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FACULTY OF ENGINEERING

DEPARTMENT OF CIVIL & CONSTRUCTION ENGINEERING

**Phytoremediation of Hexavalent Chromium in Effluent Tannery Sludge and
Chromium Contaminated Soils by Using *Ricinus Communis* Plant**

MSc Thesis

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**A thesis submitted in partial fulfillment of the requirements for the award of the
Degree of Master of Science in Civil Engineering (Environmental Health
Engineering) of the University of Nairobi.**

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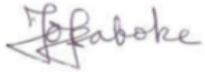
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ABSTRACT

Heavy metal pollution is a global problem of expanding apprehension due to its toxic effects on the environment which in turn adversely affects Flora and Fauna. Tanning industries have a sludge effluent that is highly contaminated with chromium which is mostly disposed in sludge pits hence polluting the environment. Given the use of chromium in the tanning process and handling of solid wastes in tanning industries, there is high chromium contamination both in the soils surrounding tanning industries and high chromium levels in the tannery effluent sludge after treatment process. The objective of this research is therefore to establish the concentration of chromium VI in tannery effluent sludge; determine the chromium phytoremediation potential of *Ricinus Communis* (castor oil plant) and Compare efficacy of citric acid as a chelating agent in phytoremediation of chromium VI from chromium contaminated soil and tannery sludge.

Samples of tannery sludge were collected from Aziz Tanneries Ltd in Nairobi, and the concentration of Hexavalent Chromium determined using Atomic Absorption Spectrophotometer (AAS). The *Ricinus communis* seeds were be collected from local castor oil bean plant farmers within Kenya, Germinated, and the Seedlings were transferred to trial pots and watered twice a day and weeded as it deemed necessary. On, thirtieth, forty fifth and sixtieth days the plants were harvested from the pots, cleaned using faucet water and deionized water, and isolated into shoots, stems and roots ready for analysis using the AAS. Bio-Concentration Factor (BCF) and Translocation Factor (TF) were calculated to give the indication of the phytoremediation potential of *Ricinus Communis* plant.

The average concentrations of Hexavalent Chromium (CrVI) Level from the Tannery sludge collected was as 14.936mg/kg this exceeded the United States Environmental Protection Agency (U.S. EPA) regulatory limits for protection of human health and the environment of 0.01mg/kg and the National Environmental Management Authority and WHO limits of 0.05mg/kg. the Hexavalent Chromium concentrations were high at the roots compared to the areal parts in five of the pots at the 30th and 45th day. On the 60th day there was high concentration of hexavalent chromium in leaves, stem and roots of *Ricinus communis* in tannery sludge media, which infers translocation of the metal.

Application of the chelate on the tannery sludge and red soil mixture of ratio 1:1, increased absorption of Hexavalent Chromium. At the 30th day the percentage increase was 39% and more than 100%, from the 45th day. The total accumulation of Hexavalent chromium in *R. Communis* plant at the end of the exposure period was 11.74 ppm in the pot without chelate and 43.54ppm in the pot with chelate which is approximately 3.7 times more. The bio concentration factor ranged between 0.01 and 2.68. The results in this study showed that *Ricinus Communis* planted on

Tannery sludge had BCF values > 1 from the 45th day to 75th day. The highest translocation factor (2.524), was noted at 75days exposure time, followed by 1.997 at exposure time of 75days in the chromium polluted soil and soils mixed with tannery sludge (1:1 ratio) respectively. Basically, since the translocation factors were all greater than one at the exposure time of 60 days; this means that *Ricinus communis* plant has potential for phytoremediation by phytoextraction of chromium with exposure time of between 60 to 75 days. This agrees with Rani, et.al. (2017) on the study on “stabilization of tannery sludge amended soil using *Ricinus Communis*”, where they concluded that *Ricinus Communis* plant is suitable for growth in heavy metal rich tannery sludge soil.

The *Ricinus communis* plant, demonstrated potential for phytoremediation of hexavalent chromium by both Phyto stabilization and phytoextraction which may be attributed to its tolerance and considerable biomass production.

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LIST OF ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectrophometer
BCF	Bio Concentration Factor
TF	Translocation Factor
NEMA	National Environmental Management Authority
USEPA	United States Environmental Protection Agency
ROS	Reactive Oxygen Species
Chromium VI	Hexavalent Chromium
CCA	Chromated Copper Arsenate
DNA	Deoxyribonucleic Acid
UNIDO	United Nations Industrial Development Organization
DDTs	Dichlorodiphenyltrichloroethane
R. Communis	Ricinus Communis
EDTA	Ethylenediamine Tetraacetic Acid
HMs	Heavy Metals
WHO	World Health Organization
°C	Degree Centigrade
ppm	Parts per million
ppb	Parts per billion
mg/l	Milligrams per liter
pm	picometer

CHAPTER 1: INTRODUCTION

1.1 Background

Pollution from heavy metals is a global issue of expanding apprehension due to its toxic effects on the environment which in turn adversely affects Flora and Fauna. Metallic component with a usually high density is referred to as a heavy metal and could be harmful and toxic at low and high concentrations (Rao et.al.2018). They include, lead (Pb) cadmium (Cd), Arsenic (As) Thallium (TI), Chromium (Cr), and mercury (Hg) among others. Geological and human-caused activities are both sources of heavy metal contamination. Mining, smelting, military operations, fuel production, fertilizer use, and waste water from tanning industries and municipal waste disposal are among them. Overwhelming metals are typical crustal components that cannot be corrupted or annihilated, but can be extracted. “Physical, chemical, and biological” methods can be used to clean up heavy metal-contaminated soil (Zaidi et.al 2014). These remediation techniques include “precipitation, ion-exchange, reverse osmosis and phytoremediation” (Ghosh and Singh, 2005).

Oliveira, P.(n.d) records that “Chromium (III) salts, especially chrome alum and chromium (III) sulfate, are used in the tanning of leather”,(p. 393). The chromium (III) balances out the calfskin by cross connecting the collagen filaments inside the cowhide. Rippner, D. (n.d). Furthermore, Rippner, D. (n.d) records that “Chromium tanned leather can contain between 4 and 5% of chromium, which is tightly bound to the proteins”. Good administration “of chromium in tanning industry”, for example, recuperation and reuse, “direct/indirect recycling”, utilization of less chrome are “practiced” to more readily oversee chromium use in tanning (Sreeram, & Ramasami, 2003). Speciation of chromium in the effluent environment, pH and Redox causes for conversion from chromium III to chromium VI (Ghosh and Singh, 2005)

Phytoremediation, is the utilization of flora and their associated microorganisms to mitigate the ecological problems without the need to dig out the contaminant material and dispose of it elsewhere, it offers a viable, minimal effort and sustainable intends to accomplish the ideal outcomes (Hannink *et.al.*, 2001).

Tanneries are a standout amongst the most conspicuous wellsprings of chromium contamination to the amphibian condition. Pawlikowski *et.al.* (2006), argues that if wastewater from tanneries is not sufficiently treated, it contaminates surface water and sediments to inadmissible levels. This is also true with various investigations from Poland, India and numerous different nations. (Molik *et.al.*, 2004; Khwaja *et.al.*, 2001; Ward *et.al.* 1999). Tanning industries have a sludge effluent that is highly contaminated with chromium which is mostly disposed in sludge pits. “Fleshing and

slime are noteworthy strong solid wastes radiating from “tanning and treatment of tannery wastewater” (Ahamed & Kashif ,2014). “It is reported that about 140-200 kg of fleshing, which are putrescible by nature, are generated for every tonne of leather processed” (Ahamed & Kashif ,2014). Correspondingly huge amount of sludge is created when tanning industries treat their waste water. In Tamil Nadu state tanning industries produce around 100 tons of slime daily and since the “sludge has chromium”, it is categorised as dangerous matter (Ahamed & Kashif ,2014). In most countries tenable landfill sites are lacking, hence the “solid waste and sludge are dumped in low-lying areas in an inappropriate and uncontrolled manner or are just piled up within the tannery premises”, (Ahamed & Kashif ,2014). Consequently, the dumping of solid wastes including chrome-containing wastes presents significant issue because of stringent ecological guidelines. The present administration of these strong waste triggers some auxiliary and tertiary natural effects, (Ahamed & Kashif 2014).

This research will therefore come up with a remediation strategy to rehabilitate chromium contaminated soils in various tanning industries in Kenya and tannery effluent sludge.

1.2 Problem Statement

Tanning Industry as an agricultural-based area is considerably the major “source” of perilous “wastes” (Mwinyihija *et.al.*, 2005). Past studies have linked “leather tanning” and dying as one of the focal businesses that generate harmful and toxic wastes (Khwaja A.R. 1998).

Given the use of chromium in the tanning process and handling of solid wastes in tanning industries, there is high chromium contamination both in the soils surrounding tanning industries and high chromium levels in the tannery effluent sludge after treatment process. “In Kenya Chromium occurrence in the Asili tanneries surroundings exceeded NEMA set standard of 2.0 mg/l in soil sampled around the dump site by 2631.38mg/L”, (Oruko *et.al* 2014). “Upon ingestion by animals, chromium causes irritations in the stomach, ulcer and anemia while for humans, it causes skin disturbance, gastric trouble, liver harm, and yellow discoloration of the tongue and teeth” (Torresdey *et.al.*, 2005). According to Kolomaznik *et.al.*, (2008), about 30% of cancer risk was identified among the tannery workers in Italy and Sweden. Furthermore, research has likewise demonstrated that even refined calfskin items especially “those in direct contact with the skin”, for example, “gloves or shoes” have raised degrees of a “toxic” compound; Hexavalent Chromium which is, viewed as a solid allergen causing skin responses like dermatitis (Hayes, 1997).

Furthermore, most of the tanning industries have sludge pits where they dispose the effluent sludge from the industry processes which contain very high level of chromium. The *Ricinus Communis* plant has been spotted to grow in various tannery effluent disposal pits in Kenya

Several species of plants grow in the natural wetland and watercourse, for instance, papyrus, reeds, and shrubs, all of which aid in the absorption of heavy metals in the effluent. However, the extent to which plants extract chromium is a topic that has received little research (Irumba N. 2014). Therefore, there is need to study the phytoremediation potential of plants that have been found to grow at tannery effluent disposal pits and wetlands receiving waste water from tanneries. This study assessed the Hexavalent chromium levels of tannery effluent sludge of Aziz Tanneries Ltd and the phytoremediation potential of *Ricinus communis* plant in a 75-day period.

1.3 Justification of the study

The leather industry is one of the key agricultural subsectors and it has a high potential towards economic growth and employment in Kenya. Mwinyihija M, (2014) states that “The tanning sector in Kenya through the reviewed period of 2013 accrued Kenya Shillings 13.6 billion in earnings from the leather operating tanneries and leather units”. Besides, it was delineated that in any event “22,000 persons were perceived to directly be employed in the leather sector”, (Mwinyihija M, 2014). All the tanneries in Kenya utilize chromium in tanning of calf skin. Considering deposition of solids, “it gets apparent that crude unsettled tannery wastewaters can cause encrustation (of calcium carbonate) and genuine rust of metals as well as concrete sewers due to H₂S natural oxidation to H₂SO₄” (Balasubramanian et.al., 2000).

Chromium in waste water is never reduced by the conventional methods of wastewater treatment but will find itself in the effluent sludge of the treatment system. Da silva et.al. (2011) Notes that “Chromium salts (particularly chromium sulphate) are the most widely used tanning substances today”. Ahamed M. et.al (2014) argues that “Hides tanned with chromium salts have a good mechanical resistance, an exceptional dyeing suitability and improved hydrothermic resistance in relation to hides treated with vegetable substances regrettably only a portion of the chromium salts utilized in the tanning process react with the skins” (Ahamed M. et.al 2014). Alfatih A. et.al (2015) noted that the “remainder of the salts in the tanning exhaust shower are subsequently sent to a depuration plant where the chromium salts end up in the slime.” According to Ahamed & Kashif (2014), among the main emergent ecological issues in “the tanning” business “is the disposal of sludge” created as a side-effect of “tannery wastewater treatment”.

Hence high poison loads, involving chromium, sulfates, chlorides and might without much of an extend interfere with key natural forms utilized in wastewater treatment systems. What's more these contaminations affect the nature of the tolerating terrestrial and maritime systems within the locale of the discharge centers. For instance, Oruko et.al (2014) confirmed that: “the soils sampled after treatment of solid wastes within Asili tanneries limited Kenya for selected pollutant had chromium levels at 2633.38mg/l” which is higher than limits set by National Environmental Management Authority Kenya.

Generally, “leather industry is associated with the generation of huge amounts of solid waste and disposal of this waste become a serious problem” (Amita et.al. 2005). “Chromium in the effluent is a major concern for tanning industry” (Saxena et.al.2018). Chemical precipitation techniques are ordinarily utilized in expulsion “of chromium” however this contributes to a lot of “chrome-bearing solid waste”, which is “uneconomical when the concentration of chromium in the effluent is low” (Onyanha et.al 2008). “Ion exchange and membrane separation” strategies are moderately costly (Onyanha et.al 2008). All the above challenges call for a strategy that is economical and environmental friendly. Assessing the rate of remediation using the plants would promote remediation efforts through growth of plants that accumulate most chromium. These plants can be planted at tannery effluent disposal sites to help in phytoremediation, of chromium.

This study therefore explored phytoremediation of chromium contaminated soils and tannery sludge by use of *Ricinus Communis* as a means of protecting the environment from pollution due to chromium.

1.4 Research Objectives

The overall objective of this study was to investigate the quantity of Hexavalent Chromium in the tannery sludge as well as determine the chromium phytoremediation potential of *Ricinus Communis* Plant.

1.4.1 Specific objective

1. Establish the concentration of Hexavalent Chromium in tannery effluent sludge.
2. Determine the Hexavalent Chromium phytoremediation potential of *Ricinus Communis* (castor oil plant)

3. Compare efficacy of citric acid as a chelating agent on phytoremediation of Hexavalent Chromium from chromium contaminated soil and tannery sludge using *Ricinus Communis* Plant
4. Effect of plant exposure period on phytoremediation of Hexavalent Chromium from chromium contaminated soil and tannery sludge using *Ricinus Communis* Plant.

1.5 Research questions

1. What is the concentration of Hexavalent Chromium in Tannery effluent sludge?
2. What is hexavalent chromium phyto remediation potential of *Ricinus Communis*?
3. Does citric acid as a chelating agent affect the phytoremediation of hexavalent chromium from chromium contaminated soil and tannery sludge?

CHAPTER 2: LITERATURE REVIEW

2.1 Chromium

Chromium (Cr) is among the extremely lethal heavy metals discharged into the environment from tanning industries, in nature it's normally a component in the rocks, soils flora and fauna. The three major forms of chromium are chromium (0), chromium (III) and chromium (VI)" (Singh, V. P. 2005 p.272). The chromium lethality "depends on its oxidation state, Cr (VI) species", for example, chromate (CrO_4^{2-})-and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) are harmful, "mutagenic" and cancer-causing, whereas Cr(III) is fundamental to people in managing the digestion of glucose. (Li, et.al., 2008). Due to the toxicity of Hexavalent chromium, deserted chromium generation locales require natural clean up. Chromium "has an atomic number of 24, density of 7.19 gcm^{-3} "at 20^0 C "melting point of 1907^0 C and a boiling point of 2672^0 C ". (U.S. Department of Health and Human Services, 2014.)

2.2 Chemistry of Chromium

Chromium is an individual from the transition metals, in cluster 6. Daintith, J. (2004). Chromium (0) has an electronic setup of $4s13d5$, because of the lower vitality of the high turn arrangement. (Whitten, et.al. 2014). Chromium displays extensive scope of conceivable "oxidation states" (Table 2.1). "The most widely recognized oxidation conditions of "chromium are +2, +3, and +6, with +3" being the steadies and "+1, +4 and +5" states uncommon" (Greenwood & Earnshaw, 2016).

Table 2. 1: Common states of chromium

Oxidation state	Availability	Representative compound
-2	Not common	$\text{Na}_2\text{Cr}(\text{CO})_5$
-1	Not common	$\text{Na}_2\text{Cr}_2(\text{CO})_{10}$
0	common	$\text{Cr}(\text{C}_6\text{H}_6)_2$
+1	Not common	$\text{K}_3\text{Cr}(\text{CN})_5\text{NO}$
+2	Not common	CrCl_2
+3	common	CrCl_3
+4	Not common	K_2CrF_6
+5	Not common	K_3CrO_8
+6	common	K_2CrO_4

2.2.1 Trivalent Chromium

Trivalent chromium is very stable; this agrees with Oliveira P. (n.d) in the book the “*Elements*” where he describes the properties of trivalent chromium broadly. Following is an excerpt on the same:

The oxidation state +3 is the most stable, and a large number of chromium (III) compounds are known. Chromium (III) can be obtained by dissolving elemental chromium in acids like hydrochloric acid or sulfuric acid. The Cr^{3+} ion has a similar radius (63 pm) to the Al^{3+} ion (radius 50 pm), so they can replace each other in some compounds, such as in chrome alum and alum. When a trace amount of Cr^{3+} replaces Al^{3+} in corundum (aluminium oxide, Al_2O_3), the red-colored ruby is formed.

Chromium ions tend to form complexes; chromium ions in water are usually octahedrally coordinated with water molecules to form hydrates. The commercially available chromium(III) chloride hydrate is the dark green complex $\text{CrCl}_2(\text{H}_2\text{O})_4\text{Cl}$, but two other forms are known: pale green $\text{CrCl}(\text{H}_2\text{O})_5\text{Cl}_2$, and the violet $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$. If water-free green chromium(III) chloride is dissolved in water then the green solution turns violet after some time, due to the substitution of water for chloride in the inner coordination sphere. This kind of reaction is also observed in chrome alum solutions and other water-soluble chromium(III) salts. “The reverse reaction may be induced by heating the solution”. (Oliveira P. n.d. p.383)

Chromium(III) hydroxide ($\text{Cr}(\text{OH})_3$) is “amphoteric” in nature, dissolving in acidic arrangements to make “ $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ”, It is dried out by heating to create the “green chromium (III) oxide (Cr_2O_3)”, which is a stable oxide with a crystal configuration alike to that of “corundum” (Wiberg et.al. 2001).

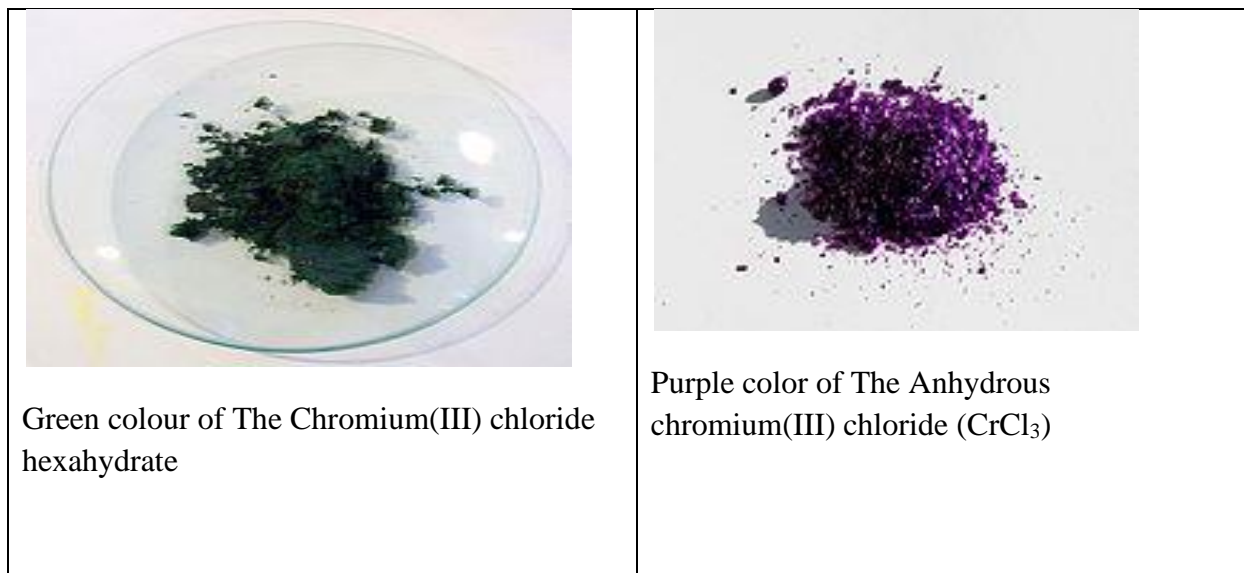


Plate 2.1: Color of chromium III compounds

source: Wiberg et.al. 2001

2.2.2 Hexavalent Chromium (Chromium VI)

Chromium (VI) compounds are strong oxidants at either low or neutral pH, and they contain oxygen as a ligand such as the chromate anion (CrO_2^{-4}) and chromyl chloride (CrO_2Cl_2).except the hexafluoride, Chromium (VI) is most commonly encountered in the chromate (CrO_2^{-4}) and dichromate ($\text{Cr}_2\text{O}_2^{-7}$) anions. (Wiberg, et.al. 2001).

“Chromate is produced industrially by the oxidative roasting of chromite ore with calcium or sodium carbonate. The chromate and dichromate anions are in equilibrium: $2 \text{CrO}_2^{-4} + 2 \text{H}_3\text{O}^+ \rightarrow \text{Cr}_2\text{O}_2^{-7} + 3 \text{H}_2\text{O}$. The dominant species is therefore, by the law of mass action, determined by the pH of the solution. The change in equilibrium is visible by a change from yellow (chromate) to orange (dichromate), such as when an acid is added to a neutral solution of potassium chromate” (Oliveira P. n.d. p.383).

“At yet lower pH values, further condensation to more complex oxidations of chromium is possible” (Wiberg, E. et.al., 2001).



Chromium (VI) oxide

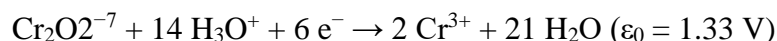


Yellow color of Sodium chromate
(Na₂CrO₄)

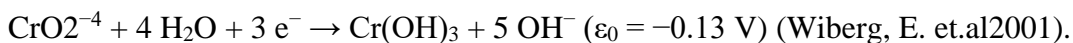
Source: (Wiberg, E. et.al., 2001).

Plate 2.2: Color of chromium VI compounds

At low pH both the chromate and dichromate anions are strong oxidizing reagents:



nevertheless, they are only moderately oxidizing at high pH:



“Chromium (VI) compounds in solution can be detected by adding an acidic hydrogen peroxide solution. The unstable dark blue chromium (VI) peroxide (CrO₅) is formed, which can be stabilized as an ether adduct CrO₅·OR₂. Chromic acid has the imaginary arrangement H₂CrO₄. Neither chromic nor dichromic acid can be isolated, but their anions are found in a variety of the chromates compounds, and dichromates.” (Wiberg, et.al 2001).

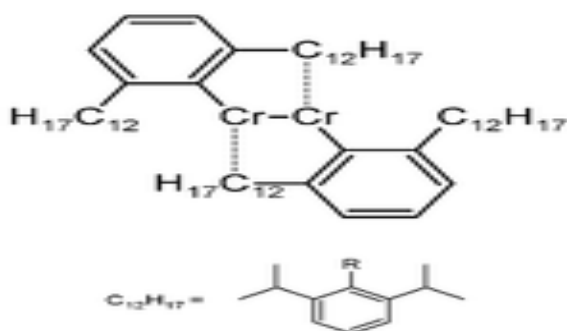
2.3 Chromium Passivation

Chromium passivates in the presence of oxygen. This agrees with Oliveira P. (n.d) where he documented that “Chromium metal left remaining in air is passivated by oxygen, forming a slender defensive oxide surface layer.” This “layer is a spinel structure” just a couple of iota “thick” and forestalls the dispersion of “oxygen into the basic material” contrary to “iron or plain carbon steels”, in which “oxygen” converts into the “basic material” and leading to rusting (Oliveira P. n.d). The “passivation” can be expanded by brief “contact with oxidizing acids like nitric acid”. Passivated chromium is steady against acids. The inverse impact is accomplished by “treatment with a strong reducing reactant” that annihilates the defensive “oxide layer on the metal”. “Chromium metal treated in this way” promptly breaks down “in weak acids” (Holleman, et.al 1985).

Chromium, dissimilar to metals, for example, “iron and nickel”, experiences not the ill effects of “hydrogen embrittlement (Oliveira P. n.d). Oliveira further states that chromium, “does suffer from nitrogen embrittlement, reacting with nitrogen from air and forming brittle nitrides at the high temperatures necessary to work the metal parts”.

2.4 Chromium Quintuple bond

A “quintuple bond in chemistry” is an anomalous sort of “chemical bond”, earliest “reported in 2005 for a dichromium compound”. (Wikipedia contributors 2019, January 18). Experimentally it was determined that Chromium compound contains a Cr-Cr quintuple bond. (Winter M. et.al. n.d.). According to Winter M.et.al (n.d), “Chromium is notable for its ability to form quintuple covalent bonds” (Figure 2.1). Winter M. et.al further found out that “the product of a reaction between chromium(I) and a hydrocarbon radical was shown via X-ray diffraction to contain a quintuple bond of length 183.51(4) pm joining the two central chromium atoms and extremely bulky monodentate ligands stabilize this compound by shielding the quintuple bond from further reactions”.



Source: Winter M. et.al n.d

Figure 2.1: Chromium Quintuple bond

2.5 Physical characteristics and use of Chromium

Chromium has good magnetic properties, this agrees with Fawcett, E. (1988) who documented that “Chromium is remarkable for its magnetic properties: it is the only elemental solid which shows antiferromagnetic ordering at room temperature (and below), above 38 °C, it transforms into a paramagnetic state”. Oliveira P. in the book the “elements” outlines the properties of chromium. Following is an extract on the same:

2.5.1 Metal technology

The fortifying impact of shaping steady metal carbides at the grain boundaries and the strong increment in corrosion resistance made chromium an imperative alloying fabric for steel. The high-speed device of steels contains between 3 and 5% chromium. Stainless steel, the essential corrosion-proof metal alloy, is shaped when chromium is introduced to iron in sufficient, typically greater than 11% concentration. For its formation, ferrochromium is brought to the molten iron. Also nickel-based alloys enlarge in strength due to the formation of discrete, stable metallic carbide particles at the grain boundaries. For example, Inconel 718 carries 18.6% chromium. Because of the high-quality excessive temperature properties of these nickel magnificent alloys, they are used in jet engines and gas generators in lieu of frequent structural materials.



Plate 2.3: Decorative chrome plating on a motorcycle

2.5.2 Coloring and pigment

The mineral crocoite (lead chromate $PbCrO_4$) was used as a yellow pigment quickly after its discovery. After a synthesis approach grew to be on hand starting from the greater abundant chromite, “Chrome yellow was, together with cadmium yellow, one of the most used yellow pigments. The pigment does no longer degrade in the light and has a strong color. The signaling effect of yellow was once used for school buses (Plate2.4) in the United States and for Postal Service in Europe. The use of chrome yellow declined due to environmental and safety concerns and was substituted with the aid of organic pigments or other lead-free alternatives. Other pigments primarily based on chromium are, for example, the brilliant red pigment Chrome red, which is a primary lead chromate ($PbCrO_4 \cdot Pb(OH)_2$). Chrome green is a combination of Prussian blue and chrome yellow, while the Chrome oxide green is Chromium (III) oxide.” (Worobec, et.al 1992).



Source: Worobec

Plate 2.4: School Bus Painted in Chrome Yellow

2.5.3 Wood Preservation

The “toxicity of chromium (VI) salts is used in the preservation of wood. For example, chromated copper arsenate (CCA) is used in curing trees to forestall wood from decay fungi, timber attacking insects, along with termites, and marine borers. The formulations contain chromium based totally on the oxide CrO_3 between 35.3% and 65.5%”. (Oliveira P. n.d) For instance in the year 1996; United States used 65,300 metric tons of CCA solutions.

2.5.4 Chromium in Tanning

The chromium (III) is used to stabilize the leather through cross connecting the collagen fibers within the leather. “Chromium (III) salts, particularly chrome alum and chromium (III) sulfate, are used in the tanning of leather.” (Brown E.M 1997). Chromium tanned leather-based can include between four and 5% of chromium, which is tightly sure to the proteins. Better administration of chromium in tanning enterprise such as recuperation and reuse, direct/indirect recycling, use of less chrome or chrome much less tanning are practiced to better influence chromium in tanning.

2.5.5 Chromium as a “Refractory material”

“The lofty heat resistivity and lofty melting point makes chromite and chromium (III) oxide a material for high temperature refractory applications, like cement kilns, blast furnaces, and molds for the firing of bricks and as foundry sands for the casting of metals”. (Business advisory April 2018). In these applications, the refractory materials are made from mixtures of chromite and magnesite. The use is declining because of the environmental guidelines due to the possibility of the formation of chromium (VI).

2.5.6 Additional uses of chromium

The following are some of the other uses of chromium:

- a. Catalyst: Several chromium compounds. For instance, the combinations of “chromium and silicon dioxide” or combinations of “chromium and titanium and aluminium oxide” manufacture Phillips catalysts. Heimbach, J. T., & Anderson, R. A. (2005).
- b. Manufacture of Magnetic compounds: Example Chromium (IV) oxide (CrO_2) is a magnetic compound which is used in the production of “magnetic tape used in high performance audio tape and standard audio cassette”. (Gerd A. et.al)
- c. Corrosion prevention in steel under wet conditions, hence the addition of chromates to drilling muds (Oliveira, P, p. 393).
- d. Gasoline additive e.g Chromium hexacarbonyl $\text{Cr}(\text{CO})_6$
- e. Chromium (III) oxide is applied in a metal polishing.
- f. Cleaning of laboratory glassware: For instance, “Chromic acid is an effective oxidizing agent and is a useful compound for cleansing laboratory glassware of any trace of organic compounds and Potassium dichromate is a chemical reagent, used in cleaning laboratory glassware and as a titrating agent” (Oliveira, P, p. 394). It is additionally “used as a mordant (i.e., a fixing agent) for dyes in fabric” (Oliveira, P n.d , p. 394).

2.6 Chromium lethality

Chromium is a very lethal element depending on its state. Gupta, R. C. (2014) notes that “Water insoluble chromium (III) compounds” and “chromium metals” are never again seen as a wellbeing peril, while the lethality and cancer-causing “properties of chromium (VI)” have been perceived for quite a while (Oliveira, P n.d. p. 717)

Chromium (III) absorbed into the cell of the plant; can damage the DNA. This agrees with Oliveira, P. (n.d) in the book *The Elements* where he recorded that depending on the transport systems, just restricted measures of chromium (III) enter the cells. Furthermore, “Several in vitro studies indicated that high concentrations of chromium (III) in the cell can lead to DNA damage. Acute oral toxicity ranges between 1500 and 3300 $\mu\text{g}/\text{kg}$ ” (Oliveira, P n.d p. 394). The proposed gainful impacts of chromium (III) and the utilization as dietary enhancements yielded some questionable outcomes, however late audits recommend that moderate take-up of chromium (III) through dietary enhancements represents no hazard (Wikipedians B. n.d p. 277).

The intense oral danger for chromium (VI) extends somewhere in the range of “50 and 150 $\mu\text{g}/\text{kg}$ ”. “In the body, chromium (VI) is reduced by a a number of mechanisms to chromium (III) in the blood before it enters the cells”. (Atroschi, F. 2014.). According to, Atroschi, “The acute toxicity of chromium (VI) is due to its strong oxidational properties and after it reaches the blood stream, it

damages the kidneys, the liver and blood cells through oxidation reactions”. (Atroshi, F. 2014. p. 49). “Hemolytic, renal and liver failures are the results of these damages. Aggressive dialysis can improve the situation” (Atroshi, F. 2014.).

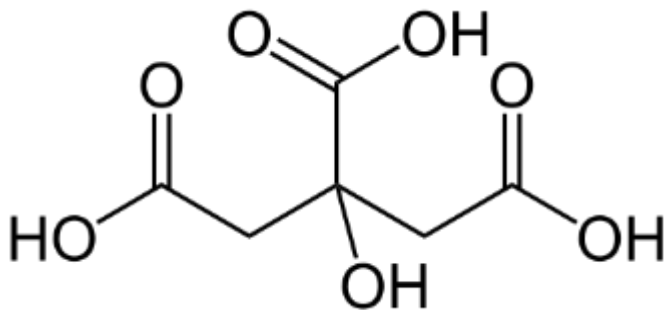
The cancer-causing potential of chromate dust has been famous “for a long time, and in the first publication in 1890 the elevated cancer risk of workers in a chromate dye company” was described. (Chen, Q., & Thouas, G. 2015). According to Atroshi, F. (2014), three instruments “have been proposed to describe the genotoxicity of chromium (VI)”. Firstly, inclusion of “highly reactive hydroxyl radicals and other reactive radicals which are by products of the reduction of chromium(VI) to chromium(III)”, secondly inclusion of “the direct binding of chromium(V), produced by reduction in the cell, and chromium(IV) compounds to the DNA” and lastly “binding to the DNA of the end product of the chromium(III) reduction” (Atroshi, F. 2014).

Oliveira notes that “contact with products containing chromates can lead to allergic contact dermatitis and irritant dermatitis, resulting in ulceration of the skin, sometimes referred to as chrome ulcers” (Oliveira, P.n.d). Oliveira further explains that “this condition is frequently found in personnel that have been exposed to strong chromate solutions in tanning electroplating, and chrome-producing manufacturers”. In addition “as chromium mixes were utilized in colors and paints and the tanning of leather, these mixes are regularly found in soil and groundwater at abandoned industrial locales”, presently requiring natural cleanup and remediation (Wikipedians B. n.d p. 277).

2.7 Chemistry of Citric acid

The soft school’s website (2005-2019) published an article with the title “citric acid formula”, which gives a lot of information on the chemistry of citric acid, its occurrence, preparation and properties. Below is an excerpt from the article:

“Citric acid is a natural tri-carboxylic acid which is a critical metabolite in all plants and animal life. The molecular formula of citric acid is $C_6H_8O_7$ and its molar mass is 192.12 g/mol. The chemical shape of citric acid is shown underneath (Figure 2.2). Citric acid is an alpha-hydroxy acid with a three-carbon skeleton, which has three carboxylic acid organizations (COOH), and one hydroxyl institution (OH)”. Soft schools’ website (2005-2019)



Source: Soft schools' website

Figure 2.2: Citric Acid Molecular Pond

Occurrence: Citric acid is found in nature in numerous fruits and vegetables, with the leading quantities in citrus fruits such as lemons limes, and oranges and a “paramount metabolic” intermediary “in the biochemical citric acid cycle and exists in all living matters”. Soft schools' website (2005-2019)

Preparation: “Citric acid is usually produced with the aid of the microbial fermentation of carbohydrates such as molasses, corn sugar, cane sugar, beet, among others. It is additionally extracted from citrus fruits as they comprise up to 8% of citric acid”. Soft schools' website (2005-2019)

Properties: The physical properties of include it having odorless and colorless crystals with an acidic taste. It has a density of 1.66 g/mL, melting point of 153 °C and boiling point of one hundred seventy-five °C. It is pretty soluble in water to giving an acidic, bitter tasting solution. On the Chemical properties Citric acid is a weak organic acid and “it commonly exists as anhydrous (water-free) form or as a monohydrate (with one molecule of water). The monohydrate can be transformed to the anhydrous structure when it is heated to about 78 °C. For temperatures above 175 °C, it decomposes with loss of carbon dioxide”. Citrate complexes with metallic ions are readily formed by citric acid. Soft schools' website (2005-2019).

2.7.1 Chelating properties of Citric acid

Citric acid is a superb “chelating agent”, which binds metals by making them soluble. It is employed to eliminate and deter the “buildup of limescale from boilers and evaporators”. (Frank H. Verhoff 2014). “It can be used to treat water, which makes it beneficial in enhancing the effectiveness of soaps and laundry detergents. It chelates metals in hard water, making the cleaners

create foam hence work excellent without the need of water softening. Citric acid is the active ingredient in some lavatory and kitchen cleaning solutions”. (Frank H. Verhoff 2014). In 1940s during the Manhattan Project, “Citric acid was the first successful eluant used for total ion exchange separation of the lanthanides” due to its chelating properties though it was replaced by EDTA in the 1950s. Wikipedia contributors. (2019, July 19).

2.8 Removal of Heavy Metals

Toxic heavy metals and organic contaminations are the real focuses for phytoremediation. Diverse “physical and chemical techniques” utilized for expulsion of heavy metals from the soils and water experience the ill effects of genuine constraints like high-cost expense, escalated work, and modification of soil properties and aggravation of soil local microflora (Ali, Khan, & Sajad, 2013). In contrast, phytoremediation is a better way out to the problem of heavy metals. Phytoremediation is defined as "the use of green plants and the associated microorganisms, along with proper soil amendments and agronomic techniques to either contain, remove or render toxic environmental contaminants harmless" (Das, Pratyush Kumar, April 2018).

According to (Ali, Khan, & Sajad, (2013), “It is a relatively recent technology and is perceived as cost-effective, efficient, novel, eco-friendly, and solar-driven technology with good public acceptance”. “Phytoremediation is based upon several processes such as phytodegradation, phytovolatilization, phytoaccumulation and phytoextraction”, (Sivaramakrishnan, et.al, 2018). Ghosh & Singh, (2005) notes that phytoremediation includes the mechanisms of contaminant removal as stipulated in Table 2.2.

Table 2. 2: Phytoremediation Mechanisms

No.	Process	Mechanism	Contaminant
1)	Rhizofiltration	Rhizosphere accumulation	organic/inorganics
2)	Phytostabilization	complexation	Inorganics
3)	Phyto extraction	Hyper-accumulation	Inorganics
4)	phytovolatilization	volatilization by leaves	organic/inorganics
5)	phytotransformation	Degradation in plants	organics

Source: Ghosh & Singh (2005)

2.8.1 Plants that can be employed in phytoremediation of heavy metals

Flora that contains potential to uptake heavy metals have been acknowledged in various clusters or families. According to Hemantaranjan, A. (2012) “Up to 45 families have been identified to have hyperaccumulate plants including Brassicaceae, Scrophulariaceae, Lamiaceae, Asteraceae,

Euphorbiaceae, and Fabaceae”. These plants in general have a high tolerance to metal stress and biomass production.

2.9 Phyto-remediation Potential in Kenya

Phytoremediation technology is a potent area that can be embraced in Kenya due to its numerous advantages on cleanup of environment. Kenya as a developing country faces challenges on pollution from various anthropogenic activities, which can easily be handled by phytoremediation technology.

2.10 Ricinus Communis (Castor Bean)

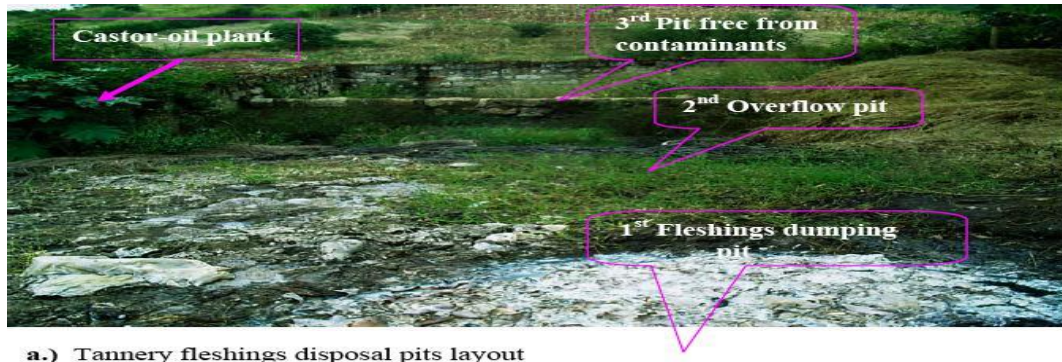
Castor bean oil, is under the Euphorbiaceae Family and it typically “grows to an average of 10 to 15 feet”, Martin, J. H., Waldren, R. P., & Stamp, D. L. (2006). The plant is incredibly changeable “in habit and appearance with the recognized sorts being numerous in Africa” (Grieve, M. n.d.).

Mwinyikione (2012) notes that “The castor bean plant is very variable in habit and appearance with the known varieties being numerous in Africa, its characterized by being drought tolerant, highly toxic if any part of the plant is ingested, grows in soils which are mildly acidic (pH 6.1 to 6.5) to neutral (pH 6.6 to 7.5) and it has been observed that moles, and other pests are driven away by the plant”.

Mwinyikione Mwinyihija Published an article on “Pollution Control and Remediation of the Tanning Effluent” which looks further on the issues associated “to pollution emanating from the tannery environment”. The article quotes:

“During the field survey related to this study, a certain type of plant (*Ricinus communis*) was observed to grow in a tannery effluent disposal pit”.

Mwinyikione Mwinyihija proposes that a range of studies be carried out to assess the phytoremediative potential of *R. communis* in relation to the tannery effluent. The studies should include both laboratory investigation to explore phytoremediation mechanisms as well as field studies to quantify phytoremediative performance under conditions encountered in the vicinity of Kenyan and other tropical tanneries. *Ricinus communis* is a type of plant that has been observed to grow in a tannery effluent disposal pit (Mwinyikione 2012) as shown in Plate 2.5. This suggested a potential plant-based, decontamination strategy (i.e. phytoremediation).



a.) Tannery fleshings disposal pits layout



Plate 2.5: Flourishing Castor Oil Plant (*Ricinus Communis*) at a Tannery Effluent Disposal Pit in Kenya

2.11 Negative Effects of chromium from tannery industries

Chromium is broadly utilized in the tanning business, and tannery laborers are under consistent risk of unfavorable wellbeing impacts because of being in contact with it (Abebe, Alebel. 2010). In a research done by Khan,, Mushtaq, Khan, & Khan, M. (2012) on Toxic effects of chromium on tannery workers at Sialkot (Pakistan), they found out that ; “The workers had hematological, hepatic and renal function impairment because of oxidative stress on body systems” the research further “concluded that about half of the workers had excessive exposure to chromium in the tanneries at Sialkot and had significantly raised chromium levels in their biological fluids and adverse health effects due to enhanced oxidative stress and inflammatory changes” (Khan et.al 2012, p. 209-215).

Tech blog *Gizmodo* in June 2014 published an article with the title “How Leather is Slowly Killing the People and Places that Make It,” By Talantola Andrew. The expose gives a lot of information on the negative effects of tanneries, particularly those in “developing countries”. Following is a quotation from the article:

“The tanning industry poses many dangers to both the environment and those that work within it. The primary environmental threat involves the dumping of solid and liquid waste that contains leftover chromium and other hazardous compounds. This is commonplace in regions without strong environmental protection standards, which also happen to be the primary regions where leather is tanned, such as China, India, and Bangladesh”.

“Even in fully modernized and carefully managed facilities, it is nearly impossible to reclaim all of the pollutants generated by the tanning process. As a rule of thumb, tanning one ton of hide typically results in 20 to 80 cubic meters of wastewater with Chromium concentrations around 250 mg/L and sulfide concentrations at roughly 500 mg/L, not to mention the offal effluence from the preparation phase and the pesticides often added to keep mold growth down during transport to the facility. Hell, 70 percent of an untreated hide is eventually discarded as solid waste—the hair, fat, meat, sinew, all goes straight into the trash.” However, as the UNIDO study authors wrote, "even though the chrome pollution load can be decreased by 94 percent on introducing advanced technologies, the minimum residual load 0.15 kg/t raw hide can still cause difficulties when using landfills and composting sludge from wastewater treatment on account of the regulations currently in force in some countries".

“Still, the most dangerous part of modern tanning is handling chromium. In humans, chromium causes a myriad of ailments depending on how it is absorbed. When inhaled, chromium acts as a lung irritant and carcinogen, affecting the upper respiratory tract, obstructing airways, and increasing the chances of developing lung, nasal, or sinus cancer. Chromium normally is absorbed this way as fine particulate dust that is produced when both raw and tanned leathers are buffed, smoothed, and ground up. Chromium has been linked to increased rates of asthma, bronchitis, polyps of the upper respiratory tract, pharyngitis, and the enlargement of the hilar region and lymph nodes (Tech blog *Gizmodo* June 2014).

It doesn't play well with your skin either. Once absorbed through unprotected handling, chromium can cause dry, cracked, and scaled skin; as well as erosive ulcerations that refuse to heal known “chrome holes” (Tech blog *Gizmodo* June 2014).

2.12 Leather industry in Kenya

The Kenyan leather industry principally relies on the huge livestock supply base of domestic animals, like Camel Goats, Sheep and Cattle for its raw materials. Mwinyihija M, (2014) states that “The tanning sector in Kenya through the reviewed period of 2013 accrued K.sh 13.6 billion in earnings from the leather operating tanneries (Table 2.3) and leather units”. Besides, “it was delineated that in any event 22,000 persons were perceived to directly be employed in the leather sector”, (Mwinyihija M, 2014). The Embassy of Kenya Rome (2019) website on Leather Hide and Skins notes that “tanneries in Kenya have installed 60% capacities for wet-blue, 25% for crust leather at and 15% finished leather taking” (<http://www.embassyofkenya.it/?p.406>).

Most tanning industries in Kenya do not have appropriate waste water treatment system, this results in dumping of tannery effluent sludge into pits, consequently polluting the environment. The tanning processes in most of the industries and the wastes generated are outlined in Figure 2.3.

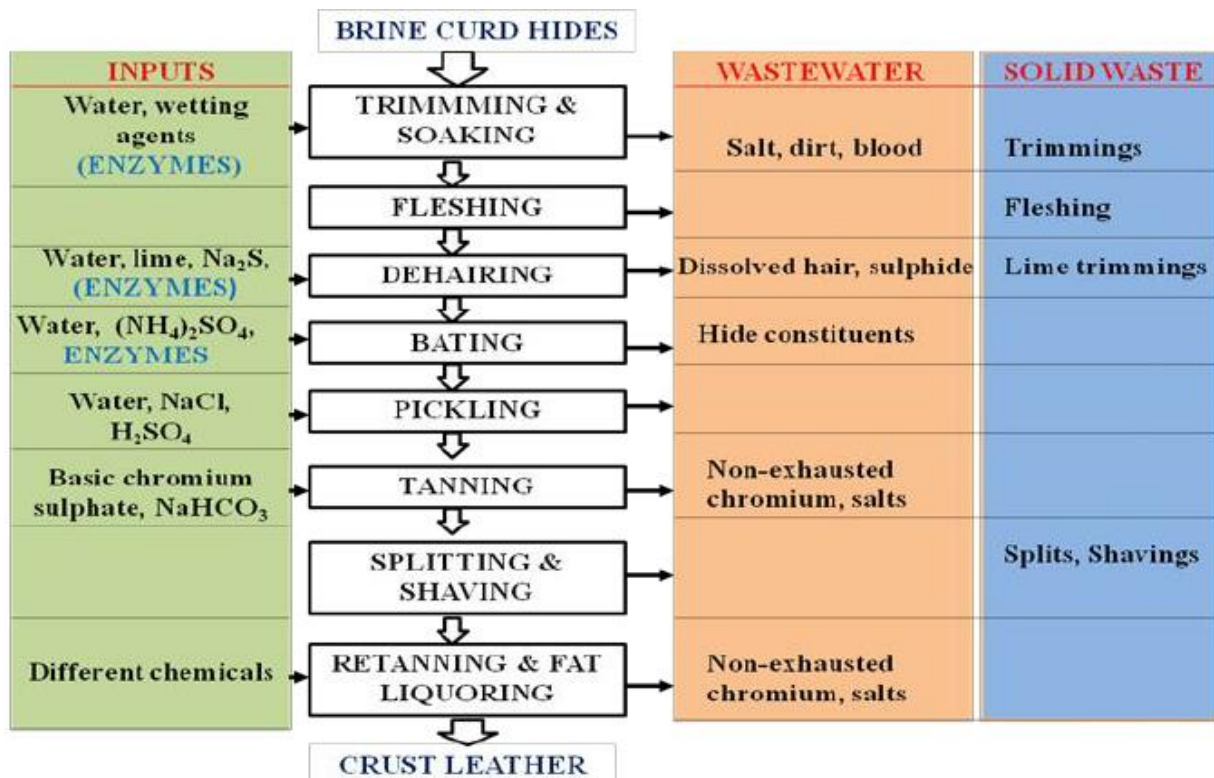


Figure 2.3: Tanning processes and waste generation

Table 2. 3: Details of tanneries operating in Kenya

Tannery	Quantity of wet salted hides per month	Goat and sheep skin (pieces per month)	Capacity utilization (%)	Level of production		
				Wet blue	Crust	Finished
Bata Shoe Limited (Limuru Town)	Crust / Finished 600,000 sq. ft.	N/A	100	X	X	X
Alpharama Ltd. (Athi River)	650 tons	400,000	100	X	X	X
Leather Industries of Kenya (Thika)	300 tons	100,000	50	X	X	X
Aziz Tanneries Ltd. (Njiru Market)	300 tons	200,000	N/A	X	X	X
Sagana Tanneries Ltd. (Sagana Town)	200 tons	50,000	N/A	X	X	X
Nakuru Tanneries Ltd. (Nakuru Town)	200 tons	150,000	N/A	X		
Dogbones Ltd. (Nairobi)	300 tons	N/A	N/A	X		
Nairobi Tanneries Ltd. (Nairobi)	50 Tons	50,000	70	X		
East Africa Tanneries Ltd. (Njiru Market)	N/A	250,000	85	X	X	X
Faaso Import and Export (Nairobi)	100 tons	50,000	N/A	X		
Athi River Tanneries (Athi River)	250 tons	100,000	N/A	X		
MAS Trading Company (Nairobi)	200 tons	N/A	100	X		
Zingo Tanneries (Nairobi)	300 tons	200,000	80	X		
Ondiri Tannery (Kikuyu)	Insignificant	Insignificant	N/A	X	X	X
Abdulwadood Tanners Ltd.	Not in operation	Not in operation	N/A	X		

Source: Alpharama

2.12.1 Leather Effluent Treatment Process in Kenya

In Kenya, most of the effluent treatment systems are as outlined in Figure 2.4 (Mwinyihija, M. 2006).

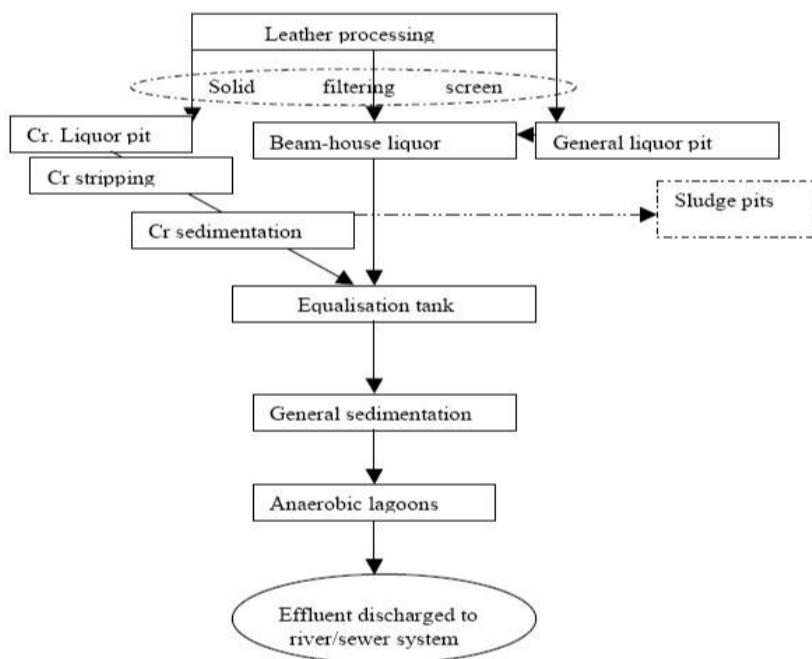


Figure 2.4: Typical Tannery Effluent treatment process

2.13 Previous studies on phytoremediation in Kenya

In Kenya not so much research has been done on phytoremediation of heavy metals. The few researches that have been done in Kenya include: phytoremediation of polychlorobiphenyls in land fill e-waste leachate with water hyacinth by Erick Omondi Auma (2014); Phytoremediation by means of bamboo to lessen hazards of chromium exposure from polluted tannery locations in Kenya by Farida H. Were, Geoffrey W. and Simon W. (2017); Phytoremediation of heavy metals in sewage sludge using plants from Brassicaceae family by Emily Kilungu (2017). All the above researchers recommended more research on phytoremediation using various plants since it's an efficient and economical way of rehabilitating the environment.

2.14 Disposal of Plants after phytoremediation

Disposal of the plant biomass after phytoremediation is of great concern, to ensure the heavy metal is not returned into the environment. In a review done by Liu Zhongchuang, et.al (2021) they concluded that “Synthesis of nanomaterials incineration, pyrolysis, and gasification are especially suitable for the disposal of high biomass plants (e.g. *Ricinus communis* L., *Pteris vittata* L., *Brassica juncea*) with HMs because of the strong capacity of plant biomass reduction. Hydrothermal modification, extraction, and microbial treatment are suitable for the disposal of low biomass plants (e.g. *Oxalis corniculata* L.) due to the low reduction rate of plant biomass”. Incineration and gasification are especially suitable for the disposal of plants with high boiling point HMs (e.g. Ni, Cr, Cu), considering the secondary pollution caused by the transformation of HMs into gaseous state. Pyrolysis and hydrothermal modification is especially suitable for the disposal of plants with medium and high boiling point HMs (e.g. Pb, Cd, Zn, Ni, Cr, Cu). Extraction and synthesis of nanomaterials are especially suitable for the disposal of plants with low boiling point HMs (e.g. Hg, As) for the low risk of secondary pollution by extraction or synthesis of nanomaterials. Microbial treatment and compression landfill are suitable for the disposal of plants with low contents of HMs, as the disposal process can cause secondary pollution. All methods have by-products that can be recycled as resources. Each method has some shortcomings, which are the focus of future research” (Liu et.al 2021).

A challenging issue for phytoremediation technique is how to properly dispose of plant biomass that contains heavy metals. (Liu et.al 2021). “A predominant setback in the remediation technique is the metals amassed in plant biomass after harvesting” Orooj Surriya, et.al. (2014). There is presently no effective way to eliminate metal accumulation in biomass. but the biomass can be disposed of as risky waste in compliance with the recommended rules and regulations. However, i hypothesize that the biomass won't be as risky as formerly assumed because of diverse

mechanisms that arise after heavy metal accumulation in biomass. “*R. communis*, is extensively famous for stabilizing, demobilizing, and binding heavy metals in the soil medium mostly with high levels in the roots, thereby decreasing its bioavailability in the soil” (Yan et.al.. 2020).

Bacteria are helpful in breakdown of pollutants in the root system. This agrees with Favas et.al. (2014) where they documented that “Dehalogenases” and “Nitroreductases”, which breakdown pollutants, are produced by the root system. Micropores in the root cell walls may also be able to breakdown metals (Negri et.al.. 1996; Ojuederie and Babalola 2017). “Hence, the enzymes and micropores in the root cell wall can degrade some of the accumulated metals in *R. communis* plants. Additionally, some microorganisms have high affinity for heavy metals, and roots may attract these microbes, which can help degrade the accumulated metals making them lower in the biomass.” (Sas-Nowosielska et.al.. 2008) Additionally, heavy metals can volatilize into the atmosphere at comparatively lower amounts when they are transferred to leaves. (Erakhrumen and Agbontalor 2007). Given the above-mentioned information, I hypothesize that while some heavy metals may be present in the biomass, they may not be at dangerous levels, leading me to the conclusion that *R. communis* can be successfully employed to clean up areas that have been contaminated with chromium. But this gap in the literature provides an intriguing topic of study in regard to the phytoremediation technique.

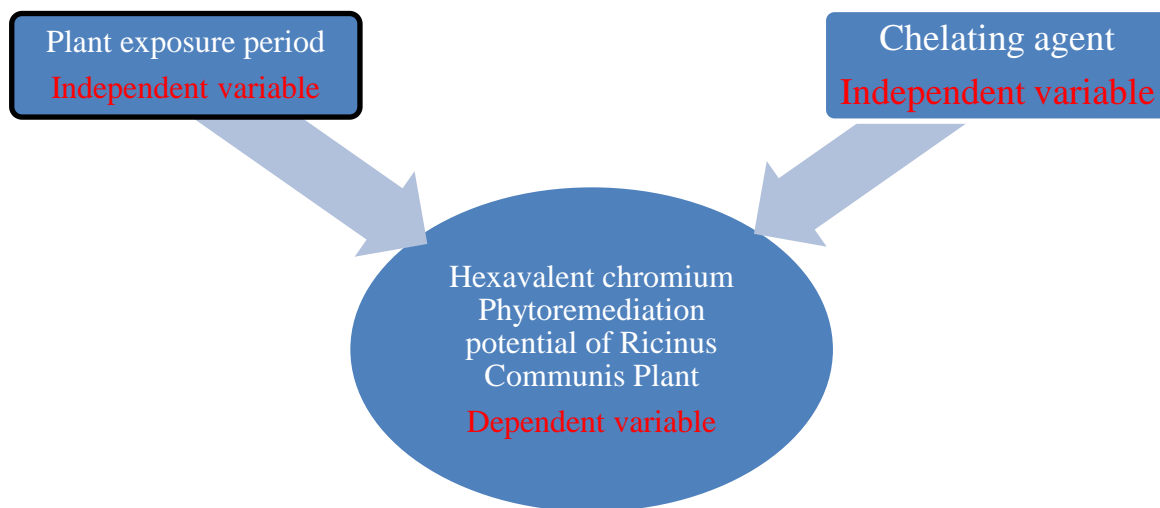
2.15 Previous Research on phytoremediation potential of Ricinus Communis on heavy metals

Various researches have been done to evaluate the potential of *Ricinus Communis* (Castor bean) on phytoremediation of various heavy metals. According to Boda R.K et.al (2017) “During 2013-2017, about 60 research papers have appeared focusing the role of castor bean in phytoremediation of co-contaminated soils, co-generation of biomaterials, and environmental cleanup, as bioenergy crop and sustainable development”. Some of the researches conducted include: “Phytoremediation impact of *Ricinus Communis*, *Malva parviflora* and *Triticum repens* on crude oil contaminated soil” (Sakina Saadawi et.al 2014); “Phytoremediation of Cadmium by *Ricinus communis* L. in Hydroponic Condition” (Fazal Hadi, et. al 2015); “*Ricinus communis* L. (Castor bean), a potential multi-purpose environmental crop for improved and integrated phytoremediation” (Narasimha et.al 2017), “The phytoremediation potential of bioenergy crop *Ricinus communis* for DDTs and cadmium co-contaminated soil” (Huagang Huang et. al 2011); “Potential of castor bean (*Ricinus communis* L.) for phytoremediation of mine tailings and oil production”(Ruiz Olivares A et.al 2012). All the above studies acknowledge that *Ricinus communis* is a wizard of phytoremediation, however there’s no research done with respect to phytoremediation of hexavalent chromium.

This study will examine the heavy metal Hexavalent Chromium which hasn't been studied on in connection with Ricinus Communis as a phytoremediator.

2.16 Conceptual Framework

A conceptual framework enables a researcher to comprehend how various study variables link to and influence one another. The framework, which serves as the researcher's "map" for carrying out the inquiry, outlines the variables needed in the research investigation (Regoniel, 2015). The conception framework describes the main variables which in this case are hexavalent chromium concentration levels in the plant tissues, Citric acid (chelate), time of plant exposure and their effects on Ricinus plant phytoremediation ability as shown on the figure 2.5. It is expected that the chelate and exposure period will affect positively the Hexavalent Chromium absorption by the plant. The Hexavalent Chromium absorbed by the plant in various parts, leave, stems, and roots will be used to calculate the Translocation factor and Bioconcentration factor which will inform the phytoremediation potential of Ricinus communis plant.



Source: Author

Figure 2. 5 Conceptual framework

2.17 Summary of Literature review

R. Communis is a wide glorious for “stabilizing, demobilizing, and binding significant metals within the soil matrix principally with high levels within the roots, thereby decreasing its bioavailability within the soil”. (Favas et a.2014). The stabilization of metals taken up by the roots reduces their transfer to other regions of the plant. It is widely known that the roots produce

contaminant-degrading enzymes in the form of “dehalogenases” and “nitro reductases” (Favas et.al., 2014).

2.18 Knowledge gaps

Literature review shows that *R. Communis* has been used as a phytoremediator for various heavy metals, but the extent to which *Ricinus Communis* plants extract chromium is a topic that has received little research (Irumba N. 2014). Mwinyikione 2012 et.al observed *R. Communis* growing in tannery effluent disposal pit which calls for assessing phytoremediative potential of the plant. This study examined the heavy metal chromium VI which hasn't been studied on in connection with *Ricinus Communis* as phytoremediator.

CHAPTER 3: METHODOLOGY

3.0 Introduction

This chapter describes the procedures that were followed and materials used to achieve the objectives of this study as mentioned in chapter one. The potential of *Ricinus communis* plant to Phytoremediate Hexavalent chromium contaminated soils was evaluated by transplanting the plant into twenty-four experimental pots. The plant was harvested at different periods, separated into roots, stem, and leaves and analyzed. The methods and materials are further described in the following sections

3.1 Source of soil media and tannery sludge

The tannery sludge was collected from Aziz tanneries in Nairobi City County. Aziz tanneries is located in Njiru sub county, and “processes 300 tons of wet salted hides per month and 200,000 pieces of goats and sheep skin per month” (World Bank Group, June 2015). The Aziz tanneries “directs wastewater from Trimming and soaking, dehairing, bating, tanning, re-tanning and liquoring streams into a pit for a period of 7 days then transfers the settled sludge into sludge drying bed, from the drying beds the sludge after dewatering is dumped to the environment”. (World Bank Group, June 2015). The red soil was collected from Karen area, and the chromium contaminated soil was contaminated by using potassium dichromate, to get a concentration of 20ppm of hexavalent chromium. The 20ppm concentration of Hexavalent chromium was selected on the basis of having a higher value than the one of the collected and analyzed tannery sludge from Aziz tanneries. Aziz tanneries is located at -1.244521 latitude and 36.9446691 longitude, in Njiru subcounty, Nairobi County.

3.2 Sampling of sludge for analysis of both total and Hexavalent chromium

Tannery sludge samples were collected from both the drying beds and the tannery sludge pit that had wet sludge. The wet sludge was collected in plastic containers whereas the tannery sludge from the drying beds was collected into 25 kilograms sacks. To obtain a representative sample, the sludge was sampled by scooping at different points and 1.0 and 1.5 m depth of the tannery effluent sludge pits and then mixed thoroughly before analysis. The dry tannery sludge from the sludge drying beds was collected from the sludge drying bed, from the middle and all the corners of the bed.

3.3 Determination of Hexavalent Chromium contamination levels in tannery sludge

The chromium concentration in the tannery sludge samples were analyzed utilizing Atomic Absorption Spectrophotometer (AAS) at Spectralab laboratory. The concentration of chromium VI in the tannery sludge and red soil was compared to the authorized theoretical threshold of chromium (VI) as set by NEMA in national environment regulations and US-EPA.

3.4 Ricinus plant seeds

The *Ricinus communis* seeds were collected from local castor oil bean plant farmers in Nakuru county Kenya. The seed were germinated in a nursery bed for 21 days before transplanting to the experimental pots.

3.5 Preparation of chemicals

The chemicals used during the study are citric acid, used as chelate and potassium dichromate used as hexavalent chromium pollutant. They were prepared as described below.

3.5.1 Preparation of chelate

Citric acid, a chelating agent was added to evaluate its efficacy in the uptake of heavy metal and tolerance. Principally “chelators are substances that render insoluble cations soluble making them available to plants” (Norvell, 1972; Lindsay, 1974). The availability and uptake of metals by plants are increased by chemical amendments such chelating agents, according to numerous studies (Wu et.al., 1999; Kirkham, 2000; Madrid et.al., 2002). In this study, citric acid of 0.1 M was prepared by dissolving 19.21g of anhydrous citric acid in 1liter of distilled water, this was used as a chelate. Plate 3.1 shows the kind of citric acid used.



Plate 3.1: Citric acid used as chelate

3.5.2 Preparation of hexavalent chromium contaminant

To prepare 20ppm of hexavalent chromium solution that was used to contaminate red soil, 56.497grams of potassium dichromate was dissolved in 1 liter of distilled water, forming a solution as shown in plate 3.2.



Plate 3.2: Potassium Dichromate mixture used to contaminate the red soil.

3.6. Experimental setup

The Seedlings were transplanted in various pots having 0.07842ppb (control), tannery sludge (14.960ppm), and chromium polluted soil (20ppm) concentrations of Hexavalent Chromium to determine the phytoremediation potential. The various experimental pot set ups were as follows:

1. Garden soil +Tannery Sludge + plant (4 experimental pots (1:1 ratio)) Plate 3.3.
2. Tannery Sludge + plant (4 experimental pots) plate 3.4.
3. Garden soil + plant (4 experimental pots) plate 3.5.
4. Garden soil + sludge + citric acid chelating agent (4 experimental pots).
5. Hexavalent chromium contaminated soil + plant (4 experimental pots) plate 3.6 row 1.
6. Hexavalent chromium contaminated soil + plant+ Citric acid chelating agent (4 experimental pots) plate 3.7 row 2.



Plate 3.3: Pots containing mixture of tannery sludge and red soil



Plate 3.4: Pots containing Tannery sludge media



Plate 3.5: Pots with garden soil media



Plate 3.6: Pots with red soil contaminated with potassium dichromate: (i) row one with citric acid, and (ii) row 2 without citric acid



Plate 3.7: Showing all the experimental set up pots

3.7 Assessment/comparison of the uptake rate of Cr^{+6} of the plants

Seedlings were transplanted into the experimental pots and were watered twice a day and weeded as it deemed necessary. On, thirtieth, forty fifth, sixtieth and seventh fifth days the plants were gathered from the pots, separated into shoots, stems, and roots after being cleansed with tap water and deionized water (Plate 3.8).



Plate 3.8: Harvested plant separated into, roots, stem and leaves

The plants were then dried in an oven at $105^{\circ}C$ for 48 hours, carbonized by subjecting them to an hour's of heating on a hot skillet till the powder turned black. The ash was then cooled and weighed, and finally chromium VI concentrations was determined using a flame Atomic Absorption Spectrometer.

3.7 Determination of Bio-Concentration Factor and Translocation Factor

“Bio –concentration factor (BCF) is an indicator of the ability of the plant to build up the metal with regards to metal concentration in the substrate” (Giri, 2012). The translocation factor is the

capability “of the plant to translocate metals from the root to the leaves via the shoots” (Giri, 2012).

The BCF and TF were calculated using equation one and two respectively as stated below

$$\text{BCF} = \frac{C_{\text{plant part}} \left(\frac{\text{mg}}{\text{kg}}\right)}{C_{\text{soil part}} \left(\frac{\text{mg}}{\text{kg}}\right)} \quad \text{Equation 1}$$

Where

$C_{\text{plant part}}$ - the amount of chromium in the sampled plant component,

C_{Soil} - the amount of chromium in the soil.

$$\text{TF} = \frac{C_{\text{stem}} \left(\frac{\text{mg}}{\text{kg}}\right)}{C_{\text{root}} \left(\frac{\text{mg}}{\text{kg}}\right)} \quad \text{Equation 2}$$

Where:

C_{stem} - concentration of chromium in plant stem, and

C_{root} - concentration of the chromium in the root

3.8. Data analysis

The collected data was analyzed using Microsoft Excel.

CHAPTER 4: RESULTS AND DISCUSSION

This chapter first presents the results of analysis of Hexavalent Chromium concentration in Tannery sludge samples collected from Aziz tanneries limited. It then presents observations on the growth of Ricinus communis plant on red soil (control), tannery sludge, tannery sludge and the red soil mixed at a ratio of 1:1. Lastly it gives the translocation factor that is used in estimating the phytoremediation potential of the Ricinus Communis plant.

4.1 Hexavalent Chromium in tannery sludge and red loamy soil

The concentrations of Hexavalent Chromium (CrVI) Level in the Aziz Tanneries Ltd sludge pit (Table 4.1) was recorded as 14.936mg/kg which exceeded the United States Environmental Protection Agency (U.S. EPA) regulatory limits for protection of human health and the environment and the National Environmental Management Authority limits (Table 4.2). Therefore, there is need for pollution control measures to limit the release of Hexavalent Chromium into the environment.

Table 4. 1: Concentration of Hexavalent Chromium in Aziz Tanneries Ltd sludge

Concentration of Hexavalent chromium in Aziz tanneries ltd sludge		
source	units	Value
Sludge Pit	ppm	19.640
Sludge Drying Bed	ppm	14.936

Table 4. 2: Hexavalent Chromium effluent disposal limits

Organization	Units	Permissible Limit	Source
U.S EPA	ppm	0.01`	U.S EPA(May 2012)
WHO	ppm	0.05	World Bank. Project guidelines: Industry sector guidelines. Pollution Prevention and abatement Handbook (1998)
NEMA	ppm	0.05	NEMA Water quality regulations (2006)

The control soil was sourced from Karen area and it had a Hexavalent Chromium level of 0.07842 ppb.

4.2 Growth of *Ricinus cummunis* plant

Ricinus communis were planted in a seed bed for 21 days as shown in the plates



Plate 4.1: *Ricinus Communis* plant at the seed bed

The seedlings planted on the tannery sludge were stressed after transplantation as shown in Plate 4.2 but later coped and grew as expected as shown in plate 4.3. This stress can be associated with higher concentration of chromium (VI) in the tannery sludge media.



Plate 4.2: *Ricinus communis* plant 5 days after transplanting



Plate 4.3: Ricinus plant growth at 21 days after transplanting

4.3 Accumulation of Hexavalent Chromium Concentrations in Different Parts of the Ricinus Communis Plant

The hexavalent concentrations in the leaves, shoots and roots harvested at from 30th day at interval of 15 days were recorded as shown in Table 4.3. The Hexavalent Chromium accumulation from tannery sludge and their distribution in root shoot and leaves showed variable patterns as shown in Table 4.3. As shown in Table 4.3, at 30 days (Appendix 4.3), the roots of the Ricinus Communis plant in the Tannery sludge had the highest Hexavalent Chromium accumulation. Furthermore, it was observed that out of the six pots, the Hexavalent Chromium concentrations were high at the roots compared to the areal parts in five of the ports after 30 days. This agrees with López-Luna et.al (2009) who found that “roots of wheat, oat, and sorghum accumulated more Cr than shoots; however, in spite of that, wheat, oat, and sorghum showed Cr translocation from roots to shoots”. Furthermore, Zayed et.al. (1998); tested “Cr(III) and Cr(VI) translocation in several crops and found that translocation of both Cr forms from roots to shoots was very low and accumulation of Cr by roots was 100-fold higher than in shoots, despite of the Cr species”.

However, Skeffington et.al (1976) found that “the chromium isotope (^{51}Cr) was transported from root to shoot when Cr(VI), rather than Cr(III), was supplied to the plant. At high Chromium doses (1 mM CrCl_3) roots accumulated very high levels of Chromium and translocation was mainly to cotyledonary leaves and only small amounts in hypocotyls”.

On the 45th day the highest concentrations (Appendix 4.4) were accumulated in the roots of the plant that was planted on the tannery sludge, mixture of tannery sludge a red soil, and the mixture

of tannery sludge, red soil and chelate. This is a common characteristic as observed by (Ghosh and Singh, 2005; Erenoglu et.al., 2007; Dong et.al.. 2007; Zhang et.al.. 2007; Zayed et.al 2003; Pulford and Watson 2003).

Table 4.3 and Appendices 4.4 to 4.6 further shows that there was high accumulation of Cr (VI) in the leaves stem and roots of the plant planted in both the tannery sludge and the mixture of tannery sludge, red soil and chelating agent at 60th. This is associated with the high concentration of chromium (VI) in the pots having tannery sludge and mixture of tannery sludge, red soil and chelating agent.

Table 4. 3: Hexavalent Chromium concentrations in the plant

Period of exposure		30 th day	45 th day	60 th day	75 th day
Media	Plant part	Accumulation (ppb)	Accumulation (ppb)	Accumulation (ppm)	Concentration (ppm)
Garden soil (control)	Leaves	9.691±0.236	Nil	0.004±0.0051	1.331±0.0034ppb
	Stems	11.659±0.457	3.16±0.027	0.001±0.0005	3.992±0.0048ppb
	Roots	10.625±0.249	7.95±0.032	0.008±0.001	5.984±0.0072ppb
Garden soil +Tannery sludge+ chelate	Leaves	7.718±0.463	3.67±0.460	5.987±0.0072	3.995±0.0040
	Stems	23.866±0.454	3.16±0.034	6.378±0.0041	8.784±0.0091
	Roots	14.900±0.697	4405.40±0.473	5.984±0.0096	7.962±0.0093
Garden soil +tannery sludge	Leaves	15.742±0.006	3.93±0.031	1.588±0.0048	1.995±0.0006
	Stems	4.687±0.065	3.13±0.028	0.995±0.0033	0.797±0.0004
	Roots	12.972±0.539	1964.77±0.666	3.963±0.0012	0.399±0.0003
Tannery sludge	Leaves	15.534±0.439	3.99±0.0024ppm	8.587±0.0913	3.983±0.0030
	Stems	40.496±0.013	3.16±0.014ppm	1.988±0.0038	13.995±0.0047
	Roots	51.880±0.829	12.20±0.421ppm	12.391±0.0028	7.909±0.0248
chromium polluted soil	Leaves	9.053±0.906	3.15±0.037	2.589±0.0034	1.996±0.0017
	Stems	2.260±0.230	3.57±0.084	0.691±0.0004	3.993±0.0052
	Roots	19.098±0.690	1273.67±0.304	2.837±0.0005	1.582±0.0007
Chromium Polluted Soil+Chelate	Leaves	19.654±0.229	4.590±0.116ppm	2.487±0.0047	12.824±0.0068
	Stems	93.996±0.098	5.160±0.010ppm	15.193±0.0617	17.995±0.0102
	Roots	101.778±0.0015	13.2±0.0251ppm	13.789±0.0024	16.921±0.00196

Values are means of three replicates ± standard error.

It was also noticed that there was no concentration in the leaves of the plant in the control. This could be due to low concentration of chromium VI in the red soil which was also acting as a control.

There was significant accumulation of Hexavalent chromium in the leaves stem and roots of the plant planted in both the tannery sludge and the mixture of tannery sludge, red soil and chelating agent at 60th day, and the chromium polluted soil with chelate as shown on Table 4.3 and Figure 4.1, this signifies that movement of the Cr (VI) from the roots to the aerial parts depends on time of exposure and also the hexavalent chromium concentration in the media. Metal accumulation pattern showed that chromium six concentrations in the plant were highest between the 45th and 60th days of growth.

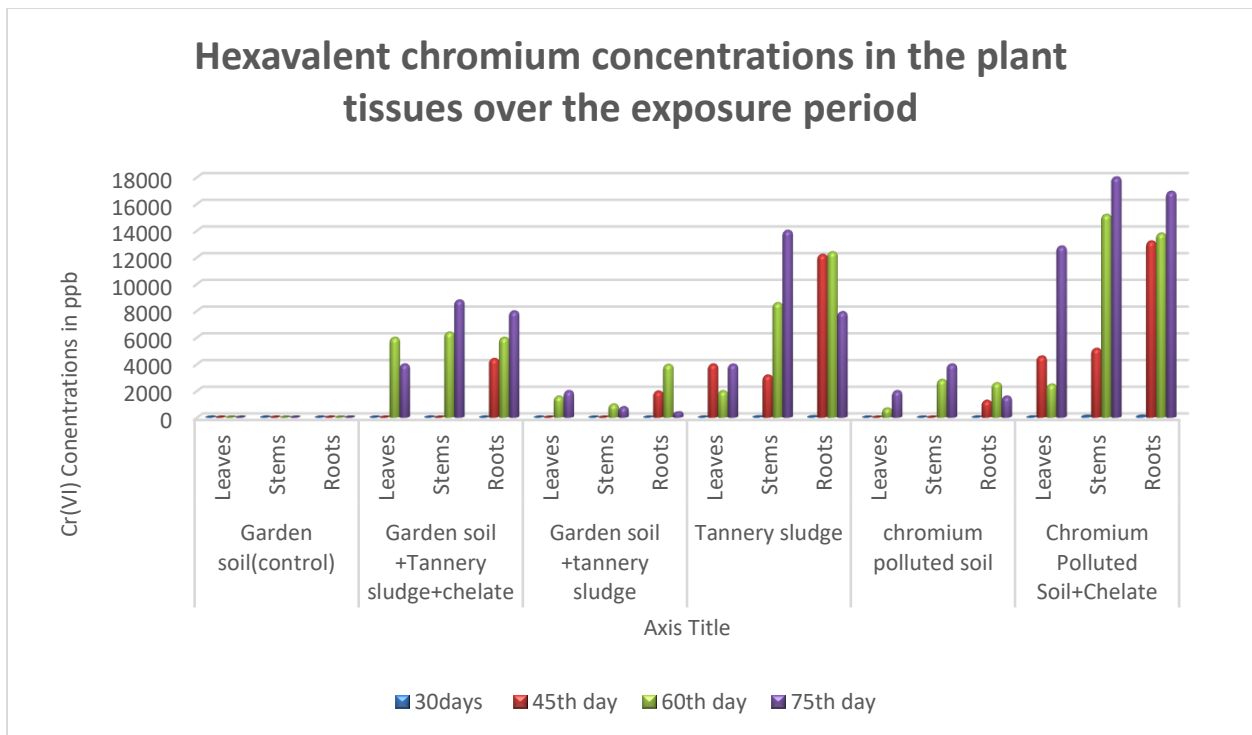


Figure 4.1: Hexavalent chromium concentrations in the plant tissues over the exposure period

The amount of Cr (VI) concentration in the plant was higher than the amount of it in the media. This could be due to chromium speciation, oxidation in the presence of manganese in the media. Bartlett et.al (1979); “observed that Cr (III) was oxidized to Cr(VI) in soils with high elemental contents of manganese as compared with other soils”. “Chromium (III) can be oxidized into Cr(VI) in soils, mostly by Manganese oxides, especially quadrivalent Manganese” (Kim et.al., 2002); and Fendorf et.al., 1993).

4.4 Effect of Application of the Chelating Agent Citric Acid

4.4.1 Effects of chelate on Absorption of Hexavalent Chromium using Mixture of tannery sludge and Red soil as media

As shown on Table 4.4, Citric acid as a chelate had a very high impact on phytoremediation of chromium from the soil, especially from the 45th day (Figure 4.2). This concurs with the results of Bursztyn Fuentes (2018) et.al, who found out that “Citric acid was the most effective chelating agent in increasing the concentration of Cu, Cr, and Pb in root and in the aerial part of chicory and castor bean”.

Figure 4.2 illustrates the comparative accumulation of Hexavalent Chromium for the different parts of *Ricinus Communis* plants grown with and without citric acid first on mixture of tannery sludge and red soil and on chromium polluted soil. The highest concentration of the chromium was in the stems and roots of the *R. Communis* plant in tannery sludge media with chelate.

Table 4. 4: Comparison of chromium concentration in the *Ricinus Communis* planted in the media with and without Chelate

Part Of Plant	Duration (Days)	Without chelate	With chelate	Concentration Units
LEAVES	30 th day	15.742±0.006	7.718±0.463	ppb
	45th day	3.93±0.031	3.67±0.460	ppb
	60th day	1.588±0.0048	5.987±0.0072	ppm
	75th day	1.995±0.0006	3.995±0.0040	ppm
STEMS	30 th day	4.687±0.065	23.866±0.454	ppb
	45th day	3.13±0.028	3.16±0.034	ppb
	60th day	0.995±0.0033	6.378±0.0041	ppm
	75th day	0.797±0.0004	8.784±0.0091	ppm
ROOTS	30 th day	12.972±0.539	14.900±0.697	ppb
	45th day	1964.77±0.666	4405.40±0.473	ppb
	60th day	3.963±0.0012	5.984±0.0096	ppm
	75th day	0.399±0.0003	7.962±0.0093	ppm

Values are means of three replicates ± standard error.

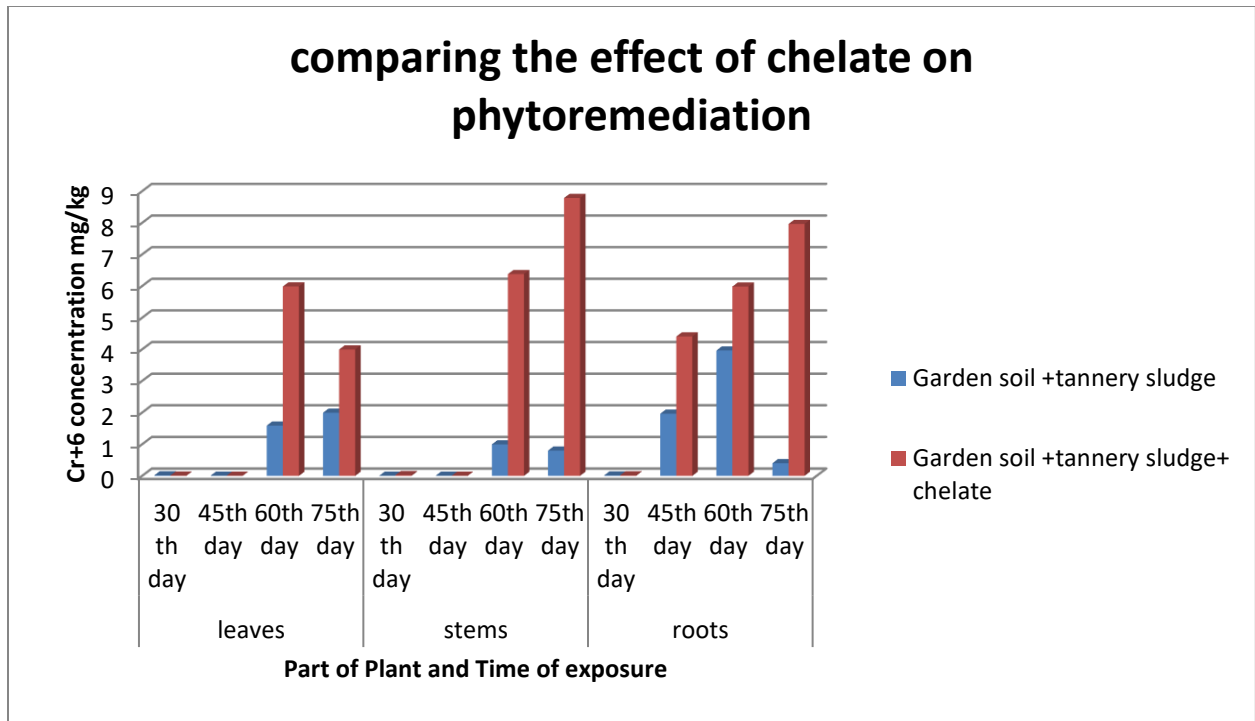


Figure 4.2: Comparing the effect of Citric acid chelate on absorption of hexavalent chromium

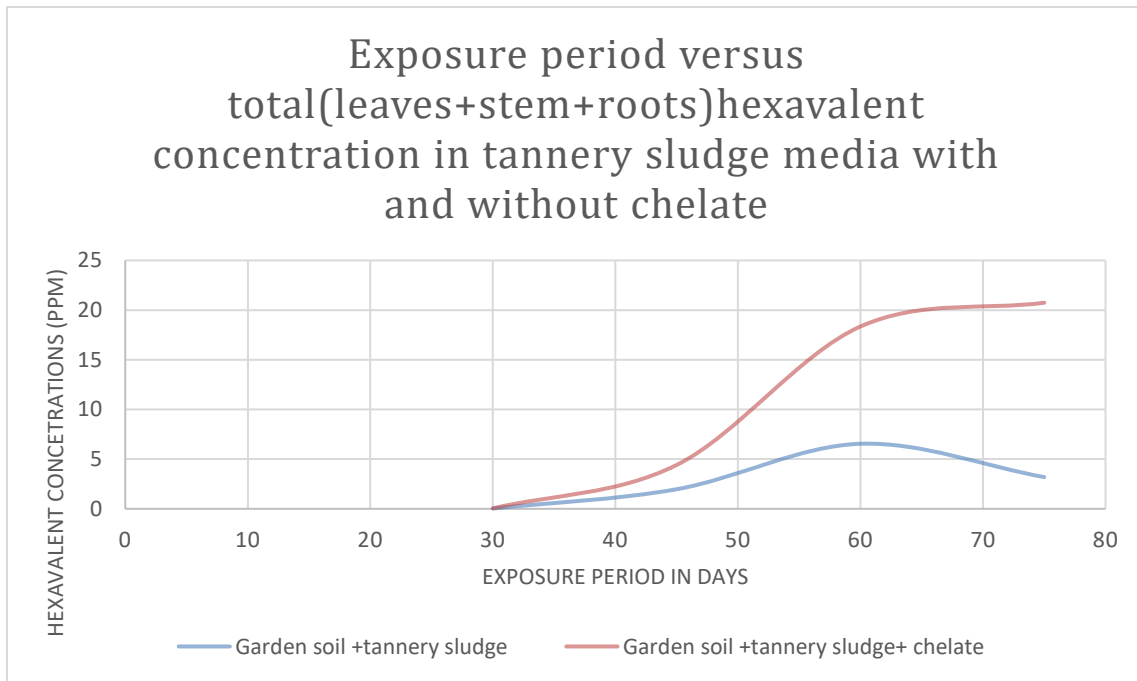


Figure 4.3: Effects of chelate on Hexavalent chromium absorption by Ricinus communis plant (using Tannery sludge soil as media)

The chelate increased absorption of chromium in the roots on the 45th day likewise there's also an increase of the chromium absorption by the roots and the stems of the Ricinus Communis plant planted in chromium contaminated soil after 75 days as shown in Figure 4.3 . From Figure 4.3, the

graph tends to flatten from day 65, this could imply saturation point in terms of hexavalent chromium absorption of the plant. The drop of Hexavalent chromium concentration in the plant for the media without chelate could be due to reduction of chromium in the soil media.

Application of the chelate on the tannery sludge and red soil mixture of ratio 1:1, showed and increased absorption of Hexavalent Chromium as shown in Figure 4.3. At the 30th day the percentage increase was 39% and more than 100%, from the 45th day (Table 4.4). This demonstration that Citric acid can be used as a chelate in phytoremediation of chromium contaminated soils. The total accumulation of Hexavalent chromium in *R. Communis* plant at the end of the exposure period was 11.74ppm in the pot without chelate and 43.54ppm in the pot with chelate which is approximately 3.7 times more. These demonstrations that Citric acid can be used as a chelate in phytoremediation of chromium contaminated soils which agrees with Madrid et.al., (2002) in his research on “Heavy metal displacement in chelate-irrigated soil during phytoremediation”.

The ANOVA statistical analysis (Appendix 4.7), showed statistically significant difference (p value = 0.0196961) =less than 0.05, between tannery sludge containing chelate and the one without chelate. The p value show that the Hexavalent concentration results in the *Ricinus communis* plant are significantly different hence we reject the null hypothesis: there’s no difference between the hexavalent chromium concentrations in the plant planted in pots with chelate and without chelate.

4.4.2 Effects of chelate on Absorption of Hexavalent Chromium using in the chromium polluted red soil

Citric acid was also applied in the media contaminated with 20ppm hexavalent chromium. The results are as shown in Table 4.5.

Table 4. 5: Comparison of concentration in the *Ricinus Communis* planted in the chromium polluted media with and without Chelate

Exposure period (days)	Cr(VI) concentration (ppb) in <i>Ricinus</i> plant planted chromium polluted	Cr(VI) concentration (ppb) in <i>Ricinus</i> plant planted chromium polluted chelate
30	30.411	215.428
45	1280.39	22950
60	6117	31469
75	7571	47740

Comparing the concentration of hexavalent chromium in the plant biomass in the media with and without the chelate, the chelate increased phytoextraction by more than 100% from the 45th day. This is further illustrated in Figures 4.4 and 4.5.

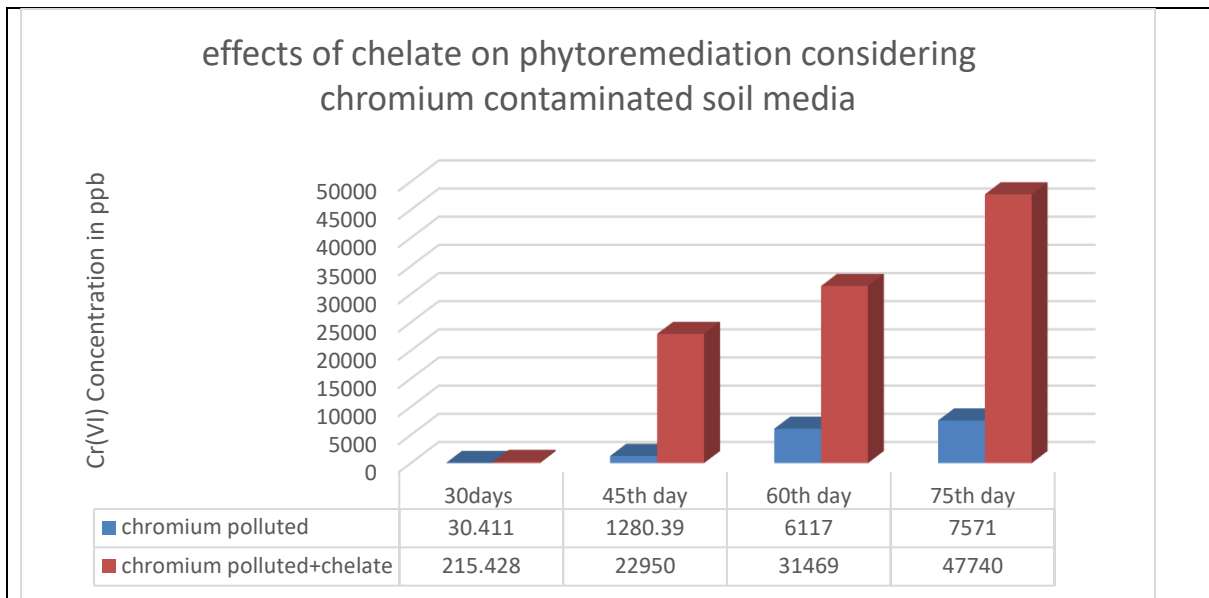


Figure 4.4: Effects of chelate considering the chromium polluted soil media

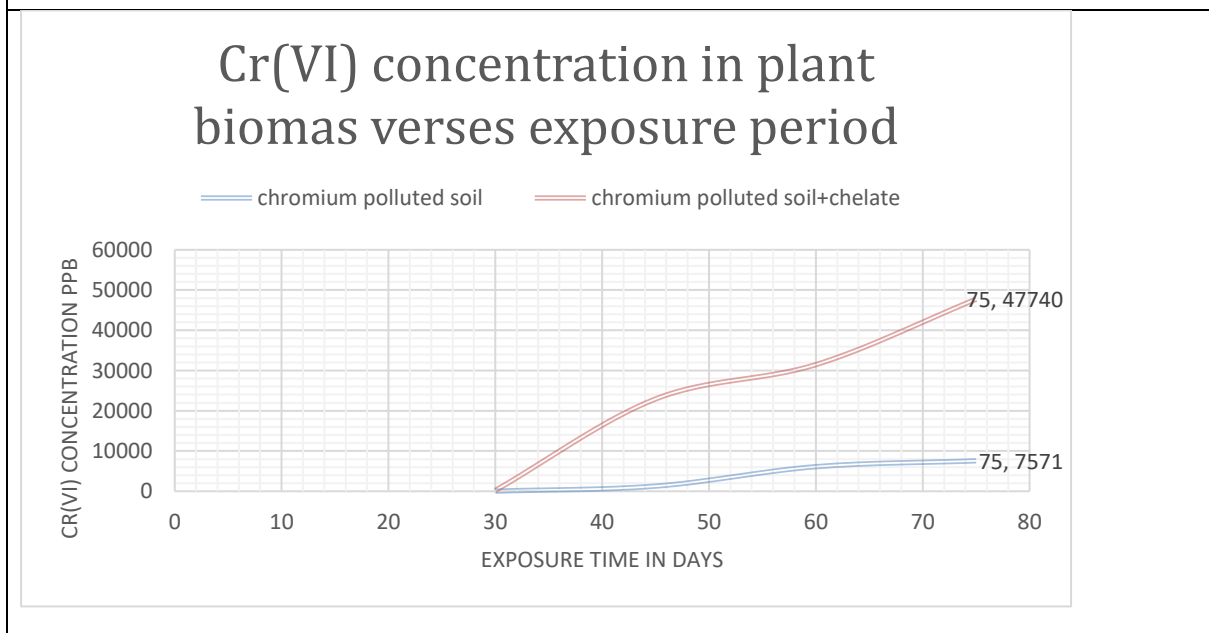


Figure 4.5: Graph showing effects of chelate considering the chromium polluted soil media

4.5 Translocation Factor

The Translocation Factor (TF) generally shows the movement of chromium from root to shoot, indicating the efficiency to uptake the bio-available Hexavalent Chromium from the soils. Metals that are accumulated by plants and largely stored in the roots are indicated by TF values of <1. Values greater than one indicate translocation to the aerial parts of the plant. (Ma, et.al. 2001). Plants with TF values > 1 are classified as high-efficiency plants for metal translocation from the roots to shoots (Ma, et.al. 2001). The translocation coefficient (TF) was described as the ratio of heavy metal concentration in the plant shoot to that in the root of the plant (Yanqun et.al 2005). This ratio is an indication of the ability of the plant to translocate metals from the roots to the aerial parts of the plant (Marchiol et.al 2004)

The translocation factors were calculated and recorded as shown in Table 4.6. The highest translocation factor (2.524), was noted at 75th day exposure time, followed by 1.997 after exposure time of 75 days in the chromium polluted soil and soils mixed with tannery sludge (1:1 ratio) respectively as shown in Table 4.6.

Table 4. 6: Translocation Factors of the Ricinus Communis Plant at different plant exposure period

time	Translocation factors at different exposure period			
	30 th day	45th day	60th day	75th day
Garden soil(control)	1.097	0.397	0.125	0.66711
Garden soil +Tannery sludge+Chelate	1.60	0.0007	1.066	1.1032
Garden soil +tannery sludge	0.361	0.0015	0.2511	1.997
Tannery sludge	0.781	0.259	0.1604	1.770
Chromium polluted	0.118	0.0028	0.2436	2.524
Chromium polluted + Chelate	0.924	0.3909	1.1018	1.063

The Translocation factors greater than one, show that Ricinus communis plant can be used for phytoextraction, since it allowed translocation of the heavy metal into the shoots Figure 4.6, on the other hand the TF<1, show that the Plant accumulated hexavalent chromium in the roots, possibility of phytoremediation by phytostabilization.

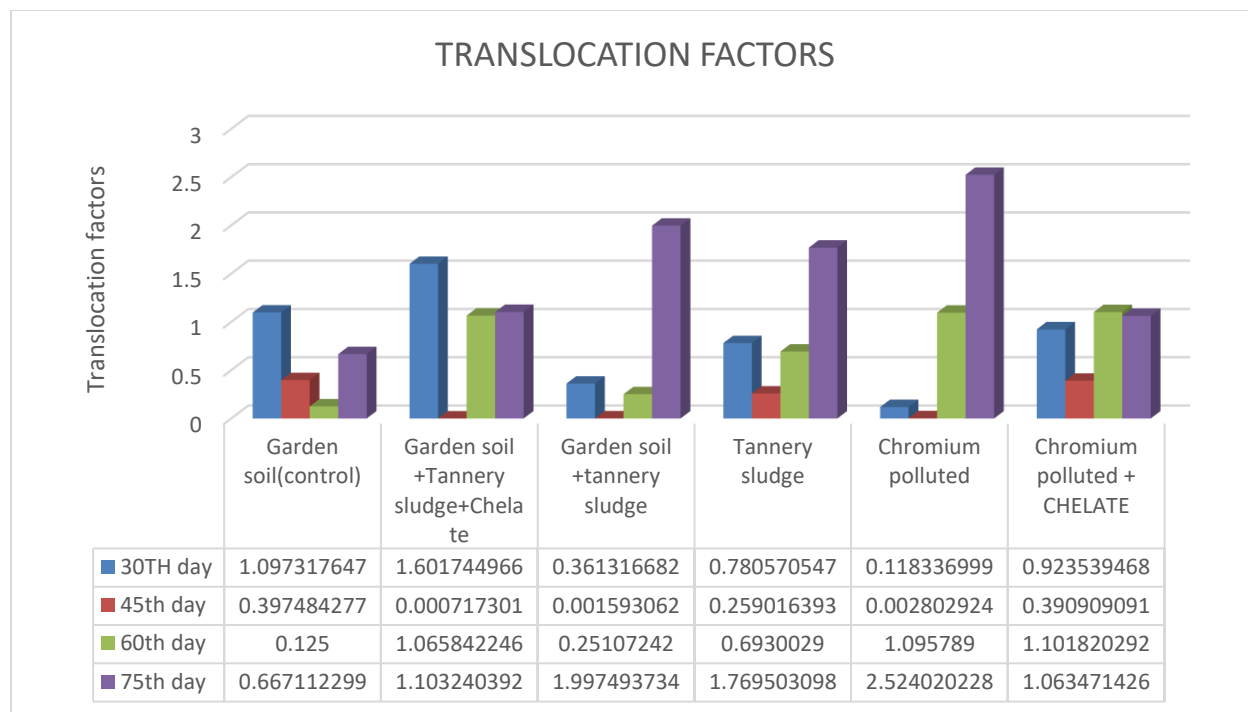


Figure 4.6: Translocation factors at different exposure time

Generally, since the translocation factors were greater than one at the exposure time of 75 days except in the control pot; this means that *Ricinus communis* plant has potential for phytoremediation of chromium with exposure time of between 60 to 75 days. This agrees with Rani et.al (2017) on “Stabilization of tannery sludge amended soil using *Ricinus communis*”, where they concluded that *Ricinus communis* plant is suitable for growth in “heavy metal rich” tannery sludge soil “vis a vis for phytostabilization of heavy metals”. Translocation to the shoot is one of the methods of resistance to high Cr concentration, therefore a better translocation is helpful to phytoextraction as it can reduce Cr concentration and thereby minimize the toxicity potential to the root. (Ghosh et.al; 2005)

4.6 Bio concentration Factor

The “bio concentration factor (BCF) is the ability of the plant to accumulate heavy metal with respect to the metal concentration in the surrounding medium” (Zayed et.al. 1998). BCF values at different exposure time (days) calculated from initial concentration of metal in the effluent are given in Table 4.6. The bio concentration factor ranged between 0.01 and 2.68. This study assumed that plants with BCF values > 1 are accumulators, while plants with BCF values < 1 are excluders Baker A. J. M.

The outcomes in this study exhibited that *Ricinus Communis* planted on Tannery sludge had BCF values > 1 from the 45th day to 75th day, indicating that the plant has the potential to be used as

accumulator of Hexavalent Chromium, while before 30th day the plant had a BCF value < 1 for chromium as shown in Table 4.7. This agrees with Rani, et.al. (2017), that “Majority of the metals” were “accumulated in root part (BCF >1) and meagre translocation (TF <1) in aerial part”, concluding that *R. communis* can be utilized effectively to clean up environments contaminated with Hexavalent chromium. The “success of the phyto extraction process depends on heavy metal removal by the shoots” (Usman et.al 2009). Consequently, “it is suggested that the plant species having the higher metal concentration in its shoots than in its roots can be considered as accumulator for phytoremediation” (Alori et.al 2018).

Table 4. 7: Bioconcentration factors at various exposure period

	30 th day	45 th day	60 th day	75 th day
Garden soil(control)	0.003316909	0.00115249	0.001348548	0.001172925
Garden soil +Tannery sludge + Chelate	0.004821992	0.45770021	1.903423237	2.151556017
Garden soil +tannery sludge	0.003464834	0.20454668	0.679045643	0.331016598
Tannery sludge	0.011193983	2.00726141	2.382365145	2.685373444
Chromium polluted	0.00152055	0.0640195	0.30585	0.37855
Chromium polluted + Chelate	0.0107714	1.1475	1.57345	2.387

The results in Figure 4.7 show that the bioconcentration factors are also affected by exposure period, as seen in the results from the garden soil+tannery sludge+chelate; tannery sludge; chromium polluted soil and chromium polluted soil + chelate pots.

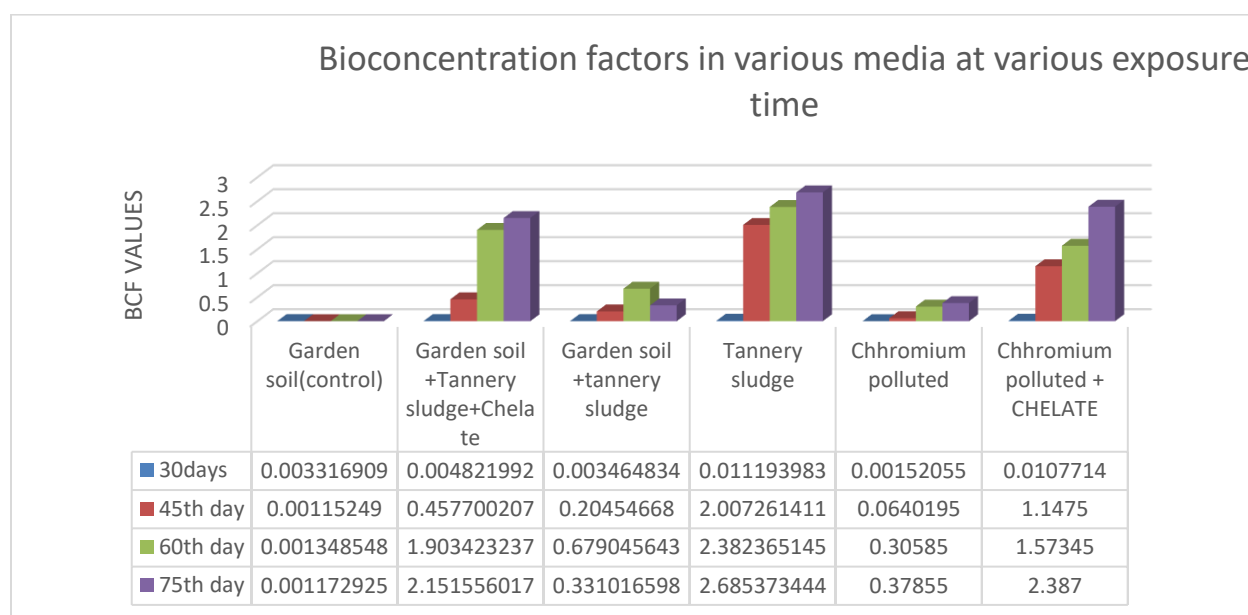


Figure 4.7: Bioconcentration factors in various media at various exposure period of the plant

Considering the pot with tannery sludge, the bioconcentration factor were 2.0, 2.38 and 2.68 at day 45th, 60th and 75 respectively (Table 4.7 and Figure 4.7). This signifies *Ricinus communis* plant to be a hyper accumulator, since $BCF > 1$. Therefore, *R. communis* plants can be used for successful reclamation of Chromium contaminated soils- based its $BCF > 1$ effectively from 45th day.

4.7 General discussions

The *Ricinus communis* plant, demonstrated potential for phytoremediation of hexavalent chromium by both phytostabilization and phytoextraction which may be attributed to its tolerance and considerable biomass production. The roots of the *Ricinus Communis* plant planted in the Tannery sludge had the highest Hexavalent Chromium accumulation. Furthermore, out of the six pots, the Hexavalent Chromium concentrations were high at the roots compared to the areal parts in five of the ports after 30 days and on the 45th day the highest concentrations were accumulated in the roots of the plant that were planted on the tannery sludge, mixture of tannery sludge and red soil, and the mixture of tannery sludge, red soil and chelate. This means that the plant can be used for phytostabilization of chromium contaminated soils hence reducing the mobility of the heavy metal by accumulation of the contaminants by the plant roots.

Basically, since the translocation factors were all greater than one at the exposure time of 75 days except for the control; this means that *Ricinus communis* plant has potential for phytoremediation by phytoextraction of chromium with exposure time of between 60 to 75 days. This agrees with Rani P. et.al (2017) on the study on “stabilization of tannery sludge amended soil using *Ricinus Communis*” where they concluded that *Ricinus Communis* plant is suitable for growth in “heavy metal rich” tannery sludge soil vis a vis for “phytostabilization of the heavy metals”.

Citric acid as a chelate applied on the tannery sludge and red soil mixture of ratio 1:1, increased absorption of Hexavalent Chromium from the 45th day with a percentage increase of more than 100%, at 60th day the percentage increase was 25% and 24% at 75th day. This shows that Citric acid can be used as a chelate in phytoremediation of Hexavalent chromium contaminated soils, since it enables the plant to absorb more of the contaminants.

The amount of Cr (VI) concentration in the plant is higher than the amount of it in the media. This could be due to chromium speciation, oxidation in the presence of manganese in the media. Bartlett and James (1979); observed that “Cr (III) was oxidized to Cr (VI) in soils with high elemental contents of Manganese as compared with other soils”. In addition; Kim et.al., (2002); Fendorf

et.al., (1993) concluded that “Chromium (III) can be oxidized into Cr (VI) in soils, mostly by Manganese oxides, especially quadrivalent Manganese”.

The data collected from the tests that were done was able to show that *Ricinus Communis* can extract Cr (VI) from tannery waste, mixture of tannery waste and red soil; mixture of tannery waste and red soil plus chelate. The result also showed that chelating the contaminated soil and tannery waste positively influenced extraction of Cr (VI). The results also showed that phytoextraction of Cr (VI) by *Ricinus Communis* can be best achieved at 75days since all the Translocation factors were higher than one. It was also evident from the results that the more the exposure period of the plant the more the extraction and accumulation of Cr (VI) in the *Ricinus Communis* plant.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study evaluated the phytoremediation of Hexavalent chromium from Tannery sludge which was sourced from Aziz tanneries limited. The study established the concentration of hexavalent chromium metal in the Tannery sludge, and determined the phytoremediation potential of *Ricinus communis* plant Planted on different media including Tannery sludge, Red soil and tannery sludge in the ratio of 1:1 with and without addition of a chelating agent, and artificially hexavalent contaminated soil.

Observations were made on the growth of *Ricinus communis* plant on red soil (control), tannery sludge, tannery sludge and the red soil mixed at a ratio of 1:1, and artificially contaminated soil for a period of 75 days. Lastly translocation factors and bioconcentration factors were calculated and used to check whether *Ricinus communis* plant can be used to decontaminate hexavalent chromium contaminated soils. The following were the conclusions of the study.

1. The average concentrations of Hexavalent Chromium (CrVI) Level from the Tannery sludge collected was as 14.936mg/kg this exceeded the United States Environmental Protection Agency (U.S. EPA) regulatory limits for protection of human health and the environment of 0.01mg/kg and the National Environmental Management Authority and WHO limits of 0.05mg/kg.
2. The Hexavalent Chromium accumulation from tannery sludge and their distribution in root shoot and leaves showed variable patterns while the roots of the *Ricinus Communis* plant planted in the Tannery sludge had the highest Hexavalent Chromium accumulation. Furthermore, it was observed that out of the six pots, the Hexavalent Chromium concentrations were high at the roots compared to the areal parts in five of the pots at the 30th and 45th day. On the 60th day there was high concentration of hexavalent chromium in leaves, stem and roots of *Ricinus communis* in tannery sludge media, which infers translocation of the metal. This capability is a result of the *Ricinus Communis* plant roots' great capacity to accumulate heavy metals in their cell walls, high biomass production, and strong antioxidant capacity to remove Reactive Oxygen Species (ROS).
3. Application of the chelate on the tannery sludge and red soil mixture of ratio 1:1, increased absorption of Hexavalent Chromium. At the 30th day the percentage increase was 39% and

more than 100%, from the 45th day. The total accumulation of Hexavalent chromium in *R. Communis* plant at the end of the exposure period was 11.74 ppm in the pot without chelate and 43.54ppm in the pot with chelate which is approximately 3.7 times more. These demonstrates that Citric acid can be used as a chelate in phytoremediation of hexavalent chromium contaminated soils.

4. The bio concentration factor ranged between 0.01 and 2.68. The results in this study showed that *Ricinus Communis* planted on Tannery sludge had BCF values > 1 from the 45th day to 75th day, indicating that the plant has the potential to be used as accumulator of Hexavalent Chromium and good for Phytostabilization; Consequently, environment contaminated with hexavalent chromium can be successfully cleaned up with *R. communis*.
5. Translocation factors were all greater than one at the exposure time of 75days except in the control pot. The highest translocation factor (2.524), was noted at 75days exposure time, followed by 1.997 at exposure time of 75days in the chromium polluted soil and soils mixed with tannery sludge (1:1 ratio) respectively. *Ricinus communis* plant has potential for phytoremediation by phytoextraction of chromium with exposure time of between 60 to 75 days.

5.2 Recommendations

From the research findings, *Ricinus communis* showed potential of hexavalent chromium phytoremediation via both phytoextraction and Phyto-stabilization. Given this was a pot experiment its therefore recommended that the plant be used under field conditions to reclaim chromium contaminated soils and reduce chromium levels in tannery sludge. Secondly from the study Citric acid can be used as a chelate in phytoremediation of hexavalent chromium contaminated soils and tannery sludge.

5.3 Recommendations for further research

1. Management techniques that could lead to a buildup of metals in the *R. communis* shoots and prevent the roots from reintroducing the metals into the soil.
2. Evaluation of the effect of Manganese and other oxidants in converting the Cr (III) to Cr (VI).
3. Establish the optimal dosage of chelating agent verses the maximum metal absorption without retarding plant growth.

4. Investigation on enzymes interaction with the accumulated hexavalent chromium in the roots and shoot of the plant.

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APPENDICES

Appendix 3.1: Photographs of planting media and materials



Plate 3.1: Soil media and tannery preparation



Plate 3.2: Ricinus communis seeds



Plate 3.3: Potassium dichromate used for contamination



Plate 3.4: Citric acid, chelating agent

Appendix 4.1: Plant growth and harvesting



Plate 4.1.1: Plant growth in the nursery bed



Plate 4.1.2: Plant growth 7 days after transplanting



Plant 4.1.3: Plant growth at day 15



Plate 4.1.4 plants harvested and separated into leaves, stem and roots

Appendix 4.2: Sample Labelling

Sample Labelling				
	day 30	45	Day 60	Day 75
Media	Sample ID	Sample ID	Sample ID	Sample ID
Garden soil	GP 1-	GP C-	Sample 1-	GP 1-
garden soil +sludge + chelating agent	GP 2-	GP D-	Sample 2-	GP 2-
tannery sludge +garden	GP 3-	GP E-	Sample 3-	GP 3-
tannery sludge	GP 4-	GP B-	Sample 4-	GP 4-
chromium polluted	GP 5-	GP A-	Sample 5-	GP 5-
chromium polluted+ chelate	GP 6-	GP F-	Sample 6-	GP 6-

Appendix 4.3: Analysis of plant tissues after 30 days

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CERTIFICATE OF ANALYSIS

CoA No:SAS /CA/RD/19029-19046

Client: NYAKUNDI EVERLYNE KEMUNTO
Contact Person: Ms. Nyakundi Everlyne Kemunto
Date Received: Jan 3, 2019
Client's Code: SAS-KC-126

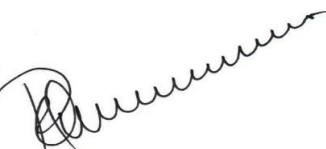
Sample Name:	Castor oil Plant
Customer ID	Plant Tissues
Laboratory ID	SAS-RD-19029-19046
Date Reported	6-Feb 2019

Sample ID	Lab Nos.:	Analytical	Units	Reading 1	Reading 2	Reading	Average
GP 1- Leaves	SAS-RD-	AAS Met	ppb	9.9641	9.5656	9.5443	9.691
GP 1- Stems	SAS-RD-	AAS Met	ppb	11.9261	11.9197	11.1309	11.659
GP 1- Roots	SAS-RD-	AAS Met	ppb	10.7689	10.3381	10.7689	10.625
GP 2- Leaves	SAS-RD-	AAS Met	ppb	7.9824	7.9886	7.1842	7.718
GP 2- Stems	SAS-RD-	AAS Met	ppb	23.6035	24.3902	23.6035	23.866
GP 2- Roots	SAS-RD-	AAS Met	ppb	15.7052	14.4971	14.4971	14.900
GP 3- Leaves	SAS-RD-	AAS Met	ppb	15.7387	15.7384	15.7497	15.742
GP 3- Stems	SAS-RD-	AAS Met	ppb	4.6476	4.6512	4.7628	4.687
GP 3- Roots	SAS-RD-	AAS Met	ppb	13.5809	12.7796	12.5564	12.972
GP 4- Leaves	SAS-RD-	AAS Met	ppb	15.8573	15.7097	15.0346	15.534
GP 4- Stems	SAS-RD-	AAS Met	ppb	40.5108	40.4866	40.4916	40.496
GP 4- Roots	SAS-RD-	AAS Met	ppb	52.4344	52.2778	50.9270	51.880
GP 5- Leaves	SAS-RD-	AAS Met	ppb	8.9824	9.9927	8.1842	9.053
GP 5- Stems	SAS-RD-	AAS Met	ppb	2.3928	1.9940	2.3928	2.260
GP 5- Roots	SAS-RD-	AAS Met	ppb	19.4695	19.5225	18.3019	19.098
GP 6- Leaves	SAS-RD-	AAS Met	ppb	19.9187	19.5219	19.5219	19.654
GP 6- Stems	SAS-RD-	AAS Met	ppb	93.8977	93.9941	94.0961	93.996
GP 6- Roots	SAS-RD-	AAS Met	ppb	101.7769	101.7799	101.7776	101.778

Remarks

* ppb - parts per billion

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Appendix 4.4: Analysis of plant tissues after 45 days

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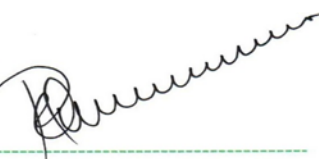
CoA No: SAS /CA/RD/19227-19244

Client: NYAKUNDI EVERLYNE KEMUNTO
Contact Person: Ms. Nyakundi Everlyne Kemunto
Date Received: Jan 18, 2019
Client's Code: SAS-KC-126

Sample Name:	Castor oil Plant
Customer ID	Plant Tissues
Laboratory ID	SAS-RD-19227-19244
Date Reported	29-Jan -19

Sample ID	Lab Nos.:	Analytical	Units	Reading 1	Reading 2	Reading 3	Average
GP C-	SAS-RD-19227	AAS Met	ppb	Nil	Nil	Nil	Nil
GP C-	SAS-RD-19228	AAS Met	ppb	3.1746	3.1311	3.1809	3.1622
GP C-	SAS-RD-19229	AAS Met	ppb	7.9840	7.9208	7.9523	7.9524
GP D-	SAS-RD-19230	AAS Met	ppb	3.9761	3.1373	3.8835	3.6656
GP D-	SAS-RD-19231	AAS Met	ppb	3.1558	3.1936	3.1250	3.1581
GP D-	SAS-RD-19232	AAS Met	ppb	4660.2000	4660.9000	4660.0000	4405.4000
GP E-	SAS-RD-19233	AAS Met	ppb	3.9216	3.9604	3.8986	3.9269
GP E-	SAS-RD-19234	AAS Met	ppb	3.0948	3.1311	3.1496	3.1252
GP E-	SAS-RD-19235	AAS Met	ppb	1964.2000	1964.6000	1965.5000	1964.7667
GP B-	SAS-RD-19236	AAS Met	ppm	3.9944	3.9968	3.9920	3.9944
GP B-	SAS-RD-19237	AAS Met	ppm	3.1564	3.1784	3.1527	3.1625
GP B-	SAS-RD-19238	AAS Met	ppm	12.6883	11.9427	11.9784	12.2031
GP A-	SAS-RD-19239	AAS Met	ppb	3.1128	3.1496	3.1873	3.1499
GP A-	SAS-RD-19240	AAS Met	ppb	3.5398	3.5011	3.6613	3.5674
GP A-	SAS-RD-19241	AAS Met	ppb	1273.3200	1273.7900	1273.8900	1273.6667
GP F-	SAS-RD-19242	AAS Met	ppb	4590.0026	4590.2051	4590.0070	4590.0716
GP F-	SAS-RD-19243	AAS Met	ppb	5160.1765	5159.9853	5160.0015	5160.0544
GP F-	SAS-RD-19244	AAS Met	ppb	13200.0283	13200.0183	13199.9807	13200.0091

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Appendix 4.5: Analysis of plant tissues after 60 days

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CERTIFICATE OF ANALYSIS

CoA No:SAS/CA/RD/19406-19423

Client: NYAKUNDI EVERLYNE KEMUNTO
Contact Person: Ms. Nyakundi Everlyne Kemunto
Date Received: February 5, 2019
Client's Code: SAS-KC-126

Sample Name:	Castor oil Plant
Customer ID	Plant Tissues
Laboratory ID	SAS-RD-19406-19423
Date Reported	6-March-19

Sample ID	Lab Nos.:	Analytical	Units	Reading 1	Reading 2	Reading 3	Average
Sample 1-	SAS-RD-19406	AAS Met	ppb	3.9928	3.9833	3.9912	3.9891
Sample 1-	SAS-RD-19407	AAS Met	ppb	1.1966	1.1962	1.1971	1.1966
Sample 1-	SAS-RD-19408	AAS Met	ppb	7.9943	8.0255	8.0021	8.0073
Sample 2-	SAS-RD-19409	AAS Met	ppm	5.9832	5.9892	5.9976	5.9871
Sample 2-	SAS-RD-19410	AAS Met	ppm	6.3745	6.3821	6.3758	6.3775
Sample 2 -	SAS-RD-19411	AAS Met	ppm	5.9856	5.9737	5.9928	5.984
Sample 3-	SAS-RD-19412	AAS Met	ppm	1.5857	1.5854	1.5939	1.5883
Sample 3-	SAS-RD-19413	AAS Met	ppm	0.9946	0.9988	0.9923	0.9952
Sample 3-	SAS-RD-19414	AAS Met	ppm	3.9683	3.969	3.9667	3.963
Sample 4-	SAS-RD-19415	AAS Met	ppm	8.4962	8.6788	8.5874	8.587467
Sample 4-	SAS-RD-19416	AAS Met	ppm	1.9857	1.9924	1.9861	1.988067
Sample 4-	SAS-RD-19417	AAS Met	ppm	12.3909	12.3881	12.3937	12.3909
Sample 5-	SAS-RD-19418	AAS Met	ppm	2.5927	2.5865	2.5871	2.588767
Sample 5-	SAS-RD-19419	AAS Met	ppm	0.6906	0.6903	0.691	0.690633
Sample 5-	SAS-RD-19420	AAS Met	ppm	2.8373	2.8367	2.8377	2.837233
Sample 6-	SAS-RD-19421	AAS Met	ppm	2.4915	2.4821	2.4876	2.487067
Sample 6-	SAS-RD-19422	AAS Met	ppb	15193.113	15193.004	15193.0143	15193.04
Sample 6-	SAS-RD-19423	AAS Met	ppb	13789.043	13789.01	13788.9982	13789.02

Remarks

* ppm - parts per million

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Appendix 4.6: Analysis of plant tissues after 75 days

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CERTIFICATE OF ANALYSIS

CoA No: SAS /CA/RD/19564-19581

Client: NYAKUNDI EVERLYNE KEMUNTO
Contact Person: Ms. Nyakundi Everlyne Kemunto
Date Received: Feb 19, 2019
Client's Code: SAS-KC-126

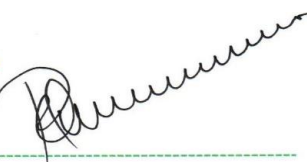
Sample Name:	Castor oil Plant
Customer ID	Plant Tissues
Laboratory ID	SAS-RD-19564-19581
Date Reported	4th-March -19

Sample ID	Lab Nos.:	Analytical	Units	Reading 1	Reading 2	Reading 3	Average
GP 1- Leaves	SAS-RD-19564	AAS Met	ppb	0.0019936	1.9936	1.9984	1.331
GP 1- Stems	SAS-RD-19565	AAS Met	ppb	3.9872	3.9928	3.9968	3.992
GP 1- Roots	SAS-RD-19566	AAS Met	ppb	5.9809	5.9928	5.9797	5.984
GP 2- Leaves	SAS-RD-19567	AAS Met	ppm	3.9928	3.9992	3.9918	3.995
GP 2- Stems	SAS-RD-19568	AAS Met	ppm	8.7733	8.7914	8.7885	8.784
GP 2- Roots	SAS-RD-19569	AAS Met	ppm	7.9586	7.9729	7.9554	7.962
GP 3- Leaves	SAS-RD-19570	AAS Met	ppm	1.9956	1.9948	1.996	1.995
GP 3- Stems	SAS-RD-19571	AAS Met	ppm	0.7974	0.7968	0.7966	0.797
GP 3- Roots	SAS-RD-19572	AAS Met	ppm	0.3994	0.399	0.3995	0.399
GP 4- Leaves	SAS-RD-19573	AAS Met	ppm	3.9793	3.9841	3.9849	3.983
GP 4- Stems	SAS-RD-19574	AAS Met	ppm	13.9896	13.9968	13.9984	13.995
GP 4- Roots	SAS-RD-19575	AAS Met	ppm	7.9036	7.9365	7.888	7.909
GP 5- Leaves	SAS-RD-19576	AAS Met	ppm	1.9976	1.9944	1.9968	1.996
GP 5- Stems	SAS-RD-19577	AAS Met	ppm	3.9976	3.9872	3.9928	3.993
GP 5- Roots	SAS-RD-19578	AAS Met	ppm	1.5826	1.5823	1.5813	1.582
GP 6- leaves	SAS-RD-19579	AAS Met	ppm	12.7933	12.7833	12.8942	12.824
GP 6- stems	SAS-RD-19580	AAS Met	ppm	17.99501	17.995004	17.99502	17.995015
GP 6- Roots	SAS-RD-19581	AAS Met	ppm	16.92103	16.92104	16.92107	16.92105

Remarks

* ppb - parts per billion,

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Appendix: 4.7 ANOVA analysis on effect of chelate

ANOVA REGRESSION ANALYSIS ON EFFECT OF CHELATE

Anova: Single Factor						
SUMMARY						
<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>		
Without chelate	12	11742.23	978.5193	1487487.12		
With chelate	12	43548.71	3629.06	11837362.1		
ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	42152181.7	1	42152182	6.32685306	0.019696	4.30095
Within Groups	146573341.9	22	6662425			
Total	188725523.6	23				

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