sato et al. (2013) |
|                              | P.Territories | 2001                                | 0.071  | 2001                                | 0.030  | 1998                                | 0.010  | PEDCAR (2001)      |
|                              | Qatar         | 2005                                | 0.055  | 2006                                | 0.058  | 2005                                | 0.043  | Sato et al. (2013) |
|                              | Syria         | 2002                                | 1.364  | 2002                                | 0.550  | 2003                                | 0.550  | Sato et al. (2013) |
| Tunisia                      | 2010          | 0.246                               | 2010   | 0.226                               | 2001   | 0.021                               | Saloua (2012)                                |                    |

| Continent          | Country      | Wastewater Generated                |  | Wastewater Treated                  |  | Wastewater Used                     |  | References                |
|--------------------|--------------|-------------------------------------|--|-------------------------------------|--|-------------------------------------|--|---------------------------|
|                    |              | Reporting year annual <sup>-1</sup> | Amount (km <sup>3</sup> year <sup>-1</sup> ) | Reporting year annual <sup>-1</sup> | Amount (km <sup>3</sup> year <sup>-1</sup> ) | Reporting year annual <sup>-1</sup> | Amount (km <sup>3</sup> year <sup>-1</sup> ) |                           |
| Sub-Saharan Africa | Turkey       | 2010                                | 3.582  | 2010                                | 2.719  | 2006                                | 1.000  | TURKSTAT (2012)           |
|                    | Yemen        | 2000                                | 0.074  | 1999                                | 0.046  | 2000                                | 0.006  | Sato et al. (2013)        |
|                    | Ethiopia     | 2009                                | 0.049  | 2009                                | 0.002  | 2009                                | 0.009  | Van Rooijen et al. (2010) |
|                    | Ghana        | 2006                                | 0.280  | 2006                                | 0.022  | -                                   | NA   | Gyampo (2012)             |
|                    | Senegal      | 2010                                | 0.067  | 2010                                | 0.015  | 2010                                | 0.002  | Kayiizzi et al. (2012)    |
|                    | Seychelles   | 2003                                | 0.009  | 2003                                | 0.0009                                       | 2003                                | 0.000006                                     | Sato et al. (2013)        |
|                    | South Africa | 2000                                | 3.200  | 2000                                | 3.20   | 2008                                | 0.030  | Jiménez et al. (2010)     |
|                    | Swaziland    | 2002                                | 0.012  | 2002                                | 0.009  |                                     | NA   | Sato et al. (2013)        |
| Oceania            | Australia    | 2008                                | 2.094  | 2008                                | 1.779  | 2008                                | 0.348  | ABS (2010)                |
| Asia               | India        | 2012                                | 13.99  | 2012                                | 4.302  | 2000                                | 0.450  | Kaur (2012)               |
|                    | Japan        | 2009                                | 27.00  | 2009                                | 14.65  | 2009                                | 0.204  | WB (2012)                 |
|                    | Mongolia     | 2002                                | 0.126  | 2002                                | 0.083  | -                                   | NA   | Basandorj (2002)          |
|                    | Nepal        | 2006                                | 0.135  | 2006                                | 0.006  | -                                   | NA   | Nyachhyon (2008)          |
|                    | Pakistan     | 2011                                | 6.849  | 2011                                | 0.548  | -                                   | NA   | Murtaza (2012)            |
|                    | Viet Nam     | 2003                                | 1.100  | 2009                                | 0.070  | 2003                                | 0.175  | Sato et al. (2013)        |

### **2.4.1 Wastewater treatment scenario in Africa**

In many developing countries, the effect of surface water pollution the result of the discharge without treatment of untreated industrial wastewater containing heavy metals. This affects people living along river banks, in the towns as well as in the country. Untreated/polluted industrial wastewater is a main problem for many people living around river basins as it causes various health problems. As treatment is costly, many industries are not interested in participating in safe waste disposal activities and there are no binding rules on how to dispose of the waste without affecting nearby communities. In Kenya, for example, wastewater is discharged from sugar and coffee factories into nearby waterways without sufficient treatment (Wandiga, 1977).

From the above information  $0.049 \text{ km}^3 \cdot \text{year}^{-1}$  wastewater was generated in Ethiopia. Eighteen percent (18%) of this wastewater is used for agricultural production and other purposes without treatment; the rest of the water is discharged to the surrounding rivers and streams (GTP-MoFED, 2010). According to Kebena and Krishna (2011) in 2009,  $161,668 \text{ m}^3 \cdot \text{day}^{-1}$  liquid waste was generated, and of this, only  $6,728 \text{ m}^3 \cdot \text{day}^{-1}$  (4%) was treated (Krishna, 2011). These figures show that advanced wastewater treatment technologies are expensive and unaffordable, and the literature shows that, as yet, there is no available wastewater treatment in the country. However, it is important that low-cost adsorptive technologies are developed for a sustainable environment and healthy life.

### **2.4.2 Current status of wastewater treatment in Ethiopia**

The geographical coordinates of Ethiopia, are  $8^{\circ}00\text{N}$  and  $38^{\circ}00\text{E}$  and the total area of the country is 1.1 million  $\text{km}^2$ . It is located on the horn of the African continent (NSCRB, 2011) and the total population of the country is around one hundred million (CSA, 2016/17). The industries in the country are rapidly growing from year to year due to the policies of the country. For example, chemical, metal processing, agro-processing, and other, industries are increasing and expanding throughout the regions of Ethiopia. The country also has different climatic conditions and rainfall (Alemayehu, 2014; Said, 1993).

Table 2.9 Volume of wastewater production, treatment, and reuse in Africa

| Country      | Wastewater Generated |   | Wastewater Treated |   | Wastewater Used |   | References                        |
|--------------|----------------------|---|--------------------|---|-----------------|---|-----------------------------------|
|              | Reporting year       | Volume (km <sup>3</sup> .year <sup>-1</sup> ) | Reporting year     | Volume (km <sup>3</sup> .year <sup>-1</sup> ) | Reporting year  | Volume (km <sup>3</sup> .year <sup>-1</sup> ) |                                   |
| Algeria      | 2010                 | 0.730   | 2010               | 0.150   | -               | NA  | Sato et al. (2013)                |
| Egypt        | 2011                 | 8.500   | 2011               | 4.800   | 2010            | 0.700   | Sato et al. (2013)                |
| Ethiopia     | 2009                 | 0.049   | 2009               | 0.002   | 2009            | 0.009   | Kaur et al (2012); Krishna (2011) |
| Ghana        | 2006                 | 0.280   | 2006               | 0.022   | -               | NA  | Gyampo (2012)                     |
| Libya        | 1999                 | 0.546   | 1999               | 0.040   | 2000            | 0.040   | Sato et al. (2013)                |
| Morocco      | 2010                 | 0.700   | 2010               | 0.124   | 2008            | 0.070   | Sato et al. (2013)                |
| Senegal      | 2010                 | 0.067   | 2010               | 0.015   | 2010            | 0.002   | Kayiizzi (2012)                   |
| Seychelles   | 2003                 | 0.009   | 2003               | 0.0009  | 2003            | 0.000006                                      | Sato et al. (2013)                |
| South Africa | 2000                 | 3.200   | 2000               | 3.200   | 2008            | 0.030   | Jiménez et al. (2010)             |
| Swaziland    | 2002                 | 0.012   | 2002               | 0.009   | -               | NA  | Sato et al. (2013)                |
| Tunisia      | 2010                 | 0.246   | 2010               | 0.226   | 2001            | 0.021   | Saloua (2012)                     |
| Yemen        | 2000                 | 0.074   | 1999               | 0.046   | 2000            | 0.006   | Sato et al. (2013)                |

Increased industrialization in Ethiopia has contributed significantly to the Gross Domestic Product (GDP) of the country. However, wastewater discharge from this industrial sector is increasing from year to year and is being discharged into the environment without treatment. It is affecting the health of living organisms both, biotic and abiotic. Therefore, treatment of these toxic heavy metals is becoming a critical issue in the country. Moreover, there is limited information on treatment options available which are suitable for application in the country.

Industrial wastewater is released every day into streams and is significantly affecting the quality of water (Ogedengbe, 2004). The effect is exponentially raised every year because most countries tend to be industrialized. Similarly, in Ethiopia different industries discharge their wastewater into nearby surface water bodies. For example, in the town of Hawassa, wastewater from the textile industry is released into the Tikur Wuha River (Mekuyie, 2014). Kombolcha is one of the main industrial corridors of Northern Ethiopia and the few existing industries are steel products, textiles, tannery, and brewery, meat processing (ELFORA) and flour production. These industries release contaminated wastewater containing toxic heavy metals into the nearby rivers, namely the Borkena, Worka and Leyole Rivers (Zinabu, 2011). The Shinta River is located around the Gonder town, and wastewater containing various pollutants from factories is discharged into this river bodies and onto the open fields around the factories. Some factories for example MOHA soft drinks, plastics, Dashen beer and other existing factories, are affecting the health of many living organisms (Belay and Sahile, 2013). Domestic and municipal wastewater is discharged into the Huluka river of Ambo. The amount of the wastewater released into the Huluka River varies from between 10,000 to 15,000 l.day<sup>-1</sup> (Padanilly et al., 2008) and the Bahir Dar tannery is discharging its effluent into the Blue Nile River (Wosnie and Wondie, 2014). Wastewater containing harmful elements from non-point source of pollution flows into the Awetu and Kito rivers at Jimma town, and like other towns, urbanization and the increase population and industrial growth increases pollution in the water bodies (Haddis et al., 2014). The socio-political and industrial corner of Ethiopia, and the capital Addis Ababa generates an estimated annual volume of 49 million m<sup>3</sup> total wastewater from which about 4 million m<sup>3</sup> is industrial wastewater (van Rooijen et al., 2010). Rivers in Addis Ababa are contaminated with heavy metals because more than two thousand industries in the town are established along the river ways. According to Environmental Protection Authority (EPA) three-quarters of the industries in Ethiopia are established in Addis Ababa, Around 90% of these

industries release their waste directly into these water bodies. Others have some form of on-site treatment plant, and subsequently discharge effluents into adjacent streams (Leta, 2004; Tong, 2012).

Figure 2.3 shows that around 13 thousands  $\text{m}^3 \cdot \text{day}^{-1}$  wastewater is discharged from various industries to nearby water bodies and into the Akaki River in Addis Ababa where 65% of all the industries in the country are found (CSA, 1999). Most toxic heavy metals are found in industrial waste (Schmuhl et al., 2004). For example, in the Ejersa area of East Shoa, in Ethiopia, textile and tannery industries release waste that contains heavy metals such as Cr, Cu, Pb, Fe, Zn and Cd (Asfaw, 2007).

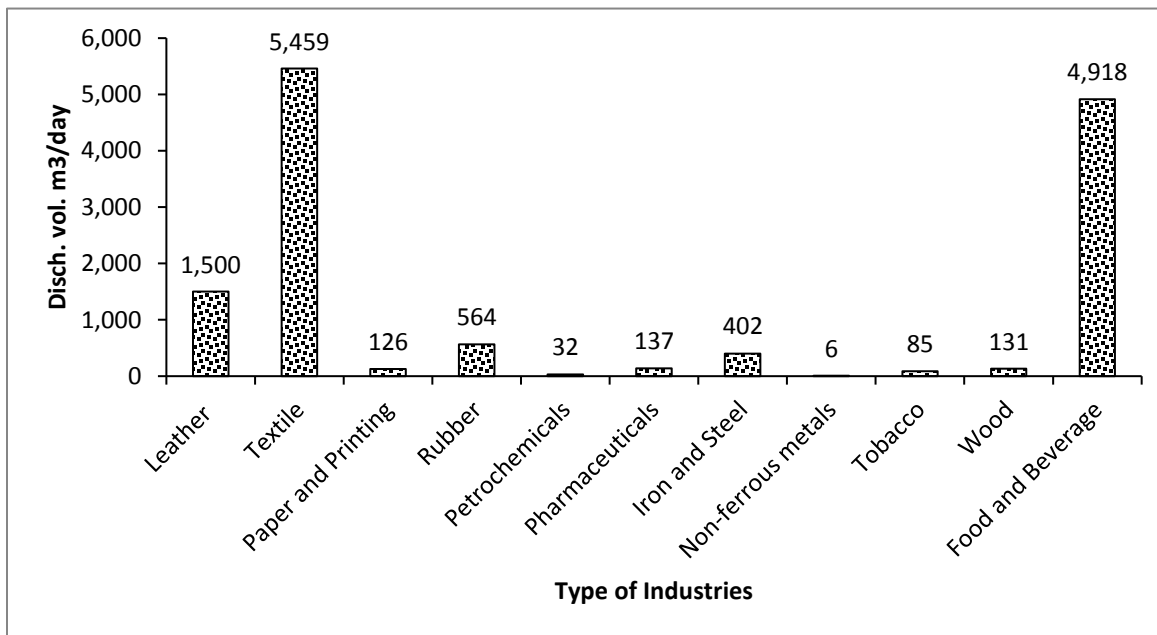


Figure 2.3 Amount of wastewater daily discharged from various industries (Asfaw, 2007)

There is around 390 hectares of irrigated land along the Akaki River in Addis Ababa, on which vegetables are grown, for example potatoes, which have some toxic elements such as Zn, Ni, Hg, Cu, Cd and Cr, as do red beet and onions, which contain Cr (Gebre et al., 2009). For a long time, it has been known that intake of food that contains high amount of heavy metals, affect to human health (Pendias, 1984). These toxic hazardous elements have a significant effect on biotic, abiotic and other living organisms (Sari et al., 2007). Disease includes asthma, malarial, respiratory

infections, skin infections, pregnancy problems, cancer and mortality (Gebre et al., 2009; Zinabu, 2011). It is important to remove toxic hazardous elements from contaminated water discharged into nearby surface water bodies by using low-cost locally available materials. Examples are minerals like clay, industrial byproducts, agricultural waste and other easily available materials (Agrawal et al., 2004; Kurniawan et al., 2006a). Generally, the discharge of untreated effluent wastewater from industries contains heavy metals, which is the main source of water pollution in developing countries like Ethiopia.



Figure 2.4 Wastewater used for vegetable production (390 ha) (Ethiopia)

#### 2.4.2.1 Volume of wastewater discharge in Ethiopia

In Addis Ababa 90-96%, of industries discharge their wastewater without treatment into nearby water bodies (Getachew, 2006). Table 2.10 displays the industries' total wastewater generation and discharge from industries into the *Akaki River*, without the application of any treatment (Getachew, 2006).

Table 2.10 Industrial wastewater generation

| Industry                        | Water Consumption<br>(m <sup>3</sup> .year <sup>-1</sup> ) | Source of water               | Wastewater Generation<br>(m <sup>3</sup> .year <sup>-1</sup> ) |
|---------------------------------|--|-------------------------------|--|
| Akaki Textile S.C.              | 208,050  | Tap water, river and borehole | 98,550   |
| Ethiopia Iron and Steel Factory | 43,800   | Borehole                      | 3,650  |
| Fewes Pharmaceuticals PLC       | 284,700  | Tap water                     | 1,095  |
| Kadisco Chemical Industry       | 2,628  | Tap water                     | 219  |
| Kality Metal Products Factory   | 3,212  | Borehole and tap water        | 3,212  |
| Meher Fiber Products Factory    | 18,615   | Tap water and borehole        | 18,615   |
| Kality Foods S.C.               | 27,193   | Borehole                      | -  |
| MAMCO Paper Products Factory    | 7,300  | Tap water                     | -  |

Source: (Getachew, 2006)

Table 2.10 displays the data obtained from interviews at different business in Addis Ababa, Ethiopia (Getachew, 2006). It shows that these firms generate high volumes of wastewater containing heavy metals. For example, Akaki Textiles generates 98,550 m<sup>3</sup>.year<sup>-1</sup> of wastewater and releases it, without treatment, into the nearby water bodies (*i.e.* rivers and boreholes). These water bodies are contaminated with pollutants. Hence, it is important that generated wastewater is treated with low-cost locally available adsorbents.

Table 2.11 Amount of wastewater discharged and treated trend in Addis Ababa

| Indicators  | Annual Trend |         |         |         |         |
|---|--------------|---------|---------|---------|---------|
|   | 2005         | 2006    | 2007    | 2008    | 2009    |
| Daily wastewater generated in m <sup>3</sup> .day <sup>-1</sup> | 136,893      | 136,027 | 149,392 | 155,013 | 161,668 |
| Daily wastewater treated in m <sup>3</sup> .day <sup>-1</sup>   | 8,530        | 8,592   | 8,768   | 8,024   | 6,728   |
| Percent (%)   | 6%           | 6%      | 6%      | 5%      | 4%      |

Source: (CSA, 2010)

According to Table 2.11, the daily wastewater discharge from industries is increasing, while, on the other hand, the amount of wastewater treated has decreased annually from 6% to 4% (Krishna, 2011). This indicates that the introduction of low-cost treatment techniques that use local and abundantly-available raw materials is becoming a crucial issue.

## 2.5 Conclusions

Environmental problems that arise due to the release of untreated wastewater, particularly industrial wastewater, have been increasing along with a global expansion of industry. Various treatment techniques like membrane filtration, coagulation, ion exchange, adsorption, irradiation, oxidation, biological treatment and others have been developed and used to remove hazardous heavy metals from contaminated wastewater. However, high capital, a complex operation and high costs, plus the need for skilled man power and the generation of secondary sludge limits the application of these modern technologies in developing countries. So far, adsorption principles have been considered the best because of their simplicity of design, operation, cost-effectiveness and possibility of regenerating the spent adsorbent media for re-use. The adsorptive removal efficiency of any adsorbent media is greatly affected by a number of experimental parameters, both under batch adsorptive experimental design. Above all, dissolution problems, the need for pH adjustment and low removal efficiency make locally available adsorbent media unsuitable for toxic chemical removal from aqueous environments. However, further research exploring low-cost locally-available materials for the adsorptive removal of pollutants, is required to develop practically-applicable techniques in developing countries.

## 2.6 References

- Abas, S, Ismail, M, Kamal, M and Izhar, S. 2013. Adsorption process of heavy Metals by low-cost adsorbent: A Review. *World Applied Sciences Journal* 28: 1518-1530.
- ABS. 2010. Australian Bureau of Statistics. Water Account Australia 2008–2009. [http://www.ausstats.abs.gov.au/ausstats/subscriber.nsf/0/D2335EFFE939C9BCCA2577E700158B1C/\\$File/46100\\_2008-09.pdf](http://www.ausstats.abs.gov.au/ausstats/subscriber.nsf/0/D2335EFFE939C9BCCA2577E700158B1C/$File/46100_2008-09.pdf) [accessed 07.10.11].

- Agrawal, A, Sahu, K and Pandey, B. 2004. A comparative adsorption study of copper on various industrial solid wastes. *AIChE journal* 50: 2430-2438.
- Ahalya, N, Ramachandra, T and Kanamadi, R. 2003. Biosorption of heavy metals. *Research Journal Chemistry and Environment* 7: 71-79.
- Ahluwalia, S and Goyal, D. 2005. Removal of heavy metals by waste tea leaves from aqueous solution. *Engineering in Life Sciences* 5: 158-162.
- Ahluwalia, S. and Goyal, D. 2007. Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresource Technology* 98: 2243-2257.
- Ahmaruzzaman, M. 2009. Role of fly ash in the removal of organic pollutants from wastewater. *Energy and Fuels* 23: 1494-1511.
- Ahmaruzzaman, M. 2011. Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Advance Colloid Interface and Scienc* 166: 36-59.
- Ahn, K, Song, K, Cha, H and Yeom, I. 1999. Removal of ions in nickel electroplating rinse water using low-pressure nanofiltration. *Desalination* 122: 77-84.
- Akkaya, G and Güzel, F. 2013. Optimization of Copper and Lead removal by a novel biosorbent: Cucumber (*Cucumis Sativus*) Peels kinetic, equilibrium, and desorption Studies. *Journal of Dispersion Science and Technology* 34:1295-1307.
- Aksu, Z and Tezer, S. 2005. Biosorption of reactive dyes on the green algae *chlorella vulgaris*. *Process Biochemistry* 40: 1347-1361.
- Al-Farraj, A, Al-Sewailem, M, Aly, A, Al-Wabel, M and El-Maghraby, S. 2013. Assessment and heavy metal behaviors of industrial waste water: A case study of Riyadh city, Saudi Arabia. *Proceedings of the International Academy of Ecology and Environmental Sciences* 3: 266-277.
- Alemayehu, A. 2014. Source and determinants of water pollution in Ethiopia: Distributed Lag Modeling Approach. *Intellectual Property Rights* 2: 2-10.
- Alfarra, R, Ali, N and Yusoff, M. 2014. Removal of heavy metals by natural adsorbent: review. *International Journal of Biosciences* 4: 130-139.
- Ali, H, Khan, E and Sajad, M. 2013. Phytoremediation of heavy metals-concepts and applications. *Chemosphere* 91: 869-881.

- Alluri, H, Ronda, S, Settalluri, V, Bondili, J, Suryanarayana, V and Venkateshwar, P. 2007. Biosorption: An eco-friendly alternative for heavy metal removal. *African Journal of Biotechnology* 6: 1-1.
- Amarasinghe, B and Williams, R. 2007. Teawaste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chemical Engineering Journal* 132: 299-309.
- Apak, R, Guclu, K and Turgut, M. 1998. Modelling of copper (II), cadmium (II), and lead (II) adsorption on red mud. *Journal of Colloid Interface Science* 203: 122-130.
- APHA. 2005. Standard methods for examination of water and wastewater. American Public Health Association, American Water Works Association and the Water and Environment Federation, 21th ed, Washington.
- Appel, C and Ma, L. 2002. Concentration, pH, and surface charge effects on cadmium and lead sorption in three tropical soils. *Journal of Environmental Quality* 31: 581-589.
- Appel, C, Ma, L, Dean, R and Kennelley, E. 2003. Point of zero charge determination in soils and minerals via traditional methods and detection of electroacoustic mobility. *Geoderma* 113:77-93.
- AQUAREC. 2006. Integrated concepts for reuse of upgraded wastewater: Report on integrated water reuse concepts. AQUAREC. EVK1-CT-2002-00130, Deliverable D19. RWTH Aachen University, Aachen.
- Argun, M, Dursun, S, Ozdemir, C and Karatas, M. 2007. Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics. *Journal of Hazardous Materials* 141: 77-85.
- Arora, M, Kiran, B, Rani, S, Rani, A, Kaur, B and Mittal, N. 2008. Heavy metal accumulation in vegetables irrigated with water from different sources. *Food Chemistry* 111: 811-815.
- Asfaw, F. 2007. Modeling on Akaki rivers liquid waste disposal and base flow separation, Addis Ababa University, Ethiopia.
- Atun, G, Hisarli, G, Sheldrick, W and Muhler, M. 2003. Adsorptive removal of methylene blue from colored effluents on fuller's earth. *Journal of Colloid Interface Science* 32: 261-269.
- Aziz, A and Aws, A. 2012. Wastewater production, treatment and use in Iraq: country report , presented at the second regional workshop of the project 'safe use of wastewater in agriculture', 16–18 May 2012, New Delhi  
<http://www.ais.unwater.org/ais/mod/page/view.php?id=62> [accessed 21.12.12].

- Babel, S and Kurniawan, T. 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials* 97: 219-243.
- Bailey, S, Olin, T, Bricka, R and Adrian, D. 1999. A review of potentially low-cost sorbents for heavy metals. *Water Research* 33: 2469-2479.
- Barakat, M. 2011. New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry* 4: 361-377.
- Basandorj, D. 2002. Water resource management in Mongolia the national seminar on water quality improvement, Ulaanbaatar, 12–13 June. Cited by: Dore, G., Nagpal, T., 2006. Urban transition in Mongolia: pursuing sustainability in a unique environment. *environment: science and policy for sustainable development* 48: 10–24.
- Belay, A and Sahile, S. 2013. The effects of Dashen brewery wastewater treatment effluent on the bacteriological and physicochemical quality of Shinta river in Gondar, North West Ethiopia. *World Environment* 3:29-36.
- Benavente, M. 2008. Adsorption of metallic ions onto chitosan: equilibrium and kinetic studies. *Water Research* 23: 246-247.
- Bennour, H. 2012. Influence of pH and ionic strength on the adsorption of copper and zinc in Bentonite Clay. *Chemical Science Transactions* 1: 371-381
- Beyene, H and Banerjee, S. 2011. Assessment of the pollution status of the solid waste disposal site of Addis Ababa city with some selected trace elements, Ethiopia. *World Applied Sciences Journal* 14: 1048-1057.
- Bhatnagar, A, Minocha, A, Pudasainee, D, Chung, H, Kim, Lee, G, Min, B and Jeon, B. 2008. Vanadium removal from water by waste metal sludge and cement immobilization.. *Chemical Engineering Journal* 144: 197-204.
- Bhattacharyya, K and Gupta, S. 2008. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. *Advances in Colloid and Interface Science* 140: 114-131.
- Biney, C and Ameyibor, E. 1992. Trace metal concentrations in the pink shrimp *Penaeus notialis* from the coast of Ghana. *Water, Air and Soil Pollution* 63: 273-279.
- Bocca, B, Pino, A, Alimonti, A and Forte, G. 2014. Toxic metals contained in cosmetics: A status report. *Regulatory Toxicology and Pharmacology* 68: 447-467.

- Boparai, H, Joseph, M and O'Carroll, D. 2011. Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. *Journal of Hazardous Materials* 186: 458-465.
- Carvalho, J, Araujo, J and Castro, F. 2011. Alternative low-cost adsorbent for water and wastewater decontamination derived from eggshell waste: an overview. *Waste and Biomass Valorization* 2: 157-167.
- Çay, S, Uyanık, A and Özasık, A. 2004. Single and binary component adsorption of copper (II) and cadmium (II) from aqueous solutions using tea-industry waste. *Separation and Purification Technology* 38: 273-280.
- Chakraborty, D and Mukhopadhyay, K. 2014. Water pollution and abatement policy in India: A study from an economic Perspective, pp 237-245.
- Chang, K, Hsieh, J, Ou, B, Chang, M, Hsieh, W, Lin, J and Chen, S. 2012. Adsorption studies on the removal of an endocrine-disrupting compound (Bisphenol A) using activated carbon from rice straw agricultural waste. *Separation Science and Technology* 47: 1514-1521.
- Charemtanyarak, L. 1999. Heavy metals removal by chemical coagulation and precipitation. *Water Science and Technology Journal* 39: 135-138.
- Chaturvedi, D and Sahu, O. 2014. Adsorption of heavy metal ions from wastewater. *Global Journal of Environmental Science and Technology* 2: 020-028.
- Chen, K, Wang, Y and Chang, Y. 2009. Using catalytic ozonation and biofiltration to decrease the formation of disinfection by products. *Desalination Journal* 249: 929-935.
- Christmann, K. 2010/11. Lecture series modern methods in heterogeneous catalysis research institut für Chemie and Biochemie, Freie Universität Berlin, England
- Corcoran, E. 2010. Sick Water the central role of wastewater management in sustainable development: a rapid response assessment, UNEP/Earthprint. pp387-391
- CROSTAT. 2012. Public sewage system, 2011. [http://www.dzs.hr/default\\_e.htm](http://www.dzs.hr/default_e.htm). [accessed 21.12.12].
- CSA. 1999. Central Statistics Agency, Addis Ababa, Ethiopia.
- CSA. 2010. Central Statistics Agency, Addis Ababa, Ethiopia.
- CSA. 2016/17. Central Statistics Agency, Addis Ababa, Ethiopia.

- CSBL. 2011. Central Statistical Bureau of Latvia. Database: Environmental Protection. <http://www.csb.gov.lv/> [accessed 21.09.11].
- Daifullah, A, Girgis, B and Gad, H. 2003. Utilization of agro-residues (rice husk) in small waste water treatment plans. *Materials Letters* 57: 1723-1731.
- Deepali, G and Gangwar, K. 2010. Metals concentration in textile and tannery effluents, associated soils and ground water. *New York Science Journal* 3: 82-89.
- Deras, M. 2012. Wastewater production, treatment and use in El Salvador, Presented at the forth regional workshop of the project 'safe use of wastewater in agriculture', 11–13 December 2012, Lima: [http://www.ais.unwater.org/ais/pluginfile.php/378/modpage/content/127/EL\\_SALVADOR.pdf](http://www.ais.unwater.org/ais/pluginfile.php/378/modpage/content/127/EL_SALVADOR.pdf) [accessed 21.12.12; in Spanish].
- Dimitrova, S. 1996. Metal sorption on blast furnace slag, *Water Resource Journal* 30: 228-232.
- Dişli, E. 2010. Batch and column experiments to support heavy metals (Cu, Zn, and Mn) transport modeling in alluvial sediments between the Mogan Lake and the Eymir Lake, Gölbaşı, Ankara. *Groundwater Monitoring and Remediation* 30: 125-139.
- Dore, G and Nagpal, T. 2006. Urban transition in Mongolia: pursuing sustainability in a unique environment. *Environmental Science and Policy for Sustainable Development* 48: 10-24.
- Du, Z, Deng, S, Bei, Y, Huang, Q, Wang, B, Huang, J and Yu, G. 2014. Adsorption behavior and mechanism of perfluorinated compounds on various adsorbent: A review. *Journal of Hazardous Materials* 274: 443-454.
- Duruibe, J, Ogwuegbu, M and Egwurugwu, J. 2007. Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences* 2: 112-118.
- Ekengele, M and Ombolo, A. 2008. Metal pollution in freshly deposited sediments from river Mingoa, main tributary to the Municipal lake of Yaounde, Cameroon. *Geosciences Journal* 12: 337-347.
- El Gendy, M, Hassanein, N, Ibrahim, E, Abd, H and El Baky, D. 2011. Evaluation of some fungal endophytes of plant potentiality as low-cost adsorbents for heavy metals uptake from aqueous solution. *Journal of Applied Sciences Research*, 7: 108-117.
- El Zayat, M. 2014. Adsorption of heavy metals cations in wastewater using cement kiln dust. <http://dar.aucegypt.edu/handle/10526/4138>
- EUROSTAT. 2012. Generation and discharge of wastewater.

- <http://epp.eurostat.ec.europa.eu/portal/page/portal/environment/data/database> [accessed 21.12.12].
- FAO. 2011. The wastewater database.  
<http://www.fao.org/nr/water/infores/databases/wastewater.html>. [accessed 21.09.1].
- Fasinu, P and Orisakwe, O. 2013. Heavy metal pollution in sub-saharan Africa and possible implications in cancer epidemiology. *Asian Pacific Journal Cancer Prevantion* 14: 3393-3402.
- Fatoki, M. 2001. An assessment of heavy metal pollution in the East London and Port Elizabeth harbours. *Water Journal S 27*: 2-13.
- FDRE-CRGE. 2011. Federal Democratic Republic of Ethiopia. Addis Ababa, Ethiopia,
- Fianko, O, Adomako, D, Adotey, D and Serfor-Armah, Y. 2007. Assessment of heavy metal pollution of the Iture Estuary in the central region of Ghana. *Environmental Monitoring and Assessment* 131: 467-473.
- FIE. 2012. French Institute for the Environment, sewage treatment: treatment and sludge (water and sanitation survey).  
<http://www.stats.environment.developpementdurable.gouv.fr/Eider/seriesdo#> [accessed 21.12.12; in French].
- Freundlich, H. 1906. Uber die adsorption in losungen. *Zeitschrift für Physikalische Chemie* 57:385–470.
- Fu, F and Wang, Q. 2011. Removal of heavy metal ions from wastewaters: a review. *Journal of Environmental Management* 92: 407-418.
- Fufa, F, Alemayehu, E and Lennartz, B. 2014. Sorptive removal of arsenate using termite mound. *Journal of Environmental Management* 132: 188-196.
- Gao, Z, Badosz, T, Zhao, Z, Han, M and Qiu, J. 2009. Investigation of factors affecting adsorption of transition metals on oxidized carbon nanotubes. *Journal of Hazardous Materials* 167: 357-365.
- Gebre, G, Rooijen, D and Shaw, R. 2009. Urban water pollution and irrigated vegetable farming in Addis Ababa. Water, sanitation and hygiene: sustainable development and multisectoral approaches. Proceedings of the 34th WEDC International Conference, United Nations Conference Centre, 18-22 May 2009 .Addis Ababa, Ethiopia,

- Getachew, T. 2006. Industrial waste management practices in Addis Ababa: A Case Study on Akaki-Kality Industrial Zone, Addis Ababa, Ethiopia.
- Ghiloufi, I, Khezami, L and El Mir, L. 2014. Nanoporous activated carbon for fast uptake of heavy metals from aqueous solution. *Desalination and Water Treatment Journal* 33: 1-10.
- Goswami, D and Das, A. 2000. Removal of arsenic from drinking water using modified fly-ash bed. *International Journal of Water* 1: 61-70.
- GSOE. 2011. Opportunities for kaolin resource development in Ethiopia, Geological survey of Ethiopia. Addis Ababa, Ethiopia.
- GTP-MoFED. 2010. Growth and Transformation Plan of Ethiopia Government (2010/2011-2014/2015). Addis Ababa, Ethiopia.
- Gunay, A, Arslankaya, E and Tosun, I. 2007. Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics. *Journal of Hazardous Materials* 146: 362-371.
- Gupta, K, Gupta, M and Sharma, S. 2001. Process development for the removal of lead and chromium from aqueous solution using red mud: An aluminum industry waste. *Water Research Journal* 35: 1125-1134.
- Gupta, V. 2009. Application of low-cost adsorbents for dye removal: a review. *Journal of Environmental Management* 90: 2313-2342.
- Gupta, V, Mohan, M and Sharma S. 1998. Removal of lead from wastewater using bagasse flyash: A sugar industry waste material. *Separation Science and Technology Journal* 33: 1331-1343.
- Gupta, V, Jain, R, Saleh, T, Nayak, A, Malathi, S and Agarwal, S. 2011. Equilibrium and thermodynamic studies on the removal and recovery of safranin-T dye from industrial effluents. *Separation Science and Technology Journal* 46: 839-846.
- Gupta, V, Jain, C, Ali, I, Sharma, M and Saini, S. 2003. Removal of cadmium and nickel from wastewater using bagasse fly ash a sugar industry waste. *Water Research Journal* 37: 4038-4044.
- Gyampo, M. 2012. Wastewater production, treatment, and use in Ghana, Presented at the Third Regional Workshop of the Project 'Safe Use of Wastewater in Agriculture', 26–28 September, 2012. Johannesburg <http://www.ais.unwater.org/ais/mod/page/view.php?id=61> [accessed 21.12.12].

- Habuda-Stanić, M., Ravančić, M and Flanagan, A. 2014. A Review on adsorption of fluoride from aqueous solution. *Materials Journal* 7: 6317-6366.
- Haddis, A, Getahun, T, Mengistie, E, Jemal, A, Smets, I and Bruggen, B. 2014. Challenges to surface water quality in mid- sized African cities: conclusions from Awetu- Kito Rivers in Jimma, south- west Ethiopia. *Water and Environment Journal* 28: 173-182.
- Handa, G and Kumar, A. 1983. Pollution of natural waters by industrial waste effluents in some parts of North and Northwestern India. *Asian Environment Journal* 21:13-19.
- Hua, R and Li, Z. 2014. Sulfhydryl functionalized hydrogel with magnetism: Synthesis, characterization, and adsorption behavior study for heavy metal removal. *Chemical Engineering Journal* 249: 189-200.
- Isah, U and Lawal, M. 2012. Acid activated tea bag waste as an adsorbent for the removal of chromium ions from tannery waste water. *Advances in Applied Science Research Journal* 3: 4033-4035.
- Itanna, F. 2002. Metals in leafy vegetables grown in Addis Ababa and toxicological implications. *Ethiopian Journal of Health Development*, 16: 295-302.
- IWRG701. 2009. Sampling and analysis of waters, wastewaters, soils and wastes. pp 856-879
- Jain, M, Garg, V and Kadirvelu, K. 2013. Chromium removal from aqueous system and industrial wastewater by agricultural wastes. *Bioremediation Journal* 17: 30-39.
- Jiménez, B and Asano, T 2008a. Water reuse: An international survey of current practice, issues and needs. IWA, London.
- Jiménez, B, Drechsel, P, Koné, D, Bahri, A, Raschid-Sally, L and Qadir, M. 2010. Wastewater, sludge and excreta use in developing countries: an overview. *Wastewater Irrigation Journal* 12:1-47
- Juang, R and Shiau, R. 2000. Metal removal from aqueous solutions using chitosan-enhanced membrane filtration. *Journal of Membrane Science* 165: 159-167.
- Kan, C, Ibe, A, Rivera, K, Arazo, R and Luna, M. 2017. Hexavalent chromium removal from aqueous solution by adsorbents synthesized from groundwater treatment residuals. *Sustainable Environment Research Journal* 27:163-167
- Kapanji, K. 2009. *The removal of heavy metals from wastewater using South African clinoptilolite*. Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, South Africa.

- Kara, Y. 2005. Bioaccumulation of Cu, Zn and Ni from the wastewater by treated *Nasturtium officinale*. *International Journal of Environmental Science and Technology* 2: 63-67.
- Kaur, R., Wani, S, Singh, A and Lal, K. 2012. Wastewater production, treatment and use in India, Presented at the Second Regional Workshop of the Project 'Safe Use of Wastewater in Agriculture', 16–18 May 2012, New Delhi  
<http://www.ais.unwater.org/ais/mod/page/view.php?id=61> [accessed 21.12.12].
- Kaushal, R. 2013. Treatment of waste water with low cost adsorbent:A review. *International Journal of Technical and Non-Technical Research*, 4: 15-23
- Kaushal, R and Upadhyay, K. 2014. Treatability study of low cost adsorbents for heavy metal removal from electroplating industrial effluent: a review. *International Journal of ChemTech Research* 6: 1446-1452.
- Kayiizzi, R, Tomusange, T, Paskwale, K and Lal, K. 2012. Wastewater production, treatment, and use in Uganda, Presented at the Third Regional Workshop of the Project 'Safe Use of Wastewater in Agriculture', 26–28 September 2012, Johannesburg  
<http://www.ais.unwater.org/a s/mod/page/view.php?id> [accessed 21.12.12].
- Keng, P, Lee, S, Ha, S, Hung, Y and Ong, S. 2013. Cheap materials to clean heavy metal polluted waters. *Green Materials for Energy, Products and Depollution*. 3: 335-414.
- Khan, S and Khan, M. 1995. Adsorption of chromium (III), chromium (VI) and silver (I) on bentonite. *Waste Management Journal* 15: 271-282.
- Kırbyık, K, Epeliog˘ullar, O˘ and Pu˘tu˘n, A. 2012. Use of sesame stalk biomass for the removal of Ni(II) and Zi(II) from aqueous solutions. *Water Science and Technology Journal* 66: 231-238.
- Kishe, M. 2003. Distribution of heavy metals in sediments of Mwanza gulf of Lake Victoria Tanzania. *Environment International Journal* 28: 619-625.
- Krishna, K. 2011. Environmental Impact Assessment: a study on liquid waste management in Addis Ababa, Ethiopia. *Abhinav National Monthly Refereed Journal of Research in Science and Technology* 3:29-36
- Kufa, T. 2012. Recent coffee research development in Ethiopia, Ethiopian coffee export conference: Strengthening the legacy of our coffee 8-9 November 2012, Hilton Hotel, Addis Ababa, Ethiopia.

- Kulkarni, S and Kaware, J. 2014. Fixed bed removal of heavy metal, a review. *International Journal of Research* 1: 861-871.
- Kurniawan, T, Chan, G, Lo, W and Babel, S. 2006a. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Science of the Total Environment Journal* 366: 409-426.
- Kurniawan, T, Chan, G, Lo, W and Babel, S. 2006b. Physico-chemical treatment techniques for wastewater laden with heavy metals. *Chemical Engineering Journal* 118: 83-98.
- Langmuir, I. 1916. The constitution and fundamental properties of solids and liquids. *Journal of the American Chemical Society* 38:2221-2295
- Lawrence, P, Meigh, J and Sullivan, C. 2002. The water poverty index: an international comparison, Department of Economics, Keele University. [www-docs.tu-cottbus.de](http://www-docs.tu-cottbus.de)
- Lazaridis, N, Hourzemanoglou, A and Matis, K. 2002. Flotation of metal-loaded clay anion exchangers. Part II: the case of arsenates. *Chemosphere Journal* 47: 319-324.
- Lee, S. 2001. Removal of Cu(II) and Cd(II) from aqueous solution by seafood processing waste sludge. *Water Research Journal* 35: 534-540.
- Leta, S. 2004. Developing and optimizing processes for biological nitrogen removal from tannery wastewaters in Ethiopia, Biotechnology. Addis Ababa, Ethiopia.
- Li, Q, Xu, X, Cui, H, Pang, J, Wei, Z, Sun, Z and Zhai, J. 2012. Comparison of two adsorbents for the removal of pentavalent arsenic from aqueous solutions. *Journal of Environmental Management* 98: 98-106.
- Li, Q, Zhai, J, Zhang, W, Wang, M and Zhou, J. 2007. Kinetic studies of adsorption of Pb (II), Cr (III) and Cu (II) from aqueous solution by sawdust and modified peanut husk. *Journal of Hazardous Materials* 141: 163-167.
- Liang, S, Guo, X, Feng, N and Tian, Q. 2010. Effective removal of heavy metals from aqueous solutions by orange peel xanthate. *Transactions of Nonferrous Metals Society of China* 20: 187-191.
- Lim, A and Aris, A. 2014. A review on economically adsorbents on heavy metals removal in water and wastewater. *Reviews in Environmental Science and Bio/Technology Journal* 13: 163-181.

- Lin, H, Rong, C, Jiu, B, Li, B, Yu, Q, Gan, L and Zhang, Z. 2018. Effects of chromium on pyrolysis characteristic of water hyacinth (*Eichornia crassipes*). *Renewable Energy Journal* 115: 676-684.
- Liu, C and Evett, J. 2003. Soil properties-testing, measurement, and evaluation. Banta Book Company, USA. ISBN:0-13-093005-9.
- Long, C, Li, A, Wu, H and Zhang, Q. 2009. Adsorption of naphthalene onto macroporous and hypercrosslinked polymeric adsorbent: effect of pore structure of adsorbents on thermodynamic and kinetic properties. *Colloids and Surfaces A: Physicochemical and Engineering Aspects Journal* 333: 150-155.
- Mahmoud, M and El-Halwany, M. 2014. Adsorption of cadmium to orange peels: isotherms, kinetics, and thermodynamics. *Journal of Chromatograph and Separation Techniques* 5: 2-8.
- Majeed, M, Muhammed, A and Rasheed, K. 2014. The removal of zinc, chromium and nickel from industrial waste water using rice husk. *Iraqi Journal of Science* 55: 411-418
- Malarkodi, M. 2007. Characterization of heavy metal contaminated soils of coimbatore district in Tamil Nadu. *Journal of Agronomy* 6: 147-151.
- Mandal, N. 2014. Performance of low-cost bio adsorbents for the removal of metal ions; a review. *International Journal Science and Research, ISSN* 3: 2319-7064
- Marshall, W and Champagne, E. 1995. Agricultural byproducts as adsorbents for metal ions in laboratory prepared solutions and in manufacturing wastewater. *Journal of Environmental Science and Health Part A* 30: 241-261.
- Meck, L and Mapani, B. 2006. Zimbabwean mine dumps and their impacts on river water quality: a reconnaissance study. *Physics and Chemistry of the Earth Journal* 31: 797-803.
- Mekuyie, M. 2014. Heavy metals concentration in effluents of textile industry, Tikur Wuha River and milk of cows watering on this water source, Hawassa, Southern Ethiopia. *Journal of Natural Sciences Research* 4: 47-56.
- Memon, A and Schröder, P. 2009. Implications of metal accumulation mechanisms to phytoremediation. *Environmental Science and Pollution Research Journal* 16: 162-175.
- Mersha, Z. 2008. Water quality monitoring design for Little Akaki River. Addis Ababa University, Ethiopia.
- Metcalf, E. 2004. Wastewater engineering: treatment and reuse McGraw-Hill, Boston, USA.

- Mihelcic, J. and Zimmerman, J. 2010. Environmental engineering; fundamental sustainability, design: Wiley, USA.
- Mohanty, K, Das, D and Biswas, M. 2006. Preparation and characterization of activated carbons from *Sterculia alata* nutshell by chemical activation with zinc chloride to remove phenol from wastewater. *Adsorption Journal* 12: 119-132.
- Mohod, C and Dhote, J. 2013. Review of heavy metals in drinking water and their effect on human health. *International Journal of Innovative Research in Science, Engineering and Technology* 2: 2992-2996
- Mombeshora, A and Osibanjo, O. 1998. Pollution studies on Nigerian rivers: toxic heavy metal status of surface waters in Ibadan city. *Environment of International Journal* 5: 49-53.
- MONSTAT. 2010. Statistical Office of Montenegro (MONSTAT), Statistical Year Book 2010. Monstat, Podgorica.
- Moreno-Piraján, J. and Giraldo, L. 2012. Heavy metal ions adsorption from wastewater using activated carbon from orange peel. *Journal of Chemistry* 9: 926-937.
- Muiruri, J, Nyambaka, H and Nawiri, M. 2013. Heavy metals in water and tilapia fish from Athi-Galana-Sabaki tributaries, Kenya. *International Food Research Journal* 20: 891-896.
- Mungray, A, Kulkarni, S and Mungray, A. 2012. Removal of heavy metals from wastewater using micellar enhanced ultrafiltration technique: a review. *Central European Journal of Chemistry* 10: 27-46.
- Murtaza, G. 2012. Wastewater production, treatment and use in Pakistan, presented at the second regional workshop of the project 'Safe use of wastewater in Agriculture', 16–18 May 2012, New Delhi:  
<http://www.ais.unwater.org/ais/mod/page/view.php?id=62> [accessed 21.12.12].
- Muwanga, B. 2006. Impact of industrial activities on heavy metal loading and their physico-chemical effects on wetlands of Lake Victoria basin (Uganda). *Africa Journal of Science Technology* 7: 51-63.
- Naiya, T, Bhattacharya, A, Mandal, S and Das, S. 2009. The sorption of lead (II) ions on rice husk ash. *Journal of Hazardous Materials* 163: 1254-1264.
- Narain, S, Ojha, C, Mishra, S, Chaube, U and Sharma, P. 2011. Cadmium and chromium removal by aquatic plant. *International Journal of Environmental Sciences* 1: 1297-1304.

- Naseem, R and Tahir, S. 2001. Removal of Pb (II) from aqueous/acidic solutions by using bentonite as an adsorbent. *Water Research* 35: 3982-3986.
- NASI, S. 2012. National Statistics Institute, Spain. Survey on water supply and sewage. <http://www.ine.es/welcoing.htm> [accessed 21.12.12].
- NIWP. 2010. National Institute for Water, Portugal, Portuguese acronym for national inventory on urban water supply and sewerage systems. Cited by: National Institute of Statistic. Wastewater discharged (m<sup>3</sup>) by Geographic localization and existence of treatment. [http://www.ine.pt/xportal/xmainxpId=INE&xpgid=ine\\_indicadores&indOcorrCod=0001879&contexto=bd&selTab=tab2](http://www.ine.pt/xportal/xmainxpId=INE&xpgid=ine_indicadores&indOcorrCod=0001879&contexto=bd&selTab=tab2) [accessed 21.12.12].
- NSCRB. 2011. National Statistical Committee of the Republic of Belaru. Statistical Yearbook NSCRB, Minsk, Belaru., 2011.
- NSSRA. 2012. National Statistical Service of the Republic of Armenia. Statistical Yearbook of Armenia 2012. NSSRA, Yerevan.
- Nyachhyon, B. 2008. Service Enhancement and Development of Sanitary Sewage System in Urban and Semi-Urban Setting in Nepal, Policy Paper 23 , Prepared for Economic Policy Network, Ministry of Finance (MOF)/HMGN, ADB Nepal Resident Mission, pp. 86–94 (Cited by: Tuladhar, B., Shrestha, P., Shrestha, R., 2008. Decentralised wastewater management using constructed wetlands. In: Wicken, J., Verhagen, J., Sijbesma, C., Silva, C, Ryan, P. (eds.) 2008. Beyond construction: use by all. A collection of case studies from sanitation and hygiene promotion practitioners in South Asia. IRC, International Water and Sanitation Centre – WaterAid, Delft and London).
- Ogedengbe, K and Akinbile, C. 2004. Impact of industrial pollutants on quality of ground and surface waters at Oluyole industrial estate, Ibadan, Nigeria. *Nigerian Journal of Technological Development* 4: 139-144.
- Oliveira, W, Franca, A, Oliveira, L and Rocha, S. 2008. Untreated coffee husks as biosorbents for the removal of heavy metals from aqueous solutions. *Journal of Hazardous Mater* 152: 1073-1081.
- Öncel, M. 2008. Adsorption of copper (II) from aqueous solution by Beidellite. *Environmental Geology Journal* 55: 1767-1775.
- Padanilly, N, Zerihun, T, Tadele, N, Sevanan, R, Lakew, W, Alemayehu, N, Ephrem, D, Esayas, A, Asfaw, A and Asefa, K. 2008. Characterisation of sewage wastewater and assessment

- of downstream pollution along Huluka River of Ambo, Ethiopia. *Journal of Science and Technology* 2: 440-443.
- Pal, P and Banat, F. 2014. Comparison of heavy metal ions removal from industrial lean amine solvent using ion exchange resins and sand coated with chitosan. *Journal of Natural Gas Science and Engineering* 18: 227-236.
- Palaniappan, M. 2010. Clearing the waters: a focus on water quality solutions, United Nations Environment Programme, Division of Environmental Policy Implementation. *National Environmental Programme pp* 34-39
- Pansini, M, Colella, C and De Gennaro, M. 1991. Chromium removal from water by ion exchange using zeolite. *Desalination Journal* 83: 145-157.
- Panda, H, Tiadi, N, Mohanty, M and Mohanty, C. 2017. Studies on adsorption behavior of an industrial waste for removal of chromium from aqueous solution. *South African Journal of Chemical Engineering* 23: 132-138.
- Park, D, Yun, Y and Park, J. 2010. The past, present, and future trends of biosorption. *Biotechnology and Bioprocess Engineering* 15: 86-102.
- Pawar, K, Wankhede, S, Kaul, H and Karda, S. 2014. Removal of heavy metal ions from synthetic wastewater using various low-cost natural adsorbents. *Journal of Desalination* 3:301-306
- PEDCAR. 2001. Palestinian Economic Council for Development and Reconstruction . Water sector strategic planning. environmental authority, Palestine (Cited by: Fatta, D., Salem, Z., Mountadar, M., Assobhei, O., Loizidou, M., 2004. Urban wastewater treatment and reclamation for agricultural irrigation: the situation in Morocco and Palestine. *Environmental Journal* 24, 227–236).
- Pehlivan, E, Cetin, S and Yanik, B. 2006. Equilibrium studies for the sorption of zinc and copper from aqueous solutions using sugar beet pulp and fly ash. *Journal of Hazardous Materials* 135: 193-199.
- Pehlivan, E, Yanik, B, Ahmetli, G and Pehlivan, M. 2008. Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp. *Bioresource Technology Journal* 99: 3520-3527.
- Pendias, 1984. Trace elements in soils and plants, CRC press, Boca Raton, Florida, USA.

- Pérez, A and Montás, L. 2012. Wastewater production, treatment and use in Dominican Republic, presented at the forth regional workshop of the project 'safe use of wastewater in agriculture', 11–13 December 2012, Lima :  
<http://www.ais.unwater.org/ais/mod/page/view.php?id=171> [accessed 21.12.12]; in Spanish.
- Pizano, M, Besri, M, Marcotte, M and Porter, I. 2010. United Nations Environment Programme (UNEP) 2010 Report of the methyl bromide technical options committee. *UNEP/Ozone Secretariat*, Nairobi, Kenya
- PMDFEU. 2009. Principality of Monaco, department of facilities of the environment and urban, the environment in principality of Monaco: data collection 2009. <http://www.gouv.mc/content/download/7013/108142/file/LEnvironnement%20Recueil20Donnees202009-2>. in French pdf [accessed 21.12.12]
- Qadir, M, Bahri, A, Sato, T and Al-Karadsheh, E. 2010. Wastewater production, treatment, and irrigation in Middle East and North Africa. *Irrigation and Drainage Systems Journal* 24: 37-51.
- Rafatullah, M, Sulaiman, O, Hashim, R and Ahmad, A. 2009. Adsorption of copper (II), chromium (III), nickel (II) and lead (II) ions from aqueous solutions by meranti sawdust. *Journal of Hazardous Materials* 170: 969-977.
- Rao, K, Anand, S and Venkateswarlu, P. 2010. Cadmium removal from aqueous solutions using biosorbent *Syzygium cumini* leaf powder: Kinetic and equilibrium studies. *Korean Journal of Chemical Engineering* 27: 1547-1554.
- Renge, V, Khedkar, S and Pande, S. 2012. Removal of heavy metals from waste water using low cost adsorbents: a review. *Sciences Review Chemical Communications* 2: 580-584.
- RMSSO. 2011. Republic of Macedonia, State Statistical Office. Environmental statistics, RMSSO. *Skopje*, pp 532-578
- Saad, A. 2008. Studies on the biosorption of (lead and nickel) in wastewater using the fungus *Rhizopus nigricans* and effect of the biomass pretreatment on the biosorption activity II, Al Azhar University, Egypt.
- Sahni, S. 2011. Hazardous metals and minerals pollution in India. A Position Paper, August 2011. *Indian National Science Academy New Delhi, India*, pp1-22.
- Said, R. 1993. The Nile River: Geology, Hydrology, and Utilization. Pergamon Press, Oxford, UK.

- Saloua, R. 2012. National Report: Tunisia, Presented at the First Regional Workshop of the Project ‘Safe Use of Wastewater in Agriculture’, 18–19 February 2012, Marrakech <http://www.ais.unwater.org/as/mod/page/view.php?id=59> in French [accessed 21.12.12].
- Santhy, K and Selvapathy, P. 2004. Removal of heavy metals from wastewater by adsorption on coir pith activated carbon. *Separation Science and Technology Journal* 39: 3331-3351.
- Saraswat, S and Rai, J. 2010. Heavy metal adsorption from aqueous solution using: eichhornia crassipes: dead biomass. *International Journal of Mineral Processing* 94: 203-206.
- Sari, A, Tuzen, M, Citak, D and Soylak, M. 2007. Equilibrium, kinetic and thermodynamic studies of adsorption of Pb (II) from aqueous solution onto Turkish kaolinite clay. *Journal of Hazardous Materials* 149: 283-291.
- Sari, A, Tuzen, M and Soylak, M. 2007. Adsorption of Pb (II) and Cr (III) from aqueous solution on Celtek clay. *Journal of Hazardous Materials* 144: 41-46.
- Sato, T, Qadir, M, Yamamoto, S, Endo, T and Zahoor, A. 2013. Global, regional, and country level need for data on wastewater generation, treatment, and use. *Agricultural Water Management Journal* 130: 1-13.
- Schmuhl, R, Krieg, H and Keizer, K. 2004. Adsorption of Cu (II) and Cr (VI) ions by chitosan: Kinetics and equilibrium studies. *Water SA Journal* 27: 1-8.
- Shahmohammadi-Kalalagh, S, Babazadeh, H, Nazemi, A and Manshoury, M. 2011. Isotherm and kinetic studies on adsorption of Pb, Zn and Cu by kaolinite. *Journal of Environmental Science* 9: 243-255.
- Solley, W, Pirce, R and Perlman, H. 1998. Estimated use of water in the United States in 1995. U.S. Geological Survey Circular, 1200. U. S. Geological Survey, Colorado, USA
- Soltani, R, Khorramabadi, G, Khataee, A and Jorfi, S. 2014. Silica nanopowders/alginate composite for adsorption of lead (II) ions in aqueous solutions. *Journal of the Taiwan Institute of Chemical Engineers* 45: 973-980.
- Sonde, C and Odoemelam, S. 2012. Sorption studies on the use of African breadfruit (treculia africana) seed hull as adsorbent for the removal of Cu <sup>2</sup>, Cd <sup>2</sup> and Pb <sup>2</sup> from aqueous solutions. *American Journal of Physical Chemistry* 1: 11-21.
- SORS. 2012. Statistical Office of the Republic of Slovenia . Environment, energy, and transport in figures. <http://www.stat.si/doc/pub/OET-ANG.pdf> [accessed 21.12.12].

- Srivastava, S, Gupta, V and Mohan, D. 1997. Removal of lead and chromium by activated slag a blast-furnace waste. *Journal of Environmental Engineering* 123:461-476.
- Srivastava, S, Gupta, V, Yadav, I and Mohan, D. 1995. Removal of 2,4-dinitrophenol using bagasse fly ash-A sugar industry waste material. *Fresenius Environmental Journal* 4: 550-557.
- Srivastava, S, Tyagi, R and Pant, N. 1989. Adsorption of heavy metal ions on carbonaceous material developed from the waste slurry generated in local fertilizer plants. *Water Research Journal* 23: 1161-1165.
- Srivastava, S, Singh, A and Sharma, A. 1994. Studies on the uptake of lead and zinc by lignin obtained from black liquor A paper industry waste material. *Environmental Technology Journal* 15: 353-361.
- SUSU. 2012. The State Committee of Statistics of Ukraine. Main indicators on the water resources use and protection. <http://www.ukrstat.gov.ua/> [accessed 21.12.12].
- Tajar, A, Kaghazchi, T and Soleimani, M. 2009. Adsorption of cadmium from aqueous solutions on sulfurized activated carbon prepared from nut shells. *Journal of Hazardous Materials* 165: 1159-1164.
- Tajrishy, M. 2012. Wastewater production, treatment and use in Iran , Presented at the Second Regional Workshop of the Project ‘Safe Use of Wastewater in Agriculture’, 16–18 May 2012, New Delhi  
[http://www.ais.unwater.org/ais/mod/page/view.php?id\\_62](http://www.ais.unwater.org/ais/mod/page/view.php?id_62).
- Tan, W, Ooi, S and Lee, C. 1993. Removal of chromium (VI) from solution by coconut husk and palm pressed fibres. *Environmental Technology Journal* 14: 277-282.
- Tegegn, F. 2014. Physico-chemical pollution pattern in Akaki River basin, Addis Ababa, Ethiopia. 2014 GSA Annual Meeting in Vancouver, British Columbia
- Tong, B. 2012. Wastewater production, treatment and use in Peru, presented at the forth regional workshop of the project ‘safe use of wastewater in agriculture’, 11–13 December, Lima:  
[http://www.ais.unwater.org/ais/mod/page/view.php?id\\_171](http://www.ais.unwater.org/ais/mod/page/view.php?id_171) [accessed 21.12.12]
- Tran, H, Roddick, F and O'Donnell, J. 1999. Comparison of chromatography and desiccant silica gels for the adsorption of metal ions I. adsorption and kinetics. *Water Research Journal* 33: 2992-3000.
- Tünay, O and Kabdaşlı, N. 1994. Hydroxide precipitation of complexed metals. *Water Research Journal* 28: 2117-2124.

- TURKSTAT. 2012. Environment statistics; Municipal Wastewater Statics.  
<http://www.turkstat.gov.tr/Strt.do;jsessionid=hkLSRRjHdxhKXPhMZLTwYG0w6SRJ5HLT2bGZdlpB0L0khfB9tY!-1381182142> [accessed 21.12.12].
- UNECE. 2001. UN Economic Commission for Europe. environmental performance reviews: Uzbekistan. UN Publication, New York and Geneva.
- UNECE. 2009. Environmental performance reviews: Kyrgyzstan second review. UN Publication, New York and Geneva.
- UNEP. 2010. United Nations Environment Programme, *UNEP/IPBES/3/3*.
- UNIDO. 2001. Proceeding of the national workshop on the industrial environmental policy and strategy of Ethiopia, UNIDO/EPA/Royal Netherlands Government, Addis Ababa, Ethiopia
- USEPA/SOP. 2012. U. S. EPA Environmental response team standard operating procedures. US
- Van Rooijen, D, Biggs, T, Smout, I and Drechsel, P. 2010. Urban growth, wastewater production and use in irrigated agriculture: a comparative study of Accra, Addis Ababa and Hyderabad. *Irrigation and Drainage Systems Journal* 24: 53-64.
- Veli, S and Alyuz, B. 2007. Adsorption of copper and zinc from aqueous solutions by using natural clay. *Journal of Hazardous Materials* 149: 226-233.
- Volesky, B. 2003. "Sorption and Biosorption" BV Sorbex, Inc., Montreal St. Labert, Quebec, Canada.
- Wandiga, K. 1977. Analysis of chemical pollution in some Kenyan water systems with special reference to lake Nakuru'. National academy for advancement of arts and sciences. symposium. The role of water resources in development: Proceedings of the 13th annual symposium of the East African academy, Nairobi, Kenya
- Wang, J and Chen, C. 2009. Biosorbents for heavy metals removal and their future. *Biotechnology Advances Journal* 27: 195-226.
- Wang, L and Shamma, N. 2009. Single-sludge biological systems for nutrients removal. *Advanced Biological Treatment Processes Journal* 79: 209-270
- WB. 2012. The World Bank data; GNI per capita, Atlas method (current US\$). <http://data.worldbank.org/indicator/NY.GDP.PCAP.CD> [accessed 21.12.12].
- WHO. 1984. World health Organization, Guidelines for Drinking Water Quality . Geneva,
- Wosnie, A and Wondie, A. 2014. Bahir Dar tannery effluent characterization and its impact on the head of Blue Nile River. Addis ababa, Ethiopia.

- Wu, Y, Zhang, S, Guo, X and Huang, H. 2008. Adsorption of chromium (III) on lignin. *Bioresource Technology Journal* 99: 7709-7715.
- Yadanaparthi, S, Graybill, D and von Wandruszka, R. 2009. Adsorbents for the removal of arsenic, cadmium, and lead from contaminated waters. *Journal of Hazardous Materials* 171: 1-15.
- Zinabu, E. 2011. Assessment of the impact of industrial effluents on the quality of irrigation water and changes in soil characteristics: The case of Kombolcha town. *Irrigation and Drainage Journal* 60: 644-653.
- Zouboulis, A and Kydros, K. 1993. Use of red mud for toxic metals removal: the case of nickel. *Journal of Chemical Technology and Biotechnology* 58: 95-101.
- Zwain, H, Vakili, M and Dahlan, I. 2014. Waste material adsorbents for zinc removal from wastewater: a comprehensive review. *International Journal of Chemical Engineering* 78: 657-662.

### 3. APPLICABILITY OF SOIL RICH IN KAOLINITE-FERRINATRITE FOR ADSORPTIVE REMOVAL OF Cr(VI) FROM CONTAMINATED WATER

#### 3.1 Abstract

Chromium (VI) can be found in large quantities in industrial wastewater. Since the wastewater is disposed to rivers in developing countries, adsorptive removal of Cr(VI) from polluted water is crucial for environmental protection. The aim of this research was to study the efficiency of Cr(VI) ion removal from an aqueous solution by using soil rich in kaolinite-ferrinatriite (SRKF). A batch experiment was performed to approximate the effects of shaker speed, contact time, adsorbent dose, pH solution, initial concentration, and particle size. Optimum conditions for Cr(VI) removal were observed at a shaker speed of 150 rpm, an equilibrium time of 40 minutes, adsorbent dose of 3.5 g.L<sup>-1</sup>, particle size of 0.075 mm, pH of 2 and an initial Cr(VI) concentration of 2 and an initial concentration Cr(VI) of 2 mg.L<sup>-1</sup>. Kinetic data were best fitted with the pseudo second-order kinetic model. The result showed that Freundlich's adsorption isotherm model better describes the Cr (VI) adsorption onto SRKF with a coefficient of determination ( $r^2$ ) of 0.9336. SRKF was found to be a promising applicable material for the adsorptive removal of Cr(VI) from polluted water.

**Keywords:** *Adsorption; batch; chromium(VI); removal; soil rich in kaolinite-ferrinatriite*

#### 3.2 Introduction

One of the key worldwide environmental problems is toxic heavy metal pollution. Among various toxic heavy metals hexavalent chromium is a serious problem to environment (Hokkanen et al., 2016; Lin et al., 2018). Chromium is found mostly in the form of chromium (III) and chromium (VI). Chromium (VI); is 100 times more poisonous than chromium (III), when found on a surface and in ground water (Tang et al., 2014), and it is more soluble and mobile than Cr (III). The release of Cr(VI) from industrial wastewater into the environment, degrades water quality and poses hazardous threat to human beings, as well as, other living organisms such as aquatic life due to

being soluble in water in the form of chromate ( $\text{HCrO}_4^-$ ) or dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) and transfer easily to organisms through the food chain (Saifuddin and Kumaran, 2005; Pan et al., 2014; Hokkanen et al., 2016; Sanchooli Moghaddam et al., 2016). Exposure of chromium (VI) ion can lead to severe neurological or physiological damage and severe carcinogenic problem on human health. This includes causing cancer and health problem such as bronchitis, skin dermatitis, diarrhoea and other haemorrhaging problems (Chen et al., 2011; Dehghani et al., 2015; Lin et al., 2018). For these reasons, according to the United States Environmental Protection Agency (USEPA, 2011) among various types of heavy metal pollution, Cr(VI) is the most prioritized poisonous pollutant (Tang et al., 2014). The European Union (EU) has set strong environmental regulations that set the tolerable limits of chromium (VI) ion at;  $200 \mu\text{g.L}^{-1}$ ,  $0.05 \text{ mg.L}^{-1}$  and  $0.1 \text{ mg.L}^{-1}$  for municipal and industrial wastewaters, potable water and inland surface water, respectively (Chen et al., 2011). According to the World Health Organization the recommended maximum tolerable level of chromium (VI) in wastewater discharged from industries is  $0.25 \text{ mg.L}^{-1}$  and in drinking water is  $50 \mu\text{g.L}^{-1}$  (Zhong et al., 2014; Hokkanen et al., 2016). The Ethiopian Environmental Protection Authority (EPA) has set a minimal standard to be  $0.1 \text{ mg.L}^{-1}$  for Cr(VI) containing industrial discharge (Workneh et al., 2014). Cr(VI) is generated from different industrial activities carried out in textile industries, leather tanning, electroplating, steel production, paint manufacturing, pulp processing, chromate preparation, electric and electronic components (Alfarra et al., 2014b; Pan et al., 2014; Sultana et al., 2016; Kan et al., 2017). Thus, it is critical to find effective ways to remove chromium (VI) from industrial wastewater.

Typical treatment technologies used to remove chromium (VI) from wastewater include ion exchange, chemical reduction, adsorption, chemical precipitation, membrane separation, electrocoagulation, and reverse osmosis (Yang et al., 2013; Tang et al., 2014; Zhong et al., 2014; Sultana et al., 2016). However, most of these technologies have their own limitations, such as the high investment costs and unaffordability on a large scale, the high operational costs, and their ineffectiveness for higher concentrations of Cr(VI) that are removed from contaminated water (Hokkanen et al., 2016). Amongst all the treatment technologies, the adsorption technique is one of the most feasible and promising techniques due to its naturally available raw adsorptive material sources, low cost investment, high efficiency, effectiveness, flexibility in design, easy operation and eco-friendly status (Chen et al., 2011; Yang et al., 2013; Tang et al., 2014; Zhong et al., 2014;

Sultana et al., 2016). As a result, looking for a suitable wastewater treatment technology using locally available natural materials that may be used in developing countries such as Ethiopia remains an important issue to address. Among the natural adsorbents, soil rich in kaolinite-ferrinatriite (SRKF) would meet the conditions that have been established for the wastewater treatment process due to its abundant availability in Ethiopia and suitable physical and chemical properties. The following sections in this chapter briefly present the overall condition of SRKF as well as its applicability as an industrial wastewater treatment method.

The objective of this research was to investigate the efficiency of chromium (VI) ion removal from contaminated water, determine the adsorption kinetics and the isotherms as well as pH effect, contact time effect and dosage of the initial concentration of chromium (VI) by using low-cost SRKF under a batch adsorption experiment.

### **3.3 Materials and Methods**

#### **3.3.1 Sample collection and analysis**

For this study, soil rich in kaolinite-ferrinatriite (SRKF) was abundantly found in Ethiopia (GSOE,2011). The sample (soil rich in kaolinite (40.4%) and ferrinatriite (59.6%)) was collected in October 2015 from Bilida locality, Limu-kosa Woreda, Jimma Zone, Oromia Regional National State and South-west Ethiopia. The soil samples were collected in plastic bags from three different sites, according to the standard methods of soil sampling (States, 1992). The collected soil samples were mixed thoroughly, in equal proportions, to make a composite sample at the Bishoftu Research Institute Laboratory. The particle sizes of the soil sample was analyzed according to ASTM D 422 (American Society for Testing and Materials) (Liu and Evett, 2003; Fufa et al., 2013).

The procedure for the analysis of soil rich in kaolinite-ferrinatriite parameters was carried out as per the methods described in this section. The Electrical Conductivity (EC) was measured by using an EC meter in a 1:5 soil: water ratio, the Cation Exchange Capacity (CEC) was measured at a soil pH of 7 after displacement, by using the 1 N ammonium acetate ( $C_2H_7NO_2$ ) method, after which it was estimated titrimetrically. The pH was measured in water at a soil (1) to water (2.5) ratio, the

Total Nitrogen (TN) was measured by using the Kjeldahl method, the Organic Carbon (OC) of SRKF was carried out by using the Walkley-Black method, the soil particle size distribution was measured by the Bouyoucos hydrometric method, after destroying Organic Matter (OM) using H<sub>2</sub>O<sub>2</sub> and dispersing the soils with NaPO<sub>3</sub>, and texture of the SRKF was determined by a hydrometer (Bouyoucos, 1962; Chapman, 1965; van Reewijk, 1992).

The physical characteristics of soil rich in kaolinite-ferrinatriite used for the present study. This is characterized at the Ethiopia Institute of Agricultural Research by document number: Ethiopian Institute of Agricultural Research (EIAR/F), 510-2 and effective date in February 2015. The elemental composition of soil rich in kaolinite-ferrinatriite used for the present study. This is characterized at KwaZulu-Natal University, Pietermaritzburg campus, Life Science Microscopy, and Microanalysis Unit (MMU) by using Scanning Electron Microscopy (SEM/EDS) (Model ZEISS EVO LS15, Germany) at South Africa. The mineral composition was determined using XRD at the Geological Survey Laboratory (Addis Ababa, Ethiopia). The samples were prepared and coated with gold sputter, which is a relatively stable arrangement for the penetration by electron beam and suitable for analysis by SEM and TEM. The morphology of SRKF was identified by gold sputter coat, scanning electron microscopic (SEM/EDS) (Model-ZEISS EVO LS15, Germany) and transmission electron microscope (TEM) (Model-JEOL JEM-1400 Electron Microscopy, Japan) at the University of KwaZulu-Natal, School of Life Sciences, Microscopy, and Microanalysis Unit (Pietermaritzburg, South Africa).

#### 3.3.1.1 Equipment used

- (a) Analytical Balance: used for weighting adsorbents, chemical salts,
- (b) UV-visible spectrophotometer: used for analyses of Cr(VI),
- (c) Drying oven: used for desorption of experiment,
- (d) pH meter: 3310 model-pH meters for adjustable for pH,
- (e) Orbital shaker: used for agitating of samples,
- (f) What-man filter paper, and
- (g) Glassware: Volumetric and Erlenmeyer flasks, glass beakers, cylinders, plastic, test tubes and micropipettes.

### 3.3.1.2 Chemical used

- (a) Distilled water,
- (b) Standard buffer solution: used for calibration of pH meter,
- (c) H<sub>2</sub>SO<sub>4</sub>/ NaOH /HCL; used for adjustable for pH of solution,
- (d) 1,5-Diphenylcarbazide (DPC), and
- (e) Soil rich in kaolinite-ferrinatriite.

### 3.3.2 Batch experimental procedures

The batch adsorption technique expanded with the new natural sorbent (soil rich in kaolinite-ferrinatriite) in this work for chromate removal was carried out with aqueous solution and actual chromate wastewater samples. Batch adsorptive experiments were undertaken to limit the isotherms adsorption of chromate Cr(VI) into SRKF in the 100 mL plastic bottle. The experiment was carried out at laboratory room temperature ( $22 \pm 2^{\circ}\text{C}$ ). The experiments were investigated in duplicate, in addition to the control (only Cr(VI) without SRKF) and blank (only SRKF without Cr(VI)). The chromate water pH were measured with a 3310 model-pH meter, Germany before the application with soil rich in kaolinite-ferrinatriite and chromate concentration in the solutions was determined at 540 nm by using a UV-visible spectrophotometer (HACH LANGE<sup>®</sup>, Model No: 5000).

### 3.3.3 Chemicals

The stock (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) standard solution of each of Cr(VI) (500 mg.L<sup>-1</sup>) was prepared by dissolving 1.414 g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (FINKEM) in 1000 mL distilled water in a volumetric flask. The working solution for batch adsorption experiment was prepared by proper dilution of the stock solution of Cr(VI) in distilled water. The standard solution (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) was used for calibration curve of UV-Visible spectrophotometer measurements. The concentration of 0.1 M NaOH and/or 0.1 M HCl were used for the adjustment of the pH value in the solution.

### 3.3.4 Experimental design

The experimental design of adsorptive removal of chromium (VI) ions from industrial wastewater by using SRKF involves the following treatments: shaker speed from 100 to 250 rpm at interval of, contact time (10, 20, 30, 40, 50, 50, 60, 80, 100 and 120) minutes, adsorbent dose (0.4, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0) g, adsorbent particle size (< 0.075, 0.425, 2.000 and 4.750) mm, pH (2-10) and Cr(VI) concentration (0.5 – 6.0) mg.L<sup>-1</sup>. Batch adsorption experiments were performed on thermo-stated orbital shaker at 100 rpm in 300-ml flasks containing 100 ml of test solution. Desired amount of adsorbent 0.4 SRKF was added to these flasks. The effect of different operating conditions such as shaker speed, contact time, solution pH, initial metal ion concentration, dose of SRKG and particle size was investigated by varying only one of the operating conditions at one time, while others maintained constant. Cr(VI) adsorption capacity versus shaker speed fix initial chromium concentration: 3.5 mg.L<sup>-1</sup>, pH: 7, particle size: 0.425 mm, and contact time: 120 min. (Mishra *et al.*, 2015). Optimum condition for each parameter was obtained by these experiments.

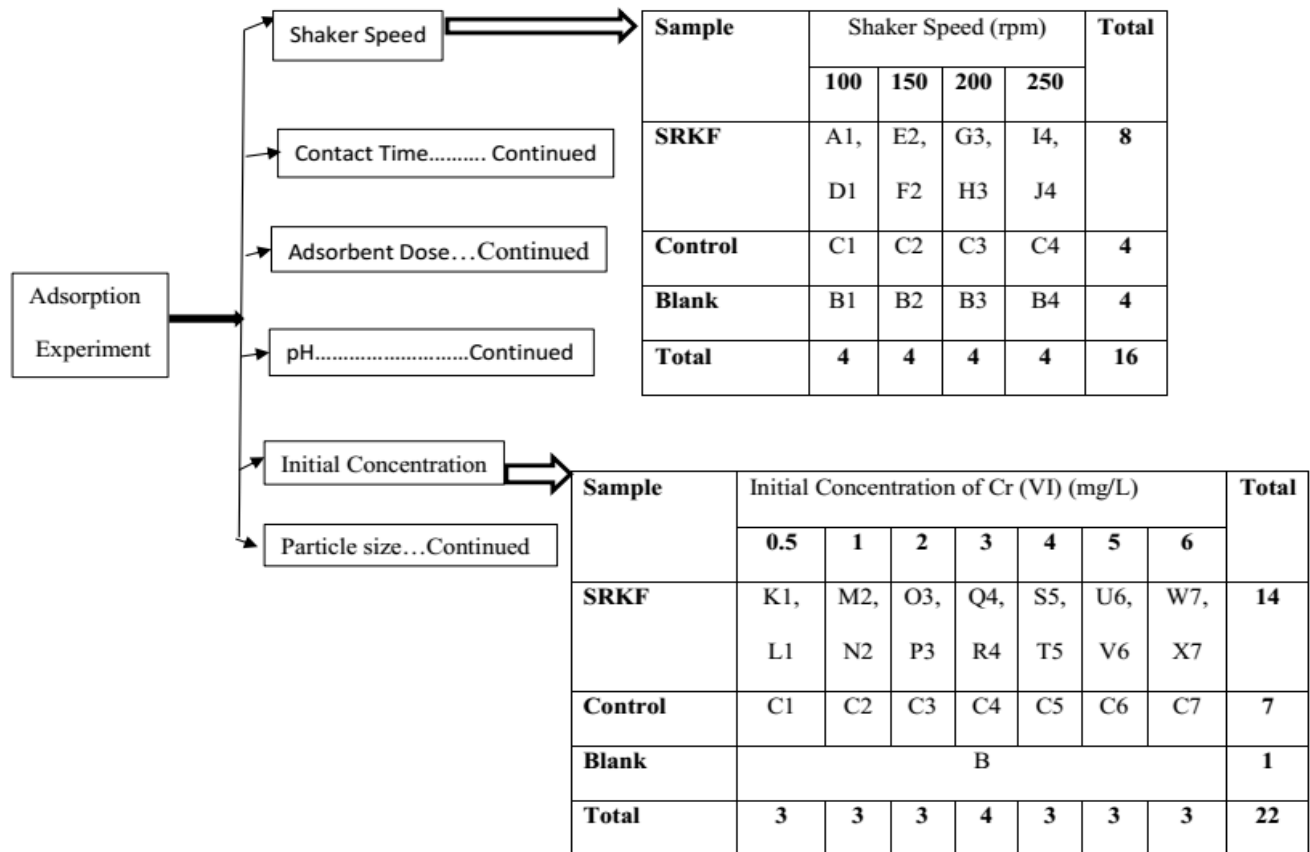


Figure 3.1 Batch adsorption experiment flow diagram (A1, E2, G3, B = sample code; continued = similar table like shaker speed)

### 3.3.5 Hexavalent chromium ions adsorption procedure

Each experiment was duplicated with one control each and one overall blank sample. The experiment was performed under controlled temperature of  $22 \pm 2^\circ\text{C}$  at Jimma University, Environmental Health Laboratory in 2016. Polyethylene plastic bottles were washed using 0.01 M  $\text{HNO}_3$  and thoroughly distilled water. The adsorbent (SRKF) was equilibrated by soaking it with 0.01 M  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  for 12 hours (overnight) a day before the main experiments. Each set of the batch adsorptive experiment effect contains: duplicate trial with blank (only SRKF without Cr(VI) ion) and control (only Cr(VI) ion without SRKF). A series of 300 mL plastic bottles were prepared for the experiments with a 100mL aqueous solution containing a known Cr(VI) ions concentration and an adjusting pH by placing Polyethylene plastic bottles containing the desired adsorbent dose. This was carried out by agitating the solution at a fixed revolution per minute on a Horizontal Thermostat Orbital shaker, for a fixed contact time and at room temperature. Thereafter, the solid soil rich in kaolinite-ferrinatriite was filtered by Whatman filter paper ( $0.45 \mu\text{m}$ ). Next, 0.2 N  $\text{H}_2\text{SO}_4$  for pH adjusted to  $\text{pH } 1 \pm 0.3$  and then, added 1 mL diphenyl-carbazide in 50 mL was added. It then stood 10 min. for color development. Residual Cr(VI) ion concentration was transferred to 1 cm absorption cell and it determined according Section 3.3.2 mentioned. The average of duplicate Cr(VI) measurements was reported.

### 3.3.6 Shaker speed effect

The effect of shaker speed on Cr (VI) removal capacity was studied. Table 3.1 shows the orbital shaker speed (rpm) evaluated for removal of Cr (VI) using SRKF as adsorbent under batch adsorption experiment. The aqueous solution in each plastic bottles was kept agitated in the various speed orbital shaker at 100, 150, 200 and 250 revolutions per minutes, at a room temperature of  $22 \pm 2^\circ\text{C}$  and for a set contact time.

Table 3.1 Identifying the optimum orbital shaker speed (rpm) for removal Cr(VI)

| Sample  | Shaker Speed (rpm) |        |        |        | Total |
|---------|--------------------|--------|--------|--------|-------|
|         | 100                | 150    | 200    | 250    |       |
| SRKF    | A1, D1             | E2, F2 | G3, H3 | I4, J4 | 8     |
| Control | Co1                | Co2    | Co3    | Co4    | 4     |
| Blank   | B11                | B12    | B13    | B14    | 4     |
| Total   | 4                  | 4      | 4      | 4      | 16    |

The analysis were conducted on 16 samples; control (only Cr,VI) without SRKF; blank only SRKF without (Cr,VI); (A1, E2, G3, ..., B14= sample code)



Figure 3.2 Orbital shaker on the time of experimental activity

Cr(VI) solution was prepared from a stock solution (35 mL) by dilution (65 mL distilled water). This was poured into a 300 mL plastic bottle and pH was adjusted at  $7 \pm 0.05$  by using 0.1 M NaOH and 0.1 M HCl. The 16 samples were prepared, of which 8 samples contained 0.4g SRKF and Cr(VI) concentration, 4 were blanks (only SRKF with 100 mL distilled water without Cr(VI) concentration) and 4 were controls (only 35 mL Cr(VI) with 65 ml distilled water without 0.4 g SRKF adsorbent). All 16 plastic bottles sample put on different agitated speed (rpm) for 120 minutes' contact time at room temperature ( $22 \pm 2^\circ\text{C}$ ). The experiment was stopped after the

equilibrium had been achieved. The solution of the experimental samples was filtered by using Whatman filter paper (0.45  $\mu\text{m}$ ) and acidified to  $\text{pH } 1 \pm 0.3$ . Thereafter, 1 mL diphenyl-carbazide in 50 mL was added and this left to stand for 10 minutes for color development. The residual Cr(VI) ion concentration was transferred to 1 cm absorption cell and it was determined using the UV-visible spectrophotometer. The average of duplicate measurements were reported. Finally, optimum stirring speed was selected based on the removal efficacy of Cr(VI) for further experiments.

### 3.3.7 Contact time effect

To fix the equilibrium of the contact time at which the adsorption was completed, the agitation time was varied from 10 to 120 minutes, until the equilibrium was achieved. A known concentration of the adsorbate in aqueous solutions at desired pH was shaken with a desired amount of the adsorbent at 150 rpm for a predetermined contact time effect using the Horizontal Thermostat Orbital shaker. The value of the chromium (VI) adsorbed over the unit mass of the adsorbent media, and the percentage adsorption was computed using Equations 3.1 and 3.2 given below, respectively (Sanchooli Moghaddam et al., 2016; Doke and Khan, 2017)

$$q_t = \frac{(C_0 - C_t) * V}{M} \quad (3.1)$$

$$A = \left(1 - \frac{C_t}{C_0}\right) * 100 \quad (3.2)$$

Where

$q_t$  = the value of Cr(VI) ions adsorbed at time (min) ( $\text{mg.g}^{-1}$ ),

$C_0$  = initial Cr(VI) ions concentration ( $\text{mg.L}^{-1}$ ),

$C_t$  = concentration of Cr(VI) in the solutions at any time(min) ( $\text{mg.L}^{-1}$ ),

$V$  = amount of the aqueous solution (L),

$M$  = mass of SRKF media used in the experiment (g), and

$A$  = the percentage of chromium (VI) ions adsorbed (%).

### **3.3.8 Effect of adsorbent dose**

To determine the optimum dose required for the reduction of average heavy metal concentration in the industrial wastewater to a desired level, different adsorbent doses ranging from (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 g.L<sup>-1</sup>) were separately added into an aqueous solution of known pH containing a desired adsorbate concentration. The mixture was agitated at a 150 rpm (revolution per minute) for equilibrium contact time determined by time series experiments.

### **3.3.9 Solution pH effect**

The solution pH effect was investigated to fix the highest pH value for the highest adsorptive removal of heavy metal over the initial pH value varying from (2, 4, 6, 8, and 10) by allowing a known optimum shaker speed = 150 rpm, contact time = 40 min., dose of SRKF 3.5 g from 0.425 mm particle size and unknown initial concentration Cr(VI) = 3.5 mg.L<sup>-1</sup> and particle size of the adsorbent.

### **3.3.10 Initial concentration of chromium (VI) effect**

Initial concentration effect was studied varying the concentration of hexavalent chromium ions (1, 2, 3, 4, 5 and 6 mg.L<sup>-1</sup>) while maintaining optimum shaker speed = 150 rpm, contact time = 40 min., dose of SRKF 3.5 g from 0.425 mm particle size, pH = 2 and unknown particle size of the adsorbent.

Table 3.2 Optimum pH for removal Cr(VI) using soil rich in kaolinite-ferrinatrinite

| Sample  | Initial Con <sup>n</sup> . of Cr (VI) (mg.L <sup>-1</sup> ) |           |           |           |           |           | Total |
|---------|---|-----------|-----------|-----------|-----------|-----------|-------|
|         | 1   | 2         | 3         | 4         | 5         | 6         |       |
| SRKF    | Y1,<br>Z1   | W2,<br>X2 | U3,<br>V3 | S4,<br>T4 | Q5,<br>R5 | O6,<br>P6 | 12    |
| Blank   |   |           |           | B         |           |           | 1     |
| Control | C1  | C2        | C3        | C4        | C5        | C6        | 6     |
| Total   | 3   | 3         | 3         | 4         | 3         | 3         | 19    |

Nineteen plastic bottles; control only Cr(VI) without SRKF; blank only SRKF without Cr(VI); (Y1, W2, U3, ..., C6 = sample code). There was only one replicated blank (B) for all the treatments.

The method was explained by Gupta et al. (2015) and was arranged with the same changes to analyse Cr(VI), using soil rich in kaolinite-ferrinatrinite

- (a) Chromium(VI) (10 mL) from stock solution + 90 mL distilled water = 3 plastic bottles,
  - (b) Chromium(VI) (20 mL) from stock solution + 80 mL distilled water = 3 plastic bottles,
  - (c) Chromium(VI) (30 mL) from stock solution + 70 mL distilled water = 3 plastic bottles,
  - (d) Chromium(VI) (40 mL) from stock solution + 60 mL distilled water = 3 plastic bottles,
  - (e) Chromium(VI) (50 mL) from stock solution + 50 mL distilled water = 3 plastic bottles,
  - (f) Chromium(VI) (60 mL) from stock solution + 40 mL distilled water = 3 plastic bottles,
- and
- (g) 100mL distilled water blank only contain SRKF without Cr(VI) concentration = 1 plastic bottle.

These 19 plastic bottles samples were agitated for 40 minutes then filtered through Whatman filter paper (0.45 µm) and analyzed by a UV spectrophotometer. Finally, the result was reported.

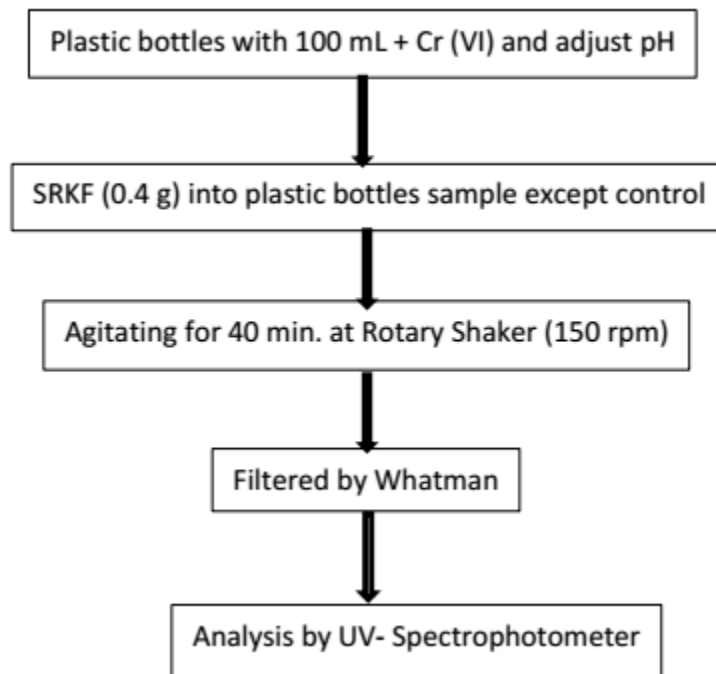


Figure 3.3 Flow diagram of experimental setup for optimization of various effects (contact time, adsorbent dose, pH, shaker speed, initial Cr(VI) concentration)

### 3.3.11 Particle sizes effect

The effect of the adsorbent particle size was investigated for adsorptive removal of heavy metal over the particle size range (<0.075, 0.425, 2.000 and 4.750 mm). This was based on the maximum/optimum value as received from the previous set of the batch equilibrium experiment.

### 3.3.12 Desorption experiment

The adsorbent /SRKF regenerate depends on the released of chromium(VI) from the soil rich in kaolinite-ferrinatriite. Cr(VI) ion laden SRKF/ adsorbent was ready by stirring a known dose of SRKF with the desired concentration of Cr(VI) by shaking at a fixed rpm for a defined equilibrium agitation time. After adsorption, the solution was identified or separated by using Whatman filter paper (0.45  $\mu\text{m}$ ). The SRKF on the Whatman filter paper was washed with distilled water. The Cr(VI) ion-laden SRKF/adsorbent was dried by oven (105°C for 12 hours). The experiments of desorption were then conducted by agitating the oven dried spent adsorbent at a fixed rpm for an equilibrium contact time in 100 mL of different concentration of NaOH solution (0.01 M, 0.1 M

and 0.5 M) separately. Equation 3.3 used to calculate the ratio of desorption (Hu et al., 2011; Singh et al., 2011; Albadarin et al., 2012)

$$\text{Desorption ratio (\%)} = \frac{\text{Amount of Cr(VI) ion desorbed}}{\text{Amount of Cr (VI) ion adsorbed}} \times 100 \quad (3.3)$$

### 3.3.13 Adsorption kinetics

The Pseudo-first-order kinetic and pseudo-second-order kinetic are the most common models used to check adsorption condition of the adsorbents (Ahluwalia and Goyal, 2007).

#### 3.3.12.1 Pseudo-first-order kinetics

The model is illustrated as the following Eq. 3.4:

$$\log(q_E - q_T) = \log q_E - \left( \frac{k_1}{2.303} \right) T \quad (3.4)$$

Where:

$q_E$  = adsorption efficiency at equilibrium ( $\text{mg.g}^{-1}$ ),

$q_T$  = is adsorption efficiency at a time ( $\text{mg.g}^{-1}$ ),

T= time (min) and

$K_1$  = kinetics constant ( $\text{h}^{-1}$ ).

#### 3.3.12.2 Pseudo-second-order kinetics

The model equation can be stated in a linear form as given in Eq. 3.5:

$$\frac{T}{q_E} = \frac{1}{K_2 q_E^2} + \left( \frac{1}{q_E} \right) T \quad (3.5)$$

Where

T= time (min), and

$K_2$  = kinetic constant ( $\text{g.mg}^{-1} \text{h}^{-1}$ ) and the rest of parameters are the same as those presented in Equation 3.4.

### 3.3.14 Adsorption isotherms

Freundlich and Langmuir isotherms were used to fix the highest value of adsorption efficiency of the adsorbents.

#### 3.3.13.1 Langmuir

The Langmuir isotherm is the homogenous molecule surface of adsorption. In this process, one molecule of adsorption cannot affect the near site of adsorption (Ahluwalia and Goyal, 2007).

Linear Langmuir equation is given as follows:

$$\frac{1}{q_E} = \frac{1}{q_M} + \frac{1}{q_M k_L} \frac{1}{C_E} \quad (3.6)$$

Where

$q_E$  = a value Cr(VI) adsorbed over gram of locally available materials,

$C_E$  = an equilibrium of Cr(VI) in wastewater, a milligram of Cr(VI) per liter,

$k_L$  = Langmuir the same, liter per milligram of Cr(VI), and

$q_M$  = maximum contain, a milligram of Cr(VI) per gram of SRKF.

Important features of the Langmuir equation stated in the forms of dimensionless separation factor (Moreno-Piraján and Giraldo, 2012),  $R_L$ , are defined as:

$$R_L = \frac{1}{(1 + K_L C_o)} \quad (3.7)$$

Where

$K_L$  = constant of Langmuir ( $\text{L.mg}^{-1}$ ),

$C_o$  = primary amount of Cr (VI) ions ( $\text{mg.L}^{-1}$ ), and

$R_L$  a result indicating the shape of the isotherms:  $1 < R_L$  indicates disapproving adsorption,  $1 = R_L$  indicates linear,  $R_L$  values between 0 and 1 indicates approving adsorption, and  $0 = R_L$  indicates adsorption nonreversible.

### 3.3.13.2 Freundlich

The Freundlich isotherm was described as the heterogeneous surface energies by multilayer adsorption (Sanchooli Moghaddam et al., 2016).

The general equation is illustrated as follows:

$$\text{Log}(q_E) = \text{Log}(k_F) + \frac{1}{n} \text{Log}(C_e) \quad (3.8)$$

Where

$q_E$  shows adsorption efficiency ( $\text{mg} \cdot \text{g}^{-1}$ )

$1/n$  values between 0 and 1 shows the suitability of adsorption. If  $K_F$  value is higher and shows the better suitability of adsorption.

### 3.3.15 Chromium (VI) analysis methods

The United States Environmental Protection Agency accepts four techniques for measuring the Cr(VI) concentration: chelation/ extraction (Pehlivan and Cetin, 2009; Chen et al., 2011). Balasubramanian and Pugalenti (1999) compared three methods of Cr(VI) analysis result from wastewater estimated by ICP-MS, FAAS and UV-visible spectrophotometry (1,5-diphenylcarbazide spectrometry). It was found that the UV- visible spectrophotometry method was better suited for Cr(VI) ions analysis when compared with the other techniques (Chen et al., 2011). This study, Cr(VI) concentration in the solutions was determined at 540 nm by using a UV-visible spectrophotometer made by HACH LANGE © (Model No: 5000). The statistical data analysis of the studies was performed by OriginPro 8 software.

### 3.4 Results and Discussion

#### 3.4.1 Characterization of soil rich in kaolinite-ferrinatrinite

Table 3.3. describes the site from where the soil samples were collected. The locations were selected from three sited to reduce the sampling bias and was randomly selected (States, 1992).

Table 3.3 Sampling location site of soil rich in kaolinite-ferrinatrinite

| Sampling Site | UTM                    | Difference (m) | Elevation (m) | Depth (m) |
|---------------|------------------------|----------------|---------------|-----------|
| 1             | 37N 0274104<br>0888816 | ± 3            | 1792          | 0.9       |
| 2             | 37N0264967<br>0879988  | ± 3            | 1816          | 1.2       |
| 3             | 37N0260722<br>0877326  | ± 3            | 1990          | 0.8       |

UTM represents Universal Transverse Mercator

##### 3.4.1.1 Particle Size

The collected soil samples were mixed thoroughly in equal proportions to make a composite sample at Bishoftu Research Institute Laboratory. The particle size of the soil sample was analyzed according to American Society for Testing and Materials (ASTM D 422) (Liu and Evett, 2003; Fufa et al., 2013). The samples were dried at room temperature and ground using hand mortar and pestle. Thereafter, the particle size was identified by using a sieve with diameter 0.075, 0.425, 2.000 and 4.750 mm. The samples were, then, stored in an airtight plastic bottles for physicochemical analysis of adsorbents and for batch adsorption experiments.

The particle size distribution of soil rich in kaolinite-ferrinatrinite were ranged from 0.075 to 4.750 mm (Figure 3.4). The Coefficient of Uniformity (CU) of the soil is equal to grain size (d<sub>60</sub>) over

effective grain size (d10). The value of CU was found to be 10.5 (Mathews and Zayas, 1989; Alaa and Mena, 2015) using the gradation curve for soil rich in kaolinite-ferrinatriite.

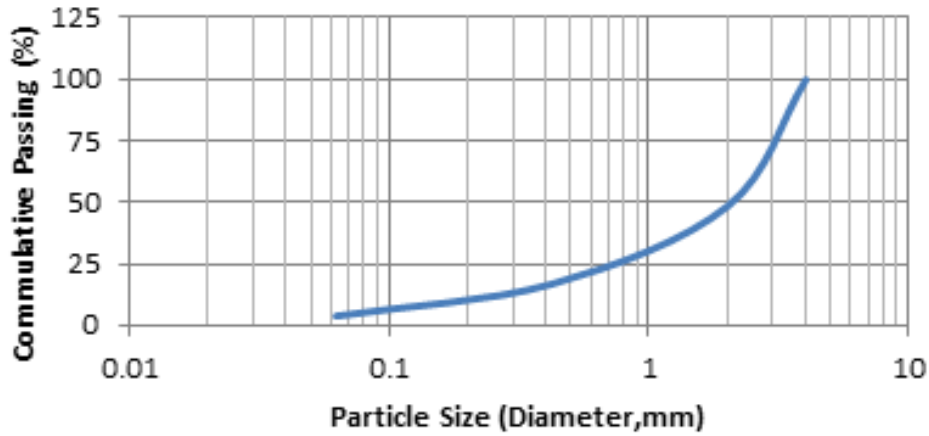


Figure 3.4 Gradation curve for soil rich in kaolinite-ferrinatriite used in present study

### 3.4.1.2 Physical and elemental analysis

Table 3.4 shows that, the amount of electrical conductivity, cation exchange capacity, total nitrogen, organic carbon, organic matter and texture of SRKF were carried out at Bishoftu Research Institute Laboratory, Ethiopia, according procedure (Bouyoucos, 1962; Chapman, 1965; van Reewijk, 1992).

Table 3.4 Physical characteristic of soil rich in kaolinite-ferrinatriite

| Sample | Parameters                                 |                                  |      |           |           |           |             |             |             |         |
|--------|--|----------------------------------|------|-----------|-----------|-----------|-------------|-------------|-------------|---------|
|        | EC<br>( $\mu\text{s}\cdot\text{cm}^{-1}$ ) | CEC (cmol.<br>Kg <sup>-1</sup> ) | pH   | TN<br>(%) | OC<br>(%) | OM<br>(%) | Sand<br>(%) | Silt<br>(%) | Clay<br>(%) | Texture |
| SRKF   | 22.80                                      | 24.00                            | 5.24 | 0.14      | 0.75      | 1.28      | 18.80       | 10.40       | 70.80       | Clay    |

CEC: Cation Exchange Capacity; EC: Electrical Conductivity; OC: Organic Carbon; OM: Organic Matter; TN: Total Nitrogen.

The elemental composition and surface morphology of SRKF was investigated by using ZEISS EVO LS15 model SEM and EDX at University of KwaZulu-Natal, South Africa. The sample was

coated with gold sputter then analysed in SEM and EDX. The SEM photo (Figure 3.5) shows the irregular structure morphology, high porous surface, and heterogeneous rough surface shape of SRKF. Consequently, SRKF is favorable/ suitable for metal ions adsorbed on the SRKF and good for the fast adsorption of adsorbate onto adsorbent that is chromium (VI) onto SRKF. This finding was similar to the findings of Albarelli et al. (2011), Aravind et al. (2013), Aravind et al. (2015), Miao et al. (2016). The amount of carbon, oxygen, sodium, magnesium, aluminum, silica, potassium, tritium, and iron in the SRKF were studied by using elemental analysis instrument EDX spectra (Figure 3.6). The surface of soil rich in kaolinite-ferrinatrinite (Figure 3.6) indicate that oxygen, silica, aluminum, and carbon about 51%, 14%, 12% and 9%, respectively and have been found rich in macronutrients weight on the surface. These Figure 3.6 also shows traces of Na, K, Ca, Ti, Mg, P and Mn.

Table 3.5 Elemental composition of soil rich in kaolinite-ferrinatrinite used in this study

| Elements | C    | O <sub>2</sub> | Na   | Mg   | Al    | Si    | P    | K    | Ca   | Ti   | Mn   | Fe    |
|----------|------|----------------|------|------|-------|-------|------|------|------|------|------|-------|
| Weight   |      |                |      |      |       |       |      |      |      |      |      |       |
| %        | 8.90 | 51.15          | 0.02 | 0.34 | 11.46 | 13.63 | 0.23 | 0.33 | 0.09 | 0.66 | 1.08 | 11.04 |

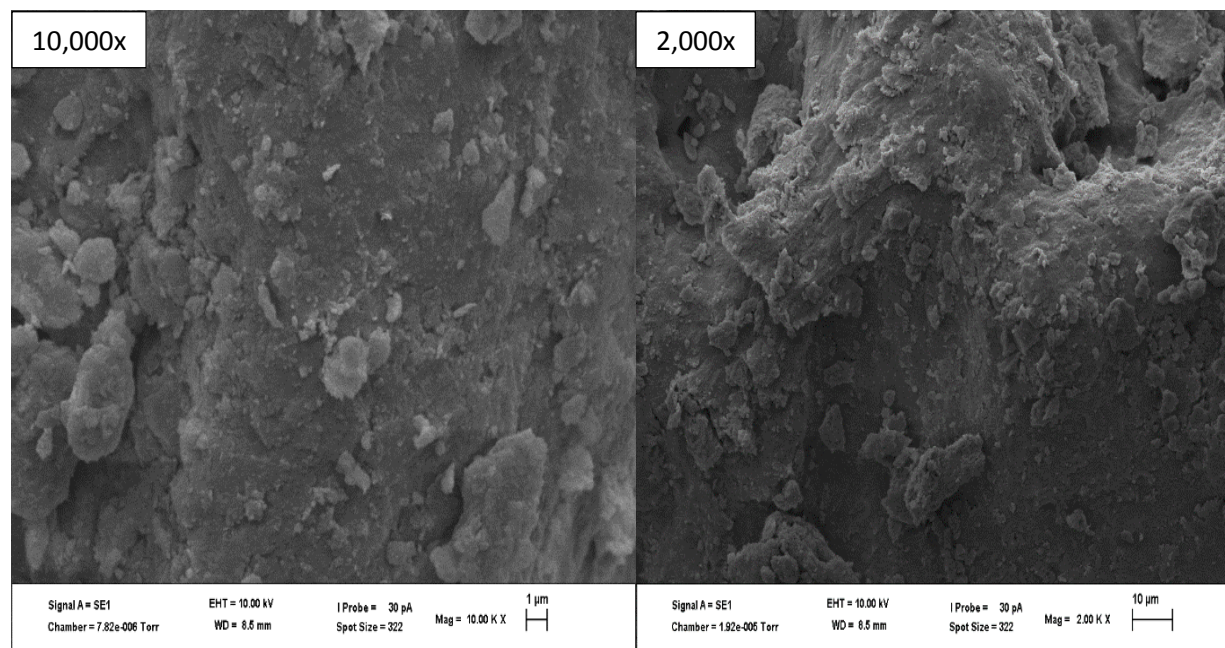


Figure 3.5 Scanning Electron Microscopy (SEM) of SRKF at 10,000X and 2,000X magnification

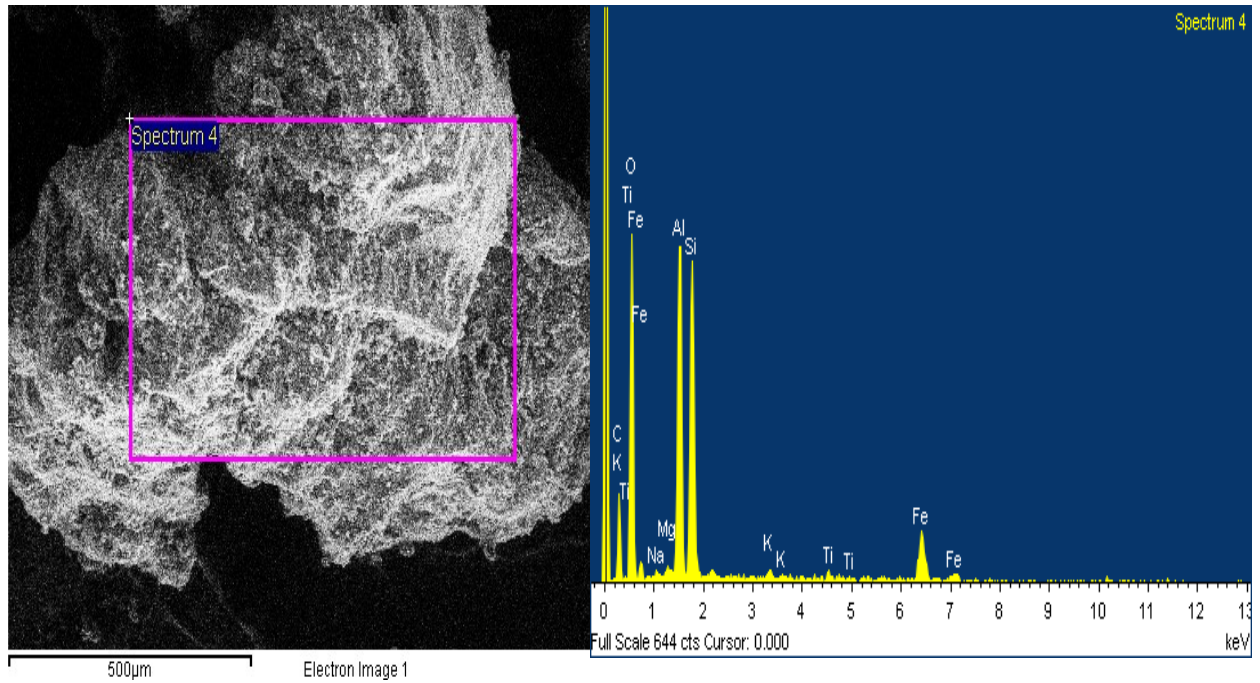


Figure 3.6 Characteristic of X-ray spectrum of soil rich in kaolinite-ferrinatriite

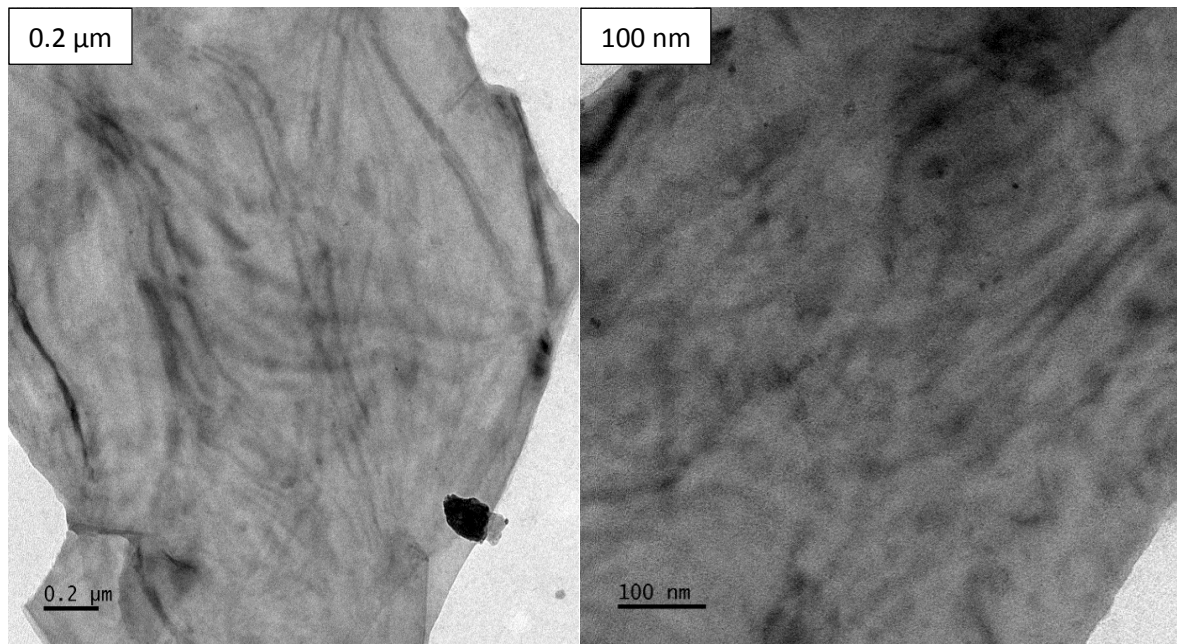


Figure 3.7 Transmission Electron Microscopy (TEM) image of soil rich in kaolinite-ferrinatriite at 0.2 µm and 100 nm magnification

### 3.4.2 The effect of shaker speed on Cr(VI) removal

The effect of shaker speed for Cr(VI) removal capacity was studied. Figure 3.8 shows the adsorptive experimental result obtained from a series of experiments performed, initial chromium concentration:  $3.5 \text{ mg.L}^{-1}$ , adsorbent dose:  $0.4 \text{ g}$ , pH: 7, particle size:  $0.425 \text{ mm}$ , and contact time: 2 hours at room temperature  $22 \pm 2^\circ\text{C}$  and various shaking speed 100, 150, 200 and 250 revolutions per minute. The adsorption removal percentage curve at various shaking speed showed that, was plotted and is shown in Figure 3.8. It showed that the string speed of 150 rpm has a greater removal efficiency of Cr(VI) then the other string speeds. Thus, the agitating speed was fixed at 150 rpm in further experiments.

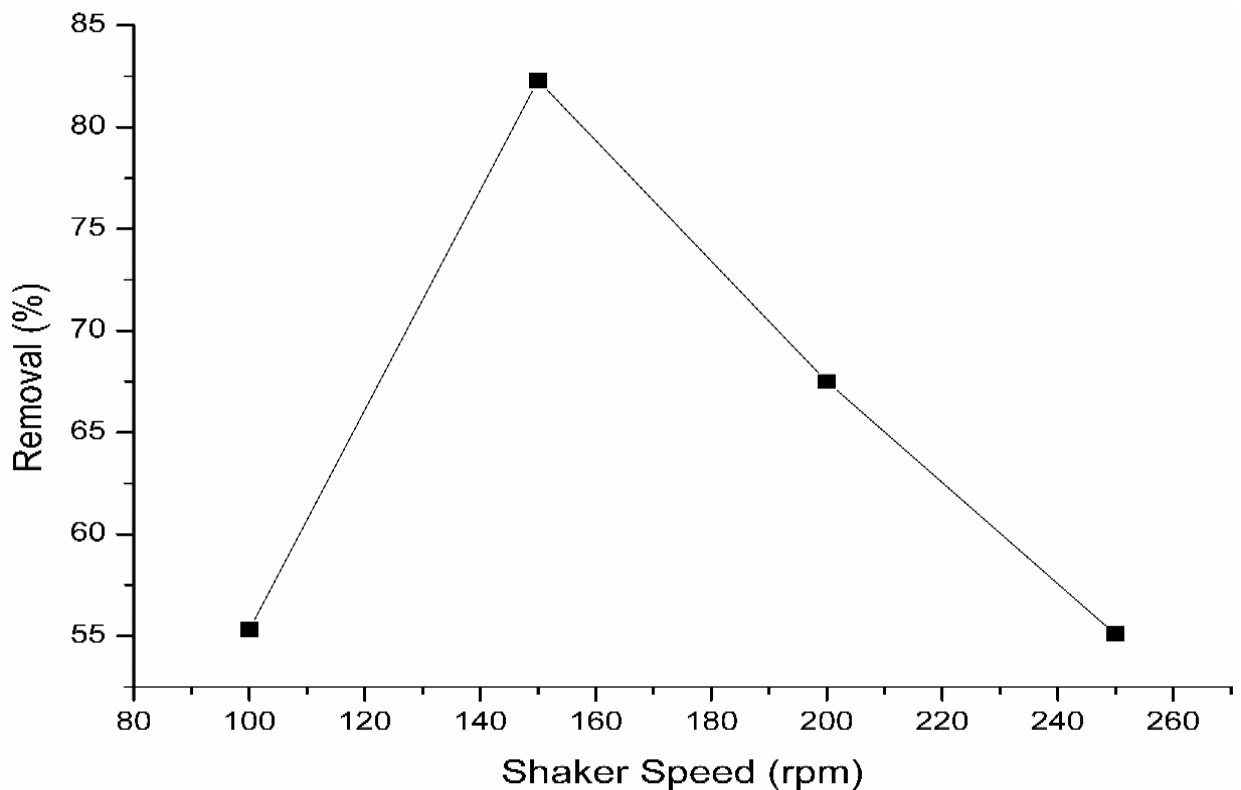


Figure 3.8 Cr(VI) adsorption capacity versus shaker speed (initial chromium concentration:  $3.5 \text{ mg.L}^{-1}$ , SRKF dose:  $0.4 \text{ g.L}^{-1}$ , pH: 7, particle size:  $0.425 \text{ mm}$ , and contact time: 120 min.)

### 3.4.3 Contact time effect

The effect of contact time on Cr (VI) adsorption and its influence on the soil rich in kaolinite-ferrinatrinite was studied by continuously increasing the contact time from 10 to 120 minutes (Figure 3.9). The contact time increased upto 40 minutes, with the increased adsorptive removal of adsorbate. After 40 minutes (the equilibrium point), the adsorption removal of adsorbate remained constant, due to the exhaustion of the binding sites (Akiode et al., 2015; Dehghani et al., 2015; Kuppusamy et al., 2016).

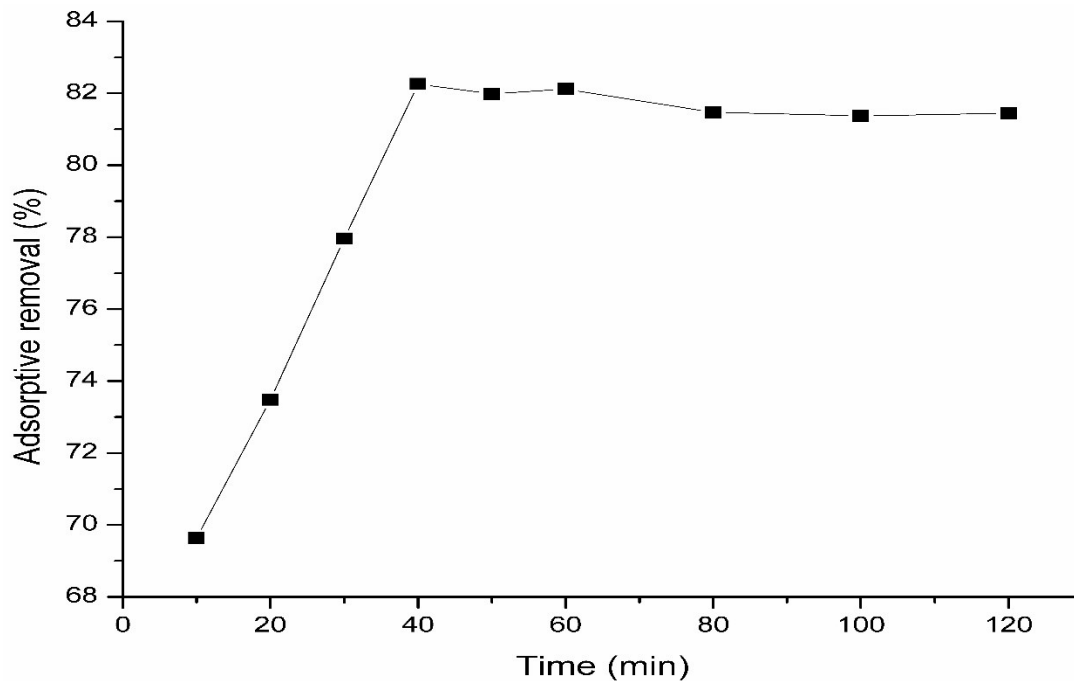


Figure 3.9 Cr(VI) adsorptive removal versus time (shaking speed: 150 rpm, initial chromium concentration:  $3.5 \text{ mg.L}^{-1}$ , adsorbent dose:  $0.4 \text{ g.L}^{-1}$ , pH: 7 and particle size: 0.425 mm)

The rate of adsorption of chromium (VI) ion was fast up to 40 minutes. This was due to soil rich in kaolinite-ferrinatrinite surface having many open spaces that could lead to strong attraction forces between Cr(VI) and adsorbent which was found to be in agreement with an observation of Wanees et al. (2012). Adsorptive removal of chromium (VI) from 10 and 40 minutes was rapidly and fast due to highly increased adsorption sites (Mekonnen et al., 2015). After 40 minutes, there was no change in the rate of adsorption of Cr(VI) on SRKF. This showed that SRKF had no sufficient open

space since the bulk solution increased. This finding was found to be in agreement with the finding of another study by Workneh et al. (2014). The adsorption capacity was high for a short period of time (40 minutes) on SRKF adsorbent. The reason for this could be due to the open space, clay texture, lower bulk density, and small particle size. This finding is in agreement with the finding repeated by Babel and Opiso (2007) and Dehghani et al. (2015).

#### **3.4.4 pH effect**

The amount of chromium (VI) removed was dependent on pH (Figure 3.10). The effect of pH on chromate removal capacity and adsorption efficiency were shown in Figure 3.10. The chromate removal capacity increased with the decreasing pH values, namely, from a pH value of 8 to a pH value of 2, and from a low at pH 2 to pH 8, which is from 98.3% to 89.2%, while the adsorption capacity decreased with increasing pH values, namely, at pH 2 = 0.097 mg.g<sup>-1</sup> and at pH 6 = 0.089 mg.g<sup>-1</sup>. The adsorption efficiency was high at the pH of 2 which is 0.097 mg.g<sup>-1</sup> while the percentage of chromate removed was found to be 98.3% (Figure 3.10).

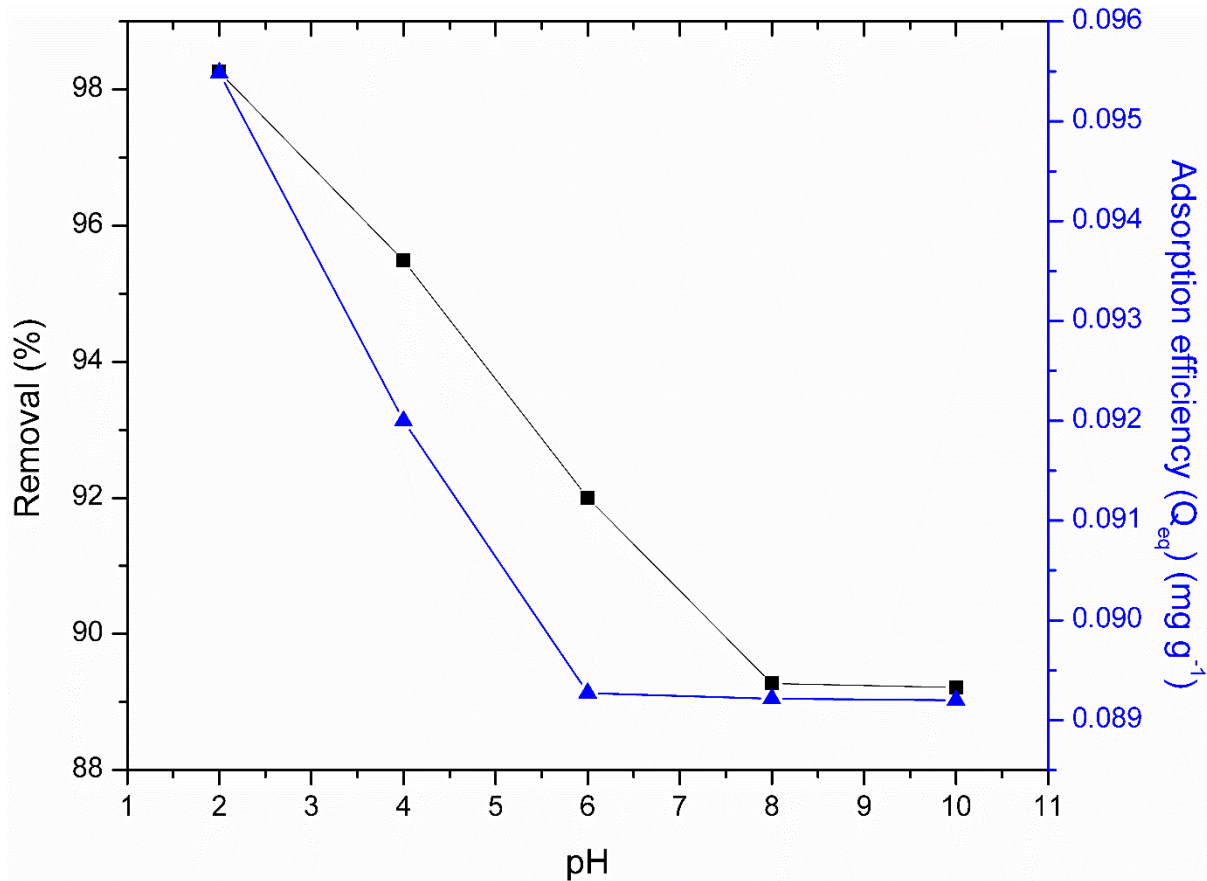
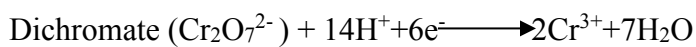


Figure 3.10 Cr(VI) removal (square) and adsorption efficiency (triangle) versus pH (initial chromium concentration: 3.5 mg.L<sup>-1</sup>, SRKF dose: 0.4 g.L<sup>-1</sup>, contact time: 40min, particle size: 0.425 mm, shaking speed: 150 rpm)

The pH value is crucial to control adsorption of metal in between solid and water interface. Figure 3.10 shows that Cr (VI) ions removal occurred at a pH of 2 within a contact time 40 minutes. This might be due to the reduction of chromium (VI) to chromium (III).



Many H<sup>+</sup> ions were presented at low pH value. The high concentration of H<sup>+</sup> neutralize the negative charge ions by diffusion of dichromate ions. This observation was similar to the finding reported by Yarkandi (2014). The percentage of chromate removal was increased from 89.2 to 98.3% by decreasing the solution pH value from 8 to 2. The value of pH decreases with an increase in HCrO<sub>4</sub> concentration. This shows that the attraction of anion high at both of the low crystalline Oxy-

hydroxides of Al and Fe and to crystalline oxides of Al and Fe. This observation also agrees with the finding of Otero et al. (2015). The increase of the adsorption efficiency of chromate in the pH value ranges from 6 to 2. This could be showed that the electrostatic attraction between chromate ions and the positive surface charge of the adsorbent (Akiode et al., 2015). The adsorbent could develop a positive surface charge due to the dissociation of metal hydroxide complexes at the solid-solution interface formed by metal oxides mainly Fe, Al, and Si, this finding agrees with an investigation by Zachara et al. (1987). In contrast, the efficiency of chromate removal decreased at an initial solution was  $\text{pH} > 2$ . The decrease in the adsorption of chromate with the increase in the pH of the solution beyond 2 might be due to the negative surface charge of the adsorbent and surface adjustment with  $\text{OH}^-$  ions that may cause repulsion between the hydroxyl ions and the chromate ions according to the study of Alemayehu et al. (2012). In addition, the decreased adsorptive removal of Cr(VI) with increasing of pH value implies the repulsion between  $\text{OH}^-$  ions and the negatively-charged chromium ions (Dehghani et al., 2015).

The pH value was decreased with increased positive charge in the SRKF due to protonization process. The adsorption chromium (VI) ion increased with increasing pH values. The pH value affects adsorption process on the surface of Al and Fe oxides. The decrease in  $\text{HCr}_2\text{O}_7^-$  in the solution resulted in increased pH values due to the  $\text{Cr}_2\text{O}_7^{2-}$  concentration. This implies that the amount of  $\text{Cr}_2\text{O}_7^{2-}$  concentration might describe the adsorption of chromium (VI) ion. The trends positively agreed with the finding reported by Guo et al. (2008) and Zhong et al. (2014).

### **3.4.5 Adsorbent dose effect**

The effect adsorbent dose variation on the chromate removal was shown in Figure 3.11. The amount of chromate removed increased from 84.1% to 94.2% as the SRKF amount increased from 1 to 3.5  $\text{g.L}^{-1}$ . The dose amount of adsorbent increased with the increasing of adsorptive removal percentage of Cr(VI) (Azouaou et al., 2010). This showed that the availability of adsorbed space for metal ion. The capacity of chromate adsorption decreased as the SRKF dose increased beyond 3.5  $\text{g.L}^{-1}$  (Figure 3.11). Hence, the minimum dose for maximum chromate removal was 3.5  $\text{g.L}^{-1}$  and 3.5  $\text{g.L}^{-1}$  of the adsorbent was considered for further adsorption experiments in this study.

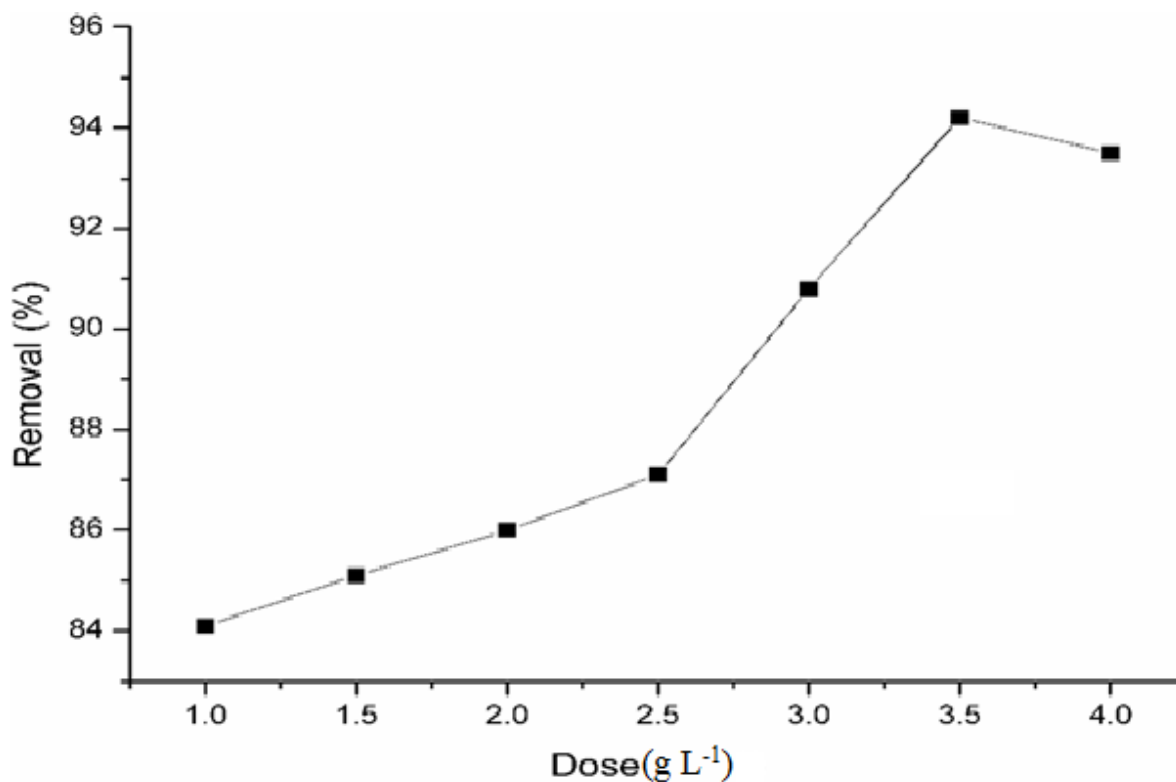


Figure 3.11 Cr(VI) removal capacity of adsorbent dose (initial chromium concentration: 3.5 mg.L<sup>-1</sup>, time: 40 min, pH: 2, speed of shaker: 150 rpm, the adsorbent particle size: 0.425 mm)

### 3.4.6 Initial chromate concentration effect

The graphical presentation of the chromate adsorption efficiency of the chromium (VI) concentration is given in Figure 3.12. The result indicated that the initial chromate concentration increased from 1 mg.L<sup>-1</sup> to 2 mg.L<sup>-1</sup> as the removal capacity of chromate increased from 99.89% to 99.92%. At 2 mg.L<sup>-1</sup>, the chromium (VI) concentration of sufficient adsorbent / SRKF sites was available for adsorption of chromium(VI) ions due to the larger number of the ions at lower concentration (Akiode et al., 2015).

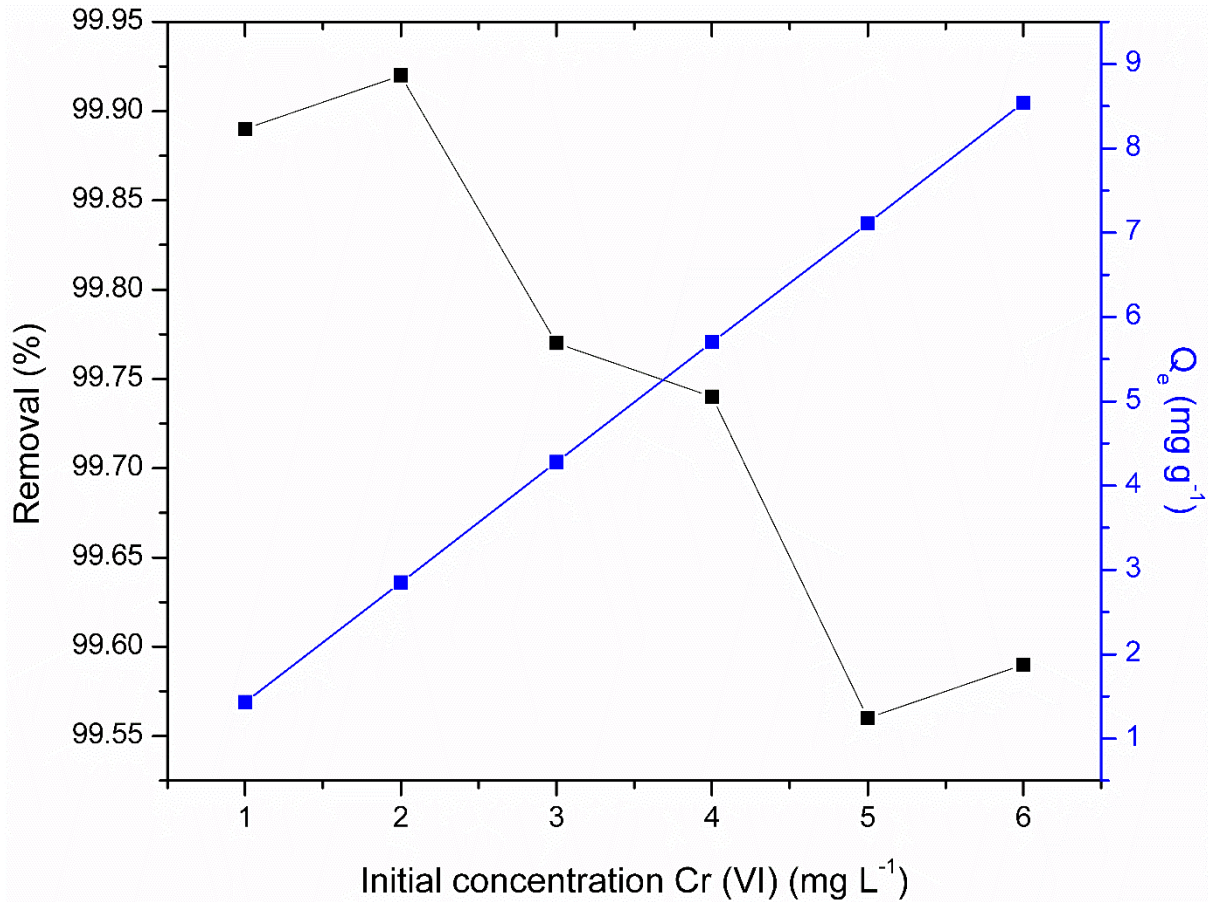


Figure 3.12 Cr(VI) removal and adsorption efficiency versus initial concentration (SRKF dose: 3.5 g.L<sup>-1</sup>, pH: 2, time: 40 minutes, shaking speed: 150 rpm, particle size: 0.425 mm)

### 3.4.7 Particle sizes effect

Adsorptive removal of chromium (VI) from wastewater decreased with increasing the particle size of SRKF that is from 98.8% to 92.5% with 0.075 mm to 4.750 mm, respectively. The small particle (0.075 mm) adsorbent shows that it has a large surface area as well as a large number of porosity used for high Cr(VI) removal from contaminated water and also decreased external mass effect (Alemayehu et al., 2011). Therefore, 0.075 mm diameter of particle size adsorbent was selected for the rest of the batch adsorption experiment.

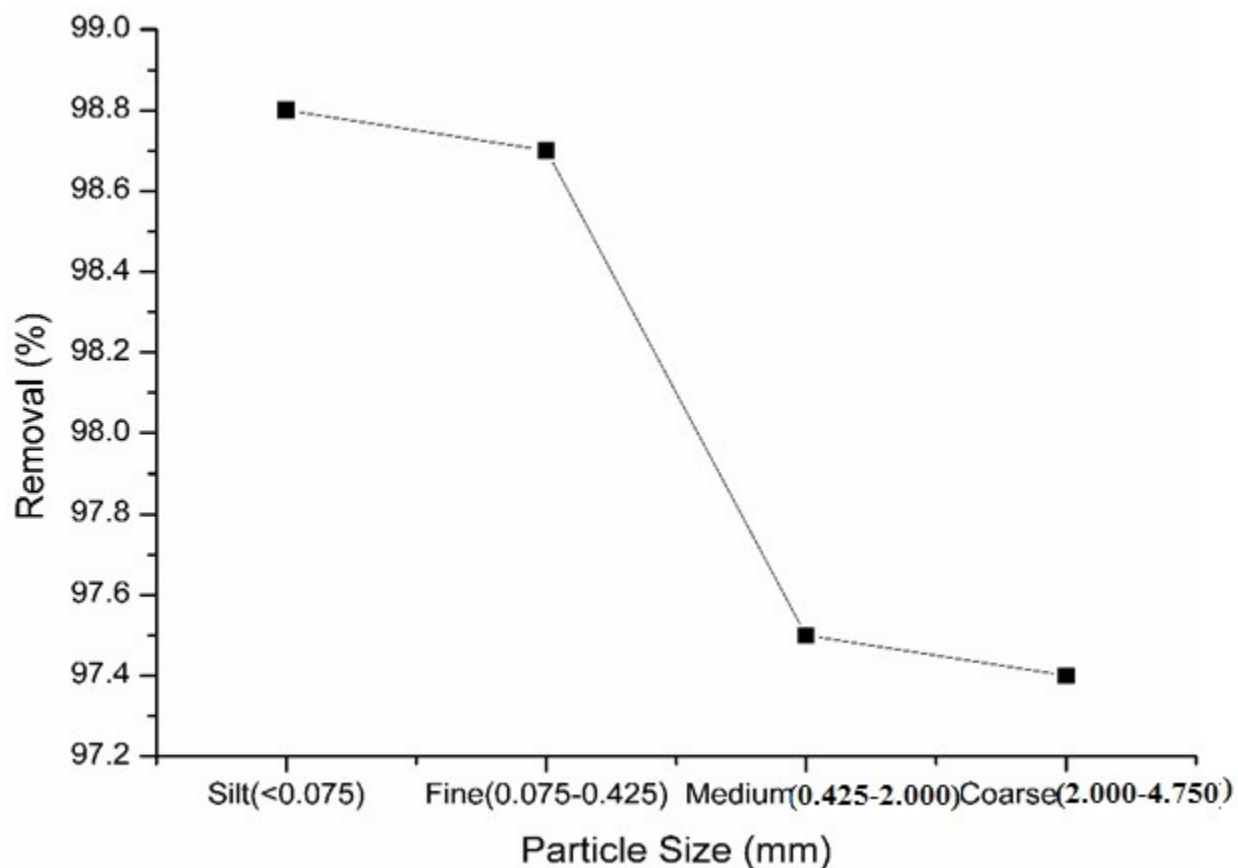


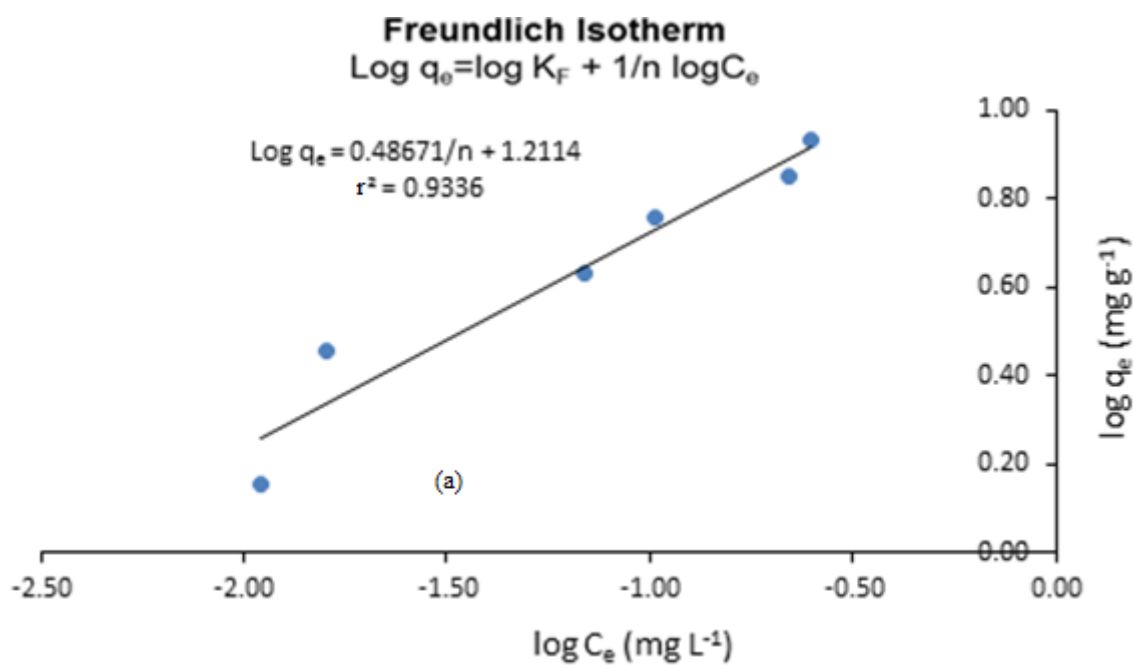
Figure 3.13 Cr(VI) removal efficiency versus particle size (adsorbent dose: 3.5 g.L<sup>-1</sup>, pH: 2, time: 40 min, speed of shaker: 150 rpm and initial concentration: 2 mg.L<sup>-1</sup>)

### 3.4.8 Adsorption isotherm

The equilibrium adsorption experiment was carried out at a pH of 2, varying the chromate amount of 2 mg.L<sup>-1</sup> using 3.5 g.L<sup>-1</sup> of the soil rich in kaolinite-ferrinatriite. The results of the chromate adsorption isotherm are given in Figure 3.14. The Freundlich and Langmuir isotherm parameters obtained from the linear equation of these models are given in Table 3.6. The values of the  $r^2$  for the Freundlich and Langmuir isotherms were 0.9336 and 0.9139, respectively. Dimensionless constant for soil rich in kaolinite-ferrinatriite was between 0 and 1 this was showing a favorable adsorption process.

Table 3.6 Langmuir and Freundlich isotherm for adsorption of chromium (VI) using SRKF

| SRKF | Dose<br>(g.L <sup>-1</sup> ) | Ci<br>(mg.L <sup>-1</sup> ) | Duplicate |      | C <sub>e</sub><br>(mg.L <sup>-1</sup> ) | Log<br>C <sub>e</sub> | Vol.<br>(L) | Q <sub>e</sub><br>(mg.g <sup>-1</sup> ) | Log            |       | Ce/Qe<br>(mg.L <sup>-1</sup> ) |      |
|------|------------------------------|-----------------------------|-----------|------|---|-----------------------|-------------|---|----------------|-------|--------------------------------|------|
|      |                              |                             | A         | B    |   |                       |             |   | q <sub>e</sub> | 1/Ce  |                                |      |
|      | 0.35                         | 10.00                       | 0.01      | 0.02 | 0.01                                    | -1.96                 | 0.10        | 1.43                                    | 0.15           | 90.91 | 0.70                           | 0.01 |
|      | 0.35                         | 20.00                       | 0.01      | 0.02 | 0.02                                    | -1.80                 | 0.10        | 2.85                                    | 0.46           | 62.50 | 0.35                           | 0.01 |
|      | 0.35                         | 30.00                       | 0.07      | 0.07 | 0.07                                    | -1.16                 | 0.10        | 4.28                                    | 0.63           | 14.60 | 0.23                           | 0.02 |
|      | 0.35                         | 40.00                       | 0.10      | 0.10 | 0.10                                    | -0.99                 | 0.10        | 5.70                                    | 0.76           | 9.71  | 0.18                           | 0.02 |
|      | 0.35                         | 50.00                       | 0.20      | 0.24 | 0.22                                    | -0.66                 | 0.10        | 7.11                                    | 0.85           | 4.52  | 0.14                           | 0.03 |
|      | 0.35                         | 60.00                       | 0.23      | 0.27 | 0.25                                    | -0.61                 | 0.10        | 8.54                                    | 0.93           | 4.04  | 0.12                           | 0.03 |



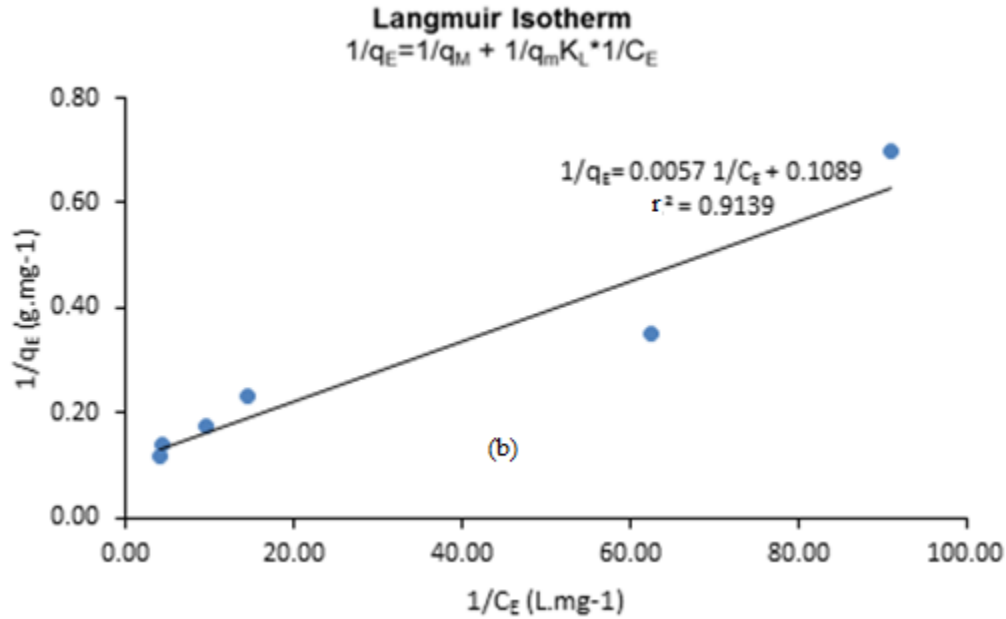


Figure 3.14 Freundlich (a) and Langmuir (b) isotherms for chromate adsorption using SRKF (initial chromate concentration: 2 mg.L<sup>-1</sup>, SRKF dose: 3.5 g.L<sup>-1</sup>, pH: 2, time: 40 min, speed of shaker: 150 rpm, particle size: 0.075 mm)

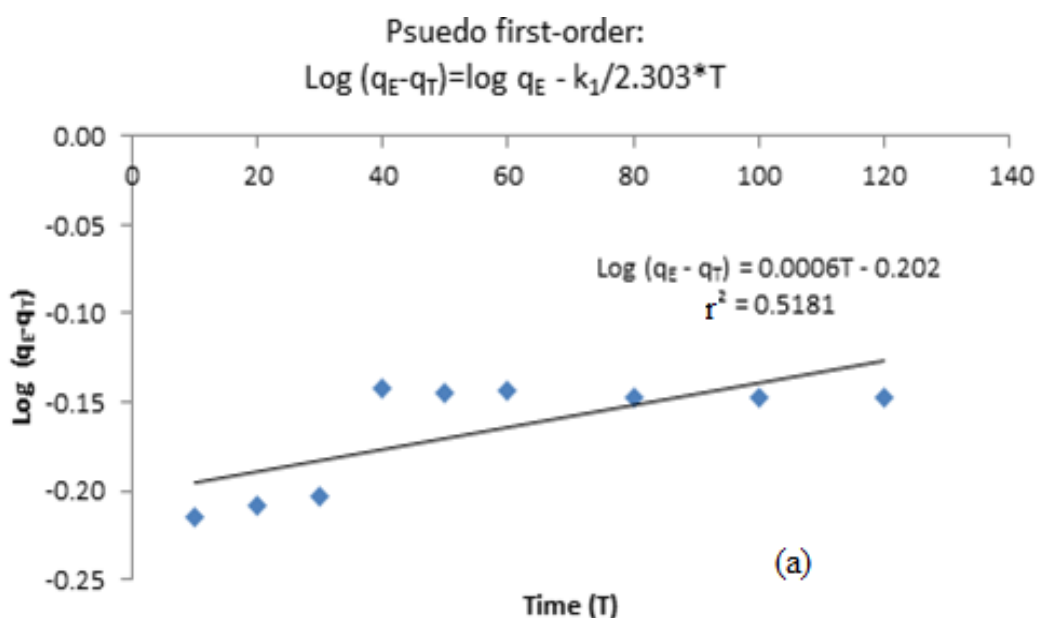
Table 3.7 Linear estimated isotherm models and its constant value for chromate adsorption

| Temp.<br>°C | Freundlich Isotherm:         |        |                | Langmuir Isotherm:             |             |                |
|-------------|------------------------------|--------|----------------|--------------------------------|-------------|----------------|
|             | $K_F$ (mg. g <sup>-1</sup> ) | 1/n    | r <sup>2</sup> | $1/q_M$ (mg. g <sup>-1</sup> ) | $1/q_M k_L$ | r <sup>2</sup> |
| 22±2        | 1.2114                       | 0.4867 | 0.9336         | 0.1089                         | 0.0057      | 0.9139         |

### 3.4.9 Adsorption kinetics

In order to state the kinetics of the chromium (VI) adsorption, the parameters for the adsorption method were carried out for contact time 10, 20, 30, 40, 50, 60, 80, 100 and 120 minutes by

assessing the percent of removal of chromium (VI) by soil rich in kaolinite-ferrinatriite. The equilibrium adsorption experiment was studied at pH 2 varying the chromate amount of 2 mg.L<sup>-1</sup> using 3.5 g.L<sup>-1</sup> of the soil rich in kaolinite-ferrinatriite at room temperature 22 ± 2°C. The results of the chromate adsorption kinetic are given in Figure 3.15. The psuedo-first and -second order kinetic parameters obtained from the linear equation of these models are showed in Table 3.8. The values of the r<sup>2</sup> for the psuedo first and second order kinetic were 0.5181 and 0.9985, respectively. Psuedo-second-order r<sup>2</sup> = 0.9985 is fitted model for SRKF.



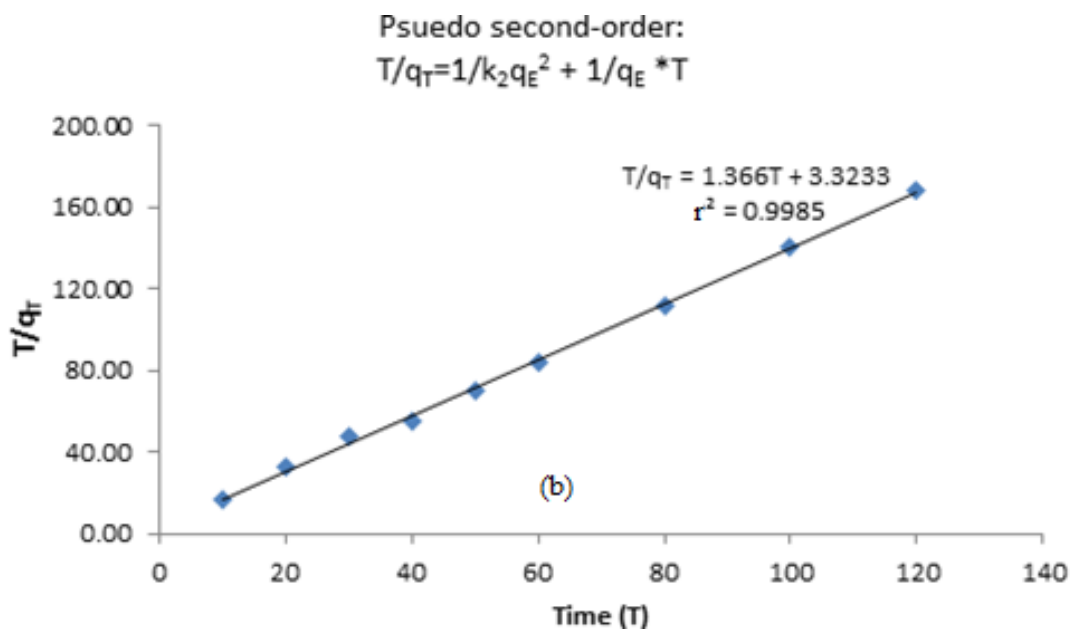


Figure 3.15 Psuedo-second and -first order for Cr(VI) adsorption onto SRKF (Cr(VI) = 2 mg.L<sup>-1</sup>; pH = 2; adsorbent dose = 3 g; time = 40min.; shaking speed=150 rpm and temp. 22 ± 2°C)

Table 3.8 Linear estimated of kinetic adsorption of chromium (VI) ions onto adsorbents

| Temp.<br>°C | Psuedo first-order:<br>Log (q <sub>E</sub> -q <sub>T</sub> ) = Log q <sub>E</sub> - k <sub>1</sub> /2.303*T |                       |                | Psuedo second-order:<br>T/q <sub>T</sub> = 1/k <sub>2</sub> q <sub>E</sub> <sup>2</sup> + 1/q <sub>E</sub> *T |                  |                |
|-------------|---|-----------------------|----------------|---|------------------|----------------|
|             | log q <sub>E</sub>  | k <sub>1</sub> /2.303 | r <sup>2</sup> | 1/k <sub>2</sub> q <sub>E</sub> <sup>2</sup>  | 1/q <sub>E</sub> | r <sup>2</sup> |
| 22±2        | 0.202   | 0.0006                | 0.5181         | 3.3233  | 1.366            | 0.9985         |

### 3.4.10 Desorption study

Figure 3.16 shows the percentage of chromate desorbed by different concentration of the NaOH solution. The result indicated that the percentage of chromate desorbed increased from 35.13% to 82.16% as the concentration of NaOH increased from 0.01 to 0.5 M in the solution. This indicates that when NaOH is at about 0.5 M concentration the adsorbent materials exhausted can be regenerated for reuse. This finding agrees with the finding repeated by Hu et al., (2011), Singh et al., (2011), Albadarin et al., (2012). This indicates that when NaOH is at about 0.5 M concentration

the adsorbent materials exhausted can be regenerated for reuse. This finding agrees with the finding repeated by Hu et al., (2011), Singh et al., (2011), and Albadarin et al., (2012).

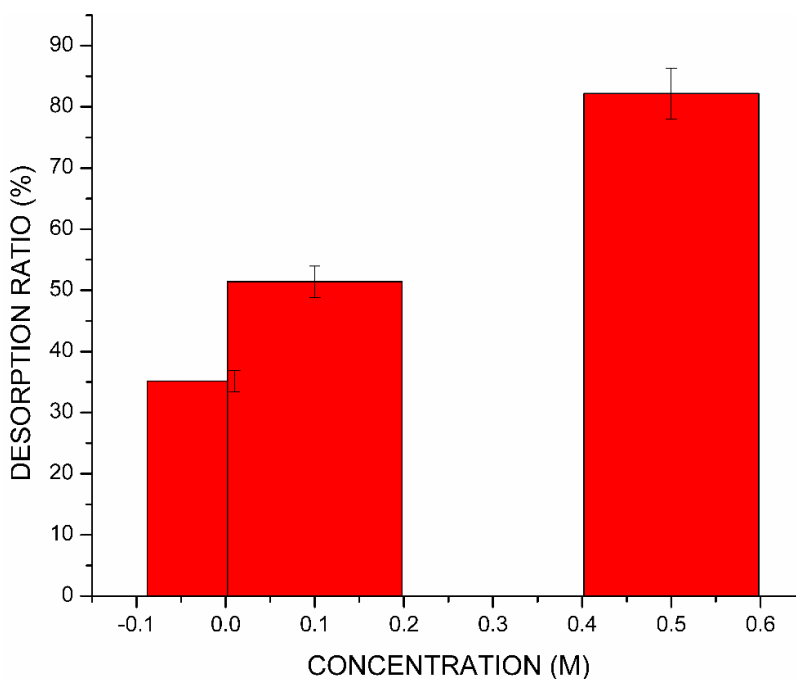


Figure 3.16 Desorption of Cr(VI) from soil rich in kaolinite-ferrinatrinite

### 3.4.11 Removal of chromate from real wastewater

The characteristics of the wastewater sample collected from Friendship Tannery PLC factory, East Showa Zone are given in Table 3.9. The wastewater contained  $0.98 \text{ mg.L}^{-1}$  chromate; this  $0.98 \text{ mg.L}^{-1}$  chromate was reduced to  $0.035 \text{ mg.L}^{-1}$  by 150 rpm shaker speed,  $3.5 \text{ g.L}^{-1}$  of the soil rich in kaolinite-ferrinatrinite within 40 min of contact time at  $\text{pH} = 2$  and  $<0.075 \text{ mm}$  particle size of the sample. This means that 96.4% of the  $0.98 \text{ mg.L}^{-1}$  chromate concentration of the wastewater was removed by  $3.5 \text{ g.L}^{-1}$  of the adsorbent. This finding similar to the finding of Rajesh, et al, (2011).

Table 3.9 Physicochemical characteristics of wastewater from Friendship Tannery PLC factory

| Composition | Cr <sup>+6</sup><br>(mg.L <sup>-1</sup> ) | PO <sub>4</sub> <sup>3-</sup><br>(mg.L <sup>-1</sup> ) | NO <sub>3</sub> <sup>-</sup><br>(mg.L <sup>-1</sup> ) | Cl <sup>-</sup><br>(mg.L <sup>-1</sup> ) | DO<br>(mg.L <sup>-1</sup> ) | COD<br>(mg.L <sup>-1</sup> ) | BOD<br>(mg.g <sup>-1</sup> ) | pH   | EC<br>(μs.cm <sup>-1</sup> ) | Turbidity<br>(NTU) |
|-------------|---|--|---|--|-----------------------------|------------------------------|------------------------------|------|------------------------------|--------------------|
| Value       | 0.98                                      | 15.91  | 1.80  | 819.30                                   | 3.45                        | 463.5                        | 941.40                       | 7.66 | 6.19                         | 14.56              |

Source: Laboratory work (refer to the methods in section 5.3.2)

### 3.4.12 Low-cost adsorbents to compared with soil rich in kaolinite-ferrinatrinite

Low-cost adsorbents as compared with naturally available materials or adsorbents, and are defined as waste products from agriculture, industries, and domestic use. These cheap adsorbents can be less expensive (Renge et al., 2012), affordable (Lim and Aris, 2014), environmentally-friendly as well as abundant (Kurniawan et al., 2006b; Kırbıyık et al., 2012; Lim and Aris, 2014) and cheap (Kurniawan et al., 2006a; Carvalho et al., 2011). They have high treatment efficiency for the removal of toxic chemicals (Tajrishy, 2012). These cheap adsorbents are simply gathered from agricultural waste, industrial byproducts, clay soil, food waste and seafood (Bailey et al., 1999; Jain et al., 2013). Hence, they are economically affordable and copiously available (Li et al., 2007; Kaushal and Upadhyay, 2014) for example, bagasse fly ash adsorbent can be available at US\$0.002 kg<sup>-1</sup> includes the transport payment to the adsorption processing site, energy used and other factors to be used as adsorbent. The final, total cost of this bagasse fly ash is around 0.009 US dollars per kilogram (Srivastava S, 1995).

Some low-cost adsorptive materials serve as a scavenger of contaminants by absorbing anions and cations. For example, clay is an environmentally suitable material for wastewater treatment containing heavy metals (Sari et al., 2007; Bhattacharyya and Gupta, 2008; Öncel, 2008) and it is an excellent adsorbent material, and also 20 times cheaper than activated carbon (Kaushal and Upadhyay, 2014).

In Ethiopia, soil rich in kaolinite-ferrinatrinite is, on average, about birr 0.15 (15 cents) per kilogram, including the transportation costs. The SRKF adsorbent is US \$ 500 kg<sup>-1</sup> (five hundred dollars per

kilogram) times cheaper than some adsorbent such as chitosan at US\$16 per kilogram (Babel and Kurniawan, 2003).

### **3.4.13 Soil rich in kaolinite-ferrinatriite removal time compared with other adsorbents**

The SRKF prepared in this study had a comparatively high adsorptive removal efficiency of chromium (VI) with short period of contact time compared with other adsorbents reviewed in the literature such as adsorptive removal of Cr(VI) by using soil rich in kaolinite-ferrinatriite : They have a contact time (minutes) that is 10 times earlier than Fe<sup>0</sup> nanorods modified with chitosan anodic alumina, a 2.5 times earlier contact time (minutes) than a graphene sand composite, a nine times earlier contact time (minutes) than magnetic graphene oxide via ethylenediamine and a 1.5 times earlier contact time (minutes) than SWCNTS and MWCNTS (Liu et al. 2011; Hamadi *et al.*, 2011; Hamadi *et al.*, 2015; Liu *et al.*, 2011; Dehghani et al., 2015).

## **3.5 Conclusions**

If chromium (VI) is present in the water and the level is more than the permitted limit, it is toxic and could lead to many health problems. The present study demonstrated the adsorptive efficiency of soil rich in kaolinite-ferrinatriite for removal technique for Cr(VI) ions from industrial wastewater. The different effect of batch adsorption, such as solution pH, contact time and the initial concentration of Cr(VI), were evaluated. The adsorption chromium (VI) on SRKF was high at a pH 2 of contact time 40 min and the initial concentration of Cr(VI) = 2 mg.L<sup>-1</sup>. Freundlich and Langmuir isotherm was examined in this study at a room temperature of 22 ± 2°C. Therefore, this behavior suggested that SRKF could be an interesting and applicable low-cost adsorbent technology for Cr(VI) removal from contaminated industrial wastewater.

## **3.6 References**

Ahluwalia, S and Goyal, D. 2007. Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresource Technology* 98: 2243-2257.

- Akiode, O, Idowu, M, Omeike, S and Akinwunmi, F. 2015. Adsorption and kinetics studies of Cu (II) ions removal from aqueous solution by untreated and treated sugarcane bagasse. *Global Nest Journal* 17: 583-593.
- Alaa, H and Mena, M. 2015. Batch experiment and adsorption isotherm of phosphate removal by using drinking water treatment sludge and red mud. *International Journal of Advanced Research in Science, Engineering and Technology* 2: 557-571.
- Albadarin, A, Mangwandi, C, Ala'a, H, Walker, G, Allen, S and Ahmad, M. 2012. Kinetic and thermodynamics of chromium ions adsorption onto low-cost dolomite adsorbent. *Chemical Engineering Journal* 179: 193-202.
- Albarelli, J, Rabelo, R, Santos, D, Beppu, M and Meireles, M. 2011. Effects of supercritical carbon dioxide on waste banana peels for heavy metal removal. *The Journal of Supercritical Fluids* 58: 343-351.
- Alemayehu, D, Singh, S and Tessema, D. 2012. Assessment of the adsorption capacities of fired clay soils from Jimma (Ethiopia) for the removal of Cr (VI) from aqueous solution. *Universal Journal of Environmental Research and Technology* 2: 411-420.
- Alemayehu, E, Thiele-Bruhn, S and Lennartz, B. 2011. Adsorption behaviour of Cr (VI) onto macro and micro-vesicular volcanic rocks from water. *Separation and Purification Technology* 78: 55-61.
- Alfarra, R, Ali, N and Yusoff, M. 2014. Removal of heavy metals by natural adsorbent: a review. *International Journal of Biosciences* 4: 130-139.
- Aravind, J, Kanmani, P, Devisri, A, Dhivyalakshmi, S and Raghavprasad, M. 2015. Equilibrium and kinetic study on chromium (VI) removal from simulated waste water using gooseberry seeds as a novel biosorbent. *Global Journal of Environmental Science and Management* 1: 233-244.
- Aravind, J, Muthusamy, S, Sunderraj, S, Chandran, L and Palanisamy, K. 2013. Pigeon pea (*Cajanus cajan*) pod as a novel eco-friendly biosorbent: a study on equilibrium and kinetics of Ni (II) biosorption. *International Journal of Industrial Chemistry* 4: 25-32.
- Atun, G, Sheldrick, W and Muhler, M. 2003. Adsorptive removal of methylene blue from colored effluents on fuller's earth. *Journal of Colloid and Interface Science* 261: 32-39.

- Azouaou, N, Sadaoui, Z, Djaafri, A and Mokadden, H. 2010. Adsorption of cadmium from aqueous solution onto untreated coffee grounds: equilibrium, kinetics and thermodynamics. *Journal of Hazardous Materials* 184: 126-134.
- Babel, S and Kurniawan, T. 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials* 97: 219-243.
- Babel, S and Kurniawan, T. 2004. Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere* 54: 951-967.
- Babel, S and Opiso, E. 2007. Removal of Cr from synthetic wastewater by sorption into volcanic ash soil. *International Journal of Environmental Science and Technology* 4: 99-107.
- Bailey, S, Olin, T, Bricka, R and Adrian, D. 1999. A review of potentially low-cost sorbents for heavy metals. *Water Research* 33: 2469-2479.
- Balasubramanian, S and Pugalenti, V. 1999. Determination of total chromium in tannery waste water by inductively coupled plasma-atomic emission spectrometry, flame atomic absorption spectrometry and UV-visible spectrophotometric methods. *Talanta* 50: 457-467.
- Bhatnagar, A, Pudasainee, D, Chung, H, Kim, S, Kim, H, Lee, G, Min, B and Jeon, B. 2008. Vanadium removal from water by waste metal sludge and cement immobilization. *Chemical Engineering Journal* 144: 197-204.
- Bhattacharyya, K and Gupta, S. 2008. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. *Advances in Colloid and Interface Science* 140: 114-131.
- Bouyoucos, G. 1962. Hydrometer method improvement for making particle size analysis of soils. *Agronomy Journal* 54: 179-186.
- Carvalho, J, Araujo, J and Castro, F. 2011. Alternative low-cost adsorbent for water and wastewater decontamination derived from eggshell waste: an overview. *Waste and Biomass Valorization* 2: 157-167.
- Chapman, H. 1965. Cation Exchange Capacity. In: C.A. Black, (Eds.), *Methods of soil analysis. agronomy* 9, Am. Soc. Agro. Inc., Madison, Wisconsin, pp: 891-901.

- Chen, S, Yue, Q, Gao, B, Li, Q and Xu, X. 2011. Removal of Cr(VI) from aqueous solution using modified corn stalks: characteristic, equilibrium, kinetic and thermodynamic study. *Chemical Engineering Journal* 168: 909-917.
- Dehghani, M, Taher, M, Bajpai, A, Heibati, B, Tyagi, I, Asif, M, Agarwal, S and Gupta, V. 2015. Removal of noxious Cr(VI) ions using single-walled carbon nanotubes and multi-walled carbon nanotubes. *Chemical Engineering Journal* 279: 344-352.
- Doke, K and Khan, E. 2017. Equilibrium, kinetic and diffusion mechanism of Cr (VI) adsorption onto activated carbon derived from wood apple shell. *Arabian Journal of Chemistry* 10: 252-260.
- Fufa, F, Alemayehu, E and Lennartz, B. 2013. Defluoridation of groundwater using termite mound. *Water, Air and Soil Pollution Journal* 224: 1-15.
- GSOE. 2011. Opportunities for kaolin resource development in Ethiopia, Geological Survey of Ethiopia. Addis Ababa, Ethiopia
- Guo, X, Zhang, S and Shan, X. 2008. Adsorption of metal ions on lignin. *Journal of Hazardous Materials* 151: 134-142.
- Gupta, P, Kumar, P and Singh, N. 2015. Adsorption of copper metal by living *Aspergillus niger* L. biomass. *International Journal of Environmental Sciences* 5: 1122-1132.
- Hamadi, N, Chen, X, Farid, M and Lu, M. 2001. Adsorption kinetics for the removal of chromium (VI) from aqueous solution by adsorbents derived from used tyres and sawdust. *Chemical Engineering Journal* 84: 95-105.
- Hokkanen, S, Bhatnagar, A, Repo, E, Lou, S and Sillanpää, M. 2016. Calcium hydroxyapatite microfibrillated cellulose composite as a potential adsorbent for the removal of Cr (VI) from aqueous solution. *Chemical Engineering Journal* 283: 445-452.
- Hu, X, Wang, J, Liu, Y, Li, X, Zeng, G, Bao, Z, Zeng, X, Chen, A and Long, F. 2011. Adsorption of chromium (VI) by ethylenediamine-modified cross-linked magnetic chitosan resin: isotherms, kinetics and thermodynamics. *Journal of Hazardous Materials* 185: 306-314.
- Jain, M, Garg, V and Kadirvelu, K. 2013. Chromium removal from aqueous system and industrial wastewater by agricultural wastes. *Bioremediation Journal* 17: 30-39.
- Kan, C, Ibe, A, Rivera, K, Arazo, R and de Luna, M. 2017. Hexavalent chromium removal from aqueous solution by adsorbents synthesized from groundwater treatment residuals. *Sustainable Environment Research* 27:163-167

- Kaushal, R and Upadhyay, K. 2014. Treatability study of low cost adsorbents for heavy metal removal from electroplating industrial effluent: a review. *International Journal of ChemTech Research* 6: 1446-1452.
- Kırbıyık, Ç, Kılıç, M, Çepelioğullar, Ö and Pütün, A. 2012. Use of sesame stalk biomass for the removal of Ni (II) and Zn (II) from aqueous solutions. *Water Science and Technology Journal* 66: 231-238.
- Kuppusamy, S, Thavamani, P, Megharaj, M, Venkateswarlu, K, Lee, YB and Naidu, R. 2016. Oak (*Quercus robur*) Acorn Peel as a low-cost adsorbent for hexavalent chromium removal from aquatic ecosystems and industrial effluents. *Water, Air and Soil Pollution Journal* 227: 1-11.
- Kurniawan, T, Chan, G, Lo, W and Babel, S. 2006a. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Science of the Total Environment Journal* 366: 409-426.
- Kurniawan, T, Chan, G, Lo, W and Babel, S. 2006b. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Science of the Total Environment Journal* 366: 409-426.
- Li, Q, Zhai, J, Zhang, W, Wang, M and Zhou, J. 2007. Kinetic studies of adsorption of Pb (II), Cr (III) and Cu (II) from aqueous solution by sawdust and modified peanut husk. *Journal of Hazardous Materials* 141: 163-167.
- Lim, A and Aris, A. 2014. A review on economically adsorbents on heavy metals removal in water and wastewater. *Reviews in Environmental Science and Bio/Technology* 13: 163-181.
- Lin, H, Rong, C, Jiu, B, Li, B, Yu, Q, Gan, L and Zhang, Z. 2018. Effects of chromium on pyrolysis characteristic of water hyacinth (*Eichornia crassipes*). *Renewable Energy Journal* 115: 676-684.
- Liu, C and Evett, J. 2003. Soil properties: testing, measurement, and evaluation, Banta Book Company, USA. ISBN:0-13-093005-9.: ISBN 0-13-093005-9.
- Liu, S, Chen, Y, De Zhang, L, Hua, G, Xu, W, Li, N and Zhang, Y. 2011. Enhanced removal of trace Cr (VI) ions from aqueous solution by titanium oxide-Ag composite adsorbents. *Journal of Hazardous Materials* 190: 723-728.
- Mathews, A and Zayas, I. 1989. Particle size and shape effects on adsorption rate parameters. *Journal of Environmental Engineering* 115: 41-55.

- Mathialagan, T and Viraraghavan, T. 2002. Adsorption of cadmium from aqueous solutions by perlite. *Journal of Hazardous Materials* 94: 291-303.
- Mekonnen, E, Yitbarek, M and Soreta, T. 2015. Kinetic and thermodynamic studies of the adsorption of Cr(VI) onto some selected local adsorbents. *South African Journal of Chemistry* 68: 45-52.
- Miao, M, Wang, Y, Kong, Q and Shu, L. 2016. Adsorption kinetics and optimum conditions for Cr (VI) removal by activated carbon prepared from luffa sponge. *Desalination and Water Treatment* 57: 7763-7772.
- Mishra, A, Dubey, A and S. Shinghal, S. 2015. Biosorption of chromium(VI) from aqueous solutions using waste plant biomass. *International Journal of Environmental Science and Technology* 12:1415–1426
- Moreno-Piraján, J and Giraldo, L. 2012. Heavy metal ions adsorption from wastewater using activated carbon from orange peel. *Journal of Chemistry* 9: 926-937.
- Öncel, M. 2008. Adsorption of copper (II) from aqueous solution by Beidellite. *Environmental Geology Journal* 55: 1767-1775.
- Otero, M, Cutillas-Barreiro, L, Nóvoa-Muñoz, J, Arias-Estévez, M, Fernández-Sanjurjo, M, Álvarez-Rodríguez, E and Núñez-Delgado, A. 2015. Cr(VI) sorption/desorption on untreated and mussel-shell-treated soil materials: fractionation and effects of pH and chromium concentration. *Solid Earth Journal* 6: 373-382.
- Pan, J, Jiang, J and Xu, R. 2014. Removal of Cr(VI) from aqueous solutions by Na<sub>2</sub> SO<sub>3</sub> and FeSO<sub>4</sub> combined with peanut straw biochar. *Chemosphere Journal* 101: 71-76.
- Panda, H, Tiadi, N, Mohanty, M and Mohanty, C. 2017. Studies on adsorption behavior of an industrial waste for removal of chromium from aqueous solution. *South African Journal of Chemical Engineering* 23: 132-138.
- Pehlivan, E and Cetin, S. 2009. Sorption of Cr (VI) ions on two Lewatit-anion exchange resins and their quantitative determination using UV-visible spectrophotometer. *Journal of Hazardous Materials* 163: 448-453.
- Rajesh, S, Anita, K, Rajender, K, Neeru Y, Narsi, R, Bishnoia, R and .Lohchaba K. 2011. Removal of sulphate, COD and Cr(VI) in simulated and real wastewater by sulphate reducing bacteria enrichment in small bioreactor and FTIR study. *Bioresource Technology Journal* 102: 667 – 682.

- Renge, V, Khedkar, S and Pandey Shraddha, V. 2012. Removal of heavy metals from wastewater using low cost adsorbents: a review. *Sciences Review Chemical Communications* 2: 580-584.
- Saifuddin, M and Kumaran, P. 2005. Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. *Electronic Journal of Biotechnology* 8: 43-53.
- Sanchooli Moghaddam, M, Rahdar, S and Taghavi, M. 2016. Cadmium removal from aqueous solutions using saxaul tree ash. *Iranian Journal of Chemistry and Chemical Engineering* 35: 45-52.
- Sari, A, Tuzen, M, Citak, D and Soylak, M. 2007. Equilibrium, kinetic and thermodynamic studies of adsorption of Pb (II) from aqueous solution onto Turkish kaolinite clay. *Journal of Hazardous Materials* 149: 283-291.
- Singh, S., Barick, K and Bahadur, D. 2011. Surface engineered magnetic nanoparticles for removal of toxic metal ions and bacterial pathogens. *Journal of Hazardous Materials* 192: 1539-1547.
- Srivastava, S, Yadav, I and Mohan, D. 1995. Removal of 2,4-dinitrophenol using bagasse fly ash-a sugar industry waste material. *Fresenius Environmental Bullent* 4: 550-557.
- States, U. 1992. EPA Preparation of soil sampling protocols : sampling techniques and strategies. environmental monitoring systems laboratory office of research and development, (July). 252: 1-169.
- Sultana, F, Uddin, M, Kabir, M, Sultana, N, Sikder, M and Rahman, S. 2016. Removal efficiency of chromium (VI) ions from aqueous solution by adsorption of rice husk and saw dust ash as a homogeneous composite. *International Journal of Environmental Sciences* 6: 987-993.
- Tajrishy, M. 2012. Wastewater production, treatment and use in Iran, presented at the second regional workshop of the project 'safe use of wastewater in agriculture', 16–18 May 2012, New Delhi:  
[http://www.ais.unwater.org/ais/mod/page/view.php?id\\_62](http://www.ais.unwater.org/ais/mod/page/view.php?id_62).
- Tang, L, Fang, Y, Pang, Y, Zeng, G, Wang, J, Zhou, Y, Deng, Y, Yang, G, Cai, Y and Chen, J. 2014. Synergistic adsorption and reduction of hexavalent chromium using highly uniform polyaniline–magnetic mesoporous silica composite. *Chemical Engineering Journal* 254: 302-312.

- Tare, V, Chaudhari, S and Jawed, M. 1992. Comparative evaluation of soluble and insoluble xanthate process for heavy metal removal from wastewaters. *Water Science and Technology Journal* 26: 237-246.
- USEPA. 2011. Ground water and drinking water , current drinking water standards, EPA 816-F-02.
- Van Reewijk, L. 1992. Procedures for soil analysis. (3rd Ed.). *International Soil Reference Center (ISRIC)*, Wageningen, Netherlands.
- Wanees, S, Monem, A, Adam, M and Mohamed, M. 2012. Adsorption studies on the removal of hexavalent chromium-contaminated wastewater using activated carbon and bentonite. *Chemistry Journal* 02: 95-105.
- Wang, H, Liu, Y, Zeng, G, Hu, X, Hu, X, Li, T, Li, H, Wang, Y and Jiang, L. 2014. Grafting of  $\beta$ -cyclodextrin to magnetic graphene oxide via ethylenediamine and application for Cr (VI) removal. *Carbohydrate Polymers Journal* 113: 166-173.
- Watson, J. 2007. Microbial feed additive. Google Patents.
- Workneh, A, Habtu, N and Beyene, H. 2014. Removal of hexavalent chromium from tannery wastewater using activated carbon primed from sugarcane bagasse: adsorption/desorption studies. *American Journal of Applied Chemistry* 2: 128-135.
- Yang, Z, Xiong, S, Wang, B, Li, Q and Yang, W. 2013. Cr (III) adsorption by sugarcane pulp residue and biochar. *Journal of Central South University* 20: 1319-1325.
- Yarkandi, N. 2014. Kinetic and isotherm of toxic hexavalent chromium adsorption onto natural adsorbent. *International Journal of Current Microbiology and Applied Sciences* 3: 1-15.
- Zachara, J, Girvin, D, Schmidt, R and Resch, C. 1987. Chromate adsorption on amorphous iron oxyhydroxide in the presence of major groundwater ions. *Environmental Science and Technology Journal* 21: 589-594.
- Zhong, Q, Yue, Q, Li, Q, Gao, B and Xu, X. 2014. Removal of Cu (II) and Cr (VI) from wastewater by an amphoteric sorbent based on cellulose-rich biomass. *Carbohydrate polymers Journal* 111: 788-796.

## 4. POTENTIAL OF COFFEE HUSK ASH FOR ADSORPTIVE REMOVAL OF Cr(VI) FROM INDUSTRIAL WASTEWATER DISCHARGE

### 4.1 Abstract

Hexavalent chromium is one of the environmental problem of the modern world. The removal of Cr(VI) from polluted water is crucial. This study examined the efficiency of Cr(VI) ion removal, using an aqueous solution of coffee husk ash (CHA). Batch experiment was performed to evaluate the effects of shaker speed, contact time, adsorbent dose, pH solution and initial concentration. Optimum condition for Cr(VI) removal were observed at shaker speed = 100 rpm, equilibrium time = 40 minutes, dosage of CHA =  $1.5\text{g.L}^{-1}$ , pH = 2 and initial Cr(VI) concentration =  $0.5\text{ mg.L}^{-1}$ . Adsorption of Cr(VI) followed pseudo second-order kinetics. Result showed that Freundlich's adsorption isotherm model better describe for the Cr(VI) adsorption onto coffee husk ash (CHA) with coefficient of determination ( $r^2$ ) of 0.9846. CHA is technically viable and promising method for removal of Cr(VI) from industrial wastewater discharge.

**Keywords:** *Adsorption; batch; chromium(VI); coffee husk ash; removal*

### 4.2 Introduction

The release of toxic chemicals from industrial wastewater into the environment degrades water quality and is hazardous threat to human beings, as well as, other living organisms such as aquatic life (Saifuddin and Kumaran, 2005; Pan et al., 2014; Sanchooli Moghaddam et al., 2016; Lin et al., 2018). Cr(VI) is generated from different industrial activities carried out in textile industries, leather tanning, electroplating, steel production, paint manufacturing, pulp processing, chromate preparation, electric and electronic components (Pan et al., 2013; Alfarra et al., 2014a; Sultana et al., 2016; Kan et al., 2017; Panda et al., 2017). According to United State Environmental Protection Agency (USEPA, 2011) Cr(VI) is the most top-prioritized poisonous pollutant (Tang et al., 2014). Chromium is found mostly in the form of trivalent chromium and hexavalent chromium. Chromium

(VI) is 100 times poisonous than chromium (III) when found on a surface and in ground water (Tang et al., 2014; Kan et al., 2017). According to the World Health Organization (WHO) the recommended maximum tolerable limit of chromium (VI) in wastewater discharged from industries is  $0.25 \text{ mg.L}^{-1}$  (Zhong et al., 2014). Thus, it is critical to find effective ways to remove chromium(VI) from industrial wastewater. Typical treatment technologies used to remove chromium from contaminated water include membrane separation, ion exchange, chemical reduction, adsorption, precipitation, reverse osmosis and electrocoagulation (Tang et al., 2014; Zhong et al., 2014; Sultana et al., 2016). Amongst all the treatment technologies, adsorption technique is one of the most feasible and promising technique, because of its wide raw material sources, low cost investment, high efficiency, effectiveness, flexibility in design and easy operation (Chen et al., 2011; Yang et al., 2013; Tang et al., 2014; Zhong et al., 2014; Sultana et al., 2016). As a result, looking for a suitable wastewater treatment technology using locally available natural materials that may be used in developing countries such as Ethiopia remains important issue to address. Among the natural adsorbents, coffee husk ash (CHA) would meet the conditions that has been established for wastewater treatment process due to coffee abundantly found in Ethiopia: coffee production coverage area is 700,000 ha and annual production is 350,000 tons per year (Kufa, 2012) and 517,084 tons per year (CSA, 2016/17) and suitable physical and chemical properties. The following section briefly presents the overall properties of coffee husk ash as well as its technical viability for industrial wastewater treatment methods.



Figure 4.1 Availability of major coffee growing areas in Ethiopia (Kufa, 2012)

The objective of the research was to investigate the efficiency of Cr(VI) ion removal from contaminated water, determine the adsorption of kinetics and the isotherms as well as the pH effect, contact time effect and dosage of the initial concentration of chromium(VI) by using low-cost coffee husk ash under a batch adsorption experiment.

### **4.3 Materials and Methods**

#### **4.3.1 Sample collection**

Coffee was abundantly found in Ethiopia (Kufa, 2012). Coffee husk was collected from four coffee wet milling plants in January 2015 from Jimma Zone, Oromial Regional National State and Southwest Ethiopia. The coffee husk from four wet milling plants were mixed in equal proportions to make a composite coffee husk sample. The composite sample was dried at  $105 \pm 5^\circ\text{C}$  for 3h. The coffee husk composite was ashed using a muffle furnace at  $700^\circ\text{C}$  for 4 hours (Xinyu et al. 2016). The samples were, then, stored in airtight plastic bottles for physicochemical analysis and for batch adsorption experiments.

#### **4.3.2 Physical characteristics**

The physical characteristics of coffee husk ash used for the present study was characterized at the Ethiopia Institute of Agricultural Research by document number: Ethiopian Institute of Agricultural Research (EIAR/F). 510-2 and effective date in February 2015. The laboratory analysis procedure of coffee husk ash parameters were determined as following: Electrical Conductivity (EC) was carried out using a EC meter in a 1:5 soil : water ratio, Cation Exchange Capacity (CEC) was measured at a soil pH of 7 after displacement by using 1 N ammonium acetate ( $\text{C}_2\text{H}_7\text{NO}_2$ ) method and thereafter estimated titrimetrically, pH was measured in water at a soil to water ratio of 1:2.5 and Organic Carbon (OC) of coffee husk ash was measured by the Walkley-Black method, (Bouyoucos, 1962; Chapman, 1965; Van Reewijk, 1992).

### 4.3.3 Chemicals

The stock solution of Cr(VI) was prepared by dissolving 2.828 g of  $K_2Cr_2O_7$  (FINKEM) in one liter of distilled water in volumetric flask to achieve concentration of  $1000 \text{ mg.L}^{-1}$ . The working solutions for batch adsorption experiment were diluted from the above stock solution. The UV-visible spectrophotometer was set with the equivalent dilution procedure as the experimental samples. 0.1 M NaOH and/or 0.1 M HCl used for the adjustment of the pH value of the adsorption experiments solution.

### 4.3.4 Cr(VI) ions adsorption

The batch adsorption set up experiment was carried out at  $22 \pm 2^\circ\text{C}$  at the Jimma University, Environmental Health Laboratory in 2016. Polyethylene plastic bottles were washed using 0.01M  $HNO_3$  and thoroughly distilled water. The adsorbent (CHA) was equilibrated by soaking with 0.01 M  $CaCl_2 \cdot 2H_2O$  for overnight (12 h) before the main experiments done the next day. Each set of the batch adsorptive experiment effect contains: duplicate trial with blank (only CHA) and control (only Cr(VI) ion). A 100 mL aqueous solution containing a known Cr(VI) ions concentration was added to a series of 300 mL plastic bottles for experiments and the pH adjusted. The desired dose of sample adsorbent was added and the bottles agitated at a fixed rpm on a Horizontal Thermostat Orbital shaker for a fixed contact time at a temperature of  $22 \pm 2^\circ\text{C}$ . Thereafter, the solid coffee husk ash was filtered by using Whatman filter paper. The pH value of the solution was adjusted with 0.1 N  $H_2SO_4$  or 0.1 N NaOH to get  $pH 1 \pm 0.3$  by adding 1 mL diphenylcarbazide in 50 mL. It then stood for 10 min for color development. Residual Cr(VI) ion concentration was transferred to 1 cm absorption cell and it determined using the UV-visible spectrophotometer made by HACH LANGE © (Model No: 5000). The average of duplicate measurements was reported.

### 4.3.5 Contact time effect

To fix the equilibrium of the contact time at which the adsorption was completed, the agitation time was varied from (10, 20, 30, 40, 50, 60, 80,100 and 120 minutes) until equilibrium was achieved. A known concentration of the adsorbate in aqueous solutions at desired pH was shaken with a desired amount of the adsorbent at 100 rpm for a predetermined contact time effect using the Horizontal Thermostat Orbital shaker. The value of the chromium (VI) adsorbed over the unit

mass of the adsorbent media, and the percentage adsorption was computed using equation 4.1 and 4.2 given below, respectively (Sanchooli Moghaddam et al., 2016).

$$q_t = \frac{(C_0 - C_t) * V}{M} \quad (4.1)$$

$$A = \frac{(C_0 - C_t)}{C_0} * 100 \quad (4.2)$$

Where

$q_t$  = value of Cr(VI) ions adsorbed at any time (min) ( $\text{mg}\cdot\text{g}^{-1}$ ),

$C_0$  = initial concentration Cr(VI) ions an any time ( $\text{mg}\cdot\text{L}^{-1}$ ),

$C_t$  = final concentration of Cr(VI) ions at any time (min) ( $\text{mg}\cdot\text{L}^{-1}$ ),

$V$  = amount of solution (L),

$M$  = mass of the CHA media used in the experiment (g) and

$A$  = percentage of chromium(VI) ions adsorbed (%)

#### 4.3.6 Adsorbent dose effect

To determine the optimum dose required for the reduction of average heavy metal concentration in the industrial wastewater to a desired level, different adsorbent doses ranging from (0.5, 1.0, 1.5, 2.0, 2.5, 3, 3.5 and 4.0  $\text{g}\cdot\text{L}^{-1}$ ) were separately added into an aqueous solution of known pH, containing the desired adsorbate concentration. The mixture was agitated at a 100 rpm (revolution per minute) for equilibrium contact time determined by time series experiments.

#### 4.3.7 Solution pH effect

The solution pH effect was investigated to fix the highest pH value for the highest adsorptive removal of heavy metal over the initial pH value varying from (2, 4, 6, 8 and 10) by allowing a known dose of the adsorbent to adsorb the desired concentration of heavy metal ions in the solution.

### 4.3.8 Effect of initial concentration of Cr(VI)

Initial concentration effect was studied varying the concentration of hexavalent chromium ions (0.5, 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 mg.L<sup>-1</sup>) while maintaining the solution pH, adsorbent dose and shaking speed at optimum and contact time at equilibrium.

### 4.3.9 Desorption experiment

The regeneration of an adsorbent basically depends on the ease with which an adsorbate is released from the spent adsorbent. For desorption experiments, Cr(VI) ion-loaded adsorbent was prepared by agitating a known dose of coffee husk ash with a desired concentration of Cr(VI) by shaking at a fixed rpm for a defined equilibrium agitation time. After adsorption, the solid was separated from the supernatant solution by filtration. The solid on the filter paper was washed with distilled water. The Cr(VI) loaded adsorbent was dried at 105°C for 12 hours in an oven. Desorption experiments was then being carried out by shaking the oven dried spent adsorbent at a fixed rpm for an equilibrium contact time in 100 mL of different concentration of NaOH solution (0.01 M, 0.1 M and 0.5 M) separately. The ratio of desorption percentage can be calculated according to Eq. 4.3 (Hu et al., 2011; Singh et al., 2011; Albadarin et al., 2012)

$$\text{Desorption ratio (\%)} = \frac{\text{Amount of Cr (VI) ion desorbed}}{\text{Amount of Cr (VI) ion adsorbed}} \times 100 \quad (4.3)$$

### 4.3.10 Adsorption kinetics

The pseudo-first-order kinetic and pseudo-second-order kinetic are the most common models for checked of adsorption condition of the adsorbents (Ahluwalia and Goyal, 2007).

#### 4.3.10.1 Pseudo-first-order kinetics

A model is illustrated as the following Eq. 4.4:

$$\log(q_E - q_T) = \log q_E - \left( \frac{k_1}{2.303} \right) T \quad (4.4)$$

Where

$q_E$  = adsorption efficiency at equilibrium (mg.g<sup>-1</sup>),

$q_T$  = adsorption efficiency at a time ( $\text{mg.g}^{-1}$ ),

$T$  = time (min) and

$K_1$  = kinetics constant ( $\text{h}^{-1}$ )

#### 4.3.10.2 Pseudo second order kinetics

A model equation can be showed as Eq. 4.5:

$$\frac{T}{q_E} = \frac{1}{K_2 q_E^2} + \left( \frac{1}{q_E} \right) T \quad (4.5)$$

Where

$K_2$  = kinetic constant ( $\text{g.mg}^{-1} \text{h}^{-1}$ ) and the rest of parameters are the same as those presented in equation 4.4.

#### 4.3.11 Adsorption isotherms

Freundlich and Langmuir isotherms were used to fix the highest value of adsorption efficiency of the adsorbents.

##### 4.3.11.1 Langmuir isotherm

The Langmuir isotherm is the homogenous molecule surface of adsorption. In this process, one molecule of adsorption cannot affect the near site of adsorption (Ahluwalia and Goyal, 2007).

Linear Langmuir equation is given as follows:

$$\frac{1}{q_E} = \frac{1}{q_E} + \frac{1}{q_M k_L} \frac{1}{C_E} \quad (4.6)$$

Where

$q_E$  = a value Cr(VI) adsorbed over gram of locally available materials,

$C_E$  = an equilibrium of Cr(VI) in wastewater, a milligram of Cr(VI) per liter,

$k_L$  = Langmuir the same, liter per milligram of Cr(VI), and

$q_M$  = maximum contain, a milligram of Cr(VI) per gram of coffee husk ash.

Important features of the Langmuir equation stated in the forms of dimensionless separation factor (Moreno-Piraján and Giraldo, 2012),  $R_L$ , are defined as:

$$R_L = \frac{1}{(1 + K_L C_o)} \quad (4.7)$$

Where

$K_L$  = constant of Langmuir (L.mg<sup>-1</sup>),

$C_o$  = primary amount of Cr(VI) ions (mg.L<sup>-1</sup>), and

$R_L$  = a result indicating the shape of the isotherms:  $1 < R_L$  indicates disapproving adsorption,  $1 = R_L$  indicates linear,  $R_L$  results in between 0 and 1 indicates approving adsorption, and  $0 = R_L$  indicates adsorption non-reversible.

#### 4.3.11.2 Freundlich isotherm

The Freundlich isotherm was described as the heterogeneous surface energies by multilayer adsorption (Sanchooli Moghaddam et al., 2016).

The general Freundlich is given as follows Eq. 4.8:

$$\text{Log}(q_E) = \text{Log}(k_F) + \frac{1}{n} \text{Log}(C_e) \quad (4.8)$$

Where

$q_E$  = shows adsorption efficiency (mg.g<sup>-1</sup>) and

$1/n$  values between 0 and 1 it shows the suitability of adsorption. The  $K_F$  value is higher and shows the better suitability of adsorption.

## 4.4 Results and Discussion

### 4.4.1 Characterization of coffee husk ash

The physical characteristic of coffee husk ash was performed using standard procedures. Characterization of the coffee husk ash was carried out electrical conductivity ( $64.30\mu\text{s cm}^{-1}$ ), cation exchange capacity ( $36.20\text{ cmol Kg}^{-1}$ ), pH (12.47), organic carbon (0.518%) and organic matter (0.893%) was done according (Bouyoucos, 1962; Chapman, 1965; van Reewijk, 1992).

Table 4.1 Physical characteristic of coffee husk ash

| Sample | Parameters                      |                                 |       |           |           |
|--------|---------------------------------|---------------------------------|-------|-----------|-----------|
|        | EC<br>( $\mu\text{s cm}^{-1}$ ) | CEC (cmol<br>$\text{Kg}^{-1}$ ) | pH    | OC<br>(%) | OM<br>(%) |
| CHA    | 64.30                           | 36.20                           | 12.47 | 0.518     | 0.893     |

The elemental analysis of coffee husk ash was examined by using SEM-EDS model ZEISS EVO LS 15 and coffee husk ash was rich in macronutrients weight such as O<sub>2</sub> (36.47 %), K (30.1%), C (25.2%), Ca (3.97%), Mg (1.83%) and other, which are useful for adsorbing Cr(VI) from contaminated water.

Table 4.2 Elemental components of coffee husk ash

| Elements | C     | O <sub>2</sub> | Na   | Mg   | Si   | P    | S    | Cl   | K     | Ca   |
|----------|-------|----------------|------|------|------|------|------|------|-------|------|
| Weight % | 25.20 | 36.47          | 0.16 | 1.85 | 0.50 | 0.83 | 0.82 | 0.56 | 30.10 | 3.97 |
| Atomic % | 38.4  | 38.7           | 0.1  | 1.4  | 0.33 | 0.49 | 0.4  | 0.29 | 14.1  | 1.81 |

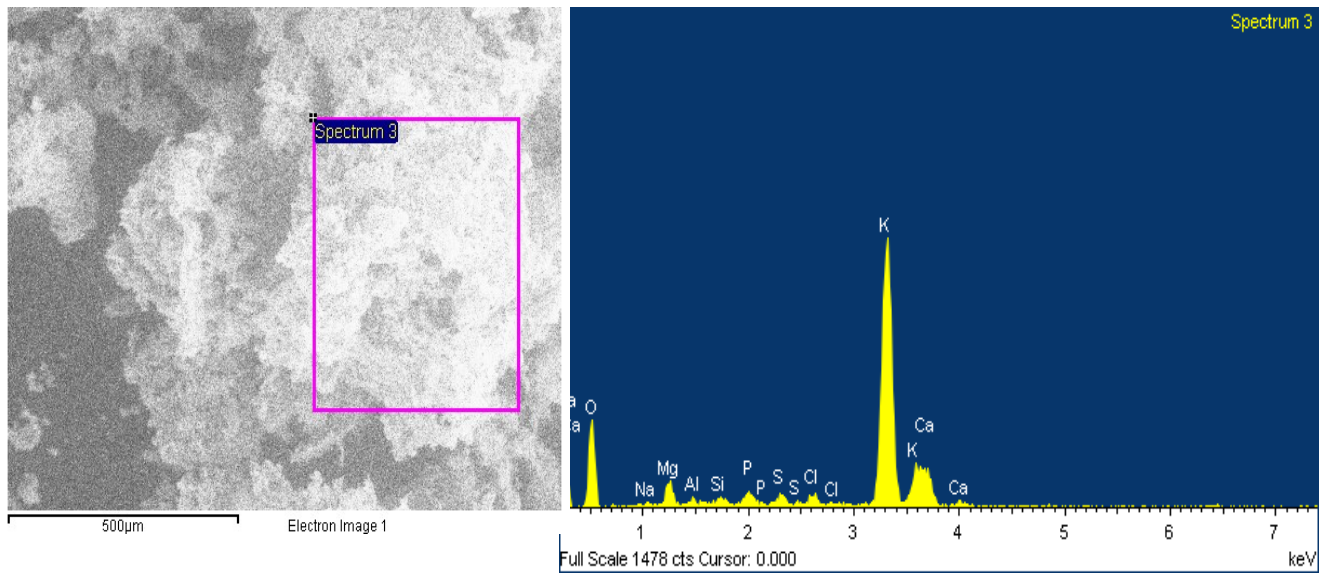


Figure 4.2 Elemental analysis of coffee husk ash by using SEM-EDX

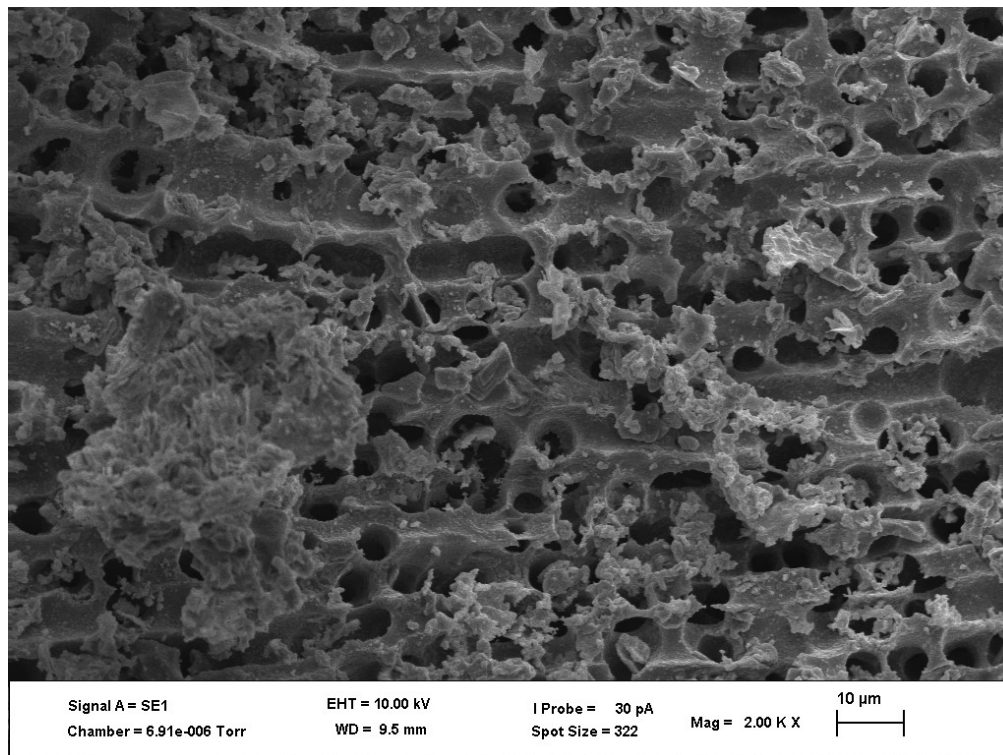


Figure 4.3 Scanning Electron Microscopy (SEM) of coffee husk ash magnified 10 µm

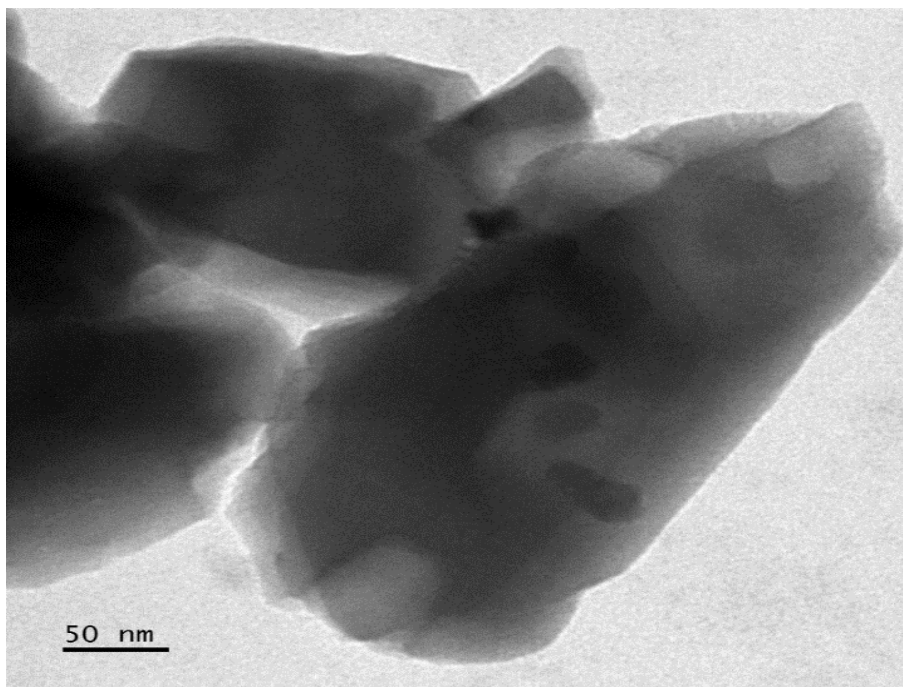


Figure 4.4 Transmission Electron Microscopy (TEM) of coffee husk ash magnified 50 nm

#### 4.4.2 Shaker speed

The effect of the shaker speed on the removal capacity of Cr(VI) was studied and Figure 4.5 shows the adsorptive experimental results obtained from a series of experiments performed, namely an initial concentration of Cr(VI) of  $3.5 \text{ mg.L}^{-1}$ , a solution pH of 7, a CHA dose of 0.4 g and a contact time of 120 minutes at room temperature, at different shaking speed from 100-250 rpm. In order to get the adsorption removal percentage, the curve was plotted at different shaking speed as shown in Figure 4.5. It showed that shaking speed of 100 rpm has a greater removal efficiency of chromium(VI) from the others string speeds The adsorption rate decreased at higher shaker speed due to the decrease in the mobility of adsorbing species (Yasemin and Zubeyde, 2006). Thus, the agitating speed was fixed at 100 rpm in further experiments.

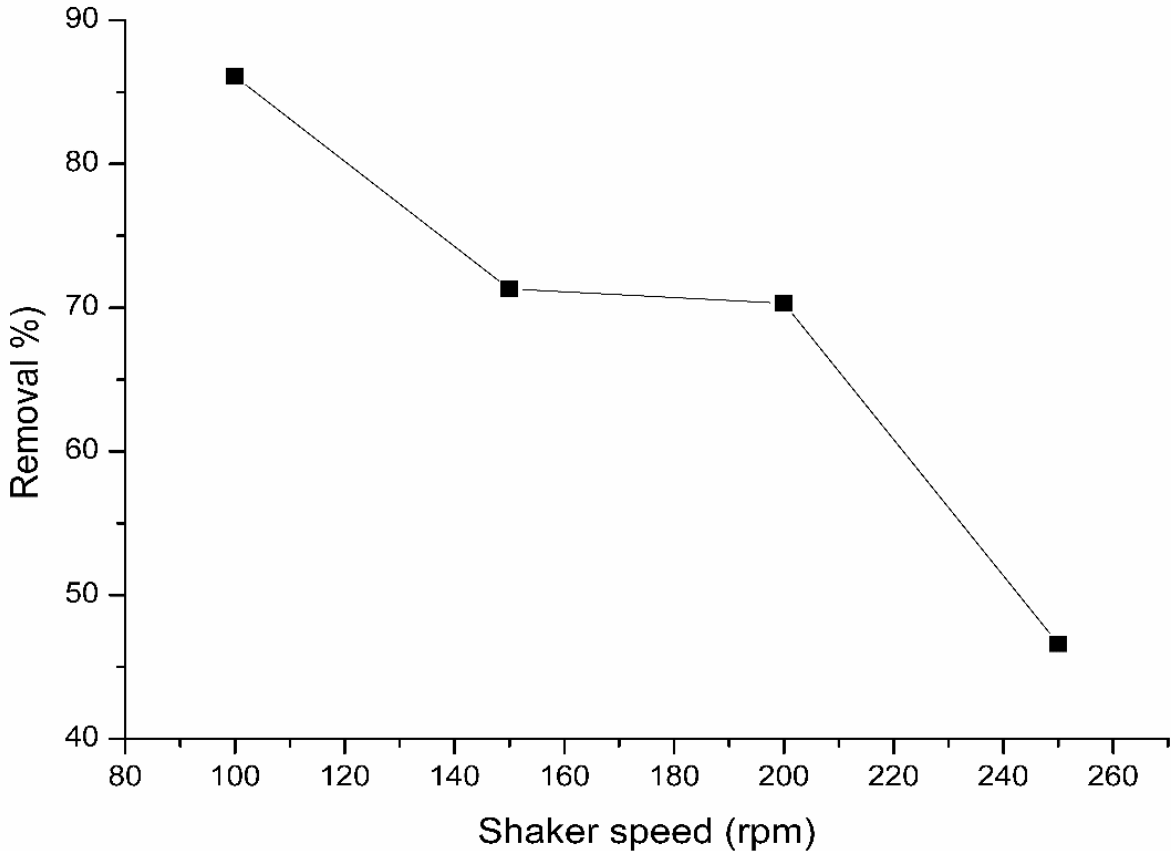


Figure 4.5 Cr(VI) adsorption capacity versus shaker speed (initial chromium concentration: 3.5 mg.L<sup>-1</sup>, dose of CHA: 0.4 g.L<sup>-1</sup>, pH: 7 and time: 2 hours)

#### 4.4.3 Contact time effect

The effect of the contact time on adsorption influence of coffee husk ash on chromium (VI) was investigated by continuously increasing the contact time (10, 20, 30, 40, 50, 60, 80, 100 and 120) minutes (Figure 4.6). The adsorptive removal of adsorbate increased with increase in contact time up to 40 minutes (Figure 4.6). After 40 minutes (the equilibrium point) the adsorption removal of adsorbate remained constant due to the exhaustion of binding sites (Akiode et al., 2015; Choudhary et al., 2015; Kuppusamy et al., 2016).

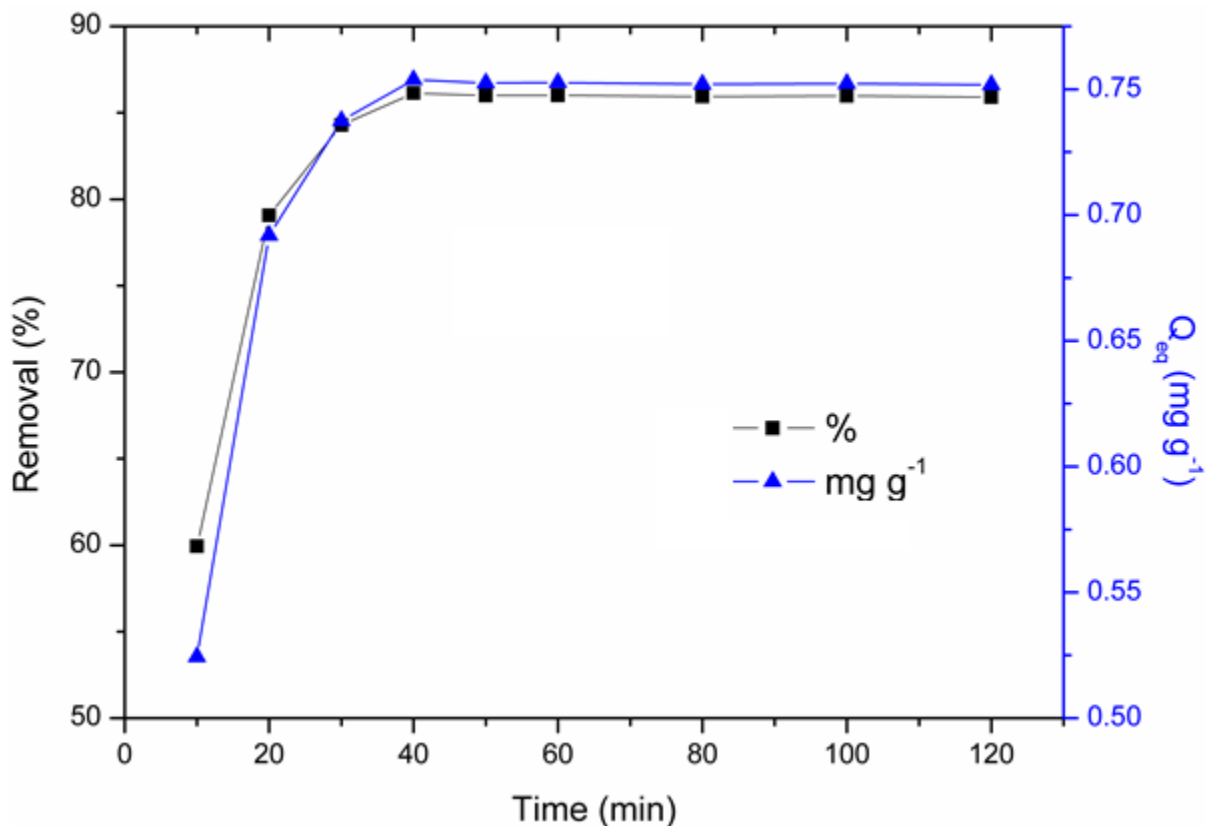


Figure 4.6 Cr(VI) adsorption capacity versus time (initial Cr(VI) amount:  $3.5 \text{ mg.L}^{-1}$ , dose of CHA:  $0.4 \text{ g.L}^{-1}$ , pH: 7, shaking speed: 100 rpm)

The rate of adsorption of chromium(VI) ion was fast up to 40 minutes. This was due to coffee husk ash surface having many open spaces that could lead to strong attraction force between Cr(VI) and adsorbent similar observation was reported by Wanees et al. (2012). Adsorptive removal of chromium (VI) from 10 and 40 minutes was rapid and fast at the beginning due to highly increased adsorption sites (Choudhary et al., 2015; Mekonnen et al., 2015). After 40 minutes, there was no change in the rate of adsorption of Cr(VI) on coffee husk ash. This showed that coffee husk ash had no sufficient open space after the bulk solution increased. Similar was reported by Workneh et al. (2014). The adsorption capacity was high for a short period (40 minutes) on coffee husk ash adsorbent. The reason for this could be due to the open space, lower bulk density and small particle size. This finding is in agreement with the finding repeated by Babel and Opiso (2007).

#### 4.4.4 pH effect

The amount of chromium (VI) removed was dependent on pH (Figure 4.7). The effects of pH on chromate removal capacity and adsorption efficiency are shown in Figure 4.7. Chromate removal and adsorption efficiency decreased with increasing pH values (2 - 8) i.e. 95.2 – 82.2% and 0.096 – 0.085 mg.g<sup>-1</sup>, respectively. The adsorption efficiency and removal efficiency at a pH of 8 were, 0.085 mg.g<sup>-1</sup> and 82.2%, respectively. The adsorption efficiency was high at the pH of 2 which is 0.096 mg.g<sup>-1</sup> while the percentage of chromate removed was found to be 95.2% (Figure 4.7).

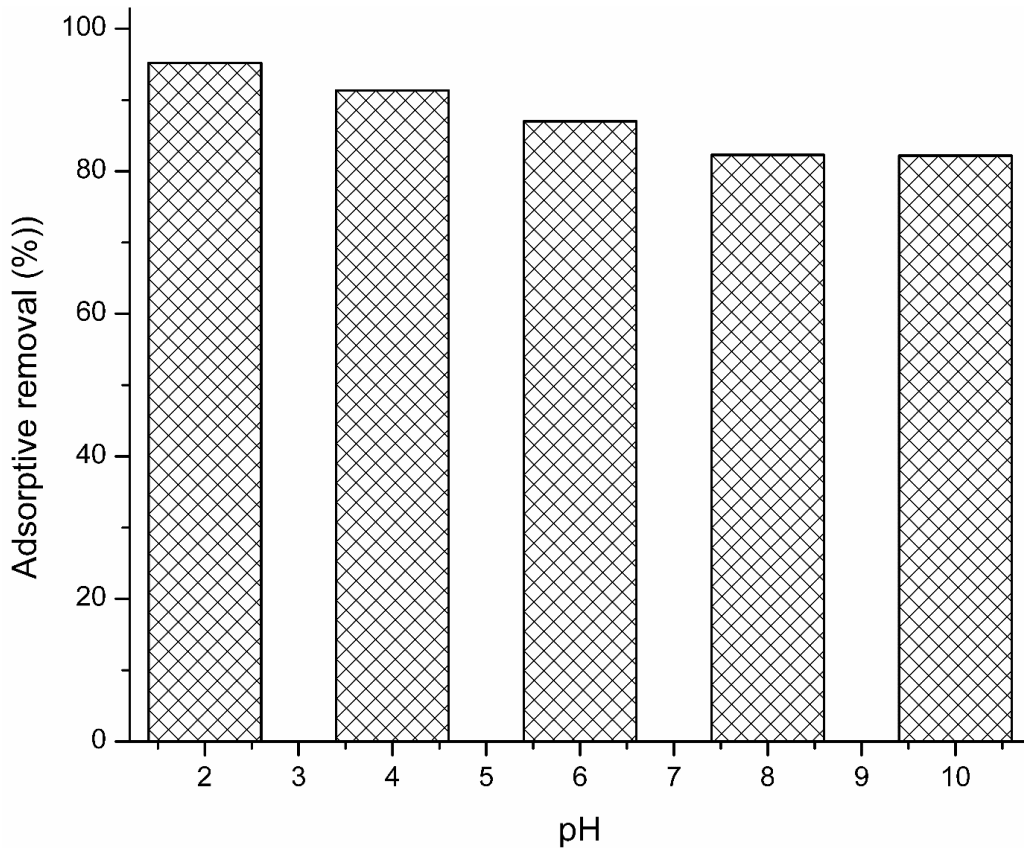


Figure 4.7 Cr(VI) removal and adsorption efficiency versus pH (initial Cr(VI) concentration: 3.5 mg.L<sup>-1</sup>, CHA dose: 0.4 g.L<sup>-1</sup>, time contact: 40min, speed of shaker: 100 rpm)

The pH value is crucial to control adsorption of metal in between solid and water interface. As can be seen from the data presented in Figure 4.7, Cr(VI) ion removal occurs at a pH of 2 within a 40 minutes contact time. This might be the hexavalent chromium reduced to trivalent chromium in solutions through various mechanisms as showed by Eq. 4.9 and 4.10, respectively (Abas et al., 2012; Li et al., 2012; Ghashghaee and Farzaneh, 2016).



Numerous  $\text{H}^+$  ions were presented at low pH value. The high concentration of  $\text{H}^+$  neutralizes the negative charge ions by diffusion of dichromate ions and hydrogen chromate ions. This observation was similar to the finding reported by Yarkandi (2014). The percentage of chromate removal was increased from 82.2% to 95.2% by decreasing the solution pH value from 8 to 2. The increase of the adsorptive removal of chromate corresponded with a decrease in pH values ranging from 8 to 2. This could be showed electrostatic attraction in between chromate ions and the positive surface charge of the adsorbent (Akiode et al., 2015). In contrast, the efficiency of chromate removal decreased at an initial solution was  $\text{pH} > 2$ . The decrease in the adsorption of chromate with the increase in the pH of the solution beyond 2 might be due to the negative surface charge of the adsorbent and surface adjustment with  $\text{OH}^-$  ions that may cause repulsion between the hydroxyl ions and the chromate ions according to the study of Alemayehu et al. (2012). The pH value was decreased with increased positive charge in the coffee husk ash due to protonization process. The adsorption chromium(VI) ion increased with decreasing pH values. The trends of this finding was positively agreed with the finding reported by Guo et al. (2008) and Zhong et al. (2014).

#### 4.4.5 Effect of adsorbent dose

The effect of variation of adsorbent dose on the removal of chromate is shown in Figure 4.8. The amount of chromate removed increased from 68.8% to 86.4% as the adsorbent dose increased from 0.5 to 1.5  $\text{g.L}^{-1}$ . The percentage of Cr(VI) removal increased with increasing coffee husk ash dose because of the abundant number of vacant adsorption site and increase effective surface area are present on the adsorbent (Dehghani et al., 2015). The capacity of chromate adsorption decreased ( $0.61 \text{ mg.g}^{-1} - 0.08 \text{ mg.g}^{-1}$ ) as the adsorbent dose increased beyond 1.5  $\text{g.L}^{-1} - 4.0 \text{g.L}^{-1}$  (Figure 4.8). Hence, the minimum dose for maximum chromate removal was 1.5  $\text{g.L}^{-1}$ , and 1.5  $\text{g.L}^{-1}$  of the adsorbent was considered for further adsorption experiments in this study.

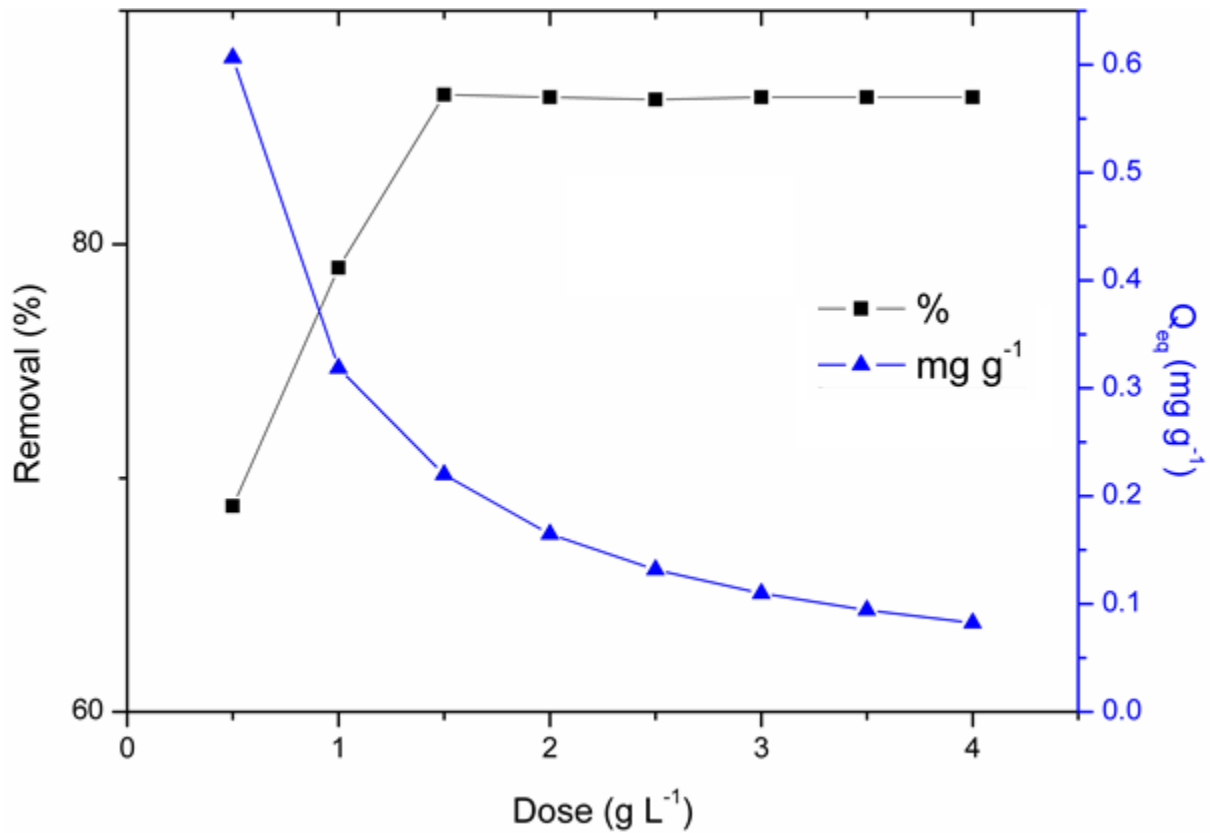


Figure 4.8 Cr(VI) removal capacity of adsorbent dose (initial chromate amount: 3.5 mg.L<sup>-1</sup>, time: 40 min, pH: 2, speed of shaker: 100 rpm)

#### 4.4.6 Effect of initial chromate concentration

The graphical presentation of the chromate adsorption efficiency as a function of the initial chromium concentration is given in Figure 4.9. The result showed that the removal efficiency of chromate decreased from 99% to 93.21% and Cr(VI) removal capacity increased (1.65 mg.g<sup>-1</sup> - 15.53 mg.g<sup>-1</sup>) as the initial chromate amount increased from 0.5 mg.L<sup>-1</sup> to 5.0 mg.L<sup>-1</sup>. At 0.5 mg.L<sup>-1</sup> Cr(VI) sufficient coffee husk ash sites were available for adsorption of chromium(VI) ions due to the larger number of the ions at lower concentration (Akiode et al., 2015).

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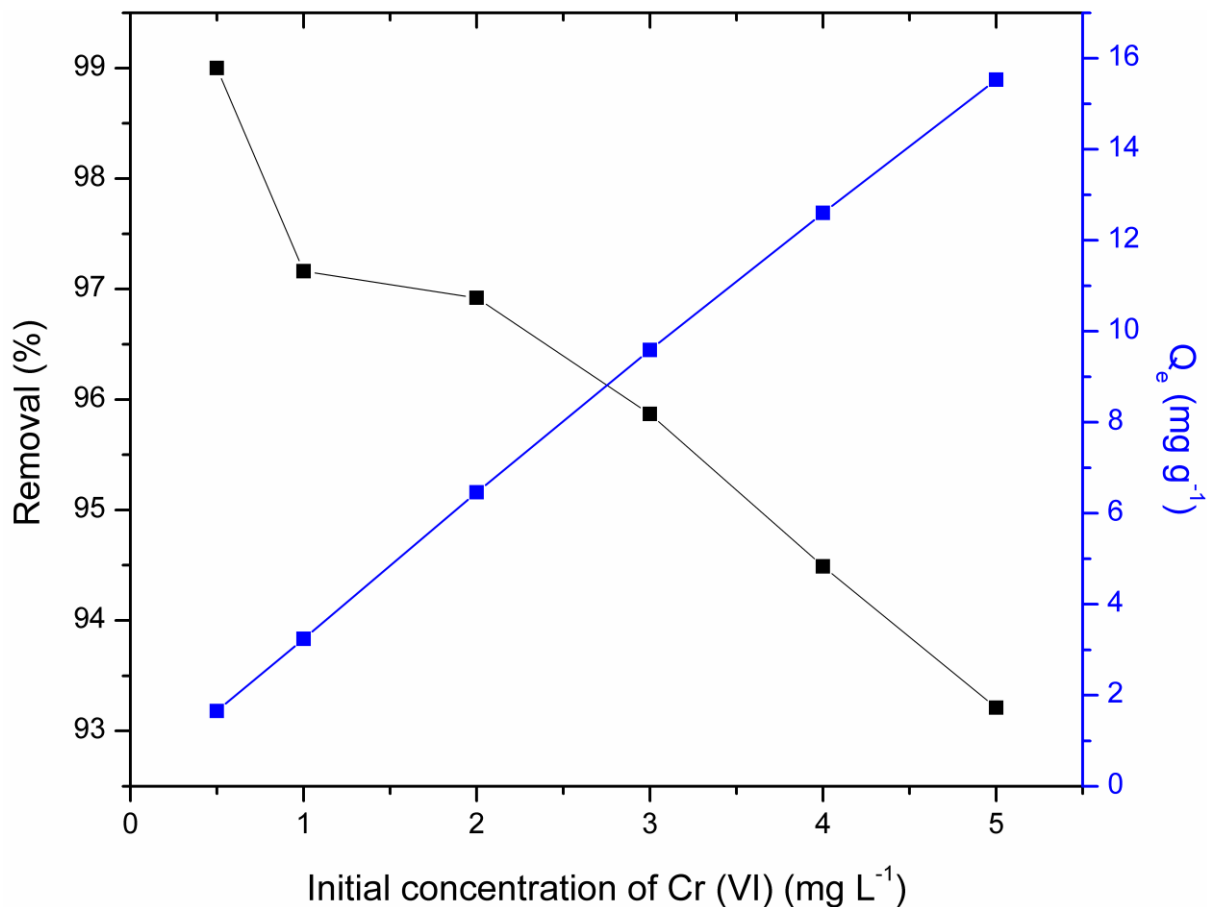


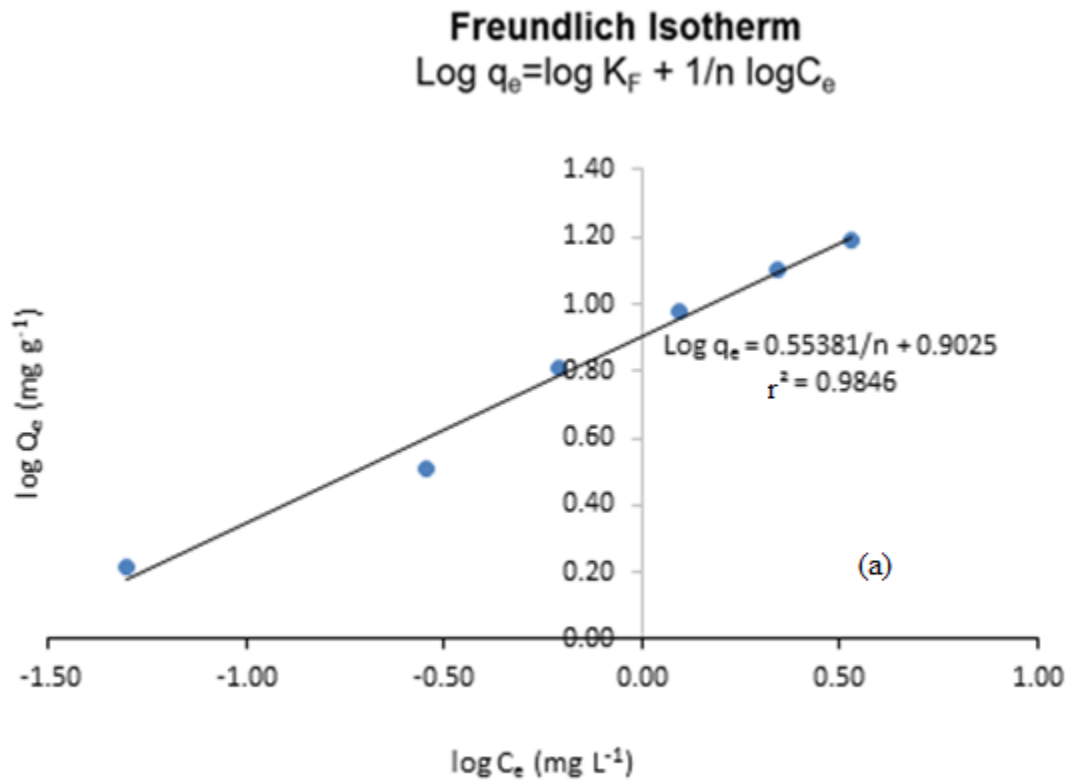
Figure 4.9 Cr(VI) removal and adsorption efficiency versus initial concentration (CHA dose: 1.5 g.L<sup>-1</sup>, pH: 2, time: 40 minutes, shaking speed: 100 rpm)

#### 4.4.7 Adsorption isotherm

The equilibrium adsorption experiment was investigated at pH 2 varying the chromate amount of 0.5 mg.L<sup>-1</sup> using 1.5 g.L<sup>-1</sup> of the coffee husk ash. The results of the chromate adsorption isotherm are shown in Figure 4.10. The Freundlich and Langmuir isotherm parameters obtained from the linear equation of these models are given in Table 4.3. The values of the correlation coefficient for the Freundlich and Langmuir isotherms were 0.9846 and 0.9444, respectively. The Freundlich isotherm model is more suitable than the Langmuir isotherm model for this adsorption process. The dimensionless constant for coffee husk ash was between 0 and 1, showing a favorable adsorption process.

Table 4.3 Freundlich and Langmuir isotherm for adsorption of Cr(VI) using coffee husk ash

| ASH Dose (g/L) | C <sub>i</sub> (mg/L) | Duplicate |      | C <sub>e</sub> (mg/L) | log C <sub>e</sub> | Volume (L) | Q <sub>e</sub> (mg/g) | log Q <sub>e</sub> | 1/C <sub>e</sub> (L/mg) | 1/Q <sub>e</sub> (g/mg) | C <sub>e</sub> /Q <sub>e</sub> (mg/L) |
|----------------|-----------------------|-----------|------|-----------------------|--------------------|------------|-----------------------|--------------------|-------------------------|-------------------------|---------------------------------------|
|                |                       | A         | B    |                       |                    |            |                       |                    |                         |                         |                                       |
| 0.15           | 5.00                  | 0.01      | 0.09 | 0.05                  | -0.74              | 0.10       | 0.30                  | 0.22               | 20.00                   | 0.61                    | 0.03                                  |
| 0.15           | 10.00                 | 0.29      | 0.28 | 0.28                  | -0.16              | 0.10       | 3.11                  | 0.51               | 3.51                    | 0.31                    | 0.09                                  |
| 0.15           | 20.00                 | 0.59      | 0.64 | 0.62                  | 0.14               | 0.10       | 6.21                  | 0.81               | 1.62                    | 0.15                    | 0.10                                  |
| 0.15           | 30.00                 | 1.10      | 1.38 | 1.24                  | 0.33               | 0.10       | 9.29                  | 0.98               | 0.81                    | 0.10                    | 0.13                                  |
| 0.15           | 40.00                 | 2.18      | 2.23 | 2.20                  | 0.44               | 0.10       | 12.42                 | 1.10               | 0.45                    | 0.08                    | 0.17                                  |
| 0.15           | 50.00                 | 3.48      | 3.32 | 3.40                  | 0.53               | 0.10       | 15.53                 | 1.19               | 0.29                    | 0.06                    | 0.22                                  |



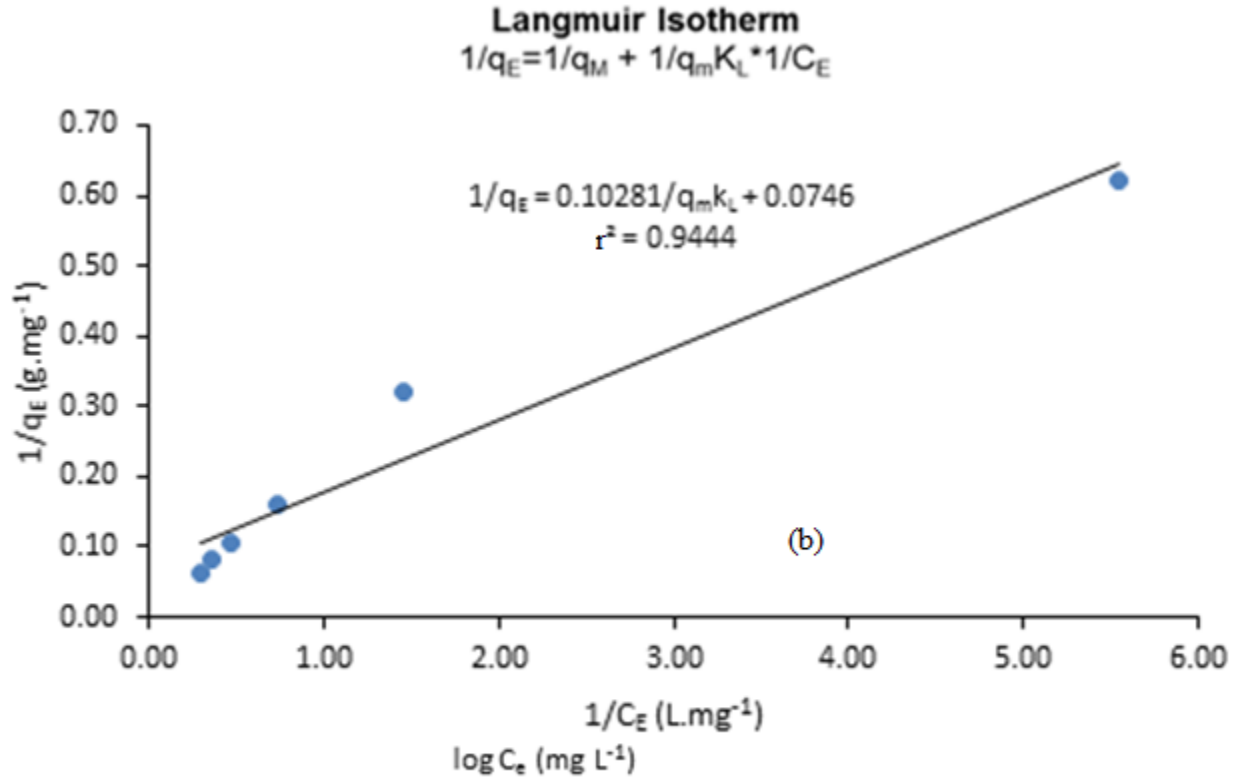


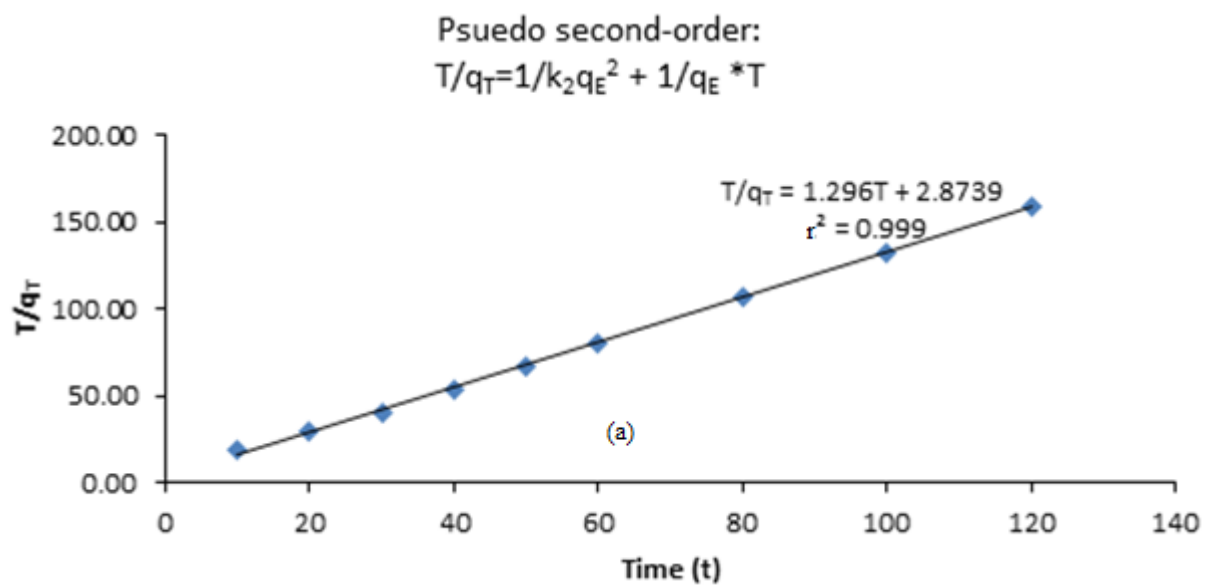
Figure 4.10 Langmuir and Freundlich isotherms for chromate adsorption using CHA (initial chromate concentration:  $0.5 \text{ mg.L}^{-1}$ , adsorbent dose:  $1.5 \text{ g.L}^{-1}$ , pH: 2, contact time: 40 min, speed of shaker: 100 rpm)

Table 4.4 Linear estimated isotherm model and its constant value for chromate adsorption

| Temp. | Freundlich Isotherm:                                       |        |        | Langmuir Isotherm:                  |             |        |
|-------|--|--------|--------|-------------------------------------|-------------|--------|
|       | $\text{Log } q_e = \text{Log } K_F + 1/n \text{ Log } C_e$ |        |        | $1/q_E = 1/q_M + 1/q_m K_L * 1/C_E$ |             |        |
| °C    | $K_F \text{ (mg.g}^{-1}\text{)}$                           | $1/n$  | $r^2$  | $1/q_M \text{ (mg.g}^{-1}\text{)}$  | $1/q_m k_L$ | $r^2$  |
| 22±2  | 0.9025   | 0.5538 | 0.9846 | 0.0746                              | 0.1028      | 0.9444 |

#### 4.4.8 Adsorption kinetics

The pseudo first and second-order kinetic models are widely used to the study of kinetics adsorption model and correlation,  $r^2$ . The rate of Cr(VI) adsorption by using coffee husk ash was studied for contact time (10, 20, 30, 40, 50, 60, 80, 100 and 120) minutes. Pseudo-second-order kinetic model was best applicable for the adsorption of chromium (VI) ions to the coffee husk ash. The mechanism may involve sharing of valence electron forces or through ion exchange between the adsorbent and the chromium(VI) ion (Chi-chuan et al, 2017).



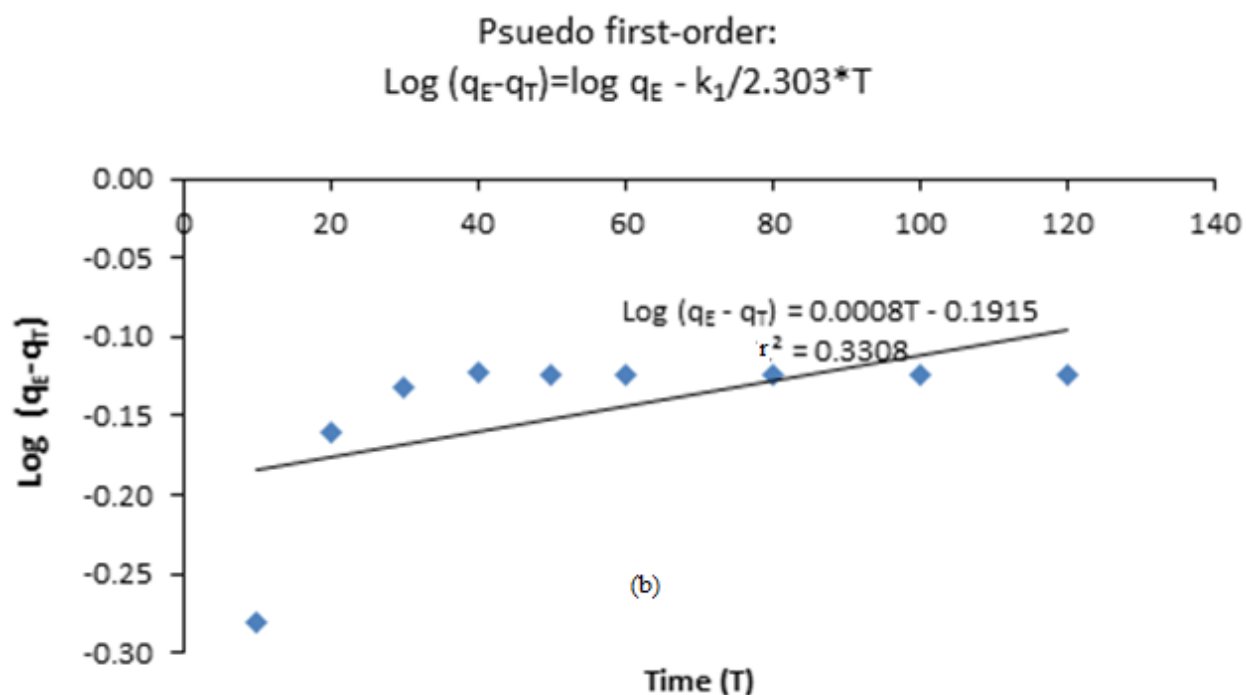


Figure 4.11 Psuedo-second and first order for Cr(VI) adsorption onto CHA (Cr(VI) = 0.5 mg.L<sup>-1</sup>; pH=2; adsorbent dose = 1.5 g; shaking speed=100 rpm and temp. 22 ± 2°C)

Table 4.5 Linear estimated kinetic adsorption of Cr(VI) ions onto coffee husk ash

| Temp.<br>°C | Psuedo-first-order:<br>$\text{Log}(q_E - q_T) = \text{Log } q_E - k_1/2.303 * T$ |             |        | Psuedo-second-order:<br>$T/q_T = 1/k_2 q_E^2 + 1/q_E * T$ |         |        |
|-------------|--|-------------|--------|---|---------|--------|
|             | $\text{log } q_E$  | $k_1/2.303$ | $r^2$  | $1/k_2 q_E^2$   | $1/q_E$ | $r^2$  |
| 22±2        | 0.1915   | 0.0008      | 0.3308 | 2.8739  | 1.2960  | 0.9990 |

#### 4.5 Conclusions

Chromium (VI) present in the water greater than the permitted is toxic and can lead to many health effects. This study demonstrated the adsorptive efficiency of coffee husk ash for the removal of Cr(VI) ions from industrial polluted water. The different effects on batch adsorption, such as solution pH, contact time, and initial concentration of Cr(VI) were evaluated. Adsorption of

chromium (VI) on coffee husk ash high at pH = 2, time = 40 minutes, dose of CHA = 1.5 g.L<sup>-1</sup> and initial amount of Cr(VI) = 0.5 mg.L<sup>-1</sup>. Freundlich and Langmuir isotherm was examined in this study at a room temperature 22 ± 2°C. Therefore, the finding suggested that coffee husk ash can be as an interesting low-cost adsorbent technology for Cr(VI) removal from contaminated industrial wastewater.

#### 4.6 References

- Abas, S, Ismail, M, Kamal, M and Izhar, S. 2012. Adsorption process of heavy metals by low-cost adsorbent: a review. *World Applied Sciences Journal* 28: 1518-1530.
- Ahluwalia, S and Goyal, D. 2007. Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresource Technology Journal* 98: 2243-2257.
- Akiode, O, Idowu, M, Omeike, S and Akinwunmi, F. 2015. Adsorption and kinetics studies of Cu (II) ions removal from aqueous solution by untreated and treated sugarcane bagasse. *Global Nest Journal* 17: 583-593.
- Albadarin, A, Mangwandi, C, Ala'a, H, Walker, G, Allen, S and Ahmad, M. 2012. Kinetic and thermodynamics of chromium ions adsorption onto low-cost dolomite adsorbent. *Chemical Engineering Journal* 179: 193-202.
- Alemayehu, D, Singh, S and Tessema, D. 2012. Assessment of the adsorption capacities of fired clay soils from Jimma (Ethiopia) for the removal of Cr(VI) from aqueous solution. *Universal Journal of Environmental Research and Technology* 2: 411-420.
- Alfarra, R, Ali, N and Yusoff, M. 2014. Removal of heavy metals by natural adsorbent: review. *International Journal of Biosciences* 4: 130-139.
- Babel, S and Opiso, E. 2007. Removal of Cr from synthetic wastewater by sorption into volcanic ash soil. *International Journal of Environmental Science and Technology* 4: 99-107.
- Balasubramanian, S and Pugalenth, V. 1999. Determination of total chromium in tannery waste water by inductively coupled plasma-atomic emission spectrometry, flame atomic absorption spectrometry and UV-visible spectrophotometric methods. *Talanta* 50: 457-467.

- Chen, S, Yue, Q, Gao, B, Li, Q and Xu, X. 2011. Removal of Cr (VI) from aqueous solution using modified corn stalks: characteristic, equilibrium, kinetic and thermodynamic study. *Chemical Engineering Journal* 168: 909-917.
- Chi-Chuan, K, Aldwin, H, Kim, K, Rivera , R, Mark, Daniel, G and De, L. 2017. Hexavalent chromium removal from aqueous solution by adsorbents synthesized from groundwater treatment residuals. *Sustainable Environment Research Journal* 27: 163-171.
- Choudhary, S, Goyal, V and Singh, S. 2015. Removal of copper (II) and chromium (VI) from aqueous solution using sorghum roots (*S. bicolor*): a kinetic and thermodynamic study. *Clean Technologies and Environmental Policy Journal* 17: 1039-1051.
- CSA. 2016/17. Central Statistics Agency, Addis ababa, Ethiopia
- Dehghani, M, Taher, M, Bajpai, A, Heibati, B, Tyagi, I, Asif, M, Agarwal, S and Gupta, V. 2015. Removal of noxious Cr (VI) ions using single-walled carbon nanotubes and multi-walled carbon nanotubes. *Chemical Engineering Journal* 279: 344-352.
- Ghashghaee, M and Farzaneh, V. 2016. Removal of Cr (VI) species from aqueous solution by different nanoporous materials. *Iranian Journal of Toxicology* 10: 15-21.
- Guo, X, Zhang, S and Shan, X. 2008. Adsorption of metal ions on lignin. *Journal of Hazardous Materials* 151: 134-142.
- Hu, X, Wang, J, Liu, Y, Li, X, Zeng, G, Bao, Z, Zeng, X, Chen, A and Long, F. 2011. Adsorption of chromium (VI) by ethylenediamine-modified cross-linked magnetic chitosan resin: isotherms, kinetics and thermodynamics. *Journal of Hazardous Materials* 185: 306-314.
- Kan, C, Ibe, A, Rivera, K, Arazo, R and de Luna, M. 2017. Hexavalent chromium removal from aqueous solution by adsorbents synthesized from groundwater treatment residuals. *Sustainable Environment Research Journal* 27:163-167
- Kufa, T. 2012. Recent coffee research development in Ethiopia, Ethiopian coffee export conference: strengthening the legacy of our coffee 8-9 November 2012, Hilton Hotel, Addis Ababa, Ethiopia.
- Kuppusamy, S, Thavamani, P, Megharaj, M, Venkateswarlu, K, Lee, Y and Naidu, R. 2016. Oak (*Quercus robur*) acorn peel as a low-cost adsorbent for hexavalent chromium removal from aquatic ecosystems and industrial effluents. *Water, Air, and Soil Pollution Journal* 227: 1-11.

- Li, W, Gong, X, Li, X, Zhang, D and Gong, H. 2012. Removal of Cr (VI) from low-temperature micro-polluted surface water by tannic acid immobilized powdered activated carbon. *Bioresource Technology Journal* 113: 106-113.
- Lin, H, Rong, C, Jiu, B, Li, B, Yu, Q, Gan, L and Zhang, Z. 2018. Effects of chromium on pyrolysis characteristic of water hyacinth (*Eichornia crassipes*). *Renewable Energy Journal* 115: 676-684.
- Mekonnen, E, Yitbarek, M and Soreta, T. 2015. Kinetic and thermodynamic studies of the adsorption of Cr (VI) onto some selected local adsorbents. *South African Journal of Chemistry* 68: 45-52.
- Moreno-Piraján, J and Giraldo, L. 2012. Heavy metal ions adsorption from wastewater using activated carbon from orange peel. *Journal of Chemistry* 9: 926-937.
- Pan, J, Jiang, J and Xu, R. 2014. Removal of Cr (VI) from aqueous solutions by Na<sub>2</sub>SO<sub>3</sub>/FeSO<sub>4</sub> combined with peanut straw biochar. *Chemosphere Journal* 101: 71-76.
- Pan, J, Jiang, J and Xu, R. 2013. Adsorption of Cr (III) from acidic solutions by crop straw derived biochars. *Journal of Environmental Sciences* 25: 1957-1965.
- Panda, H, Tiadi, N, Mohanty, M and Mohanty, C. 2017. Studies on adsorption behavior of an industrial waste for removal of chromium from aqueous solution. *South African Journal of Chemical Engineering* 23: 132-138.
- Pehlivan, E and Cetin, S. 2009. Sorption of Cr (VI) ions on two Lewatit-anion exchange resins and their quantitative determination using UV–visible spectrophotometer. *Journal of Hazardous Materials* 163: 448-453.
- Saifuddin, M and Kumaran, P. 2005. Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. *Electronic Journal of Biotechnology* 8: 43-53.
- Sanchooli Moghaddam, M, Rahdar, S and Taghavi, M. 2016. Cadmium removal from aqueous solutions using saxaul tree ash. *Iranian Journal of Chemistry and Chemical Engineering* 35: 45-52.
- Singh, S, Barick, K and Bahadur, D. 2011. Surface engineered magnetic nanoparticles for removal of toxic metal ions and bacterial pathogens. *Journal of Hazardous Materials* 192: 1539-1547.

- Sultana, F, Uddin, M, Kabir, M, Sultana, N, Sikder, M and Rahman, S. 2016. Removal efficiency of chromium (VI) ions from aqueous solution by adsorption of rice husk and saw dust ash as a homogeneous composite. *International Journal of Environmental Sciences* 6: 987-993.
- Tang, L, Fang, Y, Pang, Y, Zeng, G, Wang, J, Zhou, Y, Deng, Y, Yang, G, Cai, Y and Chen, J. 2014. Synergistic adsorption and reduction of hexavalent chromium using highly uniform polyaniline–magnetic mesoporous silica composite. *Chemical Engineering Journal* 254: 302-312.
- USEPA. 2011. Ground water and drinking water , current drinking water standards, EPA 816-F-02.
- Wanees, S, Monem, A, Adam, M and Mohamed, M. 2012. Adsorption studies on the removal of hexavalent chromium-contaminated wastewater using activated carbon and bentonite. *Chemistry Journal* 02: 95-105.
- Werkneh, A, Habtu, N and Beyene, H. 2014. Removal of hexavalent chromium from tannery wastewater using activated carbon primed from sugarcane bagasse: adsorption/desorption studies. *American Journal of Applied Chemistry* 2: 128-135.
- Xinyu, L, Xiaodong, C, Liu, Y, Hongzhuo, C, Yumei, T and Zichen, W. 2016. A review on recent advances in the comprehensive application of rice husk ash. *Research on Chemical Intermediates* 42: 893-913
- Yang, Z, Xiong, S, Wang, B, Li, Q and Yang, W. 2013. Cr (III) adsorption by sugarcane pulp residue and biochar. *Journal of Central South University* 20: 1319-1325.
- Yarkandi, N. 2014. Kinetic and isotherm of toxic hexavalent chromium adsorption onto natural adsorbent. *International Journal of Current Microbiology and Applied Sciences* 3: 1-15.
- Zhong, Q, Yue, Q, Li, Q, Gao, B and Xu, X. 2014. Removal of Cu (II) and Cr (VI) from wastewater by an amphoteric sorbent based on cellulose-rich biomass. *Carbohydrate Polymers* 111: 788-796.

## 5. APPLICATION OF SOIL RICH IN KAOLINITE-GOETHITE AS ADSORBENT ON REMOVAL OF CHROMIUM (VI) FROM INDUSTRIAL WASTE WATER

### 5.1 Abstract

Chromium (VI) can be found in industrial wastewater in high concentration which has dangerous effect on human health and the environment. This study was investigated to determine the efficiency of Cr(VI) ion removal from aqueous solution by using soil rich in kaolinite-goethite (SRKG). A batch experiment was performed on the effects of shaker speed, contact time, pH solution, adsorbent dose, initial concentration, and particle size. Optimum condition for Cr(VI) removal were observed at a shaker speed of 150 rpm, an equilibrium time of 40 minutes, a dosage of 3 g.L<sup>-1</sup>, a pH of 2, an initial concentration Cr(VI) of 1 mg.L<sup>-1</sup> and a particle size of 0.075 mm. Adsorption of Cr(VI) in SRKG followed pseudo-second-order kinetic model ( $r^2 > 0.999$ ). Result showed that Langmuir adsorption isotherm model was better describes for the Cr(VI) adsorption onto SRKG with coefficient of determination ( $r^2$ ) of 0.978. Therefore, the results of the study provided fundamental information for further evaluation of SRKG in the practical applicability for the treatment of Cr(VI) under domestic condition.

*Keywords: Adsorption; batch; chromium(VI); removal; soil rich in kaolinite-goethite*

### 5.2 Introduction

One of the key worldwide environmental problems is toxic heavy metal pollution. Among various toxic heavy metal, hexavalent chromium is a serious problem of the environment (Hokkanen et al., 2016; Lin et al., 2018). Chromium is found mostly in the form of trivalent chromium and hexavalent chromium. Chromium (VI) is 100 times poisonous than chromium (III) when found on a surface and in ground water (Tang et al., 2014; Kan et al., 2017) and more soluble and mobile than Cr (III). The release of Cr(VI) from industrial wastewater into the environment degrades water quality and poses hazardous threat to human beings, as well as, other living organisms such as aquatic life due to being soluble in water in the form of  $\text{HCrO}_4^-$  or  $\text{Cr}_2\text{O}_7^{2-}$  and transfers easily to

organisms through the food chain (Saifuddin and Kumaran, 2005; Pan et al., 2014; Hokkanen et al., 2016; Sanchooli Moghaddam et al., 2016). For these reasons, according to United State Environmental Protection Agency (USEPA, 2011) among various heavy metal pollution, Cr(VI) is the most top-prioritized poisonous pollutant (Tang et al., 2014; Panda et al., 2017). According to European Union (EU) has set in place strong environmental regulations for the maximum tolerable limit of chromium (VI) to be  $200\mu\text{g. L}^{-1}$ . World Health Organization (WHO) the recommended maximum tolerable limits of chromium (VI) in wastewater discharged from industries is  $0.25\text{ mg.L}^{-1}$  and drinking water is  $50\ \mu\text{g L}^{-1}$  (Zhong et al., 2014; Hokkanen et al., 2016). The Ethiopian Environmental Protection Authority (EPA) has set a minimal standard to be  $0.1\text{ mg.L}^{-1}$  for Cr(VI) containing industrial discharge (Workneh et al., 2014). Chromium (VI) is generated from different industrial activities carried out in textile industries, leather tanning, electroplating, steel production, paint manufacturing, pulp processing, chromate preparation, electric and electronic components (Pan et al., 2013; Alfarra et al., 2014a; Sultana et al., 2016). Thus, it is critical to find effective ways to remove chromium (VI) from industrial wastewater.

Typical treatment technologies used to remove chromium from contaminated water include chemical precipitation, chemical reduction, ion exchange, adsorption, membrane separation, reverse osmosis, and electrocoagulation. However, most of these technologies have their own limitation such as high investment costs for affordability on large scale, high operational costs, and ineffectiveness at higher concentration of Cr (VI) removed from contaminated water (Hokkanen et al., 2016). Amongst all the treatment technologies, the adsorption technique is one of the most feasible and promising techniques, due to its naturally available raw adsorptive material sources, low cost investment, high efficiency, effectiveness, flexibility in design, easy operation and eco-friendly status (Chen et al., 2011; Yang et al., 2013; Tang et al., 2014; Zhong et al., 2014; Sultana et al., 2016). As a result, looking for a suitable wastewater treatment technology using locally available natural materials that may be used in developing countries such as Ethiopia remains an important issue to address. Among the natural adsorbents, soil rich in kaolinite-geothite (SRKG) would meet the conditions that have been established for the wastewater treatment process due to its (SRKG) abundantly found in Ethiopia (GSOE, 2011) and suitable physical and chemical properties. The following sections (5.2, 5.3 and others) briefly present the overall condition of SRKG as well as its applicability for industrial wastewater treatment methods.

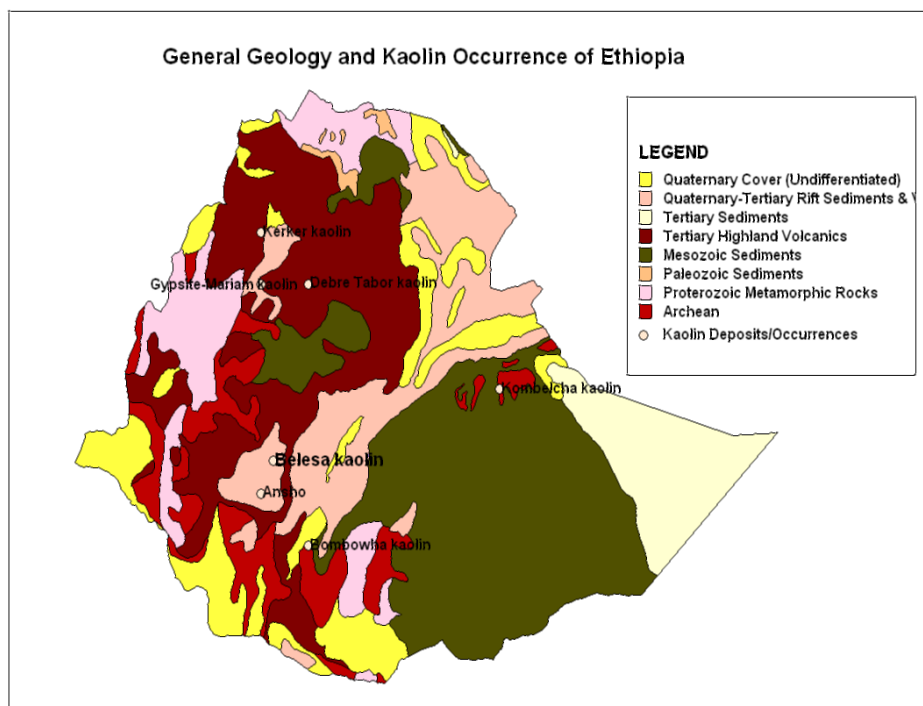


Figure 5.1 Availability of major kaolin deposit areas in Ethiopia (GSOE, 2011)

The objectives of this study were to investigate the efficiency of Cr(VI) ion removal from contaminated water, to determine the adsorption kinetics and the isotherms as well as the effect of pH, contact time and dosage of the initial concentration of chromium(VI) by using low-cost SRKG under a batch adsorption experiment.

## 5.3 Materials and Methods

### 5.3.1 Sample collection

Soil rich in kaolinite and goethite (SRKG), which is abundantly found in Ethiopia (GSOE, 2011), was used for this study. The soil samples were collected in plastic bags from three different sites according to soil sampling standard methods (States, 1992). The samples were collected from Merewa locality, Kersa Woreda, Jimma Zone, Oromia Regional National State and South-west Ethiopia, in October 2015. The collected samples were mixed thoroughly in equal proportions to make a composite sample at Bishoftu Research Institute Laboratory. The particle size of the sample

was analyzed according to ASTM D 422 (Liu and Evett, 2003; Fufa et al., 2013). The SRKG was characterized at the Ethiopia Institute of Agricultural Research, Ethiopia according to (Bouyoucos, 1962; Chapman, 1965; van Reewijk, 1992). The elemental composition and morphology of soil rich in kaolinite-goethite was characterized at KwaZulu-Natal University, Pietermaritzburg campus, Life Science Microscopy, and Microanalysis Unit (MMU) by using Scanning Electron Microscopy (SEM/EDS) (Model ZEISS EVO LS15, Germany) at South Africa.

### **5.3.2 Wastewater**

Industrial wastewater samples were collected from Friendship Tannery PLC, East Showa Zone, Oromia Regional State, Ethiopia according to standard methods for water and wastewater samples collection procedures (Federation and Association, 2005). The samples were collected in acid washed plastic bottles. The sample was acidified to a  $\text{pH} < 2$ , using 0.1 M of nitric acid or sulfuric acid, to prevent the complexation of Cr(VI) ions by organic matter in the wastewater. The physicochemical properties of the sample analyzed methods such as chromate (UV-spectrophotometer), phosphate (stannous chloride), nitrate (phphel-disulfonic), dissolved oxygen, biological oxygen demand (azid-modification of winklers) and chemical oxygen demand were determined according to standard method for water and wastewater analysis (APHA, 2005).

### **5.3.3 Equipment used**

- (a) UV-visible spectrophotometer: used for analyses of Cr(VI),
- (b) Drying oven: used for desorption of experiment,
- (c) Analytical balance: was used for weighting adsorbents, chemical salts, and others,
- (d) pH meter: 3310 model-pH meters for adjustable for pH,
- (e) Orbital shaker: used for agitating of samples, and
- (f) Glassware: Volumetric and Erlenmeyer flasks, cylinders, plastic and micro pipettes and micro-filters.

### **5.3.4 Batch experimental procedures**

The batch adsorption technique expanded with soil rich in kaolinite-goethite in this work for chromate removal was carried out with aqueous solution and actual chromate wastewater samples.

Batch adsorptive experiments were undertaken to limit the isotherms adsorption of chromate Cr(VI) into SRKG in the 100 mL plastic bottle. The experiment was investigated at laboratory room temperature ( $22 \pm 2^{\circ}\text{C}$ ). The experiments were performed in duplicate in addition to the control (only Cr (VI) without SRKG) and blank (only SRKG without Cr(VI)). The chromate water pH were measured with a 3310 model-pH meter before the application with soil rich in kaolinite-geothite and chromate concentration were measured by UV-visible spectrophotometer.

### **5.3.5 Chemicals**

All the chemicals used are of analytical reagent grade. The stock ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) standard solution of each of Cr(VI) ( $1000 \text{ mg. L}^{-1}$ ) was prepared by dissolving 2.828 g of  $\text{K}_2\text{Cr}_2\text{O}_7$  (FINKEM) in 1000 mL distilled water in volumetric flask. The working solution for batch adsorption experiment was prepared by proper dilution of the stock solution of Cr(VI) in distilled water. The UV-visible spectrophotometer was set with the equivalent dilution procedure as the experimental samples. 0.1M NaOH and/or HCl used for the adjustment of the pH value of the adsorption experiments solution.

### **5.3.6 Experimental design**

The experimental design for adsorptive removal of Cr(VI) involved the following treatments: shaker speed from 100 to 250 rpm, contact time (10, 20, 30, 40, 50, 50, 60, 80, 100 and 120) minutes, adsorbent dose (0.4, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0) g , pH = 2-10, Cr(VI) concentration from 0.5 – 6.0  $\text{mg.L}^{-1}$  and particle size (< 0.075, 0.425, 2.000 and 4.750) mm.

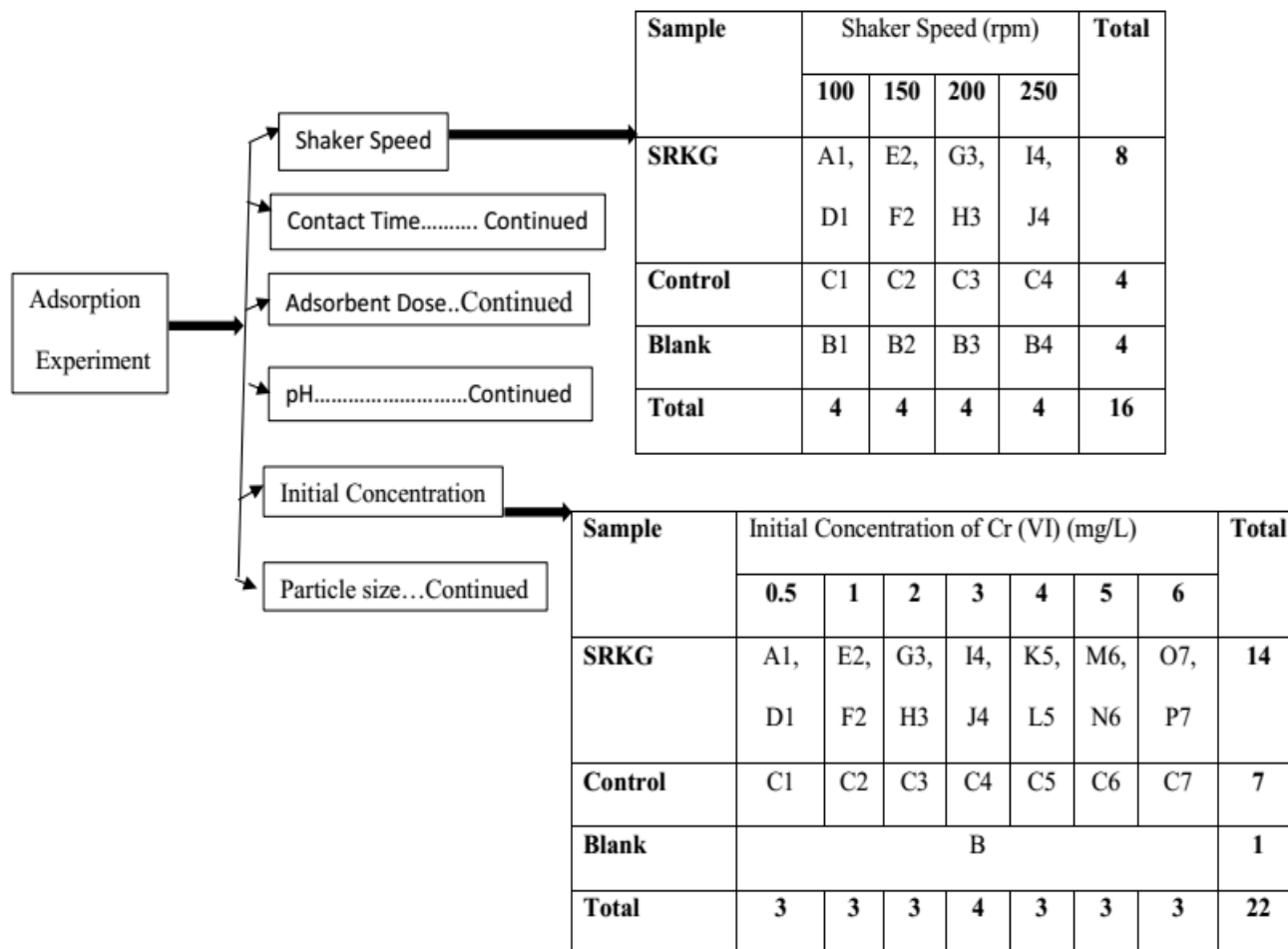


Figure 5.2 Batch adsorption experiment flow diagram (A1, E2, G3,...B = sample code; ...continued = similar table like shaker speed)

### 5.3.7 Cr(VI) ions adsorption

A series of duplicate batch adsorption experiment was conducted at  $22 \pm 2^\circ\text{C}$  at the Environmental Health Laboratory of the Jimma University, during at 2016. Polyethylene plastic bottles were washed using 0.01M  $\text{HNO}_3$  and thoroughly distilled water. The adsorbent (SRKG) was equilibrated by soaking with 0.01 M  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  for overnight (12 h) before the day of the actual experiments. Each set of the batch adsorptive experiment effect contains: duplicate trial, blank (only SRKG) and control (only Cr(VI) ion). A 100 mL aqueous solution containing a known Cr(VI) ions concentration was added into a series of 300 mL plastic bottles and the pH adjusted. The samples were shaken by a Horizontal Thermostat Orbital shaker for a fixed time, after which the samples

were removed from the shaker. The pH value was adjusted to  $1 \pm 0.3$  using 0.1 M H<sub>2</sub>SO<sub>4</sub> and/or 0.1 M NaOH. Thereafter, 1 mL diphenyl-carbazide in 50 mL was added and then stood for 10 min for color development. Residual Cr(VI) ion concentration was transferred to 1 cm cuvette absorption cell. Cr(VI) amount was then determined using the UV-visible spectrophotometer (HACH LANGE © Model No: 5000) and the average of duplicate measurements was reported.

### 5.3.8 Effect of shaker speed

The effect of shaker speed of Cr(VI) removal capacity was studied. The aqueous solution in each plastic bottles was kept agitated in the various speed orbital shaker at 100, 150, 200 and 250 revolutions per minute at a room temperature of  $22 \pm 2^\circ\text{C}$ , for set contact time.

Table 5.1 Identifying the optimum orbital shaker speed (rpm) for removal Cr(VI) using SRKG

| Sample  | Shaker Speed (rpm) |        |        |        | Total |
|---------|--------------------|--------|--------|--------|-------|
|         | 100                | 150    | 200    | 250    |       |
| SRKG    | A1, D1             | E2, F2 | G3, H3 | I4, J4 | 8     |
| Control | C1.                | C2.    | C3.    | C4.    | 4     |
| Blank   | B11                | B12    | B13    | B14    | 4     |
| Total   | 4                  | 4      | 4      | 4      | 16    |

Sample treatments involved: 16 samples in plastic bottles, control (only Cr, VI) without SRKG, blank only SRKG without Cr (VI) (A1, E2, G3, ..., B14 = sample code)



Figure 5.3 Orbital shaker speed used on the experiment

Cr(VI) solution was prepared from stock solution (35 mL) by dilution (65 mL distilled water). This was poured into 100 mL plastic bottle and pH adjusted to  $7 \pm 0.05$  by using 0.1 M NaOH and 0.1 M HCl. The 16 samples were prepared, of which 8 samples contained 0.4 g SRKG and Cr(VI) concentration, 4 were blanks (only SRKG with 100 mL distilled water without Cr (VI) concentration), and 4 were controls (only 35 mL Cr(VI) with 65 ml distilled water without 0.4 g SRKG adsorbent). All 16 plastic bottle samples were put on different agitated speed (rpm) for a 120 minutes contact time, at room temperature ( $22 \pm 2^\circ\text{C}$ ). The experiment was stopped at 120 minutes finished. The solutions were filtered by Whatman filter paper ( $0.45 \mu\text{m}$ ) and acidified to  $\text{pH } 1 \pm 0.3$  and 1 mL Diphenyl-carbazide in 50 mL was added and this left to stand for 10 minutes for color development. The residual Cr(VI) ion concentration was transferred to 1 cm absorption cell and it was determined using the UV-visible spectrophotometer made by HACH LANGE © (Model No: 5000). The average of duplicate measurements was reported. Finally, for further experiment, optimum string speed was selected depending on Cr (VI) removal efficiency

### 5.3.9 Contact time effect

To fix the equilibrium of the contact time at which the adsorption was completed, the agitation time was varied from 10, 20, 30, 40, 50, 60, 80, 100 and 120 minutes at each time four samples (two samples, one control and one blank) were taken off from shaker until equilibrium was achieved. A known concentration  $\text{Cr(VI)} = 3.5 \text{ mg.L}^{-1}$  of the adsorbate in aqueous solutions at desired  $\text{pH} = 7 \pm 0.05^\circ\text{C}$  was shaken with a desired amount of the adsorbent (0.425 mm particle size and  $0.4 \text{ g.L}^{-1}$  dose) at optimum shaker speed for Cr(VI) removal from previous set of experiment to be 150 rpm for a predetermined contact time effect using the Horizontal Thermostat Orbital shaker.

Table 5.2 Various contact time evaluated for optimization of Cr (VI) removal using SRKG

| Sample  | Time (min) |        |        |        |          |          |        |        |        | Total |
|---------|------------|--------|--------|--------|----------|----------|--------|--------|--------|-------|
|         | 10         | 20     | 30     | 40     | 50       | 60       | 80     | 100    | 120    |       |
| SRKG    | A1, D1     | E2, U2 | V3, W3 | X4, Y4 | Z.5, L5. | M.6, N.6 | O7, P7 | Q8, R8 | S9, T9 | 18    |
| Control | C.1        | C.2    | C.3    | C.4    | C.5      | C.6      | C.7    | C.8    | C.9    | 9     |
| Blank   | B.1        | B.2    | B.3    | B.4    | B.5      | B.6      | B.7    | B.8    | B.9    | 9     |
| Total   | 4          | 4      | 4      | 4      | 4        | 4        | 4      | 4      | 4      | 36    |

Sample treatments involved: 36 samples in plastic bottles, control (only Cr, VI) without SRKG, blank only SRKG without Cr (VI); (A1, E2, V3, ..., B.9 = sample code)

The amount Cr(VI) adsorbed over the unit mass of the adsorbent media, and the percentage adsorption was computed using Equations 5.1 and 5.2 given below, respectively (Sanchooli Moghaddam et al., 2016).

$$q_t = \frac{(C_0 - C_t) * V}{M} \quad (5.1)$$

$$A = \frac{(C_0 - C_t)}{C_0} * 100 \quad (5.2)$$

Where

$q_t$  = the value of Cr(VI) ions adsorbed at any time (min) ( $\text{mg.g}^{-1}$ ),

$C_0$  = initial amount of Cr(VI) ions ( $\text{mg.L}^{-1}$ ),

$C_t$  = final amount of Cr (VI) at any time (min) ( $\text{mg.L}^{-1}$ ),

$V$  = amount of the solution (L),

$M$  = mass of the SRKG media used in the experiment (g) and

$A$  = the percentage of chromium (VI) ions removed (%).

Finally, selected optimum contact time depends on removal efficiency of Cr(VI) for further experiments.

### 5.3.10 Adsorbent dose effect

To determine the optimum dose required for the reduction of average heavy metal concentration in the industrial wastewater to a desired level, different adsorbent doses ranging from (1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0  $\text{g.L}^{-1}$ ) were separately added into an aqueous solution of known  $\text{pH} = 7 \pm 0.05^\circ\text{C}$  containing a desired adsorbate concentration  $\text{Cr(VI)} = 3.5 \text{ mg.L}^{-1}$ . The mixture was agitated at optimum shaker speed = 150 rpm and at optimum contact time = 40 min.

Table 5.3 Various adsorption dose ( $\text{g.L}^{-1}$ ) evaluated for optimization on Cr (VI) removal using SRKG

| Sample  | Dose of SRKG (g) |        |        |        |        |        |        | Total |
|---------|------------------|--------|--------|--------|--------|--------|--------|-------|
|         | 1.0              | 1.5    | 2.0    | 2.5    | 3.0    | 3.5    | 4.0    |       |
| SRKG    | A1, D1           | E2, Q2 | R3, S3 | T4, U4 | V5, W5 | X6, Y6 | O7, P7 | 14    |
| Control | C                |        |        |        |        |        |        | 1     |
| Blank   | B1               | B2     | B3     | B4     | B5     | B6     | B7     | 7     |
| Total   | 3                | 3      | 3      | 4      | 3      | 3      | 3      | 22    |

Sample treatments involved: 22 samples in plastic bottles, control (only Cr, VI) without SRKG, blank only SRKG without Cr (VI); (A1, E2, R3, ..., B7 = sample code)

### 5.3.11 Solution pH effect

The solution pH effect was investigated to fix the highest pH value for the highest adsorptive removal of heavy metal over the initial pH value varying from (2, 4, 6, 8, and 10) by allowing a known optimum shaker speed = 150 rpm, contact time = 40 min., dose of SRKG 3 g from 0.425 mm particle size and unknown initial amount Cr(VI) = 3.5 mg.L<sup>-1</sup> and particle size of the adsorbent.

Table 5.4 Various pH evaluated for optimization on Cr (VI) removal using SRKG

| Sample  | pH        |           |           |           |           | Total |
|---------|-----------|-----------|-----------|-----------|-----------|-------|
|         | 2         | 4         | 6         | 8         | 10        |       |
| SRKG    | A1,<br>D1 | E2,<br>F2 | G3,<br>H3 | I4,<br>J4 | K5,<br>L5 | 10    |
| Control | C         |           |           |           |           | 1     |
| Blank   | B1        | B2        | B3        | B4        | B5        | 5     |
| Total   | 3         | 3         | 4         | 3         | 3         | 16    |

Sample treatments involved: 16 samples in plastic bottles, control (only Cr, VI) without SRKG, blank only SRKG without Cr (VI); (A1, E2, G3, ..., B5= sample code)

### 5.3.12 Effect of initial concentration of Cr(VI)

Initial concentration effect was studied varying the concentration of hexavalent chromium ions (1, 2, 3, 4, 5 and 6 mg.L<sup>-1</sup>) while maintaining optimum shaker speed= 150 rpm, contact time= 40 min., dose of SRKG 3 g from 0.425 mm particle size, pH = 2 and unknown particle size of the adsorbent.

Table 5.5 Various initial concentration of Cr (VI) evaluated for optimization on Cr (VI) removal using SRKG as adsorbent

| Sample  | Initial amount of Cr (VI) (mg.L <sup>-1</sup> ) |           |           |           |           |           | Total |
|---------|---|-----------|-----------|-----------|-----------|-----------|-------|
|         | 1   | 2         | 3         | 4         | 5         | 6         |       |
| SRKG    | A1,<br>D1                                       | E2,<br>P2 | Q3,<br>R3 | S4,<br>T4 | U5,<br>V5 | W6,<br>X6 | 12    |
| Blank   | B   |           |           |           |           |           | 1     |
| Control | C1  | C2        | C3        | C4        | C5        | C6        | 6     |
| Total   | 3   | 3         | 3         | 4         | 3         | 3         | 19    |

Sample treatments involved: 19 samples in plastic bottles, control (only Cr, VI) without SRKG, blank only SRKG without Cr (VI); (A1, E2, Q3, ..., C6 = sample code)

The method was explained by Gupta et al. (2015) and was arranged with the same changes to analysis Cr(VI) using SRKG.

- (a) Chromium(VI) (10 mL) from stock solution + 90 mL distilled water = 3 plastic bottles,
- (b) Chromium(VI) (20 mL) from stock solution + 80 mL distilled water = 3 plastic bottles,
- (c) Chromium(VI) (30 mL) from stock solution + 70 mL distilled water = 3 plastic bottles,
- (d) Chromium(VI) (40 mL) from stock solution + 60 mL distilled water = 3 plastic bottles,
- (e) Chromium(VI) (50 mL) from stock solution + 50 mL distilled water = 3 plastic bottles,
- (f) Chromium(VI) (60 mL) from stock solution + 40 mL distilled water = 3 plastic bottles, and
- (g) 100mL distilled water blank only contain SRKG without Cr(VI) concentration = 1 plastic bottle.

These 19 plastic bottles sample were agitated for 40 minutes then filtered by Whatman filter paper (0.45  $\mu$ m) and analyzed by UV- Visible spectrophotometer. Finally, the result was reported.

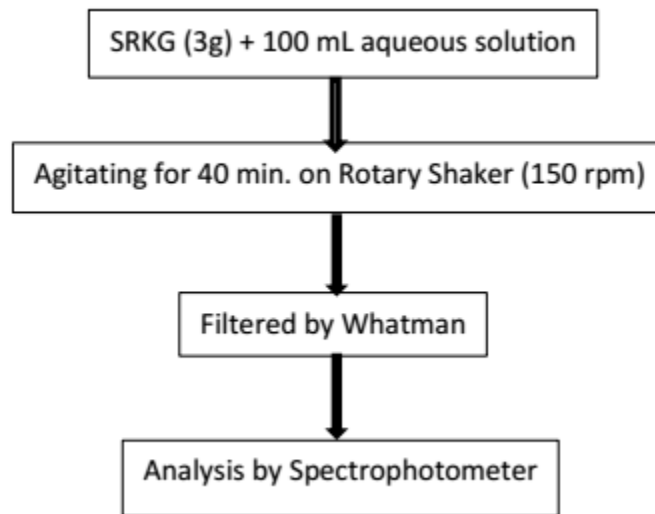


Figure 5.4 The adsorptive removal of Cr(VI) batch experimental flow chart

### 5.3.13 Particle size effect

The effect of the particle size was investigated for adsorptive removal of heavy metal over the particle size of adsorbent range (<0.075, 0.425, 2.000 and 4.750 mm).

Table 5.6 Various SRKG particle sizes evaluated for optimization on Cr (VI) removal

| Sample  | Particle size (mm) |        |        |        | Total |
|---------|--------------------|--------|--------|--------|-------|
|         | < 0.075            | 0.425  | 2.000  | 4.750  |       |
| SRKG    | A1, D1             | E2, F2 | G3, H3 | I4, J4 | 8     |
| Control | C                  |        |        |        | 1     |
| Blank   | B1                 | B2     | B3     | B4     | 4     |
| Total   | 3                  | 4      | 3      | 3      | 13    |

Sample treatments involved: 13 samples in plastic bottles, control (only Cr, VI) without SRKG, blank only SRKG without Cr (VI); (A1, E2, G3, ..., B4 = sample code)

#### 5.3.14 Desorption experiment

The regeneration of an adsorbent basically depends on the ease with which an adsorbate is released from the spent adsorbent. The desorption experiments was carried out 4 samples (duplicate, control and blank) Cr(VI) ion-loaded adsorbent was prepared by agitating on a known optimum dose = 3 g.L<sup>-1</sup> from particle size = 0.075 mm of SRKG with a desired concentration of Cr(VI) = 1 mg.L<sup>-1</sup> and pH = 2 by shaking at a fixed 150 rpm for a defined equilibrium agitation time 40 min. at room temperature 22 ± 2°C. After adsorption, the solid was separated from the supernatant solution by filtration. The solid on the filter paper was washed with distilled water. The Cr(VI)-loaded adsorbent was dried at 105°C for 12 hours in an oven. Desorption experiments was then being carried out by shaking the oven dried spent adsorbent at a fixed rpm for an equilibrium contact time in 100mL of different concentration of NaOH solution (0.5M, 0.1 M and 0.01 M) separately. Desorption percentage was calculated according to Eq. 5.3 (Hu et al., 2011; Singh et al., 2011; Albadarin et al., 2012).

$$\text{Desorption ratio (\%)} = \frac{\text{Amount of Cr(VI) ion desorbed}}{\text{Amount of Cr (VI) ion adsorbed}} \times 100 \quad (5.3)$$

### 5.3.15 Adsorption kinetics

The pseudo-first-order kinetic and pseudo-second-order kinetic are the most common models for checking of adsorption condition of the adsorbents (Ahluwalia and Goyal, 2007).

#### 5.2.15.1 Pseudo-first-order kinetics

The model equation can be shown in Eq.5.4:

$$\log(q_E - q_T) = \log q_E - \left( \frac{k_1}{2.303} \right) T \quad (5.4)$$

Where

$q_E$  = adsorption efficiency at equilibrium ( $\text{mg.g}^{-1}$ ),

$q_T$  = adsorption efficiency at a time ( $\text{mg.g}^{-1}$ ), and

$K_1$  = kinetics constant ( $\text{h}^{-1}$ )

#### 5.2.15.2 Pseudo second order kinetics

The model equation can be shown Eq. 5.5:

$$\frac{T}{q_E} = \frac{1}{K_2 q_E^2} + \left( \frac{1}{q_E} \right) T \quad (5.5)$$

Where

$K_2$  = kinetic constant ( $\text{g.mg}^{-1} \text{h}^{-1}$ ) and the rest of parameters are the same as those presented in equation 5.4.

### 5.3.16 Adsorption isotherms

Langmuir and Freundlich isotherms were used to fix the highest value of adsorption efficiency of the adsorbents.

### 5.3.16.1 Langmuir isotherm

The Langmuir isotherm is the homogenous molecule surface of adsorption. In this process, one molecule of adsorption cannot affect the near site of adsorption (Ahluwalia and Goyal, 2007).

Linear Langmuir equation is given as follows:

$$\frac{1}{q_E} = \frac{1}{q_M} + \frac{1}{q_M k_L} \frac{1}{C_E} \quad (5.6)$$

Where

$q_E$  = a value Cr(VI) adsorbed over gram of locally available materials,

$C_E$  = an equilibrium of Cr(VI) in wastewater, a milligram of Cr(VI) per liter,

$k_L$  = Langmuir the same, liter per milligram of Cr(VI), and

$q_M$  = maximum contain, a milligram of Cr(VI) per gram of SRKG.

Important features of the Langmuir equation stated in the forms of dimensionless separation factor (Moreno-Piraján and Giraldo, 2012),  $R_L$ , are defined as:

$$R_L = \frac{1}{(1 + K_L C_o)} \quad (5.7)$$

Where

$K_L$  is constant of Langmuir ( $L \cdot mg^{-1}$ ), and

$C_o$  is primary amount of Cr(VI) ions ( $mg \cdot L^{-1}$ )

$R_L$  a result indicating the shape of the isotherms:  $1 < R_L$  indicates disapproving adsorption,  $1 = R_L$  indicates linear,  $R_L$  values in between 0 and 1 indicates approving adsorption, and  $0 = R_L$  indicates adsorption nonreversible.

### 5.3.16.2 Freundlich isotherm

The Freundlich isotherm was described as the heterogeneous surface energies by multilayer adsorption (Sanchooli Moghaddam et al., 2016).

The general Freundlich isotherm is showed as follows Eq. 5.8:

$$\text{Log}(q_E) = \text{Log}(k_F) + \frac{1}{n} \text{Log}(C_e) \quad (5.8)$$

Where

$q_E$  shows adsorption efficiency ( $\text{mg.g}^{-1}$ ), and

$1/n$  values between 0 and 1 it shows the suitability of adsorption.  $K_F$  value is higher. It shows the better suitability of adsorption.

## 5.4 Results and Discussion

### 5.4.1 Characteristics of soil rich in kaolinite-goethite

Table 5.7 describes the location of the sites from where the soil samples were collected. The locations were randomly selected from the three sites to reduce the sampling bias (States, 1992).

Table 5.7 Sample taking location site of soil rich in kaolinite-goethite

| Sampling Site | UTM         | Difference (m) | Elevation (m) | Depth (m) |
|---------------|-------------|----------------|---------------|-----------|
| 1             | 37N 0269547 |                |               |           |
|               | 0850850     | ±3             | 1852          | 0.85-1.2  |
| 2             | 37N0269574  |                |               |           |
|               | 0850976     | ±3             | 1856          | 0.80-1.0  |
| 3             | 37N0269596  |                |               |           |
|               | 0850996     | ±3             | 1857          | 0.95      |

UTM represents Universal Transverse Mercator

#### 5.4.1.1 Particle size

The particle size distribution of soil rich in kaolinite-goethite ranges from 0.075 to 4.750 mm (Figure5.5). The Coefficient of Uniformity (CU) of the soil is equal to grain size ( $d_{60}$ ) over

effective grain size ( $d_{10}$ ). The value of CU was found to be 16 (Mathews and Zayas, 1989; Alaa and Mena, 2015) using the gradation curve for soil rich in kaolinite-goethite.

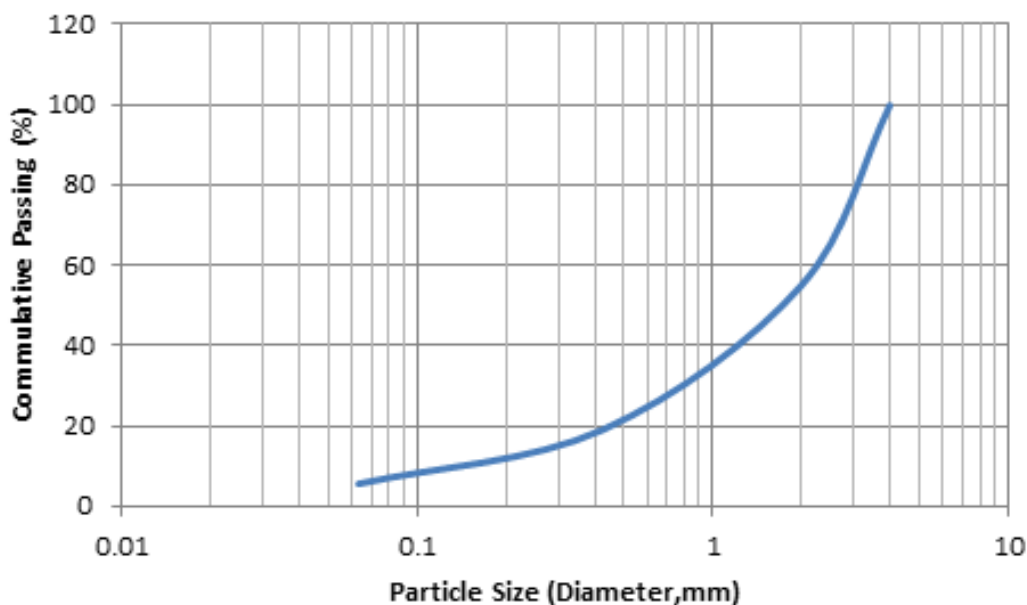


Figure 5.5 Gradation curve for soil rich in kaolinite-goethite used in present study

#### 5.4.2 Physical characteristics

Table 5.8 shows the electrical conductivity ( $20.10\mu\text{s cm}^{-1}$ ), cation exchange capacity ( $21.50\text{ cmol Kg}^{-1}$ ), pH (4.56), total nitrogen (0.13%), organic carbon (0.61%), organic matter (1.05%) and texture (clay) of soil rich in kaolinite-goethite used for the present study. This is characterized at the Ethiopia Institute of Agricultural Research by document number: Ethiopian Institute of Agricultural Research (EIAR/F) 510-2 and effective date in February 2015.

Table 5.8 Physical characteristic of soil rich in kaolinite-goethite

| Sample | Parameters                         |                                     |      |           |             |             |             |             |             |         |
|--------|------------------------------------|-------------------------------------|------|-----------|-------------|-------------|-------------|-------------|-------------|---------|
|        | E. C.<br>( $\mu\text{s cm}^{-1}$ ) | C.E.C.<br>( $\text{cmol Kg}^{-1}$ ) | pH   | TN<br>(%) | O.C.<br>(%) | O.M.<br>(%) | Sand<br>(%) | Silt<br>(%) | Clay<br>(%) | Texture |
| SRKG   | 20.10                              | 21.50                               | 4.56 | 0.13      | 0.61        | 1.05        | 12.80       | 10.40       | 76.80       | Clay    |

The elemental rich of SRKG was analysed by using SEM model ZEISS EVO LS15 such as O<sub>2</sub> (51.15%), Si (13.63%), Al (11.46%), Fe (11.04%), C (8.8%) and other which are effective for adsorbing Cr(VI) from contaminated water.

Table 5.9 Elements composition of soil rich in kaolinite-goethite

| Element | C     | O <sub>2</sub> | Na   | Mg   | Al    | Si    | P    | K    | Ca   | Ti   | Mn   | Fe    |
|---------|-------|----------------|------|------|-------|-------|------|------|------|------|------|-------|
| Weight  |       |                |      |      |       |       |      |      |      |      |      |       |
| %       | 8.90  | 51.15          | 0.02 | 0.34 | 11.46 | 13.63 | 0.23 | 0.33 | 0.09 | 0.66 | 1.08 | 11.04 |
| Atomic  |       |                |      |      |       |       |      |      |      |      |      |       |
| %       | 14.19 | 58.88          | 0.02 | 0.27 | 7.74  | 8.73  | 0.14 | 0.16 | 0.04 | 0.24 | 0.38 | 3.78  |

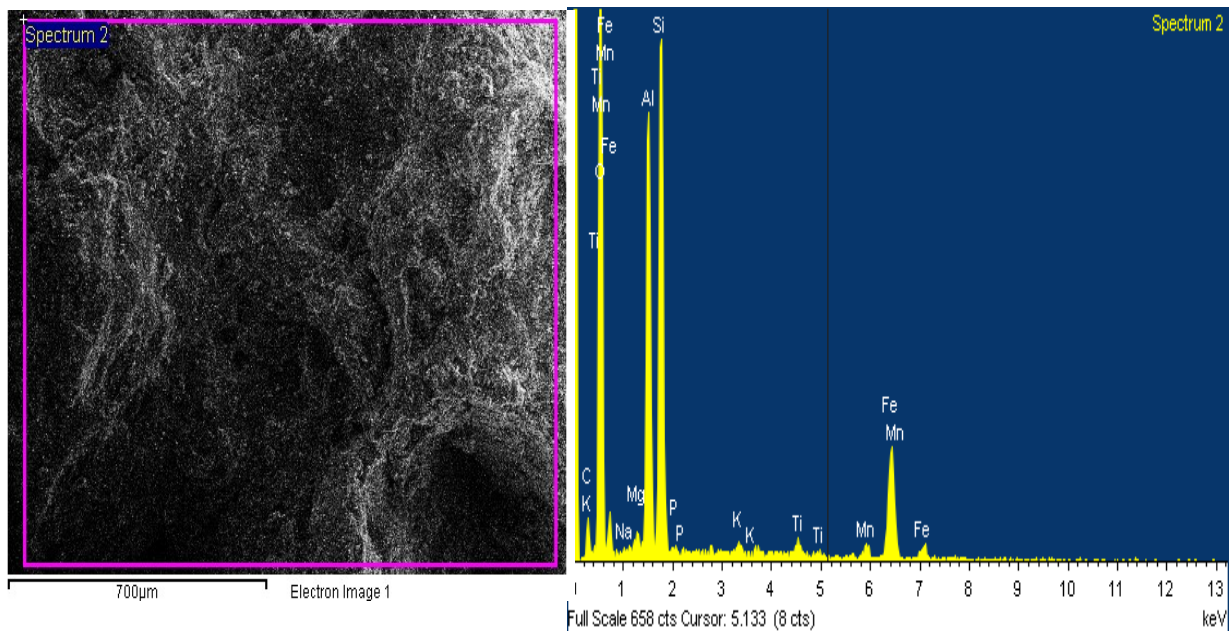


Figure 5.6 Elemental analysis of soil rich in kaolinite-goethite

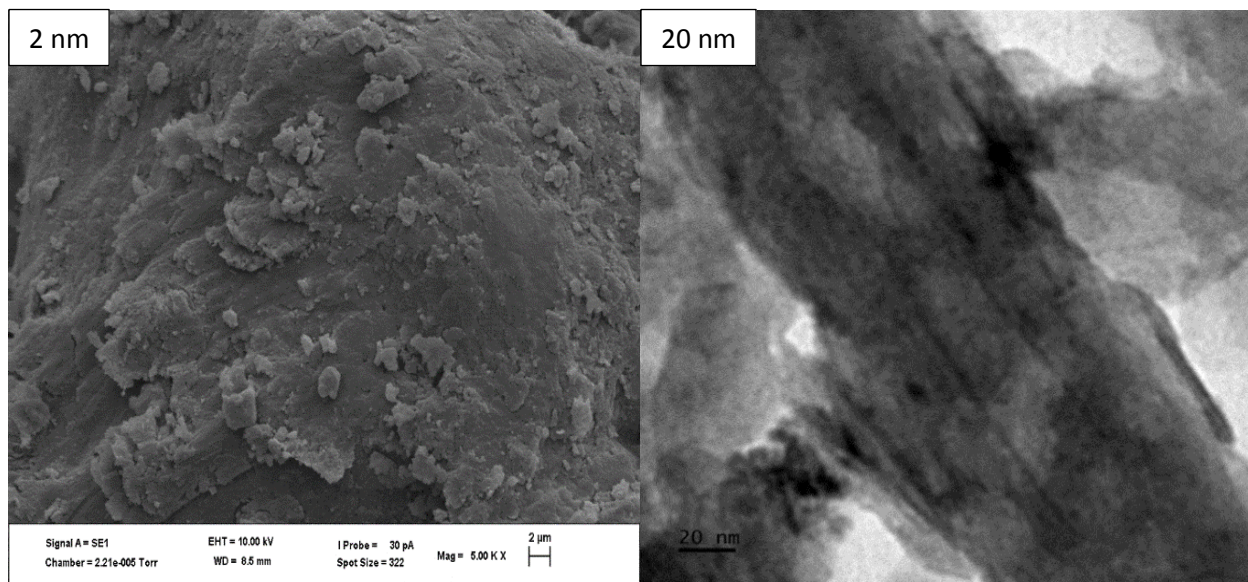


Figure 5.7 SEM and TEM image of SRKG magnified 2 nm and 20 nm, respectively

### 5.4.3 Shaker speed

The effect of shaker speed on the Cr(VI) removal capacity was studied. The experiment was carried out using contain 0.4 g dose of SRKG, at pH = 7, initial amount of Cr(VI) = 3.5 mg.L<sup>-1</sup>, 0.425 mm particle size and 120 minutes of contact time on the various shaking speed 100, 150, 200 and 250 revolutions per minute. In order to get the adsorption a plot of removal (%) curve at various shaking speed was plotted as indicated as per in Figure 5.8. It showed that string speed of 150 rpm has greater removal efficiency of Cr(VI) from the other string speeds. Thus, shaking speed was set at 150 rpm for the next experiments.

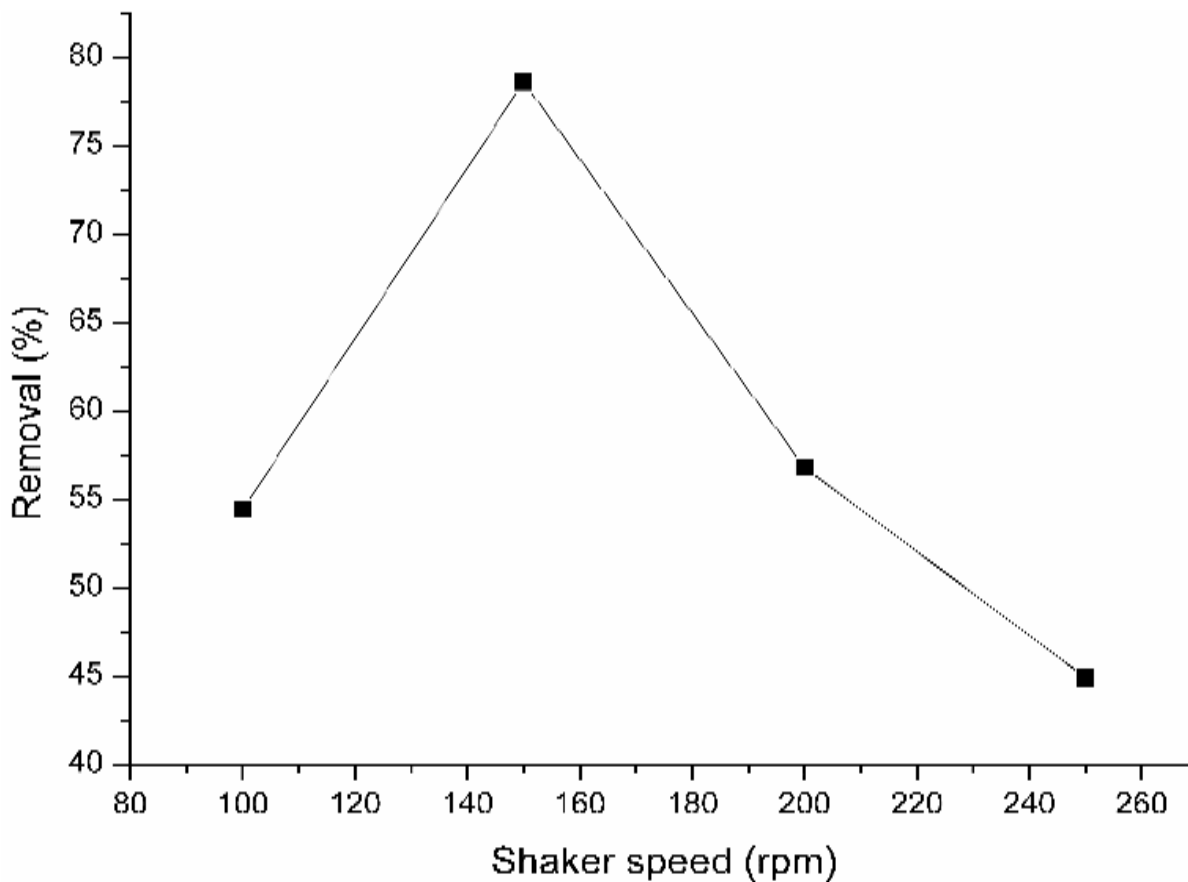


Figure 5.8 Cr(VI) adsorption capacity versus shaker speed (initial chromium concentration: 3.5 mg.L<sup>-1</sup>, dose of SRKG: 0.4 g.L<sup>-1</sup>, pH: 7, time: 120 min., particle size: 0.425 mm)

#### 5.4.4 Effect of contact time

The effect of contact time on chromium (VI) adsorption on the soil rich in kaolinite-goethite was studied by continuously increasing the contact time (10, 20, 30, 40, 50, 60, 80, 100 and 120) minutes (Figure 5.9). The contact time increased with the increasing of adsorptive removal of adsorbate up to 40 minutes. After 40 minutes (equilibrium point) showed the adsorption removal of adsorbate remained constant due to binding sites exhaustion similar was reported by Akiode et al (2015) and Kuppusamy et al (2016).

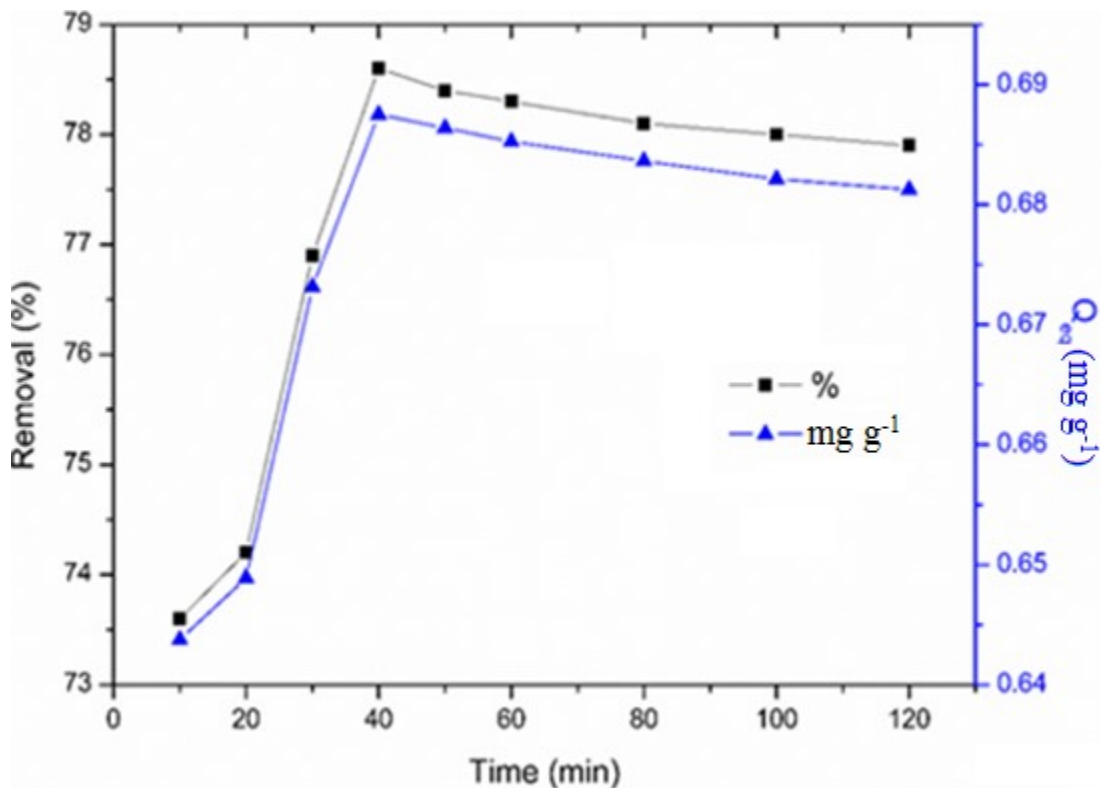


Figure 5.9 Cr(VI) adsorption capacity versus time (shaking speed: 150 rpm, initial chromium concentration: 3.5 mg.L<sup>-1</sup>, adsorbent dose: 0.4 g.L<sup>-1</sup>, pH: 7, particle size: 0.425 mm)

The rate of adsorption of chromium(VI) ion was fast up to 40 minutes. This was due to soil rich in kaolinite-goethite surface having many open spaces that could lead to strong attraction forces between Cr(VI) and adsorbent which was found to be in agreement with an observation of Wanees et al. (2012). Adsorptive removal of chromium(VI) from 10 to 40 minutes was rapid and fast due to highly increased adsorption sites (Mekonnen et al., 2015). After 40 minutes, there was no change in the rate of adsorption of Cr(VI) on SRKG. This showed that SRKG had no sufficient open space since the bulk solution increased. This concurs with the results reported by Workneh et al (2014). The adsorption capacity was high for a short period (40 minutes) on SRKG adsorbent. The reason for this could be due to the open space, clay soil texture, lower bulk density and small particle size. This finding was similar with that of Babel and Opiso (2007).

### 5.4.5 pH effect

The amount of chromium (VI) removed was dependent on pH (Figure 5.10). Chromate removal and adsorption capacity was shown in Figure 5.10. Chromate removal was low at pH 8 - 10 with the removal efficiency of 0.097 mg.g<sup>-1</sup> and the removal capacity of 96.2%. The adsorption capacity was high at the pH of 2 was 0.097 mg.g<sup>-1</sup> while the percentage of chromate removed was found to be 96.2% (Figure 5.10).

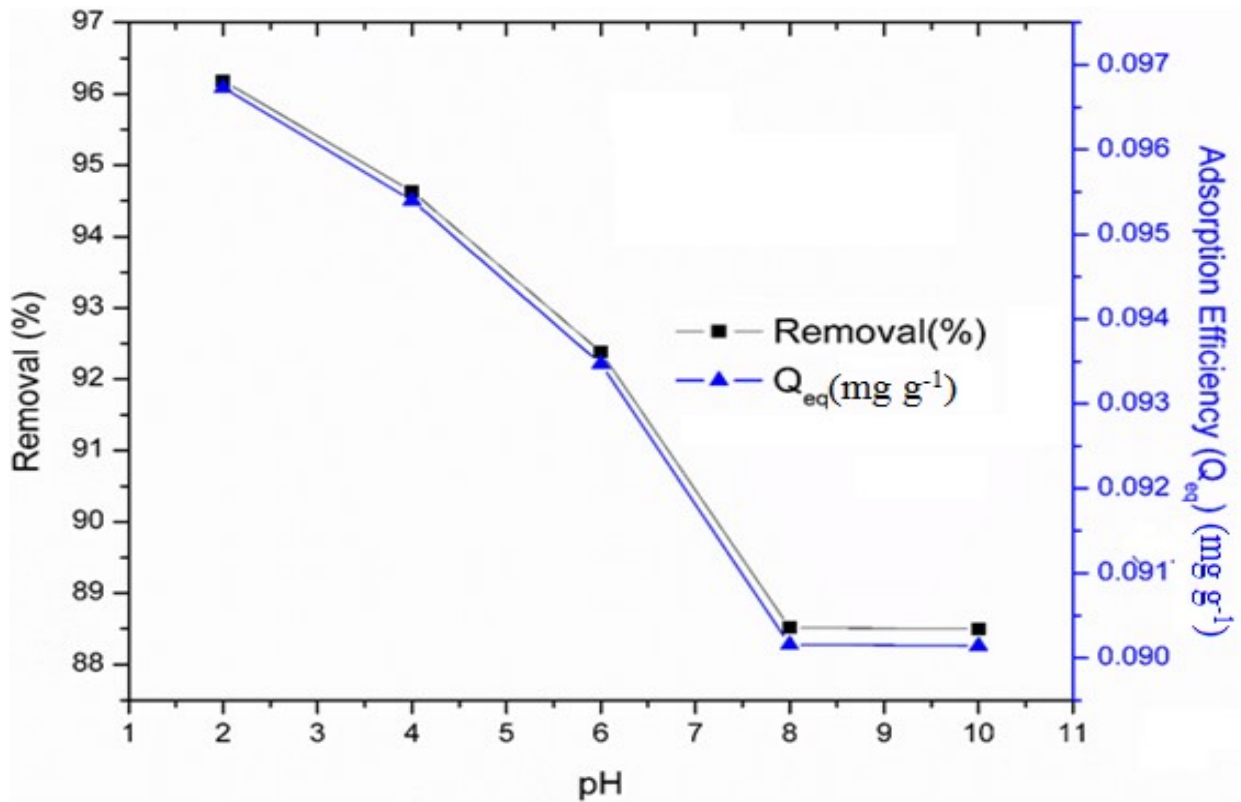


Figure 5.10 Cr(VI) removal and adsorption efficiency versus pH (shaking speed: 150 rpm, contact time: 40min, initial chromium concentration: 3.5 mg.L<sup>-1</sup>, SRKG dose: 0.4 g.L<sup>-1</sup>, particle size: 0.425 mm)

The pH value is crucial to control adsorption of metal in between solid and water interface. As shown in Fig. 5.10 Cr (VI) ion removal at pH = 2 within 40 minutes' contact time. It is might be hexavalent chromium reduced to trivalent chromium. Many H<sup>+</sup> ions were presented at low pH. The high concentration of H<sup>+</sup> neutralizes the negative charge ions by diffusion of dichromate ions.

This observation was similar to the finding reported by Yarkandi (2014). The percentage of chromate removal was increased from 88.5 to 96.2% by decreasing the solution pH value from 8 to 2. There was a decrease in pH with an increase in  $\text{HCrO}_4$  concentration. This shows that the attraction of anion high at both of the low crystalline oxy-hydroxides of Al and Fe and to crystalline oxides of Al and Fe. This observation also agrees with the finding of Otero et al. (2015). There was an increase of the removal of chromate in the as pH decreased from 8 to 2. This could be because of electrostatic attraction in between chromate ions and the positive surface charge of the adsorbent (Akiode et al., 2015). The adsorbent could develop a positive surface charge due to the dissociation of metal-hydroxide complexes at the solid-solution interface formed by metal oxides mainly Fe, Al, and Si. This finding agrees with an investigation by Zachara et al. (1987). In contrast, the efficiency of chromate removal decreased when  $\text{pH} > 2$ . The decrease in the adsorption of chromate with the increase in the pH of the solution beyond 2 might be due to the negative surface charge of the adsorbent and surface adjustment with  $\text{OH}^-$  ions that may cause repulsion between the hydroxyl ions and the chromate ions as stated Alemayehu et al. (2012). The pH value was decreased with increased positive charge in the SRKG due to protonization process. The adsorption chromium (VI) ion increased with increasing pH values. The pH values affected adsorption process on the surface of Al and Fe oxides. The amount of  $\text{HCr}_2\text{O}_7^-$  in the solution decreased, causing an increase in pH values. The trends positively agreed with the finding reported by Guo et al. (2008) and Zhong et al., (2014).

#### **5.4.6 Adsorbent dose effect**

The adsorbent dose effect of soil rich in kaolinite-goethite on the removal of chromate is shown in Figure 5.11. The amount of chromate removed increased from 78.9% to 89.4% as the soil rich in kaolinite-goethite dose efficiency decreased from 0.28 to 0.1  $\text{mg.g}^{-1}$ . The capacity of chromate adsorption decreased as the adsorbent dose increased (Figure 5.11). The trends positively agreed with the finding reported by Azouaou et al. (2010). Hence, the minimum dose for maximum chromate removal was 3  $\text{g.L}^{-1}$ . Thus the adsorbent dose of 3  $\text{g.L}^{-1}$  was considered for further adsorption experiments in this study.

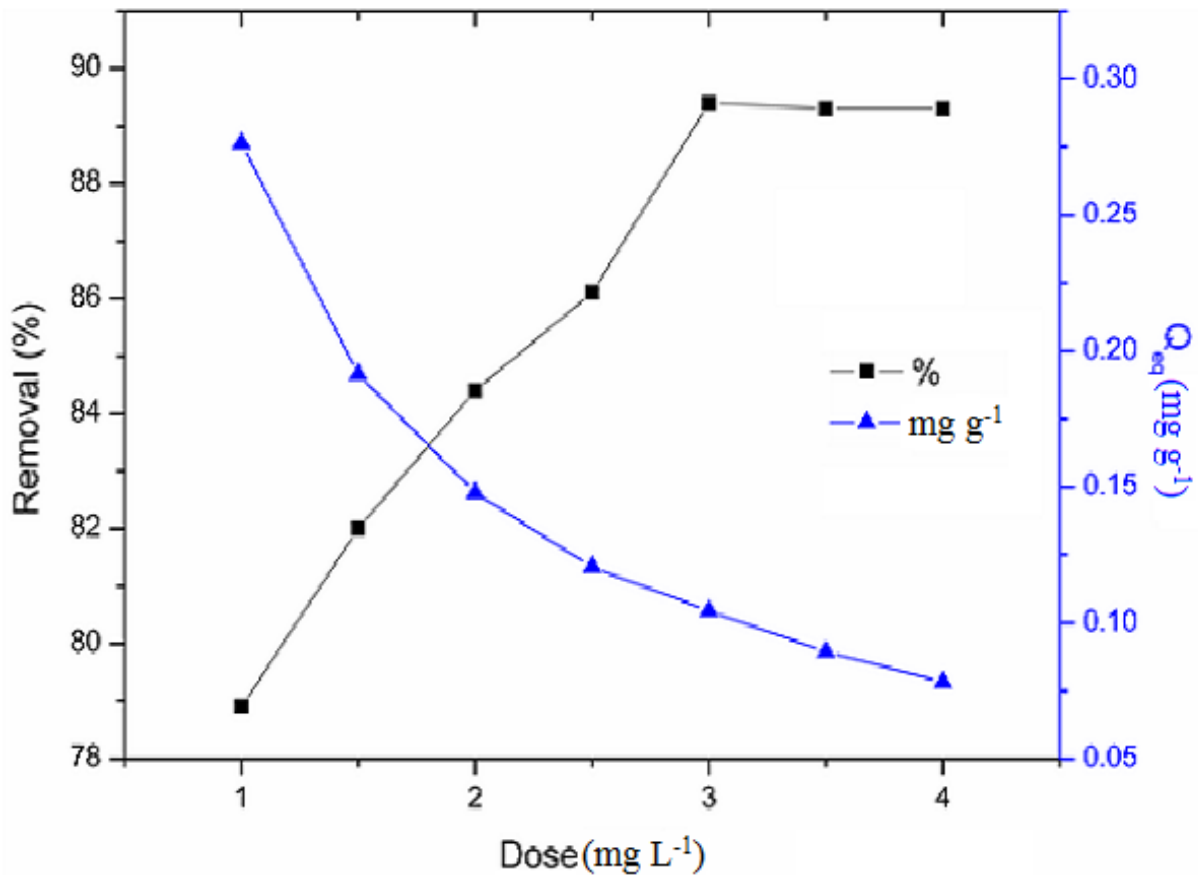


Figure 5.11 Cr(VI) removal capacity of adsorbent dose (speed of shaker: 150 rpm, contact time: 40 min, pH: 2, initial chromium concentration: 3.5 mg.L<sup>-1</sup>, particle size: 0.425 mm)

#### 5.4.7 Effect of initial chromate concentration

The graphical presentation of the chromate adsorption efficiency of the initial chromate amount is given in Figure 5.12. The result showed that the removal capacity of chromate increased from 98.5% to 99.33% as the initial chromate amount in the solution decreased from 6 mg.L<sup>-1</sup> to 1 mg.L<sup>-1</sup>. At 1 mg.L<sup>-1</sup> chromium (VI) concentration sufficient adsorbent / SRKG sites were available for adsorption of chromium (VI) ions due to the larger number of the ions at lower concentration (Akiode et al., 2015).

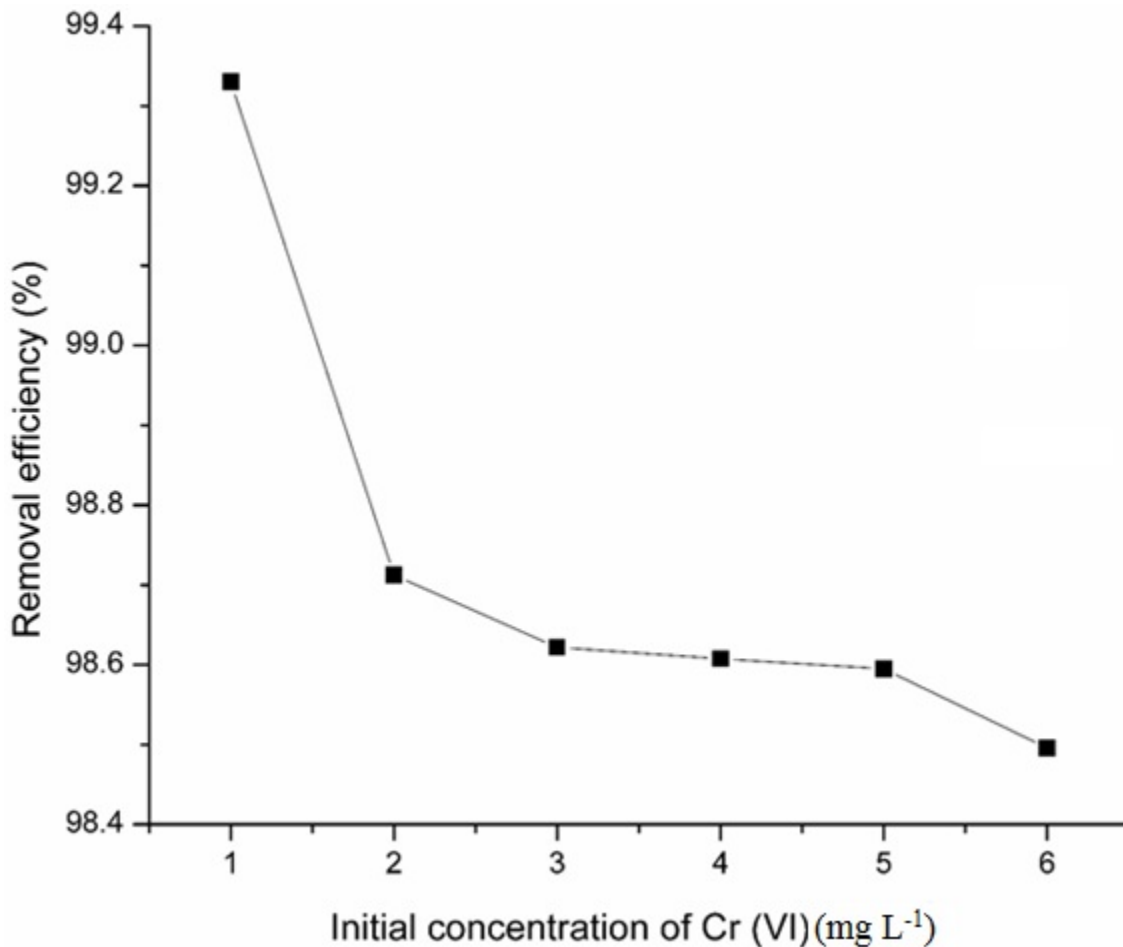


Figure 5.12 Cr(VI) removal efficiency versus initial concentration (SRKG dose: 3 g.L<sup>-1</sup>, pH: 2, time: 40 minutes, shaking speed: 150 rpm, particle size: 0.425 mm)

#### 5.4.8 Particle size effect

The effect of particle size on the optimum value of the experiment such as pH, dose of SRKG, contact time and initial concentration of chromium (VI) effect on the adsorptive removal of chromium (VI) was studied. Adsorptive removal of Cr(VI) from polluted water decreased with increasing particle size of SRKG that is from 98.8% to 92.5% with 0.075 mm to 4.75 mm, respectively.

The small particle (0.075 mm) adsorbent shows that it has a large surface area, and the large area of porosity is used for high Cr(VI) removal from contaminated water, as well as for a decreased

external mass effect (Alemayehu et al., 2011). Therefore, 0.075 mm diameter of particle size was selected as adsorbent for the rest of the batch adsorption experiment.

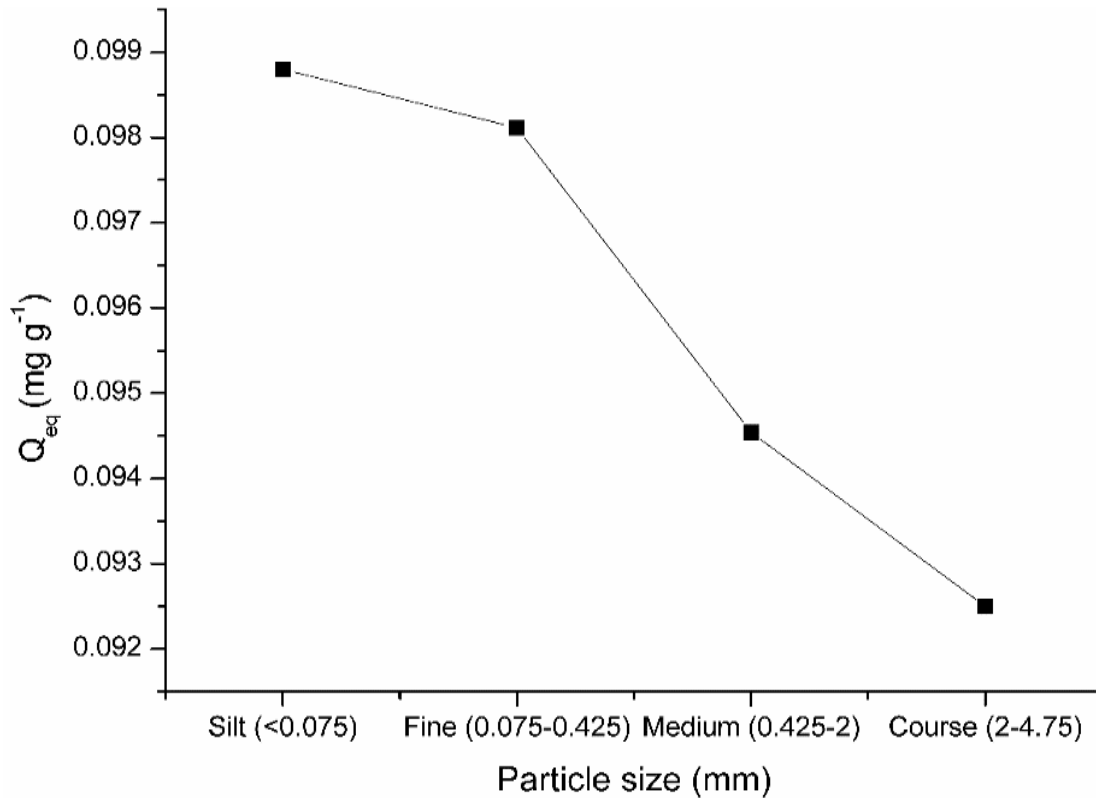


Figure 5.13 Cr(VI) removal efficiency versus particle size (adsorbent dose:  $3 \text{ g.L}^{-1}$ , pH: 2, time: 40 min, speed of shaker: 150 rpm and initial concentration:  $1 \text{ mg.L}^{-1}$ )

#### 5.4.9 Adsorption kinetics

The Pseudo first and second-order kinetic models are most used to study the adsorption kinetics. The rate of Cr(VI) adsorption by using SRKG was studied for different contact time 10, 20, 30, 40, 50, 60, 80, 100 and 120 minutes. Pseudo-second-order kinetic model coefficient of determination ( $r^2 = 0.99$ ) was found the best applicable for the adsorption of Cr(VI) ions to the soil rich in kaolinite-geothite.

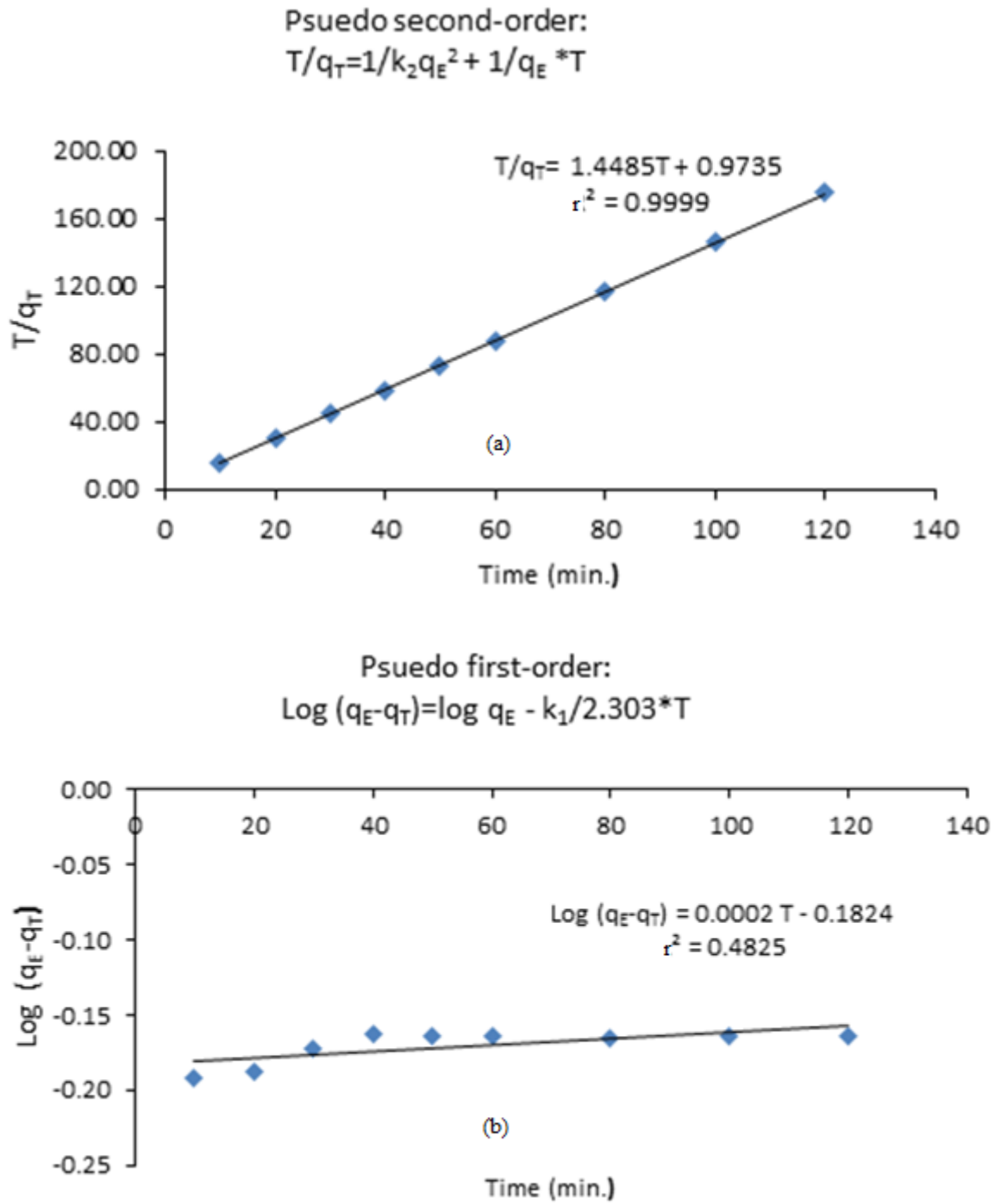


Figure 5.14 Psuedo-second and -first order for Cr(VI) adsorption onto SRKG (Cr(VI) = 1 mg.L<sup>-1</sup>; pH=7; adsorbent dose = 3 g; shaking speed=150 rpm and temp. 22 ± 2°C)

Table 5.10 Linear estimated kinetic adsorption of Cr(VI) ions onto adsorbents

| Temp.<br>°C | Psuedo first-order:<br>Log (q <sub>E</sub> -q <sub>T</sub> ) = Log q <sub>E</sub> - k <sub>1</sub> /2.303*T |                       |                | Psuedo second-order:<br>T/q <sub>T</sub> = 1/k <sub>2</sub> q <sub>E</sub> <sup>2</sup> + 1/q <sub>E</sub> *T |                  |                |
|-------------|---|-----------------------|----------------|---|------------------|----------------|
|             | log q <sub>E</sub>  | k <sub>1</sub> /2.303 | r <sup>2</sup> | 1/k <sub>2</sub> q <sub>E</sub> <sup>2</sup>  | 1/q <sub>E</sub> | r <sup>2</sup> |
| 22±2        | 0.1824  | 0.0002                | 0.4828         | 0.9735  | 1.4485           | 0.9999         |

#### 5.4.10 Adsorption isotherm

The equilibrium adsorption experiment was investigated at pH 2 varying the chromate amount of 2 mg.L<sup>-1</sup> using 1.5 g.L<sup>-1</sup> of the SRKG. The results of the chromate adsorption isotherm are given in Figure 5.16. The Freundlich and Langmuir isotherm parameters obtained from the linear equation of these models are given in Table 5.11. The values of the r<sup>2</sup> for the Freundlich and Langmuir isotherms were 0.978 and 0.9576, respectively. Dimensionless constant for SRKG was in between 0 and 1 which shows a favorable adsorption process.

Table 5.11 Langmuir and Freundlich isotherm for adsorption of Cr(VI) using SRKG

| SRKG<br>Dose<br>(g L <sup>-1</sup> ) | C <sub>i</sub><br>(mg L <sup>-1</sup> ) | Duplicate |      | C <sub>e</sub><br>(mg L <sup>-1</sup> ) | log C <sub>e</sub> | Volume<br>(L) | Q <sub>e</sub><br>(mg g <sup>-1</sup> ) | log q <sub>e</sub> | 1/C <sub>e</sub> | 1/Q <sub>e</sub> | C <sub>e</sub> /Q <sub>e</sub><br>(mg L <sup>-1</sup> ) |
|--------------------------------------|---|-----------|------|---|--------------------|---------------|---|--------------------|------------------|------------------|---|
|                                      |   | A         | B    |   |                    |               |   |                    |                  |                  |   |
| 0.30                                 | 10.00                                   | 0.07      | 0.07 | 0.07                                    | -1.17              | 0.10          | 1.66                                    | 0.22               | 14.93            | 0.60             | 0.04  |
| 0.30                                 | 20.00                                   | 0.26      | 0.24 | 0.25                                    | -0.59              | 0.10          | 3.29                                    | 0.52               | 3.88             | 0.30             | 0.08  |
| 0.30                                 | 30.00                                   | 0.41      | 0.41 | 0.41                                    | -0.38              | 0.10          | 4.93                                    | 0.69               | 2.42             | 0.20             | 0.08  |
| 0.30                                 | 40.00                                   | 0.55      | 0.56 | 0.56                                    | -0.25              | 0.10          | 6.57                                    | 0.82               | 1.80             | 0.15             | 0.08  |
| 0.30                                 | 50.00                                   | 0.70      | 0.69 | 0.70                                    | -0.15              | 0.10          | 8.22                                    | 0.91               | 1.42             | 0.12             | 0.09  |
| 0.30                                 | 60.00                                   | 0.89      | 0.91 | 0.90                                    | -0.04              | 0.10          | 9.85                                    | 0.99               | 1.11             | 0.10             | 0.09  |

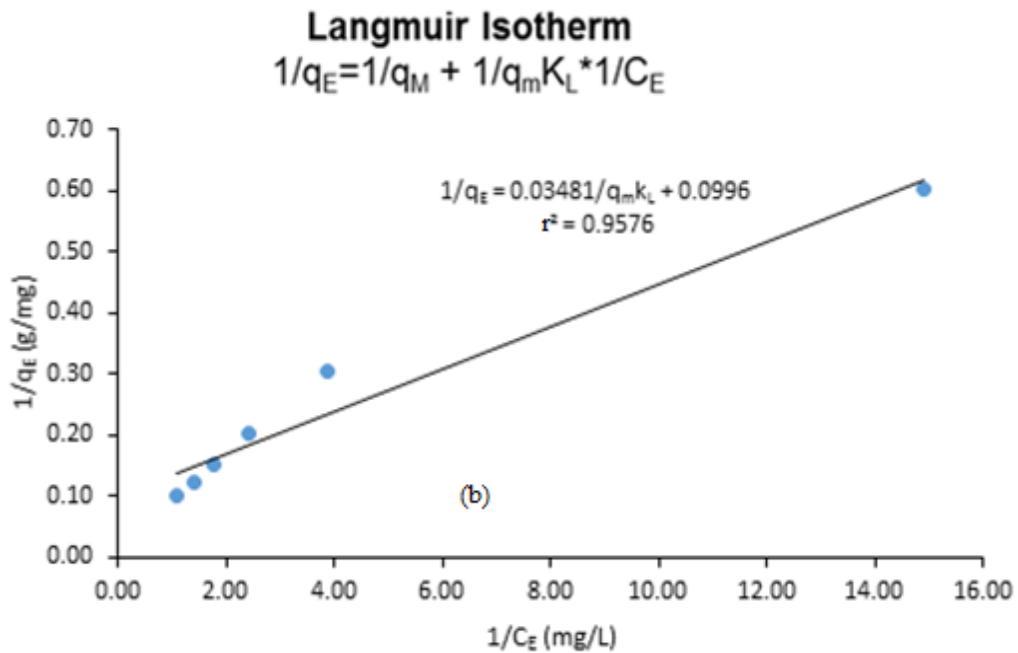
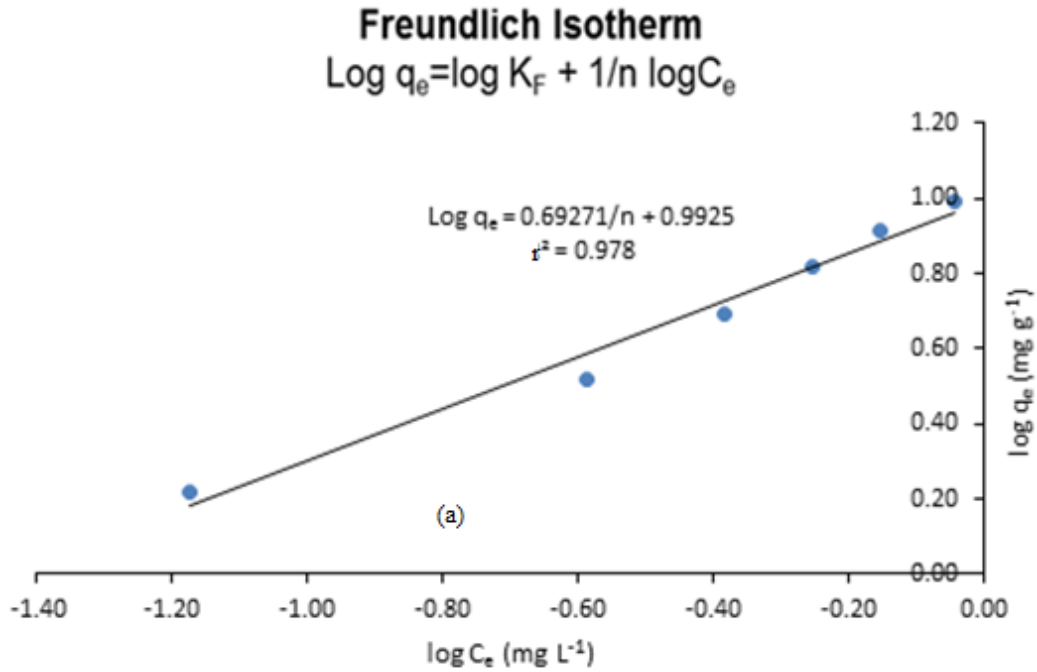


Figure 5.15 Freundlich (a) and Langmuir (b) isotherms for chromate adsorption using SRKG (initial chromate concentration:  $1 \text{ mg.L}^{-1}$ , dose of SRKG:  $3 \text{ g.L}^{-1}$ , pH: 2, time: 40 min, speed of shaker: 150 rpm)

Table 5.12 Linear estimated isotherm models and its constant value for chromate adsorption

| Temp.<br>°C | Freundlich Isotherm:<br>$\text{Log } q_e = \text{log } K_F + 1/n \text{ log } C_e$ |      |                | Langmuir Isotherm:<br>$1/q_E = 1/q_M + 1/q_M K_L * 1/C_E$ |                                 |                |
|-------------|--|------|----------------|---|---------------------------------|----------------|
|             | $K_F$ (mg g <sup>-1</sup> )  | 1/n  | R <sup>2</sup> | 1/q <sub>M</sub> (mg g <sup>-1</sup> )                    | 1/q <sub>M</sub> K <sub>L</sub> | R <sup>2</sup> |
| 22±2        | 0.99   | 0.69 | 0.99           | 0.09  | 0.03                            | 0.96           |

#### 5.4.11 Desorption study

Figure 5.16 shows the percentage of chromate desorbed studied using different concentration of the NaOH solution. The result showed that the percentage of chromate desorbed increased from 34.10% to 77.33% as the amount of NaOH increased from 0.01 to 0.5 M in the solution. This indicates that when NaOH is at about 0.5 M concentration the adsorbent materials exhausted can be regenerated for reuse. This finding agrees with the finding repeated by Hu et al. (2011), Singh et al. (2011) and Albadarin et al. (2012).

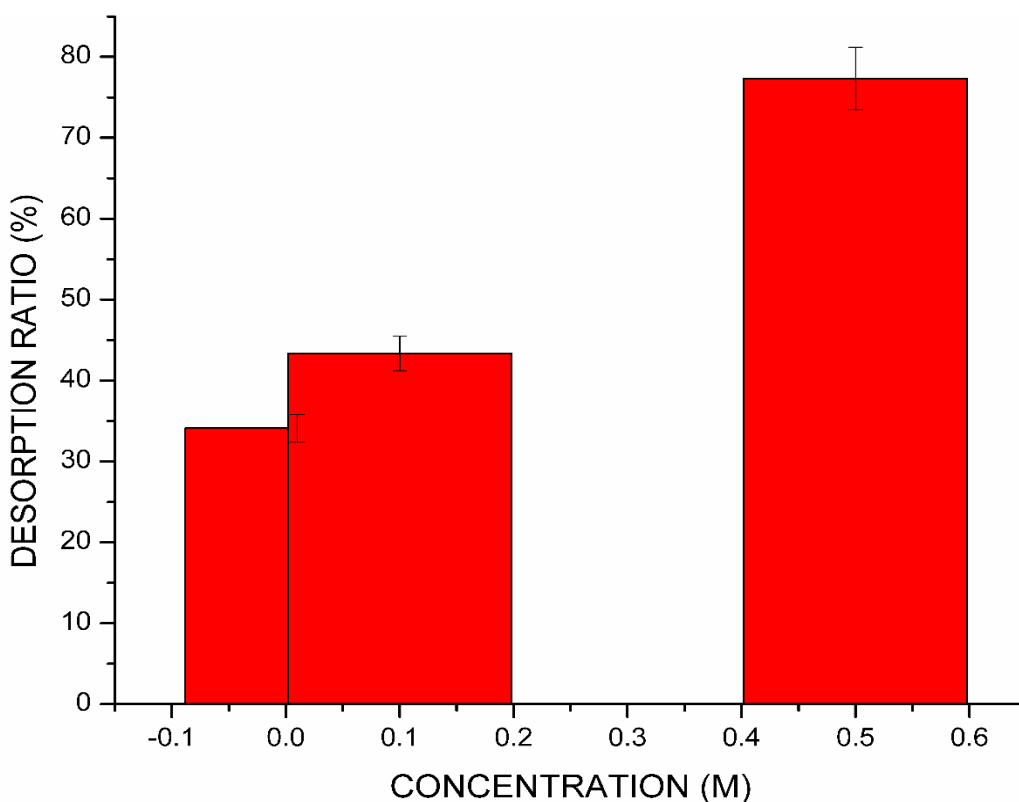


Figure 5.16 Desorption of Cr(VI) from soil rich in kaolinite-geothite

#### 5.4.12 Removal of chromate from real wastewater sample

The characteristics of the wastewater sample collected from Friendship Tannery PLC factory, East Showa Zone are given in Table 5.13. The wastewater contained 0.98 mg.L<sup>-1</sup> chromate. This 0.98 mg.L<sup>-1</sup> chromate was reduced to 0.035 mg.L<sup>-1</sup> by 150rpm shaker speed, 3.5 g.L<sup>-1</sup> of the soil rich in kaolinite-goethite of particle size <0.075mm within 40 min of contact time at pH =2 of the sample. This means that 96.4% of the 0.98 mg.L<sup>-1</sup> chromate concentration of the wastewater was removed by 3.5 g.L<sup>-1</sup> of the adsorbent.

Table 5.13 Physicochemical characteristics of wastewater from Friendship Tannery PLC factory

| Composition                   | Unit                | Value  |
|-------------------------------|---------------------|--------|
| Cr <sup>+6</sup>              | mg.L <sup>-1</sup>  | 0.98   |
| PO <sub>4</sub> <sup>3-</sup> | mg.L <sup>-1</sup>  | 15.91  |
| NO <sub>3</sub> <sup>-</sup>  | mg.L <sup>-1</sup>  | 1.80   |
| Cl <sup>-</sup>               | mg.L <sup>-1</sup>  | 819.28 |
| DO                            | mg.L <sup>-1</sup>  | 3.45   |
| COD                           | mg.L <sup>-1</sup>  | 463.50 |
| BOD                           | mg.g <sup>-1</sup>  | 941.40 |
| pH                            | -                   | 7.56   |
| EC                            | μs.cm <sup>-1</sup> | 6.19   |
| Turbidity                     | NTU                 | 14.56  |
| Temperature                   | °C                  | 25.85  |

#### 5.5 Conclusions

Chromium(VI) present in the water greater than permitted limit is toxic and could lead to several negative health effects on living organisms. The batch adsorption was evaluated by the different effects, such as the pH, the contact time, and the initial amount of Cr(VI). This study demonstrated the adsorptive efficiency of soil rich in kaolinite-goethite for Cr(VI) ions removal technique from industrial polluted water. Adsorption of chromium(VI) on SRKG was high at pH = 2, time = 40 minutes and initial amount of Cr(VI) = 2 mg.L<sup>-1</sup>. Freundlich and Langmuir isotherm was examined

in this study at a room temperature  $22 \pm 2^\circ\text{C}$ . The result showed SRKG can be used as low-cost adsorbent technology for Cr(VI) removal from contaminated industrial wastewater.

## 5.6 References

- Ahluwalia, S and Goyal, D. 2007. Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresource Technology* 98: 2243-2257.
- Akiode, O, Idowu, M, Omeike, S and Akinwunmi, F. 2015. Adsorption and kinetics studies of Cu (II) ions removal from aqueous solution by untreated and treated sugarcane bagasse. *Global Nest Journal* 17: 583-593.
- Albadarin, A, Mangwandi, C, Ala'a, H, Walker, G, Allen, S and Ahmad, M. 2012. Kinetic and thermodynamics of chromium ions adsorption onto low-cost dolomite adsorbent. *Chemical Engineering Journal* 179: 193-202.
- Alaa, H and Mena, M. 2015. Batch Experiment and adsorption isotherm of phosphate removal by using drinking water treatment sludge and red mud. *International Journal of Advanced Research in Science, Engineering and Technology* 2: 557-571.
- Alemayehu, D, Singh, S and Tessema, D. 2012. Assessment of the adsorption capacities of fired clay soils from Jimma (Ethiopia) for the removal of Cr (VI) from aqueous solution. *Universal Journal of Environmental Research and Technology* 2: 411-420.
- Alemayehu, E, Thiele-Bruhn, S and Lennartz, B. 2011. Adsorption behaviour of Cr(VI) onto macro and micro-vesicular volcanic rocks from water. *Separation and Purification Technology* 78: 55-61.
- Alfarra, R, Ali, N and Yusoff, M. 2014. Removal of heavy metals by natural adsorbent: a review. *International Journal of Bioscience* 4: 130-139.
- APHA. 2005. Standard methods for examination of water and wastewater. American public health association, American water works association and the water and environment federation, 21th ed, Washington DC, USA.
- Babel, S and Opiso, E. 2007. Removal of Cr from synthetic wastewater by sorption into volcanic ash soil. *International Journal of Environmental Science and Technology* 4: 99-107.

- Balasubramanian, S and Pugalenth, V. 1999. Determination of total chromium in tannery waste water by inductively coupled plasma-atomic emission spectrometry, flame atomic absorption spectrometry and UV-visible spectrophotometric methods. *Talanta* 50: 457-467.
- Bouyoucos, G. 1962. Hydrometer method improvement for making particle size analysis of soils. *Agronomy Journal* 54: 179-186.
- Chapman, H. 1965. Cation Exchange Capacity. In: C.A. Black, (Eds.), Methods of soil analysis. agronomy 9, Am. Soc. Agro. Inc., Madison, Wisconsin, pp: 891-901.
- Chen, S, Yue, Q, Gao, B, Li, Q and Xu, X. 2011. Removal of Cr (VI) from aqueous solution using modified corn stalks: characteristic, equilibrium, kinetic and thermodynamic study. *Chemical Engineering Journal* 168: 909-917.
- Federation, W. and Association, A. 2005. Standard methods for the examination of water and wastewater. *American Public Health Association (APHA)*: Washington, DC, USA.
- Fufa, F, Alemayehu, E and Lennartz, B. 2013. Defluoridation of groundwater using termite mound. *Water, Air and Soil Pollution* 224: 1-15.
- GSOE. 2011. Opportunities for kaolin resource development in Ethiopia, geological survey of Ethiopia. Addis Ababa, Ethiopia
- Guo, X, Zhang, S and Shan, X. 2008. Adsorption of metal ions on lignin. *Journal of Hazardous Materials* 151: 134-142.
- Gupta, P, Kumar, P and Singh, N. 2015. Adsorption of copper metal by living *Aspergillus niger* L. biomass. *International Journal of Environmental Sciences* 5: 1122-1132.
- Hokkanen, S, Bhatnagar, A, Repo, E, Lou, S and Sillanpää, M. 2016. Calcium hydroxyapatite microfibrillated cellulose composite as a potential adsorbent for the removal of Cr(VI) from aqueous solution. *Chemical Engineering Journal* 283: 445-452.
- Hu, X, Wang, J, Liu, Y, Li, X, Zeng, G, Bao, Z, Zeng, X, Chen, A and Long, F. 2011. Adsorption of chromium (VI) by ethylenediamine-modified cross-linked magnetic chitosan resin: isotherms, kinetics and thermodynamics. *Journal of Hazardous Materials* 185: 306-314.
- Kan, C, Ibe, A, Rivera, K, Arazo, R and Luna, M. 2017. Hexavalent chromium removal from aqueous solution by adsorbents synthesized from groundwater treatment residuals. *Sustainable Environment Research* 27:163-167

- Kuppusamy, S, Thavamani, P, Megharaj, M, Venkateswarlu, K, Lee, Y and Naidu, R. 2016. Oak (*Quercus robur*) acorn peel as a low-cost adsorbent for hexavalent chromium removal from aquatic ecosystems and industrial effluents. *Water, Air and Soil Pollution* 227: 1-11.
- Lin, H, Rong, C, Jiu, B, Li, B, Yu, Q, Gan, L and Zhang, Z. 2018. Effects of chromium on pyrolysis characteristic of water hyacinth (*Eichornia crassipes*). *Renewable Energy* 115: 676-684.
- Liu, C and Evett, J. 2003. Soil properties: testing, measurement, and evaluation, Banta Book Company, USA. ISBN:0-13-093005-9.: ISBN 0-13-093005-9.
- Mathews, A and Zayas, I. 1989. Particle size and shape effects on adsorption rate parameters. *Journal of Environmental Engineering* 115: 41-55.
- Mekonnen, E, Yitbarek, M and Soreta, T. 2015. Kinetic and thermodynamic studies of the adsorption of Cr (VI) onto some selected local adsorbents. *South African Journal of Chemistry* 68: 45-52.
- Moreno-Piraján, J and Giraldo, L. 2012. Heavy metal ions adsorption from wastewater using activated carbon from orange peel. *Journal of Chemistry* 9: 926-937.
- Otero, M, Cutillas-Barreiro, L, Nóvoa-Muñoz, J, Arias-Estévez, M, Fernández-Sanjurjo, M, Álvarez-Rodríguez, E and Núñez-Delgado, A. 2015. Cr (VI) sorption/desorption on untreated and mussel-shell-treated soil materials: fractionation and effects of pH and chromium concentration. *Solid Earth* 6: 373-382.
- Pan, J, Jiang, J and Xu, R. 2014. Removal of Cr (VI) from aqueous solutions by Na<sub>2</sub>SO<sub>3</sub>/FeSO<sub>4</sub> combined with peanut straw biochar. *Chemosphere* 101: 71-76.
- Pan, J, Jiang, J and Xu, R. 2013. Adsorption of Cr (III) from acidic solutions by crop straw derived biochars. *Journal of Environmental Sciences* 25: 1957-1965.
- Panda, H, Tiadi, N, Mohanty, M and Mohanty, C. 2017. Studies on adsorption behavior of an industrial waste for removal of chromium from aqueous solution. *South African Journal of Chemical Engineering* 23: 132-138.
- Pehlivan, E and Cetin, S. 2009. Sorption of Cr (VI) ions on two Lewatit-anion exchange resins and their quantitative determination using UV-visible spectrophotometer. *Journal of Hazardous Materials* 163: 448-453.
- Saifuddin, M and Kumaran, P. 2005. Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. *Electronic Journal of Biotechnology* 8: 43-53.

- Sanchooli Moghaddam, M, Rahdar, S and Taghavi, M. 2016. Cadmium removal from aqueous solutions using saxaul tree ash. *Iranian Journal of Chemistry and Chemical Engineering* 35: 45-52.
- Singh, S, Barick, K and Bahadur, D. 2011. Surface engineered magnetic nanoparticles for removal of toxic metal ions and bacterial pathogens. *Journal of Hazardous Materials* 192: 1539-1547.
- States, U. 1992. EPA preparation of soil sampling protocols : Sampling techniques and strategies. environmental monitoring systems laboratory office of research and development, (July), 252: 1-169.
- Sultana, F, Uddin, M, Kabir, M, Sultana, N, Sikder, M and Rahman, S. 2016. Removal efficiency of chromium (VI) ions from aqueous solution by adsorption of rice husk and saw dust ash as a homogeneous composite. *International Journal of Environmental Sciences* 6: 987-993.
- Tang, L, Fang, Y, Pang, Y, Zeng, G, Wang, J, Zhou, Y, Deng, Y, Yang, G, Cai, Y and Chen, J. 2014. Synergistic adsorption and reduction of hexavalent chromium using highly uniform polyaniline–magnetic mesoporous silica composite. *Chemical Engineering Journal* 254: 302-312.
- USEPA. 2011. Ground water and drinking water , current drinking water standards, EPA 816-F-02.
- Van Reewijk, L. 1992. Procedures for soil analysis. (3rd Ed.). *International Soil Reference Center (ISRIC)*, Wageningen, Netherlands.
- Wanees, S, Monem, A, Adam, M and Mohamed, M. 2012. Adsorption studies on the removal of hexavalent chromium-contaminated wastewater using activated carbon and bentonite. *Chemistry Journal* 02: 95-105.
- Workneh, A, Habtu, N and Beyene, H. 2014. Removal of hexavalent chromium from tannery wastewater using activated carbon primed from sugarcane bagasse: Adsorption/desorption studies. *American Journal of Applied Chemistry* 2: 128-135.
- Yang, Z, Xiong, S, Wang, B, Li, Q and Yang, W. 2013. Cr (III) adsorption by sugarcane pulp residue and biochar. *Journal of Central South University* 20: 1319-1325.
- Yarkandi, N. 2014. Kinetic and isotherm of toxic hexavalent chromium adsorption onto natural adsorbent. *International Journal of Curr. Microbiology and Applied Science* 3: 1-15.

- Zachara, J, Girvin, D, Schmidt, R and Resch, C. 1987. Chromate adsorption on amorphous iron oxyhydroxide in the presence of major groundwater ions. *Environmental Science and Technology* 21: 589-594.
- Zhong, Q, Yue, Q, Li, Q, Gao, B and Xu, X. 2014. Removal of Cu (II) and Cr (VI) from wastewater by an amphoteric sorbent based on cellulose-rich biomass. *Carbohydrate polymers* 111: 788-796.

## 6. REMOVAL OF Cr(VI) FROM CONTAMINATED WATER USING SOIL RICH IN KAOLINITE-FERRINATRITE, COFFEE HUSK ASH AND SOIL RICH IN KAOLINITE-GEOTHITE

### 6.1 Abstract

This study examined the efficiency of Cr(VI) ion removal from contaminated water using locally available adsorbent media. Equilibrium contact time for Cr(VI) removal was observed within 40 minutes. Adsorption of Cr(VI) followed pseudo second-order kinetics with  $r^2 > 0.99$  for the three-adsorbent media. Results of the adsorption isotherm show that the Freundlich adsorption isotherm model better described Cr(VI) adsorption into soil rich in kaolinite–ferrinatriite (SRKF), soil rich in kaolinite–goethite (SRKG) and coffee husk ash (CHA) with coefficients of determination;  $r^2 > 0.93$ . The adsorption capacity of the adsorbent can be arranged in the order of decreasing CHA > SRKG > SRKF. These adsorbent materials could be used for the removal of Cr(VI) from wastewater. However further investigation will be required for practical application of these locally available adsorbent materials for removal of chromium from wastewater.

*Keywords:* Adsorption; adsorption capacity; chromium(VI); kinetics; isotherm

### 6.2 Introduction

The release of toxic chemicals from industrial wastewater into the environment degrades water quality and is hazardous threat to human beings, as well as; other living organisms such as aquatic life (Saifuddin and Kumaran, 2005; Pan et al., 2014; Sanchooli Moghaddam et al., 2016; Lin et al., 2018). Cr(VI) is generated from different industrial activities that are carried out in textile industries, leather tanning, electroplating, steel factory, paint manufacturing, pulp processing, chromate preparation, electric and electronic components (Pan et al., 2013, Alfarra et al., 2014; Sultana et al., 2016; Panda et al., 2017). According to the United State Environmental Protection Agency (IWRG701), Cr(VI) is the most top-prioritized poisonous pollutant (Tang et al., 2014).

Chromium is found mostly in the form of chromium (III) and chromium(VI). Chromium(VI) is 100 times poisonous than chromium (III) when found on a surface and in ground water (Tang et al., 2014; Lin et al., 2018). According to the WHO, the recommended maximum tolerable limit of Chromium(VI) in wastewater discharged from industries is  $0.25 \text{ mg.L}^{-1}$  (Zhong et al., 2014). Thus, it is critical to find effective ways to remove Chromium(VI) from industrial wastewater. Typical treatment technologies used to remove chromium from contaminated water include chemical precipitation, chemical reduction, adsorption, membrane separation, ion exchange, reverse osmosis, and electrocoagulation. Of all the treatment technologies, adsorption technique is one of the most feasible and promising technique, because of its wide raw material sources, low cost investment, high efficiency, effectiveness, flexibility in design and easy operation (Chen et al., 2011; Yang et al., 2013; Tang et al., 2014; Zhong et al., 2014; Sultana et al., 2016). Thus, looking for a suitable wastewater treatment technology using locally available natural materials that may to be used in developing countries such as Ethiopia remains an important issue to address. Among the natural adsorbents, soil rich in kaolinite-ferrinatriite (SRKF), coffee husk ash (CHA) and soil rich in kaolinite-goethite (SRKG) would meet the conditions that have been established for the wastewater treatment process due to its abundant availability in Ethiopia and suitable physical and chemical properties.

The objective of this study was to compare the efficiency of Cr(VI) ion removal from contaminated water of the three adsorbents, determine the adsorption of kinetics and the isotherms, as well as the contact time by using low-cost locally available materials under a batch adsorption experiment.

## **6.3 Materials and Methods**

### **6.3.1 Sample collection**

Soil rich in kaolinite-ferrinatriite, coffee and soil rich in kaolinite-goethite are abundantly found in Ethiopia. The samples were collected from Jimma Zone, Oromia Regional National State, and South-west Ethiopia on January 2015. The same samples from the three locations were mixed in equal proportion to make a composite sample. Then the each composite adsorbent adsorption results were compared.

### 6.3.2 Physical and chemical characteristics

Table 6.1 shows the physical characteristics of locally available materials used for the present study. This is characterized at the Ethiopia Institute of Agricultural Research by document number: Ethiopian Institute of Agricultural Research (EIAR/F) 510-2 and effective date in February 2015. The physical characteristic of locally available materials was performed using standard procedures. Characterization of the locally available materials was carried out electrical conductivity, cation exchange capacity, pH, organic carbon, and organic matter. Table 6.1 shows that, the amount of electrical conductivity, cation exchange capacity and pH content of CHA were greater than SRKF and SRKG and on the other hand, organic carbon content and organic matter content of SRKF were higher than that of CHA and SRKG. Those adsorptive removal capacity of Cr(VI) from contaminated water by the three adsorbents depend on different parameters such as contact time, pH solution, initial concentration of Cr(VI) and adsorbent dose.

Table 6.1 Physical characteristic of locally available materials

| Sample | Parameters                         |                                      |       |           |             |             |             |             |             |         |
|--------|------------------------------------|--------------------------------------|-------|-----------|-------------|-------------|-------------|-------------|-------------|---------|
|        | E. C.<br>( $\mu\text{s.cm}^{-1}$ ) | C. E.C.<br>( $\text{cmol.Kg}^{-1}$ ) | pH    | TN<br>(%) | O.C.<br>(%) | O.M.<br>(%) | Sand<br>(%) | Silt<br>(%) | Clay<br>(%) | Texture |
| SRKF   | 22.80                              | 24.00                                | 5.24  | 0.14      | 0.75        | 1.28        | 18.80       | 10.40       | 70.80       | Clay    |
| CHA    | 64.30                              | 36.20                                | 12.47 | -         | 0.518       | 0.893       | -           | -           | -           | -       |
| SRKG   | 20.10                              | 21.50                                | 4.56  | 0.13      | 0.61        | 1.05        | 12.80       | 10.40       | 76.80       | Clay    |

Scanning Electron Microscopy is a powerful tool to analyze the morphological structure of the locally available adsorbents (Zhang and Palet i Ballús, 2014). Sampling preparation is simple, and the adsorbents material used gold sputter coating arrangement is relatively stable to the penetrating electron beam. Equipment description is specified in Table 6.2:

Table 6.2 Scanning Electron Microscopy equipment description


| Equipment              | SEM  |
|------------------------|--|
| Model                  | ZEISS EVO LS15   |
| Company and country    | ZEISS, Germany   |
| Laboratory of analysis | Microscopy and Microanalysis Unit<br>(UKZN. PMB, South Africa)                     |
| Image                  |  |

Table 6.3 Transmission Electron Microscopy equipment description


| Equipment              | TEM  |
|------------------------|--|
| Model                  | JEOL JEM-1400 Electron<br>Microscopy   |
| Company and country    | JEOL, Japan  |
| Laboratory of analysis | Microscopy and Microanalysis Unit<br>(UKZN. PMB, South Africa)                       |
| Image                  |  |

Table 6.4 Elemental characteristic of locally available materials

| Samples | Elemental weight % |                |      |      |       |       |      |       |      |      |      |      |      |       |
|---------|--------------------|----------------|------|------|-------|-------|------|-------|------|------|------|------|------|-------|
|         | C                  | O <sub>2</sub> | Na   | Mg   | Al    | Si    | P    | K     | Ca   | Ti   | Mn   | P    | S    | Fe    |
| SRKF    | 19.65              | 45.89          | 0.17 | 0.36 | 9.98  | 13.23 | -    | 0.49  | -    | 0.47 | 0.08 | -    | -    | 7.35  |
| CHA     | 25.20              | 36.47          | 0.16 | 1.85 | -     | 0.50  | 0.83 | 30.10 | 3.97 | -    | -    | 0.83 | 0.82 | -     |
| SRKG    | 8.90               | 51.15          | 0.02 | 0.34 | 11.46 | 13.63 | 0.23 | 0.33  | 0.09 | 0.66 | 1.08 | -    | -    | 11.04 |

### 6.3.3 Chemicals

The stock ( $K_2Cr_2O_7$ ) standard solution of each of Cr(VI) ( $500\text{ mg.L}^{-1}$ ,  $1000\text{ mg.L}^{-1}$ ) for adsorption experiments were prepared by dissolving 1.414 g and 2.828 g of  $K_2Cr_2O_7$  (FINKEM) in 1000 mL distilled water in a volumetric flask, respectively. Working solutions were prepared by appropriate dilution of the stock solution immediately prior to their use.

### 6.3.4 Batch adsorption procedures

Sets of series of duplicate batch adsorption experiments were carried out at room temperature by shaking a mixture of a known concentration of the adsorbate and a desired dose of adsorbents at a defined mixed speed (*i.e.* 100, 150, 200 and 250) rpm on a horizontal shaker. Optimum agitation speed was determined after conducting a preliminary study. The optimum contact time was determined by agitating a mixture of 0.4 g adsorbent and  $3.5\text{ mg.L}^{-1}$  Cr(VI) concentration in a horizontal shaker at 150 rpm for SRKG and SRKF. Whereas for CHA it was at 100 rpm for over 120 minutes. Equilibrium adsorption isotherm was examined by varying the concentration of the adsorbate from 10 to  $60\text{ mg.L}^{-1}$  and maintaining the dose of the three adsorbent materials at 0.35 g and shaking speed at 100 and 150 rpm for CHA, and SRKG and SRKF respectively. In all the adsorption experiments, the pH of the solution was maintained at 2.0.

### 6.3.5 Desorption experiment procedure

The reusability of the exhausted adsorbent material was investigated Firstly, by allowing 2 mg.L<sup>-1</sup> Cr(VI) to be adsorbed onto 0.35 g adsorbent dose for all the three adsorbent materials at optimum contact time; Secondly, the exhausted solid adsorbent materials were separated from the supernatant solution through filtration and allowed to be dried in an oven at 105<sup>0</sup>C overnight; Thirdly, the oven dried, exhausted adsorbent media were added into 0.01, 0.1 and 0.5 M NaOH desorbing solution separately. The mixtures were agitated under the same experimental conditions used for adsorption experiments. Finally, the amount desorbed was determined using Eq. 6.1 given below (Sadaf et al., 2015, Bekam et al, 2016).

$$Desorption\ ratio(\%) = \frac{Amount\ of\ desorbed}{Amount\ of\ adsorbed} * 100 \quad (6.1)$$

## 6.4 Results and Discussion

### 6.4.1 Characterization of locally available materials

Figure 6.1 and 6.2 show the scanning electron microscope (SEM) and transmission electron microscopy (TEM) photos of soil rich in kaolinite-ferrinatrinite (SRKF), coffee husk ash (CHA) and soil rich in kaolinite-goethite (SRKG).

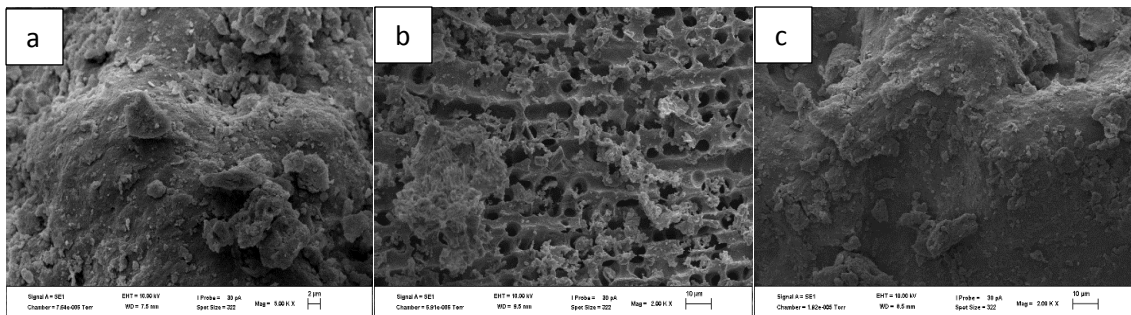


Figure 6.1 Scanning Electron Microscopy (SEM) photographs of SRKF (a), CHA (b) and SRKG (c), respectively

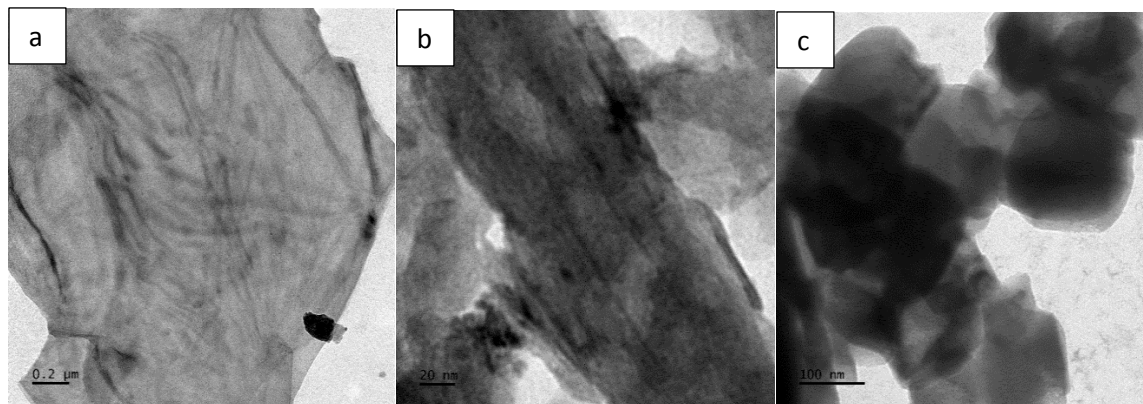


Figure 6.2 Transmission Electron Microscopy (TEM) images of SRKF (a), CHA(b) and SRKG (c), respectively

#### 6.4.2 Shaker speed

The effect of shaker speed of Cr(VI) removal capacity was studied. Figure 6.3 shows the adsorptive experimental result obtained from a series of experiments performed that comprises: initial chromium concentration:  $3.5 \text{ mg.L}^{-1}$ , adsorbent dose: 0.4 g, pH: 7, particle size: 0.425 mm, and contact time: 2 hours at room temperature  $295.5 \pm 2^\circ\text{K}$  and various shaking speed 100, 150, 200 and 250 revolutions per minute. Analysis on adsorption removal of Cr (VI) at different shaking speed. Figure 6.3 showed that string speed of 150 rpm has a greater removal efficiency of Cr (VI) by using SRKG and SRKF from the other string speeds and 100 rpm has a greater removal efficiency of Cr (VI) by using CHA. From the analysis shaker speed of 100 rpm for CHA, and 150 rpm for SRKG and SRKF were selected

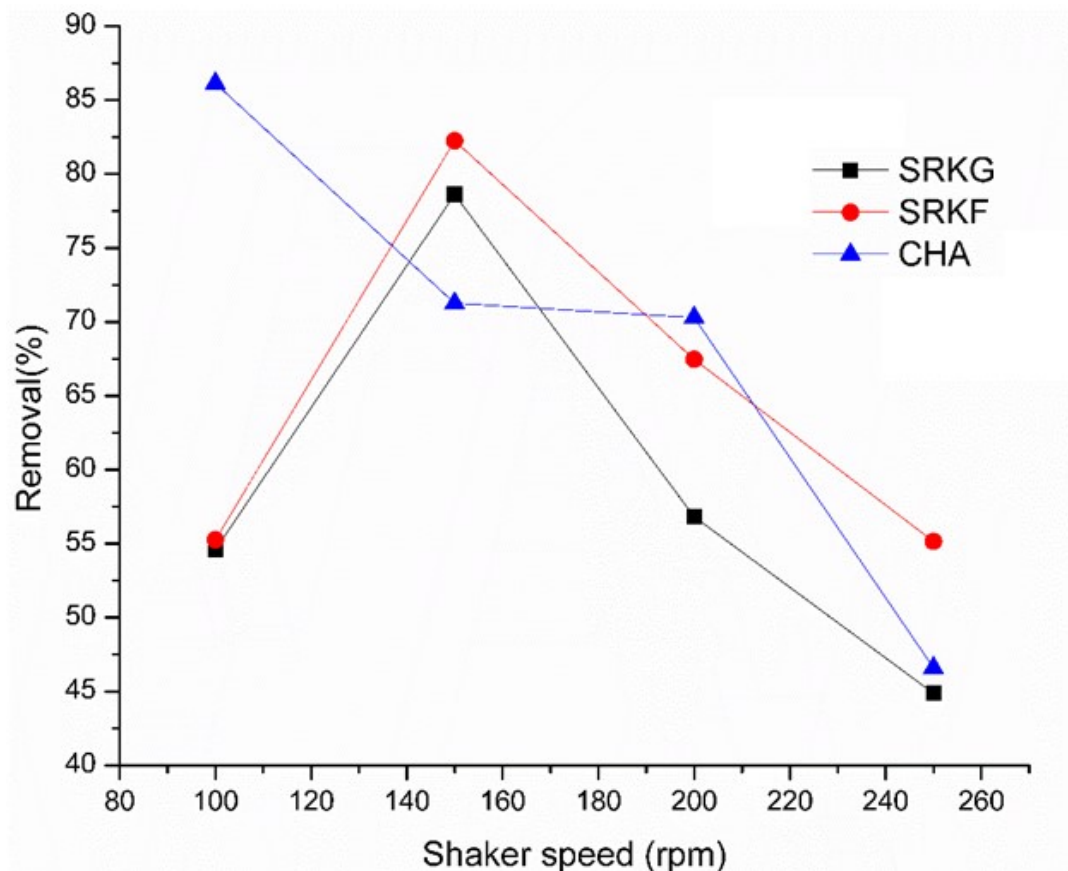


Figure 6.3 Shaker speed of locally available materials such as SRKF (circle), CHA(triangles), and SRKG (squares) were condition temperature  $22 \pm 2^\circ\text{C}$

### 6.4.3 pH effects

The amount of chromium (VI) removed was dependent on pH (Figure 6.4). The effect of pH on chromate removal capacity and adsorption efficiency were shown in Figure 6.4. The pH values was decreased with increased positive charge in the locally available materials due to protonization process. The adsorption chromium (VI) ion increased with decreasing pH values. The trends of finding was positively agreed with the finding reported by Guo et al. (2008) and Zhong et al. (2014).

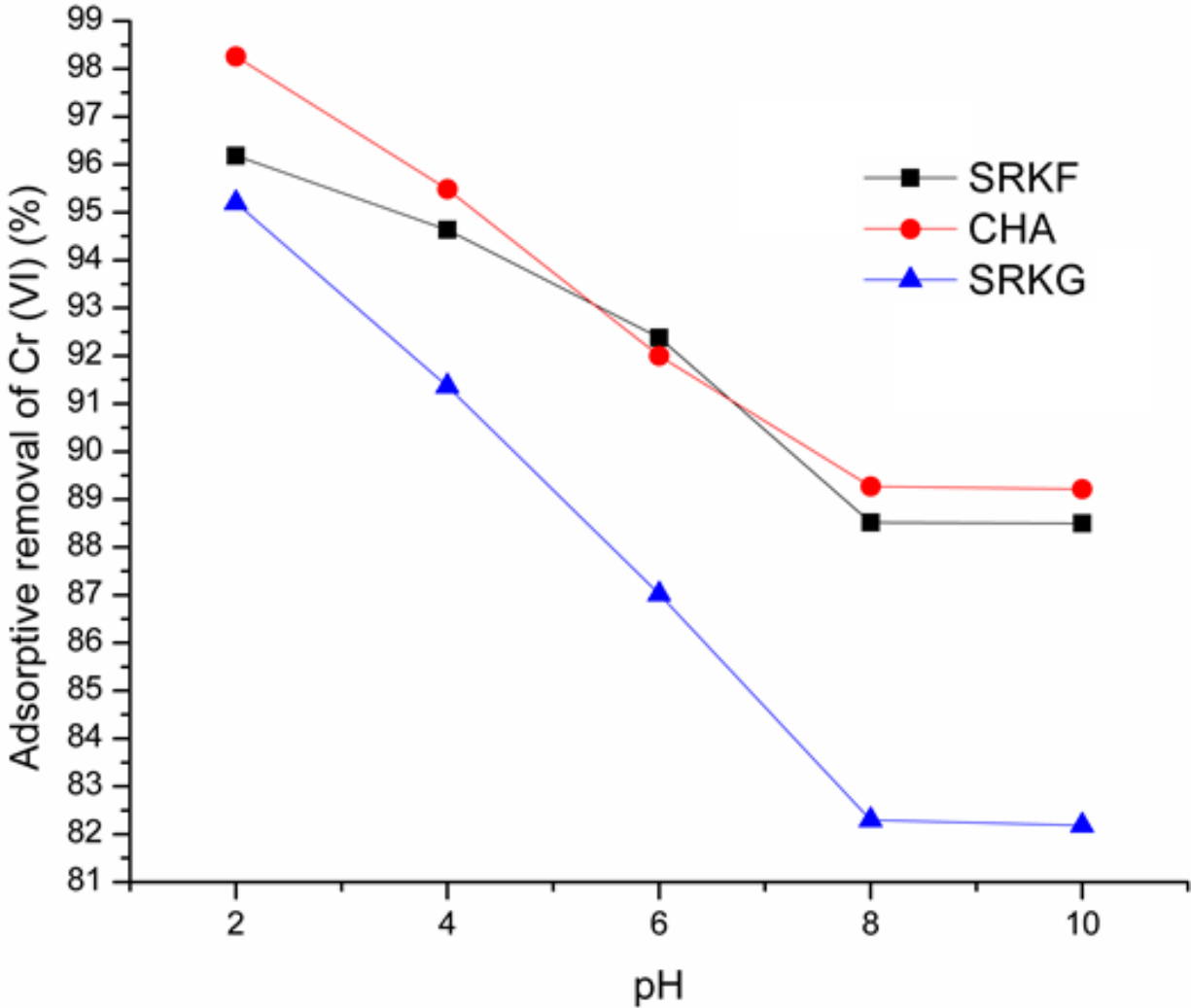


Figure 6.4 Cr(VI) adsorption on locally available materials such as SRKF (squares), CHA (circle) and SRKG (triangles) were condition temperature  $22 \pm 2^\circ\text{C}$

#### 6.4.4 Contact time

The effect of contact time on chromium (VI) adsorption on soil rich in kaolinite- ferrinatriite was studied by continuously increasing the contact time from 10 to 120 minutes. (Figure 6.5). As can be seen in Figure 6.5, the contact time increased with an increase of adsorptive removal of adsorbate up to 40 minutes. After 40 minutes (equilibrium point) the adsorption removal of adsorbate remained constant due to binding sites exhaustion (Akiode et al., 2015). The rate of adsorption of chromium (VI) ion was fast up to 40 minutes. This was due to locally available

materials (LAM) such as SRKF, CHA and SRKG which surfaces having many open spaces that could lead to strong attraction forces between Cr(VI) and an adsorbent this is confirms an observation of Wanees et al. (2012). Adsorptive removal of chromium (VI) from 10 and 40 minutes was rapidly and fast due to highly increased adsorption sites. This finding similar to the study of Mekonnen et al (2015). After 40 minutes, there was no change in the rate of adsorption of Cr(VI) on LAM. This showed that LAM did not have sufficient open space due to the fact that the bulk solution increased. This finding agreed with the observations of Workneh et al., (2014). The adsorption capacity was high for a short period (40 minutes) on LAM adsorbent. The reason for this could be due to the open space, clay texture, lower bulk density, and small particle size. This finding agrees with the finding repeated by Babel and Opiso (2007). The value of contact time 40 minutes was taken as maximum for further studies.

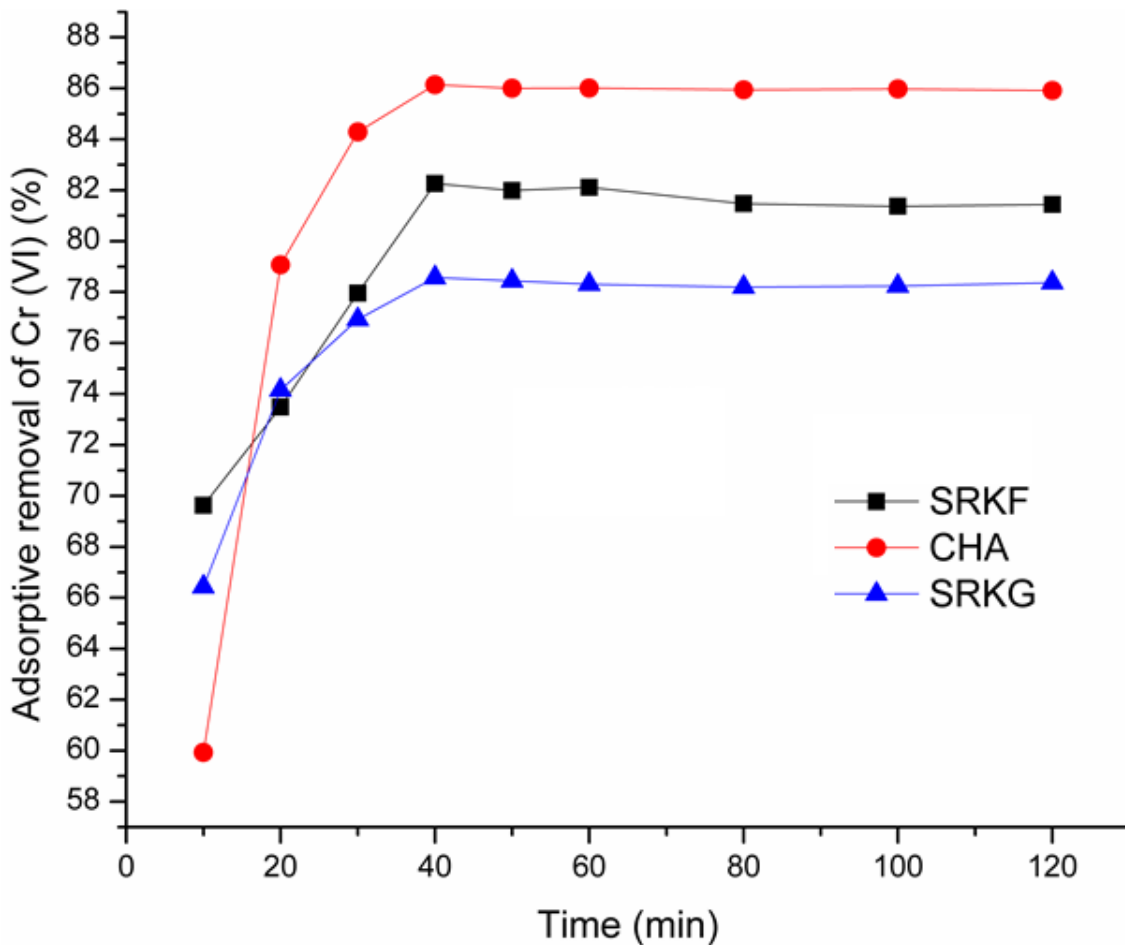


Figure 6.5 Cr(VI) adsorption on SRKF (squares), CHA (circle) and SRKG (triangles) were condition temperature  $22 \pm 2^\circ\text{C}$ , and  $\text{pH} = 2$

#### 6.4.5 Kinetic model of adsorption

The results showed that the pseudo-second order equation best described the kinetic mechanisms of chromium (VI) ions adsorption, which is evident from the high coefficient of determination value ( $r^2 > 0.99$  for SRKF, CHA and SRKG). In addition, the predicted equilibrium adsorption capacities were quite close to the experimental values for all particle sizes tested in this study, confirming the validity of the pseudo second order rate assumption. The chromium (VI) ions transports from solution to the pore of adsorbents and surface on SRKF, CHA and SRKG were responsible for the adsorption of the hexavalent chromium ions.

**Table 6.5** Summary of linear estimated kinetic parameters for adsorption of hexavalent chromium ions onto CHA, SRKF and SRKG

| Adsorbents | Pseudo-first-order:  |                       |                | Pseudo-second-order:  |                  |                |
|------------|--|-----------------------|----------------|---|------------------|----------------|
|            | Log (q <sub>E</sub> -q <sub>T</sub> ) = Log q <sub>E</sub> - k <sub>1</sub> /2.303*T |                       |                | T/q <sub>T</sub> = 1/k <sub>2</sub> q <sub>E</sub> <sup>2</sup> + 1/q <sub>E</sub> *T |                  |                |
| Ads.       | log q <sub>E</sub>   | k <sub>1</sub> /2.303 | r <sup>2</sup> | 1/k <sub>2</sub> q <sub>E</sub> <sup>2</sup>  | 1/q <sub>E</sub> | r <sup>2</sup> |
| SRKF       | 0.2020   | 0.0006                | 0.5181         | 3.3233  | 1.3660           | 0.9985         |
| CHA        | 0.1915   | 0.0008                | 0.3308         | 2.8739  | 1.2960           | 0.9990         |
| SRKG       | 0.1824   | 0.0002                | 0.4828         | 0.9735  | 1.4485           | 0.9999         |

q<sub>E</sub> = adsorption efficiency at equilibrium (mg.g<sup>-1</sup>), q<sub>T</sub> = is adsorption efficiency at a time (mg.g<sup>-1</sup>), T= time (min) , K<sub>1</sub> = kinetics constant (h<sup>-1</sup>) and K<sub>2</sub> = kinetic constant (g.mg<sup>-1</sup> h<sup>-1</sup>)

#### 6.4.6 Isotherm model of adsorption

The adsorption equilibrium is usually described by an isotherm equation whose given parameters express the surface properties and affinity of the adsorbent, at room temperature and pH. An analysis of the relationship between the adsorption capacity of the materials (SRKF, CHA and SRKG) and the initial concentration of chromium (VI) ion at equilibrium was performed, using the two most frequently employed models, namely, the Langmuir and Freundlich models. These models can be used to design and optimize an operating procedure. The data from these models

provide information to predict removal of Cr(VI) ion to the adsorbents, and an estimation of the adsorbent amounts needed to remove the hexavalent chromium ion from the solution. In all case, the result confirms that the Freundlich adsorption capacity of SRKF is greater as compared to that of SRKG. The essential characteristics of the Langmuire isotherm may be expressed in terms of the dimensionless separation factor values ( $R_L$ ). In all cases, the  $R_L$  values for the experimental data is between 0 and 1, which is also an indicative of the favorable adsorption of Cr(VI) ion on the SRKF, CHA and SRKG. In all experiments, the larger value of,  $K_L$ , obtained for the chromium (VI) ions indicate SRKF the strong interactions between the hexavalent chromium ions and SRKG and CHA. The conclusions are in conformity with the results obtained in the characterization of the adsorbents CHA has a larger CEC and EC than other two.

Table 6.6 Summary of linear estimated isotherm models and its constant value for chromate adsorption

| Adsorbents | Freundlich Isotherm:                                       |        |                | Langmuir Isotherm:                     |                                 |                |
|------------|--|--------|----------------|--|---------------------------------|----------------|
|            | $\text{Log } q_e = \text{Log } K_F + 1/n \text{ Log } C_e$ |        |                | $1/q_e = 1/q_M + 1/q_M K_L * 1/C_e$    |                                 |                |
| Ads.       | $K_F$ (mg g <sup>-1</sup> )                                | 1/n    | R <sup>2</sup> | 1/q <sub>M</sub> (mg g <sup>-1</sup> ) | 1/q <sub>M</sub> k <sub>L</sub> | R <sup>2</sup> |
| SRKF       | 1.2114   | 0.4867 | 0.9336         | 0.1089                                 | 0.0057                          | 0.9139         |
| CHA        | 0.9025   | 0.5538 | 0.9846         | 0.0746                                 | 0.1028                          | 0.9444         |
| SRKG       | 0.9925   | 0.6927 | 0.978          | 0.0996                                 | 0.0348                          | 0.9576         |

$\text{Log } q_e$  = adsorption efficiency (mg.g<sup>-1</sup>),  $\text{Log } K_F$  = Freundlich constant,  $\text{Log } C_e$ =the equilibrium concentration of adsorbate (mg l<sup>-1</sup>), 1/n values between 0 and 1 it shows the suitability of adsorption, 1/q<sub>M</sub>= maximum contain adsorbent (mg.g<sup>-1</sup>), and  $K_L$ =Langmuir constant

#### 6.4.7 Desorption

The results of desorption experiments show that the amount of Cr(VI) desorbed respectively increases from 35 to 82% for SRKF, from 34 to 77% for SRKG and 17 to 83% for CHA when the concentration of desorbent increased from 0.01 to 0.5 M NaOH. This indicates that when NaOH is at about 0.5 M concentration the adsorbent materials exhausted can be regenerated for reuse.

This finding agrees with the reports of Sadaf et al. (2015) and Bekam et al (2016). However, the regeneration cycle and adsorption capacity of the regenerated adsorbent materials requires further investigation.

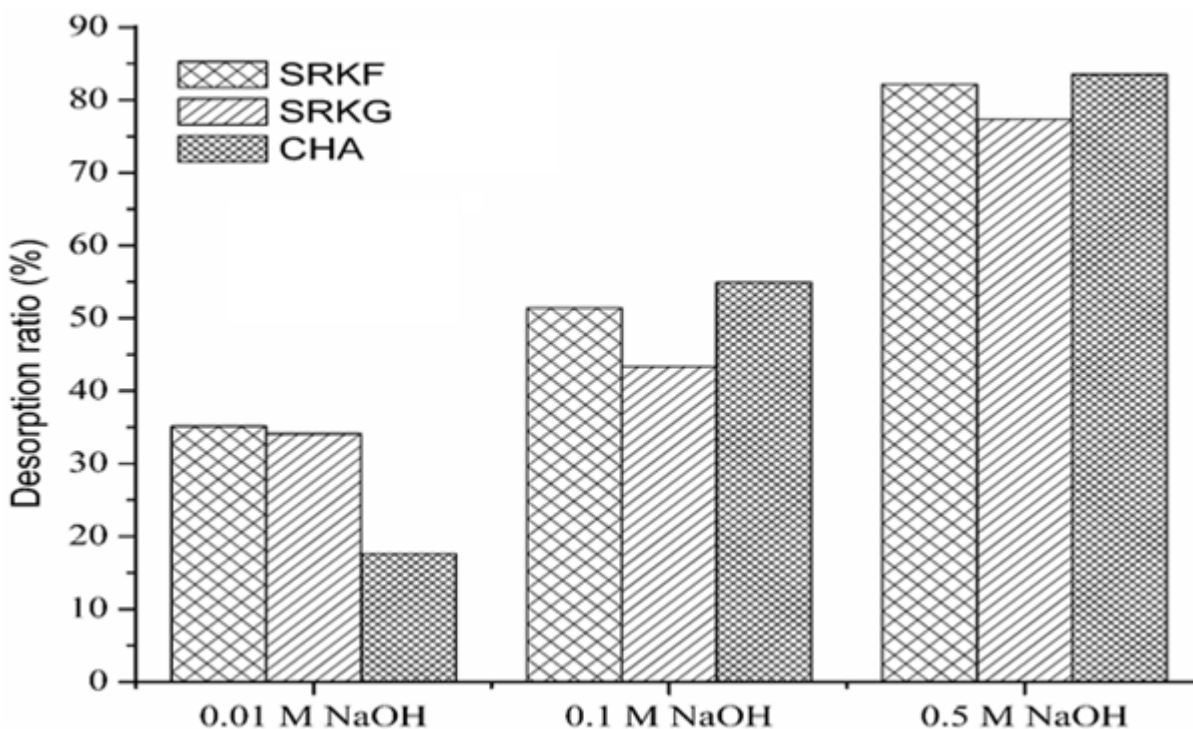


Figure 6.6 Cr(VI) desorption on SRKF, CHA and SRKG at temperature  $22 \pm 2^\circ\text{C}$ , and  $\text{pH} = 2$

#### 6.4.8 Low-cost adsorbents compared with locally available adsorbents

Low-cost adsorbents are naturally available materials or adsorbents, and are defined as waste products from agriculture, industries, and domestic use. These materials are thus, less expensive (Renge et al., 2012), affordable (Lim and Aris, 2014), environmentally friendly as well as abundant (Kurniawan et al., 2006b; Kırbıyık et al., 2012; Lim and Aris, 2014) and cheap (Kurniawan et al., 2006a; Carvalho et al., 2011). They have high treatment efficiency for the removal of toxic chemicals (Tajrishy, 2012). These cheap adsorbents are simply gathered from agricultural waste, industrial byproducts, clay soil, food waste and seafood (Bailey et al., 1999; Jain et al., 2013). Hence, they are economically affordable and abundantly available (Li et al., 2007; Kaushal and Upadhyay, 2014). For example, the cost of bagasse fly ash adsorbent which is available at

US\$0.002 kg<sup>-1</sup> includes the transport payment to the adsorption processes site, energy used and other factors. The final, total cost of this bagasse fly ash is around 0.009 US dollars per kilogram (Srivastava et al., 1995). Some low-cost adsorptive materials serve as a scavenger of contaminants by absorbing anions and cations. For example, clay is an environmentally suitable material for wastewater treatment containing heavy metals (Sari et al., 2007; Bhattacharyya and Gupta, 2008, Öncel, 2008) and it is an excellent adsorbent material, and also 20 times cheaper than activated carbon at the current market price (Kaushal and Upadhyay, 2014).

Table 6.7 Comparison between various low-cost adsorbent materials and the present used in this study adsorbents

| Adsorbents   | Price<br>(US\$kg <sup>-1</sup> ) | References                          |
|--|----------------------------------|-------------------------------------|
| Bagasse fly ash                                    | 0.009                            | Srivastava et al., (1995)           |
| Waste metal sludge                                 | 0.004-0.005                      | Bhatnagar A (2008)                  |
| Blast furnace waste                                | 0.038                            | Srivastava et al., (1995)           |
| Blast furnace slag                                 | 0.040                            | Atun et al., (2003)                 |
| Clay   | 0.040-0.120                      | Babel and Kurniawan (2003)          |
| Xanthate   | 1.000                            | Tare et al. (1992)                  |
| Perlite  | <1.500                           | Mathialagan and Viraraghavan (2002) |
| Chitosan   | 16.000                           | Babel and Kurniawan (2003)          |
| Coconut shell charcoal                             | 0.340                            | Babel and Kurniawan (2004)          |
| Bentonite  | 0.050                            | Watson (2007)                       |
| Soil rich in kaolinite- ferrinatriite <sup>a</sup> |                                  | In this study                       |
| Soil rich in kaolinite -goethite <sup>a</sup>      | <0.007                           |                                     |
| Coffee husk <sup>a</sup>                           | <0.023                           | In this study                       |

<sup>a</sup>Current market initial cost, in Ethiopia (2016)

In Ethiopia soil rich in kaolinite-ferrinatriite and goethite are at average about birr 0.15 (15 cents) per kilogram and coffee husk at birr 0.5 (50 cents) per kilogram including the transportation cost. These adsorbents (SRKF, SRKG and CHA) are US \$ 500 kg<sup>-1</sup> (five hundred dollars per kilogram)

times cheaper than some adsorbent such as chitosan at US\$16 per kilogram (Babel and Kurniawan, 2003).

#### 6.4.9 Comparison study with other adsorbents

The soil rich in kaolinite-ferrinatriite, coffee husk ash and soil rich in kaolinite-goethite prepared in this study had a comparatively high adsorptive removal efficiency of chromium (VI) with short period of contact time compared with other adsorbents reviewed in the literature such as adsorptive removal of Cr(VI) by using soil rich in kaolinite-ferrinatriite. They have a contact time (minutes) that is 10 times earlier than Fe<sup>0</sup> nanorods modified with chitosan anodic alumina, a 2.5 times earlier contact time (minutes) than graphene sand composite, a nine times earlier contact time (minutes) than magnetic graphene oxide via ethylenediamine and a 1.5 times earlier contact time (minutes) than SWCNTs and MWCNTs.

Table 6.8 Comparison between different adsorbents for the adsorptive removal time of chromium (VI) ion.

| Adsorbent  | Metal ion | Contact Time (min) | References                              |
|--|-----------|--------------------|---|
| Fe <sup>0</sup> nanorods modified with chitosan anodic alumina | Cr (VI)   | 400                | Liu et al., (2011)                      |
| Graphene sand composite  | Cr (VI)   | 100                | Wang et al. (2014)                      |
| Magnetic graphene oxide via ethylenediamine                    | Cr (VI)   | 360                | Hamadi et al. (2001)<br>Dehghani et al. |
| SWCNTs   | Cr (VI)   | 60                 | (2015)<br>Dehghani et al.               |
| MWCNTs   | Cr (VI)   | 60                 | (2015)                                  |
| SRKF   | Cr (VI)   | 40                 | this study                              |
| SRKG   | Cr (VI)   | 40                 | this study                              |
| CHA  | Cr (VI)   | 40                 | this study                              |

SWCNTs: Single-Walled Carbon Nanotubes; MWCNTs: Multi-Walled Carbon Nanotubes

## 6.5 Conclusions

The level of chromium (VI) in the water are greater than the permitted limit and are toxic, which can lead to number of health effects on living organisms and the environment. This study has demonstrated the potential of the adsorptive efficiency of SRKF, CHA and SRKG for Cr(VI) ions removal from contaminated water. The effects of shaker speed, adsorbent dose, solutions pH and contact time for removal of Cr(VI) in waste water under batch adsorption on SRKF, CHA and SRKG were investigated. The Freundlich and Langmuir isotherm was examined in this study at a room temperature of  $22 \pm 2^\circ\text{C}$ . Therefore, this behavior suggested that LAM can be as an interesting cheap adsorbents technology for hexavalent chromium removal from contaminated water.

## 6.6 References

- Akiode, O, Idowu, M, Omeike, S and Akinwunmi, F. 2015. Adsorption and kinetics studies of Cu (II) ions removal from aqueous solution by untreated and treated sugarcane bagasse. *Global Nest Journal* 17: 583-593.
- Alfarra, R, Ali, N and Yusoff, M. 2014. Removal of heavy metals by natural adsorbent: review. *International Journal of Biosciences* 4: 130-139.
- Atun, G, Sheldrick, W and Muhler, M. 2003. Adsorptive removal of methylene blue from colored effluents on fuller's earth. *Journal of Colloid and Interface Science* 261: 32-39.
- Babel, S and Kurniawan, T. 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials* 97: 219-243.
- Babel, S and Kurniawan, T. 2004. Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere Journal* 54: 951-967.
- Babel, S and Opiso, E. 2007. Removal of Cr from synthetic wastewater by sorption into volcanic ash soil. *International Journal of Environmental Science and Technology* 4: 99-107.
- Bailey, S, Olin, T, Bricka, R and Adrian, D. 1999. A review of potentially low-cost sorbents for heavy metals. *Water Research Journal* 33: 2469-2479.

- Bekam, A, Fekadu, F, Megersa, M and Michael. B. 2016. Experimental evaluation of sorptive removal of fluoride from drinking water using iron ore. *Applied Water Science Journal* 6: 57-65.
- Bhatnagar, A., Pudasainee, D, Chung, H, Kim, S, Kim, H, Lee, G, Min, B and Jeon, B. 2008. Vanadium removal from water by waste metal sludge and cement immobilization. *Chemical Engineering Journal* 144: 197-204.
- Bhattacharyya, K and Gupta, S. 2008. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. *Advances in Colloid and Interface Science Journal* 140: 114-131.
- Carvalho, J, Araujo, J and Castro, F. 2011. Alternative low-cost adsorbent for water and wastewater decontamination derived from eggshell waste: an overview. *Waste and Biomass Valorization Journal* 2: 157-167.
- Chen, S, Yue, Q, Gao, B, Li, Q and Xu, X. 2011. Removal of Cr (VI) from aqueous solution using modified corn stalks: characteristic, equilibrium, kinetic and thermodynamic study. *Chemical Engineering Journal* 168: 909-917.
- Dehghani, M, Taher, M, Bajpai, A, Heibati, B, Tyagi, I, Asif, M, Agarwal, S and Gupta, V. 2015. Removal of noxious Cr (VI) ions using single-walled carbon nanotubes and multi-walled carbon nanotubes. *Chemical Engineering Journal* 279: 344-352.
- Guo, X, Zhang, S and Shan, X. 2008. Adsorption of metal ions on lignin. *Journal of Hazardous Materials* 151: 134-142.
- Hamadi, N, Chen, X, Farid, M and Lu, M. 2001. Adsorption kinetics for the removal of chromium (VI) from aqueous solution by adsorbents derived from used tyres and sawdust. *Chemical Engineering Journal* 84: 95-105.
- IWRG701. 2009. Sampling and analysis of waters, wastewaters, soils and wastes. Retrieved March 13, 2011, from <http://www.epa.vic.gov.au/~media/Publications/IWRG701.pdf>
- Jain, M, Garg, V and Kadirvelu, K. 2013. Chromium removal from aqueous system and industrial wastewater by agricultural wastes. *Bioremediation Journal* 17: 30-39.
- Kaushal, R and Upadhyay, K. 2014. Treatability study of low cost adsorbents for heavy metal removal from electroplating industrial effluent: a review. *International Journal of ChemTech Research* 6: 1446-1452.

- Kırbiyık, Ç, Kılıç, M, Çepelioğullar, Ö and Pütün, A. 2012. Use of sesame stalk biomass for the removal of Ni (II) and Zn (II) from aqueous solutions. *Water Science and Technology Journal* 66: 231-238.
- Kurniawan, T, Chan, G, Lo, W and Babel, S. 2006a. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Science of the Total Environment Journal* 366: 409-426.
- Kurniawan, T, Chan, G, Lo, W and Babel, S. 2006b. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Science of the Total Environment Journal* 366: 409-426.
- Li, Q, Zhai, J, Zhang, W, Wang, M and Zhou, J. 2007. Kinetic studies of adsorption of Pb (II), Cr (III) and Cu (II) from aqueous solution by sawdust and modified peanut husk. *Journal of Hazardous Materials* 141: 163-167.
- Lim, A and Aris, A. 2014. A review on economically adsorbents on heavy metals removal in water and wastewater. *Reviews in Environmental Science and Bio/Technology* 13: 163-181.
- Lin, H, Rong, C, Jiu, B, Li, B, Yu, Q, Gan, L and Zhang, Z. 2018. Effects of chromium on pyrolysis characteristic of water hyacinth (*Eichornia crassipes*). *Renewable Energy Journal* 115: 676-684.
- Liu, C and Evett, J. 2003. Soil properties: testing, measurement, and evaluation, Banta Book Company, USA. ISBN:0-13-093005-9: ISBN 0-13-093005-9.
- Liu, S, Chen, Y, De Zhang, L, Hua, G, Xu, W, Li, N and Zhang, Y. 2011. Enhanced removal of trace Cr (VI) ions from aqueous solution by titanium oxide Ag composite adsorbents. *Journal of hazardous materials* 190: 723-728.
- Mathialagan, T and Viraraghavan, T. 2002. Adsorption of cadmium from aqueous solutions by perlite. *Journal of Hazardous Materials* 94: 291-303.
- Mekonnen, E, Yitbarek, M and Soreta, T. 2015. Kinetic and thermodynamic studies of the adsorption of Cr (VI) onto some selected local adsorbents. *South African Journal of Chemistry* 68: 45-52.
- Öncel, M. 2008. Adsorption of copper (II) from aqueous solution by beidellite. *Environmental Geology* 55: 1767-1775.
- Pan, J, Jiang, J and Xu, R. 2014. Removal of Cr (VI) from aqueous solutions by Na<sub>2</sub>SO<sub>3</sub>/FeSO<sub>4</sub> combined with peanut straw biochar. *Chemosphere Journal* 101: 71-76.

- Pan, J, Jiang, J and Xu, R. 2013. Adsorption of Cr (III) from acidic solutions by crop straw derived biochars. *Journal of Environmental Sciences* 25: 1957-1965.
- Panda, H, Tiadi, N, Mohanty, M and Mohanty, C. 2017. Studies on adsorption behavior of an industrial waste for removal of chromium from aqueous solution. *South African Journal of Chemical Engineering* 23: 132-138.
- Renge, V, Khedkar, S and Pandey Shraddha, V. 2012. Removal of heavy metals from wastewater using low cost adsorbents: a review. *Sciences Review Chemical Communications Journal* 2: 580-584.
- Sadaf, S, Bhatti, H, Arif, M, Amin, M and Nazar, F. 2015. Adsorptive removal of direct dyes by PEI-treated peanut husk biomass: Box–Behnken experimental design. *Chemistry and Ecology Journal* 31: 252-264.
- Saifuddin, M and Kumaran, P. 2005. Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. *Electronic Journal of Biotechnology* 8: 43-53.
- Sanchooli Moghaddam, M, Rahdar, S and Taghavi, M. 2016. Cadmium removal from aqueous solutions using saxaul tree ash. *Iranian Journal of Chemistry and Chemical Engineering* 35: 45-52.
- Sari, A, Tuzen, M, Citak, D and Soylak, M. 2007. Equilibrium, kinetic and thermodynamic studies of adsorption of Pb (II) from aqueous solution onto Turkish kaolinite clay. *Journal of Hazardous Materials* 149: 283-291.
- Srivastava, S, Yadav, I and Mohan, D. 1995. Removal of 2,4-dinitrophenol using bagasse fly ash—a sugar industry waste material. *Fresenius Environmental Bullent* 4: 550-557.
- Sultana, F, Uddin, M, Kabir, M, Sultana, N, Sikder, M and Rahman, S. 2016. Removal efficiency of chromium (VI) ions from aqueous solution by adsorption of rice husk and saw dust ash as a homogeneous composite. *International Journal of Environmental Sciences* 6: 987-993.
- Tajrishy, M. 2012. Wastewater production, treatment and use in Iran , presented at the second regional workshop of the project ‘safe use of wastewater in agriculture’, 16–18 May 2012, New Delhi  
[http://www.ais.unwater.org/ais/mod/page/view.php?id\\_62](http://www.ais.unwater.org/ais/mod/page/view.php?id_62).
- Tang, L, Fang, Y, Pang, Y, Zeng, G, Wang, J, Zhou, Y, Deng, Y, Yang, G, Cai, Y and Chen, J. 2014. Synergistic adsorption and reduction of hexavalent chromium using highly uniform

- polyaniline–magnetic mesoporous silica composite. *Chemical Engineering Journal* 254: 302-312.
- Tare, V, Chaudhari, S and Jawed, M. 1992. Comparative evaluation of soluble and insoluble xanthate process for heavy metal removal from wastewaters. *Water Science and Technology Journal* 26: 237-246.
- Wanees, S, Monem, A, Adam, M and Mohamed, M. 2012. Adsorption studies on the removal of hexavalent chromium-contaminated wastewater using activated carbon and bentonite. *Chemistry Journal* 02: 95-105.
- Wang, H, Liu, Y, Zeng, G, Hu, X, Hu, X, Li, T, Li, H, Wang, Y and Jiang, L. 2014. Grafting of  $\beta$ -cyclodextrin to magnetic graphene oxide via ethylenediamine and application for Cr (VI) removal. *Carbohydrate polymers Journal* 113: 166-173.
- Watson, J. 2007. Microbial feed additive. Google Patents.
- Workneh, A, Habtu, N and Beyene, H. 2014. Removal of hexavalent chromium from tannery wastewater using activated carbon primed from sugarcane bagasse: adsorption/desorption studies. *American Journal of Applied Chemistry* 2: 128-135.
- Yang, Z, Xiong, S, Wang, B, Li, Q and Yang, W. 2013. Cr (III) adsorption by sugarcane pulp residue and biochar. *Journal of Central South University* 20: 1319-1325.
- Zhang, H and Palet i Ballús, C. 2014. Biosorption of heavy metals from aqueous solutions using keratin biomaterials. <http://hdl.handle.net/10803/284239>
- Zhong, Q, Yue, Q, Li, Q, Gao, B and Xu, X. 2014. Removal of Cu (II) and Cr (VI) from wastewater by an amphoteric sorbent based on cellulose-rich biomass. *Carbohydrate Polymers Journal* 111: 788-796.

## **7. THEORETICAL DESIGN ON ADSORPTIVE REMOVAL OF Cr(VI) FROM SELECTED INDUSTRY WASTE WATER USING EXPLAINED DATA**

### **7.1 Introduction**

The wastewater discharge from various industries contains heavy metals such as chromium (Chai *et al.* 2014; Zwain *et al.* 2014; Hokkanen *et al.*, 2016). Improper discharge of the industrial wastewater contains heavy metals like Cr(VI) into water bodies that can affect the health of human being, living organisms and environment (Ahluwalia and Goyal, 2007; Asfaw, 2007; Belay and Sahile, 2013; Mekuyie, 2014; Padanilly, *et al.* 2008; Tong, 2012; Wosnie and Wondie, 2014; Zinabu, 2011). Hence, the adsorptive removal of hexavalent chromium from industrial wastewater discharge by using coffee husk ash (CHA), soil rich in kaolinite-goethite (SRKG) and soil rich in kaolinite-ferrinatriite (SRKF) have shown a good experimental result under the batch adsorptive experimental setup. This all adsorbents material was abundantly found in Ethiopia (GSOE, 2011, Kufa, 2012). All Chapter Three, Four and Five indicate that the adsorptive removal of Cr(VI) from aqueous solution and actual wastewater discharge from friend ship tannery PLC industry. Now, at this chapter by taking the optimum experimental result of parameters data obtained from the three chapters such as shaker speed 150 rpm for SRKF and SRKG, and 100 rpm for CHA; contact time 40 min for all three adsorbents; adsorbent dose  $3.5 \text{ g.L}^{-1}$ ,  $1.5 \text{ g.L}^{-1}$  and  $3 \text{ g.L}^{-1}$  for SRKF, CHA and SRKG, respectively. The pH value of 2 for three of them; initial concentration chromium(VI)  $2 \text{ mg.L}^{-1}$ ,  $0.5 \text{ mg.L}^{-1}$  and  $1 \text{ mg.L}^{-1}$ , respectively and particle size 0.075 mm only for SRKF and SRKG this all the experimental results were used for the design of selected wastewater discharge containing hexavalent chromium from industry. The objective of this chapter was to calculate the theoretical design of different treatment tanks by using ANSYS 17.0 software of the adsorptive removal of Cr(VI) from selected industry by adding calculated amount of SRKF, CHA and SRKG to be used for practical applicable in the industry.

## 7.1.1 Design process of treatment plant for Cr(VI) removal

### 7.1.1.1 Design consideration and specification

A process was designed for the adsorptive removal of chromium (VI) from industrial contaminated water containing hexavalent chromium, by using low cost, locally-available materials (LAM) of, such as SRKF, CHA and SRKG, to the 1500 m<sup>3</sup>.day<sup>-1</sup> discharge/ effluent capacity of the tannery industry at in Ethiopia, as mentioned in Chapter One, Section 2.3 and sub-Section 2.3.2 (Asfaw, 2007). The design was based on the optimum / maximum adsorptive removal of Cr(VI) result from batch adsorptive experiment set up and isotherm modeling; including shaker speed (rpm), contact time (min.), adsorbents (SRKF, CHA and SRKG) dose (g.L<sup>-1</sup>), pH solution, initial concentration of chromium(VI) (mg.L<sup>-1</sup>) and particle size (mm). And all the experimental data were considered for this design work.



Figure 7.1 Wastewater discharge from HAFDE tannery into river (Ethiopia)

The physicochemical characteristics of industrial wastewater were collected from Friendship Tannery PLC factory, in the Oromia regional state, the East Showa zone, near to the capital city of Ethiopia, Addis Ababa. The composition wastewater effluent from the industry characterize at Jimma University, Environmental Health Laboratory in 2015. This actual wastewater contains pH (7.56) and milligram per liter of hexavalent chromium, phosphate, nitrate, chlorine, dissolved oxygen, and chemical oxygen dissolve about 0.98, 15.91, 1.80, 819.28, 3.45 and 463.50, respectively. The physicochemical characteristics of soil rich in kaolinite-ferrinatriite, soil rich in kaolinite-goethite and coffee husk ash were characterized at Bishoftu Research Institute Laboratory, Ethiopia. The parameters contain electrical conductivity, cation exchange capacity, total nitrogen, organic matter, organic carbon and texture of the adsorbents.

Table 7.1 Physicochemical characteristics of wastewater from Friendship Tannery PLC factory (Ethiopia)

| Composition | Cr <sup>+6</sup> (mg.L <sup>-1</sup> ) | PO <sub>4</sub> <sup>3-</sup> (mg.L <sup>-1</sup> ) | NO <sub>3</sub> <sup>-</sup> (mg.L <sup>-1</sup> ) | Cl <sup>-</sup> (mg.L <sup>-1</sup> ) | DO (mg.L <sup>-1</sup> ) | COD (mg.L <sup>-1</sup> ) | BOD (mg.g <sup>-1</sup> ) | pH   | EC (μs.cm <sup>-1</sup> ) | Turbidity (NTU) | Temperature (°C) |
|-------------|--|---|--|---------------------------------------|--------------------------|---------------------------|---------------------------|------|---------------------------|-----------------|------------------|
| Value       | 0.98                                   | 15.91   | 1.80   | 819.28                                | 3.45                     | 463.50                    | 941.40                    | 7.56 | 6.19                      | 14.56           | 25.85            |

#### 7.1.1.2 Availability of local adsorbents

Soil rich in kaolinite-ferrinatriite, coffee husks and soil rich in kaolinite-goethite were collected from various districts in south-west Ethiopia, in the Oromia Regional State and the Jimma Zone. This adsorbent was collected for the physicochemical characterization and for the batch adsorptive experiment process. The Universal Transverse Mercator, difference, elevation, and sampling depth of SRKF and SRKG were indicated at Table 7.2 and Table 7.3.

Table 7.2 Sampling location site of SRKF

| Sampling Site | UTM                    | Difference (m) | Elevation (m) | Depth (m) |
|---------------|------------------------|----------------|---------------|-----------|
| 1             | 37N 0274104<br>0888816 | ± 3            | 1792          | 0.9       |
| 2             | 37N 0264967<br>0879988 | ± 3            | 1816          | 1.2       |
| 3             | 37N 0260722<br>0877326 | ± 3            | 1990          | 0.8       |

Table 7.3 Sampling location site of SRKG

| Sampling Site | UTM                    | Difference (m) | Elevation (m) | Depth (m) |
|---------------|------------------------|----------------|---------------|-----------|
| 1             | 37N 0269547<br>0850850 | ±3             | 1852          | 0.85-1.20 |
| 2             | 37N0269574<br>0850976  | ±3             | 1856          | 0.80-1.00 |
| 3             | 37N0269596<br>0850996  | ±3             | 1857          | 0.95      |

UTM represents Universal Transverse Mercator

### 7.1.2 Design process analysis

The design of adsorptive removal of chromium(VI) ion from industrial polluted water unit have a full wastewater treatment plant that is primary, secondary, and tertiary treatment as follows such as primary treatment units contain various tanks that is coagulation, flocculation, settling and sand filtration tanks; secondary treatment unit contain adsorptive removal of Cr(VI) treatment tanks as batch forms that contain locally available materials (LAM) such as soil rich in kaolinite-ferrinatriite, soil rich in kaolinite-goethite and coffee husk ash. The tertiary treatment unit has sand filtration to treat passed adsorbent contain Cr(VI) from secondary tanks, color and odor and ultraviolet lamp

used to treat microorganisms. The design considers primary, secondary, and tertiary treatment plant; specially focused on the objective and the result of research output on the secondary treatment that is adsorptive removal of chromium(VI) from industrial contaminated water discharge/effluent by using locally available materials. The following equations were used to know the dimension and the amount of the various treatment units (Rivas et al., 2008).

#### 7.1.2.1 Design of coagulation tank

The design process of coagulation tank of this work was carried out using batch adsorption experimental methods, which is most widely used experimental method for adsorption (Gerrity et al., 2015; Ronke et al., 2016). The design will be accomplished using the set up shown in Figure 7.2. The design was carried out at this coagulation pH 2 adjustment of wastewater discharge by addition of sulfuric acid ( $H_2SO_4$ ) and took  $62500 L \cdot hr^{-1}$  wastewater discharge from tannery industry (Asfaw, 2007). The design of coagulation tank consider volume ( $V = QT$ ) of wastewater discharge from industry in liters, flow rate ( $Q$ ) of the effluent wastewater from industry in liter per hour and detention time 0.25 hours, it can be typically to be between ten and thirty minutes (Michelin, 2010; Ronke *et al.*, 2016). The volume of the coagulation tank was designed, based on its length, width, and depth which was about 200, 300 and 270 cm, respectively.

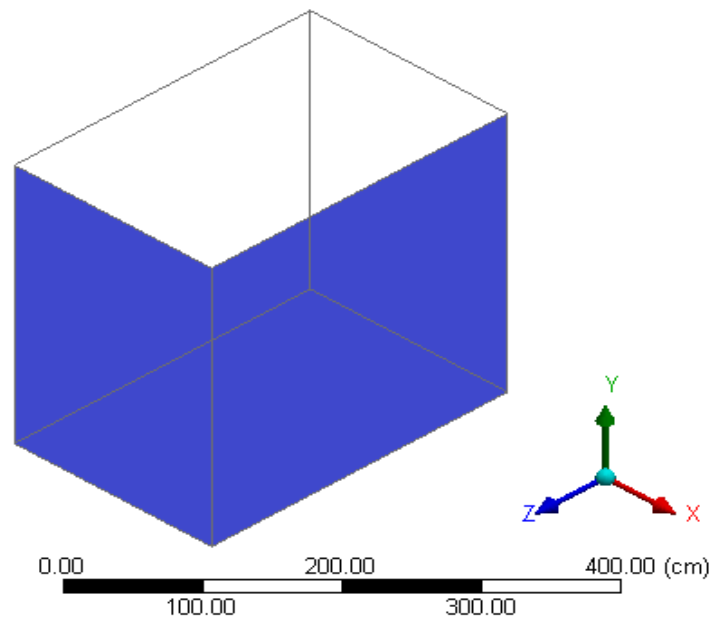


Figure 7.2 The volume of coagulation tank designed by ANSYS 17.0 software

After designing coagulation tank, the wastewater containing Cr(VI) discharge from industry was characterised at laboratory level then choice of coagulant by considering the following factors: such as nature and amount/ quantity of wastewater discharge from industry, composition of physicochemical wastewater discharge from industry, treatment condition after coagulation (filtration, settling), purity of reagents, particularly in the case of wastewater treatment process (Jin, 2005).

#### 7.1.2.2 Design of flocculation tank

The flocculation tank volume calculated by using the formula ( $V = QT$ ). At flocculation tank, the settling of colloidal material took longer time than coagulation tank (Rivas et al., 2008; Samaras et al., 2010). Therefore, the time found to be half-an-hour (30 minutes) (Michelin, 2010). Therefore  $V = 15625 \text{ L.hr}^{-1} \times 0.5 \text{ hr} = 7813 \text{ L}$ . The volume of flocculation tank was increased up to volume = 8000 L to satisfied better mixing. To know detention time;  $T = V/Q = 8,000 \text{ L}/7,813\text{L.hr}^{-1} = 1.02 \text{ hr} > 1/2 \text{ hr}$  [ok]. By taking height (H) and width (W) of flocculation tank about 27 L and 30 L, respectively. Then  $L = V/LW = 10 \text{ L}$ . Therefore, the dimension of length, width, and height of the flocculation tank about 100 cm, 300 cm, and 270 cm, respectively.

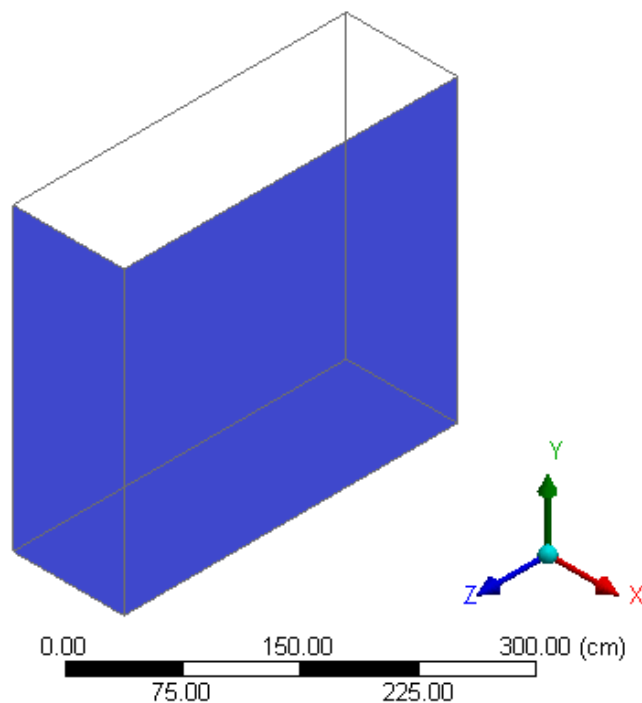


Figure 7.3 The volume of flocculation tank designed by ANSYS 17.0 software

### 7.1.2.3 Design of settling tank

The critical velocity of flow was considered for the design of the settling tank. For the removal of any particles, the value of the critical velocity ( $V_c$ ) is less than the settling velocity. The settling tank was prepared with lamella settlers to increase the removal of collides and suspended solids (Irvine et al., 1989; Shen et al., 2015). The volume of the setting tank can be calculated by ( $V = QT$ ), where Q flow rate in liter per hours, T detention time in hours. By taking the  $V = 10000$  L then  $L = 300$  cm,  $W = 120$  cm, and  $H = 300$  cm, therefore:  $T = V/Q = 10000L/15,625L.hr^{-1} = 0.64$  hr. The settling velocity of critical particle was calculated ( $V_c = Q/A$ ); therefore,  $V_c = V/TLW = 10,000/0.64 \times 30 \times 12 = 43.4$  cm.hr<sup>-1</sup>. This settling tank used for separation of particulate materials by their own weight through settling velocity designed above.

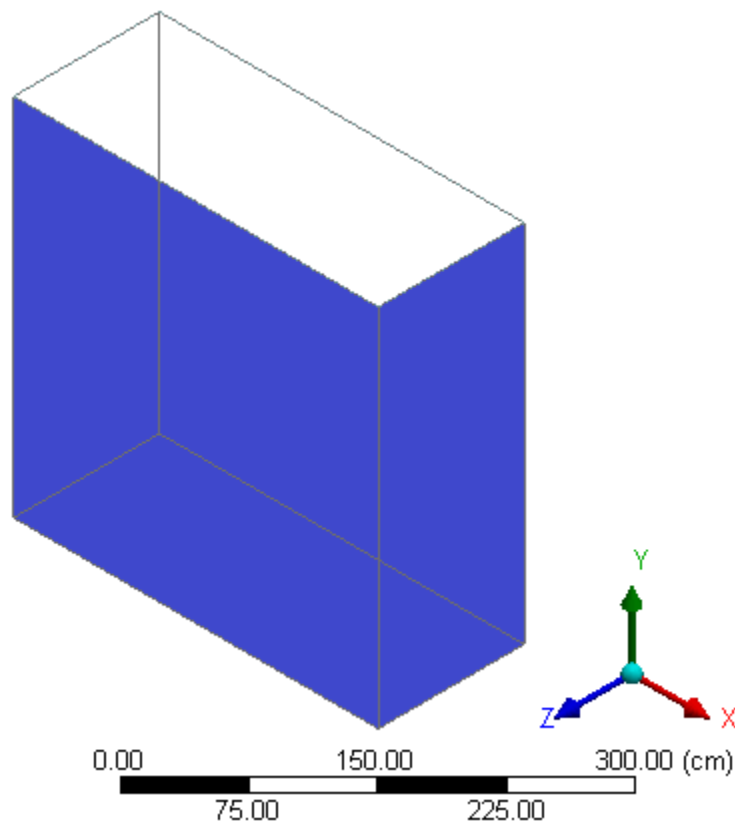


Figure 7.4 The volume of settling tank designed by ANSYS 17.0 software

The primary treatment design such as coagulation, flocculation and settling tanks summary were indicated Table 7.4 about phase I, phase II and Phase III, respectively.

Table 7.4 Summary of primary treatment design

| Phase | L (cm) | W (cm) | H (cm) |
|-------|--------|--------|--------|
| I     | 200    | 300    | 270    |
| II    | 100    | 300    | 270    |
| III   | 300    | 120    | 300    |

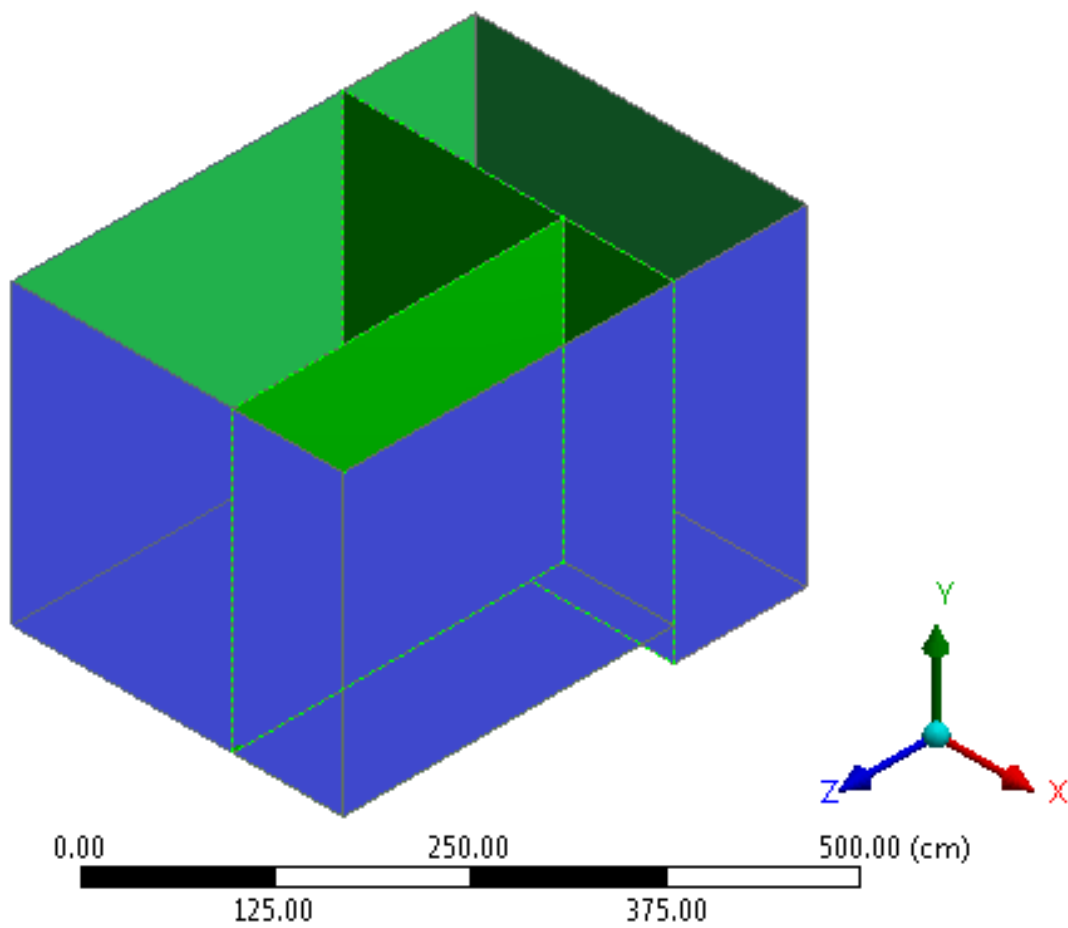


Figure 7.5 Dimension of primary treatment process tanks designed by ANSYS 17.0 software

#### 7.1.2.4 Design of filtration tank

The filtration tank removes the small particles in the industrial wastewater. However, the large particle cannot pass through the media. The primary turbidity of the industrial wastewater is also removed by the filtration process. The rapid filtration uses gravity, hence has low electrical consumption and is simple (Irvine et al., 1989). The influent industrial wastewater containing Cr(VI) is cleared by force of gravity. The advantage of this filtration process lies in its low sensitive to the quality of industrial wastewater discharge and simplicity of backwashing for regeneration by using small amount of sand (Tchobanoglous and Burton, 1991). The theoretical filtration rate is equal to flow rate of the industrial wastewater discharge divided by the area of the tank (Bahadori et al., 2013).

$$F = Q/A \quad (7.1)$$

Where

F = the filtration rate ( $\text{m}^3 \cdot (\text{m}^2 \cdot \text{hr})^{-1}$ ),

Q = flow rate in ( $\text{m}^3 \text{ hr}^{-1}$ ), and

A = area in ( $\text{m}^2$ ).

By using the above equation:  $F = 3 \text{m}^3 \cdot (\text{m}^2 \cdot \text{hr})^{-1}$  (Design standard United State ( $0.4 - 3.1 \text{m}^3 \cdot (\text{m}^2 \cdot \text{hr})^{-1}$ ) and  $Q = 7813 \text{ L} \cdot \text{hr}^{-1}$ ; Therefore,  $A = 2.6 \text{ m}^2$ ; Therefore  $D = 18.2 \text{ cm}$  around up to  $20 \text{ cm}$  and found to be  $L = 3D = 60 \text{ cm}$ . The similar size of filter media used for proper operation of sand filtration. Before the treatment process began, the sand was cleared by washing (Flores-Alsina *et al.*, 2015). The uniformity coefficient (UC) ( $d_{60}/d_{10}$ ) was approximately 1.5 due to the recommended UC between 1.3-1.8 (Paige-Green, 1999; Zouboulis et al., 2007; El Zayat et al., 2015).

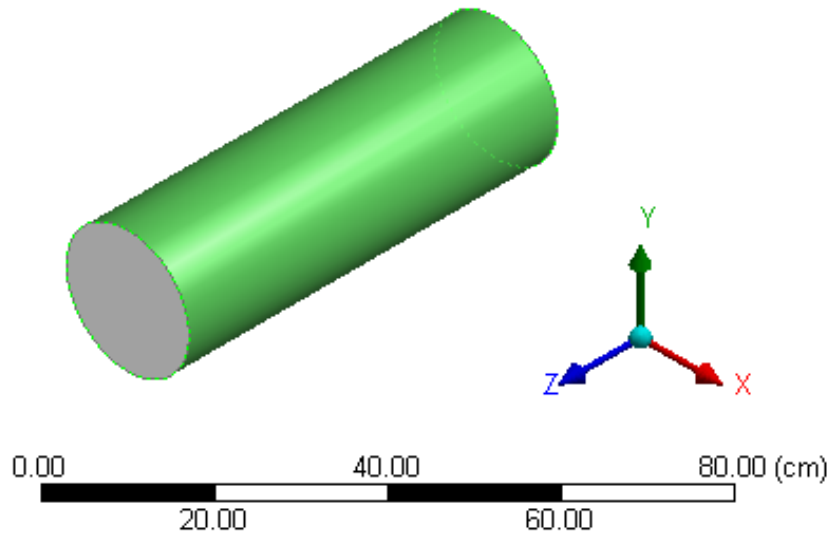


Figure 7.6 The volume of filtration tank designed by ANSYS 17.0 software

### 7.1.3 Secondary tank (design of Cr(VI) adsorptive removal tank)

Secondary tank design used for the adsorptive removal of hexavalent chromium from industrial polluted water pass through primary treatment process. Other treatment technology such as ion exchange, chemical reduction, membrane separation, reverse osmosis and electro-coagulant were expensive investment, high operational cost, and ineffectiveness at high concentration of Cr(VI) removal from industrial wastewater (Flores-Alsina et al., 2015; Hokkanen et al., 2016). Large setting basins may be required to collect the metal precipitates, usually followed by a large filtration unit. Thus, to take advantage of the benefits of adsorption while overcoming some of these drawbacks, a means has been designed for the development of a variety of economical materials for use in the removal of heavy metals from contaminated water through adsorption. Due to this adsorptive removal of Cr(VI) from industrial polluted water by using SRKF, CHA and SRKG were affordable for developing country such as Ethiopia. The following design were calculated depending on the experimental results obtained from in Chapters Three, Four and Five.

Table 7.5 Experimental result for technological viability

| No | Effects                                 | SRKF  | CHA | SRKG  |
|----|---|-------|-----|-------|
| 1  | Shaker speed (rpm)                      | 150   | 100 | 150   |
| 2  | Contact Time (min.)                     | 40    | 40  | 40    |
| 3  | Adsorbent dose (g/L)                    | 3.5   | 1.5 | 3     |
| 4  | pH solution                             | 2     | 2   | 2     |
| 5  | Initial concentration of Cr (VI) (mg/L) | 2     | 0.5 | 1     |
| 6  | Particle size (mm)                      | 0.075 | 0   | 0.075 |

From the experimental result chapter three, four and five (Table 7.5) a series cylindrical tanks with stirred tanks / orbital shaker table for batch equilibrium tank were used for adsorptive removal of hexavalent chromium from tannery industry polluted water discharge each cylindrical tank have 2 (two) tanks, one for operation and the other for reservation, in the case of SRKF, CHA and SRKG exhaustion or tank maintenance.

The design of the volume of the Cr(VI) adsorptive removal tank can be calculate depend on the experimental research result chapter Three, Four and Five (Table 7.4) as follows:

- (i) the amount of discharge from tannery industry wastewater contain Cr(VI) is  $1500 \text{ m}^3 \cdot \text{day}^{-1} = 7813 \text{ L} \cdot \text{hr}^{-1}$  (Asfaw, 2007, Chapter One Section 2.3) = 5209 L in 40 minutes (40 min from Table 7.4)
- (ii) the concentration of Cr(VI) in the tannery industry wastewater discharge is  $0.98 \text{ mg} \cdot \text{L}^{-1}$  (wastewater from Friendship Tannery PLC factory for experiment)
- (iii) the amount of pH value of wastewater from Friendship Tannery PLC factory is 7.56. The pH value of the wastewater was adjusted with  $0.1 \text{ N H}_2\text{SO}_4$  up to obtain  $\text{pH} = 2$
- (iv) the shaker speed was adjusted to 150 rpm for SRKF and SRKG adsorbents and 100 for CHA adsorbent.
- (v) the volume of cylindrical tank of adsorptive removal of Cr(VI) capacity calculated by ( $V = A H$ ), therefore,  $30\text{L} = A \times 60 \text{ cm}$ ,  $D = 80 \text{ cm}$
- (vi) the capacity of each tank is approximately 30L and assume 60 cm height.
- (vii) the diameter and height of each tank was 80 centimeters and 60 centimeters, respectively. The number of cylindrical batch adsorptive removal tanks with continuous stirred tank reactors:

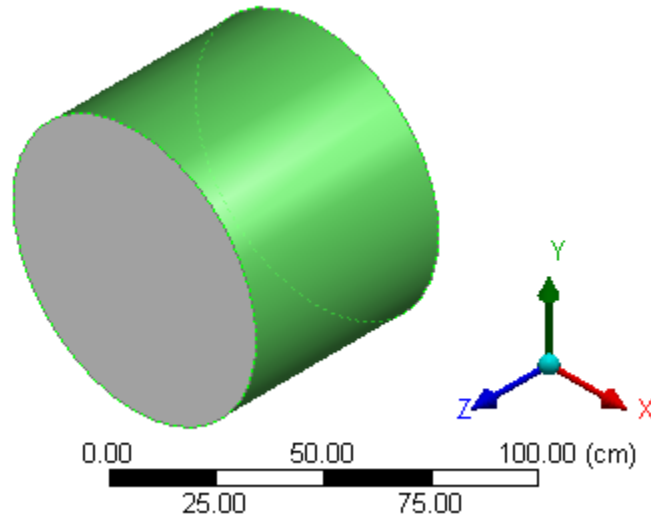


Figure 7.7 The volume of cylindrical batch adsorptive removal tank designed by ANSYS 17.0 software

Number cylindrical tank =  $Q \text{ discharge} / \text{capacity of each cylinder} = 5209 \text{ L} / 30 \text{ L}$  around 174 tanks

Therefore, 174 cylindrical tanks for process and 174 cylindrical tanks for standup, total 348 cylindrical tanks for SRKF adsorbent batch set up. For all three adsorbents (CHA, SRKG and SRKF) are 1044 tanks.

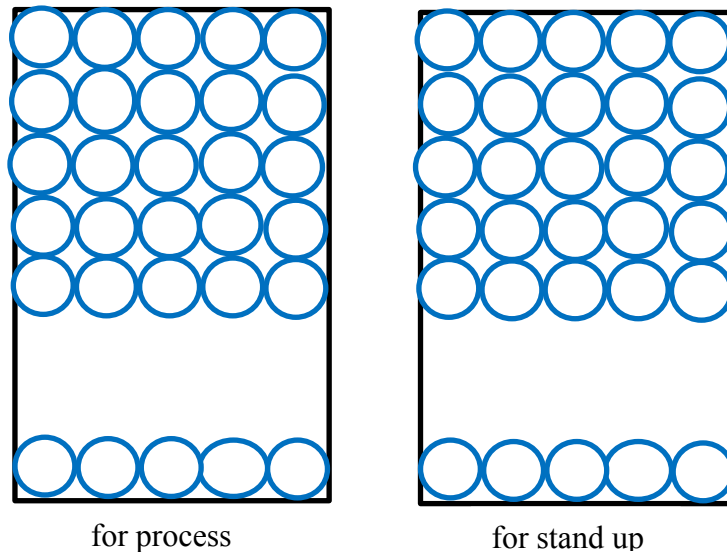


Figure 7.8 For SRKF adsorptive removal Cr(VI) batch set up block diagram (floor plan) the particle size was selected for SRKG and SRKF adsorbents (0.075 mm)

- (viii) the contact time for all adsorbents (SRKF, CHA and SRKG) are 40 minutes.
- (ix) the adsorbents (SRKG, CHA and SRKF) dose for the design:

Table 7.6 The dose of adsorbents (SRKF, CHA and SRKG)

| Adsorbent | Dose of adsorbent (g.L <sup>-1</sup> ) |                      |                     |
|-----------|--|----------------------|---------------------|
|           | Research result                        | For each tank (30 L) | For total 348 tanks |
| SRKF      | 3.5                                    | 105                  | 36,540              |
| CHA       | 1.5                                    | 45                   | 15,660              |
| SRKG      | 3                                      | 90                   | 31,320              |

- (x) the adsorbents were exhausted by Cr(VI) ion concentration, it can be regenerate by desorption process.

### 7.1.4 Tertiary treatment design

For sand filter treatment used by cylindrical shape with a diameter of 20 centimeters and a height of 60 centimeter. The tertiary treatment used for removing the adsorbents contain Cr(VI) pass from the secondary tank treatment and then to storage tanks (Tchobanoglous and Burton, 1991).

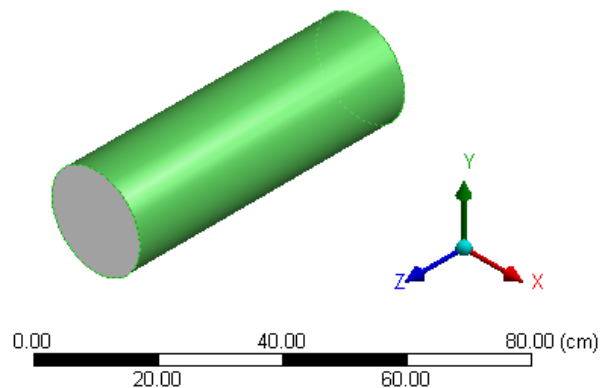


Figure 7.9 The volume of tertiary treatment tank designed by ANSYS 17.0 software

## **7.2 Adsorptive Removal of Cr(VI) from Industrial Wastewater Treatment (ARIWWT) Process Description**

The operation steps of adsorptive removal of Cr(VI) from industrial wastewater treatment and Figure 7.10 and Figure 7.11 shows the ARIWWT processes block and schematic diagram (IFC, 2007; USEPA, 2013).

1. The primary treatment process tanks were occupied with industrial wastewater containing Cr(VI).
2. Industrial wastewater contains Cr(VI) was discharged by gravity to the primary settling unit such as coagulation, flocculation, settling tanks. No chemicals or coagulants were added in the experimental runs. Suspended collides and suspended particles were removal at settling tank.
3. Wastewater discharge from settling tank to the other tank passes by gravity force for the further treatment processing.
4. The colloid and suspended unwanted materials were cleared by sand filtration process at cylindrical tanks.
5. The filter industrial wastewater was effluent to adsorptive removal of Cr(VI) tanks. The equilibrium batch cylindrical tanks have two tanks such as one for process and another standby tank used for if the exhaustion of the SRKF or maintenance of the tank. In the batch cylindrical tank around 36540 g of adsorbent dose for all 348 tanks were poured in the batch adsorptive tanks. In batch cylindrical tanks, 3.5 g.L<sup>-1</sup> of SRKF was added during the experimental runs and with 150 rpm shaker speed.
6. The sand filtration after adsorption process used for removal of some of the suspended SRKF particulate contain Cr(VI) and odor nuisance from the industrial wastewater discharge and then to storage tanks. At this storage tank it should be adjusted from a pH of 2, to a neutral pH of 7.
7. A sample was collected after adsorptive removal of Cr(VI) tank to know adsorptive removal capacity of soil rich in kaolinite-firrinatrite adsorbent.
8. The SRKF adsorbent exhausted by Cr(VI) ion the desorption process was applied.
9. The stirred/shake speed and other treatment process were controlled by an electrical control panel.

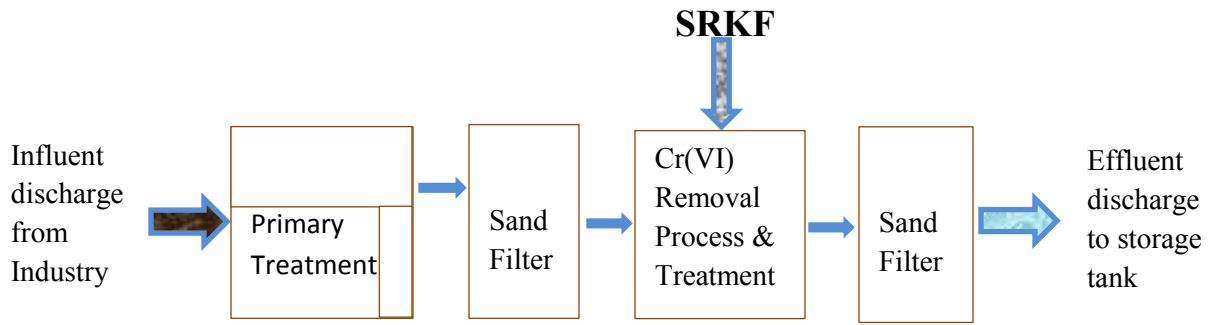


Figure 7.10 Adsorptive removal of Cr(VI) treatment processes block diagram

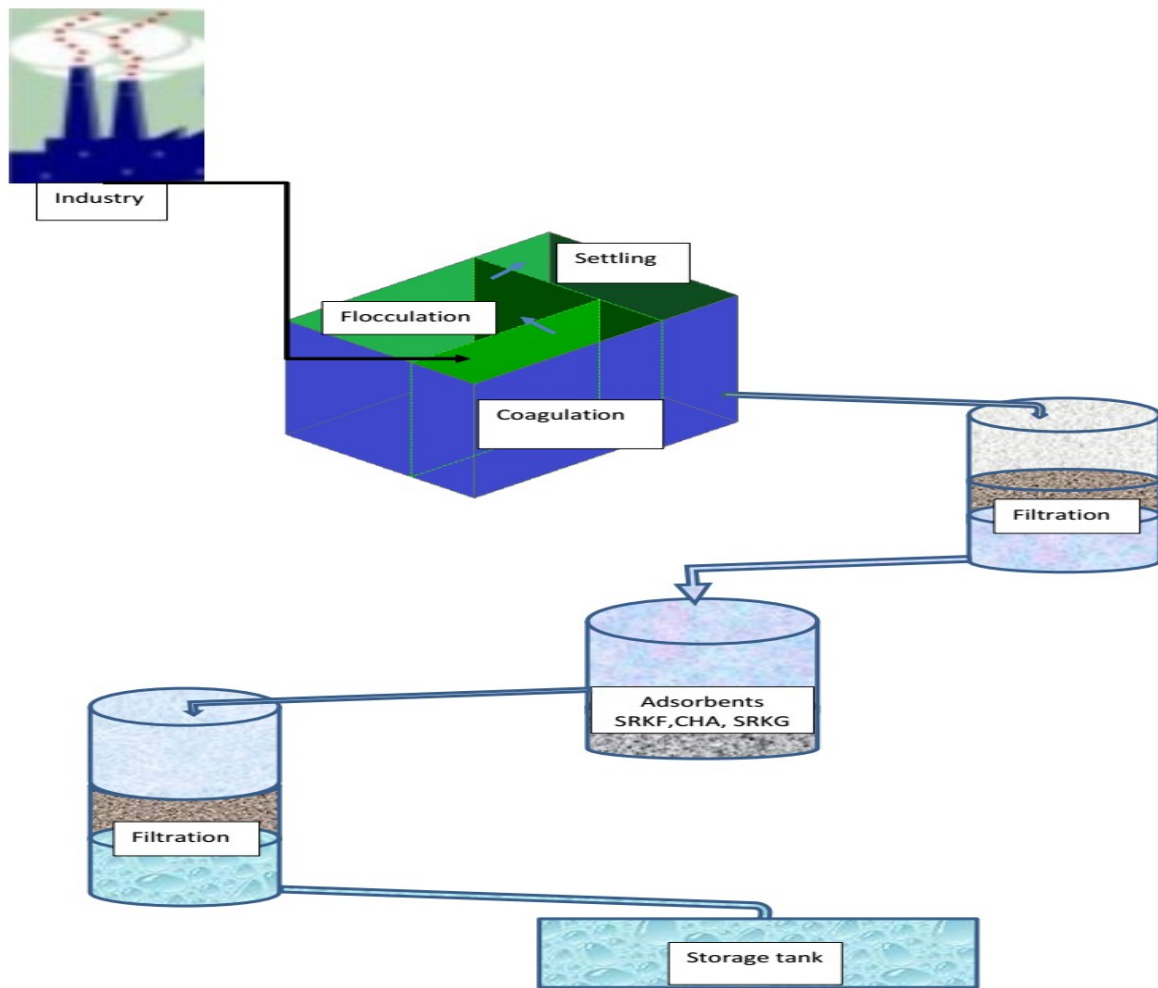


Figure 7.11 Schematic diagram of adsorptive removal of Cr(VI) by using SRKF, CHA and SRKG treatment processes

### 7.3 Conclusions

The theoretical design of adsorptive removal of Cr(VI) from industrial wastewater discharge from tannery industry was designed by taking discharge amount from the industry detention time from standard. The design considers primary treatment, filtration, and adsorptive removal of Cr(VI) tanks and it may be the major component for managing the treatment process in the developing country like Ethiopia. This all tanks volume value was calculated by using various known formulae and designed by using ANSYS software 17.0. Therefore, this local available material (SRKF, CHA and SRKG) with the design process was promising adsorbents and design for adsorptive removal of Cr(VI) from wastewaters then it will be implement at local level.

### 7.4 References

- Ahluwalia, S and Goyal, D. 2007. Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresource Technology Journal* 98: 2243-2257.
- Asfaw, F. 2007. Modeling on Akaki rivers liquid waste disposal and base flow separation, Addis Ababa University, Ethiopia.
- Bahadori, A, Clark, M and Boyd, B. 2013. Essentials of water systems design in the oil, gas, and chemical processing industries, Springer Science and Business Media Springer Briefs in Applied Sciences and Technology, DOI: 10.1007/978-1-4614-6516-4\_2.
- Belay, A and Sahile, S. 2013. The effects of Dashen brewery wastewater treatment effluent on the bacteriological and physicochemical quality of Shinta river in Gondar, North West Ethiopia. *World Environment Journal* 3:29-36.
- Chaturvedi, D and Sahu, O. 2014. Adsorption of Heavy Metal Ions from Wastewater. *Global Journal of Environmental Science and Technology* 2: 020-028.
- El Zayat, M, Sherien, E and Salah El, H. 2012. Treatment of various types of wastewater using cement kiln dust, proceeding of the 5<sup>th</sup> international perspective on water resources and environment 2012 by the environment and water resource institute of the American society of civil engineering (EWRI/ASCE): Marrakesh.

- El Zayat, M., Elagroudy, S and El Haggat, S. 2015. Economic viability of removal of heavy metal cations from industrial wastewater using innovative. *Journal of Emerging Trends in Engineering and Applied Sciences* 6: 360-370
- Flores-Alsina, X, Mbamba, C, Solon, K, Vrecko, D, Tait, S, Batstone, D, Jeppsson, U and Gernaey, K. 2015. A plant-wide aqueous phase chemistry module describing pH variations and ion speciation/pairing in wastewater treatment process models. *Water research Journal* 85: 255-265.
- Gerrity, D, Pisarenko, A, Marti, E, Trenholm, R, Geringer, F, Reungoat, J and Dickenson, E. 2015. Nitrosamines in pilot-scale and full-scale wastewater treatment plants with ozonation. *Water research Journal* 72: 251-261.
- GSOE. 2011. Opportunities for kaolin resource development in Ethiopia, geological survey of Ethiopia. Addis Ababa, Ethiopia
- Hokkanen, S, Bhatnagar, A, Repo, E, Lou, S and Sillanpää, M. 2016. Calcium hydroxyapatite micro fibrillated cellulose composite as a potential adsorbent for the removal of Cr (VI) from aqueous solution. *Chemical Engineering Journal* 283: 445-452.
- International Finance Corporation (IFC). (2007). Pollution prevention and abatement handbook. World bank group environmental, health, and safety guidelines pp 846-918
- Irvine, R, Ketchum J and Asano, T. 1989. Sequencing batch reactors for biological wastewater treatment. *Critical Reviews in Environmental Science and Technology Journal* 18: 255-294.
- Jin, Y. 2005. Use of a high resolution photographic technique for studying coagulation/flocculation in water treatment. Saskatchewan, Canada S7N5A9.
- Kufa, T. 2012. Recent coffee research development in Ethiopia, Ethiopian coffee export conference: Strengthening the legacy of our coffee 8-9 November 2012, Hilton Hotel, Addis Ababa, Ethiopia
- Mekuyie, M. 2014. Heavy metals concentration in effluents of textile industry, Tikur Wuha river and milk of cows watering on this water source, Hawassa, Southern Ethiopia. *Journal of Natural Sciences Research* 4: 47-56.
- Mihelcic, J and Zimmerman, J. 2010. Environmental engineering: fundamentals, sustainability, Designl Wiley, USA.

- Padanilly, Zerihun, T, Tadele, N, Sevanan, R, Lakew, W, Alemayehu, N, Ephrem, D, Esayas, A, Asfaw, A and Asefa, K. 2008. Characterisation of sewage wastewater and assessment of downstream pollution along Huluka River of Ambo, Ethiopia. *Journal of Science and Technology* 2: 440-443
- Paige-Green, P. 1999. A comparative study of the grading coefficient, a new particle size distribution parameter. *Bulletin of Engineering Geology and the Environment* 57: 215-223.
- Rivas, A, Irizar, I and Ayesa, E. 2008. Model-based optimization of wastewater treatment plants design. *Environmental Modelling and Software Journal* 23: 435-450.
- Ronke, R, Saidat, O and Abdulwahab, G. 2016. Coagulation-flocculation treatment of industrial wastewater using tamarind seed powder. *International Journal of ChemTech Research* 9: 771-780.
- Samaras, K, Zouboulis, A, Karapantsios, T and Kostoglou, M. 2010. A CFD-based simulation study of a large scale flocculation tank for potable water treatment. *Chemical Engineering Journal* 162: 208-216.
- Shen, Y, Linville, J, Urgun-Demirtas, M, Mintz, M and Snyder, S. 2015. An overview of biogas production and utilization at full-scale wastewater treatment plants (WWTPs) in the United States: challenges and opportunities towards energy-neutral WWTPs. *Renewable and Sustainable Energy Reviews* 50: 346-362.
- Tchobanoglous, G and Burton, F. 1991. Wastewater engineering. *Management* 7: 1-4.
- Tong, B. 2012. Wastewater production, treatment and use in Peru, Presented at the forth regional workshop of the project 'safe use of wastewater in agriculture', 11–13 December, Lima. [http://www.ais.unwater.org/ais/mod/page/view.php?id 171](http://www.ais.unwater.org/ais/mod/page/view.php?id%20171) [accessed 21.12.12]
- United States Environmental Protection Agency (USEPA). 2013. Glass manufacturing. <http://www.epa.gov/reg3hscd/bf-lr/regional/industry/glass.htm>) accessed on 08 August 2014
- Wosnie, A and Wondie, A. 2014. Bahir Dar tannery effluent characterization and its impact on the head of Blue Nile River. Addis Ababa, Ethiopia
- Zwain, H, Vakili, M and Dahlan, I. 2014a. Waste material adsorbents for zinc removal from wastewater: a comprehensive review. *International Journal of Chemical Engineering* 13: 1-13.

## 8. GENERAL CONCLUSIONS AND RECOMMENDATION

### 8.1 Summary

Industrial development along the riverbanks has caused severe problems for living organisms (Ronke et al., 2016; Ahmad and Haseeb, 2017; Kan et al., 2017). Cr(VI) is the most frequently found metal in effluent that being discharged from point source pollution such as leather, electroplating industries. The presence of higher than the permissible levels of heavy metals result in a high risk to human health (Ahmad and Haseeb, 2017; Uddin, 2017; Lin et al., 2018). It is also a known carcinogen and other chronic diseases occurrence (Ahmad and Haseeb, 2017; Kan et al., 2017; Panda et al., 2017). In many cases, particularly in developing countries, polluted water is often used for domestic as well as irrigation purposes. The lack of knowledge on the mechanisms of heavy metal removal, the relatively high cost and the complexity of providing the necessary treatment have led to either the inadequate treatment of wastewater, or no treatment at all (Ahmad and Haseeb, 2017; Panda et al., 2017). In such a case, the removal of its contaminants from wastewater is absolutely necessary. Effective and safe discharge of polluted wastewater containing heavy metals is always a challenging task for many parts of the world especially the developing countries due to the fact that cost-effective treatments are not readily available (Malik et al., 2017). Conventional technology for treating metal bearing water mainly involves precipitation of the metals and then separation of the particulate metals by setting, usually aided by chemical coagulations. This approach has several practical limitations (Kan et al., 2017; Malik et al., 2017). In many places the chemicals are expensive and they have to be imported in hard currency. Besides, precipitation is often unsuccessful if the metals are complexed or if they are existing as anions (e.g.  $\text{HCrO}_4^-$ ). In addition, these metals which do precipitate may form small particles that do not readily settle. As a result, large settling basins may be required to collect the metal precipitates, usually followed by a large filtration unit. Thus, to take advantage of the benefits of adsorption while overcoming some of these drawbacks, a means has been designed for the development of a variety of economical materials used for the heavy metals removal from industrial wastewater through adsorption.

The selection of an appropriate adsorbent is very crucial for the successful application of adsorption. The main concerns were reduction of cost, elimination of secondary pollutant generation, improving the efficiency for treatment of contaminated water with heavy metal loadings (Ronke et al., 2016). The available methods have several disadvantages, which make them not effective and/or not sustainable for non-developed areas around the globe. As a result, looking for an appropriate wastewater treatment technology using locally available natural materials that may be used in poorly developed areas such as Ethiopia remains an issue that has to be dealt with. Among the natural adsorbents, soil and coffee husk would meet the criteria that have been established for wastewater treatment processes due to their physical properties. In this work, alternative to the conventional purification agents, soil rich in kaolinite (40.4%)–ferrinatriite (59.6%) (SRKF), soil rich in kaolinite (29.4%)-goethite (70.6%) (SRKG) and coffee husk ash (CHA) were used as treatment media in order to optimize the design parameters.

Based on this, the objectives of the present work were to investigate the technological viability of SRKF, CHA and SRKG for removal of Cr(VI) ion in batch adsorption under various parameters. The effects of major design parameters ( shaker speed, pH of solution, initial concentration of chromium(VI) ion, contact time, dose of adsorbent and size of particle) onto SRKF, CHA and SRKG are optimized. In order to provide the necessary information for process optimization and design, several models have been developed using experimental data.

## **8.2 Conclusions**

The presence chromium (VI) in the water at levels greater than the permitted limit is the cause of severe to human health problems and environment. Because of this, the removal of hexavalent chromium from industrial wastewater discharge, or its minimization up to a permissible level, is necessary for human and the environment health. The present study demonstrated the technological viability of soil rich in kaolinite-ferrinatriite (SRKF), soil rich in kaolinite-geothite (SRKG) and coffee husk ash (CHA), for the adsorptive removal of Cr(VI) ions from industrial wastewater containing heavy metal discharge as effluent to nearby water bodies and/ or the environment. Batch adsorption by various effects, such as the shaker speed, contact time effect, the dose of adsorbents, the solution pH effect, initial amount of hexavalent chromium and size of particle optimum removal

efficiency was investigated. Equilibrium contact time for Cr(VI) removal was observed within 40 minutes. The fast initial uptake rate is attributed to the availability of a large number of open adsorption sites at the initial stage. The optimum adsorptive removal capacity of CHA, SRKF and SRKG adsorbents at pH value of 2. The other effects of the three locally available adsorbents are not the same optimum value of removal efficiency of chromium(VI) from aqueous solution and actual wastewater contain Cr(VI) discharge from industry. Adsorption of Cr(VI) followed Pseudo-Second-Order kinetics with coefficient of determination;  $r^2 > 0.99$  for the three-adsorbent media. Besides, the predicted equilibrium adsorption capacities were quite close to the experimental values for all particle sizes tested in this study, confirming the validity of the pseudo second order rate assumption. The transport of chromium (VI) ions from the solution to the pores of the adsorbent particles and surface of SRKF, CHA and SRKG are responsible for the adsorption of the hexavalent chromium ions.

The Freundlich and Langmuir isotherm was examined in this study at a room temperature of  $22 \pm 2^\circ\text{C}$ . Results of the adsorption isotherm show that the Freundlich isotherm model better described Cr(VI) adsorption into soil rich in kaolinite-ferrinatrinite, soil rich in kaolinite-goethite and coffee husk ash with coefficient of determination;  $r^2 > 0.93$ . The Langmuir characteristic defined by the  $R_L$  value. In all adsorbents, the  $R_L$  values for the experimental data were between 0 and 1, which is an indicative value of the favorable adsorption of chromium(VI) ions on the SRKF, CHA and SRKG. In all experiments, the larger value of,  $K_L$ , obtained for the chromium (VI) ions SRKF indicate the strong interactions between the hexavalent chromium ions than SRKG and CHA. These adsorbent materials could be used for the chromium(VI) removal from industrial wastewater and the treatment process by considering industry effluent amount and standard detention time as was designed. Therefore, this behavior suggested that soil rich in kaolinite (40.4%)-ferrinatrinite (59.6%), soil rich in kaolinite (29.4%)-goethite (70.6%) and coffee husk ash can be used as an interesting and promising cheap adsorbents technology for adsorptive removal of chromium(VI) from contaminated water. However, further investigation will be required for practical application of these three locally available adsorbent materials at local level for removal of chromium from industrial wastewater discharge.

### **8.3 Practical Relevance**

Soil rich in kaolinite-ferrinatriite, soil rich in kaolinite-geothite and coffee husk ash were locally available adsorbent materials are promising and practically viable methods for adsorptive removal of hexavalent chromium from industrial wastewater discharge. Depending on the results reported in Chapter Three, Four, Five and Six, the design of adsorptive removal in Cr(VI) from industrial wastewater discharge from tannery industry was performed by taking actual discharge amount of cubic meter per year from the industry and detention time from US standard. The design considers primary treatment, filtration, and adsorptive removal of Cr(VI) tanks and it may be the major component for managing the treatment process in the developing country like Ethiopia. The adsorptive removal tank in Cr(VI) filled with each adsorbent (SRKF, CHA and SRKG) according to the research result (experimental data) from chapters 3, 4, 5 and 6. All tanks value were calculated and designed by using ANSYS software 17.0. Therefore, this local available material (SRKF, CHA and SRKG) with the design process were promising adsorbents and design for adsorptive removal of chromium(VI) from wastewater can be recommended to be implemented.

### **8.4 Recommendations**

Promising results have been obtained for the adsorptive removal of hexavalent chromium (Cr(VI)) from contaminated water in batch adsorption experiment by using soil rich in kaolinite-ferrite, soil rich in kaolinite-geothite and coffee husk ash as adsorbents. Hence, the following can be recommended for further optimization and implementation of soil and waste for wastewater engineering:

- 1 The implementation the soil rich in kaolinite-ferrinatriite for adsorptive removal of hexavalent chromium from wastewater tested at local level depend on the design.
- 2 The practical application of the coffee husk ash will be checked as treatment technology for removal of hexavalent chromium from industrial wastewater at selected industry.
- 3 The practical application of the soil rich in kaolinite-geothite for the treatment of hexavalent chromium from contaminated water at domestic level.

- 4 Different ions and compounds present in polluted water might influence heavy metal adsorption onto the adsorbents and, hence, affect the process of adsorptive metal removal. Therefore, there is a need for a detailed investigation are required on the major inorganic ions as well as organic matters influencing the adsorptive heavy metal removal from different industrial wastewater effluents.

## 8.5 References

- Ahmad, R and Haseeb, S. 2017. Adsorption of Pb (II) on mentha piperita carbon (MTC) in single and quaternary systems. *Arabian Journal of Chemistry* 10: 412-421.
- Kan, C, Ibe, A, Rivera, K, Arazo, R and de Luna, M. 2017. Hexavalent chromium removal from aqueous solution by adsorbents synthesized from groundwater treatment residuals. *Sustainable Environment Research Journal* 27: 163-171.
- Lin, H, Rong, C, Jiu, B, Li, B, Yu, Q, Gan, L and Zhang, Z. 2018. Effects of chromium on pyrolysis characteristic of water hyacinth (*Eichornia crassipes*). *Renewable Energy* 115: 676-684.
- Malik, D, Jain, C and Yadav, A. 2017. Removal of heavy metals from emerging cellulosic low-cost adsorbents: a review. *Applied Water Science Journal* 7: 2113-2136.
- Marius, G. 2011. Hexavalent chromium reduction with zero-valent iron (ZVI) in aquatic systems. *Water, Air and Soil Pollution Journal* 222: 103-148.
- Panda, H, Tiadi, N, Mohanty, M and Mohanty, C. 2017. Studies on adsorption behavior of an industrial waste for removal of chromium from aqueous solution. *South African Journal of Chemical Engineering* 23: 132-138.
- Ronke, R, Saidat, O and Abdulwahab, G. 2016. Coagulation-flocculation treatment of industrial wastewater using tamarind seed powder. *International Journal of ChemTech Research* 9: 771-780.
- Uddin, M. 2017. A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. *Chemical Engineering Journal* 308: 438-462.

## 9. APPENDICES



Figure 9.1 Sample collection



Figure 9.2 Laboratory work



Figure 9.3 Laboratory work



Figure 9.4 Laboratory work

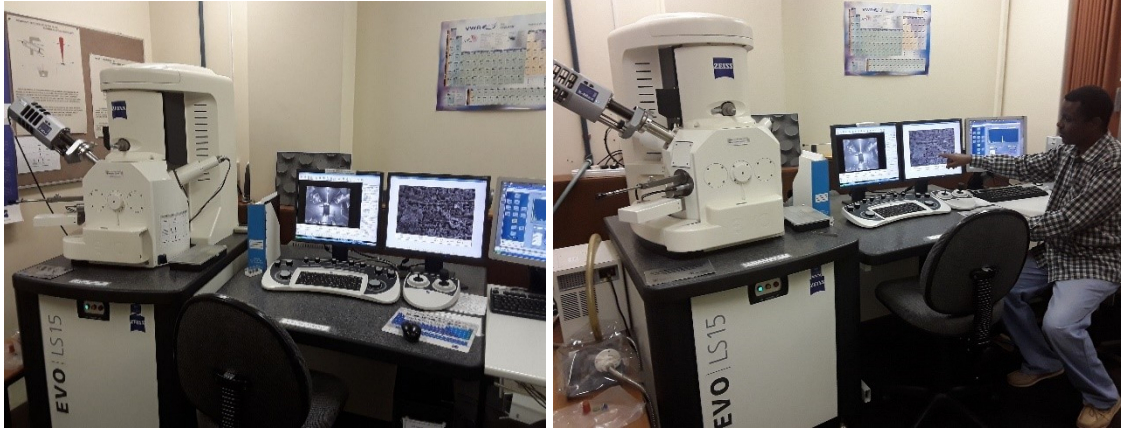


Figure 9.5 SEM and EDX analysis at Pietermaritzburg campus, UKZN

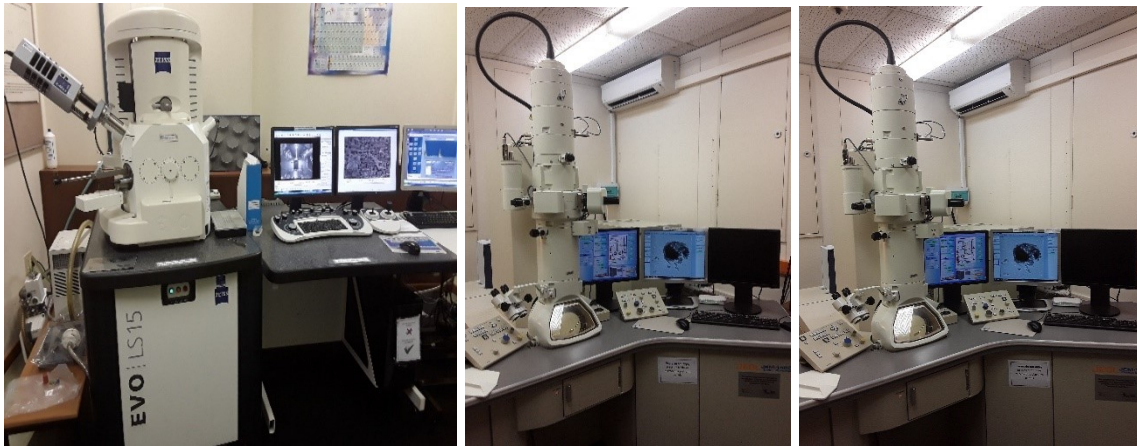


Figure 9.6 SEM and EDX analysis at Pietermaritzburg campus, UKZN

Chromium cycle (Marius, 2011)

