Evaluation of Banana Peels, Pumice and Charcoal Potential to Adsorb Chromium Ions from Tannery Wastewater

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DECLARATION

This thesis is my original work and has not been presented for a degree in any other university.

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DEDICATION

To my husband Gerald and lovely son Robbie,

You have been a great source of motivation and inspiration

When times were tough, God never let me down.

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ACRONYMS AND ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
APHA	American Public Health Association
ATSDR	Agency for Toxic Substances and Disease Registry
BD	Bulk density
BET	Brunauer, Emmett and Teller
BOD	Biochemical Oxygen Demand
CERC	Consumer Education and Research Centre
COD	Chemical Oxygen Demand
CONTANCE	Confederation of National Associations of Tanners and Dressers of the European Community
Cr (III)	Trivalent Chromium
Cr (VI)	Hexavalent Chromium
CW	Constructed wetland
DF	Dilution Factor
EHS	Environmental, Health and Safety
EPA	Environmental Protection Agency
ETAAS	Electrothermal Atomic Absorption Spectrometry
FAAS	Flame Atomic Absorption Spectrometry
GDP	Gross domestic product
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IFC	International Finance Corporation
IPPC	Integrated Pollution Prevention and Control
JKUAT	Jomo Kenyatta University of Agriculture and Technology
LIK	Leather Industries of Kenya
LOI	Loss on Ignition

MC	Moisture Content
MoEF	Ministry of Environment and Forests
NEMA	National Environment Management Authority
OECD	Organization for Economic Co-operation and Development
Rpm	Revolutions per Minute
SEM	Scanning Electron Microscope
SP	Sampling Point
SSF	Sub-surface Flow systems
UNIDO	United Nations Industrial Development Organization
USEPA	United States Environmental Protection Agency
VM	Volatile Matter
WHO	World Health Organization
IARC	International Agency for Research on Cancer

ABSTRACT

Heavy metal contamination has been a serious problem throughout the world because of the hazardous effects on the health of humans. Of major concern is chromium heavy metal which is a major pollutant from the tannery industry. Chromium often occurs in the trivalent, Cr (III), and hexavalent, Cr (VI), states under natural environmental conditions. The hexavalent state of chromium is highly toxic and carcinogenic. Although technology advancements in heavy metal removal in wastewater have been observed, conventional methods of chromium removal and recovery are expensive to implement particularly in developing countries. Research has hence focused on the use of low-cost adsorbent materials to reduce and remediating chromium metals from tannery wastewater. This research study investigated the use and effectiveness of pumice, charcoal and banana peels as adsorbents to remove chromium from stock chromium solutions in batch experiments and from tannery wastewater in a pilot study. The three adsorbents were prepared by rinsing and drying in an oven before use. Batch experiments were conducted to evaluate the effect of contact time, pH and initial concentration on chromium removal by the three adsorbents. To evaluate the practical applicability of these materials, field studies were conducted in a local tannery in Thika, Kenya. Aspects of time and adsorbent bed depth were varied to evaluate their effect on chromium removal from the tannery wastewater. The three adsorbent materials, showed high chromium removal for both batch and field studies with a range of 69.3- 98.9%. Chromium removal was observed to be effective at low pH of between 3 and 6, with reduction in the rate of chromium adsorption being observed with time. Adsorption equilibrium time for pumice and charcoal were observed at 120 min while that of banana peels was observed at 60 min. The adsorption of chromium increased with increase in concentration of the metal in solution. Adsorption results were modeled using kinetic and isotherm models. Experimental data indicated that chromium adsorption by all the three adsorbents follow the second-pseudo-order kinetics model (R^2> 0.987). The three adsorbents were also observed to have fitted well with both the

Langmuir and Freundlich isotherm models, with separation factor ($R_L<1$) and n values ($n>1$) showing favourability for the adsorption of chromium. Adsorbent depth was observed to have no significant influence on the removal of chromium from tannery wastewater. Pumice and charcoal were not significantly different in the removal of chromium, and had high desorption capabilities (>90.5%). This demonstrates their practical applicability in real life industrial waste treatment. However, banana peels applicability in the field is not viable due to the biodegradation of the peels with time, as well as the low desorption levels (29.6%). This study also recommends the evaluation of effective modification methods that would improve the adsorptive capacities of the three adsorbents.

CHAPTER ONE

INTRODUCTION

1.1 Background Information

Tanning activity is universally recognized as being a noxious industry which produces relatively high volumes of offensive wastes both liquid and solid (Winters, 1979). The estimated total wastewater discharge from tanneries is about 400 million m^3/year. About 90% of global leather production use conventional chrome-tanning processes (Rezic and Zeiner, 2008). Chrome tanning utilizes chromium in the form of basic chromium (III) sulphate for hide stabilization against microbial degradation and provision of versatility of the leather. In chrome tanning process about 60% - 80% of chromium reacts with the hides with about 20%- 40% of the chromium amount remaining in the solid and liquid wastes.

Chromium in the form of hexavalent chromium (Cr (VI)) from tannery wastewater is one of the major concerns of environmental contamination. This is due to discharge of tannery wastewater in large quantities (Lofrano *et al.,* 2008) and disposal of chromium contaminated sludge that is produced as a byproduct of tannery wastewater treatment (Chuan and Liu, 1996). Although Cr (III) is less toxic and more soluble than hexavalent chromium (Cr (VI)), Cr (III) can be oxidized to Cr (VI) under certain circumstances, resulting in more harm to environment and the public (Avudainayagam *et al*., 2003). Chromium in its hexavalent species have become a serious problem as a contaminant because it is a respiratory carcinogen and acutely toxic in high doses. According to WHO (2008), chromium is toxic, corrosive and irritant when the concentrations values exceed the threshold limit value of 0.05 mg/L in drinking water. In Kenya, the National and Environmental Management Authority (NEMA) has set the maximum allowable limit for total chromium at 2 mg/L for effluent discharge into the environment (NEMA, 2006).

Bulk of leather production is carried out in developing countries, particularly in Asia and Africa, partially because of the high labour intensity of the processes involved in the conversion of hides and skins into leather. However, the processes employed in the manufacture of leather in several developing countries remain traditional, often not optimized for chemical and water usage (Bosnic *et al*., 2003). Conventional methods of tannery wastewater treatment have been adopted to achieve the set national and international effluent discharge standards. These methods include ion exchange resins (Kocaoba and Akcin, 2002), reverse osmosis (Hafez *et al.,* 2002), electrolysis system (Vlyssides and Israilides, 1997) and chemical removal systems such as precipitation, coagulation and adsorption. However, for developing countries using these conventional methods is not only expensive but also uneconomical for small sized tanneries (USEPA, 1997). As a result, many low income countries only employ one unit treatment operation, which may be biological and physico-chemical processes or have no treatment at all. In Kenya for example, many treatment facilities for tannery wastewater either use physico-chemical methods (e.g. Kenya Industrial Research And Development Center- Leather Development Center (KIRDI-LDC,), stabilization ponds (e.g. BATA Shoe Company, Limuru) or no treatment at all (e.g. Bahati Hides and Skins Co Ltd, Machakos). Even with the conventional primary treatments, the wastewater requires further treatment to ensure chromium discharge standards are achieved before disposal to the natural environment. Thus, there is a need for the adoption of low cost, reliable, and easy-to-operate alternative secondary and tertiary treatment processes.

1.2 Problem Statement

Kenya’s leather industry has been identified as an important sector under the government’s economic recovery strategy, as well as the Strategic Recovery for Agriculture and the Vision 2030 plan (Kenyan Vision 2030, 2008). It is one of the key agricultural sub-sectors in the country and contributes an estimated 4% to agricultural GDP and 1.5% of overall GDP. The leather industry has a high potential for commodity development to address pertinent issues of socio economic importance, which impact on rural development, employment and wealth creation (Mwinyihija, 2010). Kenya's leather industry has shown an increase of tanneries from nine in year 2005 to fourteen in the year 2013, a sign that the industry is poised for growth. However, with tanneries being identified with the highest levels of water consumption and as one of the largest noxious industrial sectors, appropriate technologies are required for optimized water use and environmental quality control.

In Kenya, most of the tanneries adopt the chromium tanning process because of its high processing speed, low costs, light colour of leather and greater stability of the resulting leather. Wastewaters from these tanning industries are highly polluted with chromium, alkaline and organic substances. If this wastewater is discharged without adequate treatment it ends up in water resources causing pollution to adjacent rivers, streams as well as groundwater. This would result in serious environmental impacts including toxicity to microorganisms, plants, animals and humans (Hlihor and Gavrilescu, 2009; Xavier *et al.,* 2013). Although conventional and advanced methods of chromium removal like precipitation and coagulation, ion exchange, activated alumina and reverse osmosis are available (Rawat and Singh, 1992), these technologies are not practical for low income countries because of their high investment, operation and maintenance costs. The most common method of treatment used in Kenyan tanneries is the chemical precipitation method. Chemical precipitation is however expensive due to the high operating costs and also results in large amounts of sludge which creates a challenge in its disposal.

Adsorption technology is recognized as one of the most effective purification and separation technique used in industry especially in water and wastewater treatment (Al-Ashesh *et al*., 2000). Although the commercially available adsorbents are efficient in removal of heavy metals, they are high cost and some cannot be regenerated and recycled. A number of approaches have been recently studied for the development of cheaper and more effective adsorbents for metal removal. Many non-conventional low-cost adsorbents, including natural materials, biosorbents, and waste materials have been studied and proposed by several researchers (Bailey *et al.*, 1999; Dakiky *et al.*, 2002; Demirkas *et al.*, 2004; Kilonzo *et al.*, 2012). In Kenya however, little research has been done to explore different materials that may be employed in adsorption for the treatment of tannery wastewater.

1.3 Justification

With the high adoption of chrome tanning in Kenya, efficient methods of chromium removal from wastewater are important to attain environmental quality standards. Adsorption has been identified as one of the most promising technology for removal of dissolved heavy metal fractions from wastewater (Senthilkumar *et al.,* 2000). It has an edge over other conventional methods due to its sludge free clean operation. Although commercial adsorbents are available for use in adsorption, they are very expensive, resulting in various new low cost adsorbents being studied by researchers. Babel and Kurniawan (2003) reviewed the technical feasibility of various low-cost adsorbents for heavy metals removal from wastewater and concluded that the use of low-cost adsorbents may contribute to the sustainability of the surrounding environment and offer promising benefits for commercial purpose in the future.

Constructed wetland utilization in treatment of tannery wastewater has been observed to be an effective method. Kilonzo *et al.* (2012) using pumice as media for the constructed wetlands observed removal of chromium of up to 91%. Dotro *et al.* (2009) was able to show that about 96-98% of chromium removal was associated with media in a constructed wetland and recommended further investigation of the potential of adsorbents in chromium removal. Kilonzo *et al.* (2012) also recommended the undertaking of adsorptive studies of pumice to evaluate the exhaustion threshold during the adsorption process using models. Thus this study sought to explore the potential of using pumice, charcoal and banana peel as adsorption media for chromium ion removal from tannery wastewater. These materials, having been utilized in removal of other heavy metals from aqueous solution (Zahra *et al.,* 2013; Valdimir and Danish, 2002; Abdel-Salam *et al.,* 2011), were selected for this particular study to test them for the removal of chromium. Research studies on effect of pH, contact time, initial ion concentration and temperature on the adsorptive capacities of chromium using different adsorbent materials have also been conducted (Vinodhini and Nilanjana, 2009). Understanding how these parameters affect different adsorbents is key in evaluating the optimum adsorption conditions for the different adsorbents. This study hence sought to understand the effect of contact time, initial concentration and pH on adsorption of chromium by pumice, charcoal and banana peels using batch experiments. Apart from laboratory batch experiment, the study also evaluated chromium removal from tannery wastewater in a pilot study. The pilot study aimed at investigating the removal efficiencies in the field, and how contact time and media depth affects the adsorptive capacity of total chromium from tannery wastewater using the three adsorption materials in a constructed adsorbent bed set-up.

The results of this study provide valuable insight into the behavior and nature of chromium uptake by pumice, charcoal and banana peels, and hence help in development of techniques and methods of increasing adsorptive capacities of the chromium heavy metal. The knowledge acquired from this study also provides valuable information for tannery industries and researchers on potential use of low cost adsorbent technologies of treating the wastewater.

1.4 Objectives

Main objective:

To evaluate the potential and efficiency of natural adsorbent materials for chromium removal from aqueous solutions and tannery wastewater

Specific objectives:

1. To determine the physico-chemical characteristics of pumice, charcoal and banana peels as adsorbent materials.

2. To evaluate the effect of contact time, initial concentration and pH on removal of chromium by adsorption on pumice, charcoal and banana peels in batch studies using chromium stock solution.
3. To investigate the effectiveness of pumice, charcoal and banana peels for the adsorption of chromium from stock chromium solution using adsorption kinetic and isotherm models.
4. To determine the effect of time and adsorbent depth in chromium removal from tannery wastewater in a constructed wetland set-up.

1.5 Research Questions

1. What are the physico-chemical characteristic of the pumice, charcoal and banana peels that influence adsorption?
2. What are the characteristics of tannery wastewater?
3. How do contact time, initial chromium concentration and pH affect the adsorptive capacities of chromium ion in pumice, charcoal and banana peels?
4. Which adsorption kinetic and isotherm models best describe the adsorption of chromium by pumice, charcoal and banana peels?
5. At what bed depth in a constructed wetland will adsorbent media achieve the highest chromium removal?

1.6 Scope and Limitations of the Study

This scope of this study was to test the removal of chromium using pumice, charcoal and banana peels, which are cheap and readily available adsorbents. The study was both laboratory and field based. The laboratory batch studies were conducted using standard stock chromium solution, while the field studies were conducted using tannery wastewater. The laboratory batch studies aimed at finding out how a manipulation of contact time, initial concentration and pH, affect the adsorption capacities of pumice, charcoal and banana peels. Although temperature has been identified to have significant influence on adsorption (Gholipour *et al.*, 2011), temperature was not included among the study parameters for technical reasons. This hence means slight variations in adsorption in the study experiments were to be expected, since the study was being carried out at room temperatures. Adsorption kinetics and isotherm modeling was done using the data obtained from contact time in the batch study. Field studies were conducted to evaluate the adsorptive capacity of pumice, charcoal and banana peels as affected by time using tannery wastewater in bucket and constructed wetland setups. The field study also aimed at evaluating the effect of adsorption depth when pumice and charcoal were utilized in a constructed wetland. Banana peels were not evaluated on the effect of bed depth due to challenges experienced in obtaining significant amounts of the peels. Total chromium analyses in the wastewater were done using Atomic Absorption Spectrophotometer (AAS).

CHAPTER TWO
LITERATURE REVIEW

2.1 Kenya’s Leather Industry

Leather is one of the most widely traded commodities in the world. The leather and leather products industry plays a prominent role in the world’s economy, with an estimated global trade value of approximately US$100 billion per year (UNIDO, 2010). Africa earns only US$4 billion annually from the industry (Mwinyihija, 2012). In Kenya, the leather industry has been identified as an important sector under the government's economic recovery strategy, as well as the Strategic Recovery for Agriculture (SRA) and the Vision 2030 plan. Currently, the Leather industry sector’s contribution to Kenya’s economy currently stands at Kshs.10.6 billion, with almost all exports being wet blue. Apart from being a significant foreign exchange earner, leather industry has tremendous potential for employment generation.

Although Kenya’s leather sector has been in place since 1905, the policy and legal frameworks that have been evolving over time, have failed to revitalize the sector despite its untapped potential (Mwinyihija and Quiesenberry, 2013). The sub-sector has hardly changed over the years, and has seen little investment, despite the fact that it has the potential to become an important source of exports, particularly if it graduates from semi-processed hides to finished leather. In 2006, the government raised the export tax payable on the export of raw hides and skins to 20% and the following June doubled it to 40% (Otini, 2012). This new policy was observed to be the best after many years, improving the leather industry sector by encouraging the leather processing. The raised duty on raw hide has seen the tonnage of semi-processed hides and skins exports increased (Otini, 2012). Currently, tanneries in Kenya have installed capacities standing at 60% for wet-blue, crust leather at 25% and finished leather taking 15%. The Kenyan leather industry has also shown potential growth with the number of tanneries being observed to increase. Between years 2005-2013, the number of tanneries has grown from nine to fourteen (Mwinyihija, 2010).

2.2 Leather Tanning process

Leather tanning is the process of converting raw hides or skins into leather. It involves treating raw hide or skin to make it stronger, more flexible and resistant to decay. The tanning process involves strengthening the protein structure of the putrescible skin by creating a bond between the peptide chains (IARC, 1981). The whole tanning process uses acids, alkalis, salts, enzymes and tanning agents to dissolve the fats and non-fibrous proteins, as well as chemically bond the collagen fibers (Stellman, 1998).

The tanning process is usually accomplished in three distinct phases:

- The preparation of the hides in a beamhouse,
- The actual tanning to make leather in the tanyard and
- Finishing the leather in the post-tanning area.

In the beam house curing, fleshing, washing, soaking, dehairing, lime splitting, bating, pickling and degreasing operations are carried out. In the tanyard, the final leather is prepared by several processes. These include vegetable or chrome tanning, shaving and finishing. The finishing operation includes bleaching, stiffing, fat liquoring and coloring (IPPC, 2003).

Vegetable or mineral (chrome) tanning methods are the most widely used. Vegetable tanning uses tannin, which is a natural product found in wood, bark, leaves and fruits from oak, chestnut and hemlock trees. Vegetable tanned hide is flexible and is used for luggage, furniture leashes, belts, hats and harnesses. Mineral or chrome tanning usually uses chromium in the form of basic chromium sulfate (MoEF, 2010). Chrome tanning is the most common tanning type in the world. In the raw state chrome tanned skins are blue and therefore referred to as "wet blue". Chrome tanning is faster than vegetable tanning since it usually takes less than a day. Mineral or chrome tanning is carried out on skins needed for softer, stretchier leathers. This type of leather is found in purses, bags, briefcases, gloves, shoes, boots, pants, jackets, and sandals (CERC, 2009).

2.3 Waste Production in leather Industries

Tanneries are recognized as one of the largest sources of hazardous wastes and pollutant in the environment (Khwaja, 1998). Pollution from tanneries is from solid wastes, wastewater and air emissions produced during operation. Figure 2.1 summarises the different sources of pollutants from tanneries.

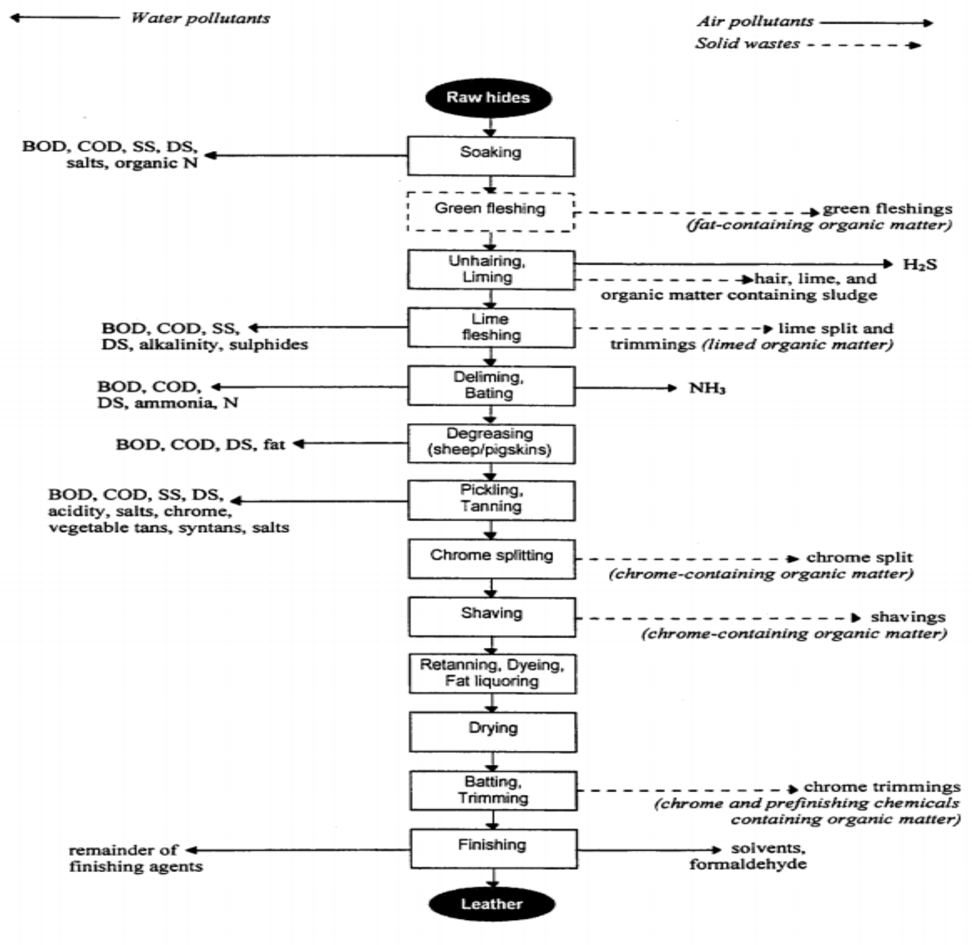


Figure 2-1: Sources and types of pollutants generated in leather processing using chrome tanning

(Source: UNEP, 1996)

2.3.1 Solid and Gaseous waste in Leather Industry

According to conservative estimates, about 600,000 tonnes per year of solid waste are generated worldwide by leather industry and approximately 40–50% of the hides are lost to shavings and trimmings (Sandeep *et al.*, 2010). Solids originate from all stages of leather making. Only 255 kg of finished leather is obtained for every 1000 kg wet salted hides processed, meaning that on average 25.5% of the raw material becomes finished leather (Aquim *et al.*, 2010).

Solid wastes produced from leather industries constitute mainly of trimmings of finished leather, shaving dusts, hair, fleshing, trimming of raw hides and skins, and remnants of paper bags. Wastewater treatment sludge also constitutes a large amount of solid waste. Nowadays, chrome tanning is the predominant method in leather manufacture, but results in a large amount of chrome-containing solid waste. A typical tannery generates huge amount of solid waste of about 56-60% fleshing; 35-4 % chrome shaving, chrome splits and buffing dust; 5-7% skin trimming and 2-5% hair (Kanagaraj *et al.,* 2006).
The high concentration of trivalent chromium along with organic/inorganic compounds in tanned solid waste such as buffing dust, shavings and sludge causes severe environmental contamination. Hence, tanneries require proper handling and disposal of the chromium containing solid wastes to prevent surface and ground water contamination in the case of land co-disposal and chronic air pollution during thermal incineration. Minimizing the quantity of waste generated and maximizing the return on by-products has been identified as two major approaches of expertly handling the vital waste streams of chrome split and shavings (MoEF, 2010; Paul *et al.,* 2013). Landfilling has been widely practiced for disposal of chrome-containing tannery wastes. This however is rather expensive because of fewer landfill sites and transportation cost increases and environmentally inappropriate way of handling a waste material that has the potentiality for utilization (Cabeza *et al.,* 1998). Landfills have been observed to have overall high pollution emissions and low energy recovery. Indiscriminate land filling leads to deterioration of water quality in neighboring areas of land fill sites due to

contamination by leachates from the landfill sites. Land fill gas, which is 50-60% methane, also contributes significantly to global warming. Hence, land fill disposal method has been discouraged by environmental experts and technological interventions such as monitoring techniques have been developed (Sekaran *et al.,* 2007). Apart from the use of landfills, other tannery solid waste disposal options have also been studied. These options include vermin composting, anaerobic digestion and thermal incineration. Air emissions from tannery occur generally in relatively small quantities. Traditionally tanneries have been associated with odour rather than any other air emissions, although the emissions of organic solvents are a major problem. Air emissions from tannery are particulate, organic solvents, hydrogen sulphide, ammonia and odour (IPPC, 2013). Emissions to air have effect beyond the tannery site, but also affect the workplace and possibly the health of the tannery workforce. The abatement of air pollutants can be done using filters and dust free chemicals to prevent particulate emissions. Scrubber units are utilized to capture organic solvents, while to prevent hydrogen sulphide generation, the liquors from the de-liming and pickling processes are treated by means of oxidising the sulphide with sodium metabisulphite or hydrogen peroxide (IPCC, 2013).

2.3.2 Wastewater in Leather Industry

The tanning process involves a significant consumption of water and generates a complex pollution consisting of a mixture of organic and inorganic substances that are rather difficult to treat. The wastewater discharge from world tanneries is about 600 million m^3 per year (Rajamani, 2010). On average 45-50 m^3 of wastewater is discharged from tanning industry per tonne of raw hide processed (Kanagraj *et al.,* 2006). Every step of the tanning process, with the exception of finishing operations, produces wastewater. The main discharge of waste water originates from wet processing stages in the beamhouse, the tanning process, and the post-tanning operations. It has been revealed that beamhouse processes and tanning processes contribute 80–90% of the total pollution load (COTANCE, 2002).

Tannery waste material varies considerably in volume and concentration due to continuous operation and intermittent discharge. The wastewater is made up of high concentration of salts, fats, protein, chromium, ammonia, polyphenolic compounds, dye and solvent chemicals. Wastewater from the tannery industry contains large quantities of biochemical oxygen demand (BOD), chemical oxygen demand (COD), sodium sulphide and suspended solids (SS) from the tannery process (Vijayaraghavan and Murthy, 1997; Szpyrkowicz *et al.,* 2001). Mean compositions of tannery wastewater are shown in Table 2-1. The tannery wastewater is characterized by substantial high organic matter content and high suspended solids content, resulting in a mean total COD concentration range of 18 to 27000 mg/l and a suspended solids concentration of between 925 to 36000 mg/l. Chloride ranged between 1500 to 28000 mg/l, which reflected high salinity levels of the tannery wastewaters.

Table 2-1: Mean Composition of tannery wastewater

Parameter	***Concentration***
BOD (mg/l)	210 – 4300
COD (mg/l)	180 - 27000
Total suspended solids (mg/l)	925 - 36000
Total chromium (mg/l)	3 - 350
Sulphides (mg/l)	1 - 500
Chlorides (mg/l)	1500 - 28000
Total phenolic compounds (mg/l)	0.4 - 100
Ammonium nitrogen (mg/l)	17 - 380
Kjehdahl nitrogen (mg/l)	90 - 630
Fats and oils (mg/l)	49 - 620
pH	1 - 13

Source: Vlyssides and Israilides, 1997

Tannery wastewaters are basic and their high organic content can cause considerable environmental pollution (Leta *et al*., 2004). It is also observed that tannery effluents are rich in nitrogen which makes possible discharge of tannery wastewaters into water bodies problematic, as they cause eutrophication. Tannery wastewaters also contain high sulphides and chromium levels ranging between 1 to 500 mg/l and 3-350 mg/l respectively. Sulphides cause an irritating, rotten-egg smell, and at concentrations above 0.01 mg/l, the toxicological exposure limits are exceeded. It can cause headaches, nausea and affect central nervous system even at low levels of exposure (ATSDR, 1999). Sulphides have also corrosive properties, which damage concrete walls of reactors, sewer systems and steel pipelines.

Conventional chrome tanning results in wastewater containing as high as 1500–3000 mg/l of chromium (Aravindhan *et al.,* 2004). For instance, in India alone about 2000–3000 tonnes of chromium escapes into the environment annually from tannery industries, with chromium concentrations ranging between 2000 and 5000 mg/l in the aqueous effluent compared to the recommended permissible discharge limits of 2 mg/l (Altaf *et al.,* 2008.)

Chromium (Cr^+) exists in two stable oxidation states, trivalent chromium Cr (III) and Hexavalent chromium Cr (VI). Chromium in its Cr (III) form is not considered a toxic element and is a required diet nutrient with recommended daily adult dosages ranging from 0.5 to 2 mg per day (ATSDR, 1998). Cr (VI) is a strong oxidizing agent that induces dermatitis and shows chronic toxic effects including carcinogenic property (Hlihor & Gavrilescu, 2009). Cr (VI) compounds are highly soluble, mobile, bioavailable and five hundred (500) times more toxic than Cr (III) species (Kowalski, 1994). Cr (III) salts are the most widely used chemicals for tanning processes, with basic chromium (III) sulphate being used in over 90% of the leather production world-wide (Rezic and Zeiner, 2008). Only a fraction of the chromium salts used in the tanning process react with the skins. In this process about 60% - 70% of chromium reacts with the hides, while about 30%- 40% of the chromium amount remains in the solid and liquid wastes. This results in Cr (III) accounting for the majority, approximately 75%, of the chromium in the wastewater stream (IFC, 2007).

Cr (III) presence, concentration and forms in the environment depend on different chemical and physical processes, such as hydrolysis, complexation, redox reactions and adsorption. Dominant forms of Cr (III) are the hydroxo complexes, $CrOH^{2+}_{(aq)}$, $Cr\ (OH)_2^{+}{}_{(aq)}$, and $Cr(OH)_{3(aq)}$, in the environment. These hydroxo complexes are dominating successively within pH 4-10 as shown in the pourbaix diagram (Figure 2-2).

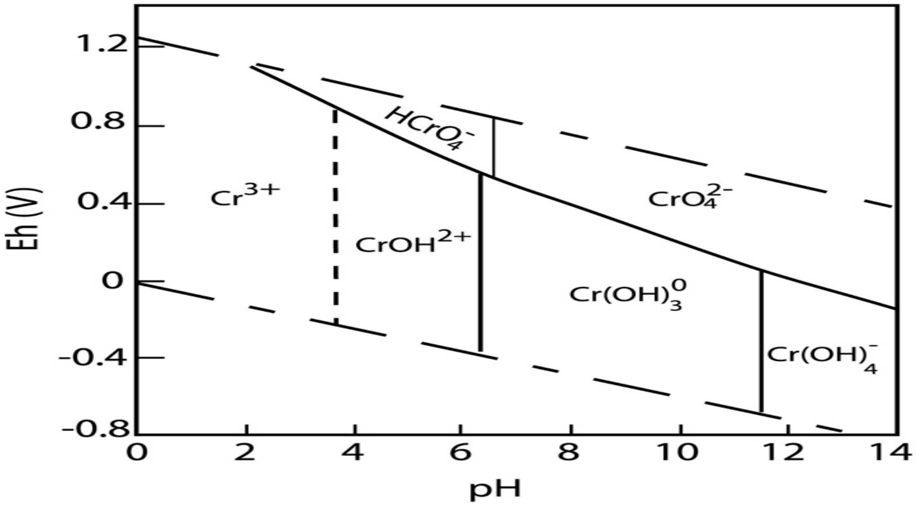


Figure 2-2: Pourbaix diagram highlighting the expected chromium compounds within the stability field of water. (Source: Rai *et al.*, 1989)

Cr (VI) can form several species, found as CrO_4^{2-}, $HCrO_4^-$ or $Cr_2O_7^{2-}$, depending on both pH of the medium and total Cr(VI) concentration. At pH less than 1 deprotonated forms of Cr (VI) is seen. Above pH 7 only CrO_4^{2-} ions exist in solution throughout the concentration range. In the pH between 1 and 6, $HCrO_4^-$ is predominant (Cotton and Wilkinson, 1980; Greenwood and Earnshaw, 1984; Nieboer and Jusys, 1988).

2.4 Tannery Wastewater Treatment Technologies

Tannery effluents contain several constituents that need to be treated to prevent environmental pollution. Wastewater treatment methods are broadly classified into physical, chemical and biological processes (Metcalf and Eddy, 2003). Various treatment method for tannery wastewater have been evaluated, including physico-chemical methods such as sedimentation (Song *et al.,* 2004); Electro floatation (Murugananthan *et al.,* 2004); Filtration (Tiglyene *et al.,* 2008) and Membrane filtration (Justina *et al.,* 2009); Precipitation (Esmaeili *et al.,* 2005); Coagulation (Sengil *et al.*, 2009); solvent extraction, Reverse osmosis, diffusion dialysis, Adsorption (Covarrubias *et al*., 2008); Ion exchange (Kabir and Ogbeide, 2008); and Biological methods (Munz *et al*., 2008; Zupancic and Jemec, 2010). The conventional and the most commonly used method for chromium removal is chemical precipitation (Young and Robert, 1986). In this method, the Cr (VI) is first reduced to Cr (III) which is then precipitated for removal. Substances used to promote the precipitation are: calcium hydroxide, sodium hydroxide, magnesium oxide or calcium magnesium carbonate. However, the high operating costs, requiring a large amount of chemicals and the production of a bulky sludge, which must be disposed, are the disadvantages of the traditional chemical treatment (Sahmoune *et al.,* 2009; Luptakova *et al.,* 2012.). On the other hand, advanced treatment techniques, such as reverse osmosis, ion exchange, membrane filtration, and electro dialysis are effective for removing chromium, but they are expensive and generate concentrated wastes that require subsequent treatment and disposal (Komori *et al*., 1990).

The choice of wastewater treatment process depends on several factors such as efficiency, cost, legistlation, environmental capability and the wastewater characteristics (Costa and Olivi, 2009). In most countries, tanneries have to carry out a pre-treatment of their wastewater for sulphide and chrome. Strict discharge limits must be met before effluents are discharged into the environment. WHO guidelines set chromium discharge limits at 0.05mg/L in drinking water (WHO, 2008), while in Kenya, the National

Environmental Management Authority (NEMA) set the maximum allowable limit of total chromium at 2.0 mg/l for effluents into the environment and public sewers (NEMA, 2006). Tanneries discharging directly to surface water,land and sewer lines have to meet additionally the requirements for COD, BOD, Cr, TSS and nitrogen so they have to treat the wastewater biologically, too (OECD, 2008).

2.5 Adsorption Technology in Wastewater Treatment

Adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. Adsorption is identified as one of the method for removal of dissolved heavy metal fractions from wastewater (Senthilkumar *et al.,* 2000). It produces a high quality product, and is a process, which is economically feasible and an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available (Choy *et al.,* 1999; Özacar and Şengil, 2003). Adsorption has an edge over other methods due to its sludge free clean operation. Although the commercially available adsorbents, including granular activated carbons and silica composites, are efficient in removal of heavy metals, they are however costly and some cannot be regenerated and recycled. As a result, attempts have been made to utilize low cost adsorbents to remove contaminants form wastewater. Babel and Kurniawan (2003) reviewed the technical feasibility of various low-cost adsorbents for heavy metals removal and concluded that the use of low-cost adsorbents may contribute to the sustainability of the receiving environment, and offer promising benefits for commercial purpose in the future. Babel and Kurniawan (2003) comparison of commercial activated carbon with low-cost adsorbents (Figure. 2-3) illustrated the adsorption capacity of some outstanding adsorbents and showed that some low-cost adsorbents such as chitosan, zeolites, waste slurry, and lignin have demonstrated outstanding removal capabilities for heavy metals, which is far better than commercial activated carbon.

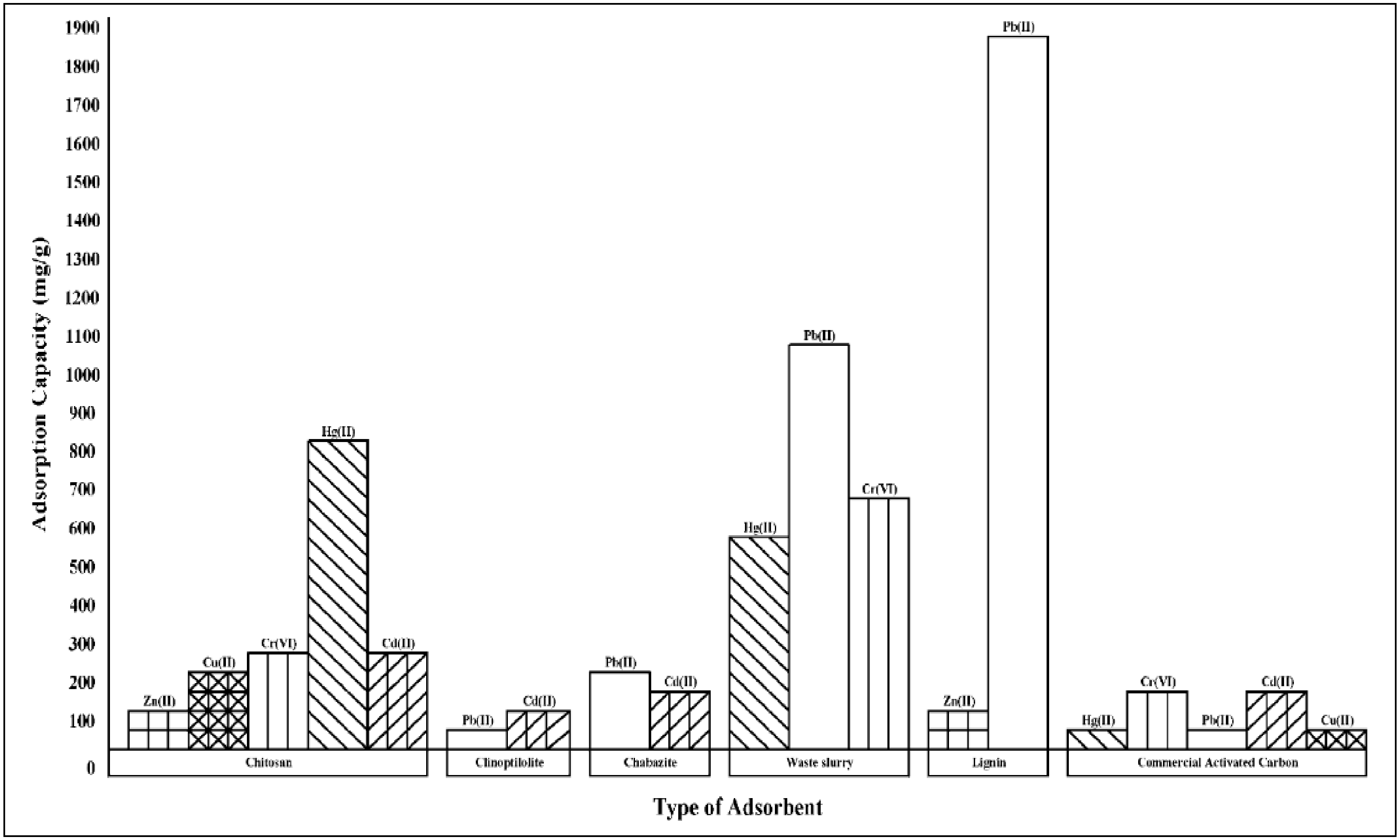


Figure 2-3: Summary of some adsorbents with high adsorption capacities (mg/g) (Source: Babel and Kurniawan, 2003)

The use of natural material and agricultural by-products has gained more attention over the years. Many natural materials such as zeolites, sapropels, peats clays and fly ash have sorption properties (Ayegi *et al.,* 2000; Kazansky and Pidko, 2005; Adeeva and Kovalenko, 2012; Zhao *et al.,* 2013). The cost of natural adsorbents is lower by tens of time in comparison to artificial ones and therefore they are often not recycled (Datsko *et al*., 2011).Various agricultural products and by-products for the removal of heavy metal from solution have been investigated by number of authors. These agricultural adsorbents include sawdust, wheat shells, soybean hulls, cottonseed hulls, rice straw, bagasse amongst others (Marshall and Champagne, 1995; Viondhini and Nilanjana, 2009). According to Kuniawan *et al. (*2006), activated carbons prepared from agriculture wastes have been found to be effective due to some specific characteristics with high Brunauer, Emmett and Teller (BET) surface area.

Removal of trivalent chromium and hexavalent chromium has been investigated on activated carbon (Valdimir and Danish, 2002; Ramos *et al.,* 1995), molecular sieves, polymeric adsorbents, and some other low-cost bio-sorbent materials including orange peels, bagasse, sawdust, coffee husks and maize husk (Chand *et al.,* 1994; Jogi, 2003; Vinodhini and Nilanjana, 2009). Compared to that of activated carbon, low cost adsorbent materials have demonstrated outstanding removal capabilities for chromium metal ions hence their viability for use in adsorption.

2.6 Pumice, Charcoal and Banana peels as Natural Adsorbents

Among the natural materials and agricultural by-products used in the removal of heavy metals from aqueous solutions are pumice, charcoal and banana peels. Previous studies conducted have also shown that these materials have effective adsorption for heavy metals including Co^{2+}, Ni^{2+} , Cu^{2+} and Zn^{2+} (Zahra *et al.,* 2013; Valdimir and Danish, 2002; Abdel-Salam *et al.,* 2011). Pumice is a volcanic stone which has a low weight, a porous structure of up to 85%, and can be found in many regions of the world (Derakhshan *et al.,* 2013). Because of its micro-porous structure, pumice has a high specific surface area, and the structure contains open channels that allow water and ions to travel into and out of the crystal structure. A scanning electron microscope (SEM) image of pumice is shown in Figure 2-4, which shows a coarse grain surface and a porous microstructure.

The use of pumice as an adsorbent to remove metals from wastewater treatment at low cost is a well-established process (Yavuz *et al.,* 2008). Recently, many researchers have used pumice for removal of heavy metals including cadmium, nickel and copper (Moraci and Calabro, 2010; Panuccio *et al.,* 2009). Zeolitized pumice was able to adsorb six metallic cations of Cu^{2+}, Ni^{2+} , Zn^{2+}, Cd^{2+} , Pb^{2+} and Cr^{3+} showing removals of metal ions between 100 and 500 mg/g in a short time and the concentration lowered under the legal limits (Catalfamo *et al.,* 2006).

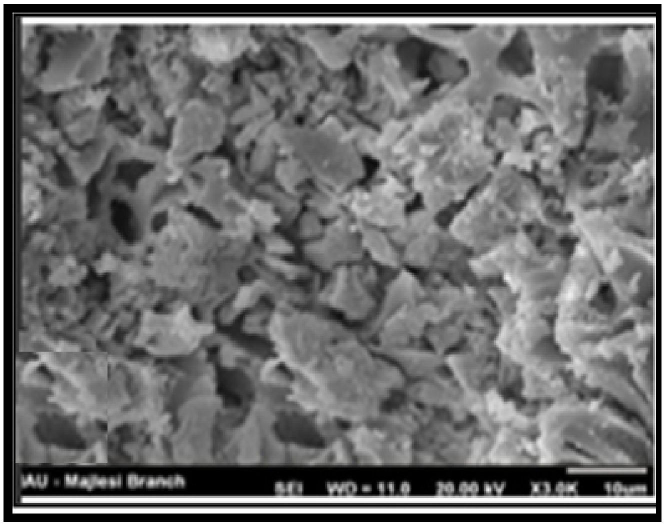
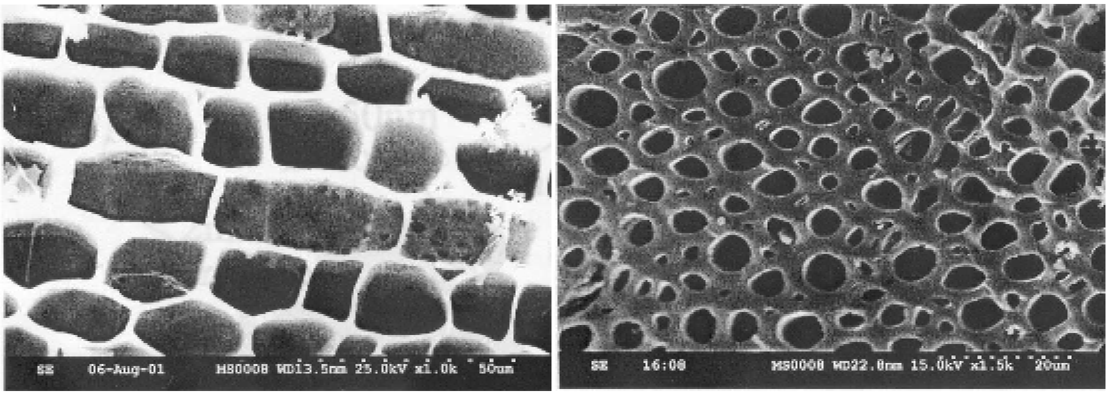


Figure 2-4: Scanning electron microscope (SEM) image for pumice showing the course grain surface (Sources: Asgari *et al*., 2012)

Charcoal, a form of amorphous carbon, is produced when wood, peat, bones, cellulose, or other carbonaceous substances are heated with little or no air present. Charcoal is a solid product of pyrolysis of biomass carried out at temperature above 300ºC. It is black in color and retains morphology of original feedstock. Charcoal is not a pure carbon or a single compound and has an elemental composition of C, H, O, N, S and ash. Analysis shows charcoals to contain quite large amounts of both oxygen and hydrogen (Janaína *et al.*, 2010), and it is probable that the initial char consists of small aggregates of graphitic crystals, having hydrogen, hydroxyl, or corresponding groups on practically all the crystal edges. This inhibition of crystal growth during formation and the random distribution of the crystals accounts for the extreme porosity of charcoal as compared with any other substances where conditions favour the formation of a more or less uniform lattice (King, 1935).The pore structure in wood derived carbons is a memory of the texture of the precursor wood and hence differ based on the type of wood/plant. A scanning electron microscope (SEM) image of charcoal is shown in Figure 2-5. The figure basically shows that wood carbons consist of slit-like voids and macropores.



a) b)

Figure 2-5: Scanning electron microscope (SEM) image of wood carbons showing the porous structures: (a) castor oil plant wood, (b) *Babool* wood
(Source; Manocha, 2003)

Charcoal is used in certain metallurgical processes and as a filter to remove organic compounds and other toxic chemicals from water and air (Baker, 1985). Various studies have been conducted on the use of charcoal and activated charcoal in heavy metal removal (Hamidi *et al*., 2005; Hasar and Cuci, 2000). Pehlivan and Kahraman (2011) carried out batch experiments on removal of chromium (IV) using Oak wood charcoal which showed maximum adsorption capacity of 30.10 mg/g at pH 2. The use of charcoal in removal of Ni, Cd, Pb and Zn heavy metals was also observed to have efficiencies of 80% (Hamidi *et al*., 2005).

The use of fruit peels in adsorption of heavy metals have also been investigated including banana and orange peels (Mandina *et al*., 2013, Pairat *et al*., 2008). The advantages of using fruit peels as the adsorption material is that they are readily available and less costly (Thirumavalavan *et al*., 2010). Research studies on banana peels shows potential to adsorb ions including lead, copper, zinc and nickel (Pairat *et al*., 2008; Annadurai *et al*., 2002; Muhammad *et al.,* 2011a). The binding of metal ions onto banana peels was found to be pH dependent and the binding efficiency was higher for acidic medium; with the optimal sorption occurring at pH 4. In a banana peel the biochemical components include cellulose, hemicelluloses, chlorophyll pigments, and pectin substances, which contain galacturonic acid, arabinose, galactose, and rhamnose. Galacturonic acids cause the pectin to strongly bind to the metal ions because of the carboxyl functions of the sugar. Cellulose also allows heavy metals to bind (Thirumavalavan *et al*., 2010). Banana peels also contain amine, hydroxyl and carboxylic groups. These structural groups are responsible for the peels' ability to bind the toxic metals and remove them from the water. The structure of banana peels is presented in the Scanning electron microscope (SEM) micrographs shown in Figure 2-6. The SEM scan shows an irregular and highly porous surface of banana peels. The many pores on its surface exhibit a micro-rough texture with crater-like pores, which promote the adsorption process.

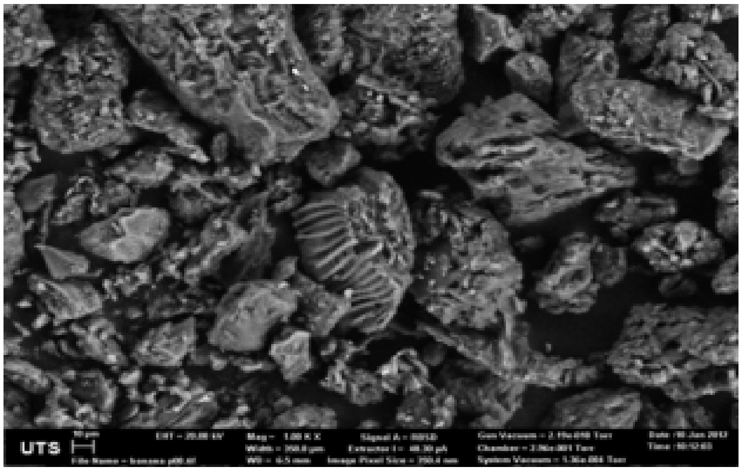


Figure 2-6: Scanning electron microscope (SEM) micrograph of banana peels
(Source: Hossain *et al.,* 2012)

Although pumice, charcoal and banana peels have been studied for the removal of heavy metal, none of these materials have been used to treat tannery wastewater in the tropics. The ability of these materials to adsorb heavy metals ions, their readily availability and low cost provides a solid research ground for the study in the removal of chromium ions especially for small scale tannery industries.

2.7 Adsorption Kinetics and Isotherm Models

Adsorption process can either be physisorption or chemisorptions or combination of both. Physisorption results in bonding by weak Van der Waals - type forces of attraction. There is no significant redistribution of electron density in either the molecule or at the substrate surface. Multilayered adsorption is possible and it is easily disrupted by increasing temperatures. However, chemisorption involves a chemical bond, involving substantial rearrangement of electron density, is formed between the adsorbate and substrate. The nature of this bond may lie anywhere between the extremes of virtually complete ionic or complete covalent character (Vashishtha *et al.*, 2008-2009). It is a process that is more akin to a chemical reaction and hence, only monolayer adsorption is possible. It takes place by chemical interaction between the surface of the solid and the molecules of the liquid (Poots *et al*., 1978). In order to understand the fate, dynamic interactions and distribution of the adsorbate species among liquid and solid phases, adsorption kinetics and isotherms are important.

2.7.1 Adsorption Kinetics

The kinetics of a given adsorbent is of great significance to evaluate the performance and gain insight into the reaction pathways and underlying mechanisms. Banat *et al.* (2003) and Hamadi *et al.* (2004) describe available adsorption kinetics and several mathematic models that have been developed to describe adsorption reaction and diffusion processes. According to Lazaridis and Asouhidou (2003) adsorption diffusion models are constructed on the basis of three consecutive steps:

1. external diffusion or film diffusion, which is diffusion across the liquid film surrounding the adsorbent particles
2. internal diffusion or intra-particle diffusion, which is diffusion in the liquid contained in the pores and/or along the pore walls; and
3. mass action, which is adsorption and desorption between the adsorbate and active sites.

However, adsorption reaction models originating from chemical reaction kinetics are based on the whole process of adsorption without considering the steps mentioned above (Lazaridis and Asouhidou, 2003)**.**

The order of adsorbate-adsorbent interactions has been described by using various kinetic models. These include pseudo-first-order model, pseudo-second-order model, Weber and Morris sorption kinetic model, Adam–Bohart–Thomas relation, first-order reversible reaction model, external mass transfer model, first-order equation of Bhattacharya and Venkobachar, Elovich's model and Ritchies's equation (Febrianto *et al.,* 2009). The pseudo-first and -second-order kinetic models are the most well-liked in the study of biosorption kinetics of heavy metals and in quantifying the extent of uptake in biosorption kinetics.

2.7.1.1 Pseudo-first-order rate equation

Lagergren presented a first-order rate equation to describe the kinetic process of liquid-solid phase adsorption. Lagergren's first order rate equation in recent years has been widely used to describe the adsorption of pollutants from wastewater in different fields (Safa and Bhatti, 2011; Ho and McKay, 1998). The pseudo- first- order equation by Lagergren is given by Equation 2.1.

$$\frac{dq}{dt} = K_1 \left(q_e \text{-} q_t\right) \tag{2.1}$$

With linear form of pseudo-first order Equation 2.1 is given by Equation 2.2.

$$\text{Log}\left(q_e \text{-} q_t\right) = \text{Log}\, q_e \text{-} \mathrm{K}_1 \frac{\mathrm{t}}{2.303} \tag{2.2}$$

Where,

q_e = adsorption capacities at equilibrium, mg/g

q_t = adsorption capacities at time t, mg/g

K_1 = pseudo-first-order rate constant for the kinetic model, min^{-1}

t = time, min.

A plot of $\text{Log}\left(q_e \text{-} q_t\right)$ versus t gives a straight line for first-order kinetics which allows computation of the adsorption rate constant, K_1 and equilibrium metal uptake q_e. The q_e value acquired by this method is contrasted with the experimental q_e value. Obtaining the linear regression correlation coefficient (R^2) from the fitting process, will show if the model justifies the experimental data.

2.7.1.2 Pseudo-second-order rate equation

Pseudo-second-order rate equation is used to distinguish kinetic equations based on adsorption capacity from solution concentration (Ho, 2006). This equation has been successfully applied to the adsorption of metal ions, dyes, herbicides, oils, and organic substances from aqueous solutions (Yan and Viraraghavan, 2003; Al-Asheh *et al.*, 2004;

Cheng *et al.*, 2008).The pseudo-second order equation based on equilibrium adsorption is expressed linearly as in Equation 2.3 (Ho and McKay, 1998)**:**

$$t/q_t = 1/K_2 q_e^2 + t/q_e \tag{2.3}$$

Regarding as the initial sorption rate as $q_t/t \rightarrow 0$ as h, hence:

$$h = K_2 q_e^2 \tag{2.4}$$

Equation (2.3) can be written as equation 2.5 (Di *et al.*, 2006):

$$t/q_t = 1/h + t/q_e \tag{2.5}$$

Where,
t = time, min
q_e = adsorption capacities at equilibrium, mg/g
q_t= adsorption capacities at time t , mg/g
K_2 = pseudo-second order rate constant, g/mg.min
h = initial adsorption rate, mg/g min.

If the pseudo second order kinetics equation is applicable, the plot of t/q_t against t gives a linear relationship, which allows computation of q_e, K_2 and h, without having to know any parameter beforehand. Obtaining the linear regression correlation coefficient values, R^2, from the data plot of t/q_t against t will show if the model can justify the experimental data.

2.7.2 Adsorption Isotherms Models

Adsorption isotherm models provide an understanding of the adsorption behaviour and are used to calculate the adsorption capacity for the adsorbent. They are mathematical models that describe the distribution of the adsorbate species between liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage, and possibility of interaction between the adsorbate species (Mohammed *et al.*, 2013). Several isotherm models are widely employed, of which the Langmuir and Freundlich equations are most widely used (Porter *et al.*, 1999; Srivastava *et al.*, 2006; Gueu *et al.*, 2007).

2.7.2.1 Langmuir Model

According to Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent, and once an adsorbate occupies a site, no further adsorption can take place at this site. The Langmuir model assumes that there is no interaction between the adsorbate molecules and the adsorption is localized in a monolayer (Xiong *et al.*, 2011). The model assumes maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The linear form of Langmuir model is given by Equation 2.6 (Ageyi *et al.*, 2000; Barkat *et al.*, 2009; Sharma & Bhattacharyya, 2004):

$$C_e/q_e = 1/K_L q_m + C_e/q_m \qquad (2.6)$$

Where,

q_m = Langmuir constant, mg/g related to the maximum monolayer adsorption capacity.

C_e = equilibrium solution concentration, mg/l

q_e= equilibrium amount of adsorbate, mg/g

K_L = Langmuir constant, l/mg related to the energy of adsorption.

A plot of C_e/q_e against C_e gives a straight line with slope of $1/q_m$ and intercept of $1/K_Lq_m$. Similarly, the values of maximum monolayer adsorption capacity (q_m (mg/g)) and adsorption energy (K_L (l/mg)) obtained from Langmuir model for the adsorbent are obtained. These values of maximum monolayer adsorption capacity (q_m (mg/g)) and adsorption energy (K_L (l/mg)) represent the favorable sorption of the metals. High values of correlation coefficient (R^2) indicate that the adsorption pattern for the metals of biomass used followed Langmuir isotherm.

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L (known as the separation factor). The R_L parameter is an essential characteristic of Langmuir isotherm model, which is considered as a more reliable indicator of adsorptions. The parameter is calculated using the Equation 2.7:

$$R_L = {}^{1}/{}_{1+K_L C_i} \tag{2.7}$$

Where,

R_L = Separation factor

K_L= Langmuir constant, L/mg

C_i = initial concentration of metal ions, mg/L.

The parameter R_L indicates the shape and type of the isotherm as shown in Table 2-2:

Table 2-2: Separation factor (R_L) value indicating the type of isotherm

R_L Value	**Type of Isotherm**
$R_L = 0$	Irreversible
$0 < R_L < 1$	Favorable
$R_L = 1$	Linear
$R_L > 1$	Unfavorable

(Source: Poots *et al.,* 1978; Hall *et al.*, 1966)

2.7.2.2 Freundlich Isotherm

Freundlich isotherm is an empirical model that is based on adsorption on heterogonous surface (Liang *et al.,* 2006). The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. It is given by Equation 2.8 (Liang *et al.,* 2006; Oguz, 2005):

The Freundlich Equation has the linear form:

$$q_e = K_f C_e^{1/n} \tag{2.8}$$

This can be presented in logarithmic form as Equation 2.9:

$$\log q_e = \log K_f + {}^{1}/_{n} \log C_e \tag{2.9}$$

Where,

q_e = metal ion uptake, mg/g

C_e = equilibrium concentration of the solution, mg/L

K_f and n = Freundlich constant, representing adsorption capacity

n = Freundlich constant, representing adsorption intensity

By plotting, log q_e against log C_e, the adsorption capacity, K_f (mg/g) and the adsorption intensity (n) can be estimated from the intercept and slope of the Freundlich isotherm, respectively. High values of correlation coefficient (R^2) also indicate that the adsorption pattern for the metals by the biomass used followed Freundlich isotherm.

The *n* value of Freundlich equation could give an indication on the favorability of sorption. High value of *n* indicates a strong bond between the adsorbent and the adsorbate (Yakubu *et al.,* 2008). The *n* value indicates the degree of nonlinearity between solution concentration and adsorption as shown in Table 2-3 (Ahlam *et al.,* 2013):

Table 2-3: *n* value based on isotherm

***n* value**	**Type of isotherm**
$n < 1$	Chemical Process
$n = 1$	Linear
$n > 1$	Physical process

Different studies provide different ranges of n value favorability. Ho and McKay (1998), Huang *et al.* (2010) and Poots *et al.* (1978), describes that $n > 1$, indicates a favorable sorption process while Hamdaoui *et al.* (2008), generally states that values of n in the range of 2 to 10 is good, 1 to 2 as moderately difficult and less than 1 as poor sorption characteristic.

CHAPTER THREE

RESEARCH METHODOLOGY

This chapter describes the laboratory batch experiments using Potassium dichromate stock solution and field pilot-plant experiments for the removal of chromium ions from tannery wastewater using pumice, charcoal and banana peels as adsorbent materials. The operational procedures, as well as the analytical methods used in the study are explained. Two different experiments were conducted during the field study; one with the use of buckets from 12th October to 9th November 2013 and the second with an existing constructed wetland from 14thDec 2013 to 15thFebruary 2014.

3.1 Description of Study Site

The field pilot plant experiments were conducted at the Leather Industries of Kenya (LIK) located about 1 km from Thika town, Kenya, along the Thika-Garissa road (Figure 3-1). Geographical Coordinates according to Google earth, of the study area are 1°3'29.045"S, 37°7'46.675"E (S01.05719, E 037.12897). The area has a flat to gently undulating volcanic upland with an altitude of about 1465 m above mean sea level. The annual mean minimum and maximum temperature are 15^0C and 28^0C respectively. The Leather Industries of Kenya factory was incepted in 1985 by a consortium of national and international development institutions. The tannery utilizes the chrome tanning process and mostly produces wet blue hides/skins, crust and finished leather.

Figure 3-1: Aerial Photograph showing the study area at Leather Industries of Kenya.

The tannery produces both wastewater and solid wastes. Studies conducted by Kilonzo *et al*. (2012) at the tannery indicate a wastewater average flow rate of 3.5 l/s and approximately 100m^3/day in an 8 hour shift. Flow generation varies across the days and over a single day depending on the "floor activities". Wastewater quality from the factory is observed to contain about 23 mg/l of chromium during tanning.

The factory utilizes an activated sludge reactor, chemical precipitation, clarifiers and ponds for treatment of wastewater. Wastewater treatment plant's final effluent levels before release to the environment are within the regulatory requirement of 2.0 mg/l of total chromium Kilonzo *et al*., 2012.

3.2 Grading of pumice, charcoal and banana peel study aggregates

Pumice used in the study was obtained from Nakuru, Kenya, while charcoal, made from acacia tree (*Acacia tortilis*), was obtained locally from Machakos, Kenya. The pumice obtained was of medium size and was graded whole for the field study experiment. Charcoal was graded whole for use in the constructed subsurface adsorbent beds. Another sample of charcoal was crushed and graded to approximate size of pumice for use in bucket field experiment. Banana peels (*Musa sapientum* biomass) were obtained from mature bananas with yellow peel from a local market. The peels were dried in the sun for fifteen days. After sun drying, the banana peels were then washed with tap water to remove any dust or foreign particles attached and sun dried. The peels were then cut into small pieces of 1-2 cm for bucket field experiments.

The pumice, charcoal and banana peels utilized in the bucket and constructed beds field studies were graded using the standard sieve analysis method. Sieves used had openings of 0.074 mm, 0.105 mm, 0.25 mm, 0.42 mm, 0.84 mm, 2 mm, 4.76 mm, 9.52 mm and 19.7 mm. The percentage of aggregate passing through each sieve was found out by calculating the percent of samples retained in each sieve, using Equation 3.1.

$$\%\ \mathrm{Re}\,tained = \frac{W_{Sieve}}{W_{Total}} x100\,\% \tag{3.1}$$

Where, W_{Sieve} was the weight of aggregate retained in the sieve and W_{Total} was the total weight of the aggregate (Mamlouk and Zaniewski, 1999). The results of sieve analysis were presented in particle-size distribution curves and effective size, uniformity coefficient, and coefficient of gradation of the three adsorbents materials were determined. The diameter in the particle-size distribution curve corresponding to 10% finer is defined as the effective size, or D_{10} (Das, 2012) Aggregates may be either poorly graded (Uniformly graded) or well graded depending on the value of coefficient of gradation and uniformity coefficient. The uniformity coefficient (C_u) is given by Equation 3.2:

$$C_U = \frac{D_{60}}{D_{10}} \tag{3.2}$$

Where, D_{60} is the diameter corresponding to 60% finer in the particle-size distribution. Its value should be more than 4 for well graded aggregates.

The coefficient of gradation (C_c) may be estimated by the Equation 3.3 as:

$$C_C = \frac{D_{30}^2}{D_{10} * D_{60}} \tag{3.3}$$

Where, D_{30} is the diameter corresponding to 30% finer in the particle-size distribution. Coefficient of gradation (C_c) should lie between 1 and 3 for well grade aggregates.

An estimation of permeability was done from the effective size using Hazen's approximation. Hazen's approximation is an empirical relation between hydraulic conductivity with grain size and the permeability and is given by the Equation 3.4.

$$k = C*D_{10}^2 \tag{3.4}$$

Where, k is the hydraulic conductivity (cm/s), D_{10} is the effective size (cm/s) and C is the Hazen's coefficient based on grain size, usually ranging between 0.8 and 1.2 (a value of 1.0 is commonly used).

3.3 Adsorbent Physico- Chemical Analysis

Adsorbent physical and chemical characterization was conducted to understand the physical and chemical compositions of the adsorbent materials. Physical analyses of the different adsorbents were done to determine the amounts of moisture content, bulk density, volatiles, ash and pore volume that were in the samples. These physical properties were determined using the analytical methods described below. Ultimate analysis was done to determine the elemental composition of the adsorbents. This chemical analysis of the adsorbents was carried out at the Ministry of Mines and Geology Laboratory in Nairobi, Kenya.

Bulk density

Bulk density (BD) of a medium is defined as its dry mass per unit of volume and is measured in g cm^{-3}. The procedure involved by pouring the ground sample into a dry graduated cylinder of 10ml. The sample was tapped several times until constant volume and then weighted. The bulk density was determined using Equation 3.5 and expressed in g cm^{-3}.

$$\text{Bulk density (BD)}=\frac{\text{Weight of sample}}{\text{volume of cylinder}} \tag{3.5}$$

Moisture content

The percentage moisture content (MC) was found by weighing 2 g of the ground sample into a crucible, and the weight of the sample plus crucible was noted. The samples were then oven dried at 105°C for 24 hours and weighed after cooling in a dessicator. This was repeated twice for all samples to obtain average moisture content value. The moisture content was then calculated using Equation 3.6.

$$Moisture, \% = \frac{A-B}{A-W_1} \times 100 \tag{3.6}$$

Where, W_1 is the weight of crucible, A is the Weight of the Crucible +dry sample and B is the weight of the crucible+ oven dried sample.

Volatile matter

The percentage volatile matter (VM) was determined by pulverizing 2 g of the ground sample in a crucible and placing it in an oven until a constant weight was obtained. The samples were then kept in a furnace at a temperature of 550°C for 10 min and weighed after cooling in a dessicator. The volatile matter was then calculated using Equation 3.7:

$$Volatile\ matter, \% = \frac{B-C}{B} \times 100 \tag{3.7}$$

Where B is the weight of the oven-dried sample and *C* is the weight of the sample after 10 min in the furnace at 550°C.

Ash Content

2g of the ground sample was placed in a crucible and the weight of the crucible plus the dry sample was noted. The sample was then placed in a furnace at temperatures of 750 ^{o}C for 6 hours. The crucible and its contents were then cooled in a dessicator and reweighed. This was repeated twice to obtain an average ash content value. The ash content was determined using the Equation 3.8.

$$Ash, \% = \frac{A-B}{W_0} \times 100 \tag{3.8}$$

Where, W_o is the original weight of the dry sample, A is the weight of the crucible+ dry sample and B is the weight of the crucible+ heated sample

Pore volume

2g of dry sample was weighed into a beaker and the weight of sample plus the beaker was noted. 50ml of distilled water was added into the beaker containing the sample and the mixture boiled for 15 minutes to displace the air in the pores. The sample was then drained, dried superficially and weighed. The procedure was repeated twice. Pore volume was calculated according to Equation 3.9.

$$Pore\ Volume = \frac{W_F - W_1}{W_1} \times density\ of\ water \tag{3.9}$$

Where, W_1 is the Initial weight of samples + beaker and W_F is the final weight of the sample. The density of water is taken to be equal to 1g/cm^3

3.4 Tannery Wastewater Characterization

The raw wastewater sample was obtained from LIK. The samples were collected from the chrome liquor stream after the precipitation process. pH and temperature were measured using the standard pH electrode meter (Hanna HI 98129 pH EC/TDS Waterproof Combo Tester/Meter, Hanna Instruments Inc., Woonsocket, Rhode Island, USA).Total dissolved solids (TDS), Total suspended solids (TSS), BOD, COD, electrical conductivity (EC), chromium and sulphides and chlorides were estimated using the standard methods for the Examination of Water and Wastewater (APHA, 1998).

3.5 Batch Experiments

This section explains the methodology used in batch experiments on the adsorption of chromium by pumice, charcoal and banana peels from standard chromium stock solution. The experiments were conducted at room temperature at the Jomo Kenyatta University of Agriculture and Technology (JKUAT) Food Science laboratory.

3.5.1 Preparation of Stock solution

Chromium (IV) stock solution was prepared by dissolving Potassium Dichromate (K_2CrO_4) in distilled water (Figure 3-2). Chromium samples at concentrations of 5 mg/l, 10 mg/l, 20 mg/l, 30mg/l, 40 mg/l and 50 mg/l were prepared by appropriate dilution of the stock solution with distilled water.

Figure 3-2: Stock chromium (IV) solution prepared from Potassium Dichromate

3.5.2 Preparation of sorbents

The pumice and charcoal were rinsed with distilled water several times until the wash water turbidity was lower than 0.1 NTU and then dried in an oven at 100°C for 24 hours. Finally the raw sample of pumice and charcoal were crushed and then sieved to particle size fraction of 20 mesh size (0.841mm) as shown in Figure 3-3.The banana peel was dried in the sun for fifteen days. After sun drying, the banana peels were then washed with tap water to remove any dust or foreign particles attached and thoroughly rinsed with distilled water. The washed peels were then cut into small pieces (1-2 cm) and then oven dried at 100^{o}C for 24h. The biomass was then crushed and sieved to particle size fraction of 20 mesh size (0.841mm) as shown in Figure 3-3.

Oven dried Pumice, Charcoal and Banana peels.

Crushed and sieved Banana peels

Crushed and sieved Pumice

Crushed and sieved Charcoal

Figure 3-3: Preparation of Pumice, Charcoal and Banana peels sorbents for batch experiments.

3.5.3 Batch Adsorption Experiments

Batch experiments were conducted in the laboratory by contacting the chromium solution with pumice, charcoal and banana peel adsorbents. The effect of initial concentration of Cr^+, contact time, and initial pH were investigated by varying any one of the parameters and keeping the other parameters constant. The experiments were conducted in triplicates and total chromium (VI) was determined using the flame atomic absorption spectrophotometer (Machine-Buck Model 210VGP AAS with a 220-GF graphite furnace, East Norwalk, USA). The total chromium determination was done using an air Acetylene/nitrous oxide burner at wavelengths of 357.9 nm

Effect of contact time on the adsorption of chromium ions

To investigate the effect of contact time on the adsorption of chromium ions, 3g of finely ground pumice was weighed and put in a 600 ml beaker. 300 ml chromium stock solution with concentrations of 20 mg/l was added to the beaker and the mixture stirred for duration of 3 hours. This was repeated for 50 mg/l concentrated stock solution. pH of the stock solution was maintained between 4.0 and 5.0 by adding 0.1N sodium hydroxide (NaOH) or 0.1N nitric acid (HNO_3) before each experiment. The solution was then stirred at a speed of 150rpm at room temperature (Figure 3-4a). 20 ml samples of the solution were taken at 1, 5, 10, 15, 20, 30, 60, 90 and 180 minutes contact time. The samples were then filtered using a Whatman filter paper No.42 (Figure 3-4b) and the filtrate was analyzed to evaluate the amount of chromium in solution. The above procedure was repeated for each of the other adsorbents (charcoal and banana peels).


a) b)

Figure 3-4: a) Sample stirring at speed of 150 rpm at room temperature and (b) filtration of the samples in the laboratory

Effect of initial concentration on the adsorption of chromium ions

To investigate the effect of initial chromium concentration on the adsorption of chromium ions, 1000 mg of finely ground pumice was weighed and put in a 250 ml beaker. 100 ml chromium stock solution with concentrations of 5 mg/l was added to the beaker and the mixture stirred for duration of 3 hours with a constant agitation speed of 150 rpm at room temperature. This was repeated using 10, 20, 30, 40 and 50 mg/l concentrated stock solution. A pH value of between 4.0 and 5.0 were maintained throughout the experiment by adding 0.1 N sodium hydroxide (NaOH) or 0.1 N nitric acid (HNO_3) solutions before each experiment. The solutions were then filtered using a Whatman filter paper No. 42 and the filtrate analyzed to determine the amount of chromium still in solution, from which the adsorbed chromium was calculated. The above procedure was repeated for each of the other adsorbents (charcoal and banana peels).

Effect of pH on the adsorption of chromium ions

To investigate the effect of pH on the adsorption of chromium ions, 1000 mg of finely ground pumice was weighed and put in a 250 ml beaker. 100 ml chromium stock solution with concentrations of 50 mg/l was added to the beaker and the mixture stirred for duration of 3 hours with a constant agitation speed of 150 rpm at room temperature. The pH range of 3.0-10.0 was used and chromium solution pH was adjusted by adding 0.1N sodium hydroxide (NaOH) or 0.1N nitric acid (HNO_3) before each experiment. The solution was then filtered using a Whatman filter paper No. 42(25 um) and the filtrate analyzed to evaluate the amount of chromium adsorbed

Desorption of chromium ions

Desorption was carried out by agitation of 500 mg of the chromium containing adsorbents with 50ml 2M HNO_3 solution at room temperature and agitated at 150 rpm for 3 hours. The mixture was then filtered using a Whatman filter paper No.42(25 um) and the filtrate analyzed using AAS to evaluate the amount of total chromium removed from the adsorbent.

3.5.4 Batch Studies Analysis

The filtrates from the batch experiments were analyzed for the remaining Cr ions concentration using the Atomic Absorption Spectrometry (AAS) method. For the analysis of Cr ions, standard calibration solutions using potassium dichromate were prepared for the calibration of the AAS machine. The amount of Cr^+ adsorbed in $mg\cdot g^{-1}$ at time *t* (min) was computed based on the mass balance for the adsorbent in the system using Equation 3.10.

$$q_t = V\,(C_o - C_t)/S \qquad (3.10)$$

Where:

q_t = Metal ion uptake capacity (mgg^{-1})

C_o = initial concentration of metal in solution, before sorption analysis (mgL^{-1}),

C_t= final concentration of metal in solution at a given time *t* (mgL^{-1})

V = volume of the solutions in (L).
S = dry weight of adsorbent (g),

The difference between the initial metal ion concentration and final metal ion concentration was evaluated to determine the concentration of metal ions bound to the adsorbent. The percent removal of chromium ion by adsorbent material was calculated using Equation 3.11:

$$\% \text{ R} = (C_0 - C_e)*100/C_0 \qquad (3.11)$$

Where;
%R = chromium ion removal
C_0 = initial chromium ion concentration, chromium in solution used (mgL^{-1});
C_e= chromium ion concentration in solution at given time (mgL^{-1})

3.5.5 Adsorption Models

In order to determine the adsorption kinetics of chromium ions, the pseudo-first and pseudo second order kinetic models were applied to data collected from the effect of time on adsorption (Section 3.5.3). A straight line of ln ($q_e - q_t$) versus time (t) indicate the application of the first-order kinetic model. The applicability of the second-order kinetic is indicated by a linear relationship of the plot of t/q_t against time (t). To successfully represent the equilibrium adsorptive behavior, the most widely accepted adsorption models for single solute systems Langmuir and Freundlich models (Porter et al., 1999) were used to fit the experimental data. Parameters of the isotherm constants (q_m, n, and K) were determined by regression of the experimental data. A measure of the goodness-of-fit, R^2, of experimental data on the isotherm's models was evaluated and the best isotherm equation identified.

3.6 Field Experiments

3.6.1 Set-up of treatment facility

a) Description of the constructed beds

The constructed adsorbent bed facility as described by Kilonzo *et al.* (2012) was utilized for wastewater treatment in the pilot study. The constructed beds were designed with considerations for possible manipulation in research of the; aspect ratio, media selection, Macrophytes selection, slope and orientation. The existing physical layout hence provides a suitable set-up for effect of depth studies, using sub-surface vertical flow systems and a randomized design for the adsorbents. The treatment facility consisted of a pumping unit, treatment cells; two wastewater holding tanks each of 5000 litres, one 500 litre holding tank and a drainage system. Pumping of wastewater was done from the wastewater flow channel after precipitation. The chrome wastewater was pumped to the 5000 litres elevated tanks, which were used to hold the water before release to the treatment cells. They acted as sedimentation basins for the wastewater and ensured gravity aided flow of wastewater to the treatment cells.

The pilot study treatment facility consisted of seven treatment cells of 1.5m by 3m as shown in Figure 3-5. Each of the cells was 1m deep and consisted of three outlet/sampling points along its depth. Sampling point 1 (SP1) and 2 (SP2) were located at 0.9 m and 0.3 m from the bottom of the treatment cells respectively, while sampling point 3 (SP3) was located exactly at the bottom of the cell. Pictorial setups of the treatment facility showing the elevated water tanks, drainage pipe, sampling points and media filled adsorbent beds are shown in Figure 3-6 and 3-7. Three of the cells were filled with pumice media which was to act as the absorbent material, while the other three cells were filled with charcoal as the adsorbent. The remaining cell was not filled with any media to act as control. Both the charcoal and the pumice in the cells were filled to a level just above the upper outlet which is about 0.1m from the top of the treatment cells (Figure 3-7). Banana peels were not utilized in this set-up due to lack of availability in large quantities.

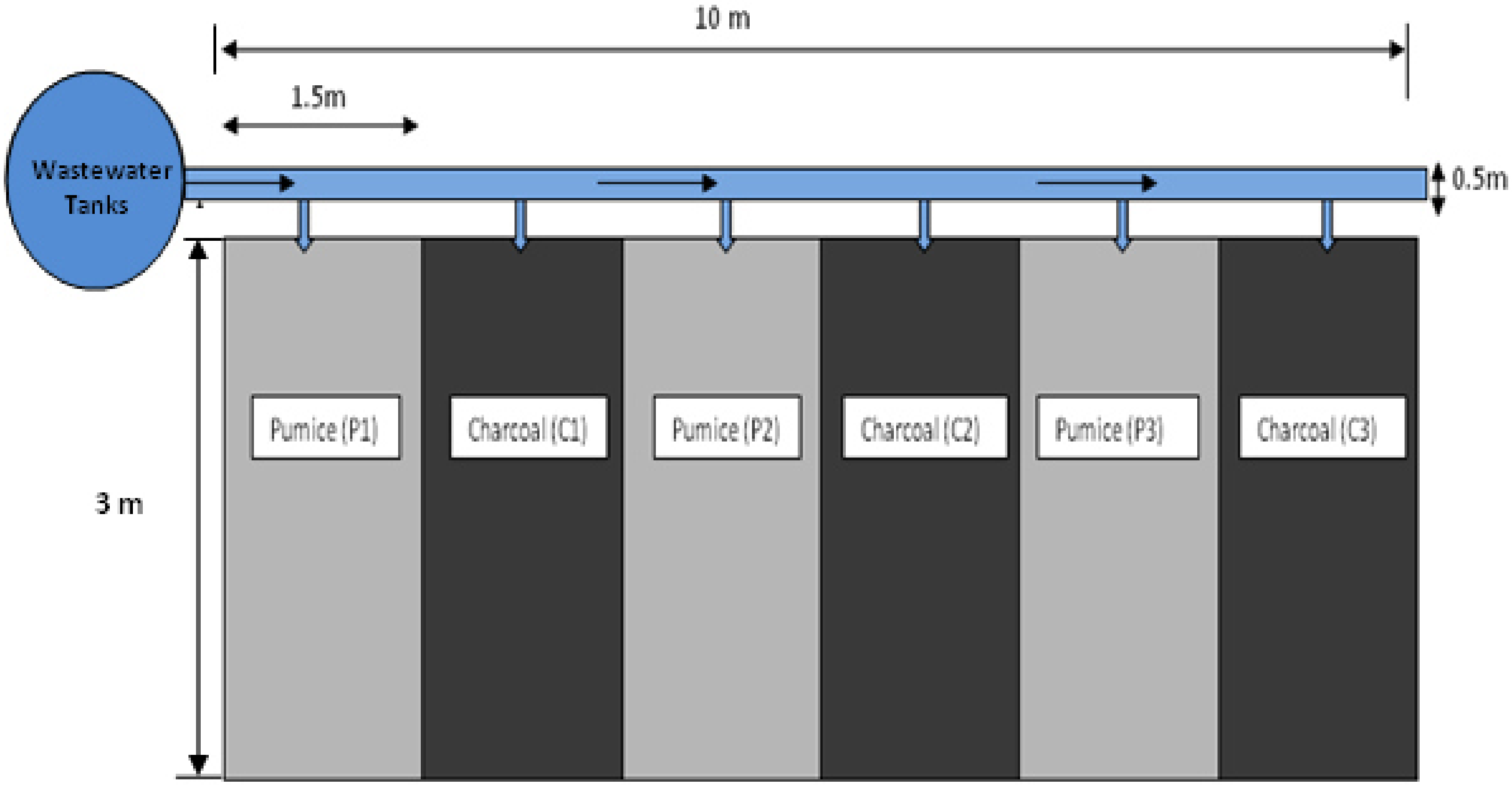


Figure 3-5: Layout of Constructed Adsorbent Cells

Figure 3-6: Set up of the constructed adsorbent bed system showing the elevated tanks, inlet and drainage pipes and the three sampling points along the depth of the adsorbent cells**.**

Figure 3-7: Constructed adsorbent beds filled with pumice and charcoal

b) Bucket Experiments

To enable the evaluation and analysis of banana peels and a comparison of banana peels with pumice and charcoal, ten 20- litre buckets were utilized. The buckets were perforated at the top and bottom which acted as the inlet and outlet points for the treated wastewater. Three buckets were filled with pumice, three were filled with charcoal, three with banana peels and one bucket without any adsorbent acted as a control.

3.6.2 Operation of treatment plant

Fresh water was first introduced into the treatment cells and buckets to flush out sediments and other impurities from the media. Raw tannery wastewater was then pumped into the two elevated tanks each having a capacity of 5000 litres. The purpose of the two tanks was to allow for sedimentation and ensure gravity-aided flow of water into a 500 litres equalization tank. The wastewater was then directed into the adsorbent cells and buckets until the adsorbent media in the cells was all flooded. A schematic flow diagram of the treatment facility is shown in Figure 3-8.

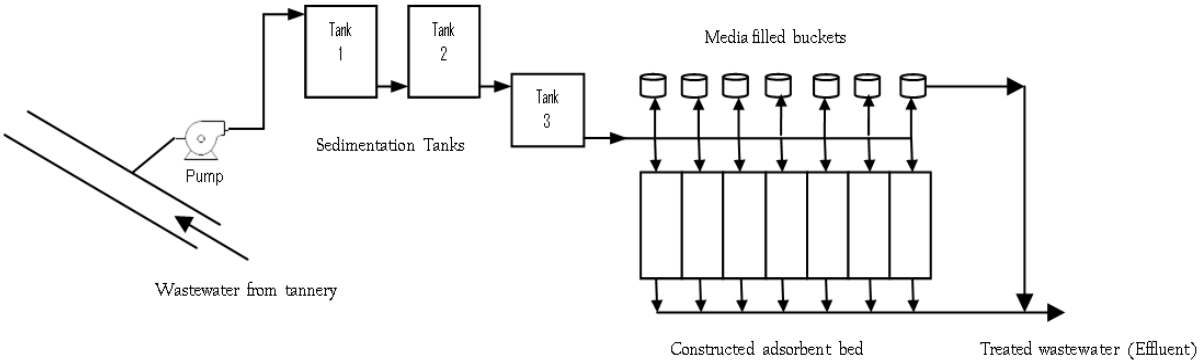


Figure 3-8: Physical Layout of the treatment facility used in the field study

3.6.3 Data collection/Sampling

An initial sample of the raw wastewater was obtained from the 500 litre tank (Tank 3-Figure 3-8) for analysis before treatment. The raw wastewater was then introduced into the treatment adsorbent beds and buckets, and retained for a duration of seven (7) days before the final sampling was done. After seven days, samples of the treated wastewater in the cells were collected from the three outlets of each treatment cells into 100ml plastic bottles. The bucket samples were collected from the outlet at the bottom of the buckets into 100ml plastic bottles for laboratory analysis. Figure 3-9 shows the three sampling points and the filled sampling bottles. After sampling, the constructed cells and buckets were then completely drained.

Figure 3-9: Photo showing the inlet pipe of the treatment cells, the sampling points and drainage pipes.

3.7 Data Analysis

Collected wastewater samples were analyzed in the laboratory using the direct determination method (U. S. EPA, 1983). For the analysis of Cr ions, standard calibration solutions using potassium dichromate ($K_2Cr_2O_7$) were prepared for the calibration of the AAS machine. The proper hollow cathode lamp for the analysis was selected and the lamp allowed to warm-up for about 15 minutes. The AAS machine was then aligned and the monochromator positioned at the correct wavelength of 375.9 nm and the proper monochromator slit width selected. The hollow cathode current was adjusted to 10 ma according to the manufacturer's recommendations. The air acetylene flame was then lit and the flow of fuel and oxidant regulated. The set of standards prepared were then run under the AAS machine to determine the Cr ion concentration. A calibration curve was then constructed by plotting the concentrations of the standards against the absorbance. The chromium solution samples from the batch experiments and the tannery wastewater were then aspirated into the flame and their respective absorbance was recorded. Standards were run each time a series of samples was run.

The results of chromium levels obtained from the AAS analysis were evaluated to determine the percentage chromium uptake. Modelling of kinetics and isotherm models were also done using the results obtained from the batch experiment, with some analysis being done using Minitab 7 statistical tool (Ryan *et al.*, 2012). The results were presented in graphs and tables.

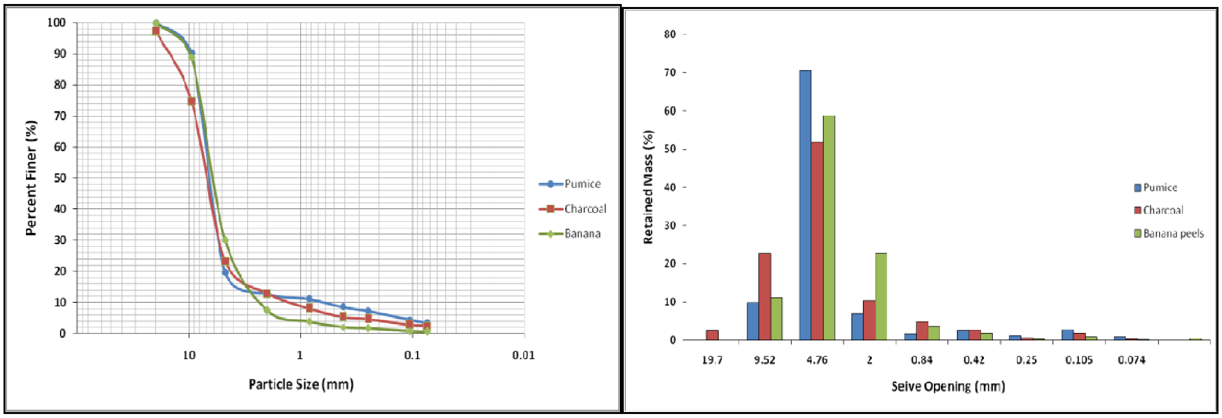
CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Adsorbent Characterization

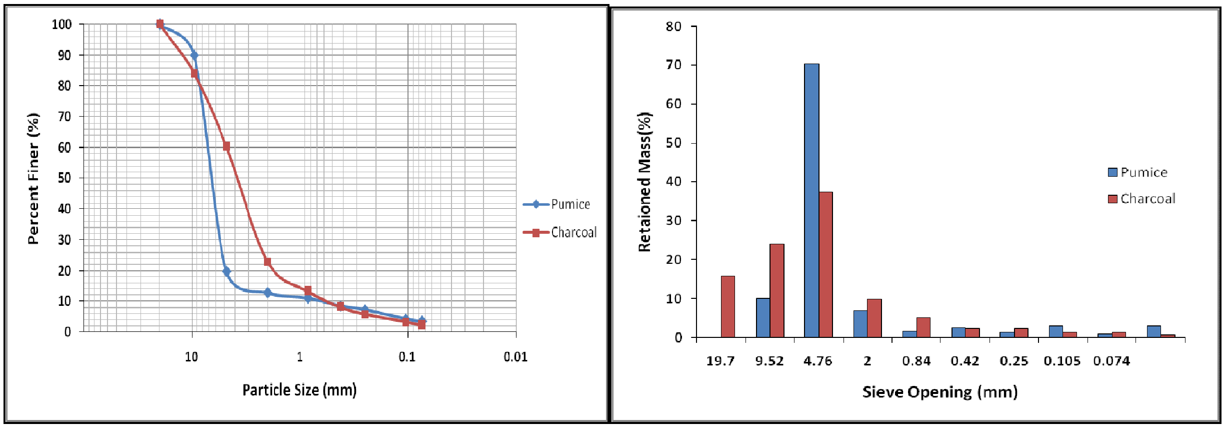
4.1.1 Classification of aggregates

The classification of the aggregates was done using the sieve analysis method. The results of the particle distribution size for three adsorbents used in the bucket and constructed beds studies are presented in Figure 4-1 and Figure 4-2 respectively.



a) b)

Figure 4-1: Particle size distribution of Pumice, Charcoal and Banana peels used in bucket experiment by sieve analysis in a) Percent finer (%) and b) Retained Mass (%)



a) b)

Figure 4-2: Particle size distribution of pumice and charcoal used in constructed bed field experiment by sieve analysis in a) Percent finer (%) and b) Retained Mass (%)

The results indicate that the aggregates used in the bucket study consisted of particles larger than 4.76mm particle size (Figure 4-1b). Pumice was composed of 80% of aggregate having particles sizes larger than 4.76mm. 70% of acacia charcoal and banana peel also consisted of particles sizes larger than 4.76mm. Pumice had an effective particle size of 0.65 and was uniformly graded and highly pervious with a hydraulic conductivity of 4.225 x 10^{-1} cm/sec as shown in Table 4-1. Pumice used for the adsorbent bed was similar to that used in the bucket study with a uniform grade consisting of 4.76mm sized aggregates.

Table 4-1: Results from the sieve analysis classification of aggregates for adsorbent materials used in the study.

Material	Effective size	Uniformity Coefficient	Coefficient of Gradation	Hazen's Approximation K(cm/sec)
Pumice	0.65	1.2	7.86	4.225 x 10^{-1}
Crushed Charcoal (Bucket study)	0.60	8.5	2.94	3.6 x 10^{-1}
Charcoal (Constructed beds)	1.20	8.0	2.17	1.44 x 10^{-0}
Diced Banana peels (Bucket study)	2.30	3.04	1.49	5.29 x 10^{-0}

Charcoal used in the adsorbent bed was composed of larger particle sizes than that used in the bucket study. Whole charcoal was used in the constructed beds, while pulverised charcoal was used in the buckets to enable comparison of all the three materials in the bucket studies. About 22% of the aggregates in the adsorbent beds were finer than the 4.76 mm size, while the pulverized bucket charcoal had particles of 13% finer than the 4.76mm size (Figure 4-2). Effective particle sizes were observed to be 1.2 and 0.6 for charcoal used in the adsorbent beds and buckets respectively. However, the charcoal was observed to be well- graded in both case as observed by the values of uniformity and gradation coefficients in Table 4-1.

Banana peels used in the bucket study were composed of 70% particle sizes greater than 4.76 mm, with an effective size of 2.3. The banana peels were also observed to be well graded with a uniformity coefficient and coefficient of gradation of 3.04 and 1.49 respectively. Both charcoal and banana peels were observed to be highly pervious from the established high hydraulic conductivity values (Table 4-1).

From the classification results, the particle sizes used in the bucket studies were generally uniform, with more than 70% of the three materials being larger 4.76 mm. This allowed for significant comparisons to be done for the three adsorbent materials. The high hydraulic conductivity of the three adsorbent materials also provides easy flow of wastewater through the adsorbent hence indicating the suitability of the materials in adsorption processes.

4.1.2 Physico- Chemical Analysis of the Adsorbent Materials

The physical characteristics of the three adsorbents are presented in Table 4-2. The pumice material used as media was lightweight with a bulk density of 0.431g/cm^3 and a moisture content of 3.3%. Charcoal had a moisture content of 6.6% and density of 0.207 g/cm^3, while banana peels had a moisture content of 10% and bulk density of 0.205 g/cm^3. Banana peels had high volatile matter content of 76.8% and an ash content of 10%. Banana peels was observed to have larger pore volume of 0.0309 cm^3 compared to charcoal (0.0096cm^3) and pumice (0.0013 cm$^{3)}$.

Table 4-2: Physical characteristics of adsorbents

Adsorbent material	**Moisture content (%)**	**Volatile matter (%)**	**Bulk Density (g/cm^3)**	**Ash Content (%)**	**Pore volume (cm^3)**
Pumice	3.3	3.4 %	0.431	0	0.0013
Charcoal	6.6	15.2%	0.207	5	0.0096
Banana peels	10	76.8 %	0.205	10	0.0309

Results from the chemical analysis of the adsorbents (Table 4-3) showed pumice was rich in silicate and aluminum oxides. This corroborates the findings reported by Moore (1937) and Williams (1942). Silica (58.7%) and aluminum oxides (12.25%) comprise a major part of the utilized pumice adsorbent, which shows the high capability of this adsorbent for absorption process as well as ion exchange. Charcoal was observed to have a high carbon content which is associated with the high loss on ignition (LOI). However the results obtained from the elemental analysis showed only 3% of CaO and 0.547% of K_2O was present.

Table 4-3: Elemental and Mineral compositions of pumice, charcoal and banana peels

Percentage (%) Elemental Compositions of Pumice and Charcoal										
Element	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	MnO	Fe_2O_3	LOI
Pumice	58.74 %	12.25 %	1.23 %	ND	5.94 %	4.02 %	0.41 %	0.16 %	9.31 %	4.75 %
Charcoal	ND	ND	3 %	ND	ND	0.547 %	ND	ND	ND	95 %

Mineral Composition of Banana peels in mg/g							
Banana peels	Cu	Ca	Mg	Na	Fe	Cr	K
mg/g	0.0088	38.1	3.4	0.117	5.7	1.04	66.3

Mineral analysis of banana peels, as shown in Table 4-3, indicated the presence of potassium (66.3mg/g), calcium (38.1mg/g), and iron at 5.7 mg/g. Chromium was also observed to be present in the banana peels at 1.04mg/g. Compared to literature values by Anhwange *et al.* (2009) and Debabandya *et al.* (2010), consistency is observed with the high levels of potassium. However, the calcium and iron levels observed in the study are higher than the 19.20mg/l and 0.61mg/g recorded by Anhwange *et al.* (2009) and Debabandya *et al.* (2010).

4.2 Characterization of Tannery Wastewater

The characteristics of the tannery wastewater from LIK are shown in Table 4-4: The tannery effluent, collected before the end of the factory's treatment process, is characterized by neutral pH, high BOD, high COD, and high dissolved solids.

Table 4-4: Characterization of tannery effluent from LIK

Parameter	**Treated Effluent**
pH	7.7 ± 0.39
Temperature (^{o}C)	25.2 ± 0.10
EC (µS/cm)	4995.7 ± 86.12
COD (mg/l O_2)	5879.4 ± 199.29
BOD(mg/l O_2)	5352.4 ± 419.24
Sulphides (S) (mg/l)	49.3 ± 11.77
Chlorides (Cl) (mg/l)	496.2 ± 15.20
Total Chromium (mg/l)	4.4 ± 0.80
Total Suspended Solids (TSS) (mg/l)	531.0 ± 76.96
Total Dissolved Solids (TDS) (mg/l)	6786.3 ± 161.80

The other major chemical constituents of the waste from the tanning industry are sulphide and chromium. Average values of 4.39 (0.80) mg/l and 49.3 (11.77) mg/l for total chromium and sulphides levels were observed respectively. These high levels of chromium and sulphides resulted from use of chromium salts and other chemicals in the tanning process. Sulphide is highly toxic to human beings. It causes an irritating, rotten-egg smell above 1 ppm, and at concentrations above 10 ppm, the toxicological exposure limits are exceeded (Midha and Dey, 2008). Excessive hardness, presence of high sulphide and total chromium, high TSS, TDS, BOD, and COD, of the tannery effluents reveals that, the tannery wastewater is highly polluted and it has to be treated to satisfy the prescribed WHO guidelines and NEMA standards. Permissible limits of sulphides and chromium of 2 mg/l are set by the NEMA standards for effluent discharge (NEMA, 2006).

4.4 Chromium Adsorption in Batch Studies

4.4.1 Standard calibration curve for AAS Analysis

The relationship between chromium concentration in the standard chromium solution and the absorbance is presented in Figure 4-3. This forms the calibration curve and formed the basis for chromium concentration analysis in the laboratory and field experiments.

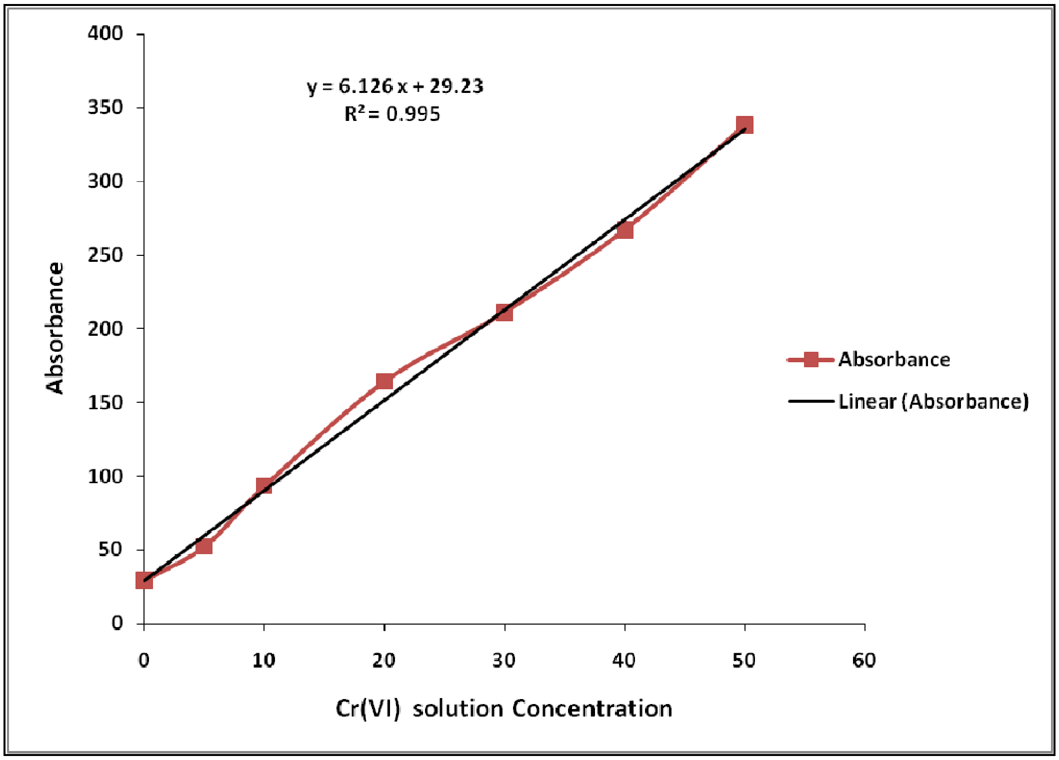
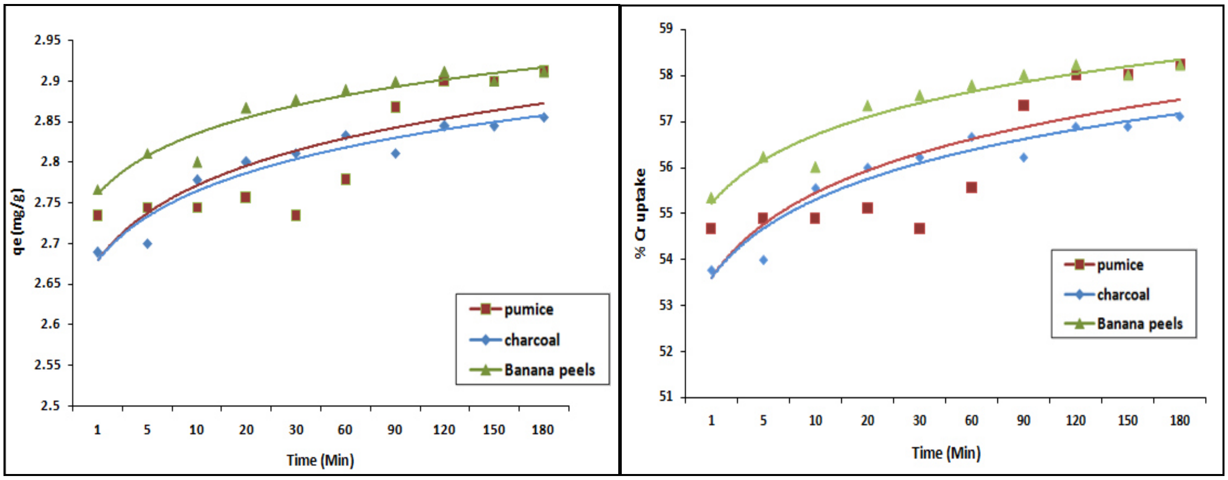


Figure 4-3: Calibration Curve of standard Chromium solution

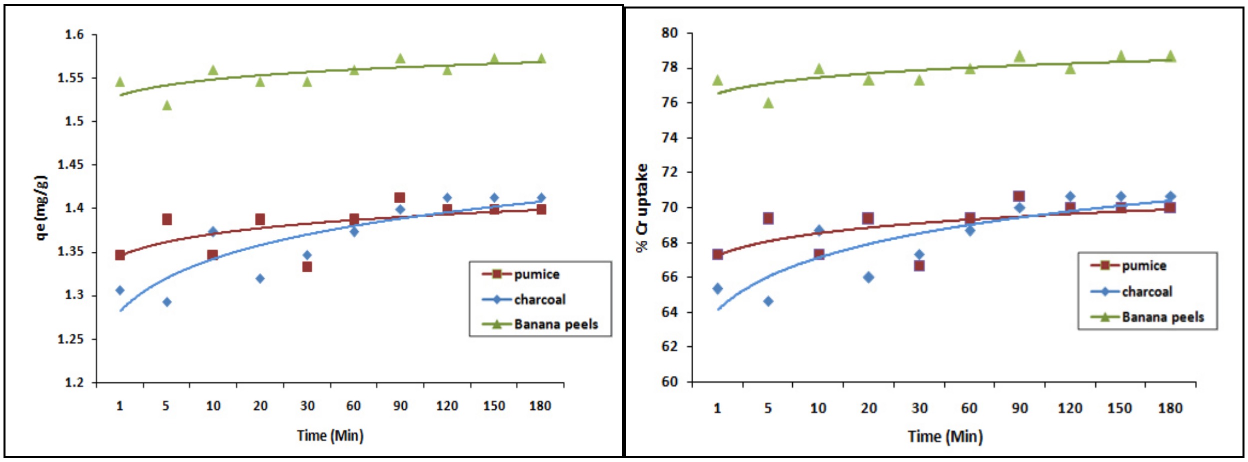
4.4.2 Effect of Time on Cr (IV) uptake

The effect of time on Cr(IV) adsorption by pumice, charcoal and banana peels in 20 mg/L and 50mg/L chromium concentrations are presented in Cr(VI) adsorbed in (mg/g) and in percentage (%) chromium uptake as shown in Figures 4-4 and 4-5.



(a) (b)

Figure 4-4: Effect of contact time on Cr (VI) removal by the adsorbents at 50 mg/l Cr^{+} stock solution concentrations; (a). Cr (VI) adsorbed in (mg/g) and (b). Cr (VI) adsorbed in % Cr (VI) uptake.



(a) (b)

Figure 4-5: Effect of contact time on Cr (VI) removal by adsorbents at 20 mg/L Cr (VI) stock solution concentrations; (a). Cr (VI) adsorbed in (mg/g) and (b). Cr (VI) adsorbed in % Cr (VI) uptake

The plots obtained for chromium removal by the different adsorbent materials present similar shape characterized by a rapid increase in chromium sorption initially followed by a slow increase and thereafter the rate of chromium ion removal tends to reach saturation with negligible effect on the percentages removal. It is observed that the removal of chromium increased with increasing contact time in the three adsorbents, especially for concentrations of 50 mg/l. Figures 4-4 and 4-5 also show the relationship between percentage adsorption and adsorption capacity in mg/g. As the percentage adsorption increases, the chromium adsorbed in mg/g also increased.

The adsorption equilibrium of Cr (VI) by pumice was observed to have been attained within 120 min after which there were no significant increases in the chromium uptake (Figure 4-4). Charcoal adsorption equilibrium was observed at 120 min. (Figure 4-5), while banana peels adsorption equilibrium was observed at 60 min, with no significant increase in chromium adsorption after 60 min (Figure 4-5). At equilibrium the uptake of chromium ions by pumice, charcoal and banana peels at initial concentrations of 20 mg/l and 50 mg/l are presented in Table 4-5. Adsorption rate of chromium on banana peel was found to be relatively higher than those reported for pumice and charcoal with equilibrium chromium uptake being 79.3% (1.6mg/g) at initial concentration of 20 mg/l and 58% (2.9mg/g) at initial concentrations of 50 mg/l.

Table 4-5: Adsorption capacities at equilibrium time for pumice, charcoal and banana peels at initial concentrations of 20 mg/l and 50 mg/l

Adsorbent	**Equilibrium time**	**Biosorption Capacity at initial concentrations of**	
		20 mg/l	**50 mg/l**
Pumice	120 hrs	69.3% (1.4 mg/g)	57.8% (2.9 mg/g)
Charcoal	120 min	70.6% (1.4 mg/g)	56.9% (2.8 mg/g)
Banana Peels	60 min	79.3% (1.6 mg/g)	58 % (2.9 mg/g)

The initial rapid increase in uptake may have resulted from the availability of large number of active binding sites in the adsorbents and consequently large numbers of chromium ions are bound onto the adsorbents. As the contact time increased the chromium removal rate decreased, as the sites available for adsorption began to decrease. After the active sites of the adsorbent gets exhausted, the chromium uptake tends towards a constant rate of removal. At this point the adsorption is said to be at equilibrium and the rate of uptake is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the biosorbent particles (Verma *et al.,* 2006). These results are typical for adsorption of metals involving no energy-mediated reactions, where metal removal from a solution is due to purely physico-chemical interactions between adsorbent and metal ions in the solution (Aksu, 2001; Balan *et al.,* 2009).

The equilibrium time for pumice of 120 min was found to be similar to studies conducted using powder pumice (Ulucinar and Nur Onar, 2005), however the removal efficiencies recorded were lower than those recorded in previous studies as shown in Table 4-6.

The charcoal equilibrium time was observed to be within the range of 20-180 min which was comparable to studies in literature conducted using activated charcoal from literature (Table 4-6). However, it was observed to be lower than that of natural untreated charcoal which attained equilibrium at 150 min, (Tahiruddin and Ya'akub, 2013). Compared to studies conducted by Tahiruddin and Ya'akub (2013) using untreated wood charcoal with adsorptive capacities of 8.73%, results from wood charcoal showed high adsorptive capacities of 70.6 %. The charcoal adsorptive capacities however were still lower than chemically activated carbon which showed adsorptive capacities of above 98% (Tamirat *et al.,* 2014; Sartape *et al.,* 2010).

Table 4-6: Literature studies of Pumice, charcoal and Banana peel as adsorbent for chromium.

Adsorbent	**Element**	**Equilibrium Time**	**Biosorption capacity**	**Reference**
pumice powder	Cr(III)	120 min	86.65%	Ulucinar and Nur Onar, 2005.
Pumice	Cr (III)	6 to 8 h	87%	Yavuz *et al.,*2008
Pumice	Cr (VI)	120 min	69.3 (1.4mg/g)	*This Study*
Untreated Charcoal	Cr (VI)	150 min	8.73 %	
Sulfuric acid modified charcoal	Cr (VI)	180min	21.06 %	Tahiruddin and Ya'akub (2013).
Nitric acid modified charcoal	Cr (VI)	120 min	11.19 %	
Chemically Activated Carbon from Bamboo	Cr(VI)	20 min	98.019%	Tamirat *et al.,* 2014
Wood apple shell activated carbon	Cr(VI)	70 min	98.05%	Sartape *et al.*,2010
Untreated Acacia charcoal	Cr (VI)	120min	70.6 (1.6 mg/g)	*This study*
Untreated Banana peels	Cr (III)	10 min	>95%	Memon *et al.*,2008
Acid treated Banana peels	Cr (VI)	60min	>90%	Kumar and Majumder , 2014
Untreated Banana peels	Cr (VI)	60min	75%	Ali and Saeed, 2014
Banana peels	Cr (VI)	60 min	79.3 %(1.4 mg/g)	*This study*

In comparison, the three adsorbent materials utilized in this study showed significant differences in the chromium adsorption with contact time. Analysis using ANOVA show *p* values < 0.001 were observed for 20 mg/l and 50 mg/l initial concentrations by the three materials (Appendix 1a and 1b). There were also significant differences observed with contact time in the removal of chromium for 50 mg/l initial concentrations. However, with *p* values of 0.998, no significant differences were observed in percentage chromium removal with contact time for 20 mg/l for all the three materials (Appendix 1a). This indicates that the initial concentrations affect the adsorptive capacities of chromium. At low initial concentrations the initial driving force for adsorption is low, hence slow adsorption takes place with time. Although the three adsorbents showed significant differences (*p* values < 0.001) , further analysis using the Turkey comparison method shows that pumice and charcoal are not significantly different. This was observed for both the 20 mg/l and 50 mg/l initial concentrations (Appendix 1a and 1b). Banana peels showed the highest potential of chromium adsorption with a mean of 57.37% and 74.8% at 20 and 50 mg/L initial concentration respectively.

The three materials showed potential for chromium adsorption with adsorptive capacities ranging from 56% to 58% and 69.3% to 79.3% at 20 mg/l and 50 mg/l concentration, respectively. These results when compared to other studies conducted using different biosorbent materials as shown in Table 4-7, show the applicability potentials of locally available natural biosorption materials.

Review of literature shows that chemical activation of adsorbents increases heavy metal removal in relation to the untreated adsorbent (Tahiruddin and Ya'akub, 2013; Wu and Chen, 2001; Usman *et al.,* 2012; Yin *et al.,* 2007). Chemical modification results in increased active surface area available for adsorption, hence exposure of more binding sites. These modifications methods include acid treatment, base treatment, heat treatment, ammonization, plasma, microwave, ozone treatment and metal impregnation (Tseng *et al.,* 2003).

Table 4-7: Other types of agricultural wastes as adsorbent for heavy metal

Adsorbent	Element	Equilibrium Time	Biosorption capacity	Reference
Neem sawdust	Cr (VI)	60 min	80%	Vinodhini and Nilanjana, 2009.
Mango sawdust	Cr (VI)	120 min	60%	,,
Wheat shell	Cr (VI)	180 min	50%	,,
Orange peel	Cr (VI)	180 min	32%	,,
Orange Peel	Cr (VI)	180 min	29.6%	Mandina *et al.,* 2013
coconut husk fibers	Cr(VI)	60 min	80%	Tan *et al.*,1993
Soybean hulls	Cr(VI)	20 min	84.96%	Ye *et al.,*2012
Activated bagasse carbon	Cr(VI)	90 min	99.975	Chand *et al.,* 1994.
Raw bagasse	Cr(VI)	90 min	93.5%	,,
Rice husk carbon	Cr(VI)	180 min	94%	Singh and Singh, 2012.

4.4.3 Effect of pH on Cr (VI) uptake

The extent to which chromium adsorption was influenced by varying pH is shown in Figure 4-6 for the case of 50 mg/l stock chromium solution.

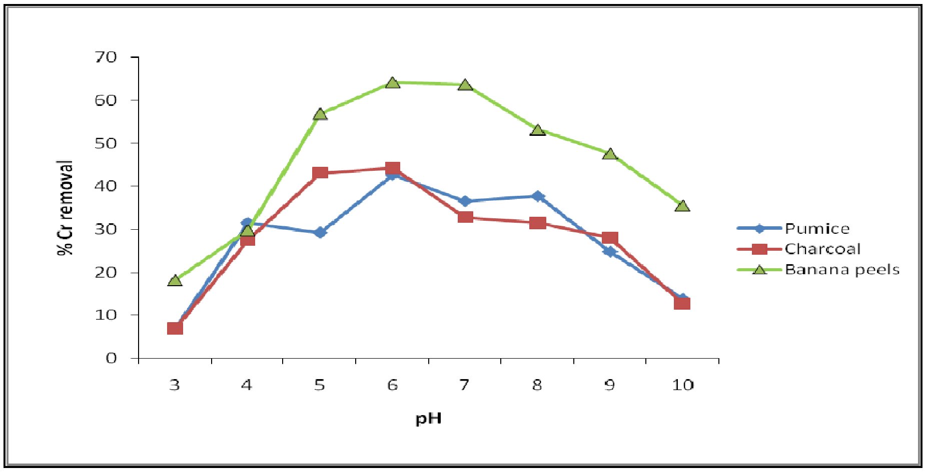


Figure 4-6: Effect of pH on chromium removal using pumice, charcoal and banana peels

The amount of adsorbed chromium is observed to increase at low pH levels, while at high pH levels the % uptake decreased for pumice, charcoal and banana peels. The amount Cr (VI) adsorbed increased with increase in pH from 3 to 6. However, banana peels indicated high chromium uptake at entire range compared to pumice and charcoal. At pH 3 the percent of chromium uptake was 6.9% for pumice and charcoal and 18.3% for banana peels. Maximum adsorption capacity of Cr (VI) was observed at pH 6 with 42.7%, 44.3% and 64.2% for pumice, charcoal and banana peels respectively. After pH 6, the % chromium uptake decreased as the pH increased towards pH 10. The results indicated that the removal of Cr (VI) was highest in acidic condition for all three adsorbents. The order of chromium adsorption capacity by the three adsorbent media was observed as banana peels > charcoal>pumice.

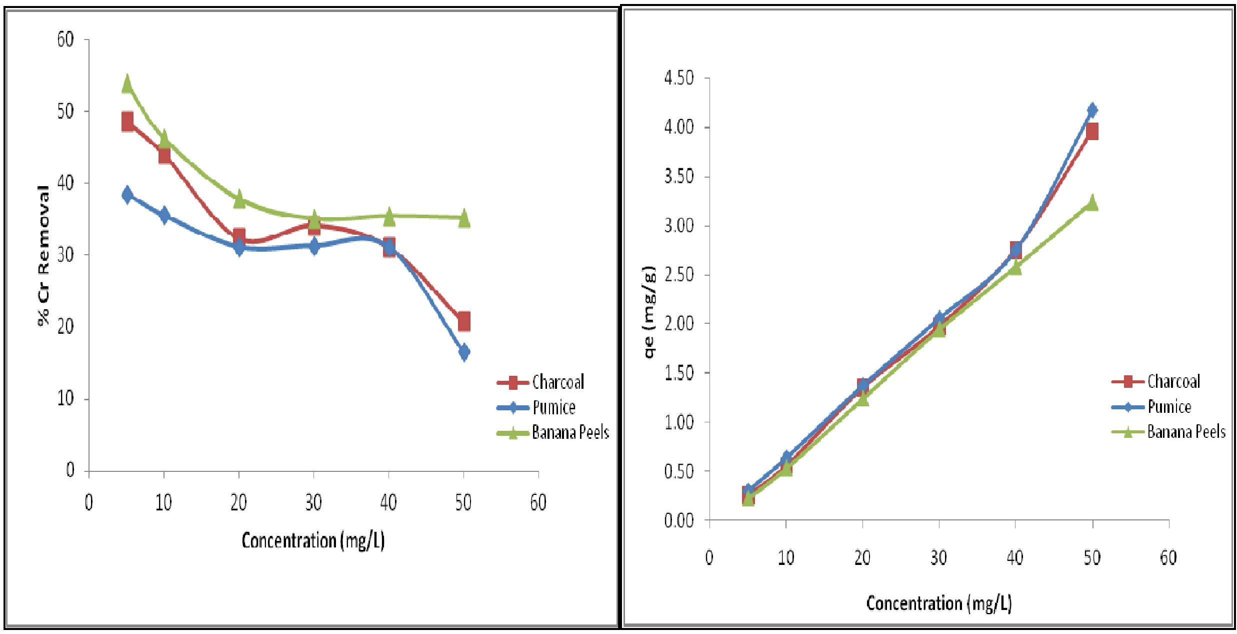
pH dependence of metal adsorption can largely be related to type and ionic state of the functional group present in the adsorbent and also to the metal chemistry in the solution (Gupta *et al.*, 2001). At low pH values, the H^+ are predominant in the solution which leads to the reduction of the adsorption sites available for metal ions, causing a decrease in metal ion adsorption (Tobin *et al.*, 1984). The H^+ compete with Cr^{6+} for the surface of the adsorbents, hindering the Cr^{6+} from reaching the adsorbent sites due to repulsive forces. This may be responsible for the low adsorption capacity of Cr (VI) onto the adsorbents at pH values <4.0. With an increase in the pH, there is a considerable reduction of H^+, which facilitates the deprotonation of the metal binding sites, which in turn increases adsorption. As the pH of the solution increases, metal ions replace H^+ from the surface of the pumice, charcoal and banana peel, thus increasing the extent of the adsorption.

High adsorption of Cr (VI) at low pH can also be explained by the species of the Cr (VI) and the adsorbent surface. According to the Chromium pourbaix diagram (Figure 2-2), the predominant Cr (VI) species in a water solution are $HCrO_4^-$(bichromate) and CrO_4^{2-} (chromate) anions in the pH range from 2 to 12 (Zhang *et al.*, 2008; Weckhuysen *et al.*, 1996; Dakiky *et al.*, 2002; Ramos *et al.,* 1994). $HCrO_4^-$ is the pre- dominant species in the 2-4 pH range whereas the $CrO_4^{2-}$is the predominant species in the 9-12 pH range (Ramos *et* *al.,* 1994; Muhammad *et al.*, 2011). As the pH of solution increased from 3.0, the amount of CrO_4^{2-} groups in the aqueous solution tended to increase. At pH 6 the molar fractions of the Cr (VI) species are 74% as $HCrO_4^-$ and 26% as CrO_4^{2-} (Ramos *et al.*, 1994). Hence, in acidic media, the adsorbent surfaces might be highly protonated and favor the uptake of Cr^+ in the ionic form, CrO_4^{2-}. This may explain the high result of Cr^+ uptake at pH 6.0. As the pH of the solution increases above pH 6.0, the sorbent undergoes deprotonation and hence decreased adsorption. High pH values result in reduction in the electrostatic attraction between negatively charged Cr (VI) species (CrO_4^{2-} and $HCrO_4^-$) and positively charged adsorbent surfaces, and hence the adsorption capacity decreases (Mor *et al.*, 2007).

Maximum adsorption of Cr (VI) at pH 6 has been reported by several researchers using activated carbon, (Ramos *et al.,* 1994; Murugesan *et al.,* 2013). Banana peels studies conducted by Annadurai *et al.* (2002) and Hossain *et al. (*2012) in the adsorption of $Cu^{2+,}$ Co^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+}, also provide similar trends as the Cr^+ adsorption, with maximum adsorption at pH 6.0. Similar trends of increased chromium uptake in the low pH range has also been observed using pumice by Yavuz *et al.* (2008).

4.4.4 Effect of Initial concentration on Chromium (VI) uptake

The effect of initial concentration on the Cr (VI) adsorption efficiency by pumice, charcoal and banana peels is shown in Figure 4-7. As the initial concentration of Cr (VI) increased from 5 mg/l to 50 mg/l, an increase in the equilibrium amount of Cr (VI) adsorbed was observed. Adsorption capacity at equilibrium increased respectively from 0.3mg/g to 4.2 mg/g, 0.3mg/g to 4mg/g and 0.2mg/g to 3.3mg/g for pumice, charcoal and banana peels. However as the amount of Cr (VI) adsorbed increased, the percentage Cr (VI) removal decreased as the initial concentration of Cr^+ was increased from 5 mg/l to 50 mg/l. For pumice, Cr (VI) removal decreased from 38.5% to 16.5% at initial Cr (VI) concentration of 5mg/l to 50 mg/l. Charcoal % Cr (VI) removal decreased from 48.6% to 20.7%, while banana peels decreased from 53.8% to 35.2% with the increase of initial concentration from 5mg/l to 50 mg/l.



aa

) b)

Figure 4-7: Effect of initial concentration on Cr (VI) adsorption in a) % Cr (VI) removal and b) equilibrium Cr (VI) adsorption (mg/g)

Increase in the Cr(VI) adsorbed (mg/g) may result from the possibility that the initial concentration of the metal ions provides the necessary driving force to overcome the mass transfer resistance of Cr (VI) between the aqueous and the solid phase (Chowdhury and Saha, 2010). The increase in the initial Cr (VI) concentration also enhances the interaction between the Cr (VI) in the aqueous phase and the biomass surface. This increase in driving force at high initial concentration, exhaustion of the adsorbents is achieved faster than when concentrations are low.

The decrease in percentage Cr (VI) uptake with increase in initial concentration can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration (Siboni *et al.,* 2011; Mor *et al.*, 2007). At lower concentration almost all the metal ions could interact with binding sites facilitating maximum adsorption (Qaiser *et al.*, 2007). As the initial concentration increases, there is an increase in number of metal ions competing for available binding sites. At higher concentration more chromium ions are left unadsorbed in the solution due to saturation of adsorption sites (Bai and Abraham, 2003), resulting in observed decreased Cr (VI) uptake. This decreasing trend with increase in initial Cr (VI) concentrations was observed to be similar to other studies conducted using activated charcoal (Gupta *et al.*, 2011; Dahbi *et al.*, 1999), Natural plant material (Devaprasath *et al.,* 2007) and Neem leaf (Gopalakrishnan *et al.*, 2013, Gupta and Babu, 2006).

Results obtained from ANOVA analysis of the experimental data, show that for both initial concentration and adsorbent material there are significant differences, with p values< 0.001(Appendix 2). The interaction of the initial concentration and the adsorbent material is also observed to be highly significant ($p< 0.001$). Meaning that the adsorption rates at different initial concentrations are different and the adsorptions by the three adsorbent materials are not equal. With the observed interaction being significant, it is clear to conclude that the initial concentration effects on Cr (VI) removal are different for the three adsorbents. Hence the removal of chromium by different adsorbent materials is dependent on the initial concentration of chromium present in the solution. Banana peels had higher Cr (VI) uptake potential with mean averages of 40.4% compared to acacia charcoal (35.1%) and pumice (33.2%) (Appendix 2).

4.4.5 Desorption of Chromium from adsorbents

Results of desorption studies using 2M HNO_3 on the metal-loaded pumice, charcoal and banana peels is shown in Figure 4-8.

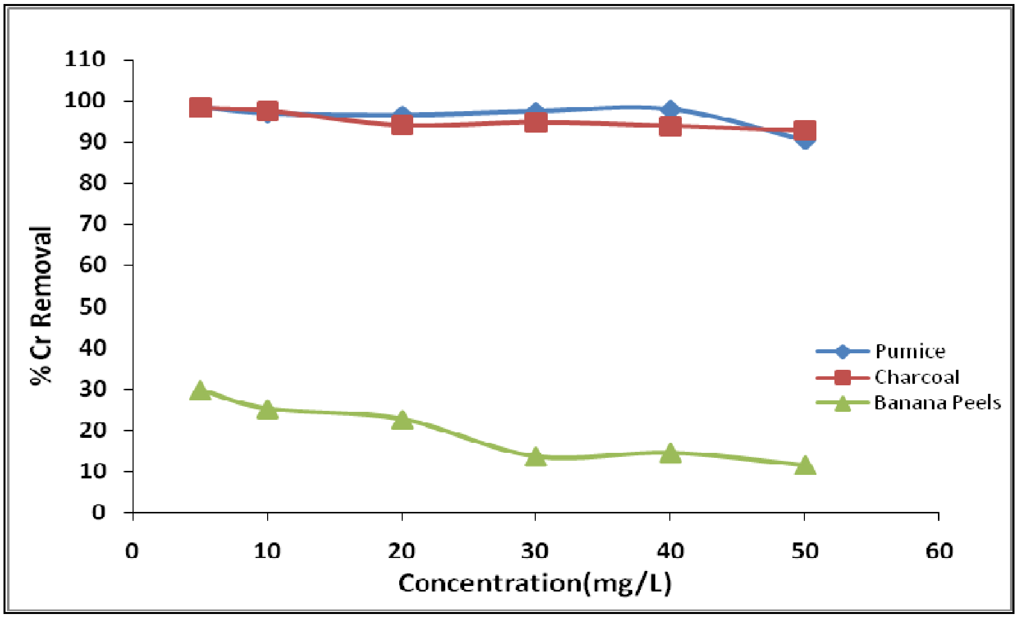


Figure 4-8: Desorption of Chromium ions from pumice, charcoal and banana peels using 2M HNO_3

There was high desorption of Cr (VI) when the metal loaded adsorbents were obtained from low initial concentrations. The results also indicated a slight decrease in Cr (VI) desorption as the initial concentration used in the adsorption process increased from 5 mg/l to 50 mg/l. Generally high desorption of Cr (VI) were observed for pumice and charcoal (>90.5%) compared to banana peels (<29.6%) when 2M HNO_3 was utilized. Maximum desorption values of 98.5%, 98.8% and 29.6% for pumice, charcoal and banana peels respectively were observed at 5 mg/l.

These results of high desorption when using metal loaded adsorbents from low initial concentrations is explained by the presence of more adsorbed Cr (VI) being present in the adsorbent. Comparative studies of adsorption and desorption (Figure 4-9) observed that at low initial concentrations of 5 mg/l, the adsorbent was most effective in adsorbing of Cr (VI) ions, hence more Cr (VI) are available for desorption.

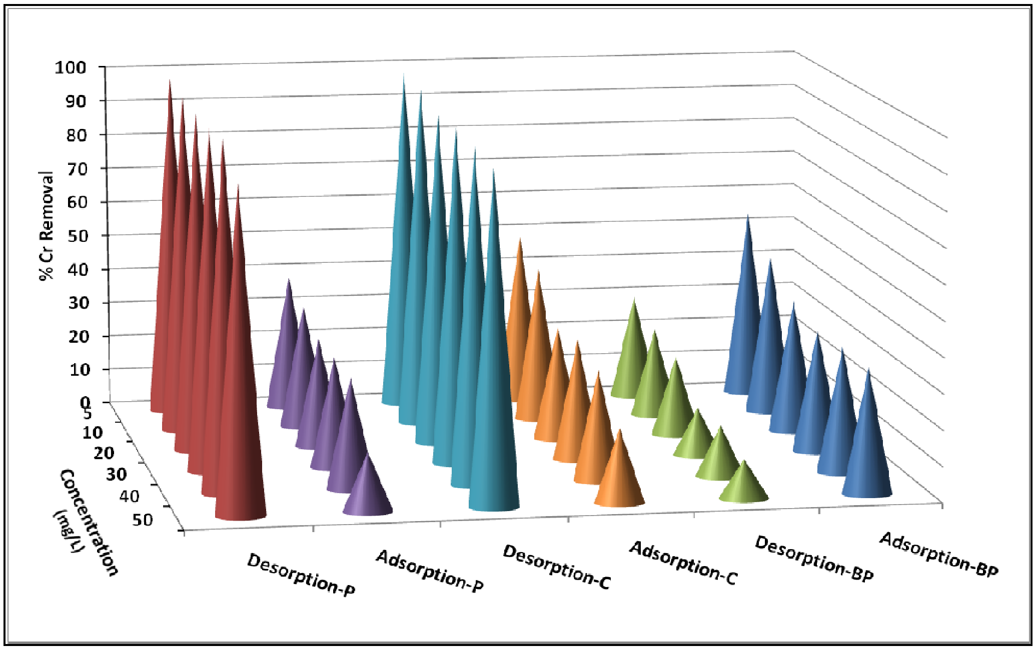


Figure 4-9: Comparative graph showing the % Cr (VI) removal from stock chromium solution (Adsorption) using pumice (P), charcoal (C) and banana peels (BP) and the % Cr (VI) from the three adsorbents using 2M HNO_3 (Desorption).

From Figure 4-9, banana peels is observed to achieve the highest levels of adsorption of chromium ions (53.8%), but had the lowest desorption levels (29.6%). This indicates that the chromium ions are strongly bound by the banana peels. This strong bonding observed is associated with the banana peel pore structure and rich organic functional groups (-OH, -NH2, -COOH) on the surface of pores (Anwar *et al.,* 2010; Castrol *et al.,* 2011). With more than 90.5% being desorped from pumice and charcoal, this indicates that the chromium ions are weakly bonded by the two adsorbents. The high desorption by pumice and charcoal indicates their potential and suitability in reuse for adsorption of chromium.

The 2M HNO_3 lowers the pH value of the solution. At low pH values, the H^+ are predominant in the solution. During desorption, the H^+ released from the acids replaces the Cr (VI) on surface of the adsorbents. As the H^+ competes for the Cr (VI) sites on the surface of the adsorbents, there is the hindering of H^+ from reaching the adsorbent sites due to repulsive forces. With low Cr (VI) being present the attractive forces binding the Cr (VI) to the adsorbent are much stronger than when the Cr (VI) are present in larger numbers, hence the low Cr (VI) removal from the adsorbent. With higher Cr (VI) ions availability in the adsorbent, replacement with H^+ is enhanced, thus resulting in higher desorption rates. Literature reviews indicate that adsorbed metals on adsorbents cannot be completely reversible (Brummer *et al.*, 1988; Farrah and Pickering, 1978). Hence this explains desorption not attaining the 100% as not all chromium adsorbed can be recovered fully. Banana peels low desorption potential may be as a result of strong bonding of Cr (VI) by the hydroxyl and carboxylic functional groups. Previous studies by Khaidar *et al.,* 2007 have shown that carboxylic groups has quasi irreversible binding in the removal of chromium which relates to banana peel desorption difficulties.

The possibility of desorption using 2M HNO_3, indicates that the adsorption of Cr (VI) process is a physical process, since H^+ released from the acids replaces the Cr (VI) on surface of the three adsorbents (Patil and Shrivastava, 2010; Zheng *et al.,* 2011; Balakrishnan *et al.,* 2010). These desorption study showed that the pumice and charcoal adsorbents could be reused for chromium adsorption, hence saving on treatment costs. However, viability of reusing banana peels is poor due to its low desorption capabilities and may result in additional costs.

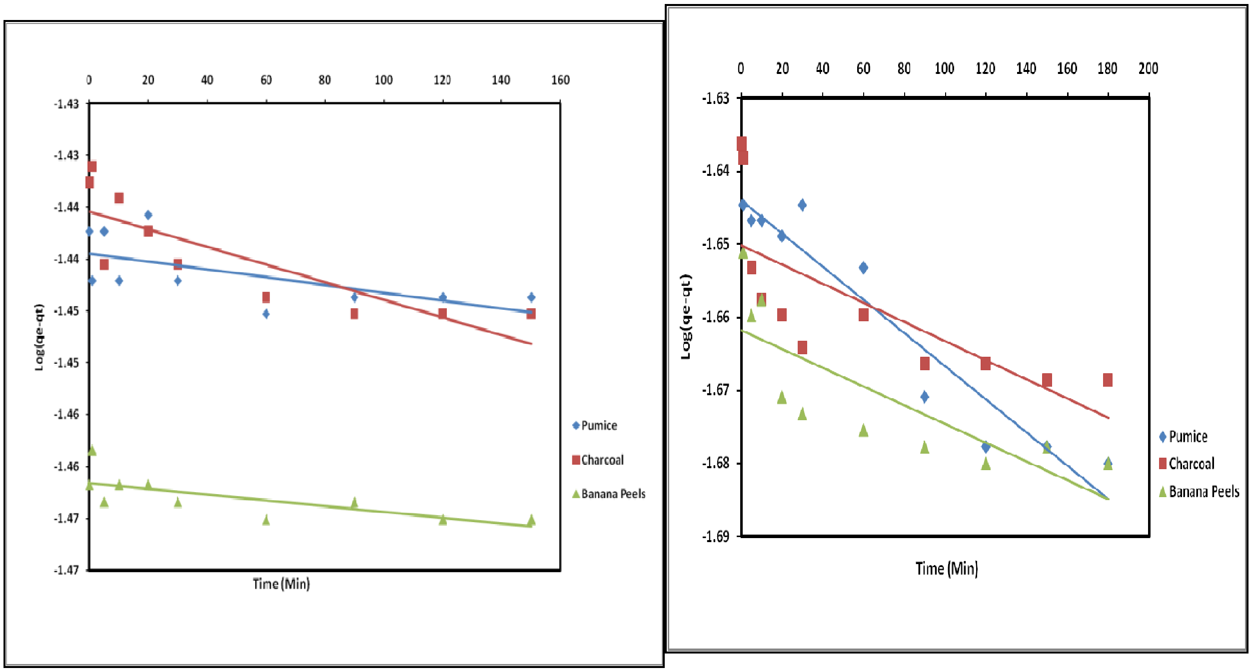
4.5 Kinetics Studies of Chromium Adsorption

The following section presents the kinetics obtained for each adsorbent material. The constants and regression coefficient were obtained by fitting the pseudo-first-order and pseudo-second-order Kinetic models to experimental data.

4.5.1 Pseudo-first-order model

The linear plots of the experimental data were obtained by plotting log (q_e-q_t) against time (t) as shown in Figure 4-10 and the calculated parameters are summarized in Table 4-8. Results observed from the pseudo-first order fit showed adsorption rates in the range of

0.001 to 0.005 min^{-1} and adsorption capacity q_e values in the range of 0.022 to 0.037 mg/g for the three adsorbent materials. From the calculated correlation coefficient, $0.921 < R^2 > 0.389$, it was observed that the experimental data is not well fitted to the pseudo- first-order kinetic equation, except for pumice in 50mg/l stock chromium solution concentration with an R^2 of 0. 921.



a) 20 mg/l b) 50 mg/l

Figure 4-10: Linear plot of Pseudo-first-order equations of Cr (VI) adsorption on pumice, charcoal and banana peels at 20 mg/l and 50 mg/l stock chromium concentrations.

Table 4-8: Parameters of the pseudo-first-order for different adsorbent materials

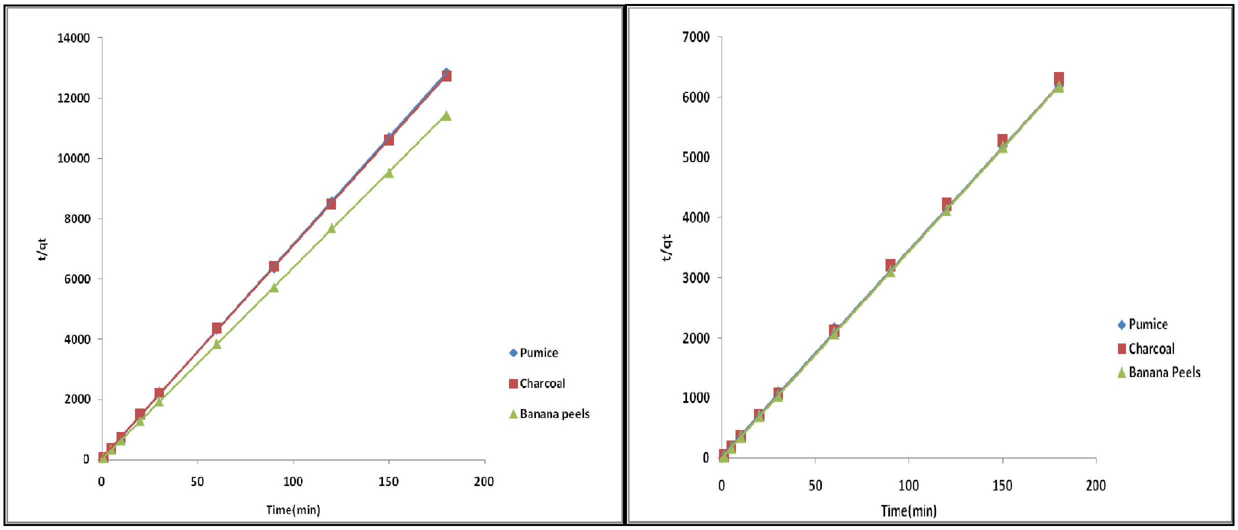
Parameter		**First –order Kinetic Model**			
Initial Cr^+ Concentration	Adsorbent	K_1 (min^{-1})	$q_{e. cal}$* (mg/g)	R^2	$q_{e. exp}$** (mg/g)
50 (mg/L)	Pumice	0.0005	0.023	0.921	0.028
	Charcoal	0.0003	0.022	0.552	
	Banana Peels	0.0002	0.022	0.676	
20 (mg/L)	Pumice	0.0001	0.036	0.389	0.011
	Charcoal	0.0002	0.037	0.693	
	Banana Peels	0.0001	0.034	0.528	

$q_{e. cal}$*- calculated values of q_e; $q_{e .exp}$** -experimental values of q_e

The linear plots also show a poor agreement between the experimental adsorption capacity ($q_{e},_{exp}$) and calculated adsorption capacity ($q_{e},_{cal}$) values. The low regression coefficient and large discrepancies in calculated and experimental q_e values indicates that the adsorption process of Cr (VI) on the three adsorbent materials is not a first-order reaction. Hence this shows that K_1 (q_e-q_t) does not represent the number of available sites and log q_e is not equal to the intercepts of the plot. Thus the analysis indicates that the pseudo-first-order model is unsuitable for describing the kinetics of the adsorption process, with pumice, charcoal and banana peels adsorbents. Tamirat *et al.* (2014) and Mohammad *et al.* (2014) also found the adsorption process does not follow the pseudo-fist –order equation for bamboo charcoal and waste pumice respectively.

5.5.2 Second -pseudo -order model

The equilibrium adsorption capacity q_e and the second-order rate constant K_2 were calculated from the slope and intercept of the plot of t/q_t against t, respectively as shown in Figure 4-11. The calculated parameters for the second-order-kinetic model are summarized in Table 4-9.



a) 20 mg/L b) 50 mg/L

Figure 4-11: Linear plot of Pseudo-Second-order equations of Cr (VI) adsorption on pumice, charcoal and banana peels at 20 and 50 mg/L stock chromium solution concentrations

Table 4-9: Parameters of the pseudo-second-order kinetics for different adsorbent materials

Parameter		**Second-order Kinetic Model**				
Initial Cr^+ Concentration(C_o)	Adsorbent	K_2 (g/mg.min)	$q_{e.\ cal}$* (mg/g)	h	R^2	$q_{e.\ exp}$** (mg/g)
50 (mg/L)	Pumice	31.382	0.029	0.026	0.999	0.028
	Charcoal	86.796	0.029	0.073	1.000	
	Banana Peels	120.09	0.029	0.102	1.000	
20 (mg/L)	Pumice	182.02	0.014	0.018	0.999	0.011
	Charcoal	78.58	0.014	0.015	0.999	
	Banana Peels	228.97	0.016	0.059	1.000	

$q_{e.\ cal}$*- calculated values of q_e; $q_{e\ .exp}$** -experimental values of q_e

It was typically observed that as the initial concentration of Cr (VI) increased, the adsorption capacity at equilibrium (q_e) and the initial sorption rate (h) increases. The Second-pseudo-adsorption rate constant (K_2) was observed to be in the range of 31.382 to 228.97 g/ mg. min. It was found that equilibrium adsorption capacity (q_e) and the initial sorption rates (h) increased with an increase in initial chromium ion concentration (C_o). Banana peels showed high initial sorption rates (h) of 0.059 and 0.102 than those of charcoal (0.015 and 0.073) and pumice (0.018 and 0.026) for initial concentrations of 20 mg/l and 50 mg/l respectively. This may be explained by the possibility that banana peels may have a larger number of available sites than that of pumice and charcoal, as well as strong bonding by hydroxyl groups. This higher availability of adsorption sites may be associated with the larger pore volume of 0.0309 cm^3 observed in banana peels compared to pumice (0.0013 cm^3) and charcoal (0.0096 cm^3).

Correlation coefficients (R^2) values were observed to be greater than of 0.999. These high values of R^2 indicated a good fit of the experimental data with the second-order kinetic equation. The linear plots also show a good agreement between the experimental adsorption capacity ($q_{e,exp}$) and calculated adsorption capacity ($q_{e,cal}$) values. This indicates that the adsorption of Cr (VI) by the three adsorbent materials follows the pseudo-second-order kinetic model and the chemical process controls the adsorption rate. The pseudo-second-order model assumption is that chemisorption is the rate-limiting step and only monolayer adsorption is possible. In chemisorptions, the metal ions stick to the adsorbent surface by forming a chemical bond and tend to find sites that maximize their coordination number with the surface (Atkins, 1995).These agrees with the findings that pseudo-second order model provides the best fit to most adsorption studies (Badmus *et al.,* 2007, Ngah *et al.,* 2004, Hossain *et al.,*2012).

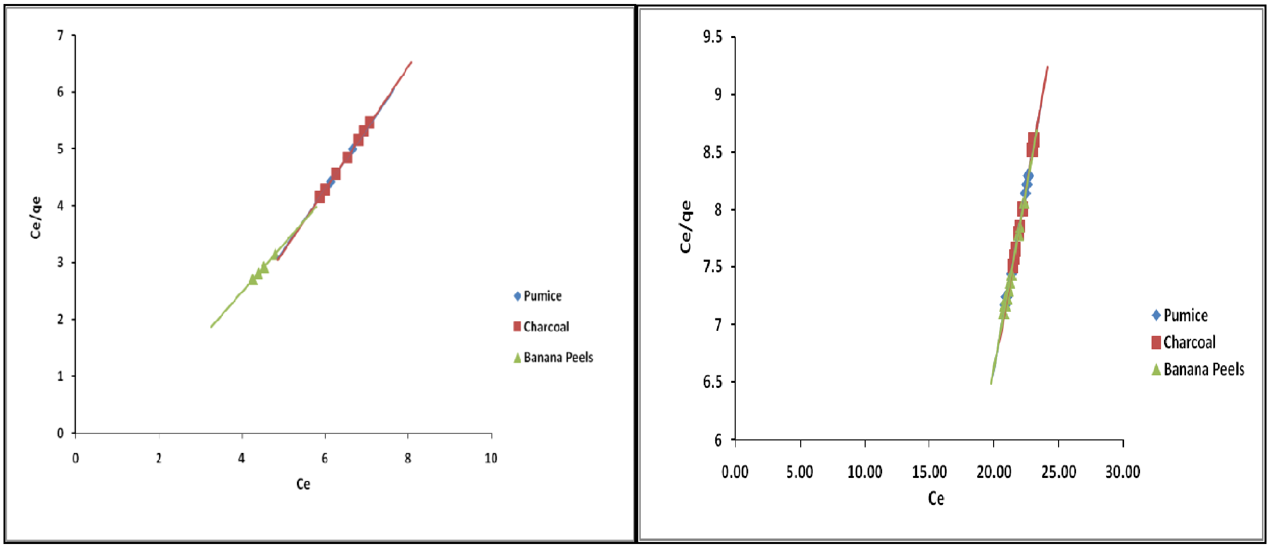
4.6 Adsorption Isotherms

For each adsorbent material, the constants and regression coefficient are obtained from graphical plots of experimental data to fit the Langmuir and Freundlich Isotherm models

(Liang *et al.*, 2006). The closer the regression coefficient, R^2, is to unity (1), the more close the data points lie on the linearized isotherm line. However, if the R^2 value is not close to unity (1), it does not mean that the experiments are unreliable; rather, it refers to the inability of the points to be linearized using the adsorption isotherm considered. Using another adsorption isotherm may perhaps yield better R^2 values; however, Langmuir and Freundlich were applied due to their widespread acceptance and application in single solute adsorption systems.

4.6.1 Langmuir isotherm

Langmuir isotherm constants and regression coefficients were determined from the linear plots of specific sorption (C_e/q_e) against the equilibrium concentration (C_e) as shown in (Figure 4-12) and the results obtained from Langmuir isotherms are presented in Table 4-10.



a) 20mg/l b) 50mg/l

Figure 4-12: Langmuir isotherm fits of Chromium at 20 mg/L and 50mg/l stock chromium solution concentration using different adsorbent materials

Table 4-10: Parameters of Langmuir and Freundlich Isotherm for different adsorbent materials at initial stock chromium concentrations of 20 mg/l and 50mg/l.

Parameter		**Langmuir isotherm**				**Freundlich Isotherm**		
Initial Cr^+ Concentration (C_o)	**Adsorbent**	**q_m**	**K_L**	**R_L**	**R^2**	**K_F**	**n**	**R^2**
50 (mg/L)	Pumice	1.592	0.105	0.160	0.999	30.409	1.297	0.999
	Charcoal	1.536	0.101	0.166	0.999	33.497	1.245	0.999
	Banana Peels	1.626	0.108	0.156	0.999	28.708	1.328	0.999
20 (mg/L)	Pumice	0.941	0.507	0.023	0.999	3.404	2.016	0.999
	Charcoal	0.920	0.486	0.022	0.999	3.365	2.045	0.998
	Banana Peels	1.200	0.986	0.056	0.999	2.564	2.967	0.988

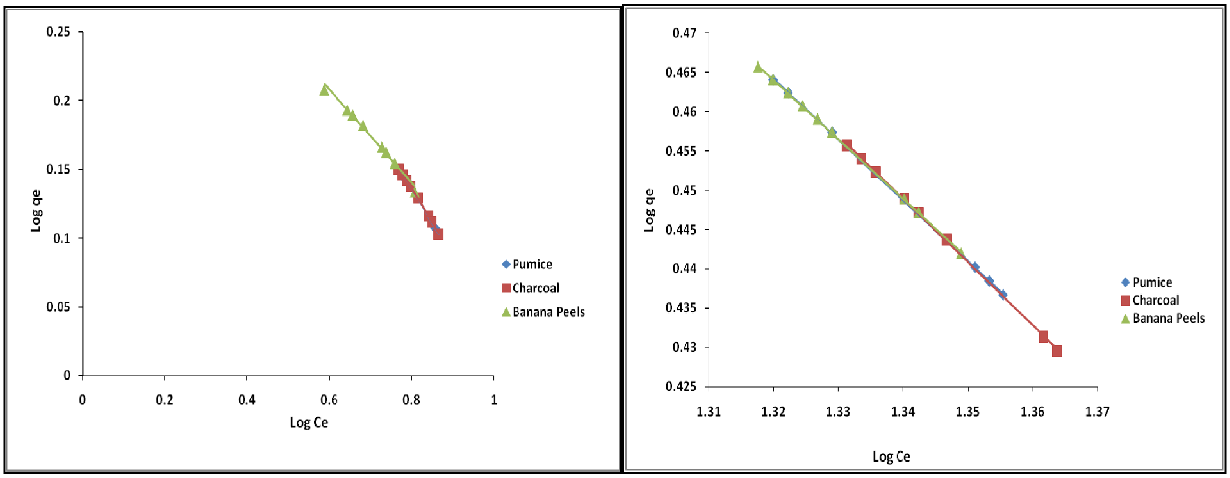
As shown in Table 4-10, the adsorption capacity, q_m, which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage showed that banana peels has a mass capacity for Cr (VI) (1.2 mg/g; 1.626 mg/g), charcoal (0.920 mg/g; 1.536 mg/g) and pumice (0.941 mg/g, 1.592 mg/g) adsorbents at initial chromium concentrations of 20 and 50 mg/l, respectively. This indicated that banana peels were more superior in the removal of chromium than pumice and charcoal. This is associated with the high pore volume in banana peels with more adsorption sites available and the presence of carboxylic and hydroxyl groups, which form strong bonds. From the q_m results, the order followed in chromium adsorption potential was banana peels> charcoal> pumice. The adsorption coefficient, K_L that is related to the apparent energy of adsorption for Cr (VI)was greater in banana peels than that of charcoal and pumice at both initial stock chromium concentrations (C_o) of 20 mg/l and 50 mg/l.

The favorability of adsorption of the chromium metal ions on the three materials was tested using the essential feature of the Langmuir isotherm model, namely the separation factor

R_L (Equation 2.7). The values of R_L obtained are listed in Table 4-10. The separation factors for the three materials are observed to be less than unity indicating that the adsorbent materials are favorable for the adsorption of Cr (VI). With the observed $0<R_L>1$value range, a highly favorable adsorption is indicated (Poots *et al.,* 1978; Hall *et al.*, 1966). The favorability of these adsorbent materials is associated to the presence of carboxylic and hydroxyl groups, silica and aluminum oxides and carbon in banana peels, pumice and charcoal, respectively, which enable ion exchange and bond formations. R_L values of banana peels are smaller compared to charcoal and pumice. This indicates that the banana peels have more available binding sites associated with the larger pore volume allowing for faster Cr (VI) binding than charcoal or pumice.

4.6.2 Freundlich isotherm

Figure 4-13 shows the Freundlich plot. The values of Freundlich adsorption capacity (K_f) and the adsorption intensity (n) were calculated from the intercept and the slope of the graph (1/n) respectively. The essential characteristics of Freundlich plot are presented in Table 4-10.



a) 20mg/l b) 50mg/l

Figure 4-13: Freundlich isotherm fits of Chromium at 20 mg/l and 50mg/l initial stock chromium concentrations using different adsorbent materials

Freundlich adsorption capacities, K_f, obtained at concentrations of 20 and 50 mg/l respectively were 3.404 and 30.409 for pumice, 3.365 and 33.497 for charcoal. Banana peels values were observed to have lower K_f values of 2.564 and 28.708 for concentrations of 20 mg/l and 50 mg/l, respectively. Increasingly large K_f values indicate high adsorption capacity, hence these results indicate that pumice and charcoal has greater adsorption capacities than the banana peels when different sites with several adsorption energies are involved in adsorption process.

The adsorption parameter (n) in the Freundlich isotherm which measures preferential adsorption of one adsorbate to other was obtained as shown in Table 4-10. 1/n is a function of the strength of the used absorbent material. Higher (1/n) values indicate that relatively small change in the solution chromium ion concentration will cause a relatively big change in chromium ions adsorbed (Wajid *et al.*, 2013). If n=1 then the partition between the two phases are independent of the concentration. If value of n is above one it indicates a normal adsorption. On the other hand, n being below one indicates cooperative adsorption (Mohan and Karthikeyan, 1997). High value of n indicates a strong bond between the adsorbent and the adsorbate (Yakubu *et al.*, 2008). The n values of banana peels (1.328, 2.967) are observed to be higher compared to pumice (1.295; 2.016) and charcoal (1.245; 2.045) at both C_o of 20 mg/l and 50 mg/l. These indicate that compared to pumice and charcoal, banana peels had stronger bond between the adsorbent and the adsorbate. These results also agreed with desorption studies conducted in this study. Pumice and charcoal was observed to desorb more than 90.5% of chromium ions compared to banana peels which desorbed less than 29.6%. The low desorption levels of banana peels indicated strong bonding compared to pumice and charcoal which weakly bonded the metal ions.

The adsorption parameter (n) value of the Freundlich equation also gives an indication of the favorability of sorption. According to Goldberg (2005), if n values lie between one and ten, this indicates a favorable sorption process. From the data in Table 4-10, the value of n is greater than unity for all the adsorbents materials at the different concentration of 20 mg/l and 50 mg/l. This indicates that the adsorption of Cr (VI) on to pumice, charcoal and banana peels is a normal adsorption and is favorable.

In terms of favorability, it is generally stated that values of adsorption parameter (n) in the range of 2 to 10 is good, 1 to 2 as moderately difficult and less than 1 as poor sorption characteristic (Hamdaoui *et al.*, 2008, Yao *et al.*, 2010). Hence from the results, adsorption at higher initial concentrations of 50mg/l was observed to be moderately difficult , with adsorption parameter (n) values ranging between 1.245 and 1.328, while at low initial concentrations of 20 mg/l, it was observed to be good with n>2. This can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated. As the initial concentration increases, there is an increase in number of metal ions competing for available binding sites. Thus as a result of limited binding sites, difficulty occurs in adsorption of Cr (VI) at the higher initial concentration. Among the three adsorbent materials, banana peels had the higher values of adsorption parameter, 1.328 and 2.967 at 20 mg/land 50 mg/l respectively, compared to pumice and charcoal. These high values of n indicate strong bonding of chromium ions onto banana peels (Yakubu *et al.,* 2008).These results agree with pseudo-second kinetic model and desorption results that describe strong bonding for banana peels.

Based on the correlation coefficients (R^2) values, the Langmuir and Freundlich isotherm models are observed to fit well with the experimental data with ($R^2 > 0.988$). Due to the bias resulting from linearization, the internal structure is not apparent at first glance of the R^2 values in Table 4-10 were determined by one-way analysis of variance (ANOVA) without replication ($P<0.05$). The summary of the statistical analysis is presented in Appendix 3.

From the ANOVA table (Appendix 3), consideration of the comparative magnitudes of the R^2 values suggest that the Freundlich isotherm model, with a mean of $R^2 = 0.9987$, provides a slightly better model for the adsorption systems compared to the Langmuir model with a mean of R^2= 0.997. However, the one -way ANOVA results (p value >0.05) indicate that the Freundlich and Langmuir isotherm models are not significantly different (Appendix 3).

The obtaining of good fits using Langmuir and Freundlich isotherm models shows the applicability of these models in practical applications of the three adsorbent materials for chromium adsorption.

4.7 Results from Field Pilot Study

4.7.1 Bucket studies

The chromium in treated wastewater were evaluated for the bucket studies using pumice, charcoal and banana peels and results are presented in Figure 4-14.

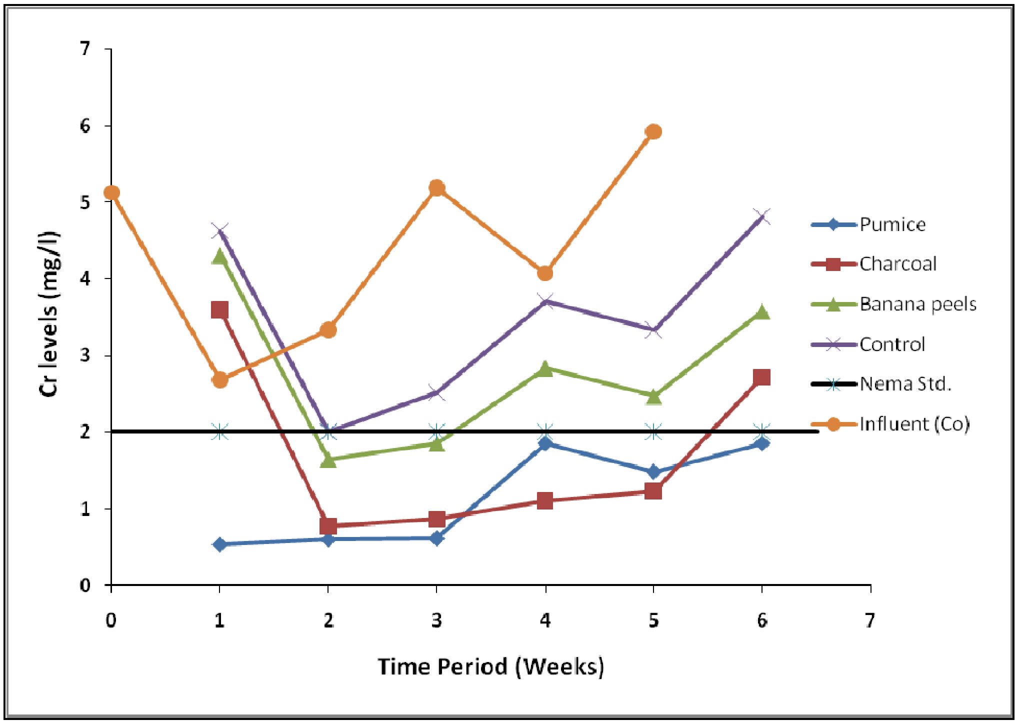


Figure 4-14: Effluent chromium concentration for the different treatment options using pumice, charcoal, banana peel and the control.

Pumice and charcoal were observed to lower the chromium levels to below those of NEMA standards of 2.0 mg/l, apart from week 1 and 6 for charcoal. The lowest chromium concentrations were observed as 0.5mg/l at week 3 and 0.8mg/l at week 2 for pumice and charcoal respectively. Chromium concentration levels were observed to be above 2mg/l for banana peels apart from week 2 which recorded the lowest chromium concentration of 1.7mg/l. The control used also indicated chromium levels above 2mg/l.

The ability of pumice and charcoal to reduce chromium levels to below the NEMA standards and WHO guidelines, prove them to be good adsorbent materials of chromium from tannery wastewater. However, based on initial concentration (C_o) and the residual chromium concentrations in the treated wastewater from the bucket studies (Figure 4-14), pumice was observed to have a higher adsorptive capacity than charcoal and banana peels. Banana peels had the lowest adsorptive capacity with levels of chromium after treatment still exceeding the NEMA standards of 2 mg/l. The low adsorptive capacity of banana peels in the bucket study contradicted the batch laboratory studies, which showed that powdered banana peels had the highest adsorptive capacities of Cr (VI) compared to pumice and charcoal. This low adsorptive capacity of banana peels in the field bucket study may be associated with the form of peels used. Al– Azzawi *et al*., 2013, showed that powdered peels had higher values of bioremoved heavy metal concentrations than those of fresh and dried peel pieces. The extreme low adsorptive capacity of banana peels may also be attributed to the decay of the banana peels which was observed to occur gradually with time.

4.7.2 Effect of time on Cr (VI) removal

The effect of time on Cr (VI) uptake for the bucket study is shown in Figure 4-15. The percentage chromium removal was calculated from the difference obtained from the influent wastewater and the sampled treated effluent after a retention period of one week in the buckets

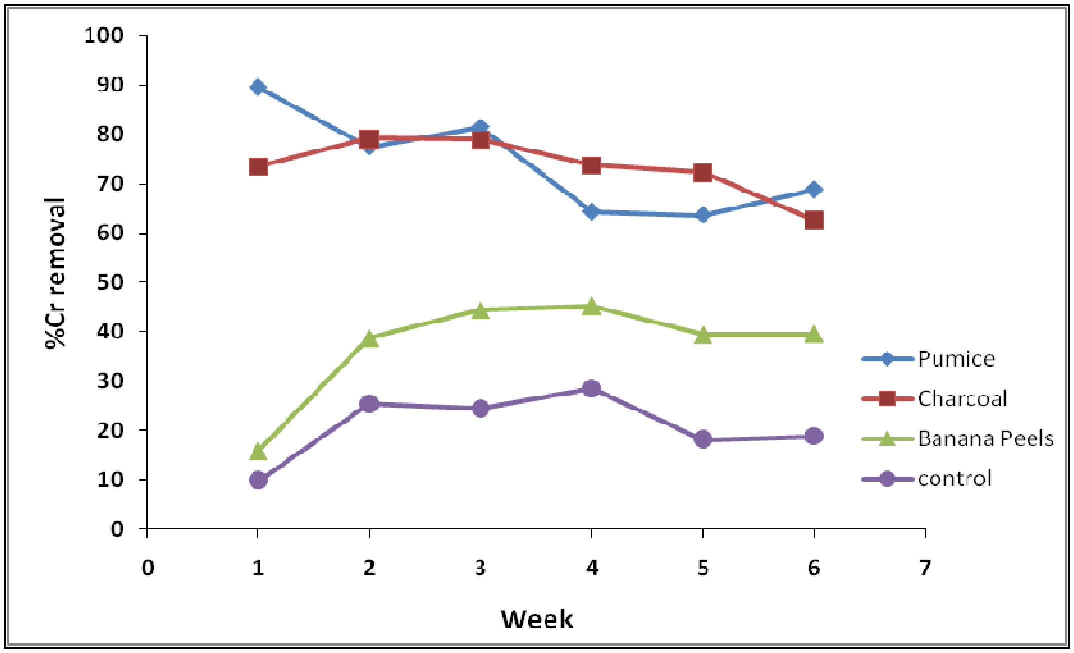


Figure 4-15: Effect of time on the Cr adsorption by Pumice, Charcoal and Banana peels in Bucket setup

Pumice was observed to have the highest potential of chromium uptake, with the initial uptake levels at 89.5%. However, with time pumice showed a declining trend in the adsorption capacity. Banana peels and charcoal were observed to have an initial gradual increase in chromium uptake followed by reduction in chromium uptake in the subsequent weeks. Maximum chromium uptake for charcoal and banana peels was observed on the third week with uptakes of 79.0% and 45.2% respectively. The control bucket in the experiment, which had no adsorption media, indicated low levels of chromium removal with maximum chromium removal of 27%. The decreasing trend in Cr (VI) uptake observed with time all the three adsorbent materials may however be associated with the gradual saturation of the adsorbent as the chromium ions fill up the available binding sites.

Reduction in Cr (VI) conentration observed in the control experiment may be associated with precipitation as well as biological transformations. Precipitation may result from the lowering of pH levels through continued reaction of aluminum sulphate (alum) with the wastewater, as well as natural precipitation of Cr (VI), although it is not a major removal mechanism (Palmer *et al.,* 1990). Bacteria can also enzymatically reduce Cr (VI) by both aerobic and anaerobic pathways. However, microbial reduction only becomes kinetically important in aerobic environments (Fendorf *et al.,* 2001).

Compared to the control, with a mean Cr (VI) removal of 22%, the three adsorbents showed potential for Cr (VI) removal in wastewater. Pumice with a mean chromium removal of 74.2% was observed to have the highest adsorptive capacity of Cr (VI) compared to charcoal and banana peels (Figure 4-16). Charcoal had a mean of 73.4% and banana peels with a mean of 37.2% had the lowest adsorption capacity.

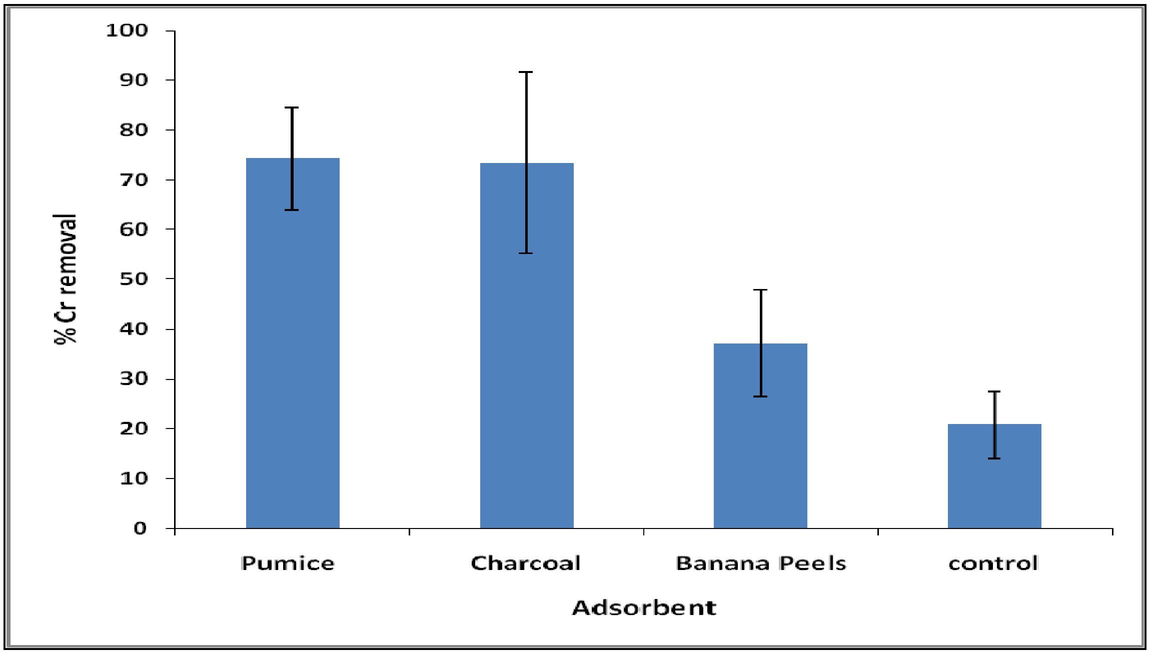


Figure 4-16: Mean % Cr (VI) removal by Pumice, Charcoal and Banana peels in Bucket setup.

ANOVA conducted using the mean % Cr (VI) removal by the three adsorbents materials shows significant differences with the p-value being less than 0.05 (Appendix 4). However, further comparison of the adsorbent materials and the control, using Tukey method, shows that pumice with a mean % Cr (VI) removal of 74.2% and charcoal with

73.4% are not significantly different. These results are comparable to the laboratory studies conducted showing agreement that pumice and charcoal are not significantly different. With their adsorption capacities being higher than those of banana peels, this means that both pumice and charcoal can be used for efficient adsorption of chromium. Although laboratory studies show high adsorptive capacities of 73.3% by banana peels, its practical applications in industries for high chromium containing wastewater is poor with only 37.2% chromium removal being observed for the bucket study using tannery wastewater. This observed low adsorptive capacity in the bucket study using banana peels may have resulted from the degradation of the peels with time. Degradation results in the breakdown of the carboxyl and hydroxyl groups involved in the binding of the chromium ions, hindering the practical applicability of banana peels in full scale wastewater treatment.

4.7.3 Adsorbent bed cells data

Mean residual chromium evaluated from the treated wastewater using pumice, charcoal and banana peels in adsorbent cells, and their mean Cr (VI) levels are presented in Figure 4-17.

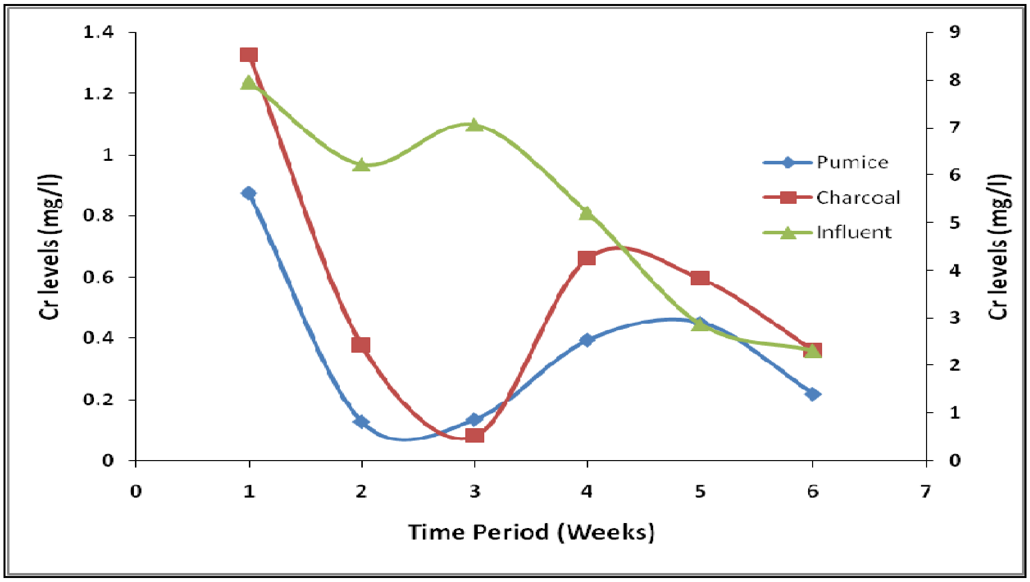


Figure 4-17: Chromium levels of Influent and after treatment using pumice and charcoal.

There was an initial reduction of chromium levels in the wastewater; however a trend of reduced adsorptive capacity was observed with passage of time. This reduction of adsorptive capacity is typical of all adsorbents, as the materials gradually get saturated. Generally, it was observed that the adsorption treatment process was effective in attenuating chromium levels from the tanning process. Chromium levels were observed to have declined from the initial high inflow levels to low levels in the effluent (Figure 4-17). The levels of chromium in the waste water were reduced to levels way below the NEMA standards (2 mg/l) by both pumice and charcoal adsorbents. This indicates a high efficiency in the removal of the chromium levels by the combined effects of pre-treatment (settling tank) and the adsorbent media. Thus, pumice and charcoal can be practically applied for chromium removal in tannery wastewater to meet the required effluent wastewater standards.

a) Influence of time on the adsorption of chromium

The results obtained on the uptake of Cr (VI) with time shows an initial % Cr (VI) uptake increase from the first week to the third week, followed by % Cr^+ adsorption decrease (Figure 4-18). On the third week, charcoal was observed to have the highest mean % Cr (VI) uptake at 98.9%, while pumice had the highest mean % Cr^+ uptake at 98%,. However, the mean % Cr (VI) uptake of pumice was observed to be higher than that of charcoal throughout the duration of study except on the third week. This high chromium uptake is associated with the presence of silica and aluminum oxide in pumice, and the carbon component in charcoal, as well as the porous structures of the two materials.

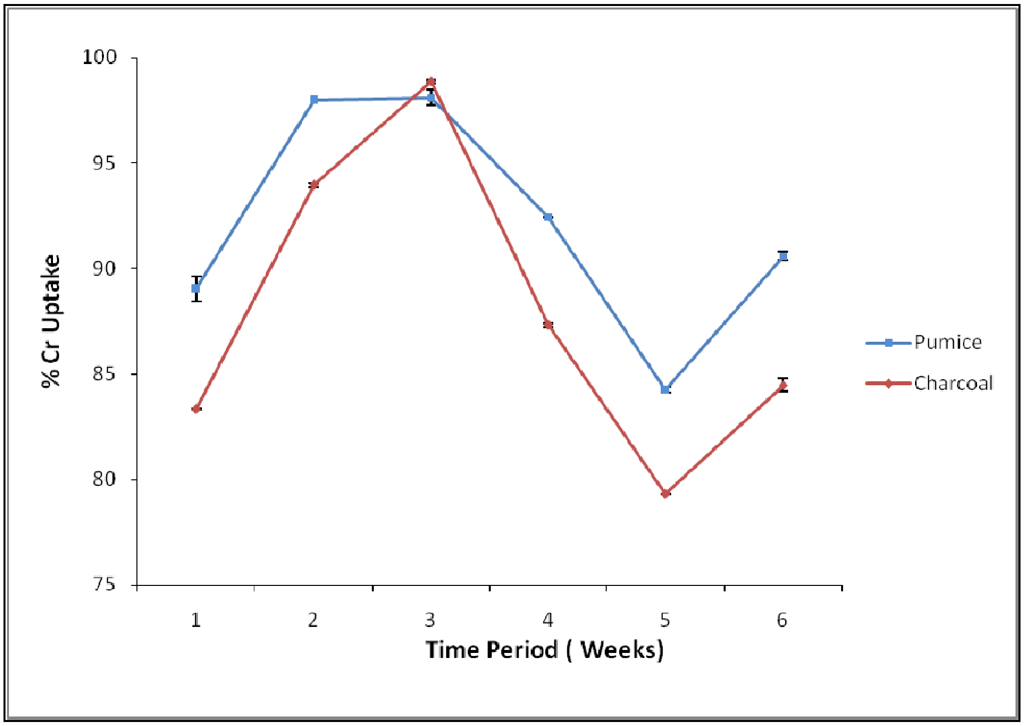


Figure 4-18: Effect of time on the mean % Cr (VI) adsorption by Pumice and Charcoal

The trend observed can be explained by the presence of high numbers of active sites for adsorption, which led to increased % Cr (VI) uptake up to the third week. As the active sites available become saturated, the adsorption of Cr^+ decreases, resulting to the decrease of % Cr (VI) adsorbed after the third week. Statistically, ANOVA carried out on % Cr (VI) removal by the pumice and charcoal adsorbents with respect to time showed that time affects the % chromium removal with a *p*-value of 0.003 (Appendix 5). On further analysis, there was no evidence of an interaction effect of time and adsorbent materials. Hence, time reduced the adsorptive capacity of the adsorbents as a result of saturation of adsorbent sites. Thus, for practical applicability, monitoring of ion chromium removal is necessary, to ensure efficient treatment processes. As saturation occurs, desorption processes may be carried out to enable reuse of the materials.

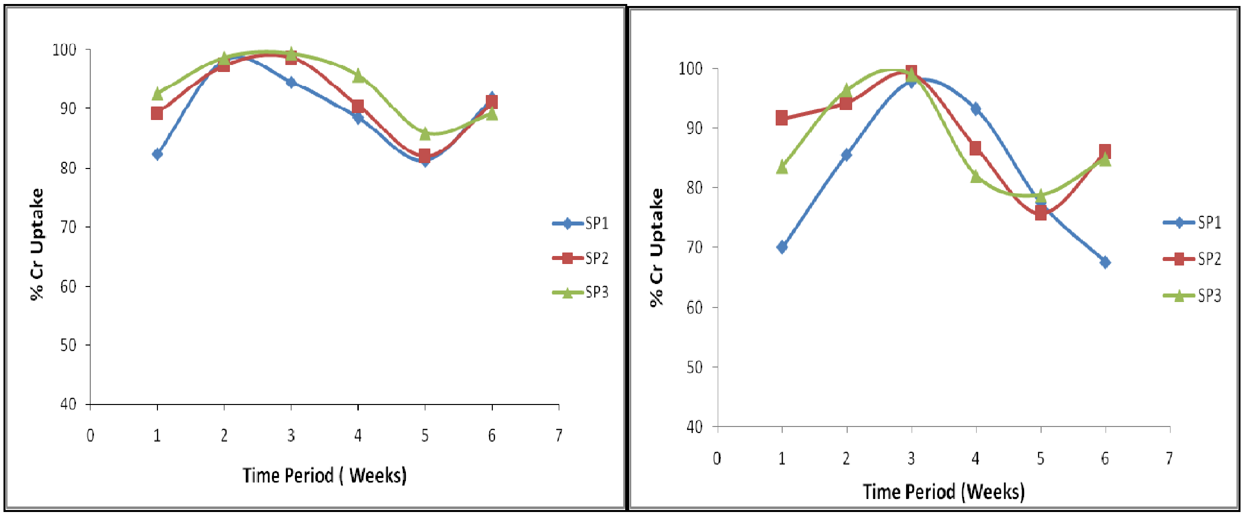
Comparing the results of pumice and charcoal obtained from the adsorbent bed and bucket studies in the field, similar adsorptive capacities with only slight differences were observed (Table 4-11). ANOVA showed that there were no significant differences observed in % chromium removal by the two adsorbent materials (Appendix 5). This means that pumice and charcoal can both be used in the removal of chromium.

Table 4-11: Comparison of the maximum % chromium removal in the laboratory and field studies

Adsorbent	Laboratory studies (Powdered)	Bucket studies	Constructed adsorbent bed study
Pumice	69.3	74.2	98
Charcoal	70.6	73.4	98.9
Banana peels	73.3	37.2	-

b) Effect of adsorbent depth on chromium uptake

Results obtained on the effect of adsorbent depth on Cr (VI) uptake are presented in Figures 4-19a and 4-19b. High % Cr (VI) uptakes were observed to occur at sampling point 3 (SP3), located at the bottom of the constructed cell. The lowest % Cr (VI) uptakes were observed at sampling point 1 (SP1), located 10 cm from the top of the adsorbent bed cell. This was observed for both the pumice and charcoal cells. At sampling point 3, pumice recorded a high % Cr (VI) uptake of 99.3% and charcoals a high of 99.1%. Lowest values were recorded at SP1 at % Cr (VI) uptakes of 81.3% for pumice and 67.5 % for charcoal. From Figure 4-19, it is also observed that with time the adsorption capacity decreased, which may be associated with saturation of the adsorbents material.



(a) (b)

Figure 4-19: Effect of depth on Cr (VI) uptake using a) Pumice and b) Charcoal

The high percentages of Cr (VI) removal observed at the lowest sampling point (SP3) may be explained by the fact that the wastewater is exposed to greater surface area as it infiltrates from the inflow at the surface of the adsorbent media to the outflow at the bottom. Wastewater at the surface was exposed to only a small fraction of the surface area of the adsorbent media (contained within the first 10 cm depth from the surface). As the depth increases the contact surface area increases, increasing the available binding sites hence increased adsorption. This effect is observed at sampling point 2 (SP2) and sampling point 3 (SP3). However, there were no significant differences in the percentage chromium removal at the different depths for both pumice and charcoal (Appendix 6a and 6b). The *p*-values for pumice and charcoal were 0.511 and 0.448 respectively. From the ANOVA table it is also observed that on average sampling point 1 had the lowest chromium removal. Hence although there is no significant difference, sampling point 3 provides a slightly higher level of chromium removal and should be recommended in design applications of adsorption systems.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

This chapter presents the conclusions based on the study results from the laboratory and field studies

1. The tannery wastewater is characterized by high acidity, high BOD, COD, TSS and high dissolved solids, with major chemical constituents of sulphide and chromium. Total chromium levels were observed at 4.4 (0.80 SD) mg/l.

2. Banana peels has high pore volumes compared to pumice and charcoal. Pumice contains high levels of silicon dioxide (SiO_2) of 58.74%, and Aluminum oxide (Al_2O_3) of 12.25%, charcoal has a high carbon content of approximately 95%, while banana peels contain high volatile matter content of 76.8%, with a chemical compositions of K (6.63%), Mg (0.34%), Fe (0.57%), Na (0.0017%) and Cr (0.104%).

3. Contact time, initial concentration and pH influence the adsorptive capacities of chromium by the three adsorbent materials namely, pumice, charcoal and banana peels. With increase in contact time, the percentage chromium removal increases, however the rate of chromium removal by the three adsorbents decrease. Removal of Cr (VI) is observed to be most effective in acidic condition for all the three adsorbents, with the amount of Cr (VI) adsorbed increasing with the raise in pH from 3.0 to 6.0. An increase in the initial concentration of Cr (VI) increased the amount of Cr (VI) adsorbed (mg/g), while the percentage (%) Cr^+ removed decrease.
4. The adsorption kinetics of the three adsorbent materials followed the Second-pseudo-order kinetics model (R^2>0.987). The three adsorbents fitted well with both

the Langmuir and Freundlich isotherm models. The Freundlich model (R^2=0.999) provided slightly better model than the Langmuir isotherm model (R^2=0.997).

5. Field experiments conducted using tannery wastewater in bucket and constructed adsorbent bed setup, showed the potential of pumice and charcoal in removal of chromium to levels below the NEMA standards of 2mg/l. Pumice and charcoal were not significantly different in their potential for chromium removal and this research demonstrates their practical applicability in real life industrial wastewater treatment. Banana peels applicability in the field was limited by biodegradation resulting in the breakdown of the carboxyl and hydroxyl groups involved in the binding of the Cr (VI) as well as low regeneration potential.

6. Depth was observed to have no considerable effect on the amount of chromium adsorbed from the wastewater in a batch feeding system.

5.2 RECOMMENDATIONS

The following recommendations are suggested from the results and the methodology used in this study

- Pumice and charcoal should be utilized in small-scale leather industries to achieve the required wastewater standards. However, Pumice provides a better option compared to charcoal to avoid environmental degradation from cutting down of trees.
- Evaluation of continuous feeding to compare with batch feeding-Batch feeding provides some rest time for the media, in real life situations, processes are more frequent a continuous flow regime even where an equalization tank exists. There is therefore need to test the robustness of the system using continuous flow feeding.
- Evaluation of cost-effectiveness and cost-benefit analysis of the adsorbent materials is necessary by use decision oriented tools to ascertain which of the three materials attain chromium removal treatment goals most efficiently and effectively.
- Evaluation of adsorbents modifications method that is efficient and cost effective of the three adsorbents materials to improve on their adsorptive capacity and practical applicability.

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APPENDICES

Appendix 1: ANOVA on effect of time on chromium removal

Appendix 1a): ANOVA on effect of time on chromium removal at 20mg/l Initial concentration

```
General Linear Model: % Cr removal- 20mg/l_1 versus Time, Adsorbent

Method
Factor coding  (-1, 0, +1)

Factor Information

Adsorbent value - Pumice (1), Charcoal (2), Banana peels (3)

Factor        Type     Levels     Values
Time          Fixed    10         1, 5, 10, 20, 30, 60, 90, 120, 150, 180
Adsorbent     Fixed     3         1, 2, 3

Analysis of Variance
Source        DF     Adj SS     Adj MS     F-Value     P-Value
  Adsorbent    2     301.07    150.533      11.88       0.001
  Time         9      14.59      1.621       0.13       0.998
Error         18     228.12     12.673
Total         29     543.78

Model Summary
     S        R-sq      R-sq(adj)    R-sq(pred)
3.55995     58.05%      32.41%        0.00%

Comparisons for % Cr removal- 20mg/l_1

Tukey Pairwise Comparisons: Response = % Cr removal- 20mg/l_1, Term =
Adsorbent

Grouping Information Using the Tukey Method and 95% Confidence
Adsorbent     N    Mean     Grouping
    3         10   74.8      A
    1         10   68.4          B
    2         10   67.8          B
Means that do not share a letter are significantly different.
```

Appendix 1b): ANOVA on effect of time on chromium removal at 50mg/l Initial concentration

```
General Linear Model: % Cr removal- 50mg/l versus Time, Adsorbent

Method
Factor coding  (-1, 0, +1)

Factor Information
Adsorbent value - Pumice (1), Charcoal (2), Banana peels (3)

Factor        Type    Levels    Values
Adsorbent     Fixed     3       1, 2, 3
Time          Fixed    11       1, 5, 10, 20, 30, 60, 90, 120, 150, 180, 200

Analysis of Variance

Source        DF    Adj SS    Adj MS    F-Value    P-Value
  Adsorbent    2    10.975    5.4875     14.21      0.000
  Time        10    41.649    4.1649     10.78      0.000
Error         20     7.725    0.3862
Total         32    60.349

Model Summary

     S        R-sq      R-sq(adj)   R-sq(pred)
0.621476    87.20%     79.52%        65.15%


Comparisons for % Cr removal

Tukey Pairwise Comparisons: Response = % Cr removal, Term = Adsorbent

Grouping Information Using the Tukey Method and 95% Confidence

Adsorbent    N     Mean    Grouping
    3       11   57.3737     A
    1       11   56.3030       B
    2       11   56.0404       B

Means that do not share a letter are significantly different.
```

Appendix 2: ANOVA for mean chromium removals at different initial concentrations

```
General Linear Model: % Cr removal versus Initial Concentration, Adsorbent

Method
Factor coding  (-1, 0, +1)

Factor Information
Initial concentration value -5 mg/l (1), 10 mg/l (2), 20 mg/l (3), 30 mg/l (4), 40 mg/l
(5), 50 mg/l (6)
Adsorbent value - Pumice (1), Charcoal (2), Banana peels (3)

Factor                  Type    Levels   Values
Initial Concentration   Fixed    6       1, 2, 3, 4, 5, 6
Adsorbent               Fixed    3       1, 2, 3

Analysis of Variance
Source                              DF     Adj SS    Adj MS   F-Value   P-Value
  Initial Concentration              5    1935.22   387.045   2660.26    0.000
  Adsorbent                          2     335.47   167.737   1152.90    0.000
  Initial Concentration*Adsorbent   10     630.05    63.005    433.05    0.000
Error                               18       2.62     0.145
Total                               35    2903.36

Model Summary
       S        R-sq    R-sq(adj)    R-sq(pred)
0.381434      99.91%       99.82%        99.64%

Comparisons for % Cr removal

Tukey Pairwise Comparisons: Response = % Cr removal, Term = Initial
Concentration

Grouping Information Using the Tukey Method and 95% Confidence
Initial Concentration   N     Mean    Grouping
          1             6   46.9865   A
          2             6   41.8011     B
          3             6   38.5598       C
          4             6   33.4123         D
          5             6   32.4359           E
          6             6   24.0629             F

Means that do not share a letter are significantly different.
```

Tukey Pairwise Comparisons: Response = % Cr removal, Term = Adsorbent

```
Grouping Information Using the Tukey Method and 95% Confidence

Adsorbent   N    Mean    Grouping
    3       12  40.3841    A
    2       12  35.0761      B
    1       12  33.1690        C
Means that do not share a letter are significantly different.
```

Appendix 3: Langmuir and Freundlich Isotherm models One-way ANOVA: R^2 versus Model

One-way ANOVA: R^2 versus Model Method

```
Null hypothesis        All means are equal
Alternative hypothesis At least one mean is different
Significance level     α = 0.05
Equal variances were assumed for the analysis.

Factor Information
Factor  Levels   Values
Model      2     Freundlich, Langmuir

Analysis of Variance
Source  DF   Adj SS    Adj MS   F-Value  P-Value
Model    1  0.000008  0.000008    0.82     0.386
Error   10  0.000101  0.000010
Total   11  0.000110
Model Summary
     S       R-sq    R-sq(adj)  R-sq(pred)
0.0031833  7.60%     0.00%       0.00%

Means
Model       N    Mean      StDev         95% CI
Freundlich  6  0.998667  0.000816  (0.995771, 1.001562)
Langmuir    6  0.99700   0.00443   ( 0.99410,  0.99990)

Pooled StDev = 0.00318329
```

Appendix 4: One-way ANOVA: Bucket study mean % Cr removal versus adsorbent

```
One-way ANOVA: % Cr removal versus adsorbent

Method
Null hypothesis         All means are equal
Alternative hypothesis At least one mean is different
Significance level      α = 0.05
Equal variances were assumed for the analysis.

Factor Information
Factor       Levels    Values
Adsorbent      4        b, c, ct, p
Adsorbent value - Pumice (p), Charcoal (c), Banana peels (bp), Control(ct)

Analysis of Variance
Source       DF     Adj SS      Adj MS    F-Value     P-Value
Adsorbent     3     5955.77     1985.26    182.60      0.000
Error         8      86.98        10.87
Total        11     6042.75

Model Summary
    S          R-sq       R-sq(adj)      R-sq(pred)
3.29734      98.56%       98.02%          96.76%

Means
Adsorbent      N       Mean       StDev         95% CI
  b            3      37.199      1.462     (32.809, 41.589)
  c            3      73.38       2.36      ( 68.99,  77.77)
  ct           3      23.43       3.34      ( 19.04,  27.82)
  p            3      74.19       4.97      ( 69.80,  78.58)
Pooled StDev = 3.29734

Tukey Pairwise Comparisons
Grouping Information Using the Tukey Method and 95% Confidence

Adsorbent     N       Mean     Grouping
  p           3       74.19       A
  c           3       73.38       A
  b           3      37.199         B
 ct           3       23.43           C

Means that do not share a letter are significantly different.
```

Appendix 5: ANOVA for constructed beds means% chromium removals with effect of time

General Linear Model: % Cr removal versus Time (Week), Adsorbent

Method

Factor coding (-1, 0, +1)

Factor Information

Adsorbent value - Pumice (1), Charcoal (2)

```
Factor          Type     Levels   Values
 Time (Week)    Fixed      6       1, 2, 3, 4, 5, 6
 Adsorbent      Fixed      2        1, 2
```

Analysis of Variance

```
Source                      DF    Adj SS    Adj MS    F-Value   P-Value
  Time (Week)                5   1175.37   235.074     5.04      0.003
  Adsorbent                  1    157.79   157.794     3.38      0.078
  Time (Week) *Adsorbent     5     48.06     9.612     0.21     0.957
Error                       24   1120.18    46.674
Total                       35   2501.40
```

Model Summary

```
     S        R-sq      R-sq(adj)    R-sq(pred)
6.83184    55.22%        34.69%       0.00%
```

<u>Comparisons for % Cr removal</u>

Tukey Pairwise Comparisons: Response = % Cr removal, Term = Adsorbent

Grouping Information Using the Tukey Method and 95% Confidence

```
Adsorbent      N    Mean       Grouping
    1         18   92.0555       A
    2         18   87.8683       A
```

Means that do not share a letter are significantly different.

Appendix 6: ANOVA on % Cr removal by pumice and charcoal versus depth

Appendix 6a): One-way ANOVA: % Cr removal versus Pumice Adsorbent depth

```
One-way ANOVA: % Cr removal versus Pumice Adsorbent depth

Method
Null hypothesis        All means are equal
Alternative hypothesis  At least one mean is different
Significance level     α = 0.05
Equal variances were assumed for the analysis.

Factor Information
Factor            Levels        Values
Pumice depth        3          P1, P2, P3

Analysis of Variance
Source           DF    Adj SS    Adj MS    F-Value    P-Value
Pumice depth      2     51.37     25.69      0.70      0.512
Error            15    549.65     36.64
Total            17    601.02

Model Summary
    S          R-sq      R-sq(adj)     R-sq(pred)
6.05335       8.55%        0.00%          0.00%

Means
Pumice  depth     N     Mean    StDev       95% CI
     P1           6    89.43     6.72    (84.17, 94.70)
     P2           6    91.46     6.04    (86.20, 96.73)
     P3           6    93.57     5.33    (88.31, 98.84)

Pooled StDev = 6.05335

Tukey Pairwise Comparisons
Grouping Information Using the Tukey Method and 95% Confidence

Pumice depth    N     Mean     Grouping
    P3          6     93.57       A
    P2          6     91.46       A
    P1          6     89.43       A

Means that do not share a letter are significantly different.
```

Appendix 6b): One-way ANOVA: % Cr removal versus Charcoal Adsorbent depth

```
One-way ANOVA: % Cr removal versus Charcoal Adsorbent depth

Method
Null hypothesis         All means are equal
Alternative hypothesis  At least one mean is different
Significance level      α = 0.05
Equal variances were assumed for the analysis.

Factor Information
Factor           Levels   Values
Charcoal depth     3      C1, C2, C3

Analysis of Variance
Source          DF    Adj SS    Adj MS    F-Value    P-Value
Charcoal depth   2     162.6     81.28      0.85      0.448
Error           15    1439.3     95.95
Total           17    1601.9

Model Summary
    S        R-sq      R-sq(adj)    R-sq(pred)
9.79564     10.15%       0.00%        0.00%

Means
Charcoal depth    N     Mean     StDev       95% CI
    C1            6     81.92    12.36    (73.40, 90.45)
    C2            6     88.89     8.15    (80.37, 97.42)
    C3            6     87.46     8.28    (78.93, 95.98)
Pooled StDev = 9.79564

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence
Charcoal depth    N    Mean    Grouping
    C2            6    88.89      A
    C3            6    87.46      A
    C1            6    81.92      A
Means that do not share a letter are significantly different.
```