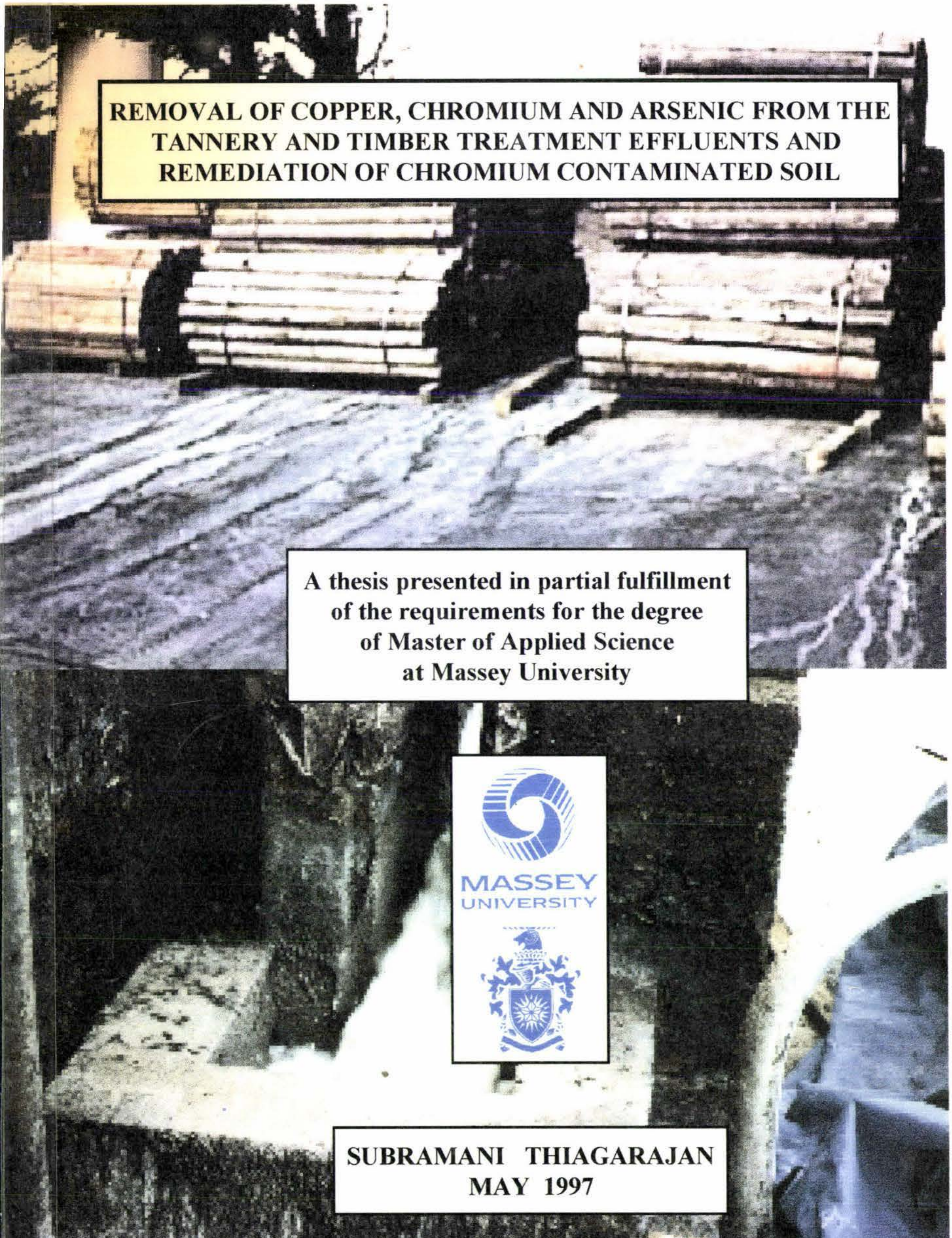

REMOVAL OF COPPER, CHROMIUM AND ARSENIC FROM THE TANNERY AND TIMBER TREATMENT EFFLUENTS AND REMEDIATION OF CHROMIUM CONTAMINATED SOIL

A thesis presented in partial fulfillment
of the requirements for the degree
of Master of Applied Science
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Dedicated to

My Beloved Parents

ABSTRACT

Tannery and timber treatment effluents are considered to be the major source of Copper (Cu), Chromium (Cr) and Arsenic (As) heavy metal contamination into the environment. Chromium is used in tanneries for the treatment of hides and skins whereas, copper, chromium, and arsenic (CCA) solution is used as the timber treatment chemical. Chromium is used as Cr (III) in tannery industry and as Cr (VI) in timber treatment industry. Arsenic and Cr (VI) which are present in the timber treatment effluent are highly toxic and carcinogenic.

An initial survey has indicated that some tannery industries in New Zealand have not developed pre-treatment practices to reduce the heavy metal concentration before discharging the effluent into soil or waterways. The heavy metal pollution due to timber treatment industries may occur from the drips, leaks and spills due to poor handling of CCA solution while treating timber.

In this project, the potential value of industrial waste materials, such as *Pinus radiata* bark, fluidised bed boiler ash (FBA), flue gas desulphurisation gypsum (FGDG) and natural resources, such as zeolite, peat soil, and two soils (Tokomaru and Egmont soils) to reduce heavy metal concentration in tannery and timber treatment effluents was examined. The value of these materials in the remediation of soil contaminated with Cr was examined using a growth experiment.

The effect of pre-treatment of *Pinus* bark with acid, alkali of formaldehyde/acid on the retention of Cr was examined. Pre-treatment of *Pinus* bark increased the heavy metal retention only at low heavy metal concentration and did not significantly improve the heavy metal retention at high concentration. The extent of adsorption increased with an increase in surface area of *Pinus* bark material. Speciation of Cr indicated that Cr (VI) is reduced to Cr (III) and adsorbed onto the *Pinus* bark.

FBA was found to be most efficient in reducing the Cr (III) concentration from tannery effluent and As and Cu concentrations in the timber treatment effluent. In the

case of Cr (VI), the highest retention was shown by the *Pinus* bark and the peat soil. The increased retention of Cr (III), Cu and As by FBA was due to the precipitation of Cr (III) as chromium hydroxide, Cu as cupric hydroxide and As as calcium arsenate. A combination of FBA + *Pinus* bark or FBA + peat soil was efficient in reducing all the three heavy metal (Cu, Cr (VI) and As) concentration from the timber treatment effluent. The effluents contaminated with Cu, Cr and As can be passed through a column containing FBA and *Pinus* bark or peat soil.

A growth experiment using sun flower (*Helianthus annus*) was set-up to examine the effectiveness of FBA, lime and *Pinus* bark to immobilise Cr in contaminated soil. FBA and lime amended soils were effective in establishing a normal plant growth of sun flower in Cr (III) contaminated soil even at high Cr (III) levels (3200 mg/kg soil). Incorporation of lime or FBA in Cr (III) contaminated soils causes precipitation of Cr (III) and thereby reduces the bioavailabilty of Cr for plants uptake. Only *Pinus* bark amended soil was found to be effective in remediating Cr (VI) contaminated soil even at 3200 mg/kg soil. *Pinus* bark material effectively retained the Cr (VI) present in the soil solution and thus reducing the toxicity and bioavailability of Cr (VI) to plants.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

There has been increasing concern on the pollution of soils and waterways resulting from the disposal of industrial effluents. With the advancement of the industrial revolution in many countries vast amounts of effluent are produced. For example in New Zealand, approximately 6,400 and 1,600 tonnes of tannery and timber treatment effluents respectively are generated annually, which contribute approximately 10 % of the total hazardous waste (Jonathan *et. al.*, 1989).

Tannery and timber treatment effluents are enriched with toxic heavy metals, such as Copper (Cu), Chromium (Cr) and Arsenic (As). Chromium sulphate is commonly used by the tanning for the treatment of skins and hides and CCA (Copper-Chromium-Arsenic) solution is used for the treatment of timber. Chromium occurs as Cr (III) and Cr (VI) ions in tannery and timber treatment effluents respectively. Hexavalent Cr is more mobile in soils and is more toxic than the trivalent Cr ion. As is present as As (V) and Cu occurs as Cu (II) in the timber treatment effluent.

Heavy metal contamination of soils and waterways occurs due to the disposal of untreated industrial effluents, drips, leaks and spills of heavy metal contaminated working solutions. Such activities are likely to elevate the heavy metal concentrations in terrestrial and aquatic environments. Dispersal of heavy metals and their largely irreversible retention by soils have long-term consequences.

In this thesis, the problems associated with the pollution by heavy metals from tannery and timber treatment effluents and their subsequent remediation is reviewed. Potential use of some industrial waste materials and natural resources to reduce heavy metal concentration in tannery and timber treatment effluents, prior to discharge to soils and waterways was examined. The effect of Cr pollution on plant growth and the efficiency of selective industrial waste materials to remediate the Cr polluted soil were also examined.

1.2 OBJECTIVES

The main aim of my thesis is to reduce the heavy metals present in the tannery and timber treatment effluents and to remediate heavy metal contaminated soils due to these effluents. The potential use of industrial waste materials, such as *Pinus radiata* bark, Fluidised Bed boiler Ash (FBA), Flue Gas Desulphrisation Gypsum (FGDG) and a few natural resources such as zeolite, peat soil, the Tokomaru and Egmont soils to reduce the heavy metal concentration was examined.

Two approaches were used to achieve the overall objective :

A. *Reduction of Cu, Cr and As concentration in the tannery and timber treatment effluents before they are discharged into the environment.*

B. *Remediation of soils previously contaminated with heavy metals due to tannery and timber treatment effluents.*

A number of specific objective were examined with in each of the above two approaches. These include :

A. *Reduction of Cu, Cr and As in the tannery and timber treatment effluents*

(i) To reduce the Cu, Cr and As concentration of the tannery and timber treatment effluents using various industrial wastes and some natural resources.

(ii) To study the reactions involved in the heavy metal reduction from the effluents by the effective materials.

B. *Remediation of soils previously contaminated with heavy metals*

Due to the time limitation of my Masters degree program, Cr contaminated soil was examined whereas soil contamination due to As and Cu was not considered. Soil contamination due to Cr (III) and Cr (VI) from the tannery and timber treatment effluents, respectively was examined.

(i) To immobilise Cr in soils, which have been already contaminated with tannery and timber treatment effluents.

(ii) To examine the effect of various amendments in reducing the phytotoxicity and bioavailability of Cr in the contaminated soils.

1.3 STRUCTURE OF THE STUDY

This thesis comprises 6 chapters. Following the introduction (Chapter 1), a general review of literature (Chapter 2) examines the heavy metal pollution problems due to the tanning and timber treatment industries. Chapter 3 reports the case studies of heavy metal pollution problems by a few tanneries and timber treatment plants in New Zealand. The effectiveness of some industrial wastes and natural resources in reducing the heavy metal concentration of the tannery and timber treatment effluents is examined using batch and column leaching experiments in Chapter 4. The most effective industrial wastes and natural resources selected from the results obtained in the batch and column leaching experiments (Chapter 4) were used to immobilise Cr in the soil contaminated with the effluents. The use of the effective industrial wastes and natural resources to immobilise and to reduce the phytotoxicity of Cr contaminated soil was examined by a growth experiment and its results are discussed in Chapter 5. A general summary and conclusion of all the results of the experiments are presented in Chapter 6 with a few recommendations to prevent and remediate heavy metal pollution due to the tanning and timber treatment industries.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Heavy metals are a major pollutant of various industrial effluents, phosphatic fertilisers, municipal sewage sludges as well as emission from power generation plants and smelters. Heavy metals can be defined as elements having an atomic density greater than 6 g cm^{-3} (Alloway, 1995). It includes non-ferrous metals and metalloids, and are grouped into essential and non-essential toxic elements, at high concentrations both the groups are toxic.

Soils are polluted with a wide range of heavy metals such as Copper (Cu), Chromium (Cr), Lead (Pb), Cadmium (Cd) etc, and metalloids such as Arsenic (As). Nriagu (1994) states that "We may be experiencing a silent epidemic of environmental metal poisoning from the ever increasing amounts of metals and metal containing materials inevitably cause environmental pollution".

In many countries, the tanning and timber treatment industries contribute a major source of effluents containing heavy metals. They are enriched with toxic heavy metals, such as Cu, Cr and As. Hexavalent Cr and As present in timber treatment effluents are carcinogenic.

This chapter deals with the reasons for the use of heavy metals in the tanning and timber treatment industries, characteristic of the heavy metals present in the tannery and timber treatment effluents, various effluent treatment processes involved in reducing the heavy metals from these effluents, reactions of Cu, Cr and As in soils and the remediation of soil contaminated with these heavy metals.

2.2. TANNERY AND TIMBER TREATMENT PROCESSES

2.2.1 Tannery treatment processes

There are different types of tanning processes namely Chrome tanning, Vegetable tanning, Aluminium tanning, and Zirconium tanning. Chrome tanning and Vegetable tanning are the two major tanning processes practised in many countries. We shall briefly look into various processes involved in tanning practices.

2.2.1.1 Vegetable tanning

Vegetable tanning was the original tanning method and this remained the only significant method until the development of commercial chrome tanning at the beginning of the 20th century. The leathers made by full vegetable tanning are used for soles, belting, saddlery, upholstery, lining, and luggage. Vegetable tannins, namely catechol tannins and pyrogallol tannins are the main chemicals involved. The source of vegetable tannins is extracts obtained from plants such as Quebracho (*Quebrachia lorentzii*), Chestnut (*Castanea dentata*), Wattle (*Acacia mollissima*), Mangrove bark etc.

The mechanism for vegetable tanning is through hydrogen bonding to the CO-NH linkage of the protein, through the phenolic hydroxyl group of the vegetable tannin. The availability of hydrogen bonds on the protein and on the vegetable tanning material is of prime importance, pH of the vegetable tannins are from 5-7 (Thomas, 1993). Nowadays, a wide range of synthetic tanning materials have been developed gradually replacing vegetable tanning. Vegetable tanning is widely replaced by chrome tanning due to the material availability and the cost of labour in harvesting the vegetable tanning materials.

2.2.1.2 Chrome tanning

The most common method of tanning is chrome tanning. Chrome tanning includes all types of hides and skins. The discovery of chrome tanning is attributed to Knapp in 1858, but the first commercial production of chrome leather is attributed to Augustus Schultz of New York in 1884.

The chemical reaction involved in the chrome tanning process is the formation of a stable compound between the hide protein and Cr (III) ions. Salts containing the Cr (III) ions are soluble in the pH range below 4-5. Chromium has variable affinity for hydroxyl ions over the entire pH range, and at pH 2-3 the fixation of Cr is moderate. The affinity of the hide for the Cr greatly increases in the pH range of 3-4. In the tanning process, the hide is brought to an acid condition at a pH of about 2. The chrome tanning salts are added and the tanning begins. Since the solution is strongly acidic the Cr salts can penetrate the hide without excessive surface fixation. After a period of time, when the Cr has penetrated the hide sufficiently, the pH is raised to promote the reaction of the Cr with the hide. The reaction is very strong and the resulting leather is resistant to decay, heat and mechanical damage. The tanning is done in a salt solution such as sodium chloride (3-5 %)to prevent osmotic swelling of the untanned hide. The solution will contain sodium sulfate at about 2 % from the sulphuric acid and chromium sulfate used. In chrome tanning, the quantity of Cr needed for a complete tannage is about 2 % or more on the weight of the hide.

The effluent generated after chrome tanning contains pollutants such as Cr, organic dyestuffs, high BOD (Biological Oxygen Demand) or COD (Chemical Oxygen Demand), suspended matter, sodium and chloride. Chromium present in the tannery effluent is of major environmental concern. Hence treatment of these effluents is essential before they are discharged into the environment. Few tanneries in New Zealand discharge untreated tannery effluent with high Cr concentration (3200 mg/L) into waterways (Thiagarajan and

Bolan, 1996). From an environmental standpoint, apart from Cr, sodium chloride and sodium sulfide may be subjects of concern depending upon the ultimate method of disposal of the effluent.

2.2.1.3 Mixed Chromium-Vegetable tanning

Mixed Chromium-Vegetable tanning is particularly interesting because it permits mechanical properties of leather to be improved by enhancing its water-repellent action and by avoiding the tendency of leather treated with Cr to contract during drying. This process is possible because leather tanned with Cr salts can fix vegetable and synthetic tannings. This capacity derives from having free peptide groups, partially immobilised amino-groups, as well as Cr atoms able to bind electron-donor groups (such as tannin anions) by co-ordinate bonds. This method is not used commonly due to the high cost of labour involved in harvesting vegetable tanning materials.

2.2.1.4 Aluminium tanning

Aluminium salts have a great affinity to leather at lower pH and have the advantage, over chrome salts, of being colourless and are used in the production of furs and some white leathers. Aluminium reacts with hide protein to produce a tanned leather. The bond between the aluminium and the hide protein is not as strong as Cr-hide protein bond, and the stabilisation of the hide protein or the tannage by aluminium is not sufficient. Because of these limitations, alum tanning is little accepted as a total replacement for chrome tanning.

2.2.1.5 Zirconium tanning

Zirconium can be used as a tanning agent for white leather. This is usually accomplished by the use of sodium citrate or citric acid as a masking agent. The high acidity and high cost of zirconium salt has limited its widespread commercial acceptance as a direct competitor to chrome tanning.

Of the different tanning processes, chrome tanning seems to be the viable, cost effective, and widely preferred method of tanning hides and skins. But the main concern is the presence of Cr in the tannery effluent. The pollution problem due to chrome tanning is widely studied and guidelines for the disposal of Cr contaminated tannery effluent are set for most of the developed countries. In this thesis, case studies of two tanneries in New Zealand were conducted and the problems associated with the pollution of Cr from tannery effluent and their subsequent remediation are reviewed (Chapter 3).

2.2.2 Timber treatment process

Various chemicals have been used to impregnate wood to prevent it from rotting. When impregnation of poles for telephone and electric wires was started on a large scale in the 1920's, copper sulphate was used almost exclusively which continued until the Second World War. During the war, Cu became unavailable and so formulation that included fluorine, zinc and arsenic came into common use. Impregnation and storage of the poles gave rise to a continuous pollution the soil and so closed vessels and tanks were used. After 1955, most industrial plants used Cr, As and F salts or Cu, Cr and As salts. These formulations gave better fixation in the timber (Ulla and Fobian, 1991). Pentochlorophenol (PCP) and dioxins had been widely used in the New Zealand timber industry for the 30 to 40 years as an anti-fungal agent. Its use ceased in New Zealand from 1988 as workers health concerns became known to the industry. Soil contaminated by PCP and dioxins were of major concern at timber treatment site.

In New Zealand, approximately 1.4 million cubic meters of timber is preservative treated each year (New Zealand Statistics, 1994). Currently in New Zealand, timber treatment is essentially of three types: Copper-Chromium-Arsenic (CCA); boron; and light organic solvent. CCA and light organic solvent treatments utilise pressure to impregnate the preservative chemicals, whereas boron treatment involves surface application and the diffusion of boron based insecticides. Approximately 150 plants throughout the country are using CCA treatment (Department of Health, 1986).

2.2.2.1 CCA treatment

Currently, CCA is the most commonly used timber treatment chemical. The Cu acts as a fungicide, Cr as a fixative and As as an insecticide. Chromium helps to hold the other components tightly to the wood to prevent leaching, while As also guards against attack by termites and copper-resistant fungi. CCA treatment of timber involves the impregnation under pressure of a 1-4 % CCA solution. The chemicals used as Cu, Cr and As sources are as follows,

Copper	- Copper sulphate
	- Copper oxide
Chromium	- Sodium dichromate
	- Chromic acid
	- Chromic oxide
Arsenic	- Arsenic pentoxide
	- Sodium pyroarsenate

Bethell (Full cell) vacuum pressure process is the most commonly used timber treatment process. The objective is to remove as much air as possible from the wood cells, and replace this with the maximum amount of preservative solution by pumping to total saturation. Other processes include Lowry (empty cell) process, alternative and oscillating pressure methods. In operation, the treatment chamber is filled with timber stacked on steel trolleys. It is sealed and a vacuum is applied to remove air from the timber, then the tank is flooded and pressurised with CCA preservative solution. The pressure is applied and the solution is pumped into the timber until total saturation is achieved. The treated timber is graded for use according to the amount of treatment solution fixed in the timber (normally 3.6-16 kg/cubic metre). After the release of the pressure the treatment solution is returned to the working tank and a vacuum is applied to the cylinder for a short period to reduce dripping. After treatment the timber must be stored in a paved area for at least 24 hours. This paved area should be sloped to drain into cylinder sump so that all the surplus solution is retained. The most significant source of soil contamination occurs because of waste disposal practices and drips, leaks and spills of stock and working solutions. Rain falling onto the freshly treated timber is also responsible for CCA contamination of ground areas. Other possible routes of soil contamination are due to the risk of wind blown dust.

2.3 COMPARISON OF CHROMIUM FIXATION ONTO HIDE AND TIMBER

Trivalent Cr is used in the tannery and hexavalent Cr is used in the timber treatment processes to increase the endurance of hide and timber, respectively. The reason for the use of different Cr species can be well understood by looking into the mechanism of Cr fixation onto hide and timber.

2.3.1 Chromium fixation onto hide

In the tanning process, the hides or skins are in a pickled state at a pH of 3 or lower, when the chrome tanning materials are introduced. At these low pH values, the affinity of the chrome tanning salt for the protein is moderate, allowing penetration of the chrome tanning agent into the hide. After proper penetration of Cr salt has been achieved, the pH is raised. This causes a reaction between the Cr salts and the hide protein. When the reaction is completed the leather is said to be full chrome tanned. Tanning action of Cr salts depends on chemical variations which takes place during alkalisation by sodium hydroxide with substitution of one or more water molecules by hydroxyl ions and with formation of basic Cr salts. Chromium sulphate is commonly used for chrome tanning.

The condition of the chromium sulphate salts in the hide treatment solution can be represented by three stages of initial reaction:

(a) *Solution* : The basic chromium sulphate dissolves, and are the sulphate ionises, a cationic complex is formed.

(b) *Masking with sodium formate* : Masking agents such as sodium formate is used to decrease the sensitivity of the tannage to pH variation. The formate ion in the solution forms a basic chromium formate complex with the displacement of some of the sulphate from the Cr complex.

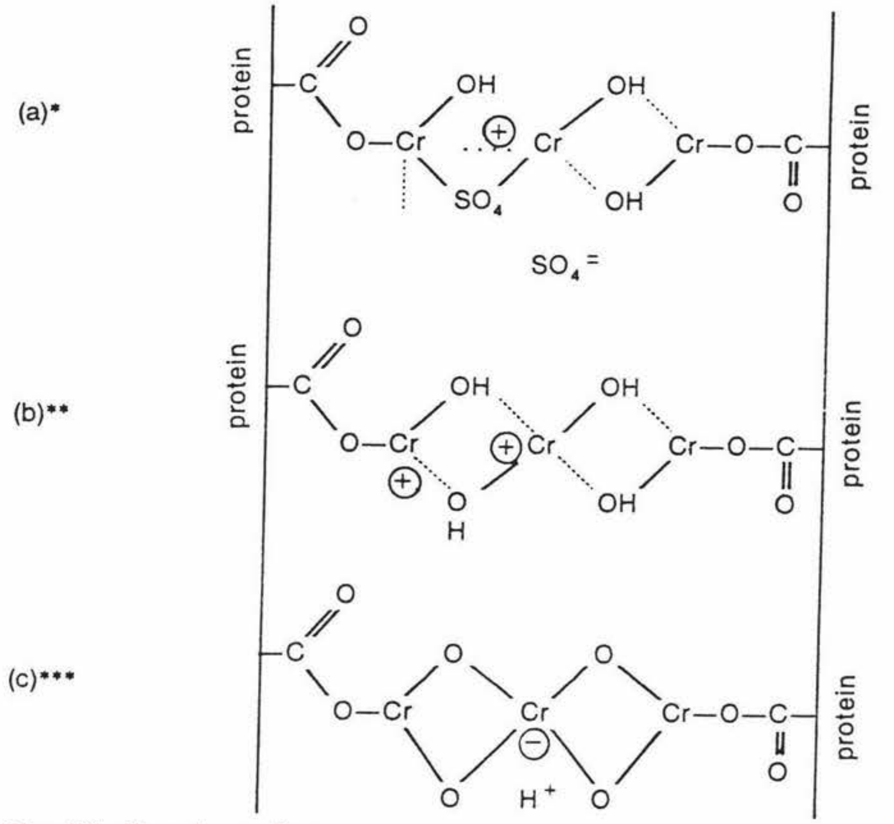
(c) *Fixation* : The cationic Cr complexes reacts with the anionic carboxyl groups of the amino acids of the hide protein in the initial tanning reaction.

The hide protein contains free carboxyl groups and other reactive sites which could, theoretically at least, form co-ordinate complexes with Cr salts. The importance of Cr salts as mineral tanning agents derives from the fact that Cr^{3+} in aqueous solution may bind to a water molecule co-ordinately. Hexawater chromium (III), $[Cr\ (H_2O)_6]^{3+}$, takes the configuration of a regular octahedral where Cr has in the middle and water molecules are at its vertices (Sandro, 1989). Trivalent Cr has a marked tendency to form stable octahedral co-ordination compounds with suitable ligands. In the absence of other ligands Cr (III) exists as $[Cr\ (H_2O)_6]^{3+}$ ions in aqueous solution. Thomas (1993) has given a simple diagram (Figure 2.1) to explain the ions exchanged during the tanning process, which involves the following process:

(a) Crosslinking : The chrome complexes react with the protein carboxyl groups.

(b) Basification-Olation : As the pH of the tannage is increased, the sulphate associated with the Cr becomes displaced by hydroxyls. The hydroxyl groups become shared by Cr atoms through olation.

(c) Oxolation : Upon drying, the tannage becomes more stable as the complex gives up hydrogen ions and oxolation results.



Simplified tanning actions:
* (a) crosslinking
** (b) basification—olation
*** (c) oxolation

Figure 2.1 Chemical bonding between Cr salt and hide protein (Thomas, 1993).

2.3.2 Chromium fixation onto timber

Hexavelent Cr is used instead of Cr (III) because the latter is adsorbed physically rather weakly to the cellulose, where as the former is fixed chemically to the cellulose in bark (Pizzi, 1981). The mechanism of Cr (VI) fixation onto cellulose is a two-step reaction. At first, Cr (VI) is chemically adsorbed by cellulose of the bark to form Cr (VI)/cellulose complexes, later the Cr (VI) adsorbed to the cellulose is reduced to Cr (III). These two steps make the Cr (VI) fix chemically to the bark material (Pizzi, 1981). Thus the bark is more efficient in retention of Cr (VI) than Cr (III).

The difference in Cr fixation onto hide and timber is that the Cr is fixed in cationic form to the hide protein by stable octahedral co-ordination compounds with suitable ligands, where as, in timber Cr in its anionic form complexes with the cellulose (Figure 2.2). Hence if Cr (III) is used to treat timber the Cr/cellulose complex is unlikely to form resulting in a weak physical adsorption of Cr (III) to the cellulose.

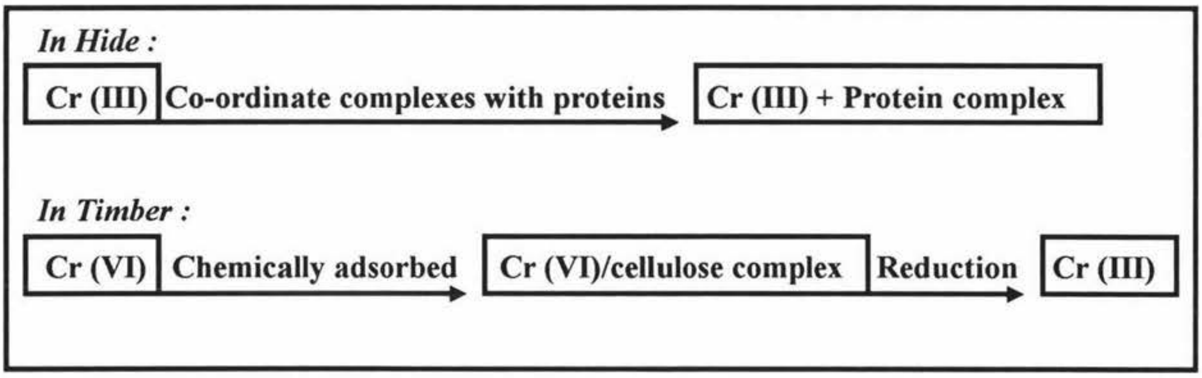


Figure 2.2 Simplified processes of Cr fixation onto hide and timber.

2.4 THRESHOLD LEVELS OF HEAVY METAL ON SOILS

The threshold limit sets the upper limit for the legal input of contaminant such as heavy metals into the soil. The threshold limit of Cu, Cr and As in different developed countries

Table 2.1 Threshold levels of As, Cr(III), Cr (VI) and Cu on soils in some developed countries.

Heavy metals	UK [a]	USEPA [b, c]	New Zealand [d]	Australia [e]	Canada [f]	Germany [g]
	(mg/kg)					
Arsenic	10	5	10	20	25	40
Chromium (III)	600	1500	600	50	250	200
Chromium (VI)	25		10	(Total)	8	
Copper	130	140	130	60	100	100

[a] UK Department of Environment (1987)
[b] US EPA (1993)
[c] Alloway (1995)
[d] Ministry of Environment/Ministry of Health (1995)
[e] ANZECC/NHMRC (1992)
[f] CCME (1995)
[g] Marshall, S (1994)

are listed in Table 2.1. The threshold level for Cr (VI) is very low compared with the Cr (III) due to the high mobility, carcinogenic and phytotoxic characteristics at very low concentration in soil of the former. Many report showing heavy metal levels exceeding the threshold levels were reported. For example recently, As soil levels exceeding the threshold levels were reported in a timber treatment plant (Stilwell and Gorny, 1997).

In New Zealand, the maximum concentration of the heavy metals that can be present in the industrial effluents, which can be discharged into soil and waterways varies among different Regional Councils. According to the Auckland Regional Council Trade and Waste Bylaws (1991), the maximum permissible concentration of heavy metal that can be present in the industrial effluents, which can be discharged are 30 mg Cr (III)/L, 5 mg Cr (VI)/L, 10 mg Cu/L, and 5 mg As/L.

2.4.1 Contamination due to tannery and timber treatment sites in New Zealand

With reference to the heavy metal contamination in New Zealand, some tanneries discharge effluents with very high concentration of Cr (3200 mg/L) into the waterways (Thiagarajan and Bolan, 1996). Contamination of soil from timber treatment plants with Cu, Cr and As exceeding the threshold limits were reported in New Zealand. McLaren (1992), Armishaw *et. al.* (1993) and CMPS & F (1995) have reported Cu, Cr and As levels found at a number of timber treatment sites. Leaching of Cu, Cr and As through some free-draining soils of New Zealand were studied recently (Carey, *et. al.*, 1996). The maximum contaminant levels found in these studies are summarised in Table 2.2. Detailed case studies on the disposal of effluent from selected tannery and timber treatment plants in New Zealand was carried out (Chapter 3).

Table 2.2 Concentration of Cu, Cr & As at CCA contaminated sites in New Zealand (Roberts *et. al.*, 1996).

Reference	Range of maximum valves (mg/kg)		
	Cu	Cr	As
McLaren, Bay of Plenty (1992)	108-6300	140-11000	80-10950
Armishaw *et. al.*, North Island (1993)	326-8020	428-4100	376-10440
CMPS & F, Canterbury (1995)	2100	2800	6100

2.5 REMOVAL OF THE HEAVY METALS FROM INDUSTRIAL EFFLUENTS

Various processes have been developed to reduce the Cr (III), Cr (VI), Cu and As concentration in the industrial effluents. The main processes involved in reducing the heavy metal concentration in industrial effluent are discussed briefly.

2.5.1 Chromium (III)

Chrome tanning wastes from the tanning processes will contribute approximately 5 kg of Cr per 1000 kg of hide (Thomas, 1993). Trivalent Cr can be removed from the industrial effluents by various methods such as precipitation, ion exchange, electrocoagulation, microfloatation, electrolysis, alum coagulation, carbon adsorption etc. But the most commonly used commercial method is by precipitation.

2.5.1.1 Precipitation

Removal of Cr (III) from industrial effluent is achieved using lime or magnesium oxide to precipitate as chromic hydroxide. Precipitation is reported to be most effective at pH 8.5-9.5, due to the low solubility of chromic hydroxide in that range (Patterson, 1985). This method will decrease the amount of Cr discharged to very low levels hence precipitation systems are very widely accepted by major tanneries.

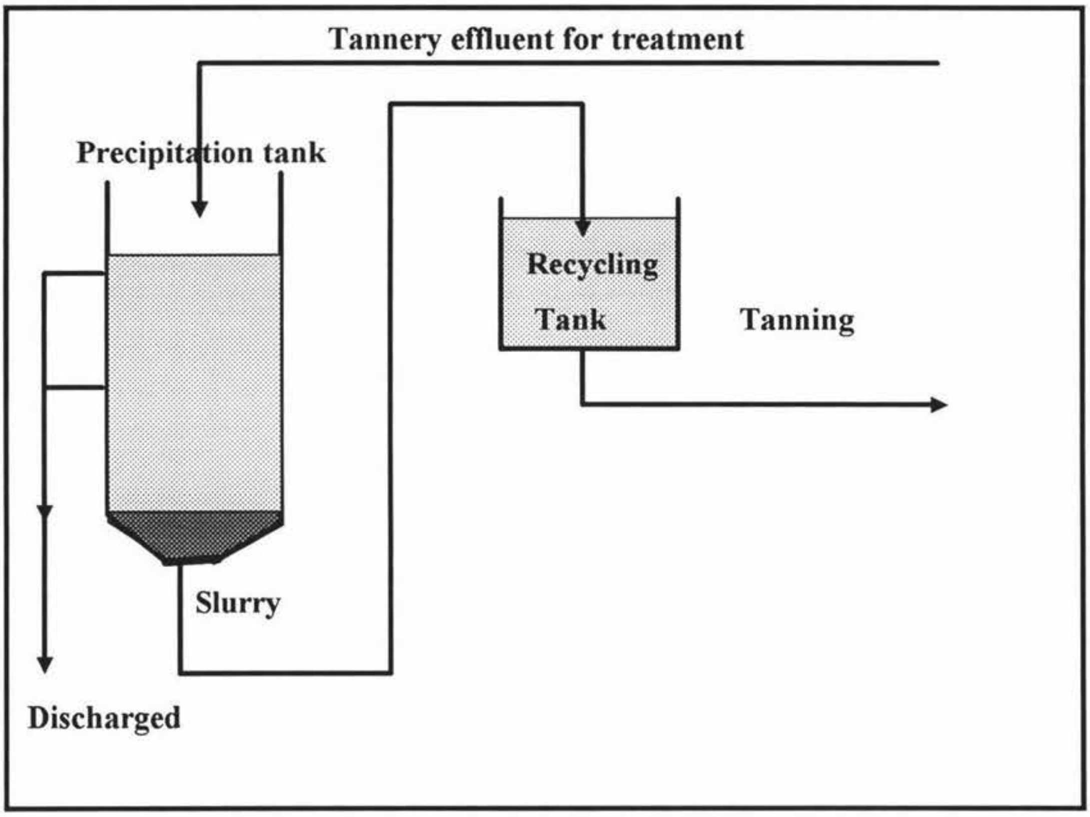


Figure 2.3 Chrome recycling drum system.

Chromium can be recycled after precipitation. Figure 2.3 illustrates the most commonly used recycling method. The spent tanning solution is discharged into the precipitation tank. The precipitation tank is equipped with a stirring mechanism for mild, non-turbulent mixing. By the addition of lime or magnesium oxide the solution in the precipitation tank is brought to pH of about 5-7 at which pH the Cr will precipitate as chromium hydroxide.

The separation of precipitated Cr from the solution is usually done by decanting the supernatant liquid using a series of cocks and the chromium hydroxide slurry left at the base of the tank is pumped into a recycling tank. The chromium hydroxide slurry can be dissolved easily in acid (sulphuric acid) and separated Cr can be recycled.

2.5.1.2 Other processes

Ion exchange treatment of Cr (III) contaminated effluent is the next preferred commercial treatment option after precipitation. This method of treatment is achieved by using ion exchange resins. A cationic type of resin is employed for removing positively charged ions. Two modes are employed, one is the concentration mechanism to recover the Cr (III). The second mode is a polishing treatment, after conventional treatment by precipitation. Ion exchange is characterised by effecting complete removal of Cr (III), until the exchange capacity of the resin is exhausted. This exchange capacity may be recovered by regenerating the resin.

Various materials were used to remove Cr from the industrial effluents like agricultural wastes (Orhan and Buyukgungor, 1993), powdered leaves (Suseela *et. al.*, 1987), *Pinus sylvestris* bark (Alves *et. al.*, 1993) and microbial organisms. A few Cr accumulating plants will remove Cr from aqueous solution, for example some water weeds (Singaram, 1994a) and sunflowers also remove Cr (Kumar *et. al.*, 1995).

2.5.2 Chromium (VI)

Reduction of Cr (VI) to Cr (III), and subsequent hydroxide precipitation of the trivalent chromic ion, is the most common method of treating Cr (VI) contaminated industrial effluent.

2.5.2.1 Reduction and precipitation

The standard reduction techniques is to lower the waste stream pH to 2-3 with sulphuric acid, and convert the Cr (VI) to Cr (III) with a chemical reducing agent such as sulphur dioxide, sodium bisulfide, metabisulfite, or ferrous sulphate. The Cr (III) is then removed, usually by hydroxide precipitate (Besseliever, 1969). The reduction of Cr (VI) is not always completely effective and depends upon a number of factors such as the length of the reaction, pH of the reaction mixture and the concentration and type of reducing agent employed. Sulphur dioxide is the most popular reducing agent used in the treatment of Cr wastes, primarily because it is relatively inexpensive.

2.5.2.2 Other processes

Other common commercial methods of Cr (VI) removal from industrial effluents are ion exchange, electrochemical reduction and evaporation recovery.

Ion exchange processes are reported to be another economical treatment option for Cr (VI) recovery. Anion exchange resin is employed to remove chromate and dichromate. When the resin is exhausted it is regenerated (usually with sodium hydroxide), and sodium chromate is eluted from the ion exchange resin. The pH of the industrial waste is a critical factor for Cr (VI) removal. At pH below 4, the oxidation power of the chromic acid begins to attack the resin. At a pH of 6, the ratio of chromate to dichromate in solution increases. Highly basic anion-exchange resins preferentially remove chromate at pH 4.5-5 (Calmon, 1974).

Electrochemical reduction is one of the processes of Cr (VI) reduction in industrial effluent. It works on the principle that an electric current applied to an iron electrode results in the release of ferrous ions into solution. These ferrous ions then reduce Cr (VI) to yield Cr (III) ions. It employs DC electric potential and consumable iron electrodes. Cr (VI) reduction of 3.5 mg/L to below to 0.05 mg/L is reported in cooling-tower wastewaters (Kraljik, 1975). Other processes to reduce Cr (VI) concentration in industrial effluents use activated carbon (Sharma and Forster, 1996), alum coagulation, evaporation recovery, sedimentation, reverse osmosis and freeze concentration.

2.5.3 Copper

Treatment processes employed for reduction of Cu in industrial effluents may involve precipitation and disposal of the resulting sludge solids or recovery processes such as ion exchange, evaporation and electrolysis.

2.5.3.1 Precipitation

Precipitation of Cu contaminated industrial waste is usually done using lime or sodium hydroxide. Precipitation as cupric oxide using lime seems to offer distinct advantages with respect to cost and solid handling. Precipitation as cupric oxide is very effective between the pH 9-10.3. Residual concentration of 0.2-1.1 mg/L has been achieved for Cu in the timber treatment effluent using lime precipitation (Teer and Russell, 1972)

2.5.3.2 Other processes

Ion exchange is capable of achieving high levels of Cu removal. Ion exchange resins such as high molecular weight organic cheletes are used in this process. When compared to other treatment methods ion exchange tends to be not feasible and does not appear to be practical from a cost standpoint.

Various other methods are used for Cu reduction in the industrial wastes. Granulated activated-carbon treatment has been reported to reduce Cu from wood chemical wastewater (Carwley, 1980). Electrodialysis has been cited as economically feasible for the treatment of process solution and rinsewaters from plating and metal-finishing operations (Anderson and Hollingworth, 1972). Reverse osmosis and evaporation are other methods of reducing Cu from industrial wastewater.

2.5.4 Arsenic

Various methods are available for treatment of As contaminated industrial effluent but the most common method is by the precipitation and co-precipitation techniques.

2.5.4.1 Precipitation

Arsenic can be precipitated using sodium sulphide, lime, ferric sulphate, ferric chloride and alum. The primary mechanism for the removal of As is by precipitation as hydroxide. Lime has been considered as a better and cheaper treatment chemical for As in industrial wastewater. Arsenic in industrial waste which also contains heavy metals in solution, can be concurrently co-preciptated upon precipitation of the heavy metals. Co-precipitation can be considered to involve both adsorption of the soluble ion onto another and bulk precipitation.

2.5.4.2 Other processes

Activated alumina has been used to adsorb As from industrial wastewater (Nriagu, 1994). Desalting techniques, such as reverse osmosis or electrodialysis, ion exchange can be other processes to remove As from industrial effluent.

In the removal of heavy metal contaminants from timber treatment effluent, a method which is suitable to reduce all three heavy metal (Cu, Cr (VI) and As) will be the most effective method in reducing the concentration of these heavy metals. Precipitation seems to be the only cheap and feasible treatment method for removing all three heavy metals from timber treatment effluent as well as the Cr (III) from the tannery effluent. But the Cr (VI) present in the timber treatment effluent should be reduced to Cr (III) and later precipitated. Chapter 4 examines the various cheap industrial wastes and natural resources that can remediate heavy metals present in the tannery and timber treatment effluent.

2.6 REACTIONS OF COPPER, CHROMIUM AND ARSENIC IN THE SOILS

When a heavy metal pollutant enters the soil environment, several different mechanisms can be involved in the retention of heavy metal ions such as cation exchange (or non-specific adsorption), specific adsorption, co-precipitation and organic complexion. The most important chemical process affecting the behaviour and bioavalibility of metals in the soil is the adsorption of heavy metals from liquid to the solid phase. All the above reactions greatly affect the bioavailablity and leaching characteristics of contaminated heavy metal in the soil environment. We shall look briefly into the various reactions of Cu, Cr and As in the soil.

2.6.1 Copper

Major sources of Cu pollution into the soil are due to smelters, fly ash captured from the burning of coal, fungicide sprays, sewage sludge, timber treatment effluent, bio-solids, etc. Copper which enters the soil as a pollutant is usually fixed by organic matter, oxides of Fe, Al and Mn, and clay minerals. Thus copper is one of the least mobile of the trace elements, thereby rendering its uniform distribution in many soil profiles (Adriano, 1986). Copper may be expected to accumulate in the surface soils due to various industrial wastes. However, considerable leaching of Cu down the soil profile can occur under certain soil conditions foe example soils with low organic matter content, acidic peats or soils with high Cu levels (Mathur and Levesque, 1986).

Copper in soil is classified into six pools according to the physico-chemical behaviour (Shorrocks and Alloway, 1987). These include : A. In soil solution, in both ionic and complexed forms ; B. On non-specific exchange sites ; C. On specific exchange sites ; D. In organic residues and living organisms ; E. Occluded in soil oxide material ; and F. In the lattice structure of primary and secondary minerals. Copper held onto the occluded oxide material and primary and secondary minerals is unavailable to plants whereas the other forms are available (McLaren and Crawford, 1973). Adsorption maxima of Cu among various soil constituents can be ranked as follows : Mn Oxides > Organic matter > Fe oxide > Clay minerals.

2.6.2 Chromium

Chromium can exist in a number of oxidation states ranging from 2^- to 6^+, but the most common and commercially significant are the metallic chromium [Cr(O)] and compounds of trivalent Cr and hexavalent Cr. Within the ranges of redox potential and pH normally found in soils, Cr exists in four states - two Cr (III), the Cr^{3+} cation and the CrO_2^- anion, and two Cr (VI) hexavalent anion forms, CrO_4^{2-} and $Cr_2O_7^{2-}$ (Alloway, 1995).

Cr (III) is adsorbed to soil particles more strongly than Cr (VI) (Mc Grath and Smith, 1995). At normal soil pH levels, Cr (VI) compounds are more toxic, more mobile and more soluble than Cr (III). Hexavalent Cr is extremely toxic and carcinogenic. Hexavalent Cr also affects the soil biological properties such as denitrification, respiration, enzyme activity. The most sensitive being denitrification at the ED_{50} value (concentration of an inhibitor results in 50 % inhibition of activity) of 63 to 730 nmol Cr (VI)/g of soil (Speir *et. al.*, 1995).

Reduction of the Cr (VI) and oxidation of Cr (III) can both occur in soils. Hexavalent Cr can be reduced to Cr (III) an environment, where a ready source of electrons is available. Suitable conditions for reduction to occur are often met where organic matter is present to act as an electron donor, and are enhanced in acid rather than alkaline soils (Cary *et. al.*, 1977). Oxidation of Cr (III) to Cr (VI) has been shown to occur but requires the presence of oxidised Mn in the soil as an electron acceptor for the reaction to proceed

(Barlett and James, 1979). However this reaction does not predominate in soils. Evidence tends to suggest that the Cr (III) is the predominant form in most soils.

2.6.3 Arsenic

Mining operations, smelting operations, arsenic pesticides, sewage sludge, timber treatment effluent etc., are major sources of As into the soil environment. The chemistry of arsenate behaviour in soil is similar to the phosphate ion behaviour. Arsenate is more unstable over a wider range of Eh and pH than phosphate, and is commonly found in the +3 oxidation state, as arsenite (AsO_3^{3-}), in mildly reducing conditions. Under reducing conditions, arsenite dominates in soils (Deuel and Swoboda, 1972), but elemental arsenic and arsine can be present (Walsh and Keeney, 1975). Arsenic would be present in well-drained soils as $H_2AsO_4^{-}$ if the soil is acidic or as $HAsO_4^{2-}$ if the soil is alkaline. The various possible forms of As in the soil environment are :

(a) *Arsenite (III)* : The reduced state of inorganic arsenic, is a toxic pollutant in natural environments. It is much more toxic and more soluble and mobile than the oxidised state of inorganic As, arsenate [As(V)] (Deuel and Swoboda, 1972).

(b) *Arsenic (V)* : At high Eh values, As (V) exists as H_3AsO_4, $H_2AsO_4^{-}$, $HAsO_4^{2-}$, and AsO_4^{3-}, whereas at low Eh values, the corresponding As (III) species is present as AsS_2^{-} (Ferguson and Gavis, 1972). Arsenate can be sorbed onto clays, especially kalolinite and montmorillonite at low pH 5.0, and becomes less adsorbed at high pH (Goldberg and Glaubig, 1988).

(c) *Organic Arsenic* : A volatile As compound, dimethyl arsinic acid seems to be present in many soils (Braman, 1975).

Chemical forms of As and their transformation in soils is illustrated in Figure 2.4. Soil components that contribute to the sorption and retention of As are oxides of Al, Fe and Mn, soil minerals and organic matter.

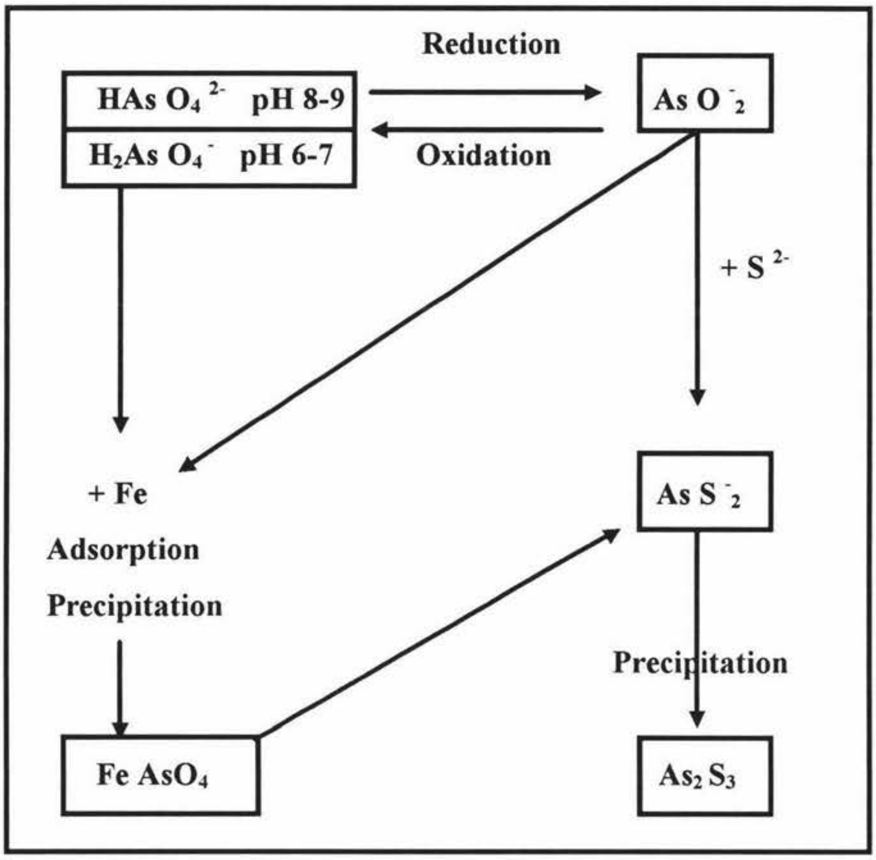


Figure 2.4 Chemical transformation of As in soils (Modified from Nriagu, 1994).

2.7 REMEDIATION OF HEAVY METAL CONTAMINATED SOIL

There are several options available for remediating heavy metal contaminated soil. The choice of the options depend on the extent of the pollution, the nature of the contaminants, the type of soil, the characteristics of the site, the relative cost of operation, and the regulations which apply in the country or region where the contaminated site is located. The remediation options vary from the minimum of reducing the bioavailability of the contaminants, to the maximum of either complete clean-up of the soil, or its removal from the site. Table 2.3 gives the characteristics of various options of methods of remediating a contaminated site.

Table 2.3 Preferred options for remediating a contaminated site (Modified from ANZECC/NHMRC, 1992).

Treatment option	Methods
1. Onsite treatment	Contaminants destroyed or reduced to an acceptable level onsite
2. Offsite treatment	Depending on the residue contamination level, soil can be removed and treated to remove contaminants.
3. Removal of soil	Excavation of contaminated material and disposal in an approved facility.
4. Barrier	Isolation of the contaminated site using a surface barrier.

2.7.1 Onsite treatment of heavy metal contaminated soil

The option of onsite treatment, which involves the in-situ remediation, is an inexpensive and rapid solution, in contrast to the problems of contaminant transport offsite (Ellis, 1992). Onsite treatment, or in-situ treatment involves the treatment of soil without excavating from the contaminated site. It is difficult in the case of contaminants present in deep sites. The in-situ treatment can be achieved through physical, chemical and biological treatment processes.

2.7.1.1 Physical in-situ treatment

The major physical in-situ treatment technologies in practice are physical mixing, soil washing and solidification.

Physical mixing results in the dilution of contaminants to levels below, which exposure is not considered a risk. This can be achieved by importing clean soil and mixing with the contaminated soil (Musgrove, 1991). This method is not a preferred option because the total contaminant loading of the site remains the same.

Soil washing is based on the desorption or dissolution of metals from the soil inorganic and organic matrix during washing with acids and chelating agents. Although soil washing is very suitable for offsite treatment of soil, it can also be used onsite using mobile equipment (Bromhead and Beckwith, 1994). The high cost of chelating agents and choice of extractants make this technology an unsuitable option (Clijsters and Vangronsveld, 1994).

Solidification involves the stabilisation of the contaminated soil into a solid mass using cement, fly ash, gypsum, asphalt or vitrification and has been applied in field scale remediation. Blast furnace slag-modified grouts were used for in-situ stabilisation of Cr contaminated soil (Allan and Kukacka, 1995). However there is a major question of long-term resistance to the breakdown of the solidified soil mass (Peters and Shem, 1992).

2.7.1.2 Chemical in-situ treatment

Various agents have been used to immobilise heavy metals chemically. Chelate ion exchange resin, cation exchange resin, hydrated lime, ferrous sulphate and silica gel, also and few natural resources, such as bentonite clay and greensand have been found to be effective in the immobilisation of a range of heavy metals. Few chemicals, such as ferrous sulphate is used to reduce Cr (VI) to Cr (III) and then precipitate Cr as chromium hydroxide (Czupyrna *et. al.*, 1989). Commercial surfactant (Surface-active-agents) such as Dowfax 8390 were effective in remediating subsurface Cr contamination (Thirumalai *et. al.*, 1996).

Chemical in-situ immobilisation is achieved by complexing contaminants using chemical additives and thereby reducing the solution phase concentration of the contaminants. If bioavaliability is a key point for remediation technologies then immobilisation may be a preferred option (Mench *et. al.*, 1994). The most widely practised form of remediating contaminated sites, particularly for removing heavy metals, is by liming the soil to pH 7 or higher, thereby rendering the metals less mobile and bioavailable (Alloway, 1995). A major inherent problem associated with immobilisation techniques is that although the heavy metals are less bioavailable the contaminants concentration has remained unchanged. The immobilised heavy metal may become plant available with time through the natural weathering process.

2.7.1.3 Biological in-situ treatment

In-situ immobilisation using biological materials to remediate contaminated soil is a viable and cheap option. Large quantities of organic matter are added to contaminated soil with the aim of locking-up metals as stable complexes with organic colloids (Harrison, 1992). Application of organic amendments such as cow dung, bermuda grass and yeast extract have been found to be effective in the reduction and immobilision of Cr (VI) contaminated soil (Cifuentes *et. al.*, 1996, Losi *et. al.*, 1994a).

Microbial bioremediation is a developing technology for contaminated soil. It involves the micro-organisms to accumulate, degrade or convert the toxic heavy metals to non-toxic forms. One such example is the use of sulphate-reducing bacteria to degrade toxic Cr (VI) to less toxic Cr (III) (DeFilippi, 1992).

Phytoremediation technique is an emerging technology for remediating contaminated soil. It involves the use of metal accumulating plants for remediating contaminated soil. This process requires the translocation of heavy metal from the soil to the easily harvestable plant parts which may be later harvested, dried and isolated as hazardous waste (Kumar, 1995).

Table 2.4 Offsite soil treatment options (Modified from Cairney, 1987).

I. Physical	II. Chemical	III. Thermal	IV. Microbial
Solvent leaching	Neutralisation	Direct heating	Bioremediation
Gravity separation	Oxidation	Indirect heating	
Particle sizing	Reduction	Incineration	
Settling velocity	Hydrolysis	Steam stripping	
Magnetic flotation	Electrolysis		
	Ozonation		
	Phytolysis		
	Cement-based		
	Polymer-based		

2.7.2 Offsite treatment

Offsite soil treatment involves the removal or destruction of the contaminants in the soil. The excavated soil can be treated before it is brought back to the site or disposed of in the disposal site. A classification of the conceptually available processes is given in the Table 2.4.

2.7.3 Removal of contaminated soil

Removal of soil involves the excavating the contaminated soil from the site and replacing it with a clean imported soil. The contaminated soil is stored in a safe place for further treatment. Mostly the contaminated soil is buried in a landfill. Complications may arise because there may be problems finding a disposal site, difficulty in finding clean fill material, hydrogeological problems, and the contaminants may have moved out of the site.

ANZECC/NHMRC (1992) guidelines suggest that soil removal may not continue to be an appropriate option due to the potential hazard associated with the transport of contaminated materials to the landfill site, contaminant migration from the landfill into adjacent environments in leachate, future limitations on the availability of secure landfill sites, and in addition other onsite, or in-situ, remediation technologies are developing rapidly.

2.7.4 Other soil remedial treatment

Table 2.5 lists the other techniques available for the remediation of contaminated soil due to inorganic substance.

Table 2.5 Treatment technologies available for soils contaminated with inorganic compounds (Logan, 1992 and Ellis, 1992).

Techniques	Objective	Processes	Common problems
Synthetic liners	Contaminants remain on site	Barrier method, minimisation of exposure	Short and long term resistance to contaminants
Modified clay liners	Contaminants remain on site	Barrier method, minimisation of exposure	Installation difficult, durability
Jet grouting	Contaminants remain on site	Barrier method, minimisation of exposure	Difficult to install, high cost
Slurry walls	Contaminants remain on site	Barrier method, minimisation of exposure	Difficult to install
Ground freezing	Contaminants remain on site	Barrier method, minimisation of exposure	High cost
Vitrification	Immobilisation	Precipitation in glass based product	Expenses, soil variability

2.8 SUMMARY

- The tanning and timber treatment industries are a major source of heavy metal pollution into soils and waterways. The tannery and timber treatment effluents (CCA) are enriched with toxic heavy metals, such as Cu, Cr and As.
- Chromium occurs as trivalent (III) and hexavalent (VI) ions in tannery and timber treatment effluents respectively. Hexavalent Cr is more mobile and toxic than the trivalent ion. As (V) is present as arsenate (AsO_4^{3-}) in the CCA solution. Copper occurs as Cu (II) in CCA solution.
- Although many alternative tanning processes such as vegetable tanning, aluminium tanning and zirconium tanning are available, Chrome tanning seems to be the most preferred and widely practised method of tanning hides and skins.
- In comparing the fixation of two species of Cr onto hide and timber, Cr (III) is fixed to hide protein by stable octahedral co-ordination compounds with suitable ligands whereas in timber, Cr (VI) complexes with cellulose and is later reduced to Cr (III).
- Most literatures confirms that heavy metal pollution from tannery and timber treatment effluent exceeds threshold levels for soils in New Zealand.
- For both tannery and timber treatment effluent, precipitation seems to be the most suitable and preferred method for removing heavy metals from the industrial effluents. But the Cr (VI) present in timber treatment effluent should be reduced to Cr (III) before precipitation.
- Various methods are available to remediate heavy metal contaminated soil of which on-site, or in-situ, treatment is widely used.

CHAPTER 3

CASE STUDIES OF THE TANNING AND TIMBER TREATMENT INDUSTRIES IN NEW ZEALAND

3.1 INTRODUCTION

Several New Zealand tanneries and timber treatment plants were selected and the pollution problems due to heavy metal contamination from those sites were studied. The effluent and soil samples from the sites were analysed and compared with the legal threshold levels for New Zealand (Ministry of Environment/Ministry of Health, 1995). Recommendations for possible remediation measures were proposed for those plants which were exceeding the heavy metal soil and effluent threshold levels. The recommendations were based on the results from the Chapter 4 and 5.

The main objectives of these case studies were,

(i) To identify the extent of the pollution problems associated with heavy metal contaminated effluent discharged from a few tanneries and timber treatment plants in New Zealand.

(ii) Based on the results of our research work, to propose possible remedial measures to those firms which were exceeding the heavy metal contaminant threshold levels.

3.2 THE TANNING INDUSTRY

Two tanneries were selected and the heavy metal pollution problems associated with the disposal of the tannery effluent were studied. The names of the tanneries were kept confidential because of the agreement signed with each tannery prior to collecting soil and effluent samples.

3.2.1 Visit to a Tannery industry in North Island

We visited a tannery in North Island where the effluent was discharged into the soil without any pre-treatment of the effluent. The pollution problem due to the disposal of tannery effluent was being investigated by the Regional Council and was subjected to court proceedings. One of the staff from the Regional Council took us to the disposal site near the tannery.

3.2.1.1 Problem of the site

This tannery generates daily between 5,000-10,000 litres of effluent depending on the level of activity of the tannery. Currently no pre-treatment of the effluent is carried out but the effluent is stored in a settlement tank before discharge. In the tannery, the effluent is first passed through a perforated drum to remove the suspended solids. The effluent is subsequently stored in a settlement tank to remove any biological sludge formed during the storage (Figure 3.1). The effluent from the settlement tank is applied to radiata pine plantation located at a distance of approximately 1.5 km from the tannery. The effluent is applied at a rate of 25,000 litres per day and the pipe is manually shifted to different areas every 1 to 4 weeks. The pine plantation is located on sand dunes resulting in free drainage of the effluent. Although the soil is considered to be ideal for effluent disposal due to the vegetation, frequent breakage of the pipe carrying the effluent makes it difficult for proper and efficient disposal. The tannery plans to expand its activity, whereby a projected future peak effluent flow of 55,000 litres per day is expected. So the tannery plans to buy a land close to the tannery, for the application of Cr effluent.

In the proposed future land treatment system, the effluent will receive some pre-treatment on the tannery site and the effluent will be pumped into a fixed irrigation system, such as a spray or micro-irrigation system onto the land beside the tannery. Under the Resource Management Act, the tannery needs to get a discharge permit if it has to

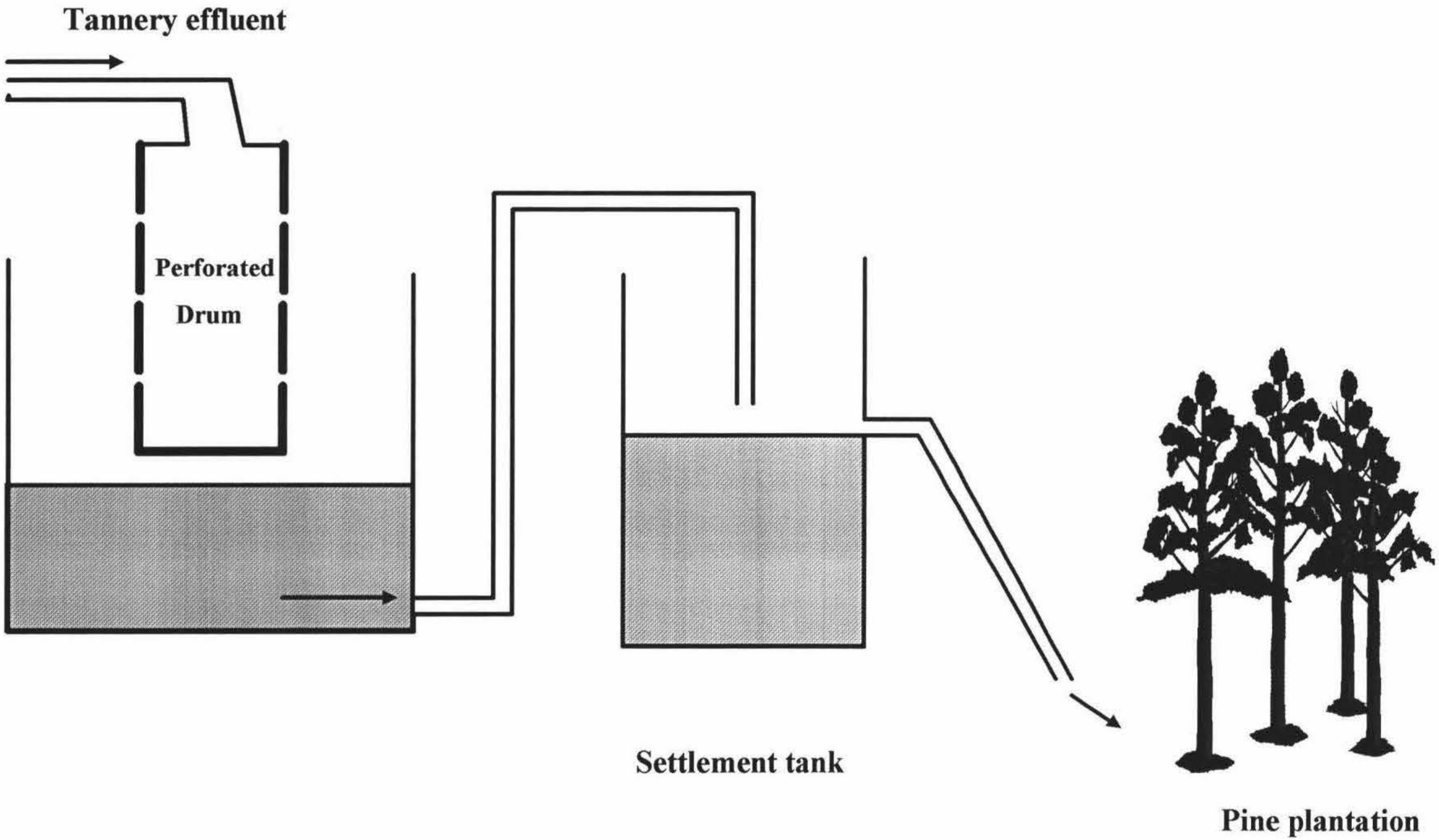


Figure 3.1 Current treatment of the tannery effluent before discharging into the soil.

dispose of the effluent onto a land. The Regional Council is responsible for the issue of a discharge permit to the tannery after investigating the problems that might arise due to the disposal of the effluent.

The soils in the area are predominantly sand, which has a high risk of ground water pollution. The water table at the site is high. The groundwater is present under the site at the depth varying between 0.5 m during winter and 2 m during the summer period. Bores exist in the vicinity and are used for stock water and in milking sheds. Few people are currently residing near the land where the tannery is planning to dispose of the effluent, but these people are fearful of the possible pollution risk.

3.2.1.2 Effluent and soil collection

We collected samples of effluent from the inlet pipe to the settlement pond. Surface soil samples (0-10 cm depth) were collected at different sites in the pine plantation. The sites were selected based on the length of time of effluent application. The soil samples were categorised as follows,

1. Control soil : No effluent was applied.
2. Soil A : received effluent for 5 years.
3. Soil B : received effluent for 12 years.
4. Soil C : received effluent for 12 years and was currently in use for effluent application.

3.2.1.3 Effluent and soil analysis

(a) *Tannery effluent*: The effluent was analysed for pH, electrical conductivity (EC) and sodium (Na) and Cr concentration. The pH of the effluent was measured using a combined glass/reference and pH electrode and the EC was measured using a conductivity meter. Analytical determination of Na concentration was measured using an emission mode at the wave length of 589.6 nm with a Flame-Atomic Absorption

Spectrophotometer (AAS) using air-acetylene flame. The Cr was measured by AAS using nitrous-oxide at 359.3 nm wave length.

(b) *Soil samples*: The soil samples were air dried and passed through a 2 mm sieve, and were analysed for pH, EC and total Cr. The soil pH was measured at a soil : water ratio of 1 : 2.5. The soil suspension was equilibrated for 1 hour and the pH of the suspension was measured using a combined glass/reference and pH electrode. Soil EC was measured at a soil : water ratio of 1 : 5 using a conductivity meter.

Total Cr was analysed using the Tri-Acid Digestion method, which is used for the total elemental analysis of soils (Bolan and Hedley, 1987). One gram of the soil sample was digested with 25 ml of tri-acid mixture of concentrated hydrochloric acid, nitric acid and perchloric acid in the ratio of 5:5:7. The mixture was heated over a hot plate at 260^0 C until white fumes built up inside the flask. After the digestion, the solution was cooled, filtered through Whatman No. 41 filter paper, and made up the volume to 100 ml. A standard soil and a blank were run with the samples. The Cr in the digest was analysed using the AAS.

3.2.1.4 Results and discussion

A. Effluent analysis (Table 3.1)

The pH of the effluent was 7.38 and the EC was 362 mS/m. The high pH and EC is attributed to the high levels of Na and salt concentration in the effluent. The Cr concentration in the effluent was 10.2 mg Cr/L. This concentration is very low compared to the other tanneries where the Cr concentration ranges around 2000-3000 mg Cr/L. Although the Cr concentration in the effluent is low the volume of effluent generation must be considered for Cr input into the soil.

Table 3.1 pH, EC and Na and Cr concentration of the tannery effluent.

pH	EC (mS/m)	Na (mg/L)	Cr (mg/L)
7.38	362	525	10.2

B. Soil samples (Table 3.2)

The data in Table 3.2 indicate that the pH of the soils irrigated with the tannery effluent was slightly higher than the control. The increase in pH is attributed to the increase in Na concentration in the soil. The EC of the soils which received effluent was much higher than the control. The increase in EC of the soils is attributed to the high salt concentration in the effluent. The Cr concentration in the soil samples which received the

Table 3.2 pH, EC and Na and Cr concentration of the soil samples.

Soil samples	pH	EC (mS/m)	Cr conc. (mg Cr/kg)
Control soil	5.06	8	14
Soil A: received effluent for 5 years.	5.12	33	19
Soil B: received effluent for 12 years.	6.55	20	1375
Soil C: received effluent for 12 years and fresh effluent application.	6.45	45	3670

effluent for the period of 5 years was not significantly different from the untreated control soil. Whereas the concentration of Cr in soils which received the effluent for 12 years increased many fold. In these soils the concentration of Cr exceeds the threshold level of Cr in soil (600 mg Cr (III)/kg soil) according to Ministry of Environment/Ministry of Health Guideline, New Zealand (Table 2.1).

The pine plantation site being a sand-plain with the groundwater under the site at depths varying between 0.5 m in the winter period and 2 m in the summer period, there is a very high risk of ground water pollution by Cr.

3.2.1.5 Recommendations

It is important that attempts should be made to reduce the Cr concentration in the effluent and to reduce the mobilisation of Cr in the contaminated soil. The following recommendations are based on the results obtained in the subsequent chapters (Chapter 4 and 5).

A. Pre-treatment of effluent using "FBA-Bark Filter System"

Since the volume of effluent generated is high, even though the Cr concentration is low in the effluent, the long term application of the effluent into the soil is likely to elevate the Cr concentration in the soil. So a proper pre-treatment system to remove the Cr from the effluent before it is discharged into the soil will lower the Cr input from the effluent into the soil.

The tannery effluent generated can be passed through a filter containing material which are effective in retaining Cr. From the results discussed in Chapters 4 and 5 it is indicated that a waste material, Fluidised Bed boiler Ash (FBA) is effective in reducing the Cr concentration in the effluent. FBA is obtained during the burning of coal with lime and contains quick lime (CaO). The alkaline CaO material precipitates Cr as $Cr(OH)_3$. So FBA can be used as a filter material through which the tannery effluent can be passed. To facilitate an easy flow of the effluent the FBA can be mixed with *Pinus* bark which also retains Cr. The filter column must be periodically changed with new material as the filter reaches saturation.

B. Precipitation tank

The most preferred option to reduce the heavy metal concentration of tannery effluent is using precipitation tank. Plate 3.1 shows the precipitation tank that is used in J.D.Wallace tannery at Waitoa to precipitate Cr before discharging the tannery effluent into the soil. The Cr which is precipitated using precipitation tank is recycled into the tannery. Similar precipitation tank can be constructed and FBA can be consider as an alternative precipitating agent instead of the lime or magnesium oxide.

C. Immobilisation of Cr in the polluted soil

The soils in which the Cr levels exceed the threshold level should be treated to avoid any possible groundwater pollution by Cr. Polluted sites can be treated with immobilising agents such as FBA or lime and tilled so that it will prevent further movement of Cr down the soil. In Chapter 5, the effect of these amendments on the immobilisation of Cr in soil is discussed. Periodical monitoring of ground water Cr must be carried out. The Cr concentration in the polluted soil must be controlled such that the groundwater Cr concentration is below the threshold level guideline of 30 mg Cr (III)/L and 0.05 mg Cr (VI)/L (Ministry of Environment/Ministry of Health, 1995).

3.2.2 Visit to a Tannery in Wanganui

This tannery is currently discharging a very high concentration of around 3200 mg/L of Cr into the public sewage system (Plate 3.2). The effluent is diluted before discharging into the pumping station, but the total amount of Cr in the tannery effluent is not reduced by pre-treatment before being discharged. The problem is that the Wanganui public sewage system does not have a sewage treatment plan, so the high Cr concentration tannery effluent is ultimately disposed of in the sea.

Plate 3.1 **Chromium precipitation tank, used to recycle Cr into the tannery at J.D.Wallace tannery, Waitoa.**

Plate 3.2 **Discharge of untreated tannery effluent with high Cr concentration (3200 mg/L) into a public sewage system, from a tannery in Wanganui.**

3.2.2.1 Recommendations

The tannery does not have any treatments plant for the effluent before it is discharged the public sewage pumping station. A pilot scale "FBA-Bark Filter System" can be set up as discussed in the Section 3.2.1.5, whereby the tannery effluent can pass through the column containing FBA + *Pinus* Bark mixture. As the Cr concentration of the effluent is very high the filter columns should be frequently changed. Another optiòn is to set up a "Precipitation tank" so that the effluent can be precipitated using FBA and then discharged. The latter method will be more effective in reducing the high concentration of Cr from the effluent.

3.3 THE TIMBER TREATMENT INDUSTRY

We visited two timber treatment plants, were the pollution problem was not as serious as the tanneries that we visited.

3.3.1 Visit to a timber treatment plant, Tangimona

In this timber treatment plant, Cr ground water pollution was reported. The Manawatu Regional council is currently undertaking frequent ground water sampling to determine the Cr pollution level. We visited the site and collected a few groundwater samples to determine the Cr concentration (Plate 3.3). Ground water samples were taken from two bores, one near the timber drip site and another bore about 20 meters away from the drip site. The concentration of Cr was measured using the Graphite furnace AAS.

The concentrations of Cr in the bore well was considered very low. The groundwater Cr water standard levels are 0.05 mg Cr (VI)/L (Ministry for the Environment/Ministry for Health, 1995). The levels found in the ground water of Tangimona timber treatment plant, was 0.007 mg Cr (VI)/L near the site bore and 0.001 mg Cr (VI)/L at the far away bore. So the concentration detected is very low and well below the legal threshold levels.

Plate 3.3 **Groundwater sampling in a timber treatment plant, Tangimona.**

Plate 3.4 **CCA treatment chamber with steam drying facility for drying the the freshly treated timber.**

3.3.2 Visit to Carter Holt Harvey Timber treatment plant, Marton

This was one of the timber treatment plant which won the "Environmental Friendly award". This plant has a well planned CCA-timber treatment system, whereby the timber is treated and steam dried (Figure 3.2, Plate 3.4), before the timber is stored on the soil surface. This steam treatment drastically reduces the amount of CCA that drips from the treated timber, so reducing the chances of heavy metal pollution of the soil. This treatment plant is an example, which should be followed by other timber treatment plants to reduce the soil and ground water pollution due to CCA effluent.

3.4 CONCLUSIONS

The heavy metal pollution problem of the tanning industry is mainly due to the untreated effluent discharge onto the soil or into the waterways whereas, in the timber treatment industry the heavy metal pollution problem is mainly due to drips and leakage of the of CCA from freshly treated timber.

To reduce the Cr concentration in the tannery effluent, the use of “FBA-Bark Filter system” or setting up a “Precipitation tank” as discussed in the Section 3.2.1.5, are the viable options.

In the case of the timber treatment plants, steam treatment of freshly treated CCA timber as practised by the Carter Holt Harvey Timber treatment plant, Marton is a preventive method to reduce the heavy metal contamination due to CCA solution. Plate 3.5 and Plate 3.6 shows the diffference between CCA treated timber, with and without steam drying process respectively.

For the treatment of CCA effluent, “FBA-Bark Filter system” can be consider to remove Cu, Cr (VI) and As from the effluents before discharging into soil or waterways.

Although the timber treatment plants that we visited did not have any major heavy metal contamination problems, some contaminated sites were reported in New Zealand (Table 2.2).

For the remediation of contaminated sites which have already been polluted with the CCA drips ,"In-situ immobilisation" using FBA and *Pinus* bark as discussed in Chapter 5, might be a possible solution to prevent further migration of heavy metals into the soil and groundwater.

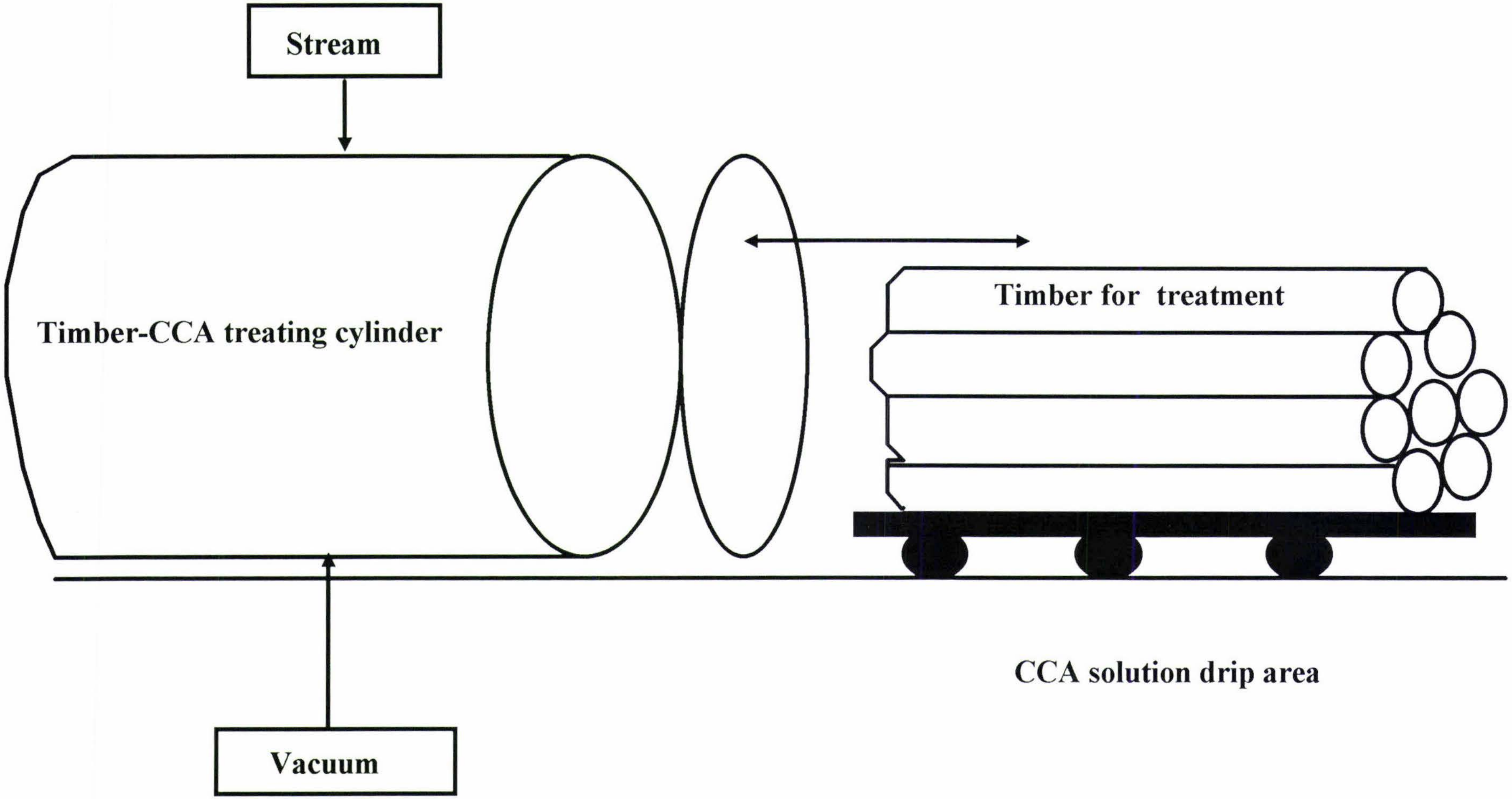


Figure 3.2 The CCA timber treatment process using vacuum and stream drying after timber treatment.

Plate 3.5 **Freshly treated timber at the Carter Holt Harvey timber treatment plant, Marton (after steam drying).**

Plate 3.6 **CCA drips from freshly treated timber in a timber treatment plant (without steam drying).**

CHAPTER 4

REDUCTION OF COPPER, CHROMIUM AND ARSENIC FROM TANNERY AND TIMBER TREATMENT EFFLUENTS

4.1 INTRODUCTION

There are various methods by which heavy metals are removed from industrial effluents before being discharged onto the soil and into waterways. These methods include precipitation, ion exchange, reverse osmosis, adsorption, freezing concentration etc. Various materials are used for the removal or reduction of heavy metals from industrial effluents such as activated carbon, synthetic resins, micro-organisms and synthetic additives. Heavy metals from tannery and timber treatment effluents are mostly removed by precipitation using materials such as lime, caustic soda or magnesium oxide.

In this chapter, we are looking into alternative cheap materials for the removal of heavy metals from tannery and timber treatment effluents. The potential value of waste material generated by some industries and cheap natural resources for reducing heavy metals from tannery and timber treatment effluents was studied. This approach enables the reuse of industrial waste as well as reducing the heavy metal concentration in the effluents was examined. A range of materials differing in their physical and chemical properties were selected and the efficiency of these materials in reducing the heavy metal concentration was examined using batch experiments.

A batch experiment was used as a preliminary screening test for selecting the efficient materials for further testing involving column leaching and plant growth experiments. Adsorption isotherms were constructed for each of these materials to determine the maximum adsorption capacity of the effective materials. The batch experiment was initially tried with individual materials and later the most effective materials were selected and the effectiveness of different combination of these materials was examined using batch and column leaching experiments.

The main objectives of the batch and column leaching experiments discussed in this chapter were :

(i) To reduce the Cu, Cr and As concentration of the tannery and timber treatment effluents before they are discharged into the soil and waterways.

(ii) To evaluate the effectiveness of a range of industrial wastes and natural resources in reducing the concentration of Cu, Cr and As concentrations from the tannery and timber treatment effluents.

4.2 MATERIALS USED

The range of industrial wastes and natural resources differing in their physical and chemical characteristics were used to reduce Cu, Cr and As concentration in the tannery and timber treatment effluents.

4.2.1 Industrial wastes

The industrial wastes used for retention of heavy metals in the batch and column leaching experiments were *Pinus* bark, Fluidised bed boiler ash (FBA) and Flue gas desulphrisation gypsum (FGDG).

4.2.1.1 *Pinus* bark

Mahimairaja *et. al.*, (1993) have shown that *Pinus* bark (*Pinus radiata*) carries a large number of cation exchange sites (ca 120 cmol/kg) and is very efficient in the retention of cations. The *Pinus* bark is a waste product obtained cheaply from saw mills. Bark from *Pinus sylvestris* and *Hardwickia binata* have been shown to retain heavy metals (Deshkar *et. al.*, 1990, Alves *et. al.*, 1993). Modified *Pinus radiata* bark was used in the removal and recovery of uranium from aqueous solution (Freer *et. al.*,1989). In the present experiments, wood chips (*Pinus radiata*) were collected from a local garden nursery, ground and sieved to less than 2 mm diameter.

The heavy metal removal capacity of *Pinus* bark can be further improved by acid treatment, alkaline treatment and by formaldehyde/acid treatment (Freer *et. al.*, 1989, Deshkar *et. al.*, 1990, Alves *et. al.*, 1993). The removal of Cu, Cr and As using both the pre-treated (Refer to Section 4.3.3.2) and untreated *Pinus* bark from the tannery and timber treatment effluents was examined.

4.2.1.2 Fluidised bed boiler ash

Fluidised bed boiler ash (FBA) is an industrial waste material obtained from fossil fuel-fired boilers. It is a gypsiferous by-products resulting from using limestone to remove SO_2 when burning high-sulphur coal. FBA was obtained from the New Zealand Dairy Corporation (NZDC) factory at Te Awamutu. The FBA was slaked with water and allowed to cool for 24 hours.

The slaked FBA was used in our experiment, its an alkaline material (37.8 % $CaCO_3$ equivalent on a wet weight basis). The major chemical composition of slaked FBA is soluble gypsum ($CaSO_4.2H_2O$) which constitutes approximately 50 % and the reminder being low soluble ettringite [Ca_6 Al_2 $(SO_4)_3$ $(OH)_{12}$..26 H_2O] (Wang *et.al.*, 1994). FBA was selected due to its very high pH of 12.4, which might be suitable to precipitate heavy metals.

4.2.1.3 Flue gas desulphrisation gypsum

Flue gas desulphrisation gypsum (FGDG) is a gypsiferous by-product from coal-fired power stations. It is obtained as a by-product after limestone is used to remove SO_2 emissions from the station. Large quantities of FGDG are obtained from coal-fired power stations as a waste material and hence was worthwhile examining for its retention capacity of heavy metals.

4.2.2 Natural resources

A zeolite sample, a peat soil, and two mineral soil samples were the natural resources used in the batch and column leaching experiments to remove heavy metals.

4.2.2.1 Zeolite

Zeolites are alumino silicate clay minerals obtained as a natural resource from the earths surface. Zeolite was selected for the retention of heavy metals due to its high cation exchange capacity of 104 cmol/kg (Table 4.1). Several researchers have reported that the zeolite minerals, such as clinoptilolite and heulandite have high cation exchange sites (Miner, 1984; Witter and Kirchmann, 1989). In the present experiment a zeolite sample (clinoptilolite) mined in New Zealand was used.

Table 4.1 Characteristics of natural resources used.

Materials	pH	CEC (cmol /kg)	Organic carbon	Sand	Silt	Clay	DOC* (mg/kg)
			(%)				
Tokomaru soil	5.80	13	3.15	12.4	60.9	24.7	96
Egmont soil	6.07	27	8.70	48.0	27.4	25.6	230
Peat soil	5.10	97	43.8	-	-	-	765
Zeolite	9.26	104	-	-	-	-	-

* Dissolved Organic Carbon

4.2.2.2 Peat soil

Peat soil was obtained from a depth of 0-75 mm in a field site at Moanatuatua Swamp, Waikato, New Zealand. Peat soil was selected due to its high organic matter content and CEC. A large fraction of the heavy metals is retained in the organic matter of the soil and hence a soil which is rich in organic carbon is considered to be useful in treating heavy metal contaminated industrial effluent.

4.2.2.3 Tokomaru and Egmont soil

Two soil samples (Tokomaro and Egmont soil) which vary in their organic matter and CEC were selected to examine the efficiency of retaining heavy metals (Table 4.1).

4.2.3 Combination of materials

From the results of the batch experiment, FBA, *Pinus* bark and peat soil were found to be the most effective materials for the removal of heavy metals from tannery and timber treatment effluents. FBA forms a solid mass when it is in contact with any liquid thereby blocking the leaching column. To overcome this problem, FBA was mixed with other materials, which were equally effective in retaining heavy metal. The retention capacity of various combination of FBA with bark and peat soil was examined in the batch experiment.

I. Three different combinations of FBA and *Pinus* bark were prepared :

1. 10 % FBA (10g FBA +90g *Pinus* bark).
2. 50 % FBA (50g FBA +50g *Pinus* bark).
3. 75 % FBA (75g FBA +25g *Pinus* bark).

II. Two combinations of FBA with the peat soil was used :

1. 50 % FBA (50g FBA +50g peat soil).
2. 75 % FBA (75g FBA +25g peat soil).

4.2.4 Chemicals used

Original tannery and timber treatment effluents were used in the batch adsorption and column leaching experiments. Tannery effluent was collected from a tannery at Wanganuai and 1 % CCA-timber treatment effluent was made up using CCA powder collected from a timber treatment plant. The original tannery effluent had a concentration of 3200 mg Cr (III)/L and the 1 % CCA effluent had a concentration of 1040, 1195 and 2475 mg/L of Cu, Cr (VI) and As respectively.

For the adsorption isotherms, standard salts, such as copper sulphate, chromium potassium sulphate, potassium dichromate and sodium arsenate were used as sources of Cu (II), Cr (III), Cr (VI), and As (V) respectively.

4.3 METHODS USED

The batch adsorption experiments were used to determine the retention capacity of the various materials and to construct adsorption isotherms. The most effective materials which were selected from the batch experiment, were used in the column leaching experiment. The various analytical techniques and experimental methods used for batch and leaching experiment are given below.

4.3.1 Measurement of Cu, Cr and As

Analytical determination of Cr and As was made by Flame-Atomic Adsorption Spectrophotometer (AAS) using nitrous-oxide at 359.3 nm and 193.7 nm wave lengths respectively. For Cu, Flame-AAS analysis was carried out using air-acetylene at 217.9 nm wave length.

4.3.2 X-ray diffraction study

X-ray diffraction (XRD) study was carried out to identify the form in which Cr was precipitated after treating the tannery effluent with the FBA. The major chemical components of the slaked FBA is $CaSO_4.2.H_2O$ and $Ca(OH)_2$, therefore the expected precipitate form was $Cr(OH)_3$.

The greenish blue precipitate formed on the surface of the FBA material after shaking the tannery effluent with the FBA was analysed mineralogically. The various fractions present in the greenish blue precipitate were examined by X-ray diffraction using a Philips PW 1710 microprocessor-controlled diffractometer after sedimentation on to glass slides. The diffractometer was used with Cobalt Kα radiation (Whitton and Churchman, 1987).

4.3.3 Retention of Cr by *Pinus* bark

A detailed study was conducted to examine the Cr adsorption onto *Pinus* bark material alone. This study was carried out to investigate the adsorption behaviour of both the Cr (III) and Cr (VI) species which have different mechanisms for fixing onto skin and hide, respectively. The effects of surface area and pre-treatment of bark on Cr adsorption, and Cr speciation after treating the Cr solution with the bark were examined.

4.3.3.1 Surface area measurement

The effect of surface area on the *Pinus* bark adsorption of Cr (VI) was examined by conducting batch adsorption using a number of particle size fractions of *Pinus* bark material ranging from > 90 micron to < 2 mm. The adsorption isotherms were obtained for various sized bark materials using a batch adsorption procedure.

The specific surface area (SSA) of different sized bark materials was measured by a simple procedure using water vapour. The dried bark was placed in a air-tight glass chamber where the relative pressure (p/p_o) is 0.2. Where, p is the vapour pressure and p_o the saturated vapour pressure at the given temperature. The pressure p is controlled by a saturated solution of potassium acetate at a room temperature of 20 °C. After setting up the samples in the glass chamber, the air in the chamber was removed using a vacuum pump and sealed with vaseline to prevent a pressure drop.

Water content (ω_m) of the samples after reaching equilibrium is determined gravimetrically and SSA is calculated by using a standard equation (Kutilek and Nielsen, 1994) :

$$SSA = 3610^* \omega_m$$

The principle of this experiment is that at 20 atmospheres pressure ($p/p_o = 0.2$) there will be only one layer of water molecules surrounding the *Pinus* bark material kept in the controlled chamber at 20 °C. So by subtracting the oven dry weight from the wet weight of the *Pinus* bark at 20 atmospheric pressure, an estimation of weight of the single layer of water vapour surrounding the surface of the *Pinus* bark material can be made. From this weight of the water content, the SSA was calculated using the above standard equation.

4.3.3.2 Pre-treatment of *Pinus* bark

The retention capacity of heavy metal by *Pinus* bark can be improved by treating with acid, alkaline or formaldehyde/acid (Freer *et. al.*, 1989, Deshkar *et. al.*, 1990, Alves *et. al.*, 1993). In this experiment, the following pre-treatments of *Pinus* bark were carried out.

A. Acid treatment

About 30 g of bark material (< 2 mm) was treated with 300 ml of 0.05 N H_2SO_4 (Alves *et. al.*, 1993). After shaking for 48 hours in an end-over-end shaker the bark mixture was washed with deionised water to neutral pH and stored in a cold room.

B. Alkali treatment

About 30 g of bark material (< 2 mm) was treated with 300 ml of 0.005 N KOH. After shaking for 48 hours in an end over end shaker the bark mixture was washed with deionised water to neutral pH and stored in a cold room.

C. Formaldehyde/Acid treatment

For this treatment, 30 g of bark material was treated with 450 ml of 3 % (v : v) nitric acid plus 0.75 ml of 40 % formaldehyde in a boiling water bath for 15 minutes (Alves *et. al.*, 1993). Later the bark material was allowed to cool to the room temperature for about 6 hours, washed with deionised water until the filtrate had the neutral pH.

4.3.3.3 Batch adsorption at low and high concentration of Cr

The adsorption of Cr (III) and Cr (VI) by the pre-treated and untreated bark materials was examined in the batch experiment at low and high concentrations of tannery and timber treatment effluents.

At low Cr concentration, the effect of pre-treatment of *Pinus* bark on adsorption of both the Cr species can be clearly observed (Alves *et. al.*, 1993). Hence the batch adsorption was carried out at a low concentration of Cr in the range of 30 mg Cr/L, which is the residual Cr concentration usually found in the tannery effluent discharge after the initial physico-chemical treatment (Hess, 1984). To compare the Cr (III) and Cr (VI) adsorption at low concentrations both the original tannery and the timber treatment effluents were diluted to a low concentration range of 30 mg Cr/L.

In the batch adsorption experiment, about 0.5 g of *Pinus* bark was treated with 10 ml of Cr solution in centrifuge tubes. The solution was shaken in an end-over-end shaker for 16 hours and centrifuged at 8000 rpm for 10 minutes. Finally the solution was filtered through Whatman No: 41 paper and the concentration of Cr in the filtrate was measured using AAS. The difference between the initial and final Cr concentration after the treatment with the *Pinus* bark materials gives the measure of Cr adsorption.

The retention capacity was calculated on the basis of the distribution coefficient (K_d). The higher the K_d value the greater the adsorption.

$$\text{Distribution coefficient } (K_d) = \frac{\text{Sorbed concentration}}{\text{Solution concentration}}$$

Chromium retention was examined for both the species of Cr at high concentration of Cr (III) (3200 mg/L) and Cr (VI) (1100 mg/L). Adsorption studies were carried out using the original effluents with various pre-treated *Pinus* bark following the batch adsorption procedure mentioned above.

4.3.3.4 Speciation of Cr adsorbed by the bark

Recently activated aluminium oxide has been used to separate Cr (III) and Cr (VI) species in the soil extracts (Prokish *et. al.*, 1995). Activated aluminium oxide adsorbs only Cr (VI) but not Cr (III), this principle was used for the speciation of Cr in the solution after treatment with *Pinus* bark. A preliminary experiment using known concentrations of Cr (III) and Cr (VI) was conducted to confirm the sensitivity of activated aluminium oxide to speciate Cr.

An initial trial experiment for speciation was carried out using a known mixture of Cr (III) and Cr (VI) in solution. Solutions containing different proportions of Cr (III) and Cr (VI) (25:75 ; 50:50 ; 75:25) were prepared. Chromium chloride and potassium dichromate were used as a source of Cr (III) and Cr (VI) respectively. The total Cr concentration in all the solutions were maintained at the same concentration of 300 mg Cr/L. These solutions were treated with the acidic aluminium oxide and the concentration of Cr in solution was measured before and after the activated aluminium oxide treatment.

The acidic aluminium oxide was pre-treated before being allowed to react with the Cr solutions. The pre-treatment was carried out by shaking 0.5 g of acidic aluminium oxide with 10 ml of 0.1 % Al (III) buffer in the form of aluminium nitrate for 1 hour. This Al (III) buffer fills the positively charged sites, therefore the adsorption of

Cr (III) is greatly decreased. The buffer solution was decanted and 20 ml of the mixture solution containing both Cr (III) and Cr (VI) was added. The Cr solution and acidic aluminium oxide was shacken in an end-over-end shaker for 1 hour so that all the Cr (VI) in the solution is adsorbed. Any Cr remaining in the solution must be in the form of Cr (III). Preliminary studies have indicated that activated aluminium oxide adsorbed only Cr (VI) not Cr (III). The concentration of Cr in the solution was measured using AAS.

Speciation of Cr adsorbed onto the bark was carried out using the following procedure. As before, acidic aluminium oxide was pre-treated using an Al (III) buffer in the form of aluminium nitrate for 1 hour and the buffer solution was decanted. The Cr (VI) solution which is to be speciated was obtained previously, shacken with a standard concentration Cr (VI) solution with the bark for 16 hours. About 5 ml of Cr solution, which was remaining after the adsorption with the bark was added to the pre-treated acidic aluminium oxide. The solution was shacken in an end-over-end shaker for 1 hour so that all the Cr (VI) in the solution is adsorbed onto the activated aluminium oxide. The concentration of Cr in the solution which is assumed to be Cr (III) was measured using AAS.

4.3.4 Batch adsorption for Cu, Cr and As

Heavy metal retention was examined at the original concentration of the industrial effluents. Adsorption studies were carried out using the original effluents with various materials. Adsorption was carried out using 0.5 g of the materials with 10 ml of the original tannery effluent and 1 % CCA solution. The experimental procedure and calculation of retention of heavy metal were similar to the batch adsorption described in the Section 4.3.3.3.

4.3.5 Adsorption isotherms for Cu, Cr and As

The adsorption isotherms were carried out for selected materials to determine the maximum adsorption of the Cu, Cr and As. The adsorption isotherms were done with a solid : solution ratio of 1 : 20 for different concentrations of Cu, Cr and As solution. dichromate and sodium arsenate were used for Cu (II), Cr (III), Cr (VI), and As (V), respectively. Adsorption isotherms with a range of increasing concentration between 0-2500 mg/L of Cu, Cr (III), Cr (VI), and As (V) were obtained following the method outlined for the batch experiment (Section 4.3.3.3).

4.3.6 Leaching experiment for Cu, Cr and As

Materials which were found to be very effective in reducing the heavy metal concentration in the effluents in the previous batch experiment were only used in the column experiment.

The various columns used were :

1. *Pinus radiata* bark column
2. Peat soil column
3. 100 % FBA column
4. 75 % FBA + 25 % *Pinus* bark column
5. 50 % FBA + 50 % *Pinus* bark column

Only for the timber treatment effluent :

6. Two successive columns
   (a) *Pinus radiata* bark column - top
   (b) 75 % FBA + 25 % *Pinus* bark column - bottom

Apart from the single column treatment, a double column treatment was used for timber treatment effluent. The double column was used based on the results of the batch experiment where FBA was effective for Cu and As whereas *Pinus* bark was effective in reducing the Cr (VI) concentration from the industrial effluents. The CCA effluent was passed through the first column containing bark alone assuming Cr (VI) might be reduced, then the leachate from the first column was passed through a second column containing 75 % FBA + 25 % bark, which might be effective in reducing the As and Cu concentration.

The practical applicability of the batch experiment can be examined by leaching the effluent through columns containing various materials. The leaching experiment results will give a better idea of the potential value of these materials to remove the heavy metals from the tannery and timber treatment effluents. The leaching experiment helps to build a break through curve (BTC), which explains the point of saturation of heavy metal retention and the capacity of the materials in reducing heavy metal concentrations from these effluents.

The objective of the leaching experiment is to access the effectiveness of various materials in reducing the concentration of heavy metals by leaching the original tannery and timber treatment effluents through the columns containing various materials. The concentration of the heavy metals can be measured in the leachate at different volumes of leachate and a break through curve can be built to locate the saturation point for each of these materials.

The leaching experiment was carried out using narrow glass tube columns of 1.5 cm diameter and 15 cms length. The adsorbent materials were packed to a height of 10 cms in the columns. Each column was separately connected to the peristaltic pump using narrow plastic tubes. The tannery and timber treatment effluents were pumped separately into the columns using a peristaltic pump at the rate of 1.2 ml/min. The leachate was collected using plastic vials at intervals of 2 minutes for the first two leachates and 5 minutes for subsequent leachates. The exact amount of the leachate was calculated by weighing the plastic vials before and after collecting the leachate. The heavy metal concentration was measured using AAS from each leachate.

4.4 RESULTS AND DISCUSSION

4.4.1 Retention of Cr by *Pinus* bark

The results of the effects of surface area of *Pinus* bark, pre-treatment of *Pinus* bark on Cr retention and the speciation of Cr are given below.

4.4.1.1 Effect of surface area of bark on Cr adsorption

The effect of surface area of bark on Cr retention was examined by constructing adsorption isotherms for various sized fractions of *Pinus* bark. The adsorption isotherm data were fitted to the Freundlich equation to simplify the description of the adsorption processes.

Freundlich equation $X = KC^{N}$

Where X is the amount of Cr adsorbed (mg/g), C is the equlibrium Cr concentration (mg/L), N is the slope constant of the Freundlich equation and K is a constant which

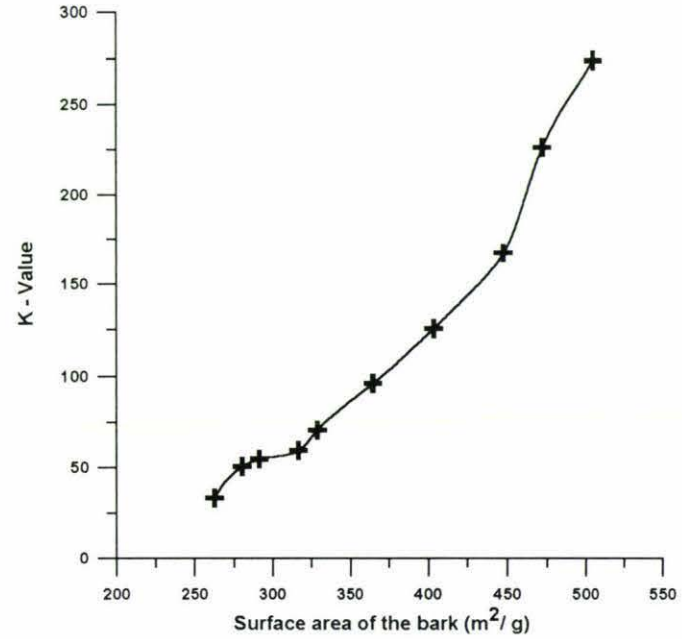


Figure 4.1 Adsorption of Cr (VI) as measured by K-value for different size fractions of *Pinus* bark.

gives the measure of sorption at unit concentration. The extent of adsorption, as measured by the K value, increases with an increase in surface area (Figure 4.1).

4.4.1.2 Effect of Pre-treatment of bark on Cr adsorption

At low concentrations of Cr (30 mg/L), the retention, as measured by the distribution coefficient (K_d), is presented in Table 4.2. It shows a clear difference between the untreated and the treated bark materials. The treated bark shows a marked increase in the retention of Cr from the effluents.

Table 4.2 Retention of Cr (III) and Cr (VI) by untreated *Pinus* bark and pre-treated *Pinus* bark at low concentration (30 mg Cr/L).

Materials used	Tannery effluent Cr (III)		Timber treatment effluent Cr (VI)	
	Amount adsorbed. (mg/g)	K_d value. (cm^3/g)	Amount adsorbed. (mg/g)	K_d value. (cm^3/g)
A. Untreated.	0.60 (± 0.04)	58	0.88 (± 0.03)	248
B. Acid treated.	0.60 (± 0.04)	73	0.92 (± 0.02)	505
C. Base treated.	0.83 (± 0.06)	416	0.95 (± 0.02)	558
D. Formaldehyde/ Acid treated.	0.77 (± 0.05)	246	0.93 (± 0.03)	672

In the case of Cr (III) the highest K_d was achieved for alkali treated bark whereas in the case of Cr (VI) the highest K_d value was shown by both the alkaline treated and the formaldehyde treated bark, which were not significantly different from each other. The improvement in the retention capacity may be due to the structural changes in the cellulose and tannins of the bark material. The tannin and cellulose are the active ion exchange compounds of the bark surfaces (Dahlgren, 1974).

For the batch adsorption at high concentration, since the alkaline treated *Pinus* bark showed a considerable increase in the retention of both forms of Cr, this treatment was compared with the untreated bark (Table 4.3).

Table 4.3 Retention of Cr (III) and Cr (VI) by untreated *Pinus* bark and alkali treated bark at high concentration (3200 mg Cr (III)/L and 1100 mg Cr(VI)/L).

Materials used	Tannery Effluent Cr (III)		Timber treatment effluent Cr (VI)	
	Amount adsorbed. (mg/g)	K_d value. (cm^3/g)	Amount adsorbed. (mg/g)	K_d value. (cm^3/g)
A. Untreated.	6538 (± 432)	2.15	38903 (± 654)	440.3
B. Alkali treated.	10190 (± 596)	3.42	33131 (± 411)	238.1

For Cr (III), the treated bark showed a slight improvement in the retention capacity but the K_d values were relatively lower for the high concentration than the low concentration treatment. Such a low K_d value for Cr (III) adsorption indicates that the *Pinus* bark was not efficient for tannery effluent at high concentration. The data for Cr (VI) showed that there was no significant difference in the Cr retention between the untreated and alkali treated bark.

The difference in the K_d value between low and high concentration of Cr effluent may be due to competition with other heavy metals for adsorption sites on the *Pinus* bark. The presence of Cu and As with the Cr (VI) particularly at high concentrations in the timber treatment effluent competes for ion exchange sites. Although the absolute amount of heavy metal retention increased with increasing concentration, there was a marked difference in K_d values between Cr (III) and Cr (VI). In the case of Cr (III), the K_d values decreased with increasing concentration whereas for Cr (VI) the K_d value increased with an increase in the concentration of heavy metals.

4.4.1.3 Speciation of Cr adsorbed by the bark

The ability of activated aluminium oxide to adsorb Cr (VI) was examined using a standard Cr solution (Cr = 300 mg/L) containing different proportions of Cr (III) and Cr (VI). The concentration of Cr (III) remaining after treatment with activated aluminium oxide indicates that most of the Cr (VI) was removed by the activated aluminium oxide. The Cr measured after adsorption indicated nearly all the Cr (VI) has been adsorbed by the activated aluminium oxide (Table 4.4). There was only a small reduction (2-9 %) in Cr (III) concentration with the Al treatment.

Table 4.4 Speciation of Cr solution using activated aluminium oxide.

Proportion of Cr (III) : Cr (VI)	Concentration of Cr (VI) (μg/ml)		Concentration of Cr (III) (μg/ml)	
	Before Al treatment	After Al treatment	Before Al treatment	After Al treatment
A. 25 Cr (III) : 75 Cr (VI)	225	0	75	68
B. 50 Cr (III) : 50 Cr (VI)	150	0	150	146
C. 75 Cr (III) : 25 Cr (VI)	75	0	225	220

To identify the form of Cr remaining after adsorption by the bark, the following experiment was carried out. Adsorption of Cr (VI) at two concentrations by two particle size fractions of *Pinus* bark was examined. At the end of the adsorption, Cr in the equilibrium solution was speciated into Cr (III) and Cr (VI) forms. Although the input solution contained only Cr (VI), the equilibrium solution after adsorption contained both Cr (III) and Cr (VI). This indicates that Cr (VI) is presumed to be reduced to Cr (III) and adsorbed. This is similar to the process occurring in the timber treatment where Cr (VI) in CCA solution is adsorbed by the timber and gets reduced to Cr (III) (Forsyth and Morrell, 1990).

Table 4.5 Speciation of Cr (VI) solution which was treated with *Pinus* bark.

Input Cr (VI) concentration (mg/L)	*Pinus* bark size (μm)	Cr (VI) after adsorption (mg/L)	Cr (III) after speciation (mg/L)
2500	< 90	279 (± 54)	13.8 (± 2.3)
2500	355-500	663 (± 81)	72.2 (± 11)
3000	< 90	380 (± 32)	16.2 (± 3.6)
3000	2000	1860 (± 143)	718.4 (± 64)

The concentration of Cr in the equilibrium solution decreased with decreasing *Pinus* bark particle size. This is attributed to the greater adsorption of Cr by the finer *Pinus* bark material due to the larger surface area. The reduction of Cr (VI) to Cr (III) is likely to depend on the nature and size of *Pinus* bark. Generally, the rate of reduction of Cr (VI) to Cr (III) increases with decreasing particle size (Table 4.5).

4.4.2 Batch adsorption of Cu, Cr and As

4.4.2.1 Tannery effluent

Of the various materials used to retain Cr (III) in the batch adsorption experiment at high concentration, FBA was found to be the most effective in reducing the Cr (III) concentration (Figure 4.2). There was no significant difference between the untreated and both the acid and alkali treated *Pinus* bark materials. Of the natural resources used peat soil had a greater retention followed by the Egmont soil, the Tokomaru soil and Zeolite. *Pinus* bark and FGDG showed a low retention capacity.

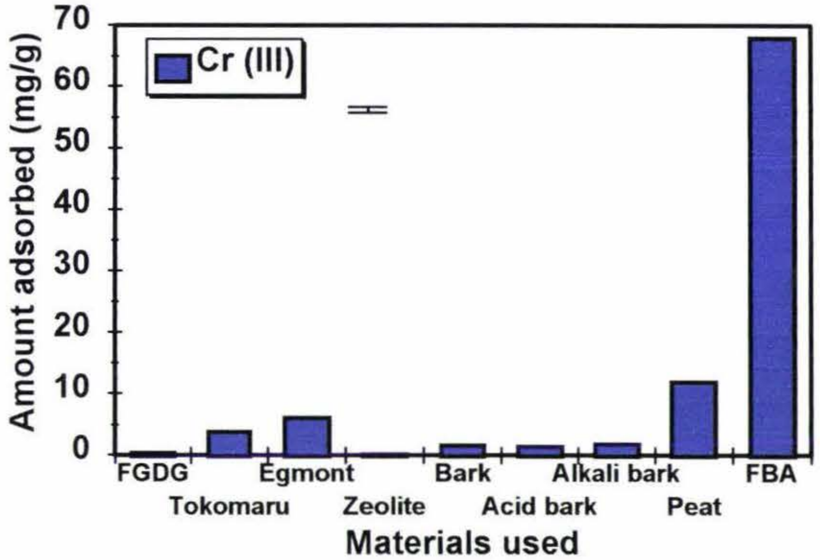


Figure 4.2 **Batch adsorption using various materials for Cr (III) in the tannery effluent (LSD =1.45 at p=0.05).**

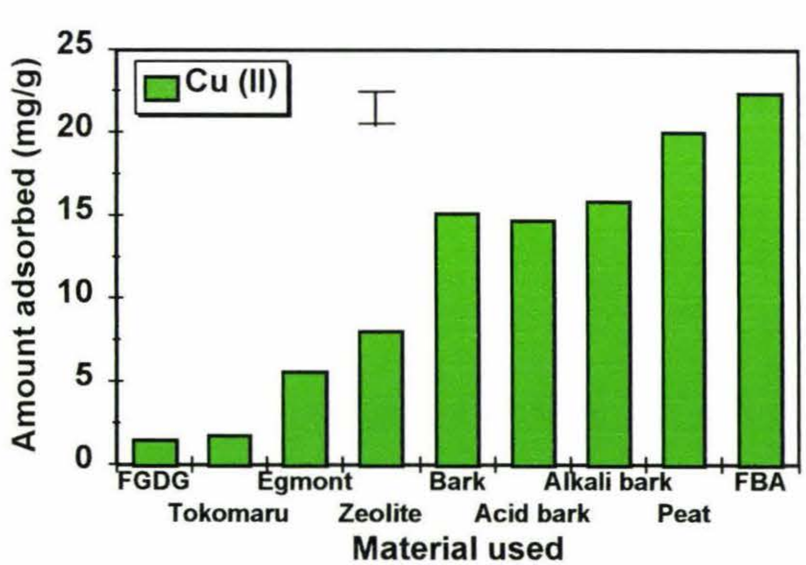


Figure 4.3 **Batch adsorption for various materials for Cu (II) in the timber treatment effluent (LSD =2.31 at p=0.05).**

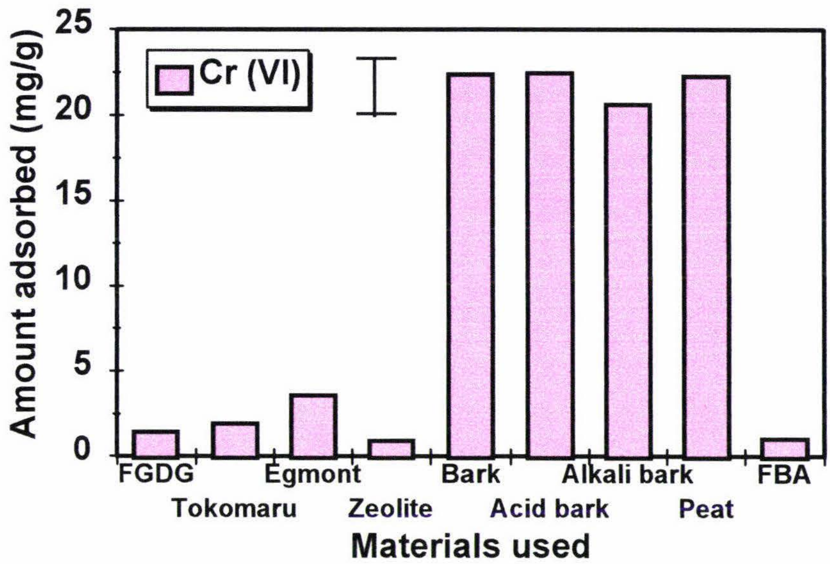


Figure 4.4 **Batch adsorption for various materials for Cr (VI) in the timber treatment effluent (LSD =2.96 at p=0.05).**

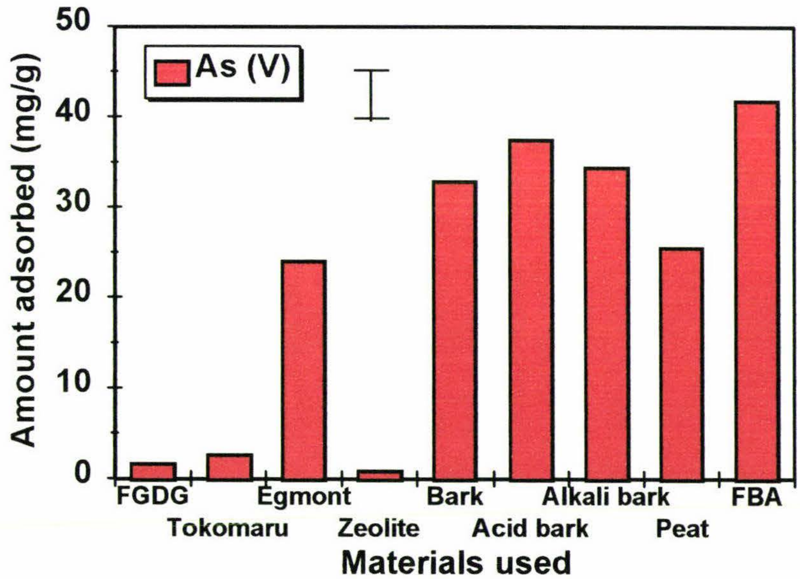


Figure 4.5 **Batch adsorption for various materials for As (V) in the timber treatment effluent (LSD =5.52 at p=0.05).**

4.4.2.2 Timber treatment effluent

The batch adsorption of Cu, Cr and As by various materials from the CCA solution is discussed below.

For Cu, FBA was the most effective in reducing the concentration of Cu in the timber treatment effluent followed by peat soil and *Pinus* bark (Figure 4.3). There was no significant difference between the treated and untreated *Pinus* bark. Zeolite and the the Egmont soils showed a greater Cu retention followed by the Tokomaru soil and FGDG.

For Cr (VI), *Pinus* bark was the most efficient in reducing Cr (VI) concentration followed by the peat soil (Figure. 4.4). There was no significant difference between the treated and untreated *Pinus* bark material. FBA, FGDG, zeolite, the Egmont and Tokomaru soils showed a low retention capacity of Cr (VI).

In the case of As (V), FBA was most efficient in reducing the As concentration in the timber treatment effluent followed by *Pinus* bark, peat soil and the Egmont soil. There was a significant difference between the untreated and acid *Pinus* bark. The acid treated *Pinus* bark showed an improvement in the retention capacity of As. Zeolite, the Tokomaru soil and FGDG showed a low retention of As (Figure. 4.5).

In general, the material which reduces the concentration of all the three elements will be the most efficient material for the treatment of timber treatment effluent. FBA was the most effective in reducing As and Cu but it retained only a low amount of Cr (VI). *Pinus* bark was effective in reducing As and Cu but showed a low retention capacity for Cr (VI). Considering the cumulative adsorption of all the three elements, *Pinus* bark, peat soil and FBA can be used in combination to reduce the Cu, Cr and As concentration of the timber treatment effluent (Figure. 4.6).

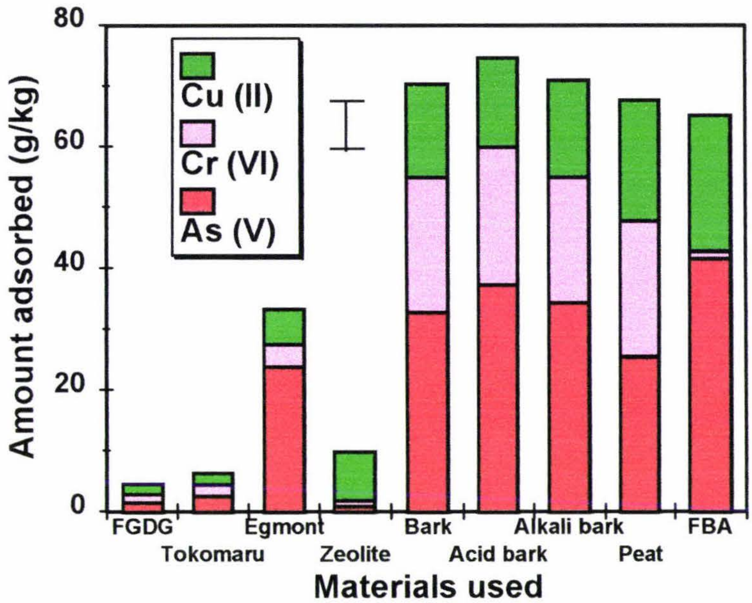


Figure 4.6 Cumulative adsorption by various materials for timber treatment effluent (LSD = 2.88 at p = 0.05).

4.4.2.3 Mechanism of heavy metal reduction in the effluents

Since FBA, *Pinus* bark and peat soil were the most effective materials in the retention of heavy metal from both the effluents, a detailed study of the mechanisms involved in the reduction of these heavy metals from the effluents was carried out.

A. Precipitation by FBA

Amongst all the treatments, FBA was the most effective for the removal of Cr (III) with a K_d value of 10486 cm^3/g . The major chemical components of the slaked FBA are gypsum and Ca $(OH)_2$ with a high pH of 12.1 (Wang *et. al.*, 1994). Chromium is likely to precipitate above pH 5.5 as Cr $(OH)_3$ (Rai *et. al.*, 1987). The pH of the FBA treated effluent was 9.62 which coincided with the effective precipitation range for Cr (III) as Cr $(OH)_3$. The increased retention of Cr (III) by the FBA is possibly due to the precipitation of Cr to insoluble Cr $(OH)_3$. To confirm this X-ray diffraction studies were conducted.

The reduction of Cu by FBA may be due to the precipitation of Cu as cupric hydroxide by Ca $(OH)_2$ and As in the form of calcium arsenate.

The x-ray diffraction patterns were obtained for Cr (III) treated FBA samples to identify the form in which Cr was precipitated after treating the tannery effluent with the FBA. It was not possible to identify the peaks for Cr $(OH)_3$ from the XRD pattern, instead the peaks for $CaSO_4.2\ H_2O$ (gypsum) and NaCl where found (Figure 4.7). The presence of $CaSO_4.2\ H_2O$ was from the FBA fraction and Na which occurs in tannery effluent is precipitated as NaCl. The absence of the peaks for Cr $(OH)_3$ may either be due to the low amounts of Cr $(OH)_3$ found or because of the amorphous nature of the precipitate.

B. *Pinus* bark retention

The mechanism by which Cr is retained in the *Pinus* bark is very similar to the process by which timber treatment is used to fix Cr (VI) onto the timber. The difference in Cr (VI) and Cr (III) retention can be well understood by studying the mechanism of fixation onto the bark (Refer to Section 2.3). Hexavelent Cr is more readily adsorbed by *Pinus* bark than the Cr (III). The reason for the difference in adsorption between the two species of Cr is because Cr (III) is adsorbed physically rather weakly to the cellulose whereas Cr (VI) is fixed chemically to the cellulose in bark (Pizzi, 1981). The hexavalent Cr is chemically adsorbed by the cellulose in the bark to form Cr (VI)/cellulose complexes, and later reduced to Cr (III). This two step process makes Cr (VI) fix chemically to the bark material (Pizzi, 1981). Thus the *Pinus* bark is more efficient in retention of Cr (VI) than Cr (III).

C. Peat soil retention

Peat soil was effective in reducing the heavy metal concentration from the effluents due to its high organic matter content. Heavy metals particularly Cu, Cr and As have been shown to be retained in the soil due to the organic matter fraction of the soil (Ulla and Fobian, 1990).

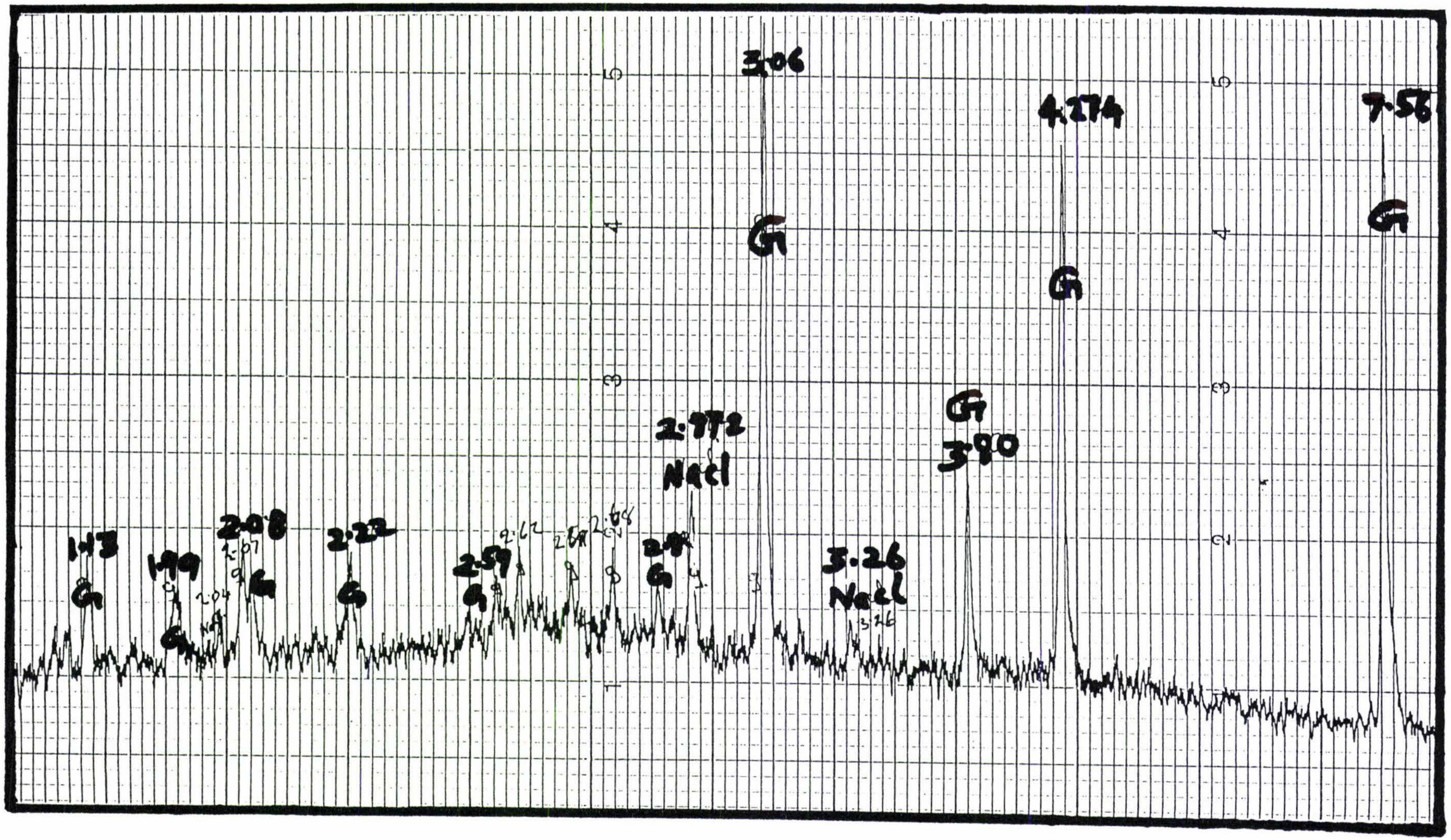


Figure 4.7 XRD pattern showing the peaks for gypsum -G - ($CaSO_4 . 2 H_2O$) and sodium chloride (NaCl).

4.4.3 Combination of materials - Batch adsorption

For tannery effluent as shown in Figure 4.8, the amount of Cr (III) retention increased with increasing amount of FBA in a mixture containing FBA + Peat or FBA + *Pinus* bark. At the 50 % FBA level, Peat + FBA retained a greater amount of Cr (III) than the Bark + Peat treatment; but at the 75 % FBA treatment both combinations retained almost similar amounts of Cr. Since there was no significant difference in the pH between the different mixtures (pH 7-8) the increase in adsorption of Cr with an increasing amount of FBA may be attributed to the increasing addition of $Ca(OH)_2$ and subsequent precipitation as $Cr(OH)_3$.

In the case of the timber treatment effluent, the retention of Cr (VI), increased with an increase in the amount of peat and *Pinus* bark in the mixture of FBA + Peat or FBA + *Pinus* bark (Figure 4.9). In contrast, higher proportion of FBA in the mixture of FBA + Peat or FBA + *Pinus* bark was effective in the retention of Cu and As.

For tannery effluent, a mixture of FBA + Peat or FBA + *Pinus* bark with high percentage of FBA should be suitable and for timber treatment effluent, use of both *Pinus* bark to reduce Cr (VI) concentration and FBA to reduce Cu and As concentration should be suitable.

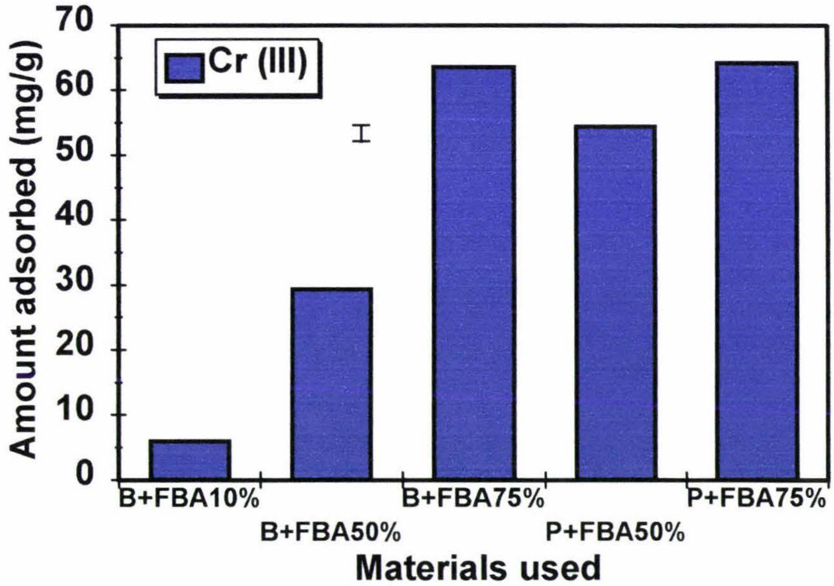
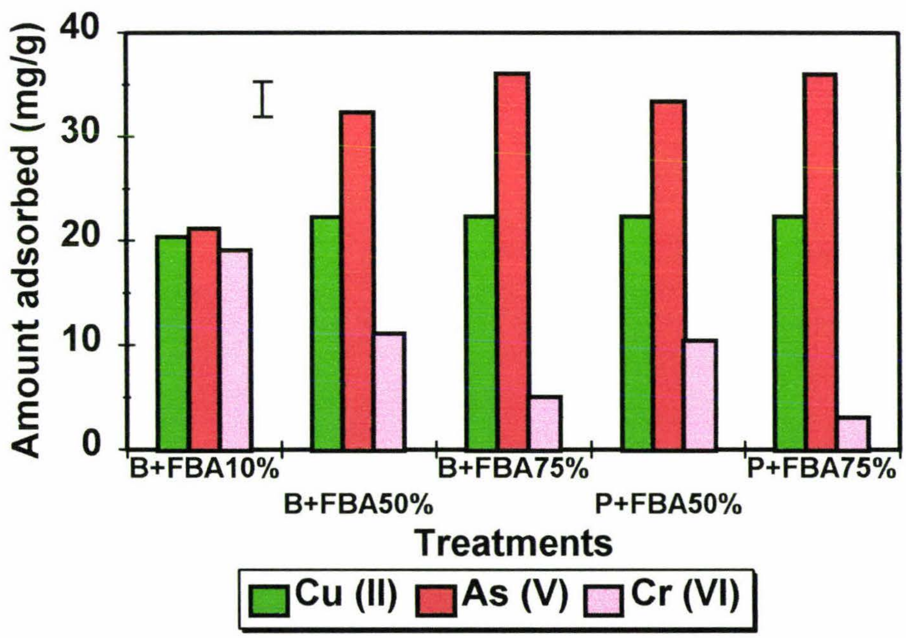


Figure 4.8 Batch adsorption using combination of effective materials for tannery effluent (LSD =2.47 at p=0.05).



* P - Peat soil ; B - *Pinus* bark.

Figure 4.9 Combination batch adsorption using various materials for timber treatment effluent (LSD = 3.92 at p = 0.05).

4.4.4 Adsorption isotherms for Cu, Cr and As

To find out the adsorption capacity of the effective materials, an adsorption isotherm was constructed for each of these materials. The adsorption isotherms were fitted to the Freundlich equation ($X = KC^{N}$) as explained in Section 4.4.1.1. Table 4.6 describes the adsorption data which were fitted to the Freundlich equation for Cr (III), Cr (VI), Cu and As.

4.4.4.1 Chromium (III)

Of the various effective materials used for the adsorption isotherms, FBA retained the highest amount of Cr (III), which involves a precipitation reaction. Usually it is not appropriate to include the precipitation reaction under an adsorption isotherm graph but to compare the efficiency between the various materials the precipitation of Cr (III) by FBA is included (Figure 4.10). The other materials which showed high adsorption were peat soil, which was significantly different from the other materials. The *Pinus* bark materials and the soil samples adsorbed low amounts of Cr (III), there was no significant difference between these materials.

4.4.4.2 Copper

FBA showed the maximum retention of Cu (II) followed by peat soil and *Pinus* bark. There was no significant difference between the untreated and acid/alkali treated bark. The other materials such as the Tokomaru and Egmont soils showed a poor retention, and were not significantly different from each other (Figure 4.11).

4.4.4.3 Chromium (VI)

Pinus bark and peat soil showed high adsorption of Cr (VI). Even though, the adsorption by alkali treated bark was higher than the untreated bark and the acid treated bark was lower than the untreated bark, there was no significant difference between the untreated and pre-treated bark. The Egmont soil, the Tokomaru soil,

Table 4.6 Freundlich equation describing the adsorption data for Cr (III), Cr (VI), Cu and As.

Materials used	Freundlich equation							
	Cr (III)		Cr (VI)		Cu		As	
	Equation*	R^2	Equation*	R^2	Equation*	R^2	Equation*	R^2
Untreated *Pinus* bark	$326{*}C^{0.21}$	96.6	$1691{*}C^{0.37}$	94.9	$1021{*}C^{0.41}$	86.2	$931{*}C^{0.71}$	76.3
Acid treated *Pinus* bark	$562{*}C^{0.29}$	85.8	$2354{*}C^{0.35}$	97.8	$848{*}C^{0.63}$	88.9	$1541{*}C^{0.81}$	84.7
Alkali treated *Pinus* bark	$606{*}C^{0.22}$	88.5	$1057{*}C^{0.42}$	91.6	$686{*}C^{0.59}$	94.3	$1094{*}C^{0.74}$	89.3
FBA	$31199{*}C^{0.11}$	97.6	$397{*}C^{0.23}$	96.1	$19990{*}C^{0.14}$	96.9	$21255{*}C^{0.12}$	98.4
Peat soil	$2869{*}C^{0.26}$	94.5	$1864{*}C^{0.36}$	93.2	$2939{*}C^{0.39}$	81.7	$892{*}C^{0.52}$	86.1
Tokomaru soil	$658{*}C^{0.23}$	82.1	$376{*}C^{0.22}$	98.2	$484{*}C^{0.25}$	80.5	$113{*}C^{0.44}$	88.6
Egmont soil	$515{*}C^{0.76}$	77.6	$529{*}C^{0.29}$	94.2	$2383{*}C^{0.21}$	97.8	$133{*}C^{0.76}$	71.8

*$X = KC^N$, Where K - Sorption at unit concentration ; X - Amount adsorbed (mg/g) ; C - Equilibrium concentration (mg/L) ; N - Slope.

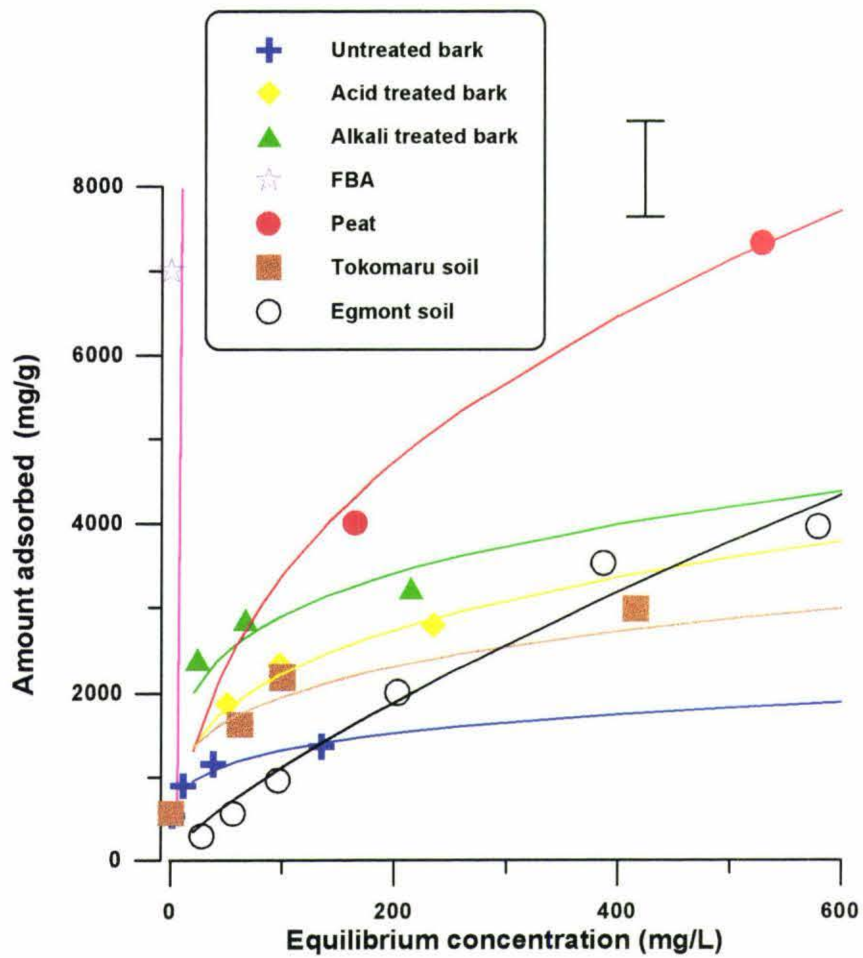


Figure 4.10 Adsorption isotherm of various effective materials for Cr (III) (LSD = 1112 at p = 0.05).

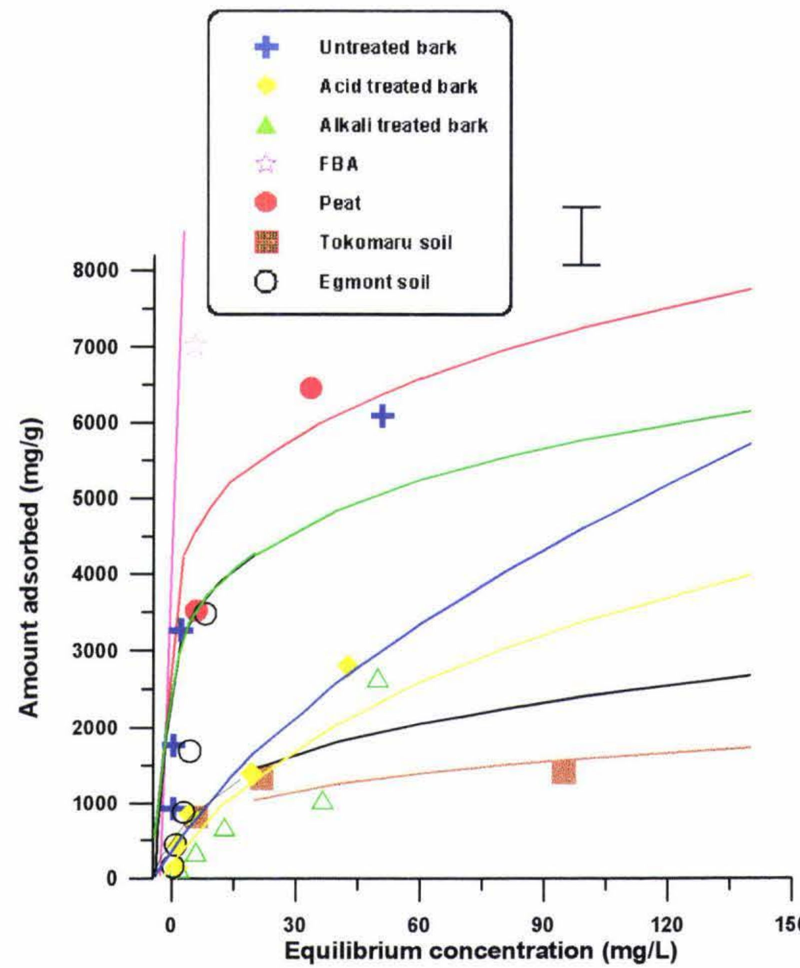


Figure 4.11 Adsorption isotherm of various effective materials for Cu (II) (LSD = 892 at p = 0.05).

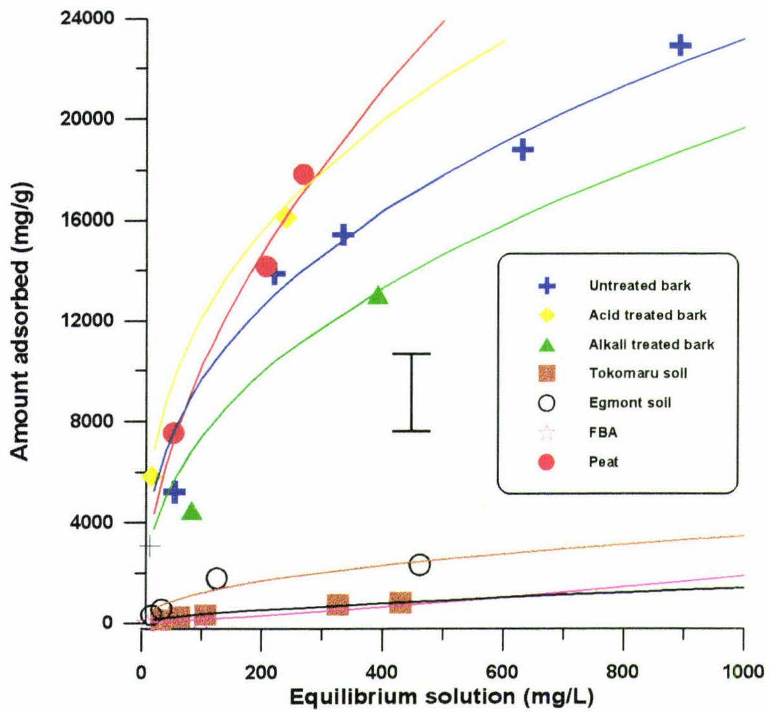


Figure 4.12 Adsorption isotherm of various effective materials for Cr (VI) (LSD = 2458 at p = 0.05).

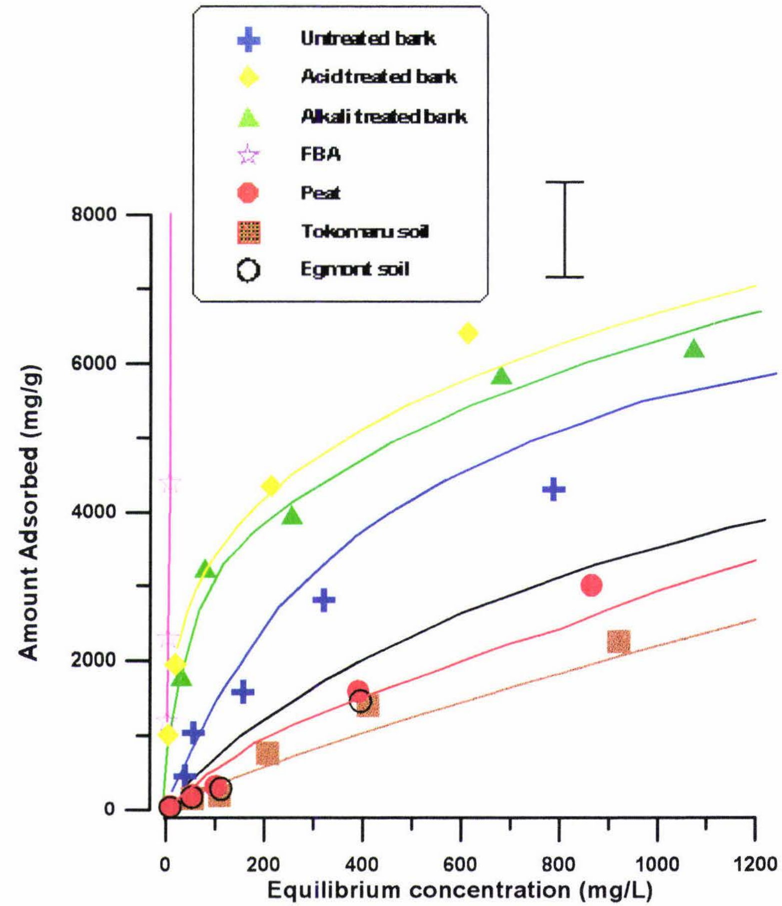


Figure 4.13 Adsorption isotherm of various materials for As (V) (LSD = 1344 at p = 0.05).

FGDG and FBA were not effective for Cr (VI) and showed saturation at very low concentration and were not significantly different from each other (Figure 4.12).

4.4.4.4 Arsenic

FBA was the most effective material and showed high retention of As (V) followed by *Pinus* bark. There was no significant difference between the untreated and the pre-treated bark. Other materials, such as the Egmont soil, the Tokomaro soil and the peat soil showed poor retention (Figure 4.13).

4.4.5 Leaching experiment for Cu, Cr and As

4.4.5.1 Tannery effluent

Of the different materials used for Cr (III) retention in the column leaching experiment for tannery effluent, 75 % FBA + 25 % Bark was the most effective in reducing Cr (III) concentration followed by the 50 % FBA + 50 % Bark column. The peat and bark columns were not effective in the retention of Cr (III) compared to the FBA column. The 100 % FBA was not successful as the tannery effluent was not able to pass through the column due to the solid cement like structure formed by FBA when contacted with effluent. This problem can be overcome by mixing FBA with porous materials such as bark or peat. These results were similar to those obtained in the batch experiment.

The Figure 4.14 shows the breakthrough curve which gives the relationship between the concentration of the leachate and the volume of the effluent leached. The concentration of Cr in the leachate from the peat and bark column reached the input concentration after 25 ml of leachate, but for the 50 % FBA + 50 % Bark column and 75 % FBA + 25 % Bark column reached saturation after 45 ml of leachate, showing a better efficiency. The reduction in the concentration of Cr (III) by the columns containing FBA is due to the precipitation of the Cr (III).

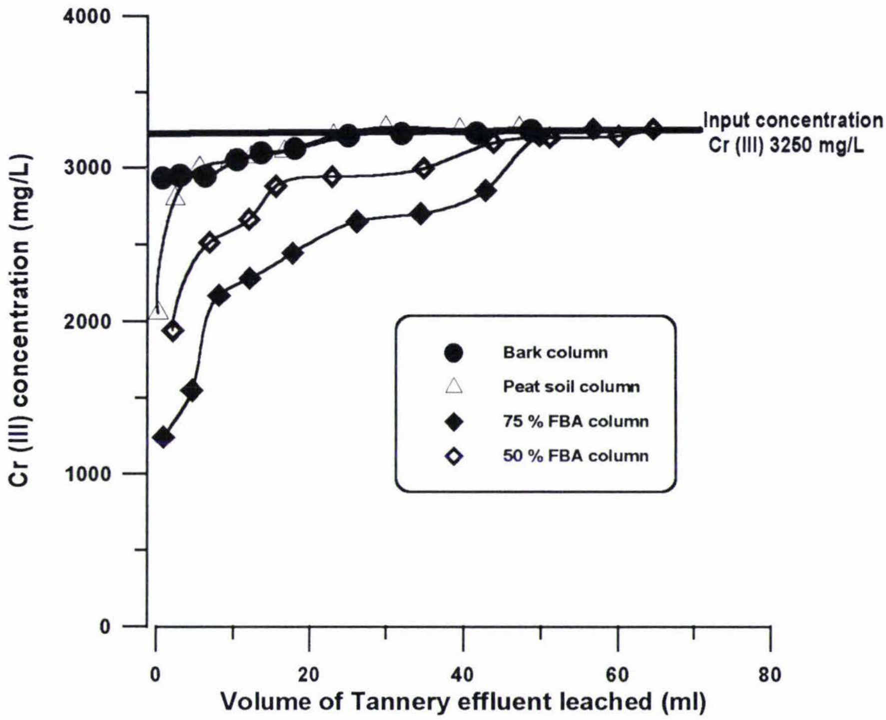


Figure 4.14 Breakthrough curves for Cr (III) in the tannery effluent.

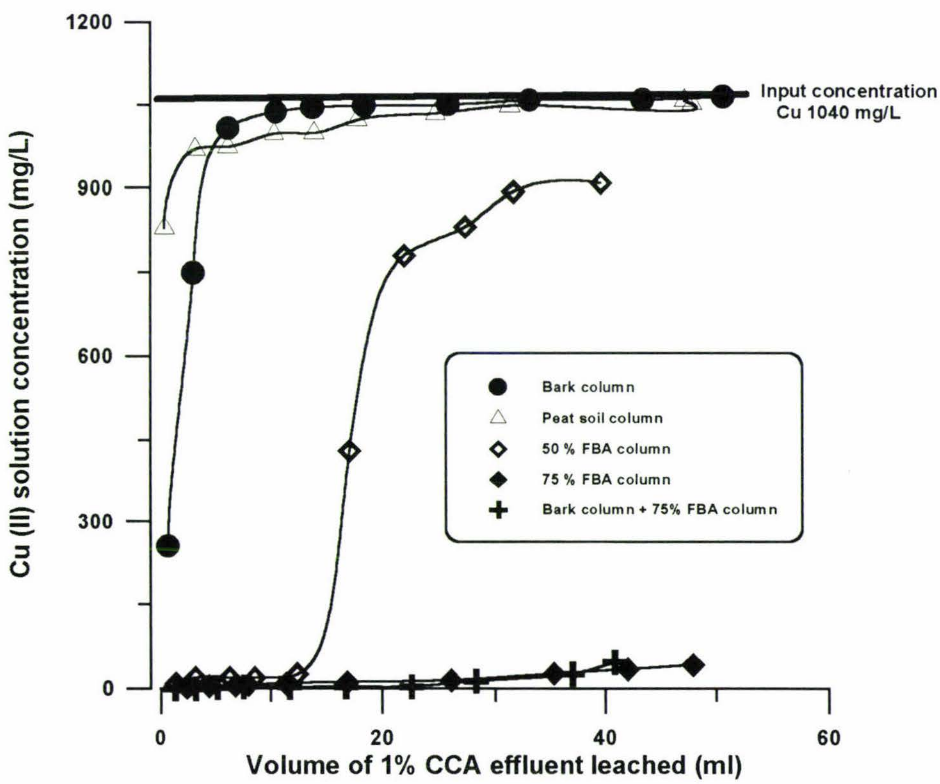


Figure 4.15 Breakthrough curves for Cu (II) in the timber treatment effluent.

4.4.5.2 Timber treatment effluent

Of the columns used for the retention of Cu, the double column (*Pinus* bark and 75 % FBA + 25 % bark) and the single column containing 75 % FBA + 25 % Bark were the most effective columns (Figure 4.15). The concentration of the leachate from these columns remained low (100 mg Cu/L) even after 40 ml of leachate were passed through. There was not much difference between the double column and 75 % FBA + 25 % Bark column for Cu retention but the double column remains effective in reducing the concentration of all the three elements from the CCA effluent. The 50 % FBA + 50 % Bark column showed better retention than the peat soil column and the bark column in which saturation was reached around 10 ml and 25 ml of leachate for the bark and peat column respectively. The reduction of Cu in the leachate by columns containing FBA is due to the precipitation of Cu as cupric hydroxide by the FBA. The *Pinus* bark and peat soil columns showed a reasonable adsorption but were not as effective as FBA in reducing the Cu concentration in the leachate.

For Cr (VI), the double column used was the most effective in the retention of Cr (VI) followed by the bark column. The *Pinus* bark column, although effective in the initial stage reached saturation within 25 ml of leachate (Figure 4.16). Comparing the results for all the three heavy metals present in CCA solution, the *Pinus* bark column was effective only for Cr (VI).

The As concentration in the leachate was reduced to a great extent by the double column followed by 75 % FBA + 25 % Bark, 50 % FBA + 50 % Bark, bark column and peat column. The concentration of As in the leachate of the double column was below 800 mg As/L after 40 ml of leachate (Figure 4.17). The reduction in As concentration is due to the precipitation of As as calcium arsenate and partial retention by the bark material. The leachate from the peat column reached saturation at less than 15 ml of leachate, showing a poor retention which confirms the batch experiment results.

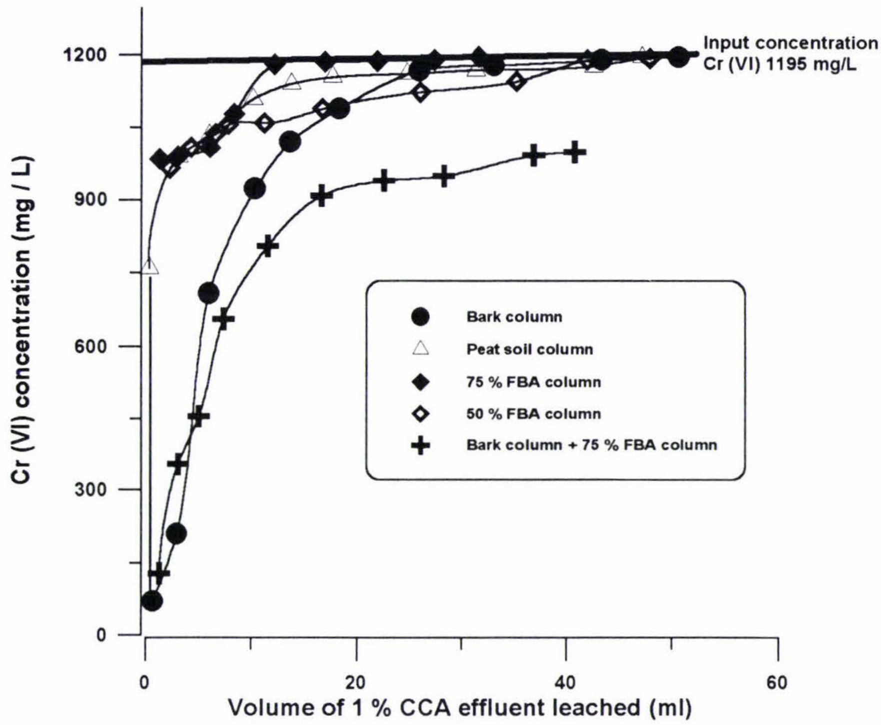


Figure 4.16 Breakthrough curve for Cr (VI) in the timber treatment effluent.

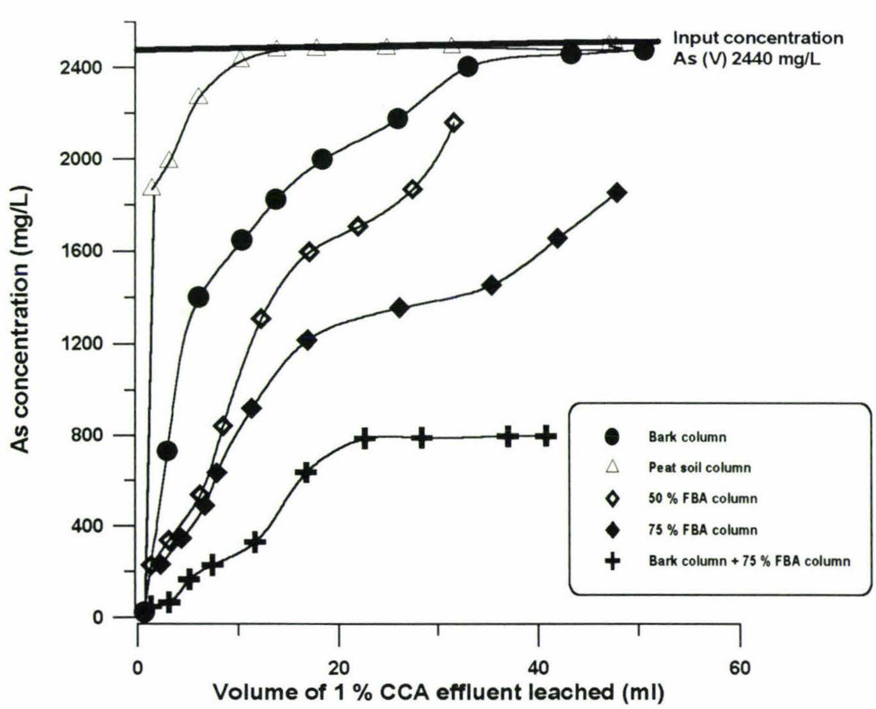


Figure 4.17 Breakthrough curve for As (V) in the timber treatment effluent.

In the double column, the amount of material is twice the amount of single column and therefore this factor also should be considered while comparing the effectiveness of the material between the single and the double column.

4.5 CONCLUSIONS

4.5.1 Tannery effluent

Of all the materials used, FBA was the most efficient for reducing Cr (III) concentration. The Cr (III) contaminated tannery effluents can be treated with FBA to reduce Cr concentration in the effluent before discharging into soils and waterways. Currently lime or magnesium oxide are used in some tanneries for the precipitation process. An alternative cheap waste material like FBA can be considered for the precipitation process.

The tannery effluent generated can be passed through a filter column containing materials which are effective in retaining Cr. FBA will be a very efficient filtering agent to reduce the Cr concentration in the tannery effluent. To facilitate easy flow of the effluent, the FBA can be mixed with *Pinus* bark or peat soil, which also retain Cr. The tannery effluent can be passed through a column filter containing 75 % FBA + 25 % *Pinus* bark and the filter column can be periodically changed with new material after the filter reaches a saturation.

The pre-treatment of the *Pinus* bark with acid, alkali and formaldehyde/acid has improved the retention of Cr only at low concentration (30 mg/L). At the original, high concentration of heavy metals, pre-treatment of bark was not efficient for retaining the Cr present in the tannery and timber treatment effluents.

4.5.2 Timber treatment effluent

FBA was efficient in reducing As and Cu concentration and *Pinus* bark was efficient in reducing Cr (VI) concentration of the timber treatment effluent. So a combination of both FBA + *Pinus* bark or FBA + peat soil may be efficient in reducing all the three heavy metal concentrations. The leachate passing through the filter must be periodically analysed for the heavy metal concentration and maintained below the guidelines set for the disposing the industrial effluent into soils and waterways. A further detailed pilot scale study is essential to examine the feasibility of this filter system.

In a timber treatment site, where freshly treated timber is dried, FBA + *Pinus* bark or FBA + Peat soil combinations can be spread. This should might absorb the heavy metal drips from the timber as well as preventing any possible heavy metal leaching through the soil into the groundwater. Further experiments, with these effective materials in immobilising heavy metals in contaminated soils will prove the practical applicability of these effective materials.

4.5.3 Disposal of the heavy metal retained materials

The entire experiment is aimed at concentrating the heavy metals onto a particular material such as FBA or *Pinus* bark or peat. These heavy metal enriched materials must be suitably treated to remove the heavy metals or be disposed off safely. For *Pinus* bark and peat soil, two ways of treatment can be considered, either to incinerate the bark material so that the heavy metals will be left out in the ash or leaching the bark with sulphuric acid to extract the heavy metal. For FBA, disposal into hazardous waste sites can be a viable option.

CHAPTER 5

IMMOBILISATION OF CHROMIUM IN CONTAMINATED SOIL

5.1 INTRODUCTION

Immobilisation of heavy metals in contaminated soils can be accomplished by adding natural or synthetic chemical additives to the soil. These additives must have certain desirable properties to successfully immobilise heavy metals in soil. The additives must be resistant to chemical and microbial degradation in the soil environment so that the heavy metals are not released from the additives over a long period of time. The additives must also be able to adsorb, complex, precipitate and/or chelate heavy metals and must not hydrolyse nor be desorbed under exposure to varying conditions in the soil, such as low pH or a varying redox conditions (Eh) which tends to solubilse the metals. For example, low Eh of soil causes reduction of Fe (III) to Fe (II) which is more soluble than the former resulting in an elevated concentration of Fe in the groundwater.

Various synthetic chemical additives, such as chelate ion exchange resin, cation exchange resin, hydrated lime, ferrous sulfate and silica gel and few natural resources, such as bentonite clay and greensand have been found to be effective in the immobilisation of a range of heavy metals (Czupyrna *et. al.*, 1989). Studies on reduction and immobilisation of Cr (VI) in the contaminated soil by organic amendments such as cow dung, bermuda grass and yeast extract have been examined (Cifuentes *et. al.*, 1996, Losi *et. al.*, 1994a).

In this experiment, we examined the potential value of cheap industrial wastes, such as *Pinus* bark and FBA to immobilise Cr in soils contaminated with industrial effluents. Results obtained in the previous batch and column leaching experiments (Chapter 4), indicated that among the various materials used, *Pinus* bark and FBA were found to be the most efficient materials in reducing Cr concentration in the tannery and timber treatment effluent. These materials were subsequently used in the experiment described in this chapter to immobilise Cr in the contaminated soil. The major chemical components of the FBA is Ca SO_4. $2H_2O$ and Ca $(OH)_2$ (Wang *et. al.*, 1994), which resembles the traditional lime used for immobilisation of heavy metals of heavy metals. To compare the effectiveness of FBA with the traditional lime, hydrated lime [Ca $(OH)_2$] was also used as a comparative immobilising agent.

For remediating Cr (VI) contaminated soil, recently a novel technique based on "Remediation-by-Reduction" strategies has been developed (James, 1996). This technique involves immobilisation of Cr (VI) in the contaminated soil by precipitating with lime after reducing Cr (VI) to Cr (III). Various factors affecting chemical and biological reduction of hexavalent Cr in soil have been studied (Losi *et. al.*, 1994b). In this experiment, no attempt was made to reduce Cr (VI) to reduce Cr (III) by adding reducing agents, because the behaviour of the different amendments on both the Cr (III) and Cr (VI) species in the contaminated soil was examined.

5.2 MATERIALS AND METHODS

A growth experiment was set up to investigate the potential to immobilise Cr (III) and Cr (VI) in the contaminated soils by using FBA, lime and *Pinus* bark amendment.

Soil samples were incubated with different Cr levels with chemicals used in the tannery and timber treatment industries. The soils were incubated artificially with Cr (III) and Cr (VI) salts because we were unable to obtain soils contaminated with Cr through the discharge of tannery and timber treatment effluents. No company was willing to provide us with contaminated soil sample. The "Cr contaminated soil" was later amended with FBA, lime and *Pinus* bark and phytotoxicity and bioavailablity of Cr was examined by a plant growth experiment. Triplicates of all the treatments were maintained.

5.2.1 Soil Cr levels

Manawatu silt loam soil was collected from the Massey Dairy No : 1, air dried and sieved to less than 1 mm diameter. The soils were then artificially contaminated using Cr solution in separate polyethylene bags for different Cr concentration. Soils were incubated with 300, 600, 1200, 3200 mg/kg of Cr (III) and Cr (VI) separately for a month. Chromium potassium sulphate and potassium dichromate were used to supply Cr (III) and Cr (VI) respectively. After incubation of the soil samples with Cr solution for a month, the soils treated with the following amendments.

5.2.2 Soil amendments

FBA and *Pinus* bark materials were selected from the results of the previous batch adsorption and column leaching experiments as the most effective materials for reducing the Cr concentration and hence used in immobilising Cr in the contaminated soil. Lime was also used as one of the amendments to compare the effectiveness of the FBA and *Pinus* bark with traditional lime amendment.

The levels of amendment were based on pH of the soil (soil pH raised to 8) for FBA and lime amended soils and 10 % w/w for *Pinus* bark amended soil. The traditional immobilisation of heavy metal contaminated soils by liming is carried out by raising the soil pH to 7 or higher (Alloway, 1995).

5.2.3 Plant used

Sunflower (*Helianthus annus* - gigantica) was used for the glasshouse trial to assess the toxicity and bioavalibility of different levels of soil Cr (III) and Cr (VI). Sunflower plant was selected due to its ability to tolerate high pH and salt concentration.

5.2.4 Pot experiment

After incubating the soils with various amendments, the unamended and amended soils were transferred to the plastic pots of 500 cm^3 capacity. About 7-8 sunflower seeds were sown in each pot, the seeds were sown to a depth of 1 mm of soil and covered with soil. The experiment was conducted in a glasshouse environment with ideal temperature of 20-25°C for the growth of sunflower. During the germination period the moisture was maintained at 80 % of the field capacity. Yellowing of leaves were observed in three weeks after sowing. This was due to lack of major and minor nutrients. After three weeks of sowing, nutrient solution containing all the major and minor nutrient elements were added. The nutrient solution was added at the rate of 60 ml/week for 6 weeks. The yellowing of leaves disappeared after two weeks time of adding nutrient solution. The moisture contents of the pots were maintained at field capacity until harvest. The location of the pots were randomly changed in regular intervals of 2 weeks to allow equal distribution of sunlight among various treatments. The plants were harvested before flowering on the 60th day after sowing.

The plant samples were harvested, washed and roots were separated from shoot. The leaves were seperated from the stem and the leaf area was measured using Licor Model 3100 Leaf Area Meter. The plant samples were air dried, ground and weighed. The Cr content of the shoot was analysed after digestion.

5.2.5 Plant analysis

The shoot samples of the plants were digested by dry ashing method and analysed for Cr uptake. Dry ashing of the plant samples was done using the following procedure. About 0.5 g of plant samples was ashed in glass test tube by combusting in an oven at 550°C for 12 hours. After cooling, the plant samples were removed from the oven and 5 ml of 2M HCl was added to the ashed plant sample and was heated to boil and mixed with a stirrer. The Cr content of the digest was measured using a Graphite-furnace AAS.

5.2.6 Soil analysis

5.2.6.1 Soil pH

The soil pH was measured using deionised water and 1M KCl at a soil : water ratio of 1 : 2.5. The soil suspension was equilibrated for 1 hour and the pH of the suspension was measured using a combined glass/reference and the pH of the supernatant solution was measured using a pH glass electrode.

5.2.6.2 Soil Cr sequential extraction

Soil samples from the growth experiment were sieved to less than 1 mm size and samples were stored at field-moist condition in polyethylene bags. Soil samples were kept at field-moist condition in order to minimise oxidation and/or reduction of Cr into different species. The results were expressed on an oven dry weight basis by determining moisture content of all samples.

Chromium contaminants in the soil are retained onto a variety of mineral and organic constituents. Remediation of Cr contaminated soil can be well understood by examining the amount of Cr held onto various components of soil. Sequential extraction of Cr, which is a series of chemical extractions, is performed to extract elements held onto different fractions of soil. Usually the first few steps of extraction tend to selectively target specific components of soil and later steps of the procedure are less specific and more rigorous and destructive (Beckett, 1989).

The procedure and type of extractants used in this study were adapted primarily from studies of Radmila and Janez (1995), Asikainen and Nikolaidis (1994), Radmila *et.al.*, (1992), and Bartlett (1991). The procedure was used to study the water soluble Cr, exchangeable Cr, organic bound Cr, Fe/Mn oxide bound Cr and residual Cr in the soil. In sequential extractions the weight of the soil residue in the centrifuge tubes before adding the extractant and after removing the extractant is noted, which gives the amount of entrain solution present. The Cr concentration in the entrain solution was corrected with the subsequent soil extracts.

A. Water soluble Cr and Cr (VI) in soil

James and Bartlett (1983) have recommended potassium-phosphate buffer as extractant for the water soluble fraction of metals bound to the soil because it contain PO_4^{-3}, which has shown to effectively compete with CrO_4^{-2} at exchange sites (Eary and Rai,1989), it contain a cation, K^+ which should be effective in displacing other exchangeable metals from the soil. Two grams of soil was shaken in an end-to-end shaker with 20ml of 0.015 M KH_2PO_4 for 2 hours in centrifuge tubes. The extractant solution was collected after centrifuging at 10,000 rpm for 10 min and filtered through Whatman No. 41 filter paper.

Hexavelant Cr present in the 0.015 M KH_2PO_4 extraction was measured by colorimetric method using azide reagent. Determination of Cr (VI) in the water soluble fraction was done by adding 1 ml azide reagent to 8 ml of water soluble extract. The mixture was allowed to stand for 20 min and the colour was compared with standard Cr solutions (0.5 to 50 μm) at 540 nm in a spectrophotometer. The azide reagent was prepared by adding 120 ml of 85% phosphoric acid, diluted with 280 ml of distilled water, to 0.4 g of s-diphenylcarbazide dissolved in 100 ml of 95 % ethanol (Bartlett, 1991). Total Cr present in the 0.015 M KH_2PO_4 extraction was measured by AAS. The difference between the total Cr and Cr (VI) will give the measure of Cr (III) in the water soluble fraction.

B. Exchangeable Cr

To measure the exchangeable Cr fraction in soil, 20 ml of 1 M ammonium chloride was added to the centrifuge tube containing the soil from which water soluble Cr has been extracted. The extractant was collected after 4 hours of shaking and centrifuging at 10,000 rpm for 10 min and analysed in AAS for exchangeable Cr.

C. Organic bound Cr

Sodium pyrophosphate ($Na_4P_2O_7$) can be used to extract organic fraction of Cr. Pyrophosphate has an advantage over many other reagents in that it is more specific to organic substances (Asikainen and Nikolaidis, 1994). 20 ml of 0.1 M $Na_4P_2O_7$ at pH 10 was added to the centrifuge containing the soil from which water soluble and exchangeable Cr have been extracted before and shaken for 16 hours. The extractant was collected after centrifuging at 10,000 rpm for 10 min and filtration and analysed in AAS for organic bound Cr.

D. Fe/Mn oxide bound Cr

Hydroxylamine hydrochloride ($NH_2OH.HCl$) is used to extract Cr bound to Fe/Mn oxides because it has an advantage of not adding a new potential reactive substances to the reaction mixtures. Reductants that are stronger than $NH_2OH.HCl$, such as sodium dithionite, often add sulfides, which would react with other substances (Asikainen and Nikolaidis, 1994). Extraction with 0.04 M NH_2 $OH.HCl$ in 25% v/v acetic acid at pH 2 was performed using the soil samples from which water soluble, exchangable, and organic Cr have been extracted before. The extractant was collected after 5 hours of shacking the soil with the extractant in an end-over-end shaker, centrifuging at 10,000 rpm for 10 min, filtration with Whatman No . 41 filter paper and was analysed for Fe/Mn oxide bound Cr in AAS.

E. Residual Cr

The last extraction involves refluxing the remaining soil residue with tri-acid mixture to extract the Cr remaining in the residue. The Tri-acid mixture consists of conc HNO_3 :

conc HCl: conc $HClO_3$ in the ratio of 5: 5: 7. This reagent is commonly used for the total elemental analysis of soil (Bolan and Hedley, 1987).

5.3 RESULTS AND DISCUSSION

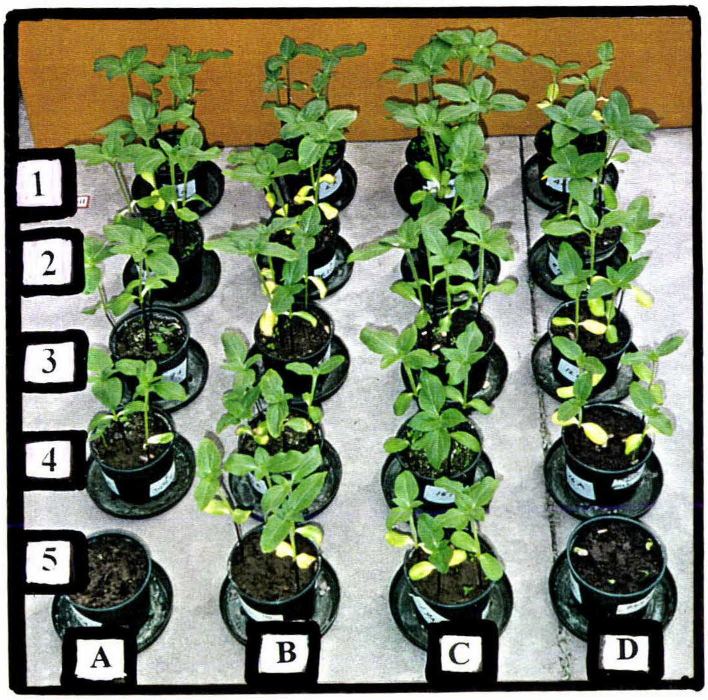
5.3.1 Plant growth

In general, there was a greater plant grown in the soils contaminated with Cr (III) than Cr (VI) (Plate 5.1 - plant growth after 18 days of sowing). These results were similar to the toxicity of Cr species examined on other plants such as paddy (Mishra *et. al.*, 1997), onion (Srivastava *et. al.*, 1994), soybean (Turner and Rust, 1971) and corn (Mortvedt and Giordano, 1975), which indicated that the plant yield was reduced in Cr (VI) treatments than that of Cr (III) treated soils. The difference in toxicity between Cr (III) and Cr (VI) may be due to the latter being more available in soil solution and more phytotoxic, where as the former is immobile, and mostly unavailable to plants (Bartlett and James, 1988).

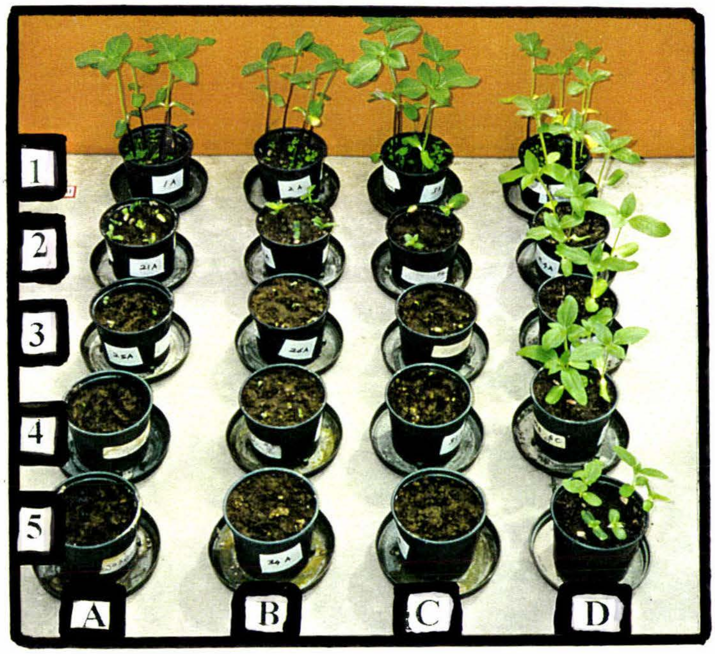
For Cr (III) contaminated soil, amending the soil with FBA and lime was effective in reducing the phytotoxicity, which is attributed due to the precipitation of Cr by FBA and lime. In the case of Cr (VI) contaminated soil, the bark treated soil alone was effective in maintaining normal plant growth. This is mainly due to the adsorption of Cr (VI) by bark resulting in less phytotoxic levels of Cr in the soil solution.

Plant growth in soils treated with either Cr (III) and Cr (VI) decreased with increasing amount of soil Cr concentration. Even in soil samples treated with various amendments, the plant growth decreased with increasing level of soil Cr but the decrease was much less than in the unamended soil.

Trivalent Cr contaminated soil



Hexavalent Cr contaminated soil



A - NO amendment C - LIME amended soil 1 - 0 mg Cr/kg 3 - 600 mg Cr/kg
B - FBA amended soil D - BARK amended soil 2 - 300 mg Cr/kg 4 - 1200 mg Cr/kg
5 - 3200 mg Cr/kg

Plate 5.1 Difference in the plant growth between Cr (III) and Cr (VI) contaminated soil.

5.3.1.1 Effect of soil Cr on germination

In soils where no Cr was added, germination was achieved within the normal duration of 8 to 10 days. In Cr contaminated soils, germination was delayed with increasing concentration of soil Cr and germination failed at high Cr soil. Similar adverse impacts on germination due to Cr were reported in other plants (Mukherji and Roy, 1977 ; Bishnoi *et. al.*, 1993 ; Rani *et. al.*, 1990).

A. Soil Cr (III)

In the unamended and bark amended soils, germination was slow with increasing levels of Cr (III) and there was no germination at the 3200 mg Cr/kg soil. FBA and lime amended soils showed complete and normal germination at all the Cr (III) levels including 3200 mg/kg, but the germination was delayed at high levels of soil Cr. The soil with 0 mg Cr/kg showed slower germination than the 300 mg Cr/kg soil, this may be due to the presence of potassium nutrient in the chromium potassium sulphate used. But this effect was not evident at higher Cr (III) concentration due to an increase in the phytotoxicity of Cr.

B. Soil Cr (VI)

In bark amended soil, germination occurred 8, 10 and 12 day after sowing for the 300, 600 and 1200 mg Cr/kg soil respectively. For unamended, lime and FBA amended soils the germination failed at 600, 1200 and 3200 mg Cr/kg soil levels and germination was delayed at the 300 mg Cr/kg and the seeds germinated after 15 days of sowing.

5.3.1.2 Effect of soil Cr on dry matter production

In general, Cr (III) contaminated soil was able to establish more dry matter than Cr (VI). This is attributed to Cr (VI) being more available in soil solution and more

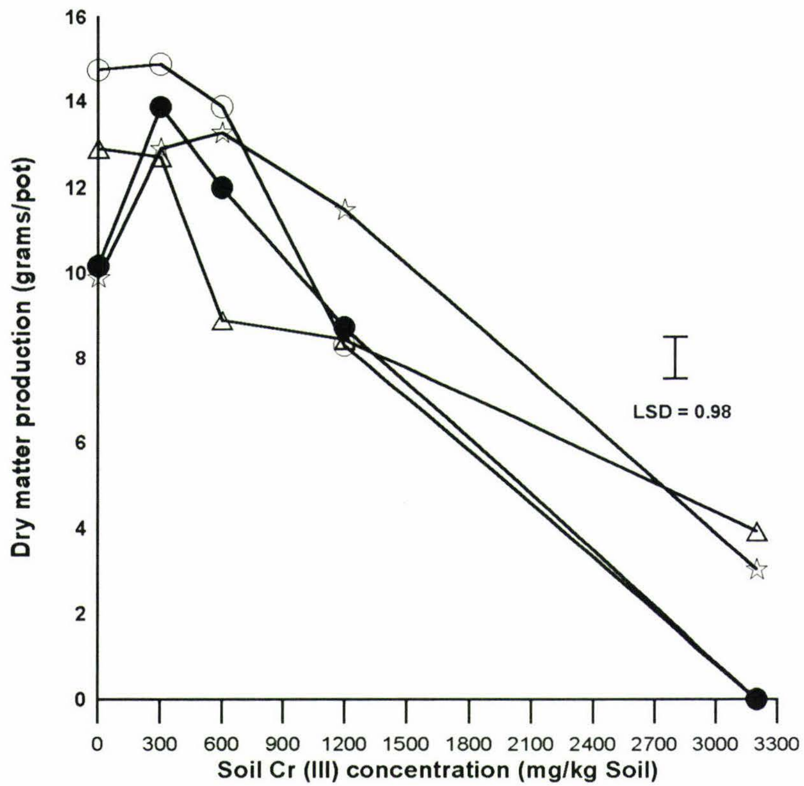


Fig. 5.1a - Cr (III)

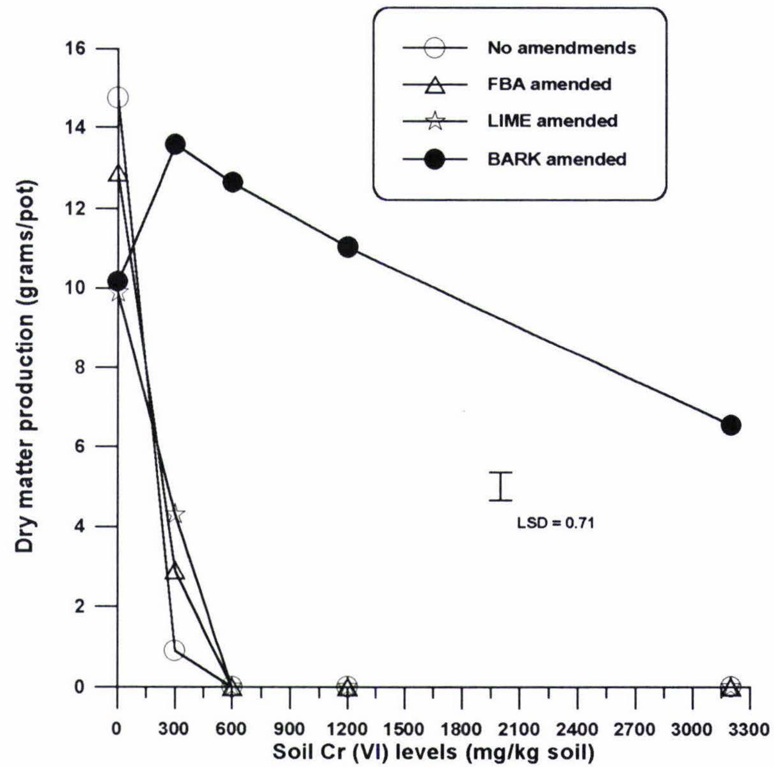


Fig. 5.1b - Cr (VI)

Figure 5.1 Effect of soil Cr on the dry matter production.

phytotoxic, where as the soil Cr (III) is less phytotoxic and mostly unavailable to plants (Bartlett and James, 1988). This was particularly evident at high Cr concentration.

A. Soil Cr (III)

The FBA and lime amended soils produced plant growth even at high concentration of 3200 mg Cr/kg, where as bark and unamended soils were unable to produce plant growth beyond 1200 mg Cr/kg levels (Figure 5.1a). Dry matter of the FBA treated soil dropped from 12.89 g at 0 mg/kg to 3.91g at 3200 mg Cr/kg of soil, for lime treated soil it dropped from 9.88 g at 0 mg/kg to 3.02 g at 3200 mg Cr/kg. The unamended soil showed no growth at 3200 mg Cr/kg of soil and caused a reduction in the dry matter from 14.74 g at 0 mg/kg to 8.43 g at 1200 mg Cr/kg soil. The reason for the growth failure at very high concentration may be due to the saturation of Cr (III) ions in the soil solution. Presence of excess Cr (III) in the soil solution has inhibited the plant growth at high concentration Cr soils.

B. Soil Cr (VI)

Only the bark amended soil was able to produce dry matter at all levels of Cr including 3200 mg Cr/kg soil, where as all the other treatments did not produce drymatter in Cr treatment beyond 600 mg Cr/kg soil. The bark amended soil was able to produce 6.53g of dry matter even at 3200 mg Cr/kg soil. This may be mainly due to adsorption of Cr (VI) by the bark material, thus reducing the phytotoxicity (Figure 5.1 b).

5.3.1.3 Effect of soil Cr on leaf area

A. Soil Cr (III)

The data for leaf area showed a similar trend to that of dry matter, FBA and lime treated soils were able to produce a leaf area of 270.4 and 259.3 m^2 respectively even at

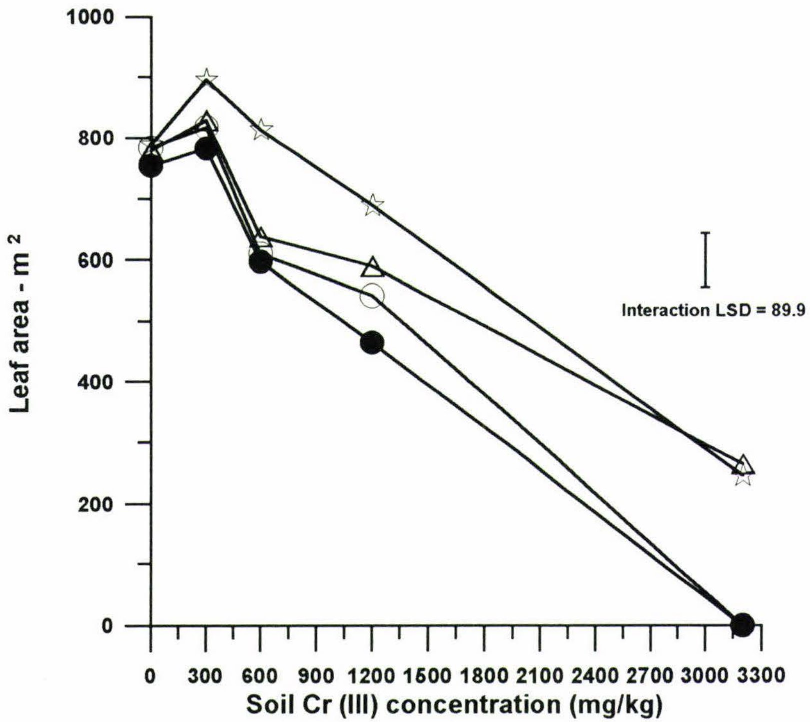


Fig. 5.2 a - Cr (III)

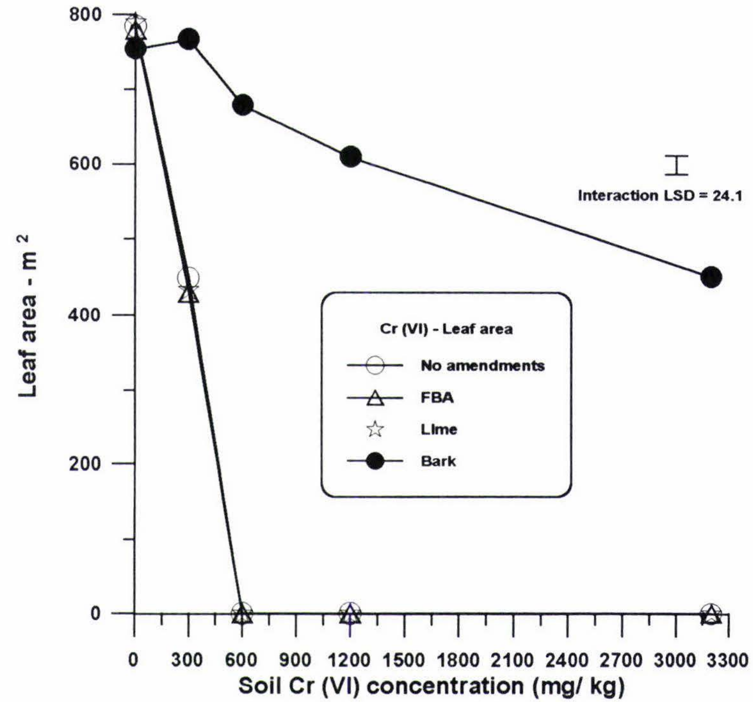


Fig. 5.2 b - Cr (VI)

Figure 5.2 Effect of soil Cr on leaf area.

3200 mg Cr/kg of soil. Unamended and bark amended soil were able to produce leaf area only for the first four levels (0 to 1200 mg Cr/kg soil). Leaf area of all the treatments decreased with increasing soil Cr concentration (Figure 5.2 a).

B. Soil Cr (VI)

The bark amended soil produced a leaf area of 754.8 m^2 at 0 mg Cr/kg soil and 431.7 at 3200 mg Cr/kg soil , where as all the other treatments were unable to produce leaf area above 300 mg Cr/kg (Figure 5.2 b). All the plant growth factors such as germination dry matter production, and leaf area shows a similar trend with increasing soil Cr toxicity. From the growth parameters we can conclude that FBA and lime can be used as amendments to immobilise Cr (III) in soil even upto 3200 mgCr/kg level. For Cr (VI) contaminated soil, bark alone seems to be effective in producing plant growth and it reduced the phytotoxicity of Cr (VI) even upto 3200 mg Cr/kg soil level.

5.3.2 Plant analysis

Chromium analysis in the plant samples (Figure 5.3) indicated that the FBA, lime and *Pinus* bark amended soils have reduced the Cr uptake by the plants. In the Cr (III) contaminated soil, FBA and lime amendments were effective in reducing the bioavailablity of Cr even at the soil Cr levels of 3200 mg/kg, whereas *Pinus* bark amendments was effective in reducing the Cr uptake until 1200 mg Cr/kg level. In the case of Cr (VI) contaminated soil, the *Pinus* bark amendment alone was able to reduce the bioavailable Cr and establish plant growth even upto 3200 mg Cr/kg level. Similar reduction of Cr uptake were observed in plants grown in Cr (VI) contaminated soil amended with cattle manure (Losi *et. al.*, 1994a). FBA, lime and unamended soils were not able to produce any plant growth. This is due to the presence of toxic Cr (VI) in soil solution inhibiting plant growth.

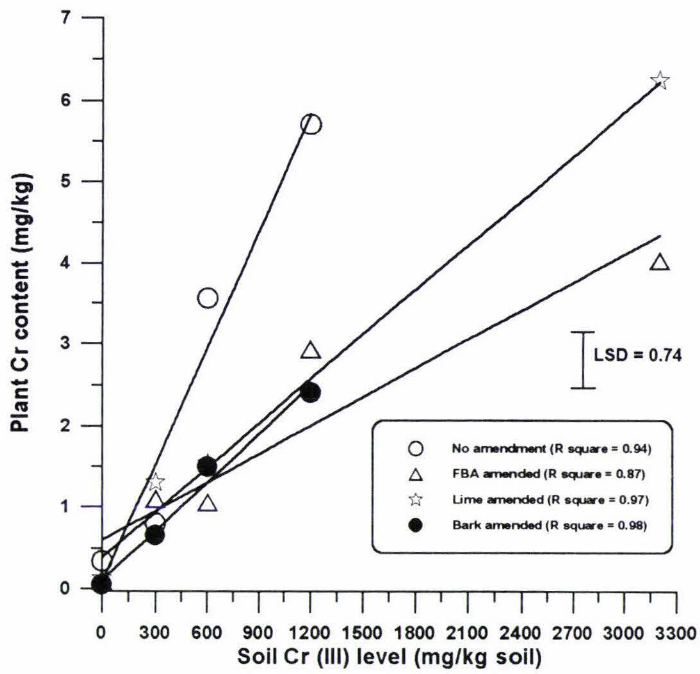


Fig. 5.3 a - Cr (III)

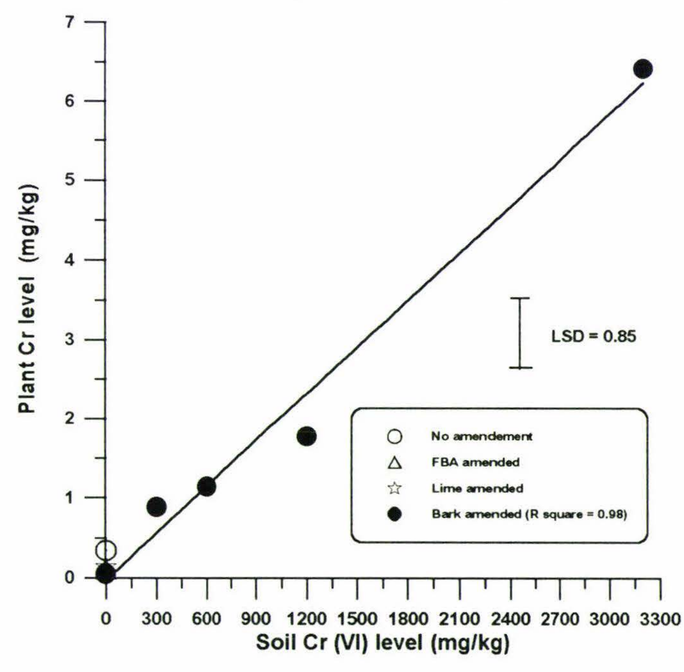


Fig. 5.3 b - Cr (VI)

Figure 5.3 Plant uptake of Cr grown on unamended and FBA, lime and *Pinus* bark amended soils.

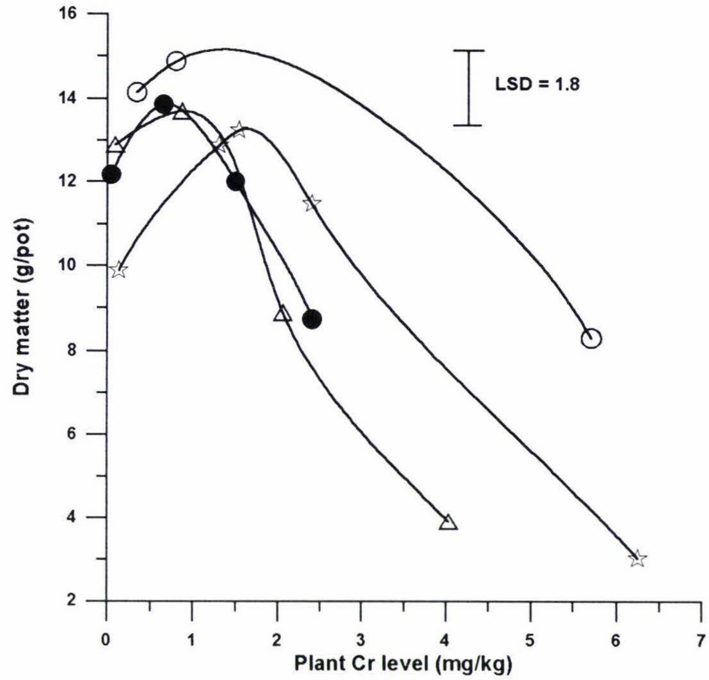


Fig. 5.4 a - Cr (III)

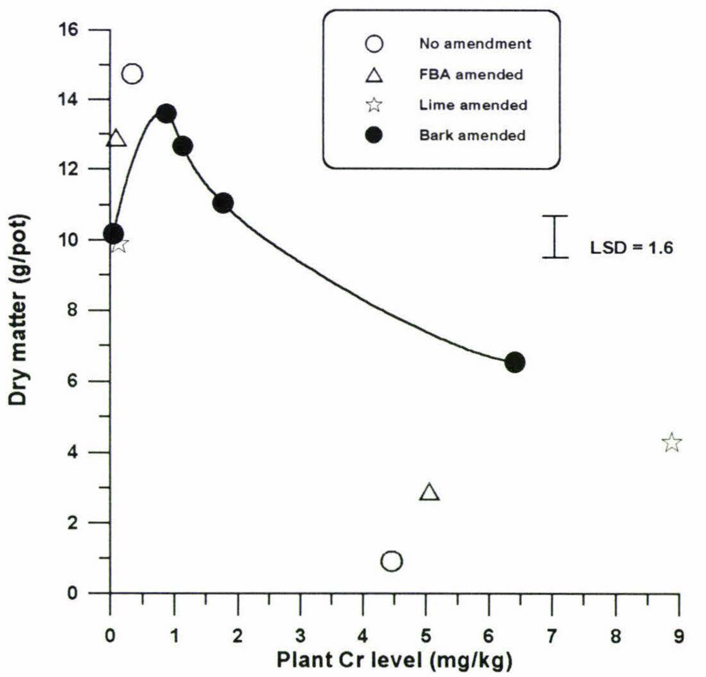


Fig. 5.4 b - Cr (VI)

Figure 5.4 **Relationship between plant Cr levels and dry matter production at varying levels of soil Cr grown on unamended and FBA, lime and bark amended soils (Except for the bark amended soil, there was no growth above the soil Cr(VI) level of 300 mg/kg in all the soils).**

Figure 5.4 gives the relationship between plant Cr uptake and dry matter production. For both the Cr (III) and Cr (VI) contaminated soils, generally there was a decrease in dry matter with increasing Cr content in plants. There was however slight increase in dry matter at the second Cr level (300mg Cr/kg) in both amended and unamended soil, which may be attributed due to the potassium added through chromium potassium sulphate and potassium dichromate used to supply Cr to the soils.

In general, the uptake of Cr by the plant was low, which are similar to the results of previous work, in which plants were grown in Cr (III), tannery waste or sewage sludge amended soil (Cunningham, *et. al.*, 1975). Comparision of Cr (III) and Cr (VI) uptake and translocation by paddy has been studied recently (Mishra *et. al.*, 1997). The phytotoxicity concentrations of Cr reported in other plants are as follows : 18-24 mg/kg in tobacco, 4-8 mg/kg in corn, and 10 mg/kg in barley seedlings (Alina and Hendryk, 1992). Figure 5.4 shows an approximate Cr threshold level of 4-6.5 mg/kg for *Helianthus annus*. To determine the exact threshold level for *Helianthus annus*, further examination with different concentration of soil Cr is needed.

5.3.3 Soil analysis

5.3.3.1 Effect of soil Cr on pH of the soil

A. Soil Cr (III)

The pH measured both in deionised water and KCl showed lower pH levels for KCl, which is mainly due to K^+ displacing the reserve pH. The pH of the soil decreased with increasing soil Cr (III) concentration for all the amendments. The FBA amended soil showed the least drop in pH from 7.81 to 7.33, where as the lime amended soil dropped more than 2 units of pH from 7. 84 to 5.58 (Figure 5.5 a). The bark amended soil dropped from 5.38 to 3.53 and unamended soil dropped from 5.64 to 3.56. Of all the treatments, FBA treated soil showed the most resistance to pH change with Cr addition.

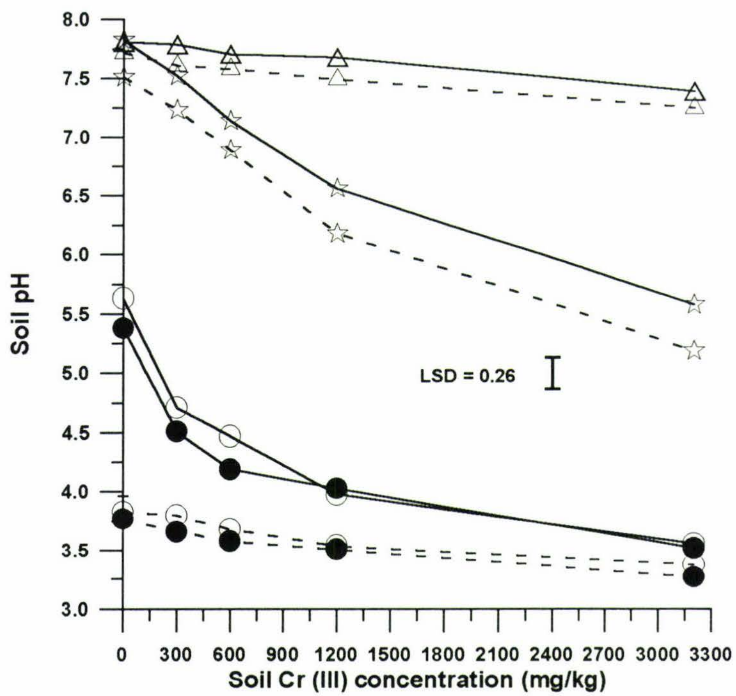


Fig. 5.5 a - Cr (III)

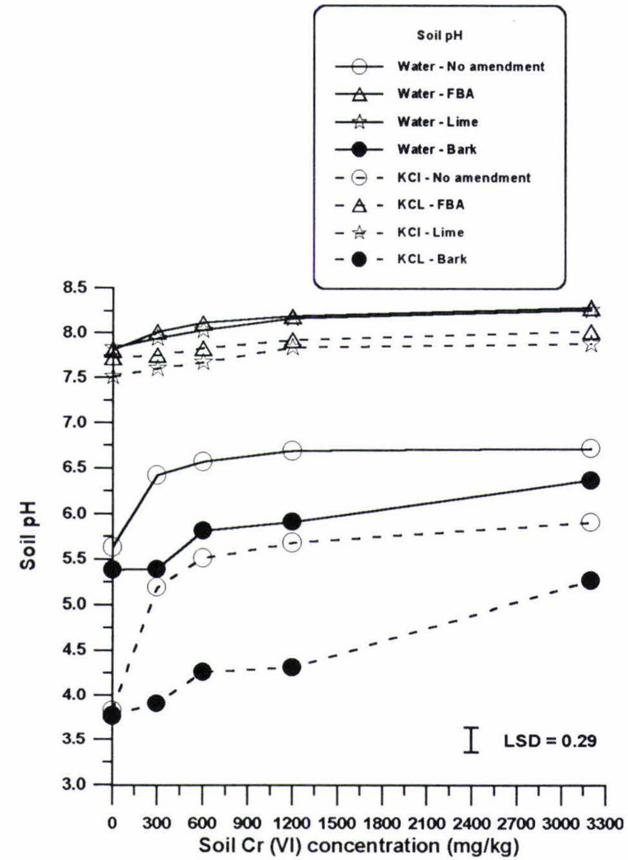


Fig. 5.5 b - Cr (VI)

Figure 5.5 **Effect of soil Cr addition on pH as measured in deionised water (- - - -) and KCl (__) for the various soil amendments.**

Grove and Ellis (1980), has previously reported the decrease in soil pH with the addition of Cr (III) salt and have proposed the following hypothesis for the decrease in soil pH :

$$Cr^{3+} + 6\,H_2O \rightleftharpoons Cr\,(H_2O)_6^{\;3+} \rightleftharpoons [Cr\,(OH)x\;\;(H_2 0)_{6\text{-}x}]^{\;3\text{-}x} + x\,H^+$$

This reaction is likely to act as a source of H^+ release in the Cr (III) contaminated soil, which tends to decrease the soil pH.

B. Soil Cr (VI)

The pH of the all the soils increased with increasing concentration of soil Cr (VI). Both the FBA and lime treated soil showed slight increase in pH from 7.81 to 8.29 and 7.84 to 8.09 respectively. The pH of the bark amended soil increased from 5.38 to 6.69. The unamended soil also showed a slight increase in the pH from 5.64 to 6.58 (Figure 5.5 b). Similar increase in soil pH was reported in Cr (VI) contaminated soil and the reason for the increase in soil pH was concluded due to the reduction reaction of Cr species, which involves the consumption of protons (H^+) (Grove and Ellis, 1980).

$$Cr_2\,O_7^{\;2-} + 14\,H^+ + 8\,e^- \longrightarrow 2\,Cr^{\;3+} + 7\,H_2O$$

The above reaction might be the reason for the increase in soil pH with Cr (VI) addition into the soil.

5.3.3.2 Soil Cr sequential extraction

The sequential extraction was used to identify and quantify the partitioning of Cr to various components of soil. The degree of remediation of soil contaminated with Cr depends on how strong the chemical bonds are between the various components of the soil and Cr. Sequential extraction also helps to elucidate the mechanism of various amendments in reducing the phytotoxicity and bioavailability of Cr in soil.

A. Soil Cr (III)

Among the various fractions of Cr (III), the exchangeable and water soluble Cr were high in the unamended and the bark amended soils (Table 5.1). The FBA and lime amended soil showed a low amount of water soluble and exchangeable Cr which may be due to precipitation of Cr by FBA and lime. Thus for the unamended soil and bark amended soil there is a risk of Cr movement into ground water, and the risk increases with increasing soil Cr concentration. Similar high concentration of water soluble and exchangeable Cr fraction were found in sandy soils, when compared with the soils with high organic matter (Radmila and Janez, 1995).

The organic Cr fraction was high in the bark amended soil followed by unamended soil (Figure 5.6). This is due to the retention of Cr by the bark and the organic matter in the bark amended and the unamended soils, respectively. In the FBA and lime amended soil, the Cr retained by the organic matter was relatively lower than that in the bark amended and unamended soil. This may be due to solubilisation of organic matter by FBA and lime at high pH and also due to the precipitation of most of Cr in the FBA and lime amended soil resulting in less Cr for retention onto organic matter. This is clearly evident from the presence of high amount of Cr in the residual fractions which included the precipitated Cr fraction in the FBA and lime amended soil. These results are similar to the high amount of Cr found in the residual fraction in the sequential extraction performed in the drilling fluid wastes soil where Cr was observed to be precipitated as insoluble chromium hydroxides (Ghode *et. al.*, 1995).

Figure 5.6 gives the effect of amendments on various fractions of Cr at two levels of soil Cr (III) (300 and 3200 mg/kg). The soil Cr at 300 mg/kg mostly tends to distribute in the organic, Fe/Mn oxide and residual fraction but as the soil Cr levels increase the Cr is mostly found in the residual portion. This is mainly due to the saturation of the organic and Fe/Mn oxide sites and therefore accumulate in the residual Cr fraction. FBA and lime amended soils are effective in precipitating soil Cr (III) levels and making them immobile and reducing the risk of groundwater pollution.

Table 5.1 Sequential extraction of soil Cr (III).

SOIL Cr (III) LEVELS	SOIL FRACTIONS					
	Water soluble	Exchan geable	Organic	Fe/Mn oxide	Residual	Total Cr
No amendment						
0 mg / kg	0	0	3.9	4.2	30	38
300 mg / kg	1.3	1.2	115	40	155	314
600 mg / kg	2.5	4.5	178	67	296	549
1200 mg / kg	4.3	12	279	121	557	988
3200 mg / kg	54	72	341	256	1488	2213
FBA amended						
0 mg / kg	0	0	4.1	2.9	28	35
300 mg / kg	0.1	0.7	120	58	145	325
600 mg / kg	0.6	1.3	217	111	307	638
1200 mg / kg	1.3	2.3	326	165	658	1153
3200 mg / kg	30	11	399	341	1642	2424
LIME amended						
0 mg / kg	0	0	7.2	4.9	35	48
300 mg / kg	0.3	1.1	111	39	183	335
600 mg / kg	0.6	3.5	182	79	331	598
1200 mg / kg	2.3	9.2	288	146	759	1206
3200 mg / kg	22	27	350	261	1719	2380
Bark amended						
0 mg / kg	0	0	4.5	4.5	27	36.5
300 mg / kg	0.6	2.8	151	38	131	325
600 mg / kg	0.4	4.7	231	69	251	557
1200 mg / kg	3.6	8.6	419	118	538	1088
3200 mg / kg	46	44	462	214	1097	1865
CV %	19	3.6	17	8.5	1.4	34
Interaction LSD	3.1	0.7	36	16	63	155

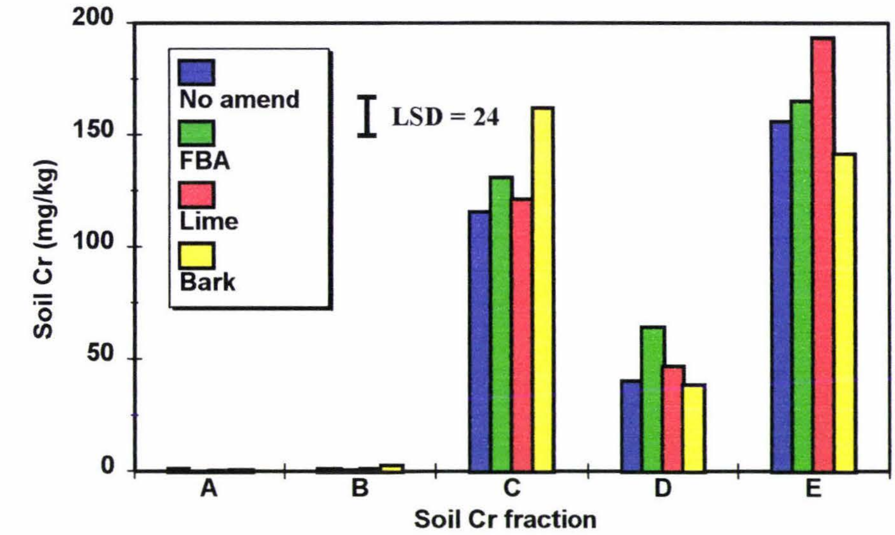


Fig 5.6 a Soil Cr (III) - 300 mg/kg

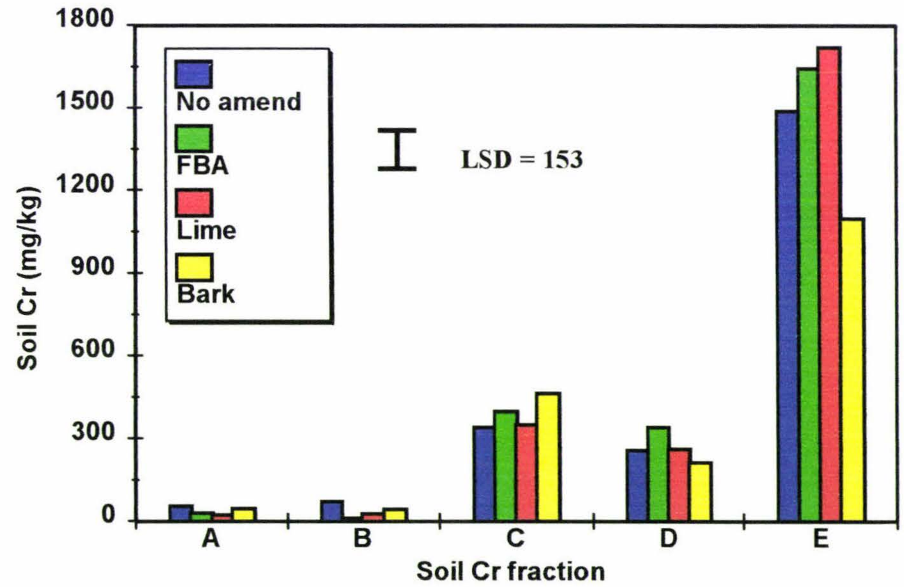


Fig 5.6 b Soil Cr (III) - 3200 mg/kg

A - Water soluble Cr B - Exchangable Cr C - Organic bound Cr
D - Fe/Mn oxide bound Cr E - Residual Cr

Figure 5.6 Comparison of sequential extraction of soil Cr at low (300 mg/kg) and high soil Cr (3200 mg/kg) levels in the Cr (III) contaminated soil.

The concentration of Cr (VI) was measured only in the water soluble fraction. Detectable levels of water soluble Cr (VI) were present only at high levels of Cr treatment (>600 mg/kg). No Cr (VI) was detected in the Cr (III) contaminated soil indicating that there was no evidence of oxidation of Cr (III) to Cr (VI) in these soils. The low levels of water soluble Cr (VI) in Cr (VI) contaminated soil may be mainly due to the leaching of Cr (VI) from the soil while watering the plants (Table. 5.2).

Table 5.2 Concentration of Cr (VI) in the water soluble fractions.

SOIL Cr LEVELS	SOIL Cr (VI) CONCENTRATION (mg/L)			
	No amend	**FBA soil**	**Lime soil**	**Bark soil**
Control (No Cr)	**0**	**0**	**0**	**0**
Cr (III) soil				
300 mg / kg	**0**	**0**	**0**	**0**
600 mg / kg	**0**	**0**	**0**	**0**
1200 mg / kg	**0**	**0**	**0**	**0**
3200 mg / kg	**0**	**0**	**0**	**0**
Cr (VI) soil				
300 mg / kg	**0**	**0**	**0**	**0**
600 mg / kg	**0.6**	**0.8**	**0.3**	**0**
1200 mg / kg	**10.5**	**6.2**	**8.2**	**0.2**
3200 mg / kg	**6.3**	**6.4**	**9.6**	**0.9**

B. Soil Cr (VI)

The amount of Cr present in the Cr (VI) contaminated soils was less than the Cr (III) contaminated soil. The loss of Cr (VI) added to soil may be mainly due to leaching, which was clearly evident from the presence of a yellow Cr (VI) solution at the base of the pots after watering the pots. The Cr (VI) remaining in soil is mostly reduced to Cr (III) by the organic matter present in the soil (Table 5.3), but as the soil Cr (VI) concentration increases there is not enough organic matter to reduce the Cr (VI) to Cr (III) and hence Cr remains as Cr (VI) particularly at the high Cr (VI) contaminated soil. Similar results with high amount of Cr (VI) was observed in soils amended with low organic matter than the high organic matter (Losi *et. al.*, 1994 a). Bartlett and Kimble, (1976) found that lack of soil organic matter could inhibit Cr (VI) reductions in soil.

Table 5.3 Sequential extraction of in the Cr (VI) contaminated soil.

SOIL Cr (VI) LEVELS	SOIL FRACTIONS					
	Water soluble	Exchangeable	Organic	Fe/Mn oxide	Residual	Total Cr
No amendment						
0 mg / kg	0	0	3.6	4.2	30	38
300 mg / kg	2.5	2.9	156	38	172	373
600 mg / kg	14	12	200	59	327	615
1200 mg / kg	18	57	234	117	654	1082
3200 mg / kg	76	185	253	208	1145	1869
FBA amended						
0 mg / kg	0	0	4.2	2.9	26	33
300 mg / kg	0.5	1.4	147	38	139	327
600 mg / kg	5.4	9.7	268	67	248	599
1200 mg / kg	12	36	190	145	544	929
3200 mg / kg	18	135	347	202	641	1346
LIME amended						
0 mg / kg	0	0	7.2	4.6	28	40
300 mg / kg	1.9	1.4	122	36	151	313
600 mg / kg	2.1	9.8	186	68	336	603
1200 mg / kg	3.1	36	379	136	589	1145
3200 mg / kg	26	135	587	195	651	1597
Bark amended						
0 mg / kg	0	0	4.5	4.9	28	37
300 mg / kg	1.8	1.5	94	35	150	284
600 mg / kg	2.5	1.6	138	50	336	529
1200 mg / kg	3.2	22	328	69	559	984
3200 mg / kg	27	129	424	95	659	1336
CV %	7.3	12	21	7.7	23	34
Interaction LSD	1.5	9.1	69	12	157	187

In the Cr (VI) contaminated soil, the exchangeable and the water soluble Cr (VI) were least in the bark amended soil and higher levels of Cr (VI) were found in the FBA and lime amended soil (Table 5.3). This may be due to the adsorption of Cr present in soil onto the bark material in the bark amended soil and precipitation of reduced Cr (III) by FBA and lime amended soils. High amount of Cr was found in the organic matter than in the Fe/Mn oxide fraction (Figure 5.7).

Bark amended soil was effective in reducing the phytotoxicity of Cr (VI) and establish a normal plant growth even at 3200 mg Cr/kg, but the effect of bark on sequential extraction of Cr (VI) was not evident as the bark fraction of the soil samples was separated from soil by sieving before soil analysis. But in general bark amended soil retained most of the Cr (VI) added to the soil resulting in less Cr present in the soil solution thus resulting in normal plant grown in the bark amended soil.

In general, the results of sequential Cr extraction indicated that major portion of Cr was held in the organic, Fe/Mn oxide and residual fractions. Similar results were shown in Cr fractionation study in tannery waste amended soil, where organic Cr (about 35%), Fe/Mn oxide (about 25%) and residual (about 20 %) were reported (Radmila and Janez, 1995). These soil fractions play an important role in the retention of majority of Cr (III) and Cr (VI) (Korte *et. al.*, 1976, James and Bartlett, 1983). In our experiment, residual Cr formed showed the highest Cr fraction, which are similar to the results of sequential extraction of Cr from the soils contaminated with drilling fluid wastes (Ghode *et.al.*, 1995).

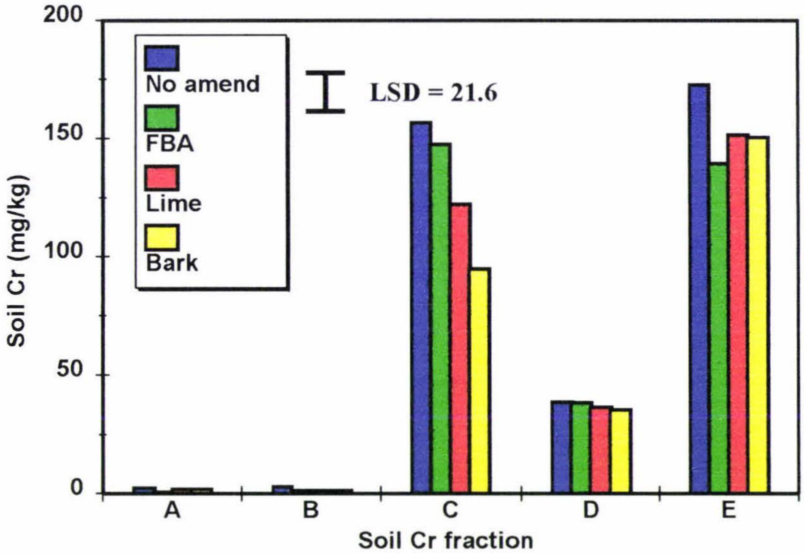


Fig 5.7 a Soil Cr (VI) - 300 mg/kg

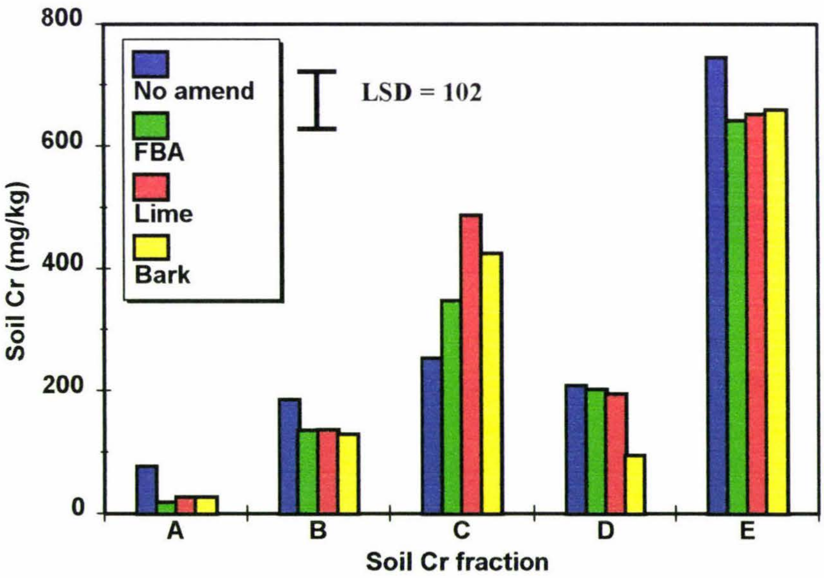


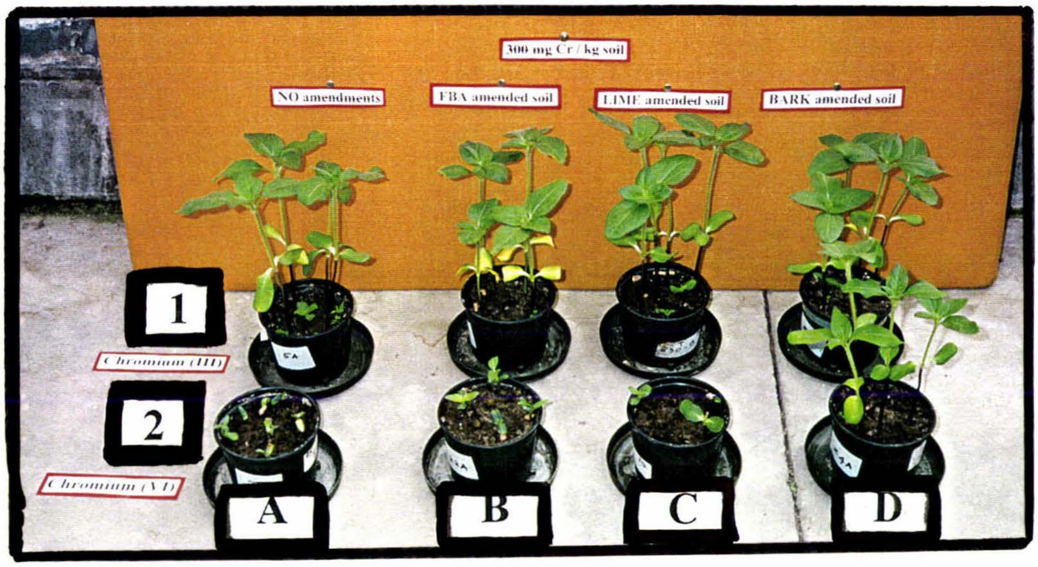
Figure 5.7 b Soil Cr (VI) - 3200 mg/kg

A - Water soluble Cr **B - Exchangeable Cr** **C - Organic bound Cr**

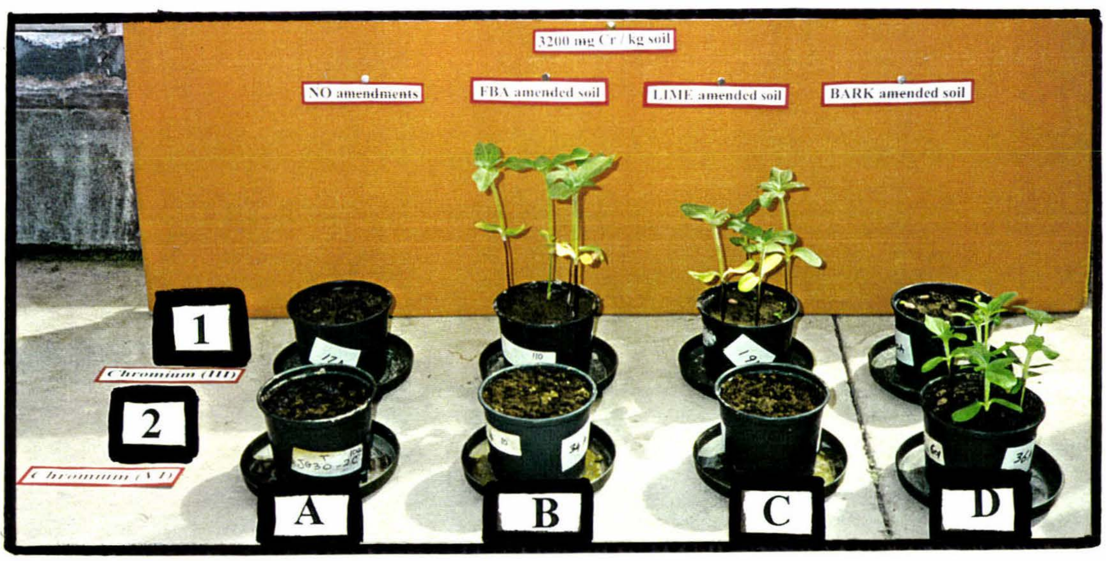
D - Fe/Mn oxide bound Cr **E - Residual Cr**

Figure 5.7 Comparison of sequential extraction of soil Cr at low (300 mg/kg) and high soil Cr (3200 mg/kg) levels in the Cr (VI) contaminated soil.

Low Cr soil (300 mg/kg)



High Cr soil (3200 mg/kg)



A - NO amendment
B - FBA amended soil
C - LIME amended soil
D - BARK amended soil
1 - Chromium (III)
2 - Chromium (VI)

Plate 5.2 Effect of FBA, lime and *Pinus* bark amended soil in remediating soils contaminated with low (300 mg/kg) and high (3200 mg/kg) Cr levels.

5.4 CONCLUSION

When comparing the Cr (III) and Cr (VI) contaminated soils, the former produced a better plant growth than the later, which is due to high phytoxicity of the Cr (VI). But the Cr (VI) contaminated soils when amended with *Pinus* bark were able to produce plant growth even at 3200 mg Cr/kg level. This was mainly due to the adsorption of Cr (VI) by the *Pinus* bark materials present in the amended soil. In the soil contaminated with Cr (III), FBA and lime amendments achieved an adequate plant growth even at 3200 mg/kg soil, but the unamended and bark amended soils were unable to produce plant growth at 3200 mg/kg soil (Plate 5.2 - plant growth after 18 days of sowing).

There was a decrease in dry matter production and increase in plant Cr with increasing level of soil Cr. The plant growth was very much reduced at plant Cr level of 4-6.5 mg/kg. FBA and lime amended soil were able to reduce the bioavailablity of Cr to plants and establish a normal plant growth in the Cr (III) contaminated soil, and in the Cr (VI) contaminated soil *Pinus* bark was effective in reducing the bioavailablity of Cr to plants.

To remediate a Cr contaminated soil by immobilisation technique, instead of using expensive chemical immobilising agents, cheap industrial waste materials, such as *Pinus* bark and FBA can be used. *Pinus* bark can be used in the immobilisation of Cr (VI) contaminated soil and FBA can be used as an equivalent to lime for the immobilisation of Cr (III) contaminated soil.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 LITERATURE REVIEW

- Heavy metal contamination of soil and waterways occurs due to the disposal of untreated industrial effluents, drips, leaks and spills of heavy metal contaminated working solution from tannery and timber treatment industries. Many reports of heavy metal contamination exceeding the legal threshold level are reported in New Zealand.

- In the case of tannery industry, although alternative tanning methods are available for tanning hides and skins, Chrome tanning seems to be the most preferred and widely practiced tanning process throughout the world. The only major disadvantage of Chrome tanning is the presence of Cr in the tannery effluent. Hence a pre-treatment of tannery effluent is required to reduce the high concentration of Cr before discharging into the soil or waterways.

- In timber treatment industry, the heavy metal soil pollution problem arises mainly due to the drips, leaks and spills due to poor handling of Copper-Chromium-Arsenic (CCA) solution while and after treating the timber. So proper collection and disposal of CCA effluent are essential while treating the timber and storing the freshly CCA treated timber. Remediation of CCA contaminated soils must be done to prevent the accumulation of toxic heavy metals in the soil and the movement of Cu, Cr and As into the groundwater.

6.2 CASE STUDIES

- The case studies examined for tannery industry, indicated that some tannery industries in New Zealand still have not developed pre-treatment practices to reduce the heavy metal concentration in the effluent before discharging into the soil or waterways. Pre-treatment of tannery effluent is essential to prevent high concentration of Cr entering the terrestrial and aquatic environment.

- The case studies carried out at the two timber treatment industries indicated that there was no major heavy metal pollution problem. This is attributed to the adaptation of proper treatment technologies by the timber treatment industries. Steam drying of freshly CCA treated timber before storing on the soil surface is one of the pollution prevention technologies adapted by Carter Holt Harvey Timber treatment industry in Martin. But many CCA contaminated sites are reported in New Zealand and remediation of CCA contaminated sites is essential to prevent the pollution of groundwater with the toxic heavy metals.

6.3 REDUCTION OF HEAVY METAL CONCENTRATION FROM THE TANNERY AND TIMBER TREATMENT EFFLUENTS

- Various methods and materials are used for the reduction of Cu, Cr and As from tannery and timber treatment effluents. Although many methods involving synthetic chemical materials are available for treatment, precipitation method using materials such as lime, caustic soda or magnesium oxide is practiced widely to reduce Cu, Cr and As concentration from the industrial effluent.

- In this project, alternative cheap methods to reduce Cu, Cr and As concentration in the tannery and timber treatment effluents were examined. The potential value of industrial waste material and cheap natural resources was considered for treating the tannery and timber treatment effluents. By this method, reuse of industrial waste is also achieved apart from reducing the heavy metal concentration in the effluents.

- Amongst the various materials used, fluidised bed boiler ash (FBA) was the most efficient material for reducing the Cr (III) concentration from tannery effluent and As and Cu concentration in the timber treatment effluent. *Pinus radiata* bark and peat soil were efficient in reducing Cr (VI) concentration of the timber treatment effluent. A combination of both FBA + *Pinus* bark or FBA + peat soil was efficient in reducing all the three heavy metal (Cu, Cr (VI) and As) concentration from the timber treatment effluent.

- The precipitation of Cr (III) to insoluble chromium hydroxide, Cu as cupric hydroxide and As as calcium arsenate was the main mechanism involved in reducing the heavy metal concentration from the effluent by FBA. *Pinus* bark and peat soil reduce the heavy metal concentration by chemical adsorption.

- Pre-treatment of *Pinus* bark with acid, alkali of formaldehyde/acid was attempted to increase the heavy metal retention capacity of the *Pinus* bark. The results indicate that the pre-treatments were effective in the retention of heavy metals only at low heavy metal concentration and did not significantly improve the heavy metal retention at high heavy metal concentration.

- In tannery industries, pre-treatment of Cr contaminated effluent can be achieved using a "FBA-Bark Filter system" i.e., the tannery effluent generated can be passed through a filter column containing FBA. To facilitate easy flow of the effluent, the FBA can be mixed with *Pinus* bark or peat soil which also retains Cr. The tannery effluent can be passed through a filter column containing 75 % FBA + 25 % Pinus bark and the filter column can be periodically changed with new material after the filter reaches a saturation.

- A most commonly practiced method to reduce the Cr concentration in tannery effluent is using "Precipitation tank" where, precipitating agents such as lime or magnesium oxide is used. FBA can be considered as an alternative cheap precipitating agent.

- In the case of the timber treatment system, the effluent disposal is not a major issue because timber treated CCA solution is recycled in a closed chamber. But a major heavy metal pollution occurs mainly due to the drips and leakage of the CCA solution at the storage site. Remediation of CCA contaminated sites can be achieved by using FBA or *Pinus* bark or peat soil.

6.4 IMMOBILISATION OF CHROMIUM IN CONTAMINATED SOIL

- A growth experiment using sun flower (*Helianthus annus*) was conducted to examine the efficiency of FBA, lime and *Pinus* bark to remediate Cr (III) and Cr (VI) contaminated soil. FBA and lime amendments were effective in establishing a normal plant growth in Cr (III) contaminated soil even at high Cr (III) (3200 mg Cr (III)/kg soil). Incorporation of lime or FBA in Cr (III) contaminated soils causes the precipitation of Cr and thereby reduces the bioavailabilty of Cr for plants uptake.

- Only *Pinus* bark was found to be effective in for remediating Cr (VI) contaminated soil even at 3200 mg Cr (VI)/kg soil. Pinus bark adsorb Cr (VI) anions from soil solution. Also the bark materials induce the reduction of Cr (VI) to Cr (III) and subsequently retain Cr (III) cations. This is likely to result in the reduction of the bioavailability Cr (VI) for plant uptake.

6.5 RECOMMENDATIONS FOR FUTURE WORK

- Further pilot scale study of using FBA or *Pinus* bark or peat soil to reduce the Cu, Cr and As concentration in the effluent is required to assess the feasibility of these material in remediating heavy metal contamination in practical situations.

- In our project immobilisation of Cr contaminated soil alone was examined, further study on remediation of Cu and As contaminated soil using FBA or *Pinus* bark is required.

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