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Phytoremediation of Hexavalent Chromium in Effluent Tannery Sludge and Chromium Contaminated Soils using Ricinus Communis Plant

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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 tannery 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 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 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 Reference [1] 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 phytosytabilization of the heavy metals

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

Keywords*: *Phytoremediation, Hexavalent Chromium, potential, Ricinus Communis, Bioconcentration factor, Translocation factor, Chelating Agent

I. INTRODUCTION

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 intents to accomplish the ideal outcomes [2].

Tanneries are a standout amongst the most conspicuous wellsprings of chromium contamination to the amphibian condition. Reference, [3] 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 [4]. 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” [7]. “It is reported that about 140-200 kg of fleshing, which are putrescible by nature, are generated for every ton of leather processed” [7]. 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 categorized as dangerous matter [7]. 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”, [7]. 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, [7].

Generally leather industry is associated with the generation of huge amounts of solid waste and disposal of this waste become a serious problem [8]. Chromium in the effluent is a major concern for tanning industry [9]. Chemical precipitation techniques are ordinarily utilized for the expulsion of "chromium" however this contributes to a lot of "chrome-bearing solid waste", in addition to it is "uneconomical when the concentration of chromium in the effluent is low" [10]. "Ion exchange and membrane separation" strategies are moderately costly [10]. 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 research will therefore come up with a remediation strategy to rehabilitate chromium contaminated soils in various tanning industries in Kenya and tannery effluent sludge.

II. RELATED WORK

Various researches have been done to evaluate the potential of Ricinus Communis (Castor bean) on phytoremediation of various heavy metals. According to reference [11] "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"[12]; "Phytoremediation of Cadmium by Ricinus communis L. in Hydrophonic Condition" [13]; "Ricinus communis L. (Castor bean), a potential multi-purpose environmental crop for improved and integrated phytoremediation" [14], "The phytoremediation potential of bioenergy crop Ricinus communis for DDTs and cadmium co-contaminated soil"[15]; "Potential of castor bean (Ricinus communis L.) for phytoremediation of mine tailings and oil production"[16]. All the above studies acknowledge that Ricinus commmunis is a wizard of phytoremediation.

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 polychlobiphenyls in land fill e-waste leachate with water hyacinth by [17] ; Phytoremediation by means of bamboo to lessen hazards of chromium exposure from polluted tannery locations in Kenya by [18]; Phytoremediation of heavy metals in sewage sludge using plants from Brassicae family by [19]. All the above researchers recommended more research on phytoremediation using various plants since it's an efficient and economical way of rehabilitating the environment.

This study examined the heavy metal Hexavalent chromium which hasn't been studied in connection with Ricinus Communis as a phytoremediator.

III. METHOD

III.I Sampling of sludge for analysis of Hexavalent chromium

Tannery sludge samples were collected from both the drying beds and the tannery sludge pit that had wet sludge. To obtain a representative sample, the sludge was sampled by scooping at different points and depths of the tannery effluent sludge pits and then mixed thoroughly before analysis. The mixed tannery sludge samples were collected in plastic containers, properly labeled taken for Hexavalent Chromium analysis.

III.II Determination of Hexavalent Chromium contamination levels in tannery sludge

The chromium concentration in the tannery sludge samples were analyzed utilizing Atomic Absorption Spectrophotometer (AAS). The concentration of chromium VI in the tannery sludge and red soil was compared with the maximum permissible limit of chromium (VI) as set by NEMA in national environment regulations and US-EPA.

III.III Ricinus plant seeds

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

III.IV. Experimental setup

The Seedlings were transplanted in various pots having various concentrations of Chromium to determine the phytoremediation potential. The various experimental pot set ups were as follows:

i. Garden soil + plant(4 experimental pots)
ii. Garden soil +Tannery Sludge + plant (4 experimental pots(1:1ratio))
iii. Tannery Sludge + plant (4experimental pots)
iv. Garden soil + sludge + chelating agent(4 experimental pots)
v. Heavy metal polluted soil + plant(4 experimental pots)
vi. Heavy metal polluted soil + plant+ chelating agent (4experimetal pots)

III. VI Assessment/comparison of the uptake rate of cr^{+6} of the plants

Seedlings were in trial pots 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, cleaned using faucet water and deionized water, and isolated into shoots, stems and roots

The plants were then dried in an oven at 105^0c for 48 hours, carbonized by heating them on a hot plate for an hour until the powder turns black. The ash was then dried using a furnace (500-600^0c), cooled and weighed, and finally chromium VI concentrations was determined using a flame Atomic Absorption Spectrometer.

III.VII Determination of Bio-Concentration Factor (BCF) and Translocation Factor (TF)

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 [20] The translocation factor is the capability of the plant to translocate metals from the root to the leaves via the shoots. The BCF and TF were calculated using equation one and two respectively as stated below

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$$\textbf{BCF} = \frac{C\ plant\ part\ (mg/kg}{C\ soil\ part\ (\frac{mg}{kg})} \quad \textbf{(1)}$$

Where
$C_{plant\ part}$-chromium concentration in the plant part sample,
C_{Soil} -chromium concentration in the soil.

$$\textbf{TF} = \frac{C\ stem\ (mg/kg}{C\ root\ (\frac{mg}{kg})} \quad \textbf{(2)}$$

Where:
$\mathbf{C}_{stem}$ - concentration of chromium in plant stem, and $\mathbf{C}_{root}$ - concentration of the chromium in the root

IV. RESULT

IV. I Concentration Of Hexavalent Chromium In Aziz Tannery Sludge

The concentrations of Hexavalent Chromium Cr(VI) Level in the Aziz Tannery sludge pit was recorded 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 and the National Environmental Management Authority limits (table 1). Therefore, there is need for pollution control measures to limit the release of Hexavalent Chromium into the environment

Table 1:Aziz tannery hexavalent chromium concentrations

source	units	Value
Sludge Drying Bed	ppm	9.640
Sludge Pit	ppm	14.936

IV.I Absorbed Hexavalent chromium concentrations

The Hexavalent Chromium accumulation from tannery sludge and their distribution in root shoot and leaves showed variable patterns as shown in Table 2.

As shown in table 2, at 30 days, 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 ports after 30 days.
On the 45th day the highest concentrations 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 [23,24].
[29] 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, [24] 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 the Cr species.

However, [30] found that more 51Cr was transported from root to shoot when Cr (VI), rather than Cr (III), was supplied to the plant. At high Cr doses (1 mM $CrCl_3$) roots accumulated very high levels of Cr and translocation was mainly to cotyledonary leaves and only small amounts in hypocotyls.

Table 2 further shows that there was high accumulation of CrVI 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 Hexavalent chromium in the pots having tannery sludge and mixture of tannery sludge, red soil and chelating agent

Table 2 Accumulation of Hexavalent Chromium Concentrations in Different Parts of the Ricinus Communis Plant during the experimental period

Period of exposure		30days	45th day	60th day	75th day
Media	**Plant part**	**Accumulation(ppb)**	**Accumulation(ppb)**	**Accumulation(ppm)**	**Concentration**
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±0.0017	5.984±0.0072ppb
Garden soil +Tannery sludge (1:1 ratio)	Leaves	7.718±0.463	3.67±0.460	5.987±0.0072	3.995±0.0040ppm
	Stems	23.866±0.454	3.16±0.034	6.378±0.0041	8.784±0.0091ppm
	Roots	14.900±0.697	4405.40±0.473	5.984±0.0096	7.962±0.0093ppm
Tannery sludge	Leaves	15.534±0.439	3.99±0.002ppm	8.587±0.0913	3.983±0.0030ppm
	Stems	40.496±0.013	3.16±0.014ppm	1.988±0.0038	13.995±0.0047ppm
	Roots	51.880±0.829	12.20±0.421ppm	12.391±0.0028	7.909±0.0248ppm
chromium polluted soil	Leaves	9.053±0.906	3.15±0.037	2.589±0.0034	1.996±0.0017ppm
	Stems	2.260±0.230	3.57±0.084	0.691±0.0004	3.993±0.0052ppm
	Roots	19.098±0.690	1273.67±0.304	2.837±0.0005	1.582±0.0007ppm

Values are means of three replicates ± standard error

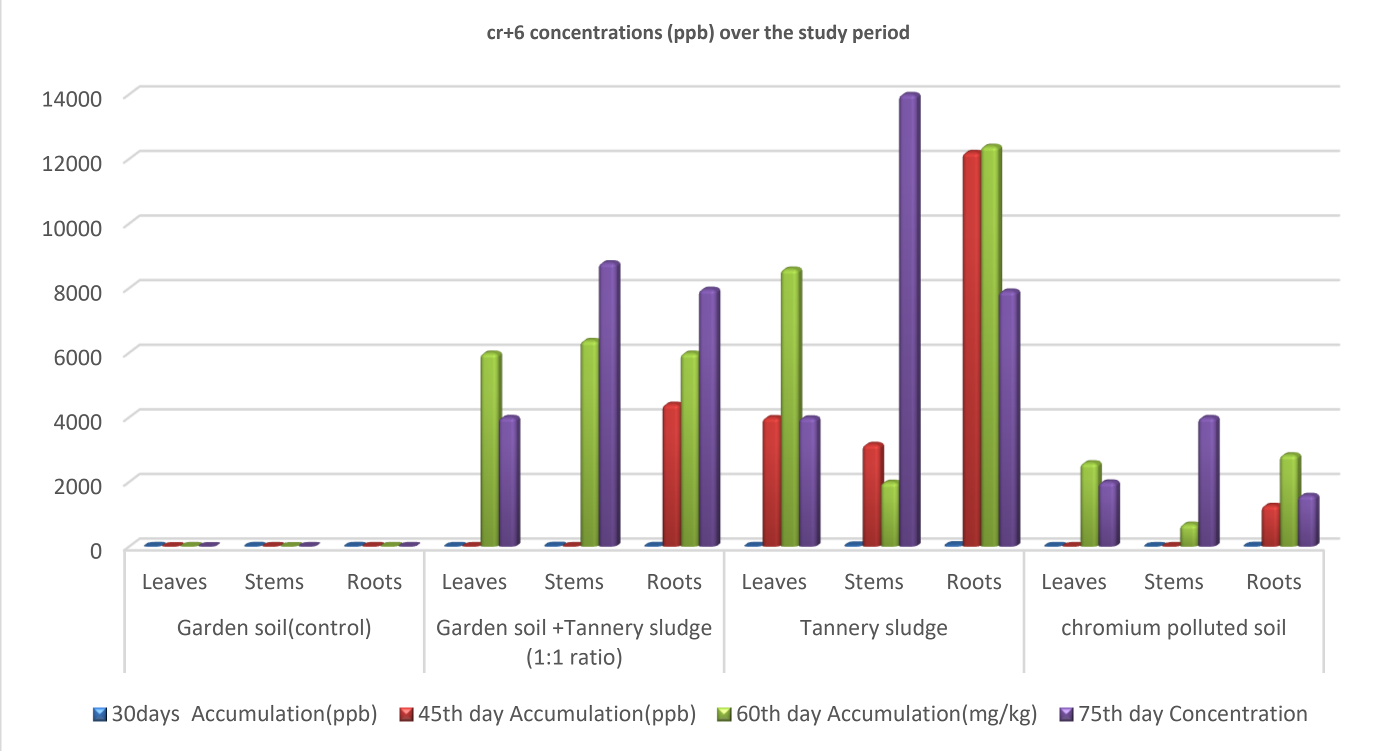

Figure 1: concentrations of hexavalent chromium in the roots, stem and leaves of Ricinus plant over the exposure period

VI: II EFFECTS OF CHELATE ON ABSORPTION OF HEXAVALENT CHROMIUM USING MIXTURE OF TANNERY SLUDGE AND RED SOIL AS MEDIA

As shown on table 3. Below, Citric acid as a chelate had a very high impact on phytoremediation of chromium from the soil, especially from the 45th day. This concurs with the results of [21] 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.

The highest concentration of the chromium was in the stems and roots of the R. Communis plant in tannery sludge media with chelate.

Application of the chelate on the tannery sludge and red soil mixture of ratio 1:1, showed an increased absorption of Hexavalent Chromium from the 45th day onwards as shown in figure 2. At the 45th day the percentage increase was more than 100%, at 60th day the percentage increase was 25% and 24% at 75th day (Table 3). 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. This shows that Citric acid can be used as a chelate in phytoremediation of chromium contaminated soils.

Table 3 Hexavalent chromium concentrations in leaves, stem and roots of the Ricinus communis plant in tannery sludge media with and without chelate.

Part Of Plant	Time (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

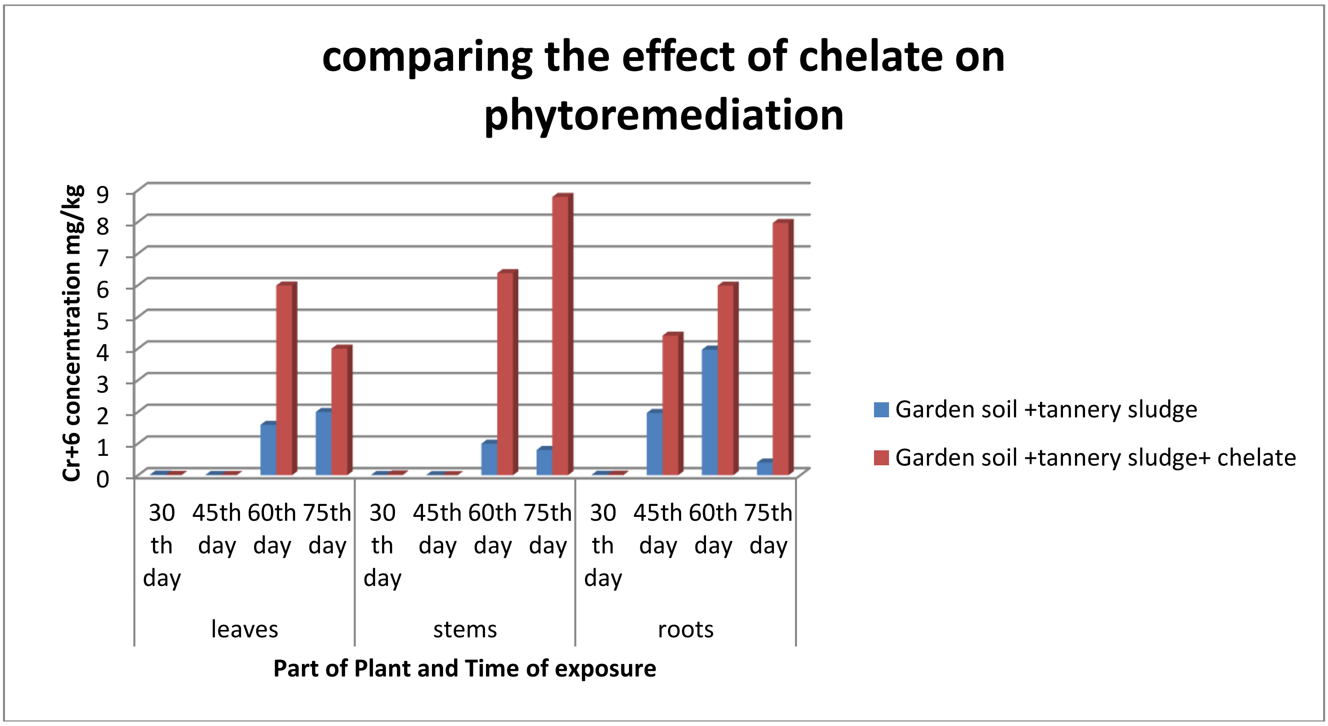

Figure 2a: figure showing effects of citric acid chelate on hexavalent phytoremediation

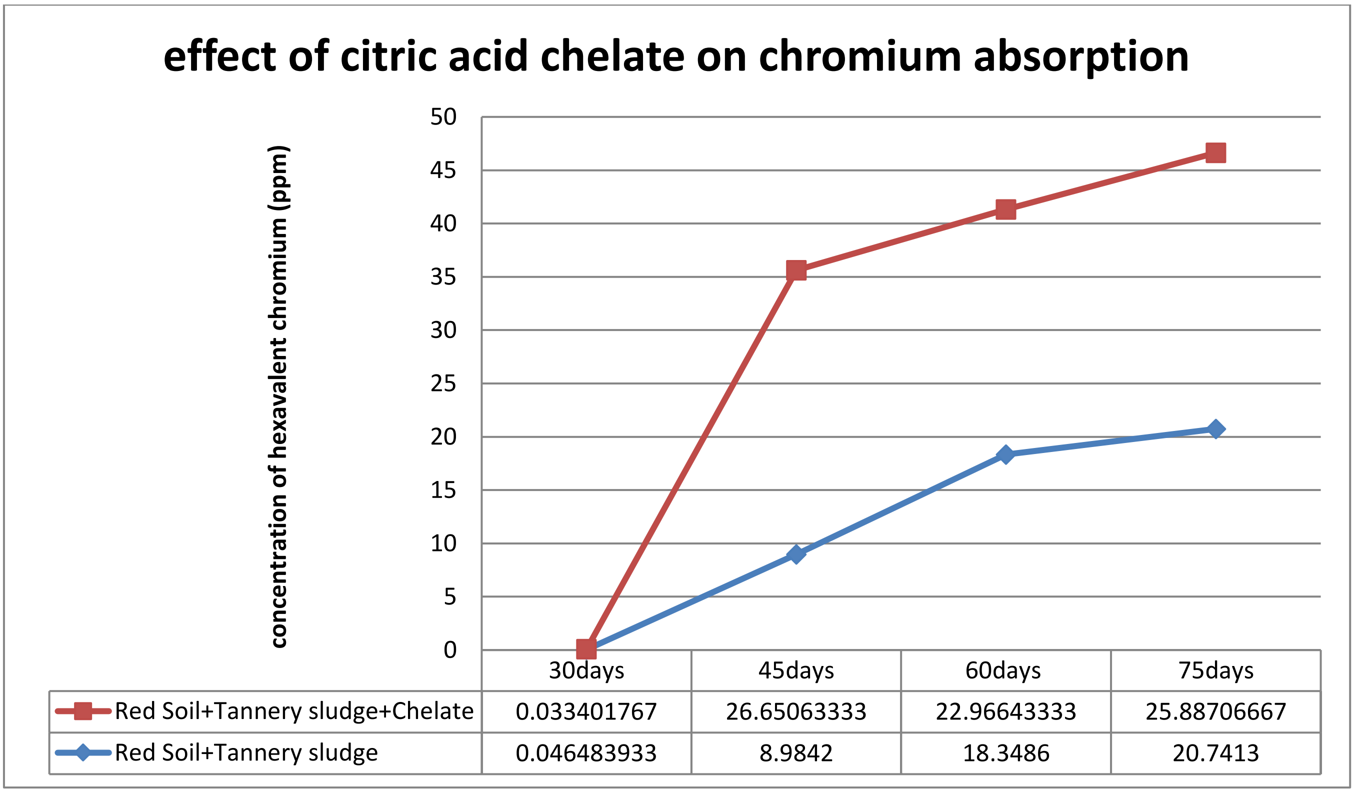

Figure 3b: figure showing effects of citric acid chelate on hexavalent phytoremediation

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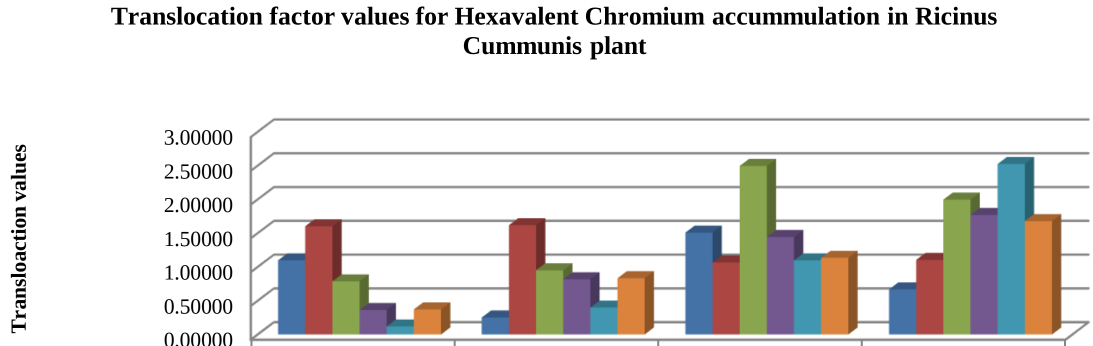
VI: III TRANSLOCATION FACTOR (TF)

The Translocation Factor 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. Plants with TF values > 1 are classified as high-efficiency plants for metal translocation from the roots to shoots [22].

The translocation factors of the Ricinus communis Plant as per the experimental design are shown (table 4.) The highest translocation factor (2.524), was noted at 75days exposure time, followed by 2.495 after exposure time of 60days in the soils mixed with tannery sludge (1:1 ratio) and the tannery sludge respectively.

Generally, since the translocation factors were all greater than one at the exposure time of 60days; this means that Ricinus communis plant has potential for phytoremediation of chromium with exposure time of between 60 to 75 days. This agrees with [1] 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 Phyto stabilization of heavy metals. A better translocation is advantageous to phytoextraction as it can reduce Cr concentration and thus reduce the toxicity potential to the root, and translocation to the shoot is one of the mechanisms of resistance to high Cr concentration [23]

Table 4 Table showing the translocation factors, given various medias (Tannery sludge, chromium polluted red soil and red soil) at different exposure time



	30days	45days	60days	75days
Control	1.09728	0.25149	1.50705	0.66710
Garden+tannery	1.60175	1.61751	1.06576	1.10325
Tannery sludge	0.78563	0.94996	2.49512	1.99583
garden+tannery+c	0.36132	0.81707	1.44291	1.76941
HP	0.11833	0.39764	1.09598	2.52362
HP+C	0.37077	0.83278	1.13432	1.67757

IV: IV BIOCONCENTRATION FACTOR (BCF)

The bioconcentration factor is the ability of the plant to accumulate heavy metal with respect to the metal concentration in the surrounding medium [24]. BCF values at different exposure time (days) calculated from initial concentration of metal in the effluent are given in Table 4.6. Maximum bio concentration factor ranged between 0.04 and 4.9. Maximum BCF value for Hexavalent Chromium was 4.98 on day 45. This study assumed that plants with BCF values > 1 are accumulators, while plants with BCF values < 1 are excluders [25].

The results in this study showed that Ricinus Communis planted on Tannery sludge had BCF values > 1from 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 (Table 5) This agrees with [1], 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 successfully used to remediate heavy metal contaminated environments

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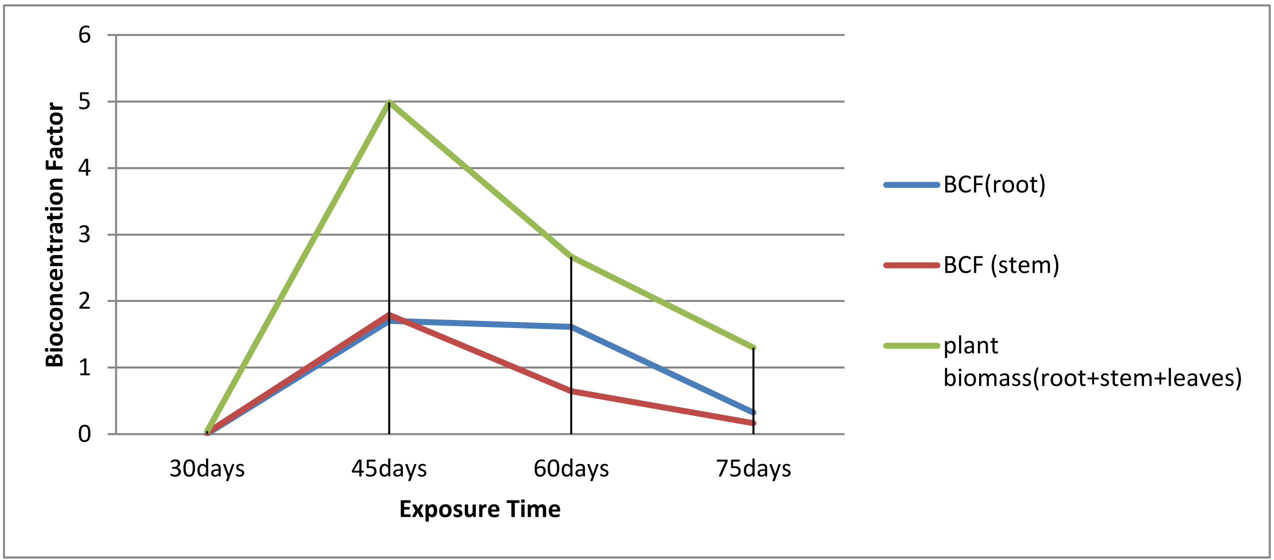
The success of the phytoextraction process depends on heavy metal removal by the shoots [26]. Therefore, it is suggested that the plant species having the higher metal concentration in its shoots than in its roots can be considered as accumulator for phytoremediation. For the fact that this plant also showed BCF value < 1, it could also be an excluder in phytoremediation processes

Table 5 Bioconcentration factors

	Bioconcentration Factors		
Exposure Time	BCF(root)	BCF (stem)	plant biomass(root+stem+leaves)
30days	0.00606274	0.020974284	0.043773031
45days	1.70286743	1.792561849	4.986965739
60days	1.61254883	0.646280924	2.663777669
75days	0.324273	0.162475586	1.298706055

Values are means of three replicates ± standard error



Values are means of three replicates ± standard error

Figure 4 Bioconcentration factors of the Ricinus Communis plant in tannery sludge

From the (Figure 4) above, the Bioconcentration factor considering the plant biomass was highest at day 45, and generally there was reduction of the bioconcentration factors as the exposure days increased. Therefore, *R. communis* plants can be used for successful reclamation of Chromium contaminated soils-contaminated soil based on its BCF>1 from the 45th day

V. DISCUSSION

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. 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 an red soil, and the mixture of tannery sludge, red soil and chelate. This means that the plant can be used for Phyto stabilization 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 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 [1] 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 phytosytabilization 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; [27] and [28] concluded that Chromium (III) can be oxidized into Cr (VI) in soils, mostly by Manganese oxides, especially quadrivalent Manganese.

VI. CONCLUSION

This paper aims to compare nine supervised algorithms' performance towards DDoS intrusion. DDoS attack will result

1. 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 ports after 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 ability is due to its high biomass production, strong antioxidant capacity to eliminate reactive oxygen species (ROS), and high capacity to accumulate heavy metals in the cell walls of roots [31].
2. Application of the chelate on the tannery sludge and red soil mixture of ratio 1:1, increased absorption of Hexavalent Chromium. At the 45th day the percentage increase was more than 100% while 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 chromium contaminated soils.

3. The bio concentration factor ranged between 0.04 and 4.9. Maximum BCF value for Hexavalent Chromium was 4.98 on day 45.The results in this study showed that Ricinus Communis planted on Tannery sludge had BCF values > 1from 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 hence that R. *communis* can be successfully used to remediate heavy metal contaminated environments,

4. Translocation factors were all greater than one at the exposure time of 60days; The highest translocation factor (2.524), noted at 75days exposure time, followed by 2.495 after exposure time of 60days in the soils mixed with tannery sludge (1:1 ratio) and the tannery sludge respectively. This means that Ricinus communis plant has potential for phytoremediation of chromium with exposure time of between 60 to 75 days.

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