STUDIES ON THE EFFECT OF TANNERY EFFLUENT ON SOIL AND CROP SYSTEM

Thesis submitted in part fulfillment of the requirements for the award of degree of Master of Science in Environmental Sciences to the Tamil Nadu Agricultural University, Coimbatore

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COIMBATORE

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CERTIFICATE

This is to certify that the thesis entitled "**STUDIES ON THE EFFECT OF TANNERY EFFLUENT ON SOIL AND CROP SYSTEM**" submitted in part fulfillment of the requirements for the degree of Master of Science in Environmental sciences to the Tamil Nadu Agricultural University, Coimbatore is a record of *bonafide* research carried out by **Ms.K.Indra** under my supervision and guidance and that no part of this thesis has been submitted for the award of any other degree, diploma, fellowship or other similar titles or prizes and that the work has not been published in part or full in any scientific or popular journal or magazine.

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(K.INDRA)

ABSTRACT

STUDIES ON THE EFFECT OF TANNERY EFFLUENT ON SOIL AND CROP SYSTEM

By

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Tanning industry is generating enormous quantities of effluent every day. The scientific ways and means of utilizing this liquid waste in reducing the pollution load is the main objective of this present investigation. Information on the utilization of tannery effluent for cultivation purposes is meager. The present study, therefore, was aimed at assessing the impact on soil by the effluent by conducting laboratory and incubation experiments using black and red soils.

Application of effluent to the soil at all the tested dilutions increased the salinity, sodium and chloride content of the soils. However, the above parameters were lower with 25 and 50 per cent diluted effluents, though they contain less toxic materials and at the same time they supplied considerable amounts of nutrients. In general, application of tannery effluent at 50 per cent concentration may be used for irrigation purposes.

Germination study with food crops like ragi, black gram and Amaranthus revealed that they are affected adversely by high concentrations (75 and 100 per cent) of tannery effluent. Though the effluent contains more amounts of dissolved solids

and the germination and growth of crops were affected, sodium and chloride were found to be the cause for the inhibition. But, these growth parameters got increased at higher dilutions of effluent (25 and 50 per cent). The study which was also conducted with simulated Cr(VI) and salt effluent, revealed that at all the concentrations affected the germination adversely. The percent germination as well as vigour index of crops got suppressed under all concentrations of chromium and salt.

In tannery wastes, Cr is of major concern and hence, laboratory studies on toxicity of chromium (VI) to microorganisms and its availability was carried out. Cr(VI) added to a soil will remain mobile only when its concentration exceeds both the adsorbing and the reducing capacities of soil. Hence, the major portion of added Cr(VI) was found reduced within 36 hours. The toxic effect of Cr(VI) before it is reduced to Cr(III) was very high on native microflora.

The distribution of Cr in the crops grown under Cr(VI) contaminated soil was in the order : root > shoot as revealed from the pot culture study. The roots of ragi, black gram and Amaranthus accumulated a considerable amount of Cr and only a small fraction was transported to the shoots. The uptake of Cr was found to be more in Amaranthus.

The results suggest that the tannery effluent at 50 per cent concentration had less pollution load and also supply more nutrients. This 50 per cent concentration as well as the more diluted effluent (25 per cent) has high ecological and economic significance as it can be used for irrigation water substitute. However, it should be test verified in the field for confirmation of this result.

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CHAPTER – 1

INTRODUCTION

Tanning industry is one of the oldest cottage industries in India, which have now taken a predominant place in the country's economy. There are more than 2500 tanneries in our country with an annual processing capacity of 7,00,000 tonnes of hides and skins. About 80% of tanneries are adopting in chrome tanning process. It is estimated that 30-35 L of water is used per kilogram of leather processed and the tannery industries generate about $680x10^6$ L of effluent per year. During the process of leather making, several toxic pollutants like $Cr_2(SO_4)_3$, NaCl, $Ca(OH)_2$, H_2SO_4, phenolic compounds, dyes, etc., are extensively used. Therefore, the resultant effluent is enriched with Chromium (Cr) and salts (Na, Chloride and SO_4). This has necessitated the tanners to look for long lasting and safe solution arising from the discharge of 'chemicals rich' tannery effluent into the environment.

Chromium in effluent is primarily in the less toxic trivalent form [Cr(III)]. When the effluent is discharged into the soil, due to varying environmental conditions, Cr(III) is oxidized to hexavalent form [Cr(VI)] (Bartlett and James, 1979), which is highly toxic with its potential carcinogenic effect (Bartlett and Kimble, 1976a) and mutagenic effect (Petrilli and Deflora, 1977).

Generally the tannery effluent contains about 2 to 6500 mg Cr L^{-1}. The permissible concentration of Cr in drinking and irrigation water is 50 µg L^{-1} in the effluent. A high concentration of Cr, ranging from 50 to 996 µg L^{-1} in bore well waters and 150 to 70,000 mg kg^{-1} in soils was detected near the tanneries in Vellore district of Tamil Nadu (Mahimairajah *et al.* 2000a).

Potassium, ammonium, phosphate, nitrate and protein matter present in the effluent is considered as good nutrients for various plants (Selvarangan, 1981). But, presence of large amount of chromium and salts affect the physico-chemical and

biological characteristics and are toxic to plant, animal and microorganisms. Hence, the impact of tannery effluent pollution on agriculture and allied activities and its indirect influence on socio- economic conditions of the farming community should be considered and the disposal of effluent has to be scientifically managed to avoid pollution to the ecosystem.

In order to minimize the pollution hazard a number of measures have been recommended. In many parts of India, Common Effluent Treatment Plants (CETP) has been setup to cater the tanning industry. The CETPs are effective in reducing the total solids (TDS), Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) of the effluent. But, Cr content in the effluent remains unchanged. Though the treated effluent contains more inorganic nutrients, the presence of heavy metal makes it toxic to the environment.

With this background, the present investigation was taken up to study the toxic effects of tannery effluent on the soil; plant and microorganism were taken up with the following objectives.

- Characterization of tannery effluent and evaluating the effect of raw and diluted tannery effluent on the properties of soil
- Evaluating the impact of tannery effluent and simulated effluent with chromium and NaCl at various concentrations on germination of crops
- Assessing the toxicity of chromium in soil by using simulated effluent at various concentrations and the uptake of chromium by crops.

CHAPTER - 2
REVIEW OF LITERATURE

Industrial pollution has emerged as a major environmental hazard in India. Most of the industries use water in varying proportions as a solvent or as a medium for chemical reactions for cooling or washing purposes. The resulting wastewater (effluent) containing toxic heavy metals and other hazardous chemicals are discharged from the factories and these effluents move through the unlined channels to nearest dispersion and percolate into the soil causing ground water pollution.

Though the international and local communities appreciate the potential of tanning industry in terms of economy and employment; there has been an increased awareness among the public about the adverse impacts of tannery wastes on agro-ecosystem. The tanning industries, its waste characteristics, the chemistry of chromium and environmental impact by the effluent are briefly reviewed in this chapter.

2.1. Tanning industry

A survey of the growth of Indian leather industries over the past few decades reveals that there are 1008 small scale and 75 large-scale tanneries in India. The hub of leather production in the country are Vellore, Erode and Dindigul in Tamil Nadu (50 per cent), Kolkatta in West Bengal (15 percent), Kanpur in Uttar Pradesh (12 per cent), and Jalandhar in Punjab (5 per cent). The Indian tanning industry occupies an important position in world leather market and is competing for foreign exchange. The export of leather and leather products has contributed more than $7x10^7$ rupees to Indian economy and its export share in global market is 6.7 per cent (Ramasamy and Naidu, 2000). It is not only a potential sector for export but also provides employment for about 1.4 million people. Tanning industries of Tamil Nadu contribute a share in

the foreign exchange income. These industries are highly labour intensive and most of the operations are done manually.

2.1.1.Process in leather making

The manufacture of leather can be divided into three separate phases. They are (a) beam house processing (removal of impurities in the skin and hides) (B) Tan yard processing (making the purified collagen of the skin made by the beam house processing to absorb the tannin or chromium) and (C) finishing process (hides will be further processed according to their intended end use)(Manivasakam, 1987).

2.1.2.Tanning processes

Tanning is the process by which animal hides and skins are converted into stable, non-biodegradable and non-putrescible leather. The tanning involves vegetable tanning, chrome tanning, zirconium tanning, aluminium tanning and iron tanning (Bailey *et al.,* 1981). Of which, vegetable and chrome tanning have greater commercial importance in India are briefly described hereunder.

2.1.3.Vegetable tanning

Vegetable tanning was the traditional tanning method until the development of commercial chrome tanning at the beginning of the twentieth century. Functionally, the vegetable tannins are polyphenolic compounds, which are divided into two groups: the hydrolysable tannins (derivatives of pyrogallol) and the condensed tannins (derivatives of catechol) (Bailey *et al.,* 1981). Vegetable tannins are extracted from different plant parts using chemical extraction methods and commonly used vegetable tannins are extracted from *Acacia nilotica* var *adansonii, Parkia clapperloniana, Eucalyptus citriodora* (Dashe *et al.,* 1999) *Salix phylicifolia, Mimosa crown*, myrobolan and tara (Vatanparast *et al.,* 1999).

It was understood that hydrogen bonds are formed as a result of vegetable tanning. This is resulted from displacement of hydrogen-bonded water molecules by the phenolic groups of the tannins with the formation of hydrogen bonding between these groups and the peptide bonds of the protein chains (Bailey *et al.,* 1981). The availability of hydrogen bonds on the protein and on the vegetable tanning materials at a pH from 5-7 is of prime importance in this process (Thomas, 1997). Currently vegetable tanning is widely replaced by chrome tanning due to the material availability and the high cost of labour in harvesting the vegetable tanning materials. But, this process is still in practice in the district of Dindigul in Tamil Nadu.

2.1.4.Chrome tanning

Chrome tanning has been used in the manufacture of almost all types of leathers. It is generally carried out by adding the acidified hide to an aqueous solution of trivalent chromium sulphate of 30-50 per cent basicity. The various processes involved are bating, pickling and tanning sequentially.

The chemical reaction involved in the chrome tanning process is the formation of stable compound between the hide protein and chromium (III) ions. Salts containing the Cr(III) ions are soluble only at pH of 2.8. During tanning, the hide is brought to an acid condition (pH less than 3) and the chrome tanning solution is added and the tanning begins. Since the solution is strongly acidic, the Cr can penetrate the hide without excessive surface fixation. After a period of time, when the Cr has penetrated the hide sufficiently, the pH raised to 3.4-3.6 by the addition of sodium carbonate the chrome has reacted with the collagen to produce a fully preserved, tanned hide. In the chrome tanning, the quantity of Cr needed for a complete tanning is about 2 per cent or more on the weight of the hide.

The importance of chromium salts as mineral tanning agents derives from the fact that Cr(III) in aqueous solution may bind to a water molecule coordinately and

form hexa water molecules Cr(VI) $[Cr(H_2O)_6]^{3+}$. The free carboxyl group in the hide protein displaces water molecules from the $[Cr(H_2O)_6]^{3+}$ and forms monodentate and bidentate co-ordinate complexes (Shuttleworth, 1958).

Chromium complexes, although more difficult to form, have the advantage over other complexing cations of reacting much more slowly in these ligand replacement reactions and therefore producing leather that is more stable and serviceable in use. Chromium (III) is also unique in its resistance to oxidation.

2.2.Chemistry of chromium in the environment

Chromium exists in different oxidation states ranging from –2 to +6. However, only +3 and +6 are normally found within the range of pH and redox potential common in environmental systems (Mertz, 1969). Chromium (III) is non toxic but essential for the maintenance of glucose, lipid and protein metabolism in living organisms. In contrast, Cr (IV) is toxic and mutagenic. Environmental chemistry of Cr(III) is more complex than Cr(VI) and found predominantly in insoluble forms in soils, such as sparingly soluble Cr_3O_3 and $Cr(OH)_3$, where as Cr(VI) exists in soils as a relatively soluble anion under most conditions (CrO_4^{2-} and $HCrO_4^-$).

The redox potential (Eh) and the pH determine the chemical forms in which chromium may be present in aqueous environment (Rai *et al.,* 1989). At very low pH (near 0), $H_2Cr\ O_4^-$ is the dominant species, while between the pH values 0 and 5.9 $HCrO_4^-$ dominates, at or above pH 6.0 CrO_4^{2-} prevails. Since the pH in environment matrices would generally not be expected to fall near zero, only CrO_4^{2-} and $HCrO_4^-$ should be present in natural systems. Also, at concentration greater than 0.01 M (520 mg L^{-1}) dimerization of the chromate ion occurs, yielding the dichromate ion.

$$2\ CrO_4 + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Bartlett and James (1979) and Das *et al.* (1990) found that Cr(III) oxidized readily to the Cr(VI) form in fresh aerobic field soils. The key to the oxidation appears to be the presence of oxidized manganese (Mn), which serves as electron acceptor in the reaction. A study by James and Bartlett (1983b) showed that freshly precipitated Cr(III) such as $CrCl_3$, Cr $(OH)_3$ and some fraction of Cr(III) in tannery wastes were oxidized to Cr(VI) by soil borne Mn (III, VI) (hydro) oxides.

In addition, reduction reaction of Cr(VI) by organic matter and other reducing agents may occur simultaneously with the oxidation of Cr(III) (Bartlett and Kimble, 1976 b). Chromium (VI) reduction by Fe (II) minerals, organic compounds (especially fulvic acids) and H_2S is most rapid under acidic conditions (Schroder and Lee, 1975; Bartlett and Kimble, 1976 b; Rai and Szelmeczka, 1990; Eary and Rai, 1991). The soil pH is a master variable in both oxidation and reduction reaction, with maximum occurring at approximately pH 6 to 7. Reduction of Cr(VI) by electron donors is favored by lower pH. Conversely both reactions are inhibited under more alkaline conditions (James *et al.,* 1997).

The early work on Cr(III) solubility in soils indicated that as solution pH was raised above pH 4.0, the solubility of Cr(III) decreased with apparent complete precipitation occurring at pH 5.5. (Bartlett and Kimble, 1976 b; Eary and Rai, 1991). However Cr(III)- organic complexes (e.g.DTPA, fulvic and humic acids) formed at low pH appeared to remain stable and soluble even when soil pHs were raised to levels where the Cr(III) would be expected to precipitate (Bartlett and Kimble, 1976 a; James and Bartlett, 1983 a).Although Cr(VI) does not form insoluble compounds in natural water it may reduce and precipitate as Cr(III) hydroxides.

The most important reaction, which determines the bioavailability of Cr in the environment, is the adsorption. At low pHs adsorption of Cr(VI) is favoured by clays and minerals such as Fe, Al, and Mn oxides and hydroxides (James and Bartlett,

1983c; Vyrodova *et al.*, 1990). Presence of orthophosphate prevented the adsorption of Cr(VI), presumably by competition for adsorption sites than Cr, NO_3^- and SO_4^- (Bartlett and Kimble, 1976 b; James and Bartlett, 1983c). The extent of Cr(III) oxidation at low pH is limited probably by the strong adsorption of the resulting anionic Cr(VI) species, which inhibits contact between the active oxidizing sites on the MnO_2 (s) surface and the Cr(III) species (James *et al.*, 1997).

Thus Cr undergoes various Chemical and biological reactions in the environment that govern its speciation behaviour and environmental toxicity.

2.3. Pollution profile of tanning industry

2.3.1. Characteristics of tannery wastes

The composition of wastes from the tanning industry contains pollutant from the hides, products formed from their decomposition and chemicals and various solutions used for preparation of the hides during the tanning process. In chrome tanning 276 chemicals and 14 heavy metals are used. It is estimated that approximately 32000 t of basic chromium sulphate (BCS) salts are used annually in Indian leathers (Ramasamy and Naidu, 2000). But the currently used methods attend a recovery of 50 - 79 per cent of chrome used (RaghavaRao *et al.*, 1999) and this amounts to an annual loss of nearly 2000 - 3000 t of Cr (on an elements basis). Thus the untreated effluent emanating from the chrome tanning sectional waste has been found to contain higher amount of Cr(III). Some important characteristics of tannery wastes are summarized in Table 2.1.

Table 2.1. Characteristics of tannery wastes

Sl.No.	Characters	Raw Effluent	Sludge
1.	Colour	Dark brown	Green
2.	Odor	Putrescible	Putrescible
3.	pH	6.0 - 12.0	7.60 - 8.46

4.	Electrical conductivity (EC) (dSm^{-1})	11.4 - 55.0	2.3 - 20.8
5.	Total suspended solids (TSS)	400 - 4000	-
6.	Total dissolved solids (TDS)	4000 - 50,000	-
7.	BOD	1,000 - 20,000	-
8.	COD	2,500 - 30,000	-
9.	Organic Carbon (per cent)	-	7.40 - 9.56
10.	Sodium	2,280 - 35,000	9,917 - 40,968
11.	Chlorides	1,805 - 15,000	287
12.	Sulphates	500 - 5000	40,000
13.	sulphides	59 - 158	-
14.	Oils and greases	1.5 - 4.0	-
15.	Chromium	7.2 - 1329	812 - 16158
16.	Copper	-	13.0 - 58.0
17.	Zinc	-	38.0 - 218

Source: Sujana and Gupta (1996); Rani Perumal and Singaram (1996); Mahimairajah *et al.* (2000b); Ramasamy and Naidu (2000); Sara Parwin Banu *et al.* (2000).

Notes : All the values except pH, EC and organic carbon are in mg L^{-1} for effluent and mg kg^{-1} for sludge.

The pH ranges from 6.0 to 12.0 and the EC is generally high which ranges from 11.4 to 55.0 dSm^{-1} in effluent. The presence of very high amount of Na^{+}, Cl^{-} and SO^{2-}_{4} contributes to higher EC value. The TDS content goes as high as 50,000 mg L^{-1}, the BOD upto 20000 mg L^{-1} and COD upto 30000 mg L^{-1}. A wide variation (from 7.2 to 1329 mg L^{-1}) was observed in the Cr concentration of the effluent.

The pH of sludge is relatively higher (7.60 - 8.46) and EC value is found to be lesser (2.3 - 20.8 dSm^{-1}) than the effluent. The sludge contains family good amount of organic carbon, which ranges from 7.40 to 9.56 per cent and also it contains higher proportion of salts (Na, Cl and SO_4) and Cr (812 - 16158 mg kg^{-1}). Other heavy metals like Cu (13 - 58 mg kg^{-1}) and Zn (38 - 218 mg kg^{-1}) are also reported in tannery sludge.

The numbers of tanneries in India and the amount of wastewater discharged per day from the factories is given in Table 2.2 which shows the impact tanning industries on the environment.

Table2.2.Pollution containment in the Indian tanning industry

Particulars	Year	
	1991	1998
Number of tanneries	2500	2500
Average volume of effluent discharged per day	60000 m^3	75000 m^3
Number of individual effluent treatment plants in operation	30	250
Number of common effluent treatment plants	2	16
Volume of effluent treated	14000 m^3 day^{-1} (23 per cent)	45000 m^3 day^{-1} (60 per cent)
Total investment	210 million rupees	1050 million rupees

Source: Buljan and Sahasranaman, 1999

2.4. Environmental impacts of tanning industries

The strict environmental protection guidelines and cost of environmental protection made a drastic decline in leather tanning in developed countries, but resulted substantial growth of leather industries, in developing countries like India. Though the progress of tanning industry is a great benefit to the economy, it poses severe threat to environment. The last twenty years of waste disposal on to productive land and river systems had resulted extensive contamination of soil, water and plant ecosystems.

2.4.1. Impact on soil

It is estimated that, in Tamil Nadu tannery pollution was severe in Erode next to Vellore; here more than 90 tanneries discharge their effluent into the land close to irrigated wetlands. The pollutants from this industry assumed serious dimensions after

most of the Erode tanneries switched over from vegetable to chrome tanning a few years ago (Anon., 1998).

It is estimated that tanning industry wastes have already degraded over 50,000 ha of productive agricultural land in Vellore district of Tamil Nadu (Ramasamy and Naidu, 2000). As a result, within 20 years the total cropped area has fallen by about 10.5 per cent in Vellore district and 41 per cent in Dindigul.

In general, tannery effluents are saline and sodic containing large amount of organic and inorganic substances. Varadarajan *et al*. (1970) reported that the tannery effluents are highly saline and contain large amounts of sodium salts, which are toxic to plants. George (1984) found that repeated irrigation of land by tannery effluents rendered vast stretches of land saline and decreased the fertility of soil. However tannery residues when applied to soil increased soil pH and available Ca, Mg and P contents.

Stomberg *et al*. (1984b) found increase in soil pH and decrease in Mn concentration of plant in the first year of application where as decrease in pH and increase in Mn concentrations was observed in successive years.

Increase in soil pH, SAR, ESP, CO_3, HCO_3, total alkalinity, Cl, water soluble salts, Na, Ca, K, Mg, P, S, Fe and NH_4O Ac extractable soil Ca, Mg, P, Fe and Morgan's solution extractable soil sulphur was reported by Pandey (1985).

Singaram (1994) reported that tannery pollution causes salt accumulation in the soil and affects the crop productivity. The increase in pH of the soil affects the urease and dehydrogenase activity (Rao and Ghai, 1985).

Dhulasi Birundha and Saradha (1994) reported that the land at Chinnapallapatti, Pudupatti and Kottapatti had become barren due to the pollution caused by the wastewater of the tanneries. The salt rich tannery wastes discharged to the land are thought to cause Na accumulation in the soils.

Research on the short term and long term effects of chromium on soil enzyme activities on a wide variety of soils are meagre. Chromium affects the microbial activity there by reducing the urease, phosphatase and dehydrogenase enzymes in the soil. The phosphatase enzyme which inferences the release of inorganic P from organically bound P. Doelman and Haanstra (1989) reported that phosphatase activity is very much affected by the application of tannery waste.

2.4.2. Impact on water

Hexavalent chromium is classified as a primary contaminant by the USEPA and the national drinking water standard has been set at 0.05 ppm. But in the effluent discharged areas, a concentration of greater than 500 mg Cr L^{-1} was obtained for the ground water sampled at 10 m depth inside the Palar river (Teekaraman *et al.,* 1984). Mahimairajah *et al*. (2000a) examined the concentration of total Cr in bore well waters around the tanning industries in Vellore and reported that Cr concentration ranged from 50 to 996 mg L^{-1}.

Similarly due to uncontrolled discharge and dumping of wastes from tanning industries at Kanpur, Uttar Pradesh the Cr content in the ground water was higher than 31 mg L^{-1} (Sujana and Rao, 1997).

The seepage of excess NaCl and Cr present in the effluent affect the ground water quality seriously. Due to this contamination there was an increase in chloride content from 80 to 180 mg L^{-1} and the effect of contamination was observed upto a dimension of 8 km (Sastry and Prasad, 1980) in the effluent discharged areas.

Nandakumar *et al.* (1993) reported that the salinity ranged from 5-219mgL^{-1} and 96-680 mg L^{-1} in Patthangal and Kotthap reservoirs respectively due to tannery pollution.

2.4.3. Impact on plants

Plant roots may affect the solubility and oxidation, reduction behaviour of Cr added to soils, and Cr in soil surrounding roots may alter the growth and nutrition of the plant. Organic exudates may reduce Cr(VI) or complex Cr(III); HCO_3^-, H^+, OH^- and other exuded ions may alter the pH of the rhizosphere. The effect of Cr on roots will depend on its forms in the soil: oxidized, reduced, chelated, Precipitated and adsorbed (James and Bartlett,1984).

The uptake of Cr occurs in either chromate or chromic form by the plant. Chromate uptake is an active process and follows Michelis - Mentan kinetics via a sulfate carrier and is mostly accumulated by the shoot. In contrast, the uptake of chromium ion is a passive process occurring mostly in roots (Peterson and Girling, 1981).

Chromium may affect crop growth firstly as a salt like chloride and sodium and by affecting chlorophyll, reducing the weight of plant parts and other metabolites of the crops as well as by inhibiting nitrification. Studies on the distribution of Cr in plants revealed that Cr generally appeared to accumulate in roots and poorly translocated to the aerial parts (Cary *et al.,* 1977). Srivastava *et al*. (1999) reported that wheat plants growing in nutrient solution containing 2 mg Cr(III) L^{-1} retained 70-80 per cent of Cr in roots. Lyon *et al*. (1969) reported that in the Cr accumulator plant, *Leptospermum scoparium*, Cr was translocated in the xylem sap as chromate and was present in roots and leaves as anionic Cr complexes one of which was trioxalatochromate ion.

Kamalam (1978) reported that the germination percent, root and shoot length in ragi were reduced markedly by increased concentrations of tannery effluent. These effects were more pronounced in black soil followed by garden land soil. Kamalam and Raj (1980) observed considerable reduction in germination, dry matter production and nutrient uptake of crops due to increase in concentration of the tannery effluent.

Teekaraman *et al*. (1982) found that irrigation with tannery effluent affected well water resulted in poor germination of paddy, cumbu, sorghum and reduction of sugarcane growth. The tannery waste affected the germination and growth of the sweet corn (Stomberg *et al.,* 1984 b). Saxena *et al*. (1986) found that untreated tannery effluents had toxic chemicals, which retarded germination and growth of crops like pulses. The germination study conducted on paddy, *Leucaena* and *Acacia* with 100 percent concentration of tannery effluent showed complete inhibition of germination (Karunyal *et al.* 1994).

Application of untreated effluent affected the growth of maize, though the crop germinated. Crop withered and dried before flowering when irrigated with the undiluted tannery effluent (Singaram,1992). *Lins culinaris* performed very badly under undiluted composite tannery effluent irrigation. The viability of pollen grain and consequently the reproductive growth showed marked retardation. The economic yield (g plant^{-1} day^{-1}) was nearly reduced to about 23 per cent compared to the control (Anjum Farooqui, 1994).

GuruprasadRao and Nandakumar (1981) reported that chromate at higher concentrations completely inhibited germination whereas there was no profound effect at lower concentrations. They further stated that tannery effluent at 25, 50, 75 and 100 per cent resulted in the reduction (except 5 and 10 per cent) in chlorophyll content due to the effect of chromium in the effluent (Bharti *et al.,* 1979).

They also observed that decrease in the yield of paddy cultivated under the tannery effluent contaminated reservoir (total chromium (2.6 ppm) and they attributed this with the significant reduction in chlorophyll caused by high amounts of salinity (1723 ppm) and chromium compounds.

Srivastava (1989) reported that chromium at different levels (10, 25, 50 and 100 mg kg^{-1} of soil) affected the growth and yield of three vegetable crops *viz*., spinach, lettuce and fenugreek. The growth and yield of spinach and lettuce were affected at 10 mg kg^{-1} levels while fenugreek growth and yield were affected at 50 mg kg^{-1} levels.

James and Bartlett (1984) reported that the nodules of beans appeared as elliptical, swollen tissue rather than as distinct spheres, which is grown in 10 mmol $Cr(OH)_3$. These roots had fewer branches of fine roots.

$Cr(OH)_3$ or other hydrated oxides of Cr(III) are so invert that they do not constitute an effective source of Cr for plants unless these hydrated oxides are present in the soil in very large amounts (Cary *et al*., 1977).

Stomberg *et al.* (1984a) reported that delayed germination and stunting were apparent in the corn grown on soils that received the tannery waste.

High rates or repeated applications of tannery waste increased soil total Cr levels four to eight fold and the most consistent feature was the pronounced tendency of soluble Cr added to soils to revert the forms that are insoluble and unavailable for plant uptake (Cary *et al.,* 1977).

2.4.4. Impact on microorganisms

Cr(III) is less toxic than Cr(VI). Inorganic Cr(III) is not mobile in soils and is not readily taken up by cells. Probably because of its low solubility and tendency to

form large hydroxy polymers at neutral pH levels. On the other hand, Cr(VI) is mobile in soils and it penetrates cell membranes readily. Once it is reduced inside cells, its toxicity probably results from oxidation of all components (National Research Council, 1994). After reduction to Cr(III) inside the cell, it may interfere with protein function. Mutations have been observed in bacteria grown in the presence of Cr(VI), moderating DNA susceptibility (Petrilli and Deflora, 1977).

The toxic and mutagenic effects of chromates on microorganisms are well documented Luli *et al*. (1983) found that 10-12 mg Cr(VI) L^{-1} was inhibitory to most soil bacteria in liquid media, while, at this level Cr(III) had no effect. Ajmal *et al*. (1984) reported that chrome electroplating waste was toxic to saprophytic and nitrifying bacteria, with toxicity increasing directly with the Cr(VI) content of the waste. In other studies, organisms exhibiting sensitivity to Cr compounds at environmentally relevant concentrations include various tomato pathogenic fungi (Naguib *et al*., 1984), mixed bacterial populations (Lester *et al*., 1979), fresh water algae (Bharti *et al.,* 1979) etc.

According to Petrilli and Deflora (1977), the effect of hexavalent chromium on *S.typhimurium* has strains shifted from toxicity to mutagenicity depending on concentration of the metal. Cr(VI) causes both frame shift errors and base pair substitutions in bacterial DNA.

Ogawa *et al.* (1989) while studying the influence of Cr on microbial growth and nucleic acids synthesis, observed the inhibition effect of $K_2Cr_2O_7$ and $CrCl_3$ present in the tannery effluent on DNA synthesis.

Heavy metals occur naturally at high concentrations in various environmental systems. So, resistance/tolerance mechanisms (methylation, demethylation, oxidation or reduction) have been evolved within microbial communities since the advent of

life. Based on this, some of the chromium tolerant microbes have been isolated from water (Simon - Pujol *et al.,* 1979), sediments (Luli *et al.,* 1983) and soil (Losi *et al.,* 1994).

Ramasamy and Naidu (2000) reported that there was an increase in the number of bacteria and fungi, whereas the population of actinomycetes was reduced, of the sludge composters, *Pseudomonas, Bacillus, Penicillium, Aspergillus, Beijerinckia* and *Sreptomyces* were the predominant organisms observed in the sludge composts.

Sudha and Krishnamurthy (1999) reported, that *Pseudomonas aeruginosa* not only tolerated chromium but also can accumulate it. It binds roughly ten times more of chromium (III) from basic chromium sulphate than chromium (VI) from potassium dichromate and that the chrome uptake characteristics was linked to electrostatic attractions between oppositely charged chromium complexes and the side chain sites available in the cell wall with the environmental parameters like pH additions, concentration of metal and cell age playing a role.

Petrilli and Deflora (1977) reported that the bacterial reduction of Cr(VI) to Cr(III) are mediated by cell membrane bound or soluble proteins. The crude extract of the bacteria (Crude enzyme) readily reduced Cr(VI) to Cr(III). However, the addition of NADH (50 μm) to the cell - free extract has increased the Cr reduction. The bacterium *Arthrobacter sp.,* has a great potential for use in detoxification of Cr(VI) in contaminated soil and water. The resistance mechanisms of microorganisms involved in the developing of commercially viable bioremediation techniques.

CHAPTER – 3
MATERIALS AND METHODS

The details of experiments, the methodologies followed regarding analysis of effluent and soil and various experiments conducted during the study to assess the impact of tannery effluent are presented below.

3.1. Analysis of tannery effluent

3.1.1. Collection of effluent samples

The tannery effluent samples let out of the factory were collected from EKM and Sons tannery unit, Agraharam, Erode and analysed for physical, chemical and biological properties. The effluent was subjected to primary and secondary treatments in the factory prior to disposal. This treated tannery effluent was used for the present investigation.

3.1.2. Sampling of effluent for microbial analysis

Samples for microbiological examinations were collected in sterilized bottles. The empty sampling bottles were closed with a ground glass stopper having an overlapping rim. The bottles were protected by covering with aluminium foil and sterilized in an autoclave at 20 psi for 15 minutes. The bottles were opened only at the time of sampling.

3.1.3. Preservation of Samples

The sample collected in acid washed clean containers thoroughly rinsed with the effluent was used for collecting the effluent samples. The collected effluent samples were stored in a walk-in cold room and used for other analytical purposes.

3.1.4. Analysis of effluent

The physical, chemical and biological characteristics of the effluent were analysed as per the methods detailed in Standard Methods for the Examination of Water and Waste Water (APHA,1989).

3.1.4.1. Physical properties

i. Color and foam : Assessed by visual comparison with distilled water.

ii. Suspended solids : A known quantity of the effluent was filtered using Whatman No. 1 filter paper and the residue was dried at 105°C to a constant weight.

iii. Dissolved solids : The filtrate obtained from the suspended solids was evaporated, dried at 105°C to a constant weight.

iv. Total solids : The sum of suspended and dissolved solids gave the total solids.

3.1.4.2. Chemical properties

i. pH

The pH of the effluent was measured using a pH meter with glass electrode (Jackson, 1973).

ii. Electrical conductivity (EC)

The EC of the effluent was measured by using a conductivity bridge (Jackson, 1973).

iii. Dissolved oxygen (DO)

The dissolved oxygen in the effluent was determined by azide modification of iodometry method (APHA,1989). The analysis was done immediately after the collection of samples at the factory itself. The samples were taken in BOD bottles and fixed with the addition of $MnSO_4$ and KI and the samples in the precipitate form was transported to the lab for DO analysis.

iv. Biochemical Oxygen Demand (BOD)

The biochemical oxygen demand was determined as per the standard procedure (APHA, 1989).

v. Chemical Oxygen Demand (COD)

The chemical oxygen demand of the effluent was determined as detailed in APHA (1989).

vi. Organic carbon

The organic carbon content of the effluent was estimated by the wet digestion method of Walkley and Black as described by Piper (1966).

vii. Nitrogen

The nitrogen content of the sample was estimated by Bremner method (Jackson, 1973).

viii. Phosphorus

This was estimated colorimetrically as described by Olsen *et al.* (1954).

ix. Potassium

This was estimated as described by Jackson (1973) using an EEL flame photometer.

x. Calcium

The calcium content was estimated by versanate titration method as detailed by Jackson (1973).

xi. Magnesium

The magnesium content was estimated by the difference between the value of calcium plus magnesium and calcium alone as estimated in the versanate titration method (Jackson, 1973).

xii. Sodium

The sodium content of the effluent sample was determined by using EEL flame photometer with sodium filter as described by Jackson (1973).

xiii. Sulphate

The sulphate content of the effluent sample was determined by Turbidimetric method using spectrophotometer at 420 nm (Jackson, 1973)

xiv. Chloride

The chloride content of the effluent sample was determined by Mohr's method as described by Jackson (1973).

xv. Carbonates and bicarbonates

Carbonates and bicarbonates were determined by titrating the solution against standard acid using phenolphthalein and methyl orange as indicators (Jackson, 1973).

3.1.4.3. Microbial properties

The microorganisms were enumerated following serial dilution and plating method (Jenson, 1968) using appropriate media for bacteria, fungi and actinomycetes as given below.

Organisms	Medium	References
Bacteria	Nutrient glucose agar	Rangaswami (1966)
Actinomycetes	Ken Knight's agar	Rangaswami (1966)
Fungi	Martin's rose bengal agar	Martin (1950)

3.1.4.4. Chromium estimation

(i) Hexavalent Chromium

To determine the Cr (VI) fraction in effluent, a known quantity of effluent was added with 10 ml of 1N H_2SO_4, 0.4 ml of H_3PO_4 and 4 ml of 1,5- diphenyl carbazide reagent. The diphenyl carbazide reagent was prepared by dissolving 0.25 g of 1,5-diphenyl carbazide and 4 g of pthalic anhydride in 100 ml of 95 per cent ethyl

alcohol. After making the contents to 50 ml, the samples were allowed to stand for 30 min. and the purple-violet color was compared with that in standards prepared at the same time by reading at 540 nm in a UV-Vis spectrophotometer.

(ii)Total chromium

The concentration of total chromium in the effluent samples was measured by digesting the effluent with triacid mixture. Ten ml of effluent was digested with 20 ml of tri acid mixture on a hot plate for 2 hrs. Then the digest was made to 100 ml and filtered through Whatman No.1 filter paper. The total Cr present in the solution was measured in an Atomic Absorption Spectrophotometer (AAS, Varian spectra AA 200) using air acetylene flame at 357.9 nm (USEPA, 1979). The difference between the total hexavalent will give the measure of concentration of Cr(III) in the effluents.

3.2. Laboratory Incubation experiment

The impact of tannery effluent on soil chemical and biological properties was assessed by an Incubation experiment.

3.2.1.Treatment details

The experiment was conducted with the following treatments

Tannery effluent

T_1 - Soil +Distilled water (Control)

T_2 - Soil + Raw tannery effluent

T_3 - Soil + 75 per cent tannery effluent

T_4 - Soil + 50 per cent tannery effluent

T_5 - Soil + 25 per cent tannery effluent

Soils : Two

Design : CRD

Replications : Three

The impact of different dilution of effluent on soil was studied through a closed laboratory incubation experiment. Two hundred grams of air-dried soils (<2 mm) were weighed in 150 cm^3 plastic cups and different concentrations of effluents were calculated to 200 gm of soil and mixed thoroughly. Calculated quantity of distilled water was added to achieve final moisture content equivalent to field capacity. The moisture content was corrected at weekly intervals and maintained throughout the incubation period. The plastic cups were covered with polyethylene bags containing small pin-sized holes to permit aeration. Each treatment was replicated three times and incubated for 45 days. Samples were drawn at 0, 15,30 and 45 days after incubation for various analysis.

3.2.2. Collection, preservation and characterization of soil samples

Two types of soils namely black and red respectively from wetland and garden land of Tamil Nadu Agricultural University, collected, air dried and kept in polythene bags were used for various physical, chemical and biological properties.

3.2.3. Soil physical properties

The soil used for incubation experiment was analysed for its physical properties viz., bulk density, particle density and water holding capacity prescribed by Chopra and Kanwar (1982).

3.2.4. Chemical properties

Sl.No.	Particulars	Remarks	Author
1.	pH	1:2.5 soil water suspension	Jackson (1973)
2.	EC	1:2.5 soil water suspension	Jackson (1973)
3.	Organic carbon	Wet digestion	Piper (1966)
4.	Available N	Alkaline permanganate method	Subbiah and Asija (1956)
5.	Available P	Calorimetric method	Olsen *et al.* (1954).
6.	Available K	Neutral normal ammonium acetate method (ELICO flame photometer)	Jackson (1973)
7.	Exchangeable Ca, Mg and Na	Ammonium acetate Extract method (ELICO flame photometer)	Jackson (1973)
8.	Chloride	Mohr's Method	Jackson (1973)
9.	Sulphate	Turbidimetric method	Jackson (1973)

3.2.5. Microbiological properties

The population of different groups of microorganisms namely bacteria, fungi and actinomycetes were enumerated from soil by using standard serial dilution plate techniques (Rangaswami, 1966).

3.2.6. Enzyme activities

a. Urease

The urease activity in soils was measured according to the method prescribed by Hoffman (1965) and was expressed as mg of ammoniacal-N released kg^{-1} soil hr^{-1}.

b. Phosphatase

The phosphatase activity of the soil was measured by the procedure prescribed by Tabatabai and Bremner (1969) and was expressed as mg of phenol released kg^{-1} soil hr^{-1}.

c. Dehydrogenase

The dehydrogenase activity of the soil was measured according to the method prescribed by Casida *et al.* (1964) and was expressed as mg of TPF released kg^{-1} soil hr^{-1}.

3.3. Laboratory batch experiment

A batch experiment was conducted to study the impact of Cr(VI) on soil microbial activity and chromium transformation using simulated effluent

3.3.1. Preparation of Chromium (VI) simulated effluent

The reduction and oxidation of chromium in soil was studied through a batch experiment using different dilution of simulated effluent. It was prepared by using potassium dichromate salt ($K_2Cr_2O_7$) at various concentrations (25,50 and 75 ppm).

3.3.2. Treatments (simulated chromium (VI) effluent)

The experiment was conducted with the following treatments

T_1 - Soil + Distilled water (Control)

T_2 - Soil + 75 ppm of Chromium (VI) effluent

T_3 - Soil + 50 ppm of Chromium (VI) effluent

T_4 - Soil + 25 ppm of Chromium (VI) effluent

Soils :Two

Design : CRD

Replications : Five

Hundred grams of air-dried soils (<2 mm) were weighed in 150 cm^3 plastic cups and different concentration of simulated effluents were added to 100 gm of soil and mixed thoroughly. Calculated quantity of distilled water was added to achieve final moisture content equivalent to field capacity throughout the experiment period. The plastic cups were covered with polyethylene bags containing small pin-sized holes to permit aeration. Each treatment was replicated five times and incubated for 48 hours. Samples were drawn at 0, 12,24,36 and 48 hours after incubation for various analysis.

3.3.3. Speciation of chromium

A method described by Noble and Hughes (1991) was employed to determine the nature (species) of retained Cr in the experiments as outlined below.

Step 1 (Water soluble): Weighed five gram of air-dried sample in a 40 ml polypropylene centrifuge tube and added 25 ml of distilled water. It was then shaken in an end-to-end shaker for 2 hrs at room temperature (25 ± 2^{o} C). Then centrifuged the samples at 10,000 rpm for 20 minutes and filtered through Whatman No.42 filter paper. A known quantity of extract was added with 10 ml of 1N H_2SO_4, 0.4 ml of H_3PO_4 and 1,5- diphenyl carbazide reagent. The diphenyl carbazide reagent was prepared by dissolving 0.25 g of 1,5- diphenyl carbazide and 4 g of pthalic anhydride in 100 ml of 95 per cent ethyl alcohol. After making the contents to 50 ml, the samples were allowed to stand for 30 min. and the purple-violet color was compared with that in standards prepared at the same time by reading at 540 nm in a UV-Vis spectrophotometer. (USEPA, 1979).

Step 2: To the residue from step 1, 25 ml of 0.5 M phosphate buffer was added and shaken for 16 hrs. followed by centrifugation, filtration and measurement as in step 1.

The tube plus contents was weighed before and after extraction to calculate the volume of entrained solution and transfer of chromium from proceeding extractions. The amounts of Cr extracted by each extractant were computed by using the following equation.

Cr extracted (mg kg^{-1}) =C x (E +M) - (C' x M)

Where,

C-Concentration of Cr in the extraction solution (mg L^{-1})

E- Mass (g) of the extractant added (25 cm^3/ ml)

M- Mass (g) of the entrained solution carried over from previous extraction (g)

C'- Concentration of Cr in the extraction solution of preceding step of the sequence (mg L^{-1}).

3.4. Germination studies

3.4.1. Details of germination test

Test crops and variety	:	Ragi (TMV 1) Black gram (CO 13) Amaranthus (CO 2)
Design	:	CRD
No. of treatments	:	Five treatments (T_1-T_5) with tannery effluent Four treatments (T_1-T_4) with two Simulated effluents
No. of replications	:	Five
Duration	:	Ragi (14 DAS) Black gram (7 DAS) Amaranthus (7 DAS)

3.4.2. Preparation of NaCl effluent

Besides chromium, the presence of salts like Na, Chlorode, etc also makes the tannery effluent not fit for irrigation. To know the effect of Cr(VI) and salt separately

on germination of crops, simulated NaCl effluent was prepared, by mixing calculated quantity of NaCl salt in distilled water to get 1050 ppm, 2100 ppm and 4200 ppm.

The simulated Cr(VI) effluent was prepared as per the procedure described in 3.3.1.

3.4.3. Treatment details

The experiment was conducted with the following treatments.

(i) Tannery effluent

T_1 - 0 percent effluent (100 per cent tap water)-control

T_2 - Raw tannery effluent

T_3 - 75 per cent tannery effluent

T_4 - 50 per cent tannery effluent

T_5 - 25 per cent tannery effluent

(ii) Simulated chromium (VI) effluent

T_1 - 0 percent effluent (100 per cent tap water)-control

T_2 - 75 ppm of Chromium (VI) effluent

T_3 - 50 ppm of Chromium (VI) effluent

T_4 - 25 ppm of Chromium (VI) effluent

(iii) Simulated Salt effluent

T_1 - 0 percent effluent (100 per cent tap water)-control

T_2 - 4200 ppm of NaCl effluent

T_3 - 2100 ppm of NaCl effluent

T_4 -1050 ppm of NaCl effluent

Germination test conducted to assess the impact of tannery effluent and simulated effluent on germination of ragi, black gram and Amaranthus. Germination test was carried out in a germination room maintained at a temperature of 25 ± 1.5°C

and relative humidity of 95 ± 2 per cent with diffused light (approximately 10 hrs.) during the day.

3.4.4. Germination percentage

The counts on number of seeds germinated were taken as per the ISTA rules (1993) and expressed in percentage.

3.4.5. Root length

The normal seedlings were taken at random and the distance between the collar and tip of the primary root were measured and the mean value was arrived and expressed as centimeter (cm).

3.4.6. Shoot length

The seedlings were again measured for the distance between collar and tip of the primary shoot. The mean value of the shoot length was recorded and expressed as cm.

3.4.7.Dry matter production (g 10 seedlings^{-1})

Ten normal seedlings of each replications were dried at first in shade and then dried in a hot air oven maintained at 105± 2°C for 16 hrs, then cooled in a desiccator and weighed.

3.4.8. Vigour index (VI)

The VI was calculated for each replication by using the formula.

VI = Germination percentage x [Root length (cm) + Shoot length (cm)]

3.5. Pot culture study

The experiment was conducted with the following treatments. The simulated Cr(VI) effluent was prepared as per the procedure described in 3.3.1.

3.5.1. Treatment details (simulated chromium (VI) effluent)

T_1 - Tap water (Control)

T_2 - 75 ppm of Chromium (VI) effluent

T_3 - 50 ppm of Chromium (VI) effluent

T_4 - 25 ppm of Chromium (VI) effluent

Soil : Red

Design : CRD

Replication : Five

3.5.2. Soil and Plant analysis

Soil and plant samples were analysed at 40days after sowing to estimate the chromium content as described below. Soil samples were analyzed as per the procedure described in 3.1.4.4(ii).

In plant analysis, one gram of plant sample was weighed in an acid washed 100 ml conical flask and added 15 ml of tri acid mixture (HNO_3: H_2SO_4: $HClO_4$ 9:2:1) (McLaren and Ritchie, 1993). The samples were digested on a hot plate at 110^oC for about 2 hours. After that, the flasks were cooled, added 5 ml of distilled water and boiled for few minutes. The volume of the contents were made to 50 ml and kept for over night. Then the contents were filtered through Whatman No.1 filter paper and the Cr concentration was measured using an Atomic Absorption Spectrophotometer with air-acetylene flame. A wavelength of 357.9 nm was with a spectral slit width of 0.2 nm (USEPA.1979)

3.6. Statistical analysis

The experimental results were statistically scrutinized as suggested by Panse and Sukhatme (1985) to find out the influence of various treatments on the crop growth and soil. The critical difference was worked out at 5 per cent (0.05) probability.

CHAPTER - 4
EXPERIMENTAL RESULTS

The present study was carried out to investigate the effect of tannery effluent on soil characteristics, transformation of chromium in soil, germination of crop plants and growth of crops. The results of various experiments conducted are presented here under.

4.1. Characteristics of Tannery effluent

The effluent contained appreciable amounts of nutrients like Nitrogen (N) 20.2 mg L^{-1}) Phosphorus (P) (3.8 mg L^{-1}) and Potassium (K) (13 mg L^{-1}). Chromium, as determined by triacid digestion, was very less in quantity (0.5 ppm) and only a trace amount of chromium (VI) form (0.025 ppm) was observed in the effluent. The effluent had exceptionally high concentration of salts namely sodium (223 m.e L^{-1}), chloride
(951 ppm) and sulphate (0.4 m.e L^{-1}). The other cations like calcium (upto 1.2 m.e L^{-1}) and magnesium (0.8 m.e L^{-1}) were also observed in the effluent (Table 4.1).

While carbonate was not detected, the effluent contained considerable amounts of bicarbonate (31 ppm). With regard to microbial population the effluent was found to have lower number of bacteria and actinomycetes, but fungi were completely absent.

4.2. Characteristics of experimental soils

Black and red soils were slightly alkaline with a pH of 7.71 and 8.01 respectively. Both the soils were non-saline (EC 0.14 and 0.07 dSm^{-1} of black and red soils respectively). Low level of N, medium level of P and high level of K were recorded in both soils. The important characteristics of the soil are presented in Table 4.2.

4.3. Effect of tannery effluent on soils

The results from a laboratory incubation experiment conducted at controlled conditions to examine the effect of tannery effluent on the characteristics of black and red soils are furnished in Tables 4.3 to 4.19.

4.3.1. Effect on soil pH

The pH of black and red soils ranged from 7.70 to 8.41 and from 8.01 to 8.55, respectively, during incubation with tannery effluent at different concentrations (Table 4.3). In black soil, T_2 registered the highest pH and it was on par with T_3 and T_4 except T_5 and control. In red soil, the highest pH was observed in T_2 and T_3 was on par with T_4. In both the soils, increase in dilution reduced the pH significantly.

4.3.2. Effect on EC

In red and black soils increase in EC was observed with increasing of incubation period, but they vary widely between the soils and treatments. It ranged from 0.14 to 0.65 dSm^{-1} in black soil and 0.07 to 0.37 dSm^{-1} in red soil (Table 4.4). Among the treatments, T_2 recorded the highest EC in both the soils but interaction effect was non-significant. Like pH, increase in dilution decrease the EC also significantly.

4.3.3. Effect on organic carbon

The organic carbon of the black soil varied from 0.408 to 0.431 percent and from 0.368 to 0.388 percent in red soil. Comparison made among the 2-way interaction (period of incubation and treatment) showed that the content of organic carbon in both the soils were slightly high in raw effluent treated soils when compared to other treatments and there was no significant difference with the days of incubation (Table 4.5)

4.3.4. Effect on available nitrogen

The availability of N was increased due to effluent application and days of incubation significantly (Table 4.6), while increase in dilution decreased the availability of N. The highest value was observed in T_2 (275 kg ha^{-1} in black soil and 212 kg ha^{-1} in red soil). The interaction effect of soil and period of incubation revealed that the content of N increased from 0 day after incubation in both the soils.

4.3.5. Effect on available phosphorus

As in the case of nitrogen, available phosphorus also increased due to effluent application and days of incubation in both the soils (Table 4.7). The highest availability was found in T_2 with 19.1 kg ha^{-1} in black soil and 13.9 kg ha^{-1} in red soil. The lowest value was 16.7 kg ha^{-1} in black and 11.4 kg ha^{-1} in red soils, which were observed at 45 days after incubation in T_1 (control). The interaction effect was non-significant in both the soils.

4.3.6. Effect on available potassium

There was a general trend of increased availability of potassium during the period of incubation and level of treatments in soils. The available K content of two soils influenced by the effluent application with different concentrations is presented in Table 4.8. The available K content in black soil ranged from 297 to 312 kg ha^{-1} at 0 day after incubation and from 293 to 307 kg ha^{-1} at 45 days after incubation. In red soil 272 to 286 kg ha^{-1} at 0 day after incubation and 270 to 290 kg at 45 days after incubation was observed. The highest value was observed in both the soils that received raw effluent. The interaction effect was found to be non-significant in both soils and the level of K availability was higher in both soils.

4.3.7. Effect on calcium

The calcium content was significantly increased by the treatments when compared to control. It increased with the incubation period upto 30 days and there

was a reduction in the concentration of Ca in black and red soils at 45 days after incubation (Table 4.9). The highest value was observed in control at 30 days after incubation in black (7.61 cmol(p^+) kg^{-1}) and red (6.68 cmol(p^+) kg^{-1}) soils. The incubation effect was significant in red soil and non significant in black soil.

4.3.8. Effect on magnesium

The magnesium content ranged from 2.85 to 4.51cmol(p^+) kg^{-1} initially and from 2.84 to 4.56 cmol(p^+) kg^{-1} at 45 days after incubation in black soil. Similarly in red soil the content of Mg extended from 1.18 to 3.66 cmol(p^+) kg^{-1} initially and from 1.16 to 3.85 cmol(p^+) kg^{-1} at 45 days after incubation.

The highest value was recorded in control at 45 days after incubation in black soil (4.56 cmol(p^+)kg^{-1}) and 15 days after incubation in red soil (3.66 cmol(p^+)kg^{-1}) (Table 4.10). The incubation effect was found to be non-significant in both the soils.

4.3.9. Effect on sodium

As in case of all nutrients T_2 recorded the highest value of sodium in all days of incubation in both soils (Table 4.11). In black soil, it was 5.31 cmol(p^+) kg^{-1} and in red soil it was 5.45 cmol(p^+) kg^{-1} at 0 day incubation. There was a marked increase in treated soils when compared to untreated control (T_1). The interaction effect was found to be non-significant in both the soils. But the treatments increased the Na content significantly in both the soils, when compared to control.

4.3.10.Effect on chloride

The highest chloride content was observed in black (136.6 ppm) and red (125 ppm) soil applied with 100 per cent concentration of effluent (T_2) at 0day after incubation, while it was lowest (33.2 and 30.5 ppm in black and red soil respectively) in control (Table 4.12). In general all treatments significantly increased the chloride content of soil, but the interaction effect was non-significant in both soils.

4.3.11. Effect on sulphate

The sulphate content ranged from 1.12 to 40.32 ppm in black soil and 1.10 to 33.60 ppm in red soil. The highest value observed was in T_2 in both the soils (40.32 and 33.60 ppm for black and red soils respectively). The SO_4 content was significantly increased with the period of incubation and also with the treatments, but the interaction effect was found to be non-significant in red and black soils (Table 4.13).

4.3.12. Effect of tannery effluent on enzyme activities in soils

4.3.12.1. Phosphatase activity

Phosphatase activity was increased by the addition of effluent when compared to control in both red and black soils (Table 4.14). The highest activity was found in 75 per cent effluent application at 30 days after incubation in black (64.72 mg kg^{-1} hr^{-1}) and red soils (59.91 mg $kg^{-1}hr^{-1}$). The phosphatase activity decreased with the period of incubation with respective to all treatments in both soils. The enzyme activity was more pronounced in black soil than in red soil. In both the soils, T_3 was the best performing treatment and it was on par with T_4 in red soil.

4.3.12.2.Dehydrogenase activity

The dehydrogenase activity (Table 4.15) showed that the application of effluent significantly enhanced the dehydrogenase activity upto 30 days after incubation in T_3,T_4 and T_5 and then it was reduced in both the soils over the control. But in the case of T_2 the activity was reduced from 15 days after incubation in both soils. The highest value recorded in black soil was 67.09 mg kg^{-1} hr^{-1} and in the red soil the activity was 62.11 mg kg^{-1} hr^{-1} in T_3 at 30 days after incubation. It was evident that the effluent application at 75 and 50 per cent dilution significantly increased the dehydrogenase activity in both the soils. In red soil, T_3 was on par with T_4.

4.3.12.3.Urease activity

The urease activity of both black and red soil was influenced by effluent application is given in Table 4.16. The urease activity was highest in black soil (189.9 mg kg^{-1} hr^{-1}) receiving the effluent at 75 per cent (T_3) at 30 days after incubation while T_2 recorded the lowest value (83.8 mg kg^{-1} hr^{-1}) at 45 days after incubation. Similarly in red soil the urease activity was maximum (175.8 mg kg^{-1} hr^{-1}) due to 75 per cent application of effluent when compared to other treatments. Irrespective of soil, the urease activity increased from 15 days after incubation and decreased upto 45 days after incubation

4.3.13.Effect of tannery effluent on microbial population

Effluent application had markedly improved the microbial population in both soils. In case of bacteria (Table 4.17) the population ranged from 8.5 to 23.71 x 10^6 CFU g^{-1} and from 6.64 to 21.95 x10^6 CFU g^{-1} in black and red soils respectively. The highest population recorded in T_3 at 30 days after incubation

The population of fungi (Table 4.18) varied from 1.26 to 5.25 x 10^3 CFU g^{-1} and 1.80 to 7.5 x 10^3 CFU g^{-1} in black and red soil respectively and the highest value observed in T_5 at 15 days after incubation.

The actinomycetes population (Table 4.19) varied from 0.91 to 3.78 x10^2 CFU g^{-1} and from 1.3 to 5.40 x 10^2 CFU g^{-1} in black and red soils respectively. Irrespective of soils the microbial population was influenced by all treatments significantly and the interaction effect was also found to be significant in all cases. As in the case of enzyme activity, the microbial population also increased upto 15 days after incubation and reduced with the advancement of incubation period.

4.4. Effect of tannery effluent, simulated chromium (VI) and salt (NaCl) effluents on crop growth

4.4.1.Effect of tannery effluent on crop

4.4.1.1. Effect on germination

The germination percentage of different crops *viz.*, ragi, black gram and Amaranthus as influenced by different dilutions of effluent was studied and the results are given in Table 4.20. The effluent concentration at 100 and 75 per cent inhibited the germination of ragi, black gram and Amaranthus, by recording the lowest germination percentage of 3.8 and 40.5; 10.6 and 38.8 and 8.7 and 46.4 respectively. The germination percentage was the highest in T_5 followed by T_1 and T_4 for all the three crops. Among the crops the germination percentage was in the order of: black gram > ragi > Amaranthus in all treatments. The effluent at 25 per cent dilution showed marked improvement in germination, which was significantly more, when compared to control. In all crops, T_5 was on par with T_4 and T_1.

4.4.1.2. Effect on root length

Root length of ragi, black gram and Amaranthus was higher in 25 per cent (7.2, 12.6 and 10.7 cm respectively) effluent concentration, followed by control (6.9, 12.2, 9.4 cm respectively). T_2 inhibited the root length of all the three crops. Notable variation in root length was observed due to different effluent concentrations, compared to control. The root length recorded was the lowest in T_2 (receiving raw effluent). In all crops, T_5 was on par with T_1 (Table 4.20)

4.4.1.3. Effect on shoot length

In all the three crops, tested for germination, the shoot length was increased by 25 percent effluent concentration (T_5). The other concentrations reduced the shoot length in all the three crops (Table 4.20). The shoot length was significantly reduced in ragi, black gram and Amaranthus due to the treatment T_2. All treatments significantly influenced the shoot length of crops and in all crops T_5 was on par with control (T_1).

4.4.1.4. Effect on vigour Index

High concentration of effluents (100 and 75 per cent) significantly reduced the vigour index of crops. The highest vigour index of black gram (2387.4), ragi (905.4) and Amaranthus (900. 9) were recorded in 25 per cent effluent concentration. The vigour index of all the three crops was markedly influenced by all concentrations of effluents; while the maximum vigour index was in 25 per cent concentration, the other two concentrations significantly reduce the vigour index (Table 4.20).

4.4.1.5. Effect on dry matter production

As in the case of all parameters, the dry matter production of ragi, black gram and Amaranthus were higher in T_5 receiving 25 per cent effluent and it was reduced by all other treatments (Table 4.20).

4.4.2. Effect of chromium (VI) effluent on crop

4.4.2.1. Effect on germination percentage

The germination percentage of ragi, black gram and Amaranthus drastically reduced by chromium (VI) at all concentrations in all crops. At 75 per cent (T_2) the lowest germination percent was observed and the highest value was observed only in control (71.0, 95.2 and 65 for ragi, black gram and Amaranthus respectively). So, The treatments significantly reduced the crop germination (1.7, 3.4 and 2.9 for ragi, black gram and Amaranthus respectively). In ragi T_5 is on par with T_4 and T_1. (Table 4.21)

4.4.2.2. Effect on root length

The root lengths of various crops (ragi, black gram and Amaranthus) grown in different concentration of Cr(VI) were very much reduced. The lowest value observed was in 75 ppm (ragi-0.3, black gram-0.6 and Amaranthus-0.7 cm) and highest value in control (ragi-7.0, black gram-12.7 and Amaranthus-9.4 cm) for all crops. (Table 4.21)

4.4.2.3. Effect on shoot length

As germination and root length, the shoot length was also affected by chromium and the shoot length was very minimum in T_2 (ragi-0.5, black gram-1.10 and Amaranthus-0.1cm) (Table 4.21).

4.4.2.4. Effect on vigour index

Similar effect was also observed for vigour index. But in T_4 the vigour index was slightly higher when compared to other two (T_2 and T_3) treatments. The control had the highest (904.4 for ragi, 2268.6 for black gram an 849.7 for Amaranthus) vigour index. (Table 4.21)

4.4.2.5. Effect on dry matter production

The effect of Cr(VI) simulated effluent was very high in dry matter production of the three crops viz., ragi, black gram and Amaranths. When compared to control, all the three treatments reduced the dry matter production very much. In control, the dry matter production was 1.7, 4.3 and 1.6 g/ 10 seedlings for ragi, black gram and Amaranthus respectively, but in T_2 it was 0.01, 0.01 and 0.01 g/ 10 seedlings for ragi, black gram and Amaranthus respectively. (Table 4.21)

4.4.3. Effect of simulated salt (NaCl) effluent on crop

4.4.3.1. Effect on germination percentage

The germination percentage of ragi, black gram and Amaranthus as influenced by simulated salt (NaCl) effluent was studied and presented in Table 4.22. The highest value was in control (T_1) followed by T_4 for all crops. The lowest value observed was in T_2 followed by T_3. All the treatments influenced the germination of the crops significantly.

4.4.3.2. Effect on root length

The effect of treatments on root length was similar to germination percentage. The high concentration of NaCl (T_2) reduced the root length. The effluent at all concentrations significantly influenced the root length of crops (Table 4.22).

4.4.3.3. Effect on shoot length

As in the case of root length, shoot length also was reduced by the treatments. The highest value occurred in control (T_1) followed by T_4. The lowest value was observed in T_2 for all crops. (Table 4.22)

4.4.3.4. Effect on vigour index

Similar effect was also observed under all treatments for all crops (ragi, black gram and Amaranthus). However, the vigour index of ragi was markedly affected by all dilutions followed by Black gram and Amaranthus. The vigour index was low in ragi at T_2. All treatments significantly reduced the vigour index of crops. (Table 4.22)

4.4.3.5. Effect on dry matter production

The dry matter production of ragi was higher in control (T_1) and lower in T_2. (0.01 g 10 seedlings^{-1}). Similarly, T_2 recorded the lowest value in black gram and Amaranthus and the highest value observed was in T_1 (control). (Table 4.22)

4.5. Effect of simulated chromium (VI) effluent on soil

4.5.1. Effect on soil pH

The pH of the soil was significantly influenced by all treatments. But, the interaction effect was found to be non-significant in both the soils (Table 4.23).

4.5.2. Toxicity of chromium (VI) to microorganisms

The different concentration of chromium (VI) toxicity on bacteria is given in (Table 4.24). Irrespective of soil, microbial population was markedly affected by the

application of chromium (VI) effluent. The 0 day samples showed that the bacterial population in both red and black soils was uniform and significantly lower than control. During the incubation, the populations started declining and after 48 hours of incubation, the bacterial load was completely absent in both the soils.

In case of fungi (Table 4.25) and actinomycetes (Table 4.26) similar trend was observed. They were present upto 24 hours after incubation but after that, both the population was absent due to the toxicity of chromium. The highest populations of organisms occurred only in the control in both the soils. Irrespective of soils, all the treatments significantly arrested the growth of organisms.

4.5.3. Water soluble extraction of Cr (VI) by DPC by colorimetry

The water soluble Cr (VI) presents in the incubated soil was analysed and is presented in Table 4.27. The solubility was high initially (immediately after application) and gradually decreased with increase in incubation period in both the soils. At higher concentration (T_2) the availability of Cr (VI) in water was high in black (2.795 mg kg^{-1}) and red soils (2.954 mg kg^{-1}).

4.5.4. Phosphate buffer extraction of Cr (VI) by DPC colorimetry

The extractant has high amount of Cr (VI) at 36 hours after incubations and suddenly declined at 48 hours after incubation in both the soils. T_2 recorded high value in black (37.0 mg kg^{-1}) and red (35.65 mg kg^{-1}) soils at 36 hours after incubation followed by T_3 and T_4. All the treatments significantly influenced the availability of Cr (VI) in the soil (Table 4.28).

4.6. Pot culture study

4.6.1. Effect on pH and EC

There was a marked influence on the soil pH by the application of simulated chromium (VI) effluent. The pH value ranged from 7.82 to 8.07initially and from 7.98

to 8.01 at the end of the experiment. In general, pH showed a gradual decrease with increase in concentration of effluent. The lowest value observed was in T_2 (7.82). Varied levels of Cr addition and the interaction of Cr and plants had significant influence on pH of the soil (Table 4.29).

The EC was changed from 0.07 to 0.19 dSm^{-1} by the all treatments. Irrespective of the plants grown, increase in the rate of Cr addition significantly increased the EC of the soil. The highest EC values were recorded at higher concentration of Cr addition (75 ppm). After 45 days, there was a slight reduction in the EC in all the treatments (Table 4.30).

4.6.2. Chromium in plant species

Chromium concentration in plant species grown in the pot culture is given in Table 4.31. In roots, the uptake of Cr ranged from 0.01 to 0.4 ppm in ragi and 0.0 to 0.28 ppm in black gram and 0.01 to 0.42 ppm in Amaranthus. The high concentration of Cr reduced the uptake of Cr by plants (T_2). At 50 ppm (T_3), the uptake was high compared to other treatments. Root accumulates more Cr than in the shoot in all the three crops. Following root and shoot, the total uptake of Cr differed significantly between the three crops and the values were significantly higher in Amaranthus.

4.6.3. Residual chromium in soil

The residual Cr content in soil after removal of plants varied from addition of graded levels of Cr has significantly influenced the total Cr content in soil. In general, increase in the rate of addition of Cr progressively increased the residual Cr in soil. While, the lowest value was with control, the highest value was observed at high concentration of Cr added. The interaction effect of the amount of Cr added and the plants did not results any significant influence on residual Cr in soil (Table 4.32).

CHAPTER - 5
DISCUSSION

Industrialization is important for the growth of a nation, but at the same time it increases pollution problem, which must be tackled by proper techniques. So, utilization of industrial wastes for productive purposes has to be explored. Most of the wastes contain essential nutrients and organic matter, can enhance the availability of nutrients and enrich the soil organic matter and ultimately increase the growth of crops. Thus, utilization of effluent has two-fold advantages (1) supply of nutrients to the soil for crop growth (2) recycling of effluent as irrigation water.

However, there are some toxic constituents present in the wastes that may affect crop production. Tannery is one such significant industry, which not only brings huge amounts of foreign exchange to our country but also harms the environment with very high loads of pollution in North Arcot, Erode and Dindigul districts of Tamil Nadu. If the wastewater from the tannery industries is recycled, then that could appreciably reduce the water of the factory needs (FalkenMark and Lindh, 1974). Hence, all the tannery industries are currently trying to construct treatment plant for remediation of pollutant or they are utilizing common effluent treatment plant (CETP). Because of the treatments, the toxicity of effluent will be reduced and the possibility of crop production with treated tannery effluent without affecting the environment may be explored, reducing the quantum of fertilizers and for enhancing soil fertility.

5.1. Characteristics of effluent

Characterization of effluent is necessary to understand the physico chemical properties of effluent, which ultimately influence the properties of soil and crop growth.

In general, the effluent had abnormal characteristics when compared to irrigation water. The effluent had unpleasant smell with turbidity and was light brown in color. This may be due to the use of basic chromium sulphate and impurities of skins and hides removed during the tanning process. The degradation of skin and hides may result in the formation of bad odour. The effluent had alkaline pH with high EC and high dissolved solids due to the use of chromium, lime, sodium chloride, sodium sulphite etc. in the tanning processes. Such an unfavourable characteristics of high pH, EC, dissolved solids of the effluent was in conformity with the findings of many workers (Thabaraj *et al.* 1964; Chadha and Pandey, 1993; Dhulasi Birundha and Saradha, 1994, Mariappan *et al.* 1997).

In addition to the presence of salts, considerable amount of Cr also was detected in the effluent. However Cr was present in trivalent form [Cr (III)] in the effluent. (Manivasakam, 1987 and Rajamani and Buljan, 1997) which is not toxic like Cr (VI). Although, the effluent showed unfavourable characteristics, it had considerable amount of nutrients like N, P, K, Ca and Mg.

5.2. Characteristics of the experimental soil

The black and red soils collected from wet and garden lands of Tamil Nadu Agricultural University, were slightly alkaline in reaction (pH 7.71 and 8.01) and non-saline (EC 0.09 and 0.32 dSm^{-1}) with low organic carbon (0.408 and 0.368%). With regard to fertility status of the soil, both soils had low level of nitrogen (N), medium level of phosphorus (P) and high level or potassium (K).

5.2.1. Characteristics of incubated soil

5.2.1.1. Effect of tannery effluent on physico-chemical properties of soil

Application of effluent increased the pH of the soil. The presence of lime and sodium salts in the effluent might have resulted in increased pH initially in all treatments but among the treatments the reduction in concentration of these salts due

to dilution of the effluent resulted in decreased pH i.e. pH decreased with increase of dilution (at 25 and at 100 pet cent dilution of tannery effluent, the pH in black soil was 8.30 and 8.41 and in red soil it was 8.35 and 8.55 respectively). (Machado *et al.*, 1984 and Stomberg *et al.*, 1984a, Dadhich *et al*., 2002). The interaction effect of effluent with the soil might have influenced the buffering capacity and soil mineral compounds resulting in the increase in pH (Karuppusamy *et al*., 2001).

In respect of EC, significant increase was noticed, both in black and red soils with the application of different dilution of effluent. Such an increase in EC with highly saline water was reported by many workers (Varadarajan *et al.*, 1970; Khan and Raman, 1972; George, 1984; Ramasamy and Krishnamurthy, 1981; Singaram, 1994 and Thangavel *et al.*, 2003a).

Asghar and Dhawan (1948) reported that out of four sodium salts (Na_2CO_3, $NaHCO_3$, NaCl and Na_2SO_4), $NaHCO_3$ has contributed the most in increasing the pH and the degree of alkalization. In this study, sodium chloride was dominant in the effluent, which might have resulted in high alkalinity. Hence, the increased EC due to the effluent, which is having high NaCl or SO_4 and lime, is understandable.

The EC of the soil was increased during the period of incubation of the soil with different concentrations of the effluent (Fig 5.1). This may be due to nature and volume of effluent used. However, the leaching factor is the important one in influencing the EC. As there was no chance of leaching in lab experiment that might have helped in the accumulation of salts in the soils. Gupta (1990) reported that in the case of silty clay to clayey soil, accumulation of salts is greater as compared to sandy loam to loamy sand soils. This is the reason for high EC in black soil when compared to red soil. The results corroborate with the findings of Kumaravelu *et al*. (2000).

5.2.1.2.Effect on nutrients and fertility status

The availability of N was significantly increased by the application of effluent (Fig 5.3). This increase might be due to the presence of substances like proteins, hide fat and their degradation products in the tannery effluent (Stomberg *et al*. 1984a). This may be responsible for higher supply of N resulting in better crop growth and consistently increased the availability throughout the crop period (Thangavel *et al*, 2003a).

Similar trend as that of N was also observed in available P content of the soils also. This is probably due to instantaneous addition of effluent to the soil and the mineralization and/or solubilization of soil P. Kamalam (1978) observed such an increase in P with the application of tannery effluent at different concentrations in the soil.

Irrespective of soils, though not consistent, the available K content increased due to the effluent application, similar to N and P content. Such an increase was also observed by Chadha and Pandey (1993) at different concentrations of tannery effluent application in soil.

Similarly, Ca, Mg and SO_4 contents of both black and red soils increased due to the application of varied levels of effluent. The effluent contains varied levels of macro and secondary nutrients, which was observed in the order: K>Ca>Mg>SO_4.

High contents of these nutrients in the effluent might have increased their availability in black and red soils. Generally Ca and Mg were more in black soil (7.08 and 4.51 cmol (P^+) kg^{-1} respectively) compared to red soil (5.92 and 3.66 cmol (P^+) kg^{-1} respectively). The increase of nutrient level in tannery effluent applied soil was also reported by Kumaravelu *et al*. (2000).

5.2.1.3. Effect on salt loading

The tannery effluent application at different rates substantially increased the chloride and sodium (Fig 5.4) content in black and red soils. It is expected that the large amounts of chloride (approximately 190 ppm) in the effluent should have contributed to the soil chloride upon application. Similar results were reported by (Ramasamy and Naidu, 2000). This was in conformity with the earlier work of Iyer *et al*. (1952) and Thangavel *et al*. (2003b) who observed increased Cl and Na in soil due to tannery effluent irrigation.

5.2.1.4.Effect on enzyme and microbial activities

The tannery effluent addition has increased the activity of phosphatase, urease and dehydrogenase (Fig 5.4) enzymes, especially at higher levels of effluent concentration (75 and 50 per cent dilution). However, reduction in the enzyme activity was observed at the end of incubation. This suggests that though tannery effluent application initially increased the enzyme activities, it also has the inhibitory effect on the level of activities at higher concentration in both the soils. The inhibitory influence of chromium in the effluent on the microorganisms may be the reason for it. Tyler (1976) reported that heavy metal pollution affect the phosphatase activity and mineralization of organic phosphorus in forest soils. Similar inhibition of enzyme activity was reported by Moore and Russell (1972) for dehydrogenase and Tabatabai, (1977 for urease activity by trace elements. Doelman and Haanstra (1986) observed that the urease activity was inhibited by both short and long-term exposure of heavy metals on the urease activity of soils.

It was evident from the Tables (4.17, 4.18 and 4.19) that the microbial populations (bacteria, fungi and actinomycetes) have been increased in both the soils initially. Except the bacterial population, which was more in black soil compared to red soil, the population of other organisms (fungi and actinomycetes) was more or less

equal in respect of soils with the period of incubation. The microbial population mostly appeared to have declined initially and increased subsequently.

Similar reduction and subsequent increase in the microbial population due to the application tannery effluent was reported by Rudolfs (1950). He reported that, the effluent will affect the nitrification and the inhibition may be overcome if the microbial population is able to adjust to the stress. The tannery waste has been shown to inhibit the biological activities of soil microorganisms (Percuoco *et al.* 1973). Khan and Raman (1972) reported that the high concentration of sodium chloride present in the tannery effluent was lethal to microorganism.

Similar result that the tannery effluent contains large quantities of chloride, which affect the microbial population and depress germination of spores probably due to increased salinity, was also observed by Ramasamy and Krishnamurthy (1981).

5.3. Effect of treated tannery effluent, simulated chromium (VI) and salt (NaCl) effluents on crop growth

5.3.1. Effect of tannery effluent on crop growth

The germination study conducted with three crops (ragi, black gram and Amaranthus) with five treatments involving effluent at five different concentrations (0,25,50,75 and 100 per cent) revealed that all the three crops performed well in T_1, T_5 and T_4. i.e. control, 25 and 50 per cent of tannery effluent respectively. The germination percentage was reduced at higher concentrations i.e., 75 and 100 per cent dilutions
(Fig 5.6).

The reduction in germination of the crops in the high concentration of effluent could be due to the inhibitory effect of the effluent. The germination study also included the evaluation of the effect of diluted effluent on root length, shoot length,

dry matter production and vigour index of three crops. These growth parameters also increased at higher dilutions of effluent (25 and 50 per cent) irrespective of crops compared to lower dilutions (75 and 100 per cent). Thangavel *et al*. (2003a) observed the same result in green gram at different concentrations of tannery effluent.

Reduction in germination per cent, root and shoot length in crops at increased concentration of tannery effluent was reported by Kamalam (1978); Kamalam and Raj (1980a) Teekaraman *et al*. (1982); Kumaravelu *et al*. (2000).

Presence of salts like sodium and chloride in the effluent leads to an increase in the osmotic pressure of water thereby the seeds might have suffered water stress. This might have had an inhibitory effect and hence the germination was very less in higher concentrations.

The chlorophyll content, leaf area, biomass and protein content were increased at low concentration (25%) when the effluent was diluted with water and used for irrigation. There was a slight decrease in the chlorophyll content at 50 per cent treatment and at high concentration reduction in growth was occurring. Karunyal *et al*. (1994) also observed that the higher concentrations of tannery effluent affect the chlorophyll content of the crop.

Reduction in root and shoot weight of *Typha angustifolia* grown at higher concentration of tannery effluent was observed by Sumathi (2003).

5.3.2.Effect of simulated chromium (VI) effluent on crop growth

The tannery effluent not only contains high concentration of salt, but also high concentration of chromium. So a study was undertaken to assess the effect of salt and chromium on crops. Here, at all concentrations (25,50 and 75 ppm), the chromium inhibited the growth of all the crops viz., ragi, black gram and Amaranthus (Fig 5.8).

This might be due to translocation of Cr to the shoot. Lahouti and Peterson (1979) reported that more chromium was translocated to the shoots of plants grown in Cr (VI). Cr (VI) was considered to enter the plant via the sulphate pathway. At high concentration
(75 ppm) the germination was severely inhibited.

The plants grown in chromium-contaminated solution have stunted growth compared with control. This suggests that, the crops are affected by low concentration of chromium too.

Yamaguchi and Aso (1977) reported that decreased root and shoot elongation was observed in rice and wheat grown in chromium-contaminated soil. The roots of plants grown in chromium-contaminated soil had fewer branches of fine roots than the roots of control were reported by James and Bartlett (1984).

5.3.3. Effect of simulated salt (NaCl) effluent on crop growth

Presence of high concentration of salts like sodium and chloride in the simulated effluent leads to an increase in osmotic pressure of water and thereby lowers water availability to plants. As a result, seeds suffer from water deficit and consequent stress. The seeds might have suffered due to chloride ion-toxicity also. (Mahimairajah and Kaleeswari, 1995). The combined effect of all these factors resulted in poor germination in higher concentration of simulated effluent (4200 and 2100 ppm). This result was in conformity with the findings of Verma and Poonia (1978) who reported that, the speed of germination as well as germination percentage, shoot and root growth and their fresh weight decreased with increased in salinity except at low salinity levels in pearl millet.

The percent germination as well as speed of germination appreciably increased under low salinity levels. On the other hand, shoot and root growth decreased

progressively under all the salinity levels indicating that the adverse effect of salt stress was more pronounced on the early seedling growth rather than on initiation of growth i.e., germination (Fig 5.8). This may perhaps be due to accumulation of high amounts of salts at elongation phase causing toxicity. This work of Verma and Poonia (1978) also lends support to the present study.

5.4.Batch experiment

5.4.1.Effect of simulated chromium (VI) effluent on adsorption by soil

The toxic form of chromium is Cr(VI) which is reduced to non toxic by its conversion to Cr(III). The rate of conversion is important to reduce the toxicity. Griffin *et al.* (1977) assumed that adsorption of Cr (VI) was the only reaction, taking place for the removal of Cr (VI) from soil solution. However, Grove and Ellis (1980) suggested that reduction alone accounted for the disappearance of soluble Cr (VI) from the soils. They did not measure Cr (VI) in the soil solutions. However, James and Bartlett (1983b) proved both the process of reduction and adsorption and reported that Cr (VI) added to a soil will remain mobile only when its concentration exceeds both the adsorbing and the reducing capacities of soil.

Similar phenomenon was observed in this investigation also. The quantity of Cr (VI) was observed high up to 36 hours and more reduction occurred within the short period of addition of Cr (VI). The applied Cr (VI) was not only adsorbed but also appreciably reduced to Cr (III) immediately after addition of Cr (VI). This was in conformity with the earlier work of Thangavel *et al.* (2003b), who observed that there was 35 per cent adsorption within a short period of addition of Cr (VI) and it remained constant (50 per cent) between 10 to 30 hrs (Fig 5.8 and 5.9).

The presence of organic matter and oxidized Mn in the soil might have enhanced the reduction of Cr(VI) to Cr(III)in soil.

James and Bartlett (1983 a) reported that organically complexed Cr (III) added to soils may remain soluble, whereas the free Cr (VI) metal ion would quickly become absorbed and hydrolyzed and precipitated (Mc Growth and Smith, 1990) in the absence of soluble, complexing agent. This might be the reason for quick unavailability of Cr (VI) in extracted solution.

Ross *et al.* (1981) reported that the presence of Cr (VI) in the soil had fully disappeared with in 13 days. About three - fourths of the Cr (VI) added to the soils treated with 100 ppm of Cr (VI) was not extractable after 3 days.

5.4.2.Toxicity of Cr (VI) to microorganism

Cr (VI), a carcinogen, is highly toxic to all forms of life. But detailed information is lacking on Cr toxicity to soil microorganisms. Hence, the present study was undertaken to have preliminary indication of the effect of Cr on soil microbial activities (Tables 4.30, 4.31 and 4.32).

The various concentrations of Cr (VI) in soil initially affected the microorganisms severely. At 48 hours after incubation, the presence of microorganisms like bacteria, fungi and actinomycetes were found. This is due to the conversion of Cr(VI) which is toxic to Cr(III), a non toxic form.. However, the initial inhibition was due to the influence of Cr(VI) before it is reduced to Cr(III). But, it may be happened only for native microflora in the tannery sludge and effluents. The results of this study showed that, the toxicity of Cr (VI) to soil microflora occurred within 12 hours. Even though Cr (VI) was present for only a short time, one portion of the population of soil microorganism was inhibited. There was no direct evidence favouring the above factor. But, it is possible that the activity of organisms have been completely suppressed by Cr (VI) as evident from the reduction in the population.

5.5.Accumulation of chromium by crop species

The crop plant varied significantly in their ability to take up and accumulate Cr in their tissues. The concentration of Cr in roots and shoots was increased with increasing concentration (25 and 50 ppm) of Cr in soil. However, at higher concentration, Cr content in roots was found reduced due to the inhibition of root growth. It was observed that the roots of ragi, black gram and Amaranthus accumulated a large amount of Cr and only a small fraction was transported to the shoots (Fig 5.11). The distribution of Cr in plants was observed in the order of: root >shoot. A similar effect of Cr was observed Nand lal *et al*. (1999) in *Lemna minor L*. These results are in agreement with results of Lyon *et al*. (1969) Ramachandran *et al.* (1980) and Quereshi *et al*. (1985). The reason for the restriction of Cr transport within plant is not yet established. However, Shewry and Paterson (1974) suggested that Cr was unavailable for transport due to spatial localization in a specific sub cellular compartment in the root cells or due to the lack of specific mechanisms for transport.

Some species have an exclusion mechanism, which either prevent root uptake of these elements or subsequent translocation to the aerial parts, whereas in this investigation more uptakes in root and less in shoot was observed.

The tannery effluent used for the present study was collected from the EKM and Sons tannery industry. The effluent is treated before it is left out and the total Cr in the effluent is around 0.525 ppm which is comparatively low; however, the use of sodium chloride results in the high quantities of sodium and chloride in the effluent ie. 223 m.e L^{-1} and 951 ppm respectively. This concentration has to be reduced for the better utilization of the effluent. This is evident from the studies by the simulated sodium chloride effluent which showed that the germination and growth of all the crops tested were adversely affected by all the concentrations of the NaCl tested. However further studies are required to confirm the results and suitable remediation of the effluent is necessary for the use of the effluent for agricultural purposes.

CHAPTER - 6

SUMMARY AND CONCLUSION

Economic reasons and environmental considerations necessitate the re-use or recycling of waste materials generated by industries and communities. Such utilization process helps in avoiding or reducing the pollution load on the environment and also brings out the usefulness of these wastes. However, the contamination by toxic constituents present in these wastes restricts the use of them. Hence, the techniques for the reduction of pollution load aiming at the effective utilization of such wastes must be developed.

Tannery industry is one of the important industries, which is contributing to large-scale pollution of the environment. To examine various aspects of tannery industrial pollutions, the effects of tannery effluent with and without dilutions on soil and crops were studied by conducting laboratory experiments. As, Chromium (Cr) is one of the major constituents of tannery wastes, laboratory studies on adsorption of Cr in soil and its toxicity on microorganisms were conducted in batch experiments and a pot culture experiment was conducted to study the uptake of Cr by plants. The results obtained in all these experiments are summarized here.

The soil samples collected from various experiments were analysed for pH, EC, organic carbon, N, P, K, water-soluble elements and nutrients like Na, Ca, Mg and So_4 etc. The population of microorganisms as influenced by the treatments also was enumerated. The plant samples from pot culture were analysed for Cr uptake. In germination studies, the biometric observations like germination percentage, shoot length, root length, vigour index and dry matter production were recorded.

The adsorbed and water-soluble Cr in soil samples from batch experiments were analysed. The data obtained were statistically analysed and interpreted accordingly. From the results obtained, the following conclusions are drawn.

Characterization of effluent

- The tannery effluent was light brown in colour and had unpleasant odour due to Cr content and SO_4 - S compounds
- It was slightly alkaline (pH - 8.79), and loaded with inorganic salts recording high EC (9.61 dSm^{-1}) and TDS (4,765 mg L^{-1}) due to the use of sodium chloride and sodium sulfate for washing process.
- The effluent had considerable amounts of nutrients like N, P, K, Ca and Mg.
- The effluent contained large amounts of salts, whose concentration is in the order: Chloride > SO_4 > HCO_3.
- The effluent used in the study was having very high load of pollutants, which were exceeding the permissible limit prescribed by Tamil Nadu Pollution Control Board. It had high BOD and COD, which may likely to pollute soil - water ecosystem.
- It had high amounts of Na, therefore, which will cause sodicity problem in soil.

Impact of tannery effluent on soils

Using an incubation experiment the impact of different rates of effluent (0. 25, 50, 75 and 100 per cent) on two-soil types viz., black and red was assessed. The results showed that:

- Irrespective of soils, the effluent application increased the pH immediately after application, but slightly reduced during incubation period.
- The soil EC increased, due to accumulation of salts like chloride and Na from effluent.

- The nutrients N, P, K, Ca and Mg in soils increased due to effluent application, more in black soil than red soil.
- The effluent had increased Na content so that the higher concentration of effluent application caused sodicity problem in soil.
- Initial enhancement in enzymes (phosphatase, dehydrogenase, and urease) and microbial (actinomycetes, bacteria and fungi) activities was evident in soil amended with the effluent. However, there was significant reduction in activities was observed at the higher concentration at the end of incubation.

Impact of tannery and simulated Cr (VI) and NaCl effluent on crops

- Germination study with different dilutions of tannery effluent (0, 25, 50, 75 and 100 per cent) showed that the lower concentrations (25 and 50 per cent) of effluent had improved the germination of ragi, black gram, and Amaranthus, whereas 75 per cent concentration reduced the germination percentage significantly. The raw effluent (100 per cent) was found detrimental for seed germination. So, instead of 25 per cent dilution, 50 per cent dilution can be safely used for irrigation.
- Both NaCl (1050,2100 and 4200ppm) and Cr (VI) effluent (25,50 and 75 ppm) showed negative effect on the seed germination at all concentrations for all crops.
- The uptake of Cr by crops were analysed in pot culture and the results showed that Amaranthus had high efficiency in accumulation compared to other crops (ragi and black gram). There was more accumulation of Cr in the root than shoot.

Effect of simulated Cr(VI) effluent on soil and microorganisms

- The population of microflora was significantly reduced by the Cr(VI), even though the applied Cr (VI) was reduced very quickly to Cr(III) in the soil, the inhibition of population was observed.

Raw effluent resulted in the significant built up of salt in soil. The effect of 50 per cent dilution on germination of crops and soil properties was on par with 25 per cent dilution. It was found to be significantly less toxic than the higher concentrations and supply optimum level of nutrients to the soil and crops. So, effluent at 50 per cent dilution may be used for irrigation purposes. However, long-term field experiments are needed to confirm these results.

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* Originals not seen

Table 4.1.Characteristics of tannery effluent

Sl.No.	Parameters	Value
	Physical properties	
1.	Colour	Light brown
2.	Odour	Unpleasant
	Chemical properties	
3.	pH	8.79
4.	EC (dSm^{-1})	9.61
5.	Total dissolved solids (ppm)	5965
6.	Organic carbon (%)	0.096
7.	Total Cr (ppm)	0.5
8.	Water soluble Cr (ppm)	0.025
9.	Biological oxygen Demand (ppm)	360
10.	Chemical oxygen Demand (ppm)	1680
11.	Sodium (m.e L^{-1})	223
12.	Sulphate (m.e L^{-1})	0.4
13.	Calcium (m.e L^{-1})	1.2
14.	Magnesium (m.e L^{-1})	0.8
15.	Carbonate (ppm)	0
16.	Bicarbonate (ppm)	31
17.	Chloride (ppm)	951
18.	Total N (m.e L^{-1})	20.2
19.	Total P (m.e L^{-1})	3.8
20.	Total K (m.e L^{-1})	13
	Microbiological properties	
21.	Bacteria (10^6 CFU/ml)	8
22.	Fungi (10^3 CFU/ml)	-
23.	Actinomycetes (10^2 CFU/ml)	4

Table 4.2. Characteristics of experimental soils

Sl.No.	Properties	Black soil	Red soil
	Physical properties		
1.	Bulk density (g cc^{-1})	1.43	1.27
2.	Particle density (g cc^{-1})	1.92	2.56
3.	Maximum water holding capacity (%)	46.49	31.3
	Chemical properties		
4.	pH (1:2.5 H_2O)	7.71	8.01
5.	EC (dSm^{-1})	0.14	0.07
6.	Organic carbon (%)	0.15	0.40
7.	Available N (kg ha^{-1})	255	198
8.	Available P (kg ha^{-1})	16.7	11.4
9.	Available K (kg ha^{-1})	297	272
10.	NH_4 OAC - Ca (cmol(P^+) kg^{-1})	7.08	5.92
11.	NH_4 OAC - Mg (cmol(P^+) kg^{-1})	4.51	3.66
12.	NH_4 OAC - Na (cmol(P^+) kg^{-1})	0.10	0.15
13.	Sulphate (ppm)	1.12	1.15
14.	Chloride (ppm)	37.8	35.2
	Enzyme assay		
15.	Phosphatase (mg kg^{-1} hr^{-1})	25.59	23.69
16.	Dehydrogenase (mg kg^{-1} hr^{-1})	26.53	24.56
17.	Urease (mg kg^{-1} hr^{-1})	75.1	69.5
	Microbiological properties		
18.	Actinomycetes (10^2 CFU/g)	2.77	3.96
19.	Fungi (10^3 CFU/g)	3.85	5.50
20.	Bacteria (10^6 CFU/g)	9.38	8.68

Table 4.3. Effect of tannery effluent on soil pH

Treatment	Black soil					Red soil				
	Period of Incubation (Days)					Period of Incubation (Days)				
	0	**15**	**30**	**45**	**Mean**	**0**	**15**	**30**	**45**	**Mean**
T_1	7.70	7.99	7.97	7.92	**7.90**	8.01	8.21	8.25	8.20	**8.17**
T_2	8.41	8.35	8.33	8.31	**8.35**	8.55	8.50	8.51	8.47	**8.51**
T_3	8.37	8.34	8.32	8.31	**8.34**	8.46	8.37	8.37	8.37	**8.39**
T_4	8.34	8.31	8.29	8.30	**8.31**	8.41	8.41	8.36	8.34	**8.38**
T_5	8.30	8.29	8.25	8.24	**8.27**	8.35	8.29	8.29	8.28	**8.30**
Mean	**8.22**	**8.26**	**8.23**	**8.22**		**8.36**	**8.36**	**8.36**	**8.33**	
	T	D	TxD				T	D	TxD	
SEd	0.02	0.02	0.04			SEd	0.02	0.02	0.04	
CD (0.05)	0.04	0.04	0.08			CD (0.05)	0.04	0.04	0.08	

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

Table 4.4. Effect of tannery effluent on soil EC (dSm^{-1})

Treatment	Black soil					Red soil				
	Period of Incubation (Days)					Period of Incubation (Days)				
	0	**15**	**30**	**45**	**Mean**	**0**	**15**	**30**	**45**	**Mean**
T_1	0.14	0.19	0.18	0.16	**0.17**	0.07	0.11	0.10	0.09	**0.09**
T_2	0.58	0.57	0.65	0.64	**0.61**	0.31	0.25	0.33	0.35	**0.31**
T_3	0.46	0.47	0.48	0.51	**0.48**	0.27	0.23	0.27	0.30	**0.27**
T_4	0.38	0.35	0.37	0.41	**0.38**	0.21	0.17	0.19	0.22	**0.20**
T_5	0.27	0.27	0.30	0.32	**0.29**	0.17	0.15	0.16	0.17	**0.16**
Mean	**0.37**	**0.37**	**0.40**	**0.41**		**0.21**	**0.18**	**0.21**	**0.23**	
		T	D	TxD			T	D	TxD	
	SEd	0.02	0.02	0.04		SEd	0.02	0.02	0.04	
	CD (0.05)	0.04	0.04	NS		CD (0.05)	0.04	0.04	NS	

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

Table 4.5. Effect of tannery effluent on soil organic carbon (%)

Treatment	Black soil					Red soil				
	Period of Incubation (Days)					Period of Incubation (Days)				
	0	**15**	**30**	**45**	**Mean**	**0**	**15**	**30**	**45**	**Mean**
T_1	0.408	0.418	0.415	0.418	**0.415**	0.368	0.384	0.390	0.394	**0.384**
T_2	0.431	0.431	0.417	0.421	**0.425**	0.388	0.388	0.376	0.379	**0.383**
T_3	0.425	0.426	0.426	0.421	**0.425**	0.382	0.383	0.383	0.379	**0.382**
T_4	0.422	0.424	0.422	0.422	**0.423**	0.379	0.383	0.380	0.380	**0.381**
T_5	0.414	0.420	0.419	0.418	**0.418**	0.373	0.378	0.377	0.376	**0.376**
Mean	**0.420**	**0.424**	**0.420**	**0.420**		**0.378**	**0.383**	**0.381**	**0.382**	
		T	D	TxD			T	D	TxD	
	SEd	0.002	0.002	0.004		SEd	0.002	0.001	0.004	
	CD (0.05)	0.004	0.004	NS		CD (0.05)	0.004	0.003	NS	

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

Table 4.6. Effect of tannery effluent on soil available N (kg ha^{-1})

Treatment	*Black soil*					Red soil				
	Period of Incubation (Days)					Period of Incubation (Days)				
	0	**15**	**30**	**45**	**Mean**	**0**	**15**	**30**	**45**	**Mean**
T_1	255.0	258.0	257.0	258.0	**257.0**	198.0	200.0	202.0	201.0	**200.3**
T_2	272.0	273.0	275.0	275.0	**273.8**	211.0	209.0	210.0	212.0	**210.5**
T_3	269.0	268.0	270.0	271.0	**269.5**	208.0	207.0	208.0	209.0	**208.0**
T_4	262.0	263.0	263.0	269.0	**264.3**	205.0	202.0	203.0	205.0	**203.8**
T_5	258.0	259.0	258.0	259.0	**258.5**	202.0	200.0	201.0	203.0	**201.5**
Mean	**263.2**	**264.2**	**264.6**	**266.4**		**204.8**	**203.6**	**204.8**	**206.0**	
	T	D	TxD				T	D	TxD	
SEd	0.41	0.41	0.82			SEd	0.48	0.43	0.97	
CD (0.05)	0.83	0.83	1.65			CD (0.05)	0.98	0.87	1.95	

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

Table 4.7. Effect of tannery effluent on soil available P (kg ha^{-1})

Treatment	Black soil					Red soil				
	Period of Incubation (Days)					Period of Incubation (Days)				
	0	**15**	**30**	**45**	**Mean**	**0**	**15**	**30**	**45**	**Mean**
T1	16.7	16.9	16.8	16.7	**16.8**	11.4	11.5	11.5	11.4	**11.5**
T2	18.5	18.6	18.9	19.1	**18.8**	13.1	13.3	13.6	13.9	**13.5**
T3	18.1	18.2	18.4	18.5	**18.3**	12.7	12.8	13.2	13.5	**13.1**
T4	17.7	17.9	18.1	18.2	**18.0**	12.4	12.7	12.8	13.1	**12.8**
T5	17.3	17.5	17.7	18.1	**17.6**	12.1	12.3	12.4	12.7	**12.4**
Mean	**17.6**	**17.8**	**18.0**	**18.1**		**12.3**	**12.5**	**12.7**	**12.9**	
		T	D	TxD			T	D	TxD	
	SEd	0.09	0.08	0.18		SEd	0.08	0.07	0.17	
	CD (0.05)	0.18	0.16	NS		CD (0.05)	0.17	0.15	NS	

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

Table 4.8. Effect of tannery effluent on soil available K (kg ha^{-1})

Treatment	Black soil					Red soil				
	Period of Incubation (Days)					Period of Incubation (Days)				
	0	**15**	**30**	**45**	**Mean**	**0**	**15**	**30**	**45**	**Mean**
T_1	297.0	296.0	294.0	293.0	**295.0**	272.0	274.0	273.0	270.0	**272.3**
T_2	312.0	311.0	309.0	307.0	**309.8**	286.0	287.0	289.0	290.0	**288.0**
T_3	309.0	311.0	307.0	305.0	**308.0**	283.0	284.0	286.0	287.0	**285.0**
T_4	306.0	307.0	305.0	302.0	**305.0**	288.0	282.0	283.0	284.0	**284.3**
T_5	302.0	303.0	300.0	298.0	**300.8**	277.0	278.0	280.0	281.0	**279.0**
Mean	**305.2**	**305.6**	**303.0**	**301.0**		**281.2**	**281.0**	**282.2**	**282.4**	
		T	D	TxD			T	D	TxD	
	SEd	0.80	0.72	1.60		SEd	0.82	0.73	1.63	
	CD (0.05)	1.62	1.45	NS		CD (0.05)	1.65	1.48	NS	

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

Table 4.9. Effect of tannery effluent on soil exchangeable Ca (cmol (p^+) kg^{-1})

Treatment	Black soil					Red soil				
	Period of Incubation (Days)					Period of Incubation (Days)				
	0	**15**	**30**	**45**	**Mean**	**0**	**15**	**30**	**45**	**Mean**
T_1	7.08	7.30	7.61	7.52	**7.38**	5.92	6.50	6.68	6.51	**6.40**
T_2	4.70	4.78	4.73	4.73	**4.74**	3.19	3.25	3.24	3.22	**3.23**
T_3	5.21	5.25	5.21	5.17	**5.21**	3.37	3.42	3.40	3.38	**3.39**
T_4	5.28	5.29	5.26	5.27	**5.28**	3.66	3.59	3.66	3.63	**3.64**
T_5	5.70	5.76	5.75	5.81	**5.76**	4.11	4.15	4.14	4.14	**4.14**
Mean	**5.59**	**5.68**	**5.71**	**5.70**		**4.05**	**4.18**	**4.22**	**4.18**	
	T	D	TxD				T	D	TxD	
SEd	0.22	0.04	0.26			SEd	0.23	0.19	0.43	
CD (0.05)	0.47	0.09	NS			CD (0.05)	0.50	0.40	0.90	

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent

Table 4.10. Effect of tannery effluent on soil exchangeable Mg (cmol (p^+) kg^{-1})

Treatment	Black soil					Red soil				
	Period of Incubation (Days)					Period of Incubation (Days)				
	0	**15**	**30**	**45**	**Mean**	**0**	**15**	**30**	**45**	**Mean**
T_1	4.51	4.48	4.52	4.56	**4.52**	3.66	3.82	3.69	3.85	**3.76**
T_2	2.85	2.87	2.88	2.84	**2.86**	1.18	1.20	1.19	1.16	**1.18**
T_3	3.02	3.03	3.04	3.00	**3.02**	1.42	1.44	1.41	1.40	**1.42**
T_4	3.29	3.31	3.35	3.27	**3.31**	1.74	1.75	1.73	1.71	**1.73**
T_5	3.52	3.54	3.55	3.50	**3.53**	2.04	2.07	2.05	2.02	**2.05**
Mean	**3.44**	**3.45**	**3.47**	**3.43**		**2.01**	**2.06**	**2.01**	**2.03**	
		T	D	TxD			T	D	TxD	
	SEd	0.12	0.01	0.13		SEd	0.15	0.01	0.17	
	CD (0.05)	0.25	0.02	NS		CD (0.05)	0.32	0.03	NS	

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

Table 4.11. Effect of tannery effluent on soil exchangeable Na (cmol (p^+) kg^{-1})

Treatment	Black soil					Red soil				
	Period of Incubation (Days)					Period of Incubation (Days)				
	0	**15**	**30**	**45**	**Mean**	**0**	**15**	**30**	**45**	**Mean**
T_1	0.10	0.13	0.12	0.11	**0.12**	0.12	0.10	0.12	0.11	**0.11**
T_2	5.31	5.19	5.20	5.05	**5.19**	5.45	5.37	5.36	5.25	**5.36**
T_3	4.59	4.56	4.51	4.46	**4.53**	4.92	4.85	4.77	4.66	**4.80**
T_4	4.26	4.19	4.15	4.07	**4.17**	4.57	4.45	4.49	4.44	**4.49**
T_5	3.49	3.36	3.44	3.34	**3.41**	3.78	3.82	3.71	3.62	**3.73**
Mean	**3.55**	**3.49**	**3.48**	**3.41**		**3.77**	**3.72**	**3.69**	**3.62**	
		T	D	TxD			T	D	TxD	
	SEd	0.10	0.09	0.92		SEd	0.07	0.06	0.13	
	CD (0.05)	0.19	0.17	0.39		CD (0.05)	0.14	0.12	0.27	

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

Table 4.12. Effect of tannery effluent on soil water soluble Cl (ppm)

Treatment	Black soil					Red soil				
	Period of Incubation (Days)					Period of Incubation (Days)				
	0	**15**	**30**	**45**	**Mean**	**0**	**15**	**30**	**45**	**Mean**
T_1	37.8	35.6	34.2	33.2	**35.2**	35.2	33.6	31.2	30.5	**32.6**
T_2	136.6	128.0	133.7	126.3	**131.2**	125.1	88.8	115.6	109.7	**109.8**
T_3	114.7	113.3	106.4	102.5	**109.2**	114.3	112.9	106.9	94.5	**107.2**
T_4	106.9	102.6	96.1	85.3	**97.7**	97.6	93.2	85.1	81.5	**89.4**
T_5	97.7	86.3	84.2	77.3	**86.4**	87.4	73.0	64.7	53.9	**69.8**
Mean	**98.7**	**93.2**	**90.9**	**84.9**		**91.9**	**80.3**	**80.7**	**74.0**	
		T	D	TxD			T	D	TxD	
	SEd	9.94	2.54	12.48		SEd	1.18	5.20	6.38	
	CD (0.05)	21.37	5.46	NS		CD (0.05)	2.54	11.18	NS	

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

Table 4.13. Effect of tannery effluent on soil water soluble SO_4 (ppm)

Treatment	Black soil					Red soil				
	Period of Incubation (Days)					Period of Incubation (Days)				
	0	**15**	**30**	**45**	**Mean**	**0**	**15**	**30**	**45**	**Mean**
T_1	1.12	1.26	2.24	1.18	**1.40**	1.12	1.74	2.24	1.10	**1.40**
T_2	34.72	35.84	38.08	40.32	**37.24**	30.24	32.48	31.36	33.60	**31.92**
T_3	30.24	31.36	32.48	34.72	**32.20**	26.88	28.00	26.88	28.00	**27.44**
T_4	25.76	26.88	28.00	29.12	**27.44**	21.28	20.16	22.40	23.52	**21.84**
T_5	21.28	22.40	23.52	24.64	**22.96**	17.92	19.04	17.92	20.16	**18.76**
Mean	**22.62**	**23.52**	**24.86**	**25.98**		**19.49**	**20.16**	**20.16**	**21.28**	
		T	D	TxD			T	D	TxD	
	SEd	2.43	0.53	2.97		SEd	2.16	0.52	2.68	
	CD (0.05)	5.05	1.15	NS		CD (0.05)	4.50	1.12	NS	

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

Table 4.15. Effect of tannery effluent on soil dehydrogenase activity (mg kg $^{-1}$ hr $^{-1}$)

Treatment	Black soil					Red soil				
	Period of Incubation (Days)					Period of Incubation (Days)				
	0	**15**	**30**	**45**	**Mean**	**0**	**15**	**30**	**45**	**Mean**
T_1	26.53	32.51	32.63	33.56	**31.31**	24.56	30.09	45.81	37.43	**34.47**
T_2	25.82	44.19	38.79	29.62	**34.61**	18.77	46.23	35.91	27.42	**32.08**
T_3	25.94	55.94	67.09	48.58	**49.39**	24.12	51.79	62.11	44.98	**45.75**
T_4	24.64	55.77	60.55	46.17	**46.78**	22.81	51.63	56.06	42.75	**43.31**
T_5	26.05	43.37	56.11	45.61	**42.79**	24.12	40.15	51.94	42.42	**39.66**
Mean	**25.80**	**46.36**	**51.03**	**40.71**		**22.88**	**43.98**	**50.37**	**39.00**	
		T	D	TxD			T	D	TxD	
	SEd	0.94	0.84	1.88		SEd	1.20	1.07	2.40	
	CD (0.05)	1.90	1.70	3.79		CD (0.05)	2.43	2.17	4.86	

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

Table 4.14. Effect of tannery effluent on soil phosphatase activity (mg kg $^{-1}$ hr $^{-1}$)

Treatment	Black soil					Red soil				
	Period of Incubation (Days)					Period of Incubation (Days)				
	0	**15**	**30**	**45**	**Mean**	**0**	**15**	**30**	**45**	**Mean**
T_1	25.59	31.36	31.48	32.38	**30.20**	23.69	29.03	24.50	24.49	**25.43**
T_2	24.91	42.63	37.42	28.58	**33.39**	21.11	34.64	42.60	26.45	**31.20**
T_3	25.03	53.96	64.72	46.87	**47.65**	23.17	49.96	59.91	43.39	**44.11**
T_4	23.77	53.79	58.41	44.55	**45.13**	22.00	49.81	54.08	41.24	**41.78**
T_5	25.14	41.84	54.13	43.99	**41.28**	23.27	38.74	50.11	40.73	**38.21**
Mean	**24.89**	**44.72**	**49.23**	**39.27**		**22.65**	**40.44**	**46.24**	**35.26**	
		T	D	TxD			T	D	TxD	
	SEd	0.60	0.81	1.81		SEd	1.16	1.04	2.32	
	CD (0.05)	1.83	1.64	3.66		CD (0.05)	2.34	2.10	4.69	

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

Table 4.16. Effect of tannery effluent on soil urease activity (mg kg $^{-1}$ hr $^{-1}$)

Treatment	Black soil					*Red soil*				
	Period of Incubation (Days)					Period of Incubation (Days)				
	0	**15**	**30**	**45**	**Mean**	**0**	**15**	**30**	**45**	**Mean**
T_1	75.1	92.0	92.4	95.0	**88.6**	69.5	85.2	129.7	105.9	**97.6**
T_2	73.1	125.1	109.8	83.8	**97.9**	63.1	130.9	101.6	77.6	**93.3**
T_3	73.4	158.2	189.9	137.5	**139.8**	68.0	146.6	175.8	127.3	**129.4**
T_4	69.7	157.9	171.4	130.7	**132.4**	64.6	146.1	158.7	121.0	**122.6**
T_5	73.7	122.8	158.8	129.1	**121.1**	68.3	113.7	147.0	119.5	**112.1**
Mean	**73.0**	**131.2**	**144.4**	**115.2**		**66.7**	**124.5**	**142.6**	**110.3**	
		T	D	TxD			T	D	TxD	
	SEd	3.40	3.04	6.80		SEd	3.40	3.04	6.80	
	CD (0.05)	6.87	6.15	13.75		CD (0.05)	6.87	6.15	13.75	

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

Table 4.17. Effect of tannery effluent on soil bacteria (10^6 CFU g^{-1})

Treatment	*Black soil*					Red soil				
	Period of Incubation (Days)					Period of Incubation (Days)				
	0	**15**	**30**	**45**	**Mean**	**0**	**15**	**30**	**45**	**Mean**
T_1	9.38	11.49	17.49	14.29	**13.16**	8.68	10.64	16.19	13.23	**12.19**
T_2	8.50	15.62	13.71	10.47	**12.08**	6.64	16.34	12.69	9.69	**11.34**
T_3	9.17	19.77	23.71	17.17	**17.46**	8.49	18.30	21.95	15.90	**16.16**
T_4	8.81	19.71	21.39	16.31	**16.56**	8.06	18.25	19.00	15.19	**15.13**
T_5	9.21	15.33	19.83	16.12	**15.12**	8.23	14.19	18.36	14.92	**13.93**
Mean	**9.01**	**16.38**	**18.36**	**14.87**		**8.02**	**15.54**	**18.36**	**13.79**	
		T	D	TxD			T	D	TxD	
	SEd	0.35	0.31	0.69		SEd	0.43	0.38	0.85	
	CD (0.05)	0.70	0.63	1.40		CD (0.05)	0.86	0.77	1.72	

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

Table 4.18. Effect of tannery effluent on soil fungi (10^3 CFU g^{-1})

Treatment	Black soil					Red soil				
	Period of Incubation (Days)					Period of Incubation (Days)				
	0	**15**	**30**	**45**	**Mean**	**0**	**15**	**30**	**45**	**Mean**
T_1	3.85	4.08	3.85	3.08	**3.72**	5.50	5.83	5.50	4.40	**5.31**
T_2	1.26	2.31	1.56	2.10	**1.81**	1.80	3.30	2.23	3.10	**2.61**
T_3	2.21	3.15	3.15	2.10	**2.65**	3.15	4.50	4.50	3.00	**3.79**
T_4	3.99	3.38	2.45	3.04	**3.22**	5.70	4.83	3.50	4.33	**4.59**
T_5	4.41	5.25	4.56	4.26	**4.62**	6.30	7.50	6.50	6.08	**6.60**
Mean	**3.14**	**3.63**	**3.11**	**2.92**		**4.49**	**5.19**	**4.45**	**4.18**	
		T	D	TxD			T	D	TxD	
	SEd	0.15	0.14	0.30		SEd	0.22	0.19	0.43	
	CD (0.05)	0.31	0.27	0.61		CD (0.05)	0.44	0.39	0.88	

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

Table 4.19. Effect of tannery effluent on soil actinomycetes (10^2 CFU g^{-1})

Treatment	Black soil					Red soil				
	Period of Incubation (Days)					Period of Incubation (Days)				
	0	**15**	**30**	**45**	**Mean**	**0**	**15**	**30**	**45**	**Mean**
T_1	2.77	2.94	2.77	2.22	**2.68**	3.96	4.20	3.96	3.17	**3.82**
T_2	0.91	1.99	1.13	1.51	**1.39**	1.30	2.38	1.61	2.16	**1.86**
T_3	1.59	2.27	2.27	1.51	**1.91**	2.27	3.24	3.24	2.16	**2.73**
T_4	2.87	2.44	1.76	2.18	**2.31**	4.10	3.48	2.52	3.12	**3.31**
T_5	3.18	3.78	3.28	3.07	**3.33**	4.54	5.40	4.68	4.38	**4.75**
Mean	**2.26**	**2.68**	**2.24**	**2.10**		**3.23**	**3.74**	**3.20**	**3.00**	
		T	D	TxD			T	D	TxD	
	SEd	0.11	0.10	0.22		SEd	0.16	0.14	0.31	
	CD (0.05)	0.22	0.20	0.44		CD (0.05)	0.32	0.28	0.63	

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

Table 4.20. Effect of tannery effluent on crop germination

Treatment	Germination (%)			Root Length (cm)			Shoot Length (cm)		
	Ragi	Black gram	Amaranthus	Ragi	Black gram	Amaranthus	Ragi	Black gram	Amaranthus
T_1	71 (57.49)	95.4 (57.52)	65 (53.83)	6.90	12.20	9.40	5.70	12.80	4.20
T_2	3.8 (5.78)	10.6 (5.78)	8.7 (3.29)	1.30	3.40	2.20	1.30	1.50	1.40
T_3	40.5 (36.75)	38.8 (39.51)	46.4 (42.62)	4.60	6.30	5.30	3.50	4.60	2.30
T_4	62.6 (48.5)	77.6 (46.57)	55.9 (45.91)	5.80	9.80	7.60	4.80	7.60	4.10
T_5	76.8 (61.27)	98.6 (57.82)	73.6 (52.98)	7.20	12.60	10.70	6.00	12.80	4.50
Mean	**46.75**	**64.20**	**49.92**	**5.16**	**8.86**	**7.04**	**4.26**	**7.86**	**3.30**
SEd	2.47	4.64	0.37	0.37	0.53	0.85	0.24	1.03	0.31
CD (0.05)	5.18	9.74	0.77	0.77	1.11	1.79	0.51	2.16	0.63

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

(Figures in parantheses indicates arc sign transformed)

Table 4.20 contd. Effect of tannery effluent on crop vigour index and dry matter production

Treatment	Vigour index			DMP (g 10 seedlings^{-1})		
	Ragi	Black gram	Amaranthus	Ragi	Black gram	Amaranthus
T_1	903.4 (2.98)	2376.4 (3.37)	884.4 (2.94)	1.70	18.60	14.50
T_2	10.9 (0.44)	50 (1.07)	30.5 (1.48)	0.10	2.10	1.90
T_3	328.2 (2.46)	423.4 (2.26)	358.8 (2.58)	1.00	7.50	5.30
T_4	579.1 (2.77)	1025.3 (2.81)	536 (2.73)	1.30	14.10	10.20
T_5	905.4 (2.99)	2387.2 (3.38)	900.9 2.95)	1.80	18.80	14.70
Mean	**545.40**	**1252.46**	**542.12**	**1.18**	**12.22**	**9.32**
SEd	0.18	0.34	4.36	0.16	0.92	1.64
CD (0.05)	0.38	0.71	9.16	0.34	0.34	3.44

T_1-Control, T_2- 100 %effluent, T_3-75 %effluent, T_4-50 %effluent, T_5 -25 %effluent.

(Figures in parantheses indicates log transformed)

Table 4.21. Effect of simulated chromium (VI) effluent on crop germination

Treatment	Germination (%)			Root Length (cm)			Shoot Length (cm)		
	Ragi	Black gram	Amaranthus	Ragi	Black gram	Amaranthus	Ragi	Black gram	Amaranthus
T_1	71 (51.51)	95.2 (78.93)	65 (42.47)	7.00	12.70	9.40	5.70	11.20	4.30
T_2	1.7 (4.506)	3.4 (5.58)	2.9 (4.43)	0.30	0.60	0.70	0.50	1.10	0.10
T_3	9.3 (17.68)	11.7 (19.97)	9.1 (17.54)	1.50	1.50	1.40	1.10	3.60	0.90
T_4	20.7 (26.99)	26 (30.47)	26.5 (30.81)	3.40	4.40	4.60	2.40	4.50	1.80
Mean	**25.68**	**34.08**	**25.88**	**3.05**	**4.80**	**4.03**	**2.43**	**5.10**	**1.78**
SEd	2.46	3.36	2.51	0.23	0.35	0.29	0.09	0.94	0.19
CD (0.05)	5.19	7.77	5.31	0.48	0.75	0.61	0.19	2.00	0.40

T_1-Control, T_2- 75 ppm, T_3-50 ppm, T_4-25 ppm of Cr(VI)

(Figures in parantheses indicates arc sign transformed)

Table4.21 contd. Effect of simulated chromium (VI) effluent on crop vigour index and dry matter production

Treatment	Vigour index			DMP (g 10 seedlings^{-1})		
	Ragi	Black gram	Amaranthus	Ragi	Black gram	Amaranthus
T_1	904.4 (2.95)	2268.6 (3.35)	849.7 (2.93)	1.70	4.30	1.60
T_2	19.6 (1.04)	5.8 (0.224)	2.5 (0.43)	0.01	0.01	0.01
T_3	25.1 (1.38)	60.9 (1.56)	21.1 (1.02)	0.02	0.10	0.02
T_4	119.4 (2.07)	233.2 (2.35)	171.9 (2.22)	0.20	0.40	0.30
Mean	**267.13**	**642.13**	**261.30**	**0.48**	**1.20**	**0.48**
SEd	0.27	0.18	0.10	0.07	0.12	0.08
CD (0.05)	0.57	0.38	0.20	0.14	0.25	0.17

T_1-Control, T_2- 75 ppm, T_3-50 ppm, T_4-25 ppm of Cr(VI)

(Figures in parantheses indicates log transformed)

Table 4.22. Effect of simulated salt (NaCl) effluent on crop germination

Treatment	Germination (%)			Root Length (cm)			Shoot Length (cm)		
	Ragi	Black gram	Amaranthus	Ragi	Black gram	Amaranthus	Ragi	Black gram	Amaranthus
T_1	71 (57.51)	95.2 (78.88)	62.2 (52.14)	7.00	12.70	9.40	5.70	11.20	4.30
T_2	5.8 (12.33)	25.7 (18.26)	15 (16.55)	0.70	1.60	1.50	1.10	2.10	0.90
T_3	17.5 (24.29)	57.9 (31.82)	31.6 (33.56)	1.60	3.40	4.10	2.00	5.00	2.30
T_4	51.4 (46.42)	74.6 (59.97)	52 (46.15)	4.40	8.60	7.50	3.40	6.60	3.40
Mean	**36.43**	**63.35**	**40.20**	**3.43**	**6.58**	**5.63**	**3.05**	**6.23**	**2.73**
SEd	2.46	4.36	4.80	0.07	0.33	0.32	0.25	0.97	0.23
CD (0.05)	5.23	9.16	10.18	0.36	0.69	0.67	0.52	2.06	0.49

T_1-Control, T_2-4200 ppm, T_3-2100 ppm, T_4-1050 ppm of NaCl.

(Figures in parantheses indicates arc sign transformed)

Table 4.22. Effect of simulated salt (NaCl) effluent on crop germination

Treatment	Germination (%)			Root Length (cm)			Shoot Length (cm)		
	Ragi	Black gram	Amaranthus	Ragi	Black gram	Amaranthus	Ragi	Black gram	Amaranthus
T_1	71 (57.51)	95.2 (78.88)	62.2 (52.14)	7.00	12.70	9.40	5.70	11.20	4.30
T_2	5.8 (12.33)	25.7 (18.26)	15 (16.55)	0.70	1.60	1.50	1.10	2.10	0.90
T_3	17.5 (24.29)	57.9 (31.82)	31.6 (33.56)	1.60	3.40	4.10	2.00	5.00	2.30
T_4	51.4 (46.42)	74.6 (59.97)	52 (46.15)	4.40	8.60	7.50	3.40	6.60	3.40
Mean	**36.43**	**63.35**	**40.20**	**3.43**	**6.58**	**5.63**	**3.05**	**6.23**	**2.73**
SEd	2.46	4.36	4.80	0.07	0.33	0.32	0.25	0.97	0.23
CD (0.05)	5.23	9.16	10.18	0.36	0.69	0.67	0.52	2.06	0.49

T_1-Control, T_2-4200 ppm, T_3-2100 ppm, T_4-1050 ppm of NaCl.

(Figures in parantheses indicates arc sign transformed)

Table 4.23. Effect of simulated Chromium (VI) effluent on soil pH

Treatment	Black soil				Red soil			
	Period of Incubation (Hours)				Period of Incubation (Hours)			
	0	**24**	**48**	**Mean**	**0**	**24**	**48**	**Mean**
T_1	7.70	7.71	7.70	7.70	8.01	8.02	8.01	8.01
T_2	6.61	6.60	6.63	6.61	6.90	7.92	6.93	6.92
T_3	6.86	6.87	6.88	6.87	7.15	7.15	7.17	7.16
T_4	7.01	7.02	7.02	7.02	7.40	7.41	7.42	7.41
Mean	7.05	7.05	7.06		7.36	7.37	7.38	
	T	D	TxD		T	D	TxD	
SEd	0.31	0.01	0.32		0.28	0.01	0.29	
CD	0.67	0.02	NS		0.60	0.02	NS	

T_1-Control, T_2- 75 ppm, T_3-50 ppm, T_4-25 ppm of Cr(VI)

Table 4.24. Effect of simulated chromium (VI) effluent on soil bacteria (10^6 CFU g^{-1})

Treatment	Black soil				Red soil			
	Period of Incubation (Hours)				Period of Incubation (Hours)			
	0	**24**	**48**	**Mean**	**0**	**24**	**48**	**Mean**
T_1	9.38	10.42	11.48	**10.43**	8.98	9.48	11.41	**9.96**
T_2	7.21	3.15	0.00	**3.45**	6.50	2.50	0.00	**3.00**
T_3	8.12	3.50	0.07	**3.90**	7.50	3.18	0.06	**3.58**
T_4	8.93	3.10	0.28	**4.10**	7.95	3.25	0.30	**3.83**
Mean	**8.41**	**5.04**	**2.96**		**7.73**	**4.60**	**2.94**	

	SEd	CD (0.05)	SEd	CD (0.05)
T	0.06	0.11	0.14	0.28
D	0.05	0.12	0.16	0.33
TxD	0.10	0.21	0.28	0.57

T_1-Control, T_2- 75 ppm, T_3-50 ppm, T_4-25 ppm of Cr(VI)

Table 4.25. Effect of simulated chromium (VI) effluent on soil fungi (10^3 CFU g^{-1})

Treatment	Black soil				Red soil			
	Period of Incubation (Hours)				Period of Incubation (Hours)			
	0	**24**	**48**	**Mean**	**0**	**24**	**48**	**Mean**
T_1	3.85	4.03	4.57	**4.15**	5.17	5.22	6.50	**5.63**
T_2	2.01	1.03	0.07	**1.04**	4.24	1.25	0.07	**1.85**
T_3	2.18	1.53	0.18	**1.30**	4.51	1.98	0.17	**2.22**
T_4	2.51	1.00	0.25	**1.25**	4.62	2.13	0.33	**2.36**
Mean	**2.64**	**1.90**	**1.27**		**4.64**	**2.65**	**1.77**	

	SEd	CD (0.05)				SEd	CD (0.05)	
T	0.19	0.40				0.25	0.52	
D	0.22	0.46				0.29	0.60	
TxD	0.38	0.79				0.80	1.03	

T_1-Control, T_2- 75 ppm, T_3-50 ppm, T_4-25 ppm of Cr(VI)

Table 4.26. Effect of simulated chromium (Cr(VI)) effluent on actinomycetes (10^{-2} CFU g^{-1})

Treatment	Black soil				Red soil			
	Period of Incubation (Hours)				Period of Incubation (Hours)			
	0	**24**	**48**	**Mean**	**0**	**24**	**48**	**Mean**
T_1	2.72	2.97	0.27	**1.99**	3.96	4.00	4.10	**4.02**
T_2	2.52	1.01	0.17	**1.23**	2.22	0.88	0.17	**1.09**
T_3	2.57	1.52	0.30	**1.46**	2.73	1.47	0.30	**1.50**
T_4	2.71	1.98	0.28	**1.66**	3.00	1.93	0.33	**1.75**
Mean	**2.63**	**1.87**	**0.26**		**2.98**	**2.07**	**1.23**	

	SEd	CD (0.05)	SEd	CD (0.05)
T	0.23	0.48	0.23	0.47
D	0.27	0.55	0.27	0.55
TxD	0.46	0.96	0.46	0.95

T_1-Control, T_2- 75 ppm, T_3-50 ppm, T_4-25 ppm of Cr(VI)

Table 4.27. Water extractable chromium (VI) in soil by DPC method (mg kg^{-1})

Treatment	Black soil						Red soil					
	Period of Incubation (Hours)						Period of Incubation (Hours)					
	0	**12**	**24**	**36**	**48**	**Mean**	**0**	**12**	**24**	**36**	**48**	**Mean**
T_1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
T_2	2.795	2.072	1.457	1.37	1.319	**1.55**	2.954	2.54	2.058	0.897	0.891	**1.60**
T_3	2.388	1.795	0.652	0.46	0.437	**0.84**	1.954	1.465	1.167	0.776	0.561	**0.99**
T_4	1.435	1.254	0.424	0.29	0.094	**0.52**	1.352	1.432	1.043	0.683	0.434	**0.90**
Mean	**1.6545**	**1.28**	**0.63**	**0.53**	**0.46**		**1.57**	**1.36**	**1.07**	**0.59**	**0.47**	

	T	D	TxD		T	D	TxD
SEd	0.076	0.085	0.169	SEd	0.146	0.163	0.327
CD (0.05)	0.154	0.172	0.344	CD (0.05)	0.295	0.330	0.661

T_1-Control, T_2- 75 ppm, T_3-50 ppm, T_4-25 ppm of Cr(VI)
BDL –Below Detectable Level

Table 4.28.Phosphate buffer extractable of chromium (VI) in soil by DPC method (mg kg^{-1})

Treatment	Black soil						Red soil					
	Period of Incubation (Hours)						Period of Incubation (Hours)					
	0	**12**	**24**	**36**	**48**	**Mean**	**0**	**12**	**24**	**36**	**48**	**Mean**
T_1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
T_2	BDL	0.462	8.916	37.00	2.102	**12.12**	BDL	0.873	35.65	30.77	4.106	**17.85**
T_3	BDL	0.13	1.947	12.75	1.686	**4.13**	BDL	0.166	18.247	10.67	0.776	**7.46**
T_4	BDL	0	1.312	2.62	1.425	**1.34**	BDL	BDL	10.14	4.79	0.033	**3.74**
Mean	BDL	**0.15**	**3.04**	**18.4**	**1.30**		BDL	**0.26**	**16.01**	**18.4**	**1.23**	
		T	D	TxD				T	D	TxD		
	SEd	1.888	2.110	4.223			SEd	1.372	1.533	3.067		
	CD (0.05)	3.817	4.267	8.535			CD (0.05)	2.772	3.099	6.198		

T_1-Control, T_2- 75 ppm, T_3-50 ppm, T_4-25 ppm of Cr(VI)
BDL –Below Detectable Level

Table 4.29. Effect of simulated Chromium (VI) effluent on soil pH

Treatment	Ragi		Black gram		Amaranthus	
	0 day	**45th day**	**0 day**	**45th day**	**0 day**	**45th day**
T_1	8.07	8.01	8.07	8.01	8.07	8.01
T_2	7.82	7.98	7.83	7.99	7.85	7.98
T_3	7.92	7.97	7.94	7.97	7.95	7.98
T_4	7.94	8.00	7.94	7.99	7.94	8.00
Mean	**7.94**	**7.99**	**7.95**	**7.99**	**7.95**	**7.99**
	SEd	CD (0.05)	SEd	CD (0.05)	SEd	CD (0.05)
T	0.03	0.07	0.03	0.07	0.03	0.06
D	0.02	0.05	0.02	0.05	0.02	0.04
TxD	0.05	0.10	0.05	0.10	0.04	0.08

T_1-Control, T_2- 75 ppm, T_3-50 ppm, T_4-25 ppm of Cr(VI).

Table 4.30. Effect of simulated Chromium (VI) effluent on soil EC (dSm^{-1})

Treatment	Ragi		Black gram		Amaranthus	
	0 day	**45th day**	**0 day**	**45th day**	**0 day**	**45th day**
T_1	0.07	0.06	0.07	0.06	0.07	0.06
T_2	0.18	0.11	0.19	0.11	0.19	0.11
T_3	0.17	0.09	0.18	0.10	0.18	0.09
T_4	0.11	0.08	0.11	0.09	0.12	0.09
Mean	**0.13**	**0.08**	**0.14**	**0.09**	**0.14**	**0.09**
	SEd	CD (0.05)	SEd	CD (0.05)	SEd	CD (0.05)
T	0.01	0.03	0.01	0.03	0.01	0.03
D	0.01	0.02	0.01	0.02	0.01	0.02
TxD	0.02	0.04	0.02	0.04	0.02	0.04

T_1-Control, T_2- 75 ppm, T_3-50 ppm, T_4-25 ppm of Cr(VI)

Table 4.31. Accumulation of chromium in plant parts (mg kg^{-1})

Treatment	Ragi		Black gram		Amaranthus	
	Root	Shoot	Root	Shoot	Root	Shoot
T_1	0.01	BDL	0.01	BDL	0.01	0.01
T_2	0.15	0.04	0.19	0.07	0.21	0.10
T_3	0.40	0.19	0.28	0.09	0.42	0.13
T_4	0.21	0.12	0.13	0.05	0.23	0.08
Mean	0.19	0.09	0.15	0.07	0.22	0.08

	Root		Shoot	
	SEd	CD (0.05)	SEd	CD (0.05)
C	0.016	0.032	0.015	0.03
T	0.018	0.037	0.017	0.036
CxT	0.031	0.065	0.03	0.062

T_1-Control, T_2- 75 ppm, T_3-50 ppm, T_4-25 ppm of Cr(VI)

BDL –Below Detectable Level

Table 4.32. Residual chromium in soil (mg kg^{-1})

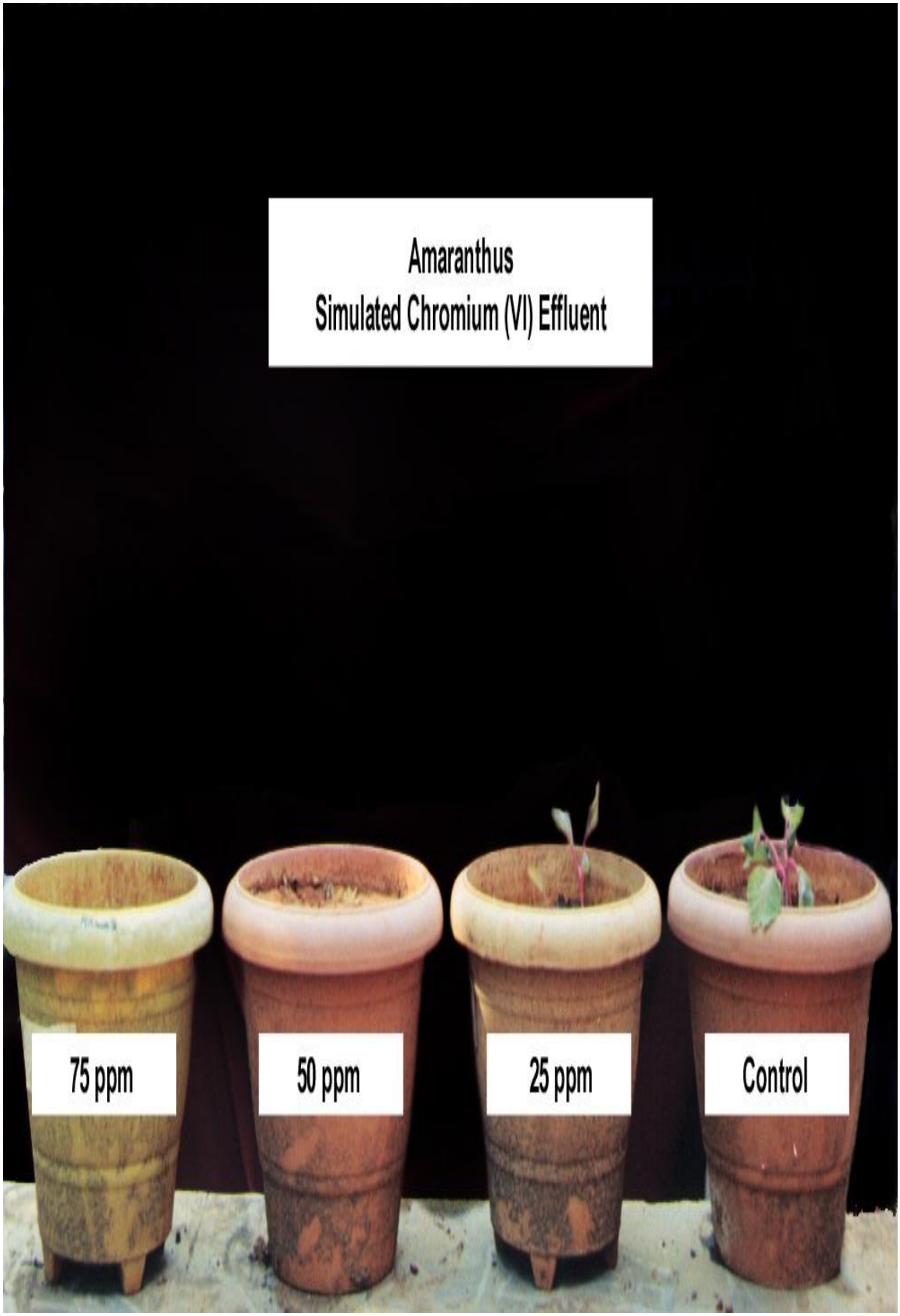
Treatment	Ragi	Black gram	Amaranthus
T_1	0.01	0.01	0.01
T_2	36.84	36.48	36.87
T_3	17.27	16.72	16.25
T_4	9.71	9.93	8.88
Mean	15.96	15.79	15.50
SEd	2.35	2.86	2.26
CD(0.05)	5.74	7.00	5.55

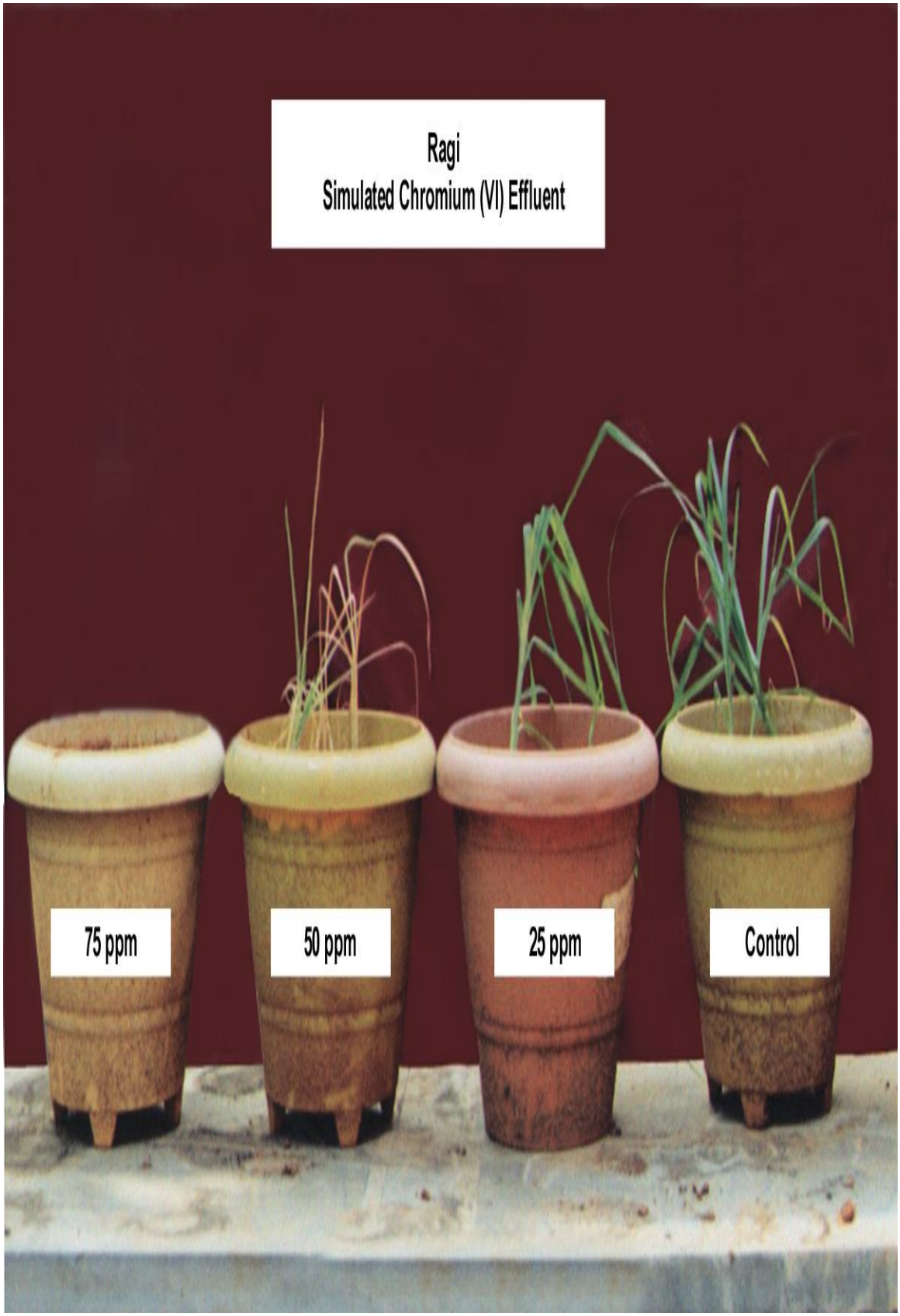
T_1-Control, T_2- 75 ppm, T_3-50 ppm, T_4-25 ppm of Cr(VI)


RAGI
CONTROL
TANNERY EFFLUENT
SPIKED CHROMIUM EFFLUENT
SPIKED SALT EFFLUENT
C25
C50
C75
C100
C25
C50
C75
C1050
C2100
C4200


AMARANTHUS
CONTROL
TANNERY EFFLUENT
SPIKED CHROMIUM EFFLUENT
SPIKED SALT EFFLUENT
C25
C50
C75
C100
C25
C50
C75
C1050
C2100
C4200


CONTROL
TANNERY EFFLUENT
SPIKED CHROMIUM EFFLUENT
SPIKED SALT EFFLUENT
C25
C50
C75
C100
C25
C50
C75
C1050
C2100
C4200
BLACKGRAM


Amaranthus
Simulated Chromium (VI) Effluent
75 ppm
50 ppm
25 ppm
Control


Ragi
Simulated Chromium (VI) Effluent
75 ppm
50 ppm
25 ppm
Control


Blackgram
Simulated Chromium (VI) Effluent
75 ppm
50 ppm
25 ppm
Control


Incubation Experiment - Tannery Effluent
L1
L2
S1
L1
L2
S1
Black soil
Red soil