REMOVAL OF CHROMIUM FROM TANNERY WASTE WATER USING NON AGRICULTURAL WASTES

M.Phil. Thesis

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SUBMITTED BY

A.B.M. Wahid Murad
Registration No. 099
Session: 2012-2013
Department of Applied chemistry
&
Chemical Engineering

UNIVERSITY OF DHAKA
Dhaka, Bangladesh
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CERTIFICATION

This is to certify that this thesis paper titled "Removal of Chromium from Tannery Waste Water Using Non Agricultural Wastes" is carried out under direct supervision of myself for the requirement of partial fulfillment for the degree of Master of Philosophy (M.Phil.) in Applied Chemistry and Chemical Engineering at University of Dhaka.

(Supervisor)

Dr. Md. Nurul Amin
Professor and Chairman
Department of Applied Chemistry and Chemical Engineering
Faculty of Engineering and Technology
University of Dhaka

DEDICATED TO MY BELOVED PARENTS

DECLARATION OF THE CANDIDATE

I do hereby declare that the thesis paper submitted as partial fulfillment for the degree of Master of Philosophy (M.Phil.) in Applied Chemistry and Chemical Engineering at University of Dhaka is the result of my own investigation. The present study work is original and has not been submitted for publishing in partially or fully or for any other degree also.

Signature of the Candidate:

....
A.B.M. Wahid Murad
Registration No. 099
Session: 2012-2013

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(A.B.M. Wahid Murad)

ABSTRACT

The removal of Cr (III) from aqueous solutions by batch adsorption technique using different low cost adsorbents was investigated. The objective of the study was to find out a suitable low cost, available, environmental friendly and highly effective adsorbent and minimization of pollution. In the present study different low cost adsorbents of non agricultural origin such as Plastic, Rubber, Hen hair, Sheep wool, Newspaper, Activated bone carbon, Goat skin trimmings, Brick powder, Concrete and Packaging (Corrugated box) boxes have been studied. Of these, Newspaper and Packaging box (Corrugated box) were found to be the most efficient adsorbents. The influences of pH, adsorbent dose, initial adsorbate concentration, contact time and particle sizes were studied. The physico-chemical properties of Newspaper and Packaging box were studied using different characterization techniques such FTIR, Langmuir adsorption isotherm, Freundlich adsorption isotherm and kinetics of the adsorption process.

The basic data obtained were interpreted kinetically using first order rate kinetics. In the case of Newspaper and Packaging box the kinetics followed first order rate equation. Experimental data for all the adsorbents were fitted to different isotherm models such as Freundlich and Langmuir isotherm. Newspaper and Packaging box were observed to be the most effective among all the selected adsorbents for the removal of Cr (III) from aqueous solution. Therefore, all further studies were carried out using these two adsorbents only. Since all adsorbents were porous in nature, it was assumed that the adsorption process might follow surface or intra-particle diffusion or both. In both the cases, the mass transfer coefficients were evaluated from the experimental data. From the values of mass transfer coefficient it was concluded that the initial faster rate was due to surface diffusion and the latter slower part was due to intra particle diffusion.

The desorption process was also studied on saturated adsorbents using different chemicals such as 0.5M of KOH, NaOH, HCL, HNO_3, H_2SO_4 solution. Among the five chemicals KOH is observed to be the strong efficient desorbent. Finally, the adsorbents were applied to the effluents emerging from tanneries and it is found effective for the removal of the Cr (III) from the effluent. Thus, the study concluded that the Newspaper and Packaging box serve as an inexpensive and easy to operate adsorbent to remove chromium from tannery waste water discharges.

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LIST OF ABBREVIATION

AAS   : Atomic Absorption Spectrophotometer

ACGIH   : American Conference of Governmental Industrial Hygienists

BCSIR   : Bangladesh Council of Scientific and Industrial Research

BOD   : Biochemical Oxygen Demand

CCLW   : Chromium Containing Leather Waste

CFR   : Code of Federal Regulations

COD   : Chemical Oxygen Demand

DAF   : Dissolved Air Flotation

DNA   : Deoxyribo Nucleic Acid

DS   : Dissolved solids

FT-IR   : Fourier Transform Infrared

IARC   : International Agency for Research on Cancer

LEL   : Lower Explosive Limit

NTP   : National Toxicology Program

OEHHA   : Office of Environmental Health Hazard Assessment

OSHA   : Occupational Safety and Health Administration

SS   : Suspended Solids

WHO   : World Health Organization

UNIDO   : United Nations Industrial Development Organization

TDS   : Total Dissolved Solids

TERI   : The Energy and Resources Institute

US EPA   : United States Environmental Protection Agency

VOC   : Volatile Organic Compound

CHAPTER 1

INTRODUCTION

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1.1 General background

Leather is the major industrial product made from hides and skins of animals. Leather processing has evolved from a traditional artisanal practice to an industrial activity. Leather industry provides the necessities, such as leather shoes and garments, while using the by-products of the meat industry. However, the leather-making process, in turn, generates by-products and wastes. It is known that only 20% of wet salted hides and skins are converted into commercial leather, while 25% becomes chromium-containing leather waste (CCLW), and the remainder becomes non-tanned waste or is lost in wastewater as fat, soluble protein and solid suspended pollutants (Alexander et al., 1991). Environmental pollution is a difficult problem for world leather industry (Kumaraguru et al., 1998; Cabeza et al., 1998). The real problem, however, that the leather industry presently faces the environmental challenge (World Leather Magazine, 2002).

The main process of skin or hide converting into leather is tanning. Skin is made up of many bundles of interwoven protein fibers which are able to move in relation to one another when the animals are alive. When the animals die, these fibers tend to shrivel and stick together. Essentially, the purpose of tanning is to permanently fix the fibers apart by chemical treatment, and to lubricate them so they can move in relation to one another. Well-tanned leather, therefore, retains the properties of flexibility, toughness and wear. It also continues to 'breathe', allowing water vapor to pass through but remaining reasonably water-proof. It is this characteristic which accounts for the comfort of genuine leather shoes and clothing. In addition, the process of tanning imparts the advantage of resistance to heat. This is an important factor in many of the uses of leather. In conjunction with chemical processing, the tanner imparts color, texture and finish to the leather, to enhance its appearance and suit it to today's fashion requirements. Chromium has been used as primary tannage for many leathers for over 100 years.

In the early days the tanning form, Cr (III), was produced from Cr (VI) by reduction of the chrome by sugars at low pH. When basic chrome sulphate was introduced as a product ready to be used for tanning, tanneries changed to the use of these products either as an aqueous solution or a dry product (O'Flaherty et al., 1978).

Due to increasingly strict requirements for leather and with regard to recycling of leather wastes, the manufacture chromium-free leather becomes very important (Plavan et al., 2009). On the other hand, mostly researches limit the investigation evaluating those leather properties, which are most important for consumers such as shrinkage temperature and strength properties, and few chemical indexes like as content of chromium in leather, content of volatile or extractable with dichloromethane materials. (Valeika et al., 2010).

Intensive production of leather in small clusters has caused environmental concern (Ramasami, 1999). It involves the use of copious amounts of water. About 300-350L of water is employed for every kilogram of hide processed (Ramasami and Prasad, 1991). Environmental challenges from leather processing arise from the nature and quantity of chemicals used as well as the amount of wastes generated and discharged. The raw material for the leather industry namely salted hides and skins, carries with it common salt, which later forms a disconcerting source of pollution (Kronick et al,1995).

Conventional methods for pre-tanning and tanning processes discharge enormous amount of pollutants, which accounts for nearly 90% of the total pollution from a tannery (Aloy, 1976). Pre-tanning process involves 'do-undo' operations, such as curing (dehydration), soaking (rehydration), liming (swelling), de-liming (de-swelling), pickling and they contribute to 60-70% of the total pollution load in leather processing (Ludvik et al., 1997). It has been reported that the conventional de-hairing process with sodium sulfide and lime is responsible for 84% of biochemical oxygen demand (BOD_5), 75% of the COD and 92% of the suspended solids from a tannery (Marsal et al., 1999).

Generally, in conventional chrome tanning about 60-70% of chrome is taken up by the pelt and the rest is released into the environment. This excess amount of chrome increase the SS, DS, BOD, COD of the waste water which pollutes the environment and when this polluted water falls into the sea or river it also increases the pollution load of existing water which is very harmful for aquatic life.

1.2 Scope of the study

Chromium is present in aqueous solutions mainly in two oxidation states, Cr (III) and Cr (VI), and due to the difference in toxicities of hexavalent and trivalent chromium, many attempts have been made to discriminate between the two species. The main sources of Cr pollution are mining, leather tanning, the cement industry, uses in dyes, electroplating, production of steel, photographic material and corrosive paints. The principal techniques for recovering or removing Cr from wastewater are chemical reduction and precipitation, adsorption by several types of adsorbents such as activated carbon, pinus sylvester's bark, fly ash and wollastonite, sphagnum moss peat and bone charcoal, ion exchange and membrane technologies. Most of these methods suffer from some drawback such as high capital and operational costs. Therefore there is a need for the development of low cost, easily available materials which can adsorb Cr economically. For tannery effluent myself effort to Cr (III) removal from several non agricultural wastes as adsorbent.

The adsorption of chromium Cr (III) from tannery wastewater at room temperature by batch adsorption technique using different low-cost adsorbents have been investigated. The main objective of the study was to find out a suitable low cost, available, environmental friendly and highly effective adsorbent.

In the present study different low cost adsorbents (non agricultural wastes) such as animal hair, newspaper, rubber, packaging box, plastic, brick powder, bone, concrete etc. have been studied. Batch adsorption studies were carried out under varying experimental conditions of pH, adsorption dose, operational temperature, initial adsorbate concentration, contact time and particle sizes.

The physico-chemical properties of the adsorbents have been studied using different characterization techniques. The desorption process were also studied on saturated adsorbents using different chemicals such as KOH, NaOH, HNO$_3$, HCl, H$_2$SO$_4$ solution. Among the five chemicals one was selected as the most efficient desorbent.

Finally the adsorbents were applied to the effluents coming from tanneries and it is found effective for the removal of the Cr (III) from the effluent. Thus the study concluded that the selected adsorbents serve as an inexpensive and easy to operate as adsorbent to remove Cr (III) from tannery wastewater discharges.

1.3 Aim of the present work

- To find out an appropriate, low cost, environmental friendly and highly effective adsorbent
- To develop a method for removal of Cr (III) from tannery wastewater
- To minimize environmental pollution

1.4 Adsorption

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. This process differs from absorption, in which a fluid (the absorbate) permeates or is dissolved by a liquid or solid (the absorbent). Adsorption is a surface-based process while absorption involves the whole volume of the material. The term sorption encompasses both processes, while desorption is the reverse of it. Adsorption is a surface phenomenon. Adsorption has emerged as promising technique for metal removal. The processes can occur at an interface between any two phases, such as, liquid-liquid, gas-liquid, or liquid-solid interfaces (Barakat, 2011).

1.4.1 Adsorbent

We are referring to adsorbers, not absorbers, because the pollutant is adsorbed on the surface (mostly the internal surface) of a granule, bead, or crystal of adsorbent material. It is not absorbed by a chemical reaction. This is an important difference. The adsorbed material is held physically, rather loosely, and can be released (desorbed) rather easily by either heat or vacuum.

By contrast, an absorber reacts chemically with the substance being absorbed, and thus holds the absorbed substance much more strongly; requiring much more energy to release the absorbed substance. Unfortunately, one of the adsorbents is called "absorbent carbon." This persisting misnomer came from the time before adsorption became understood in the 1920's. A better term is "activated carbon." Carbon is activated by the pyrolysis of coal, wood, bark, coconut husks, etc. to remove all the volatile material as a gas or vapor, and leave only the carbon. This carbon might then also be partially oxidized to enlarge its pores. Another adsorbent is the alumino-silicate crystal structure known as "zeolite," which has uniformly sized pores (also called windows) throughout its crystal structure.

The crystal structure for the 118 established types of zeolite is determined by the ratio of silicon to aluminum in the crystal when the crystal is formed. All naturally occurring zeolite is hydrophilic (having affinity for polar molecules, such as water) and contains aluminum. Dealuminizing natural zeolite makes it hydrophobic (having affinity for non-polar substances, such as many VOC). Zeolite is dealuminized by chemical replacement of the aluminum with silicon without changing the crystal structure.

Hydrophobic zeolite can also be synthesized in crystals from 1 micron to 1 millimeter in diameter, and these can be bonded into larger granules to lower their resistance to air flow. Since synthesis is expensive, it is usually reserved for making either hydrophobic zeolite or zeolite catalysts with specific large pore size. Polymeric adsorbents have pores built in when they are manufactured. These pores can range from macro-porous through molecular sizes, but the smallest pores are usually larger than the micro-pores of an activated carbon. Polymers are used as granules or beads and, as the name implies, are plastics. They have been observed to desorb faster than carbon. Like carbon, they are not considered highly selective as to which VOC they will adsorb, although any specific polymer will adsorb some VOC better than others. Choosing the best adsorbent for the situation is not simple. There are several related problems which we will discuss to familiarize you with the different adsorbents and systems.

1.5 Why are adsorbers important?

Adsorbers have been used principally to control the emission of VOC. The control of VOC emissions typically reduces the concentrations from between 400 and 2,000 parts per million (ppm) to less than 50 ppm. Adsorption technology can now extend the range of VOC concentration from 20 ppm to one-fourth of the Lower Explosive Limit (LEL). At the lower end of this range, such small concentrations may be difficult or uneconomical to control by another technology or even by all adsorbents. Incinerators, membrane separators, and condensers may be economically feasible when used in place of adsorbers at the upper end of the range. In addition to emission control; the adsorber makes recovery of the VOC possible. Recovery of a reusable or marketable VOC can significantly offset the cost of emission control. Adsorbers can also increase the concentration of VOC to allow either destruction by incineration, or recovery by either membrane or condenser to be economically feasible.

1.6 Agricultural and non agricultural wastes

Agricultural waste is unwanted or unsalable materials produced wholly from agricultural operations directly related to the growing of crops or raising of animals for the primary purpose of making a profit or for a livelihood.

Some examples of agricultural wastes include:

- Grape vines
- Fruit bearing trees
- Vegetables
- Date palm fronds

Agricultural wastes do not include items such as:

- Trash
- Plastic
- Rubber
- Garbage
- Tires
- Pallets
- Oil filters
- Broken boxes
- Chemically treated wood
- Material containing asbestos
- Packaging material and boxes
- Pesticides and fertilizer containers
- Construction and demolition Material
- Ornamental or landscape vegetation (e.g. Grass, Weeds and Tree Trimmings)
- Any other materials produced in the packaging or processing of agricultural products

Orchard or vineyard waste or any other material, generated as a result of land use conversion to nonagricultural purposes is not agricultural waste. (Source: www.aqmd.gov/home/regulations/compliance/open-burn/agricultural-waste).

1.7 Significance of chromium

Due to increase in population coupled with mining, extraction and use of various metals as different industrial and household materials, the load of toxic metal pollution in the environment is increasing. The waste from metallurgical mining sectors, in general, creates destabilization in the ecosystem, as most of the heavy metal ions are toxic to the living organisms. But some of these heavy metals, in traces, play significant role in the human metabolism. The demand of chromium has been increasing globally due to its extensive use in various metallurgical, chemical and leather tanning industries due to its various physico-chemical properties.

Apart from industrial uses, Cr (III) plays an important role in our body (Wang et al., 2004). Without Cr (III) in our diet, the body loses its ability to use sugar, protein and fat properly, which may result in weight loss or impaired growth, improper function of nervous system and imbibe diabetic conditions. The best-known nutritional effect of chromium is to assist insulin in regulating blood sugar (glucose) levels in human body as established through radio tracing. Insulin is a protein hormone that is released in to the blood when blood glucose level gets high. Insulin then binds to the receptor cells outside, causing to absorb more glucose from blood, returning blood glucose levels to normal.

Due to its strategic importance in different metallurgical processing, chromite is traded in world market either as high-grade ore or intermediate like ferrochrome charge chrome. The finished products of modern technology use ferrochrome of various grades worldwide. There have been attempts to replace chromium by other metals like cobalt, nickel vanadium, molybdenum and columbium in the manufacture of alloy steels. But these are not universally accepted due to their higher cost and marginal advantages over chromium. Therefore, chromium is still the most sought after metal in alloy steel production in addition to its traditional outlets like stainless steel or refractory bricks. A brief list of important uses of chromium for different purposes is given in Table1.1 (TERI, 2001).

Table 1.1 Application of chromium and chromium chemicals in different sectors.

SI. No.	Use	Percentage of total consumption
1	Metal finishing and corrosion control	37
2	Pigment and allied products	26
3	Leather tanning and textiles	20
4	Wood preservatives	5
5	Drilling mud	4
6	Catalyst/batteries/ magnetic tapes etc	8

1.8 Properties of chromium

Chromium is a lustrous, brittle, hard metal. Its colour is silver-gray and it can be highly polished. It does not tarnish in air, when heated it burns and forms the green chromic oxide. Chromium is unstable in oxygen, it immediately produces a thin oxide layer that is impermeable to oxygen and protects the metal. Chromium main uses are in alloys such as stainless steel, in chrome plating and in metal ceramics. Chromium plating was once widely used to give steel a polished silvery mirror coating. Chromium is used in metallurgy to impart corrosion resistance and a shiny finish, as dyes and paints, its salts colour glass an emerald green and it is used to produce synthetic rubies, as a catalyst in dyeing and in the tanning of leather, to make molds for the firing of bricks (Source: http://www.lenntech.com/periodic/elements/cr.htm).

Fig.1.1 Several forms of chromium.

1.8.1 Chemical properties of chromium

Atomic number	24
Atomic mass	51.996 g.mol^{-1}
Electronegativity	1.6
Density	7.19 g.cm^{-3} at 20°C
Melting point	1907 °C
Boiling point	2672 °C
VanderWaals radius	0.127 nm
Ionic radius	0.061 nm (+3) ; 0.044 nm (+6)
Isotopes	6
Electronic shell	[Ar] 3d^5 4s^1
Energy of first ionisation	651.1 kJ.mol^{-1}

Energy of second ionisation	1590.1 kJ.mol^{-1}
Energy of third ionisation	2987 kJ.mol^{-1}
Standard potential	- 0.71 V (Cr^{3+} / Cr 6+)
Discovered by	Vaughlin in 1797

1.9 Hexavalent chromium

Hexavalent chromium (chromium (VI), Cr (VI), chromium 6) refers to chemical compounds that contain the element chromium in the +6 oxidation state. Chromium 6+ for high oxidizing potential is more toxic than Cr^{3+} form, Cr^{6+} within 2017 in EU will be banned for galvanic industry for this reason. Virtually all chromium ore is processed via hexavalent chromium, specifically the salt sodium dichromate. Approximately 136,000 tonnes (300,000,000 lb) of hexavalent chromium were produced in 1985.Additional hexavalent chromium compounds are chromium trioxide and various salts of chromate and dichromate, among others.

Hexavalent chromium is used in textile dyes, wood preservation, anti-corrosion products, chromate conversion coatings, and a variety of niche uses. Industrial uses of hexavalent chromium compounds include chromate pigments in dyes, paints, inks, and plastics, chromates added as anticorrosive agents to paints, primers, and other surface coatings, and chromic acid electroplated onto metal parts to provide a decorative or protective coating. Hexavalent chromium can be formed when performing "hot work" such as welding on stainless steel or melting chromium metal. In these situations the chromium is not originally hexavalent, but the high temperatures involved in the process result in oxidation that converts the chromium to a hexavalent state. Hexavalent chromium can also be found in drinking water and public water systems.Inhaled hexavalent chromium is recognized as a human carcinogen. Workers in many occupations are exposed to hexavalent chromium.

Problematic exposure is known to occur among workers who handle chromate-containing products and those who grind and/ or weld stainless steel. Workers who are exposed to hexavalent chromium are at increased risk of developing lung cancer, asthma, or damage to the nasal epithelia and skin. Within the European Union, the use of hexavalent chromium in electronic equipment is largely prohibited by the Restriction of Hazardous Substances Directive (Source: https://en.wikipedia.org/wiki/Hexavalent_chromium).

1.9.1 Toxicity

Chromium toxicity refers to the fact that chromium is toxic. Water-insoluble chromium (III) compounds and chromium metal are not considered a health hazard, while the toxicity and carcinogenic properties of chromium (VI) have been known for a long time. Because of the specific transport mechanisms, only limited amounts of chromium (III) enter the cells. Several in vitro studies indicated that high concentrations of chromium (III) in the cell can lead to DNA damage. Acute oral toxicity ranges between 1900 and 3300 µg/kg. The World Health Organization (WHO) recommended maximum allowable concentration in drinking water for chromium (VI) is 0.05 milligrams per litre. Hexavalent chromium is also one of the substances whose use is restricted by the European Restriction of Hazardous Substances Directive.

In the body, chromium (VI) is reduced by several mechanisms to chromium (III) already in the blood before it enters the cells. The chromium (III) is excreted from the body, whereas the chromate ion is transferred into the cell by a transport mechanism, one by which sulfate and phosphate ions also enter the cell. The acute toxicity of chromium (VI) is due to its strong oxidative properties. After it reaches the bloodstream, it damages blood cells by oxidation reactions. Hemolysis, and subsequently kidney and liver failure, are the results of this damage.

The carcinogenity of chromate dust has been known for a long time, and in 1890 the first publication described the elevated cancer risk of workers in a chromate dye company. Three mechanisms have been proposed to describe the genotoxicity of chromium (VI). The first mechanism includes highly reactive hydroxyl radicals and other reactive radicals which are byproducts of the reduction of chromium (VI) to chromium (III). The second process includes the direct binding of chromium (V), produced by reduction in the cell, and chromium (IV) compounds, to the DNA. The last mechanism attributes the

genotoxicity to the binding to the DNA of the end product of the chromium (III) reduction. Chromium salts (chromates) are also the cause of allergic reactions in some people. Chromates are often used to manufacture, among other things, leather products, paints, cement, mortar, and anti-corrosives. Contact with products containing chromates can lead to allergic contact dermatitis and irritant dermatitis, resulting in ulceration of the skin, sometimes referred to as "chrome ulcers". This condition is often found in workers that have been exposed to strong chromate solutions in electroplating, tanning and chrome-producing manufacturers (Source: https://en.wikipedia.org/wiki/ Chromium_toxicity).

1.10 Health effects of chromium

People can be exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. In drinking water the level of chromium is usually low as well, but contaminated waste water may contain the dangerous chromium (IV), hexavalent chromium. For most people eating food that contains chromium (III) is the main route of chromium uptake, as chromium (III) occurs naturally in many vegetables, fruits, meats, yeasts and grains.

Various ways of food preparation and storage may alter the chromium contents of food. When food in stores in steel tanks or cans chromium concentrations may rise. Chromium (III) is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much chromium (III) can cause health effects as well, for instance skin rashes.

Chromium (VI) is a danger to human health, mainly for people who work in the steel and textile industry. People who smoke tobacco also have a higher chance of exposure to chromium. Chromium (VI) is known to cause various health effects. When it is a compound in leather products, it can cause allergic reactions, such as skin rash. After breathing it in chromium (VI) can cause nose irritations and nosebleeds.

Other health problems that are caused by chromium (VI) are:

 -Respiratory problems

- Weakened immune systems

- Kidney and liver damage

- Skin rashes

- Upset stomachs and ulcers

- Alteration of genetic material

- Lung cancer

 -Death

The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in this product) is of low toxicity. The hexavalent form is toxic. Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions.

Inhalation of hexavatent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch.

Carcinogenicity- Chromium and most trivalent chromium compounds have been listed by the National Toxicology Program (NTP) as having inadequate evidence for carcinogenicity in experimental animals. According to NTP, there is sufficient evidence for carcinogenicity in experimental animals for the following hexavalent chromium compounds; calcium chromate, chromium trioxide, lead chromate, strontium chromate and zinc chromate. International Agency for Research on Cancer (IARC) has listed chromium metal and its trivalent compounds within Group 3 (The agent is not classifiable as to its carcinogenicity to humans.) Chromium is not regulated as a carcinogen by OSHA (29 CFR 1910 Subpart Z). ACGIH has classified chromium metal and trivalent chromium compounds as A4, not classifiable as a human carcinogen (Source: http://www.lenntech.com/periodic/elements/cr.htm).

The human exposure pathways to chromium are inhalation, ingestion (swallowing) and dermal (skin) contact. Chromium exposure in humans and laboratory animals is known to cause cancer, interfere with physical development and harm the skin, respiratory, reproductive and digestive systems. Chromium-VI is much more toxic than Cr-III because of its greater ability to enter cells and its strong oxidation potential (Katz and Salem, 1993). Once inside cells, Cr-VI reduction produces free radicals, Cr-V, Cr-IV and eventually Cr-III, which are believed to be responsible for toxic and carcinogenic effects (Stearns et al., 1995b; Li et al., 2011). Inhalation of Cr-VI is considered more dangerous than ingestion (OEHHA, 2011).

Significant accumulation of chromium due to Cr -III ingestion has been seen in animal tissues including liver, lungs, spleen and heart (Stearns et al., 1995a). Chromium accumulation due to Cr-VI ingestion has also been seen in human and animal tissues including blood, bone, testis, liver, spleen and kidneys (Kerger et al., 1996; Finley et al., 1997; Sutherland et al., 2000; NTP, 2007; US EPA, 2010). Workers exposed to Cr-VI in Japan had high levels of chromium in respiratory organs, spleen, liver, kidney and heart tissues, up to 30 years post-exposure (Teraoka,1981); and tannery workers exposed to Cr-III had long-term elevated chromium levels in their bloodstream (Aitio et al., 1984; Randall and Gibson, 1987).

1.11 Environmental effects of chromium

There are several different kinds of chromium that differ in their effects upon organisms. Chromium enters the air, water and soil in the chromium (III) and chromium (VI) form through natural processes and human activities.

The main human activities that increase the concentrations of chromium (III) are steal, leather and textile manufacturing. The main human activities that increase chromium (VI) concentrations are chemical, leather and textile manufacturing, electro painting and other chromium (VI) applications in the industry. These applications will mainly increase concentrations of chromium in water. Through coal combustion chromium will also end up in air and through waste disposal chromium will end up in soils.

Most of the chromium in air will eventually settle and end up in waters or soils. Chromium in soils strongly attaches to soil particles and as a result it will not move towards groundwater. In water chromium will absorb on sediment and become immobile. Only a small part of the chromium that ends up in water will eventually dissolve.

Chromium (III) is an essential element for organisms that can disrupt the sugar metabolism and cause heart conditions, when the daily dose is too low. Chromium (VI) is mainly toxic to organisms. It can alter genetic materials and cause cancer.

Crops contain systems that arrange the chromium-uptake to be low enough not to cause any harm. But when the amount of chromium in the soil rises, this can still lead to higher concentrations in crops. Acidification of soil can also influence chromium uptake by crops. Plants usually absorb only chromium (III). This may be the essential kind of chromium, but when concentrations exceed a certain value, negative effects can still occur.

Chromium is not known to accumulate in the bodies of fish, but high concentrations of chromium, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal. In animals chromium can cause respiratory problems, a lower ability to fight disease, birth defects, infertility and tumor formation (Source: http://www.lenntech.com/periodic/elements/cr.htm).

It is well established that microorganisms, plants and animals are capable of accumulating chromium from their environments. Chromium in aquatic ecosystems is known to bioaccumulate in algae, aquatic plants, invertebrates' and fish (Marchese et al., 2008; Dwivedi et al., 2010). Metal bioaccumulation varies greatly among aquatic species, as seen by a wide range of chromium bioconcentration factors observed for fish and invertebrates (Marchese et al., 2008; Kimborough et al,. 1999; Weegman and Weegman, 2007). Uptake and effects are influenced by the species, organism size, sex and developmental stage, presence of other contaminants, water temperature, pH, alkalinity and salinity (Eisler, 1986). Some algae have exhibited severe signs of toxicity from as little as 1-10 ug Cr-VI/L (Health Canada 1994). Cr (III) has also been observed to affect algae (320 μg /L) and the standard test procedure may be underestimating its toxicity

(Pawlisz et al., 1997; Vignati et al., 2010). Evidence suggests that Cr (III) in water is more toxic to fish than Cr (VI) as it damages gills, and can cause reproductive damage and even death at relatively low doses (Health Canada, 1994). Cr (VI) does not deposit on gills but enters the fish and exerts toxic effects on internal organs such as the liver and kidney.

1.12 Tannery industry

Tanning, in particular chrome leather production, is characterized by the production of highly polluted waste water, solid wastes and odour. The primary environmental issue facing tannery operations is the treatment of the toxic chromium rich waste in its wastewaters and sludge. Wastewater treatment systems must ensure high levels of metal removal, whilst sludge disposal is a major issue due to the limited availability and high cost of suitable disposal sites. In Bangladesh, leather tanning is an important industry.

Large volumes of tannery effluents containing chromium salts and other pollutants are being discharged to open fields, cultivable land, river streams and water bodies causing large scale pollution of soil, water and ecotoxicological risks. The current technology for effective chromium recovery and detoxification are practiced in modern units, but still many of the older and smaller units resort to conventional effluent treatment (Alexander et al., 1991; Covington and Alexander, 1993; James and Mc Dougall, 1996).

1.12.1 Sources of contaminants to tannery effluent

The pollution load of an effluent is due to the presence of organic and inorganic materials in it. Adsorption method is reported to be very much effective in reduction of the pollution load of an effluent. (Sastry et al., 1986 and Fahim et al., 2006) discussed the literature review on characteristics and treatment of wastewater from tanneries. In tanning industries, chromium is extensively used to convert raw skin/hide to leather and a large amount of chromium-laden effluent is discharged into the environment. Chromium in its trivalent form is an essential trace element when present at the micro level, whereas the same when present in excess is proven to be a potential soil, surface water, and air contaminant under specific condition (Rao et al., 2002). (Basu and Chakraborty, 1989) characterised tannery effluent for pH, total solids, suspended solids, BOD and COD and discussed various methods of treatment of tannery wastewater containing chlorides, sulphides and chromium. Contaminants in the effluent from tannery originate in several

ways. The most obvious source of pollution is the drag-out of various processing baths into subsequent rinses, the amount of pollutants contributed by drag-out is a function of several factors such as the design of the racks or barrels carrying the parts to be plated, the shape of the parts, plating procedures and several interrelated parameters of the process solution, including concentration of toxic chemicals, temperature, viscosity and surface tension. With conventional rinsing techniques, drag-out losses from process solutions result in large volume of rinse water contaminated with relatively dilute concentration of cyanide and metals (Cushnie et al., 1985).

Leather tanning is one of the oldest professions in the world and involves the processing of hides and skins of animals for use in numerous products such as upper leather for shoes, clothing, furniture and automotive leather for upholstery in motor vehicles (Iqbal et al., 1998). Tanneries produce different types of leather products depending on customer needs. Tanning means converting the rawhide or skin, a highly putrescible material, into leather, a stable material. In this process the very sensitive hydrogen bonds of skin proteins are replaced by chemical bonds with tanning agent like chromium, aluminum or other mineral salts, vegetable or synthetic tanning agents to stabilize the material and to protect it against microbial attack. Leather production belongs to the natural products industry. The whole process involves a sequence of complex chemical reaction and mechanical processes.

1.12.2 Production of leather

Leather tanning is the process of converting raw hides into leather and can be divided into three different processes which are briefly described below.

Beamhouse operations

In the beamhouse, hides are prepared for tanning by removing hair roots, pigment and other protein substances.

Tanning process

The hides are tanned to prevent them from being damaged by bacteria. Hides can be tanned in a number of different ways by using chrome tanning agents added as a powder or a liquid to produce wet blues, or by adding vegetable tannins to produce wet whites. Wet blues are not leather, but hides that have been tanned with chromium sulphate ($CrSO_4$). They are merely a stable form of the hide. The chrome gives the leather an initial blue grey colour. The tanned hides can be stored for long periods and are also more easily transported without fear of being damaged by bacteria (www.tanschool.co.za).

Wet blues are recognized as an internationally traded commodity. The chrome tanning method is widely applied for the preparation of finished leather (Iqbal et al., 1998). Wet whites on the other hand are skins and hides that are tanned using vegetable tanning material such as aldehydes.

Leather that is tanned using vegetable tannins has different properties and is usually much firmer. These hides will go through the dye house operations to convert the wet blue and wet whites into a product that has leather-like properties. The process in the dye house can be compared to the retan process used to produce crust leather.

Finishing process

Leather finishing is the final process that is carried out in a tannery to make the leather look better and stay looking good for longer while withstanding weather and wear. Leather finishing in very simple terms is the application of paint to the leather surface.

The retan process followed at the tanning facility

Hides are retanned to level out the structure of a hide, by filling the loose and empty parts in the bellies and necks, to improve the cutting yield. Retanning produce the highest quality. Wachsman (1999) considers this is where retanning agents with real tanning properties are necessary and where either chrome salts, syntans, glururaldehyde, vegetable extract, polymers, resins, aldehydes and metals provide these properties to the wet blues and wet whites used.
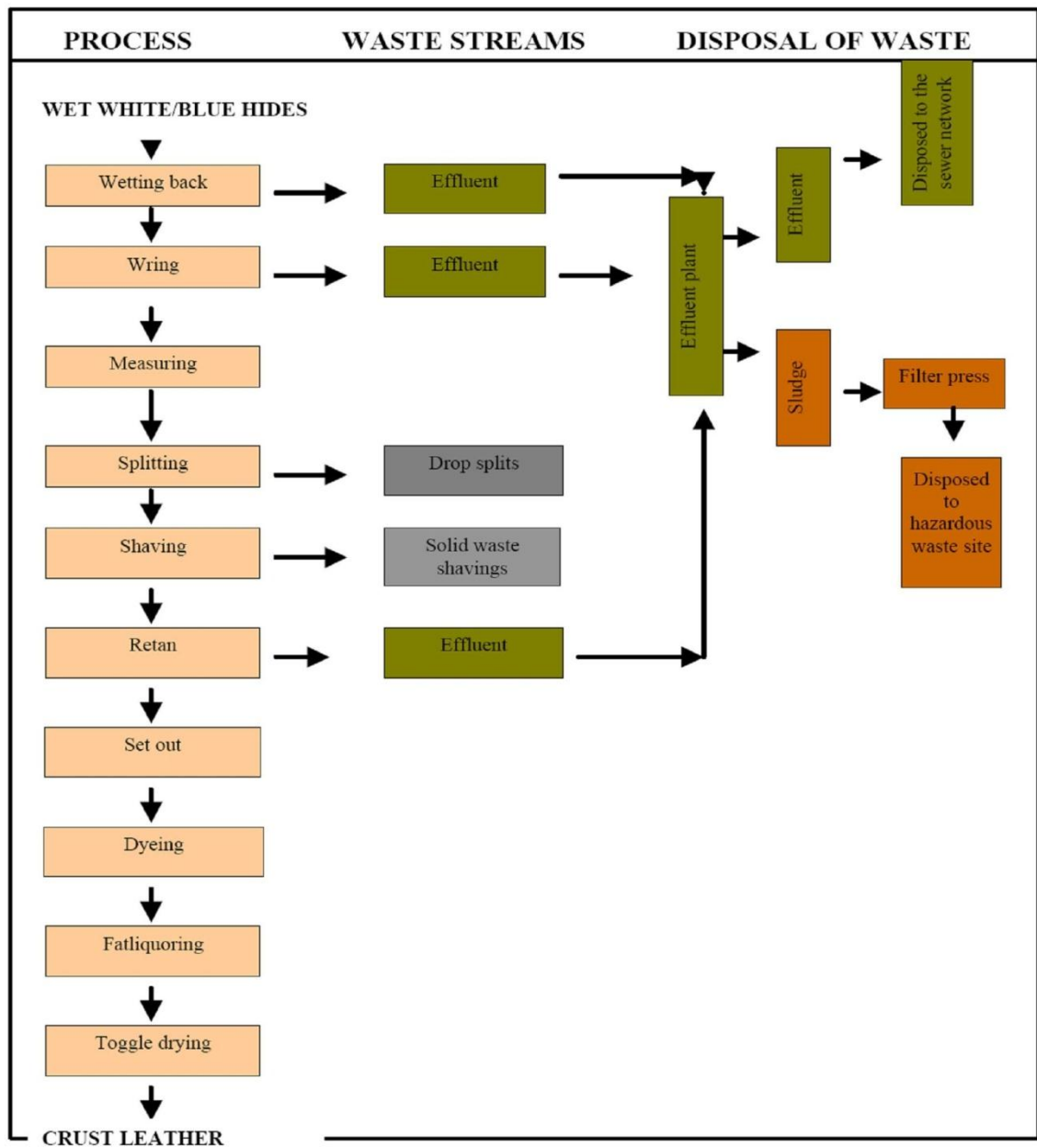
Fig. 1.2 Waste streams produced during the Retan process (Iqbal et al., 1998).

1.12.3 Waste streams generated in the retan process

During the retan process large volumes of raw materials are used in the manufacturing of crust leather. Raw materials used are chemicals, which include dyes, retanning materials, formic acids, water and the wet white or blue hides. Most of the chemicals used to prepare the hides for retanning find their way back into the environment in the form of wastes including (Iqbal et al., 1998).

-Atmospheric waste causing air pollution

-Liquid waste

-Solid waste

Fig. 1.2 explains the process and identifies the type of waste streams generated in the retan process at the tanning facility as well as the disposal options currently adopted. Waste streams produced during the tanning process include effluent and solid waste. The effluent water originates from all the areas where water is used in the tanning process, which includes the wetting back water, water from the wringer and the water dropped during the retanning process.

The partial treatment of the water results in the production of the tanning sludge and effluent that is disposed to the Municipal sewer network. Solid waste streams originate from the splitting of the hides and as a result of the effluent treatment plant. The drop splits are sold to another company for reuse, the shavings from the shaver are disposed of as general waste and the tanning sludge are disposed of to a hazardous landfill site. Although a brief description is provided for each of the wastes produced, the main focus of this dissertation is on the tanning sludge produced during the treatment of the effluent.

Atmospheric waste causing air pollution

A potential source of air pollution (atmospheric waste) may originate from the boiler. The boiler is used to produce hot water for the retan process. Possible contaminants include the release of gases. However, due to the size of the boiler used. The boiler uses less than 10 tonnes of sabufuel (a sort of paraffin) per hour and it does not use coal as an energy source. Therefore, it is expected not to have a significant impact on the environment.

<u>Liquid waste</u>

Tanneries are major consumers of water. The water in the wet processes and operations is used as a chemical carrier to facilitate all chemical reactions involved in leather processing. After completion of the process and operation, the water leaves the system as waste water in the same quantity as it is added to the system (Iqbal et al., 1998). Liquid waste or waste water includes all process water produced complex is relatively stable and slightly biologically available and therefore the chromium should not be oxidised to hexavalent chromium Cr (VI) during the retan process. The Chemical Oxygen Demand (COD) and Suspended Solids (SS) are the only constituents that are removed from the effluent through the partial treatment process, as this treatment does not throughout the retan process as described in Fig. 1.2. The waste water originates from the various stages including the wetting back, wringing and retan processes. The water volume requirements depend on each of the specific retanning processes and the specific product that needs to be manufactured at that specific time.

Effluent originating during the various stages of the process is disposed to an effluent treatment plant for partial treatment, before it is disposed of into the municipality's sewer network for further treatment. The effluent disposed of must be treated in order to comply with the local authorities' standards for disposal of industrial effluent. The water is treated through the addition of treatment chemicals (polymers, flocculants coagulants and lime), followed by dissolved air floatation of the solids. The Dissolved Air Flotation (DAF) provides successful removal of the suspended solids (SS), oil and greases, as well as any heavy metals such as chromium (Cr), Manganese (Mn), Aluminium (Al) and Iron (Fe).
Tannery effluent is characterized by a high chemical oxygen demand (COD) and high salt content measured as total dissolved solids/salts (TDS). High chloride (Cl), Sodium (Na), Sulphate (SO4) concentrations are also present in the waste stream due to their presence in the raw materials and this contributes to the high salinity levels of the effluent stream. It also contains a high level of suspended solids and chrome. According to Iqbal et al., (1998) this is characteristic of tannery waste water. The chrome (Cr) will only be present when wet blues are processed and chrome tanning salts are used. The chemical oxygen demand (COD) represents the oxygen consumption for chemical oxidation of organic material under strongly acid conditions. It only provides an indication of the potential oxygen depletion that may occur from discharging organic material into surface waters (Verheijen et al., 1996).

The suspended solids (SS) are insoluble organic and inorganic particles present in the waste water that originates from the hides and chemicals used. Suspended solids (SS) are mainly material that are too small to be collected as solid waste. Discharge of high concentrations of SS increases the turbidity of water and causes a long term demand for oxygen because of the slow hydrolysis rate of the organic fraction of the material. It has been estimated that using traditional tanning methods chromium salts which are not fixed to the collagen during the tanning process, are discharged as salinity and total dissolved salts (TDS). The chromium removes any salts in the effluent.

Solid waste

The solid waste produced includes the tanning sludge produced at the effluent plant, shaving buffings, raw material packaging (especially plastics) and general office waste. The majority of general solid waste is separated at source and recycled where possible. Empty drums, containers, plastics, white papers and carton boxes are recycled by outside contractors. All the effluent produced in the tanning facility reports to the effluent plant for partial treatment, to ensure that the water complies with the standards set by the Local Authority. The Dissolved Air Flotation (DAF) is designed to partially remove the Chemical Oxygen Demand (COD) and the Suspended Solids (SS).

Flocculants and coagulants used to remove SS and Chemical Oxygen Demand (COD) generate the tanning sludge in this process. The Dissolved Air Flotation (DAF) plant functions on the principle of flotation. Flotation is used for the removing of suspended solids from mixed effluent. Air is dissolved into the incoming effluent under pressure. When this pressure is subsequently lowered in the treatment vessel, small air bubbles are released, carrying the suspended solids to the surface. Lime, ferrous sulphate and polyelectrolyte are usually used in order to thicken tanning sludge for easier handling (Mozes, 1995). In order to reduce the tanning sludge volumes for disposal, a filter press was introduced to dewater the tanning sludge.

CHAPTER 2
LITERATURE REVIEW

2.1 Chromium removal by low cost adsorbent

The use of low-cost sorbents has been investigated as a replacement for current costly methods of removing heavy metals from solution. Use of low cost natural resource as adsorbents for removal of chromium is constantly encouraging in preference to other conventional methods. The application of activated alumina (Gupta and Tiwari, 1985), moss peat (Sharma and Forster, 1993), wood charcoal (Deepak and Gupta, 1991), carbon slurry (Singh and Tiwari, 1997) , rice straw (Samanta et al., 2000), corncob (Nigam and Rama, 2002), activated charcoal, bituminous coal and coconut shell carbon (Nagesh and Krishnaian, 2002), bagasse (Rao et al., 2003), food industrial waste (Selvaraj et al., 2003), agricultural by product (Bishno et al., 2004), different biowaste material (Joshi et al., 2003) and paper mill sludge (Ahluwalia and Goyal, 2004), rose waste biomass (Iftikhar et al., 2009), Bael fruit (*Aegle marmelos correa*) shell (Anandkumar and Mandal, 2009). Low-cost sorbents, such as *Eucalyptus* bark (Sarin and Pant, 2006), biological wastes such as sawdust, rice husk, coir pith, charcoal and naturally occurring mineral (vermiculite) have been used for removing chromium from tannery effluent through batch and column mode and adsorption capacities of the substrates were also evaluated using isotherm test and computing distribution co-efficient (Sumathi et al.,2005).

2.2 Methods for the removal of chromium

Several treatment technologies have been developed to remove chromium from water and wastewater. Common methods include reduction and precipitation (Mahajan,1985), ion exchange (Tiravanti et al., 1997; Rengaraj et al., 2001; Rengaraj et al., 2002; Rengaraj et al., 2003; Petruzzelli et al., 1995; Mahajan,1985), reverse osmosis (Ozaki et al., 2002), ultra filtration (Ghosh and Bhattacharya, 2006), electro dialysis (Mohammad et al., 2005) and adsorption (Mohan et al., 2006; Mohan and Pittman Jr, 2006; Gupta et al., 1997; 1999; 2001; Babel and Kurniawan, 2003).

2.2.1 Reduction and precipitation

This method finds wide application in the treatment of chromium. It is economical and the removal efficiency is high (98-99%). There are three steps involved in this process. 1. pH adjustment, 2. Reduction, 3. Precipitation. Adjustment of pH is achieved with the use of H_2SO_4 whereby pH is reduced to 2-3. At this pH level, the reduction of Cr^{+6} to Cr^{+3} can be achieved very efficiently. For reduction, various reducing agents such as sulfur dioxide, sodium bisulphate or sodium dithionite, sodium metabisulfate, ferricyanide and ferrous sulfate etc are used. SO2 in the waste gases is a commonly used reducing agent. Precipitation of dissolved metals to form the hydroxides by pH adjustment through the addition of alkalis is the major technique for removing chromium from aqueous wastes. For precipitation, most favorable pH is between 8 and 9. Pretreatment and separation prior to precipitation is often essential for effective metal removal. For instance, Cr (VI) should be reduced to Cr (III) in order to form the poorly soluble chromium (III) hydroxide (Mahajan, 1985).

2.2.2 Ion exchange

Ion exchange involves the reversible exchange of ions between a solution and a solid phase that are in direct contact. Both anionic and cationic exchange resins are employed for the treatment of liquid wastes containing chromium. By ion exchange, it is possible to recover chromium in the form of sodium chromate or chromic acid. In addition, the treated water can be reused in the process. Formerly this process suffered from the limitation of high cost of ion exchange resins and higher operational costs. However it is highly effective for trace metal removal depending on the chemical form of the given trace metals (Mahajan, 1985).

2.2.3 Reverse osmosis

It is a process in which heavy metals are separated by a semi-permeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids in wastewater. The disadvantage of this method is that it is expensive (Ozaki et al., 2002).In this process, the concentrated solution is subjected to high pressure (in excess of the osmotic pressure of the solution) as a result of which the solvent is forced out through a semi-permeable membrane to the dilute solution region. The concentrated solution becomes more concentrated and the chromium can be recovered from the concentrated solution. Initially reverse osmosis was used for the treatment of brackish water and desalination, but with

the development of cheaper and more efficient membranes, it was also possible to use in wastewater treatment. The three membranes most commonly used are cellulose acetate, aromatic polyamide, and NS 100. Cellulose acetate is used in wastewater treatment. The factors that affect the membrane performance are membrane leakage, membrane fouling and concentration polarization. The reverse osmosis process is expensive, i.e., both capital and operating costs are high (Mahajan, 1985)

2.2.4 Ultra filtration

They are pressure driven membrane operations that use porous membranes for the removal of heavy metals. The main disadvantage of this process is the generation of sludge. Metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. The disadvantage includes high cost and partial removal of certain ions (Ghosh and Bhattacharya, 2006).

2.2.5 Electro dialysis

In this process, the ionic components (heavy metals) are separated through the use of semi-permeable ion selective membranes. Application of an electrical potential between the two electrodes causes a migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes, cells of concentrated and dilute salts are formed. The disadvantage is the formation of metal hydroxides, which clog the membrane (Mohammad et al., 2005).

2.2.6 Adsorption

Adsorption can be a potential alternative to traditional treatment processes of metal ions removal (Ayhan, 2008; Mckay et al., 2000; Mohsen et al., 2007). The phenomenon of adsorption has been described in a wide range of non-living biomass like potato peel waste (Mohammed et al., 2009), orange peel (Ferda and Selen, 2012), crab shell (Vijayaraghavan et al., 2005), untreated coffee grounds (Azouaou et al., 2010), as well as of living biomass like, microbial cell (Gopal et al., 2002), moss (Lee and Low,1989), fungi (Sudha and Emilia, 2003), algae (Dumitru and Laura, 2012; Gupta and Rastogi, 2007; Mohammad et al., 2011) orange peel (Ferda and Selen, 2012).

Adsorption has been proved to be an excellent way to treat industrial waste effluents, offering significant advantages like the low-cost, availability, profitability, ease of operation and efficiency (Demirbas et al., 2008). The use of microbial biosorbents for removal of toxic heavy metals from wastewaters offers a relatively low cost method with potential for metal recovery.

Adsorption has distinct advantages over the conventional methods: the process does not produce sludges requiring further disposal, it could be highly selective, more efficient, easy to operate, can handle large volumes of waste waters containing low metal concentrations. The metal sequestering ability of microorganisms such as yeast, bacteria, fungi and algae have been investigated and reported .Adsorption technology based on the utilization of dead biomass offers certain major advantages such as lack of toxicity constraints, non-requirement of nutrient supply, and recovery of bound metal species by desorption (Gadd,1990).

In the last few decades, alternative sorbents for the treatment of heavy metal contamination have been investigated (Amany et al., 2007; Bayat, 2002; Cetin and Pehlivan, 2007; Mustafa et al., 2008; Wan and Hanfiah, 2008). There is a large volume of literature relating to the performance of different biosorbents for the removal of variety of heavy metals (Uysal and Ar, 2007; Qi. and Aldrich, 2008; Atalay et al., 2010).The agricultural residues seem to be preferred (Pollard et al., 1992; Nasernejad et al., 2005).

Plant materials are mainly comprised of cellulose materials that can adsorb heavy metal cations in aqueous solution. Numerous waste biomass sources are available in nature in which some experimental adsorption properties have been reported e.g rice husk (Kishore et al., 2008), saw dust (Ajay Kumar et al., 2008; Mehmet et al., 2007), tea and coffee waste (Amir et al., 2005), orange peel (Ferda and Selen, 2012), peanut shells (Qin et al., 2007) and activated carbon (Kadirvelu.et al., 2001). Venkateswarlu et al. (2007) carried out investigations on Azadirachta indica (neem) leaf powder as an adsorbent on chromium removal from aqueous solution. The results indicated that the adsorption capacity is strongly depends on equilibrium pH.

Cr (III) and Cr (VI) adsorptive removal from wastewater has been explored. The most important of these adsorbents are fly ash (Gupta et al.,1999; Rao et al., 2002; Bayat, 2002; Banarjee et al., 2004), blast furnace slag (Srivastava et al., 1997), red mud (Gupta et al., 2001; Lopez et al., 1998), lignin (Lalvani et al., 1997, 2000; Ali et al., 2004), waste sludge (Li et al., 2004; Slevaraj et al., 2003; Aksu et al., 2002), oil shale (Shawabkeh et al., 2006), tea factory waste (Malkoc et al., 2006), waste tires (Entezari et al., 2005) and residual slurry (Namasivayam and Yamuna, 1995; Singh and Tiwari,1997; Namasivayam and Yamuna, 1999).

2.3 Work done

From the literature cited, it was clear that there was a need to find a low cost process for the removal of toxic heavy metal contaminants from waste water. The process should have ease of operation so that the rural people can use it with least technical knowledge. Adsorption is universally accepted as the latest method of treating industrial and mine wastewater for removal of soluble toxic components.

The treatment process is also simple and convenient. Keeping in view the importance of treatment of Cr (III) contaminated water from industrial and mining establishments, the present study reports the feasibility of Cr (III) adsorption by using different low cost environment friendly adsorbents. Two efficient adsorbents were used in the studies which are newspaper and packaging (corrugated box) box.

Adsorption efficiency was studied as a function of contact time, pH, particle size, adsorbent dose and adsorbate concentration. Different adsorption isotherms were employed in order to evaluate the optimum adsorption conditions. Different adsorption model equations for kinetics, isotherm and rate mechanism of all the process were used to find out the best model, which fitted well to the experimental data. From the experimental results, the best adsorbent was chosen considering the metal loading capacity and kinetics. It was found that the adsorption capacity of the newspaper and packaging box was well compared to the other adsorbents reported in literature

CHAPTER 3

THEORETICAL CONSIDERATIONS

3.1 Adsorption processes

Adsorption occurs at least partly as a result of and likewise influences and alters forces active within phase boundaries, or surface boundaries these forces result in characteristic boundary energies. Classical chemistry defines a system by the properties of its mass: for surface phenomena the significant properties are those of the surface or boundary.

A pure liquid reduces its free surface energy through the action of surface tension, which is quantitatively equal to the amount of work necessary to compensate the natural reduction in free surface energy. A large number of soluble materials can effectively alter the surface tension of a liquid. Detergents, for example, lower surface tension dramatically. If a material which is active at surfaces is present in a liquid system, a decrease in the tension at the surface will occur upon movement of the solute to the surface. Migration of the substance to the surface or boundary results in a reduction of the work required to enlarge the surface area, the reduction being proportional to the concentration of adsorbate at the surface.

The energy balance of the system thus favors adsorptive concentration of such surface-active substances at the phase interface. The tendency of an impurity to lower the surface tension of water is referred to as hydrophobicity, that is, the impurity 'dislikes' water.

Adsorption of an impurity from water on to activated carbon may result from solute hydrophobicity, or it may be caused by a high affinity of the solute for the carbon. For most systems encountered in waste treatment, adsorption results from a combination of these factors. The solubility of a substance in water is significant: solubility in the sense of the chemical compatibility between the water and the solute. The more hydrophilic a substance the less likely it is to be adsorbed. Conversely, a hydrophobic substance will more likely be adsorbed.

In the context of solute affinity for the solid, it is common to distinguish between three types of adsorption. The affinity may be predominantly due to: (I) electrical attraction of the solute to the adsorbent (exchange adsorption), (II) Vander Waals attraction (physical or ideal adsorption) or, (III) chemical reaction (chemisorptions or chemical adsorption).

Many adsorptions of organic substances by activated carbon result from specific interactions between functional groups on the sorbate and on the surface of the sorbent. These interactions may be designated as 'specific adsorptions'. It is possible for specific adsorptions to exhibit a large range of binding energies, from values commonly associated with 'physical' adsorption to higher energies associated with 'chemisorptions'. The adsorptive interactions of aromatic hydroxyl and nitro-substituted compounds with active carbon, for example, are specific adsorption processes resulting from formation of donor-acceptor complexes with surface carbonyl oxygen groups, with adsorption continuing after these sites are exhausted by complexation with the rings of the basal planes of the carbon micro crystallite.

Adsorption results in the removal of solutes from solution and their concentration at a surface, until the amount of solute remaining in solution is in equilibrium with that at the surface. This equilibrium is described by expressing the amount of solute absorbed per unit weight of adsorbent q, as a function of C, the concentration of solute remaining in solution. An expression of this type is termed an adsorption isotherm. Two equations, the Langmuir equation and the Freundlich equation, find common use for describing adsorption isotherms for water and wastewater treatment applications.

The Langmuir isotherm is

$$q_e = QbC/(1 + bC)$$

in which b is a constant related to the energy or net enthalpy of adsorption, and Q is the ultimate adsorption capacity. The Freundlich equation has the general form where K_F and n are constants and n> 1.

$$q_e = K_F C^{1/n}$$

Data are usually fitted to the logarithmic form of the equation, which gives a straight line. The intercept is roughly an indicator of sorption capacity and the slope, 1/n, of adsorption intensity. The Freundlich equation generally agrees well with the Langmuir equation and experimental data over moderate ranges of concentration, C. Unlike the Langmuir equation however, it does not reduce to a linear adsorption expression at very low concentrations, nor does it agree well with the Langmuir equation at very high concentrations. The adsorption isotherm is useful for representing the capacity of an activated carbon for adsorbing organics from a waste, and in providing description of the functional dependence of capacity on the concentration of pollutant. The steeper the isotherm, the more effective is the activated carbon; that is, the sharper the rise of the isotherm to a given ultimate capacity as concentration increases, the higher will be the effective capacity at the concentration level desired for the treated water. Experimental determination of the isotherm is routine practice in evaluating the feasibility of adsorption for treatment, in selecting a carbon, and in estimating carbon dosage requirements.

The Langmuir and Freundlich equations provide means for mathematical description of the experimentally observed dependence of capacity on concentration. The adsorption isotherm relates to an equilibrium condition, however, and practical detention times used in most treatment applications do not provide sufficient time for true equilibrium to obtain. Rates of adsorption are thus significant, for the more rapid the approach to equilibrium, the greater is the fraction of equilibrium capacity utilized in a given contact time.

There are three primary rate steps in the adsorption of materials from solution by granular activated carbon. First is the transport of the adsorbate through a surface film to the exterior of the adsorbent ('film diffusion'); second is the diffusion of the adsorbate within the pores of the adsorbent (pore diffusion); third is adsorption of the solute on the interior surfaces bounding pore and capillary spaces.

For most operating conditions transport of adsorbate through the 'surface film' or boundary layer is rate-limiting, if sufficient turbulence is provided; transport of the adsorbate within the porous carbon may control the rate of uptake.

The method by which the carbon is contacted with the water determines in large part which of the transport or reaction steps is rate-limiting. For a completely and vigorously mixed batch reactor, pore diffusion may be rate-limiting. For continuous flow systems (e.g. beds of granular carbon) film diffusion is usually rate-limiting for normal flow rates.

3.2 How are pollutants adsorbed?

The Figure 3.1 shows a molecule above a surface, with the distance from the surface being the normal to the surface. There is repulsion between the cloud of electrons in atoms that form the surface and those of the molecule, and there is also a nuclear attraction force. The nuclear attraction has a much shorter radius of influence, so there is a short distance (usually nanometers) from the surface where there is a "dip" or a "well" in the potential energy curve as shown in Figure 3.2. Molecules or atoms that reach this "well" are trapped or "adsorbed" by this potential energy "well" until they can obtain enough kinetic energy to fly out of the well and escape. Kinetic energy converts to potential energy, just as when you jump upward against gravity. Therefore, kinetic energy must be added to allow the molecules to escape or desorbed. Kinetic energy of molecules exhibits itself as the temperature, with hotter being more energetic.

Historically, carbon was the first material to be observed to have a large amount of area with this property. Zeolite and polymer adsorbents have more recently been found to also have a large amount of internal surface area with this property.
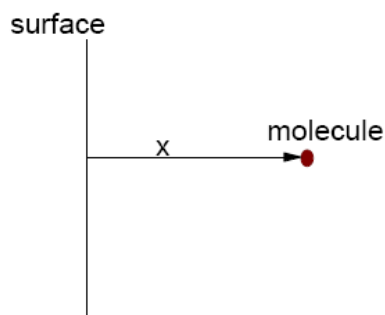
Fig. 3.1 Molecule-Surface Distance
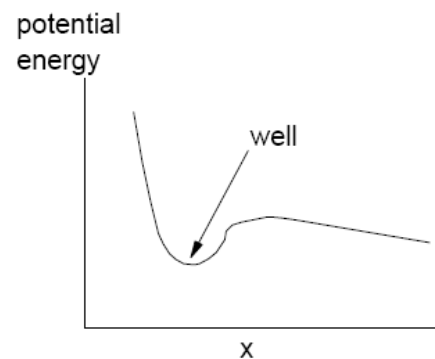
Fig. 3.2 Potential Energy vs. Distance

We have known for decades that before you can pull a "hard vacuum" (such as 1 micron Hg) even glass systems have to "outgas" adsorbed air. What is unique to these adsorbents is that they have such a large amount of area (mostly internal) with this property per unit of weight, and that this area can be desorbed so readily.

3.3 Advantages of adsorption process and adsorbents

Adsorption is an effective purification and separation technique used in industry especially in water and wastewater treatments. A number of methods for toxic metal removal from waste water have been used, but most have several disadvantages , such as continuous input of chemicals, high cost, toxic sludge generation or incomplete metal removal but the adsorption process has been found advantageous such as: low cost of adsorbent, easy availability, utilization of industrial, biological and domestic waste as adsorbents, low operational cost, ease of operation compared to other processes, reuse of adsorbent after regeneration, capacity of removing heavy metal ions over wide range of pH and to a much lower level, ability to remove complex form of metals that is generally not possible by other methods, environmentally friendly, cost effective and technically feasible.

Adsorption process is the best process for removal of metals from wastewater because it is simple, time saving and inexpensive involving no sophisticated apparatus. A definite need exists for low cost adsorbents which exhibit superior adsorption capacities and local availability.

3.4 Types of adsorption

There are two types of adsorption phenomena, physical adsorption and chemical adsorption (Jiaping, 2012).

3.4.1 Physical adsorption (Vander Waals adsorption)

Physical adsorption is the result of intermolecular forces of attraction between molecules of the solid adsorbent and the substance adsorbed. It is a readily reversible phenomenon. In industrial adsorption operations this reversibility is used for the recovery of adsorbent for reuse, for recovery of adsorbed substance or for the fractionation of the mixtures.

3.4.2 Chemisorption

Chemisorption is the result of chemical interaction between the solid adsorbent and the adsorbed substance. The adhesive force and the heat liberated are much greater those that found in physical adsorption. The process is frequently irreversible. Some substances which under condition of low temperature undergo only physical adsorption substantially. But they exhibit chemisorption at high temperatures and sometimes both the phenomena may occur at the same time. Chemisorption is of particular importance in catalysis.

3.5 Factors affecting adsorption

3.5.1 pH

The pH value of the metal solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The pH of the solution would affect both aqueous chemistry and surface binding sites of the adsorbents. The effect of pH in turn depends on the charge on the adsorbent surface. If the adsorbent surface is negatively charged, at lower pH, the large number of H^+ ions present neutralizes the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion, and a better adsorption is obtained. If the surface charge of the adsorbent is positively charged, the H^+ ions may compete effectively with the cations of the solution causing a decrease in the amount of metal ion adsorbed (Jiaping, 2012).

3.5.2 Contact time

The amount adsorbed on to the adsorbent is in a state of dynamic equilibrium with the amount desorbed from the adsorbent. The time required to attain this state of equilibrium is termed as the equilibrium time. The amount adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under the operating conditions.

3.5.3 Concentration

Whatever be the mechanism of adsorption from the solution, it is certain that the extent depends mainly on the available surface of the adsorbent. The process of adsorption is almost invariably reversible and a definite equilibrium is reached in a short time dependant on the concentration of the solution and quantity of the adsorbent.

3.5.4 Temperature and pressure

Increase of temperature and decrease of pressure increase the extent of adsorption. This fact that heat is absorbed in the process of adsorption is implied in the Le Chatliers principles. As in the case of the heat of the solution the different heats of adsorption, viz, the differential and integral heat must be distinguished.

3.5.5 Surface area (particle size)

The adsorbents with smaller particle size have a higher ability in the adsorption process with large external surface. Therefore more metal ions could be removed than the large particles. The adsorption increases as the particle size decreases, because the surface area increases when the particle size decreases. Such an effect is probably due to the inability of the large ions to penetrate all the initial pore structure of the adsorbent.

3.6 Adsorption criteria

When selecting adsorbents and absorbents, the most important properties to consider are the selectivity, surface area, and regeneration ability.

- **Selectivity** is the amount of specificity a sorbent has in the materials that it can capture. A very unselective sorbent captures many substances and a selective sorbent only removes specific ones.
- **Surface area** is the amount of material a sorbent has available for contact and determines the capacity of material a sorbent can capture, the capture rate of the sorbent, and the retention rate of the substance within the sorbent.
- **Regeneration** is the ability of a sorbent to be reused after capturing to its capacity. Many desiccants can be heat treated in order to regenerate the material after reaching water capture capacity. Other factors to consider when selecting sorbents are bulk density, chemical inertness, and ease of application.

3.7 Adsorption isotherms

Adsorption isotherm is a quantitative relationship describing the equilibrium between the concentration of adsorbate in solution and its adsorbed concentration. In the present study adsorption isotherms have been used to describe adsorption behavior and to estimate the adsorption capacity of newspaper and packaging box on the removal of chromium (III) from tannery wastewater. In this, adsorption equilibrium data has been fitted with Langmuir and Freundlich adsorption isotherm equations.

3.7.1 Langmuir adsorption isotherm

The most widely used isotherm equation for modeling the equilibrium is the Langmuir equation which is valid for monolayer sorption on to a surface with a finite number of identical sites and is given by equation

$$q = \frac{q_{max}bC_F}{(1+bC_f)}$$

Where q_{max} is the maximum amount of the metal ion per unit weight of the adsorbent to form a complete monolayer on the surface bound at high C_f and b is a constant related to the affinity of the binding sites q_{max} represents a practical limiting adsorption capacity when surface is fully covered with metal ions and assists in the comparison of adsorption performance particularly in cases where the sorbent did not reach its full saturation in experiments. q_{max} and b can be determined from the linear plot of C_f /q versus C_f (Babu and Gupta, 2008).The linearized form of this model equation is given as

$$C_f/q = C_f/q_{max} + 1/bq_{max}$$

3.7.2 Freundlich adsorption isotherm

The empirical Freundlich model also considers mono molecular layer coverage of solute by the adsorbent. However, it assumes the adsorbent has a heterogeneous surface so that binding sites are not identical. This model takes the following form for a single component adsorption (Azouaou et al., 2010).

$$q = KC_f^{1/n}$$

Where K and n are the Freundlich constants characteristic of the system. K and n are indicators of adsorption capacity and adsorption intensity respectively. Through the Freundlich isotherm is more widely used, it provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model (Aksu et al., 2003; Yu et al., 2003; Ferda et al., 2012).

3.8 Adsorption kinetic models

When the metal ion solution is mixed with the adsorbent, transport of the metal ions from the solution through the interface between the solution and the adsorbent occurs into pores in the particles. There are four main stages in the process of adsorption by porous adsorbents (i) solute transfer from the bulk solution to the boundary film that surrounds the adsorbent's surface, (ii) solute transport from the boundary film to the adsorbent's surface, (iii) solute transfer from the adsorbent's surface to active intra particular sites, and (iv) interactions between the solute molecules and the available adsorption sites on the internal surfaces of the adsorbent. One or more of these four steps controls the rate at which solute is adsorbed. The first and second steps were very slow and were found to be the rate determining step shows that the heavy metal ions diffused quickly among the particles at the beginning of the adsorption process, and then intraparticle diffusion slowed down and stabilized. In 1898, Lagergren presented the first order rate equation for the adsorption of ocalic acid and malonic acid onto charcoal (Lagergren, 1898). Lagergren kinetics equation may have been the first one in describing the adsorption of liquid-solid systems based on solid capacity. The pseudo first-order equation (Lagergren, 1898) Lagergren kinetics equation has been most widely used for the adsorption of an adsorbate from an aqueous solution.

3.8.1 Lagergren equation (pseudo-first-order)

Adsorption kinetic model Lagergren, (1898) is expressed as

$dq_e/dt = k(q_e - q_t)$

'k' can be calculated from the slope of the linear plot between log(qe-qt) vs. 't' for different adsorption parameters such as pH, temperature, adsorbate concentration, adsorbent dose, particle size and agitation speed.

The Pseudo first order or Lagergen kinetic rate equation for the sorption of liquid solid system was derived based on solid adsorption capacity. It is one of the most widely used sorption rate equations for sorption of a solute from a liquid solution (Lagergren, 1898). According to the authors, the overall adsorption rate is directly proportional to the driving force, i.e., the difference between initial and equilibrium concentrations of the adsorbate (q_e-q_t).

3.9 Principle of atomic absorption spectrophotometry

The sample solution is aspirated into a flame and the sample element is converted to atomic vapor. The flame then contains atoms of that element. Some are thermally excited by the flame, but most remain in the ground state. These ground-state atoms can absorb radiation of a particular wavelength that is produced by a special source made from that element. The wavelengths of radiation given off by the source are the same as those absorbed by the atoms in the flame.

Atomic absorption spectrophotometry is identical in principle to absorption spectrphotometry. The absorption follows Beer's law. That is, the absorbance is directly proportional to the path length in the flame and to the concentration of atomic vapor in the flame.

Both of these variables are difficult to determine, but the path length can be held constant and the concentration of atomic vapor is directly proportional to the concentration of the analyte in the solution being aspired.

Fig. 3.3 Atomic Absorption Spectrophotometer (AA-7000)

Fig. 3.4 Laboratory work

Specifications of AAS

- Item: AA-7000 Atomic Absorption Spectrophotometer

- Company : Shimadzu

- Dimensions (WxDxH) : 70.0×58.8 D $\times$ 71.4 cm (27.5 x 23.1 x 28.1 inches)

- Applications: Flame / Furnace Analysis

- Wavelength(s):185 - 900 nm

- Power Furnace : 6000 VA

- Configurations: Double Beam

- Lamp Type: Hollow-Cathode

- Vaporization : Flame

- Auto sampler : Optional

- Optics: Monochromator

- Weight :75 Kg

- Operating Environment Temperature : 10 to 35 °C

- Humidity: 20 to 80%
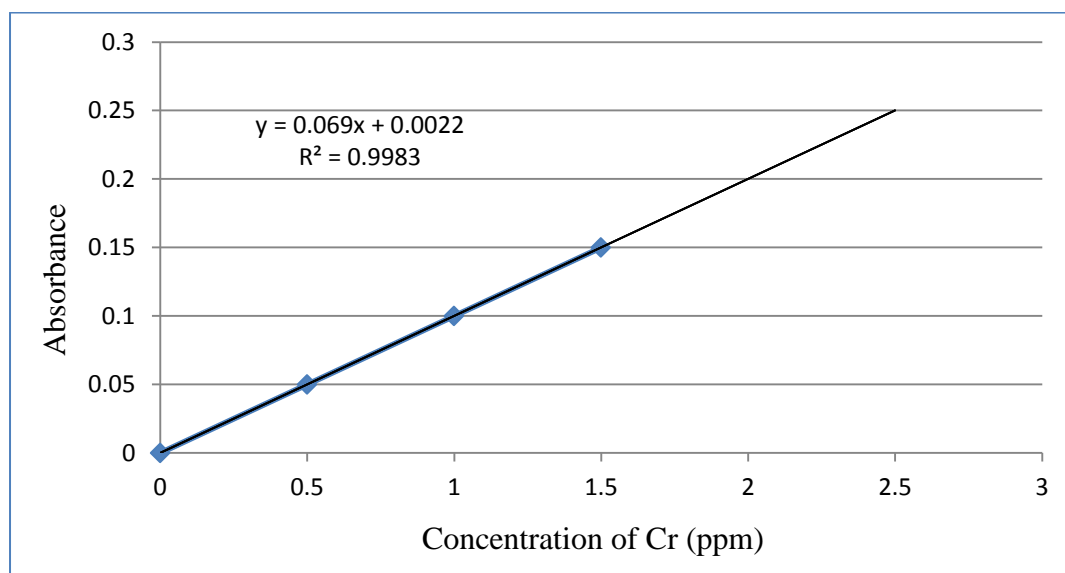
Fig.3.5 Calibration curve for AAS.

CHAPTER 4

EXPERIMENTAL

4.1 Adsorbents collection

Adsorbents which are available in our country are collected from the following points:

Table 4.1 Collection site of adsorbents.

Sl No.	Adsorbents	Collection Site
01.	Plastic	Plastic industry wastes, Household
02.	Rubber	Rubber industry wastes, Factory, Household
03.	Hen hair	Local raw market, Household, Community centre
04.	Sheep wool	Tannery industry
05.	Newspaper	Household, Office, Company, Newspaper industry wastes, Wastage paper market
06.	Activated bone carbon	Hazaribagh dumping sites , Butcher house sites
07.	Goat skin trimmings	Tannery industry
08.	Brick powder	Construction sites
09.	Concrete	Construction sites
10.	Packaging box (Corrugated box)	Household, Office, Company, Corrugated boxes industry wastes, Wastage paper market

4.2 Adsorbents digestion

The selected adsorbents available in our country were firstly collected and dried in an oven at a temperature of 100 - 105 ° C for an hour. Then the adsorbents were ground to powder form. From them 0.5 g of each of the adsorbents was mixed with 6 ml of HNO_3 (in case of hair and wool both nitrtic acid and perchloric acid used). The solution was then digested in a digester at BCSIR, Dhaka. Finally the digested solution was made to 10 ml with the addition of required amount of distilled water. The solution was further diluted if required for analysis. The solution was then analysis by using an Atomic Adsorption Spectrometer (AA-7000), Shimadzu, Japan (detection limit for chromium 0.03 ppm) to determine the chromium content in the adsorbents before adsorption experiment. From this analysis we get the following contents of chromium in different adsorbents.

Table 4.2 Chromium content in different adsorbents.

Name of the adsorbent	Chromium content (ppm)
Plastic	7.15
Rubber	7.48
Hen hair	11.67
Sheep wool	10.67
Newspaper	2.15
Activated bone carbon	0.05
Goatskin trimmings	12.58
Brick powder	0.49
Concrete	7.45
Packaging box (Corrugated box)	2.25

4.3 Adsorption experiment

Adsorption experiments were carried out in conical flasks using standard chromium solution with required amount of adsorbent. The flasks were continuously shaken for required time period by a shaker at 60 rpm rotation speed till equilibrium reached. The mixtures were filtered through filter paper and the residual Cr (III) concentration after filtration was determined spectrophotometrically using Atomic Absorption Spectrophotometer (AA-7000, Shimadzu, Japan, detection limit 0.03 ppm). Volume (V) of the solution was kept constant (100 ml). The chromium removal (%) at any instant of time was determined by the following equation-

$$\text{Chromium removal (\%)} = \frac{C_o - C_t}{C_o} \times 100$$

Where, C_o and C_t are the concentration of chromium at initial condition and at any instant of time, respectively. The effects of various parameters on the rate of adsorption process were observed by varying contact time, t (30,60, 120, 180, 240, 300, 360, 420, 480 and 540 min), initial concentration of chromium ion, Conc. (100, 200, 400, 800,1600 and 3200 ug/L), adsorbent concentration, W (1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 g/100 ml) and initial pH of solution (1.5, 2, 3, 4, 6, 8, 10 and 12). Adsorption isotherm studies were carried out with different adsorbent doses ranging from 1 to 10 g/100 mL at the same time as maintaining the initial chromium concentration at 200 μg /L. The pH of the solution was maintained at desired value by adding H_2SO_4 or NaOH before adsorption.

4.4 Adsorbent (Newspaper) preparation

Newspaper is a non agricultural waste material which is available in our country. The availability of Waste Newspaper is quite high and low cost. The Newspaper contains various functional groups, which are good chelating agents and thus good binder for various metal ions. Therefore, it has the potential to treat wastewater containing heavy metal ions. Interest in the use of Newspaper as an adsorbent has been stimulated by the good results. This newspaper collected from household, offices, wastage paper market, Dhaka, Bangladesh, has been used in this experiment. It is available in plenty. The newspaper is particularly interesting in Bangladesh because of its high availability and low cost as compared to the other adsorbents. The collected Newspaper was dried in sunlight until almost all the moisture evaporated. It was ground to a powder and sieved to 20 to 200 meshes.

Fig. 4.1Newspaper wastes

4.5 Adsorbent (Packaging box/ Corrugated box) preparation

Packaging box (Corrugated box) is a nonagricultural waste material which is available in our country. The availability of packaging box is quite high and low cost. The packaging box (corrugated box) contains various functional groups, which are good chelating agents and thus good binder for various metal ions. Therefore, it has the potential to treat wastewater containing heavy metal ions. Interest in the use of packaging box as an adsorbent has been stimulated by the good results. This packaging boxes collected from household, offices, wastage paper market, Dhaka, Bangladesh, has been used in this experiment. It is available in plenty. The wastage packaging box is particularly interesting in Bangladesh because of its high availability and low cost as compared to the other adsorbents. The collected packaging box was dried in sunlight until almost all the moisture evaporated. It was ground to a powder and sieved to 20 to 200 meshes.

Fig. 4.2 Packaging (Corrugated box) box wastes.

4.6 Standard solution preparation

Chromium having concentration 1000 ppm was taken as standard solution at volumetric flask. Experimental solutions of the desired concentrations were obtained by successive dilutions using dilution theory ($V_1S_1 = V_2S2$), where V_1 is the initial volume, S_1 is the initial concentration, V_2 is the final volume and S_2 is the final concentration of the solution. The diluted solution was taken 10 ppm and then to required concentration 100 ppb, 200 ppb, 400 ppb, 800 ppb, 1600 ppb, 3200 ppb taken for experiment.

4.7 FTIR studies

FT1R analysis of the adsorbents was carried out using IR Prestige-21 spectrophotometer. Pellets (press disk) were used for measuring absorption spectra. The samples were ground with 200 mg of ATR (spectroscopic grade) in a mortar and pressed into 10 mm diameter disks under 10 tons of pressure and high vacuum for FT-IR analysis. The conditions used were 16 scans at a resolution of 4 cm-^{1} measured between 600 and 4000 cm-$^{1.}$

Fig. 4.3 IR-Prestige-21.

4.7.1 FT-IR analysis for newspaper

Apart from electrostatic force of attraction, the adsorption might be due to formation of complex in the ligands available in the adsorbents. The adsorbent as such showed peaks at 893.06, 1029.04, 1344.41, 1422.53, 1501.61 and 1664.60 cm^{-1}. The results are shown in Table 4.3.

Table 4.3 FT-IR peaks and group assignment (Newspaper).

Peak wavelength(cm^{-1})	Assign to
893.06	=C-H bending usually strong
1029.04	C-F stretching, strong
1344.41	C-N stretching, medium weak
1422.53	-C-H bending , variable
1501.61	C=C stretch, medium weak, multiple bands
1664.60	C=C stretch usually variable

4.7.2 FT-IR analysis for packaging box

Apart from electrostatic force of attraction, the adsorption might be due to formation of complex in the ligands available in the adsorbents. The adsorbent as such showed peaks at 896.91, 1030.97, 1421.56, 1675.21, 2881.70 and 3618.52 cm^{-1}. The results are shown in Table 4.4.

Table 4.4 FT-IR peaks and group assignment of Packaging Box (Corrugated Box).

Peak wavelength (cm-1)	Assign to
896.91	=C-H bending usually strong
1030.97	C-F stretching usually strong
1421.56	-C-H bending , variable
1675.21	C=C stretch , variable
2881.70	C-H stretch , usually strong
3618.52	0-H (Stretch, free), usually strong, sharp

4.8 Real sample processing

The effluent (mainly tannery effluent) collected from Hazaribag was first sediment to remove suspending materials. Then the partially clarified effluent is filtered through filter paper of Whatman No-44. The clarified solution was stored in refrigeration system at a temperature of 0-5° C. From here 100 ml solution in each batch for 5g of adsorbent was used to testify the efficiency of adsorbent in the real sample.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Introduction

Firstly, the performances of ten adsorbents such as Plastic, Rubber, Hen hair, Sheep wool, Newspaper, Activated bone carbon, Goat skin trimmings, Brick powder, Concrete and Packaging (Corrugated box) boxes were evaluated for the removal of Chromium (III) from aqueous solutions. The removal efficiencies with Plastic, Rubber, Hen hair, Sheep wool, Newspaper, Activated bone carbon, Goat skin trimmings, Brick powder, Concrete and Packaging (Corrugated box) boxes were 13%, 14%, 28%, 58%, 63% ,37%, 27%, 12%, 47% and 69% respectively. These adsorbents had lower removal efficiencies than Newspaper and Packaging (Corrugated box) box. Therefore, they were not considered for further investigation.
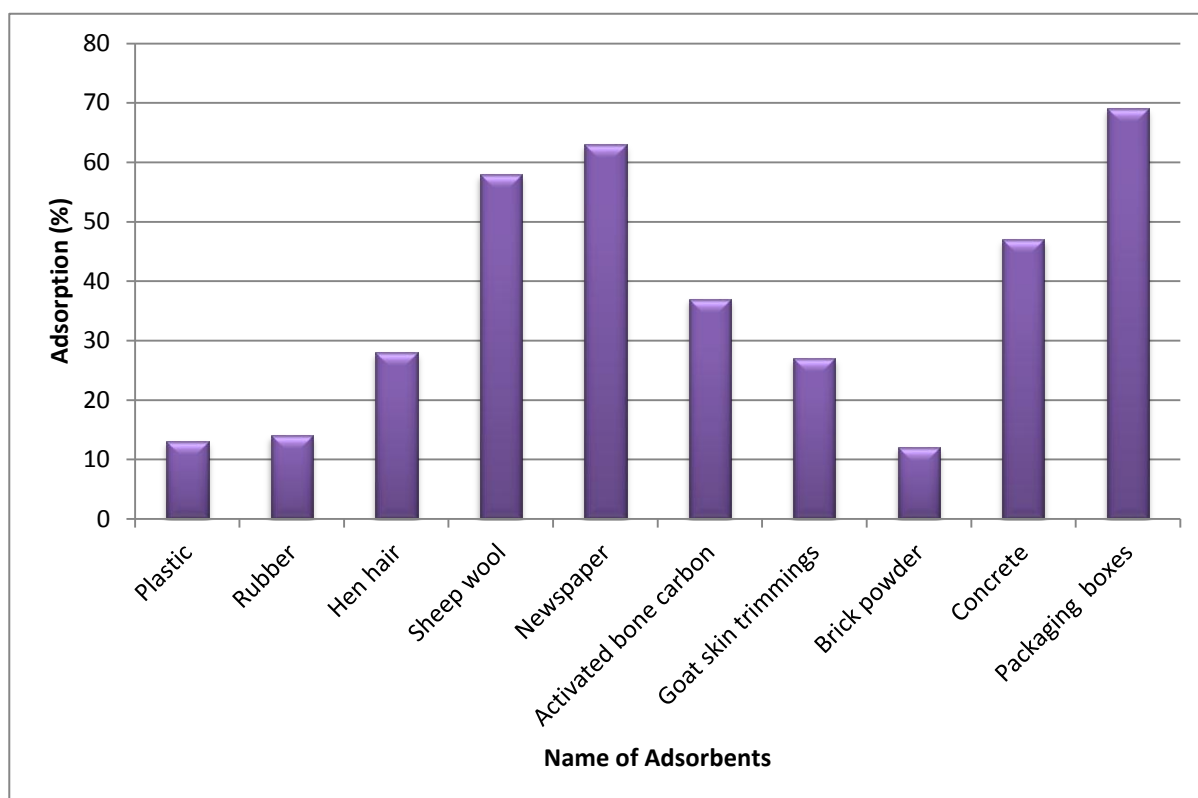
Fig. 5.1 Amount of chromium adsorbed in different adsorbents (contact time 180 min, initial cone 200 μg /L, adsorbent 1 g, initial pH 1.5, agitation speed 60 rpm).

Table 5.1 Adsorption efficiency of different adsorbent.

Adsorbents	Adsorption (%)
Plastic	13
Rubber	14
Hen hair	28
Sheep wool	58
Newspaper	63
Activated bone carbon	37
Goat skin trimmings	27
Brick powder	12
Concrete	47
Packaging box (Corrugated box)	69

5.2 Results discussion for newspaper

5.2.1 Parameters for optimization of the process

5.2.1.1 Effect of adsorbent dose on chromium adsorption

At this stage, the experiments were done under the conditions with pH of 1.5 and variable adsorbent doses (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 g/100 mL). The effect of adsorbent doses on the adsorption of chromium by newspaper was presented in Fig.5.2.1. As illustrated in Fig.5.2.1 the increase in percentage adsorption with the increase in adsorbent dose might be due to the increased number of free surface available, which caused increased number of adsorbate molecules to adsorb. The decrease in uptake might be due to the larger surface area at higher dose which remained free for adsorption at equilibrium
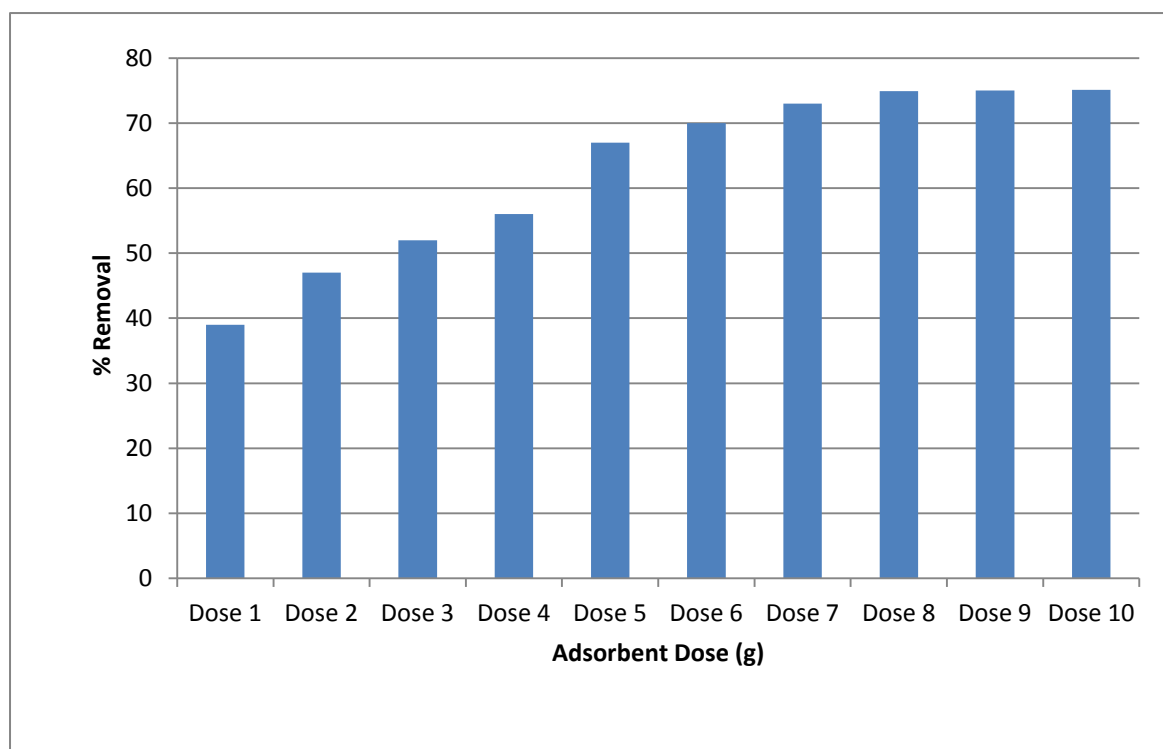
Fig. 5.2.1 Effect of adsorbent dosage on Cr (III) adsorption (contact time 120 min, initial concentration 200 μg /L, initial pH 1.5 of Cr (III) solution in the case of newspaper.

Table 5.2.1 Effect of adsorbent dosage on percentage (%) removal of Cr (III) ions for aqueous solutions (contact time 120 min, initial concentration 200 μg /L, and initial pH 1.5 of Cr (III) solution).

Adsorbent dosage (g)	Chromium (III) removal (%)
1	39
2	47
3	52
4	56
5	67
6	70
7	73
8	74.9
9	75
10	75.1

5.2.1.2 Effect of contact time on chromium adsorption

In order to find out the equilibrium contact time, experiments were carried out for 9 h. From the experimental data it was observed that percentage adsorption increased with increase in contact time up to 6 h and after that it attained a stationary phase. From Fig.5.2.2, it is observed that initially the adsorption rate was fast followed by a slower rate.

Further, the plots between times vs. percentage adsorption were smooth and continuous suggesting the possible monolayer adsorption of Cr (III) on the surface of adsorbent. As optimum adsorption was achieved in 2 h, rests of the experiments were carried out for 2 h time.

In this stage, all of the parameters except contact time, including temperature (25 °C), adsorbent dose (5 g/100 mL), pH (1.5), initial chromium concentration (200 µg /L) and agitation speed (60 rpm), were kept constant. There was no significant change in equilibrium concentration after 360 min up to 420 min and after 360 min, the adsorption phase reached to equilibrium. During the initial stage of sorption, a large number of vacant surface sites are available for adsorption. After a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the adsorbate molecules on the solid surface and in the bulk phase. Besides, the metal ions are absorbed into the meso-pores that get almost saturated during the initial stage of adsorption. Thus the driving force for the mass transfer between the bulk liquid phase and the solid phase decreases with the passage of time. Further, the metal ions have to transverse further and deeper into the pores encountering much larger resistance (Srivastava et al., 2006). This results in the slowing down of the adsorption during the later phase.
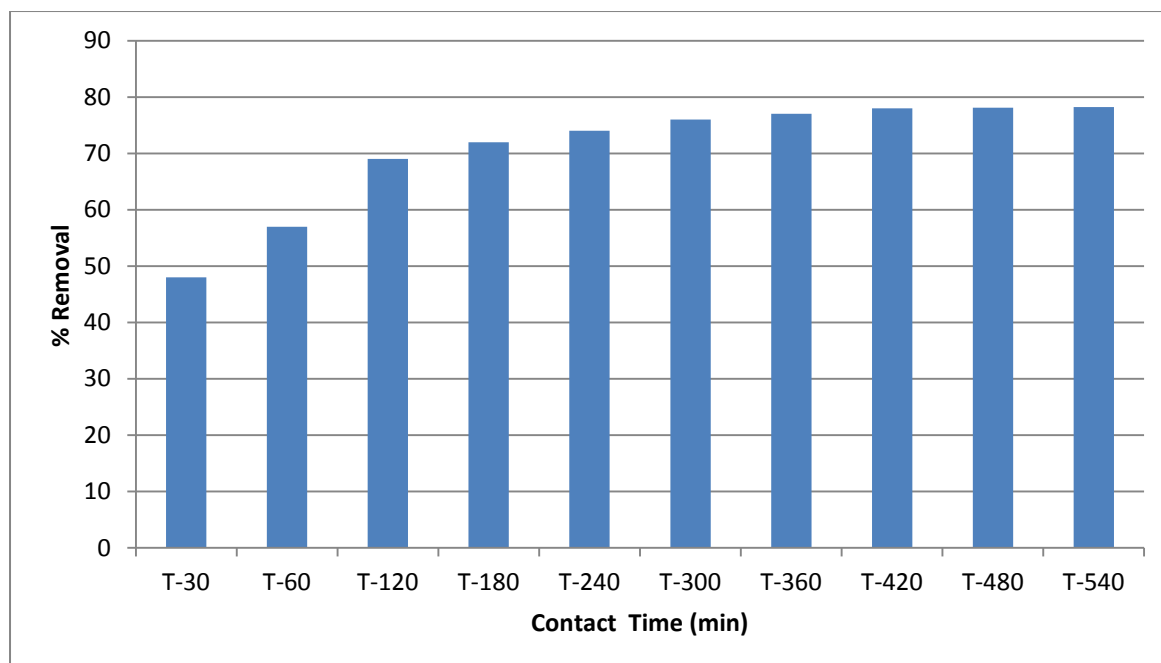
Fig. 5.2.2 Effect of contact time on Cr (III) adsorption (initial concentration 200 µg /L, initial pH 1.5, adsorbent dose 5g/100 ml, rotation speed 60 rpm).

Table 5.2.2 Effect of contact time on Cr (III) adsorption (initial concentration 200 µg /L, initial pH 1.5, adsorbent dose 5g/100ml, rotation speed 60 rpm).

Contact time (min)	Chromium (III) removal (%)
30	48
60	57
120	69
180	72
240	75
300	77
360	78
420	78.3
480	78.7
540	78.44

5.2.1.3 Effect of pH on Chromium adsorption

Adsorption experiments were performed at different pH values (1.5, 2.0, 3.0, 4.0, 6.0, 8.0, 10.0, and 12.0). From Fig. 5.2.3, it is observed that the percentage of adsorption increased from 62 to 78 percent at a pH from 1.5 to 4 then decrease the percent adsorption with the increase of pH up to 12. The increase in percentage adsorption as well as uptake at lower pH could be well explained by protonation properties of the adsorbent. At low pH values, i.e., higher hydrogen ion concentration, the negative charge at the surface of internal pore were neutralized and some more new adsorption sites were developed which provided a positive charge for anionic Cr (III) complex to get adsorbed on the surface. Again it is observed that the final pH of the solution was always greater than the initial pH of the solution, which confirmed the neutralization of H^+ ions with the negative charge at the surface and envelopment of more H^+ ions in formation of positively charged surface. As a result, the concentration of H^+ ions decreased in the solution and hence the pH of the solution increased. Many authors also reported similar results (Yu et al., 2003). From the adsorption uptake at both higher and lower pH (12 and 1.5) it is concluded that the adsorbent can be used for the treatment of Cr (III) contaminated Tannery water at lower pH.

Fig. 5.2.3 Effect of pH on Cr (III) adsorption (contact time 120 min, initial concentration 200 µg /L, adsorbent dose 5g/100 ml).

Table 5.2.3 Effect of pH on Cr (III) adsorption (contact time 120 min, initial concentration 200 μg /L, and adsorbent dose 5g/100 ml).

pH value	Chromium (III) removal (%)
1.5	62
2	64
3	67
4	78
6	69
8	65
10	53
12	41

5.2.1.4 Effect of initial chromium concentration on Cr (III) adsorption

The percentage adsorption with different adsorbate concentrations was studied by varying Cr (III) concentration from 200 ppb to 3200 ppb keeping adsorbent dose at (5g/100 ml), stirring speed (60 rpm), pH (1.5) and temperature (25^0 C) constant. Fig. 5.2.4 shows the effect of initial adsobate concentration. It was observed that the percentage of adsorption decreased with the increase of adsorbate concentration.

This may be due to the fact that at a fixed adsorbent dose, the number of active adsorption sites to accommodate the adsorbate ions remained unchanged while with higher adsorbate concentrations, the adsorbate ions to be accommodated increased. Thus, the loading was faster with higher initial concentrations of adsorbate.
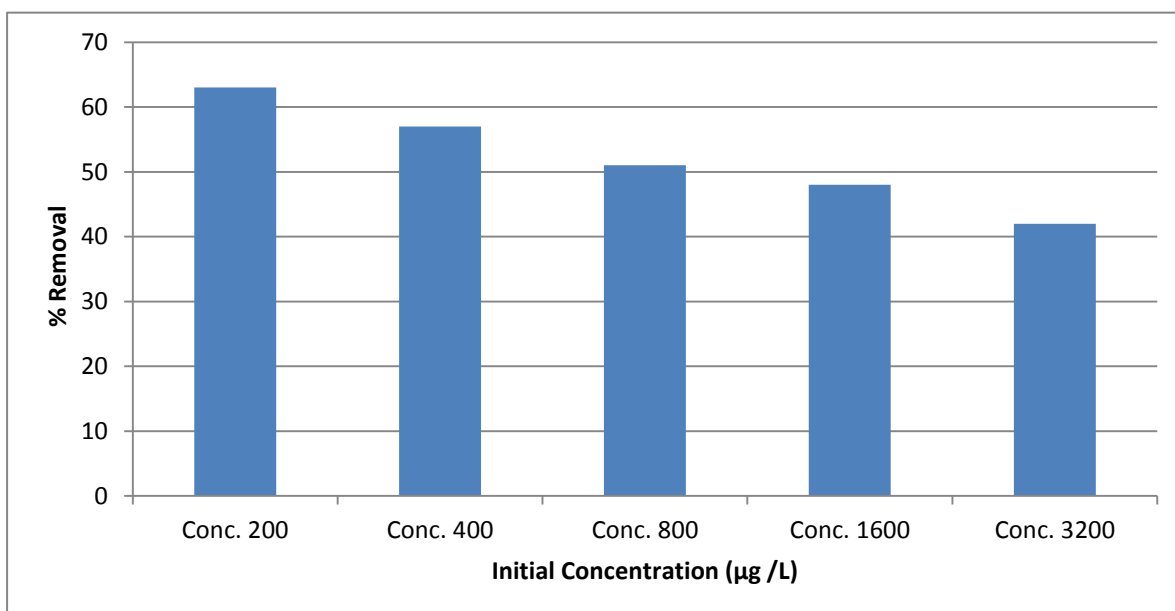
Fig.5.2.4 Effect of initial chromium concentration on adsorption (contact time 120 min, initial pH 1.5, adsorbent dose 5g/100 ml, rotation speed 60 rpm).

Table 5.2.4 Effect of initial chromium concentration on adsorption (contact time 120 min, initial pH 1.5, adsorbent dose 5g/100 ml and rotation speed 60 rpm).

Initial concentration (μg /L)	Chromium (III) removal (%)
200	63
400	57
800	51
1600	48
3200	42

5.2.1.5 Effect of particle size of adsorbent

Batch adsorption experiments were carried out for the removal of chromium from aqueous solution using five different particle sizes (0.074, 0.125, 0.177, 0.42, 0.841 mm). The results are shown in Figure. 5.2.5. With decreasing particle size, the removal increased from 61 to 77%. Munaf and Zein (1997) reported that, when the size of the adsorbents particles increased, the adsorption of metal ions decreased. Similar trends have been reported by Wong et al. (2003). These phenomena might be due to the fact that the

smaller particles offer comparatively larger surface areas and greater numbers of adsorption sites compare to larger particles.
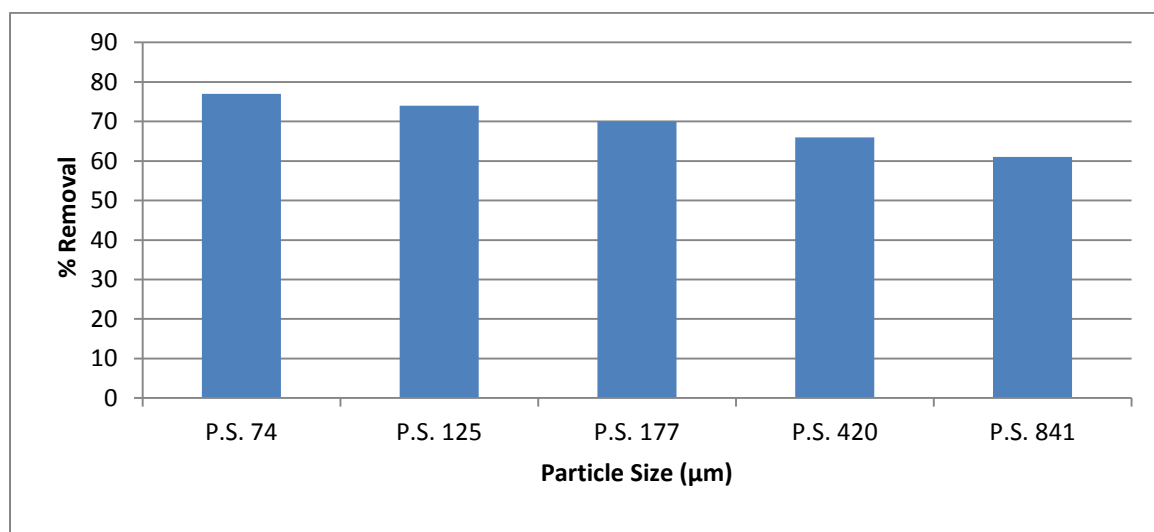
Fig. 5.2.5 Effect of particle size on Cr (III) adsorption (contact time 120 min, initial concentration 200 µg /L, adsorbent dose 5g/100 ml, pH 1.5).

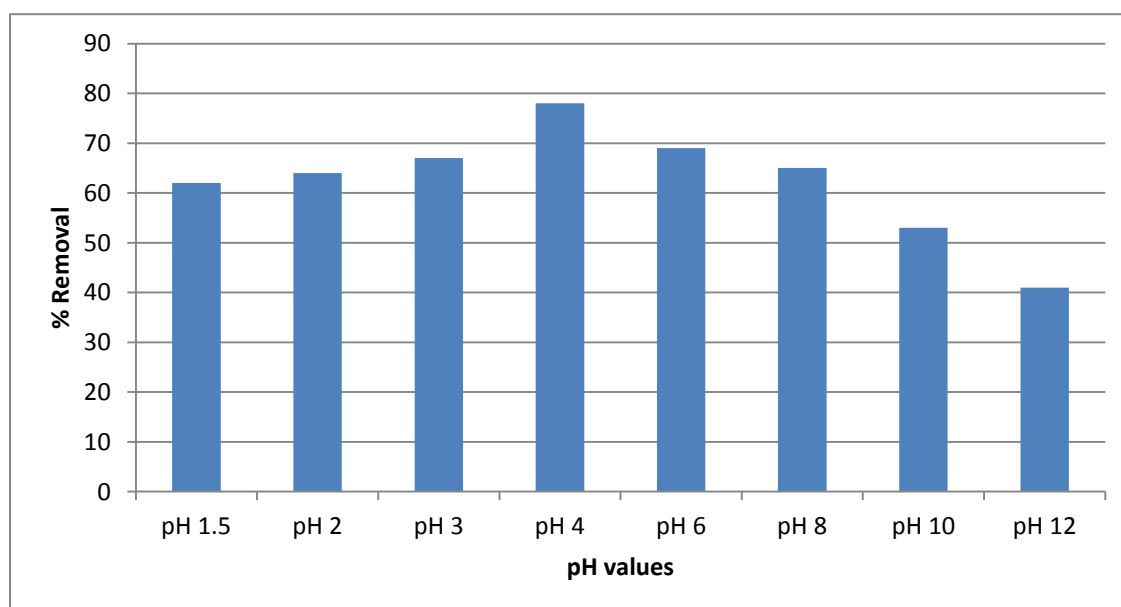Table 5.2.5 Effect of particle size on Cr (III) adsorption (contact time 120 min, initial concentration 200 µg /L, adsorbent dose 5g/100 ml, and pH 1.5).

Particle size (mesh no.)	Particle size (mm)	Particle size (µm)	Chromium (III) removal (%)
200	0.074	74	77
120	0.125	125	74
80	0.177	177	70
40	0.42	420	66
20	0.841	841	61

5.2.2 Adsorption isotherms

At a fixed initial concentration of the adsorbate (200 ug/L), the adsorbent dose was varied. Different adsorption isotherms were tested for the adsorption process. It was found that the data fitted well into the linearized Freundlich adsorption isotherm, whose mathematical expression is Log q_e= logk + 1/n logc. The plot of log q_e vs. log (Ce) in Fig. 5.2.6 shows a linear curve and hence the adsorption obeys the Freundlich adsorption isotherm.

The Langmuir adsorption isotherm whose mathematical expression is given in equation was applied for the equilibrium adsorption data and was plotted in Fig. 5.2.7. The linear plot of $1/q_e$ vs. '$1/C_e$' shows that the adsorption obeys the Langmuir adsorption isotherm also.

Table 5.2.6 Isotherm equations (Bulut and Baysal, 2006; Argun et al., 2006).

Isotherm name	Isotherm equation	Parameters
Langmuir	$q_e = \dfrac{0.b.Ce}{1+b.Ce}$	C_e: the equilibrium concentration (mg/L) q_e: the amount adsorbed per amount of adsorbent at the equilibrium (mg/g) 0 (mg/g) and b(L/mg): the Langmuir constant related to the maximum sorption capacity and energy of adsorption, respectively.
Freundlich	$q_e = KC_e^{1/n}$	K (mg/g): an indicator of the adsorption capacity. $1/n$ (mg/L) : adsorption intensity K : constant related to the adsorption energy (mol^2/KJ^2)

5.2.2.1 Freundlich isotherm

Freundlich isothermal equation is

Log q_e=logk+ 1/n logc

where 'qe' is equilibrium adsorption capacity (mg/g), 'Ce' is the equilibrium concentration of the adsorbate in solution, 'K'and 'n' are constants related to the adsorption process such as adsorption capacity and intensity respectively.
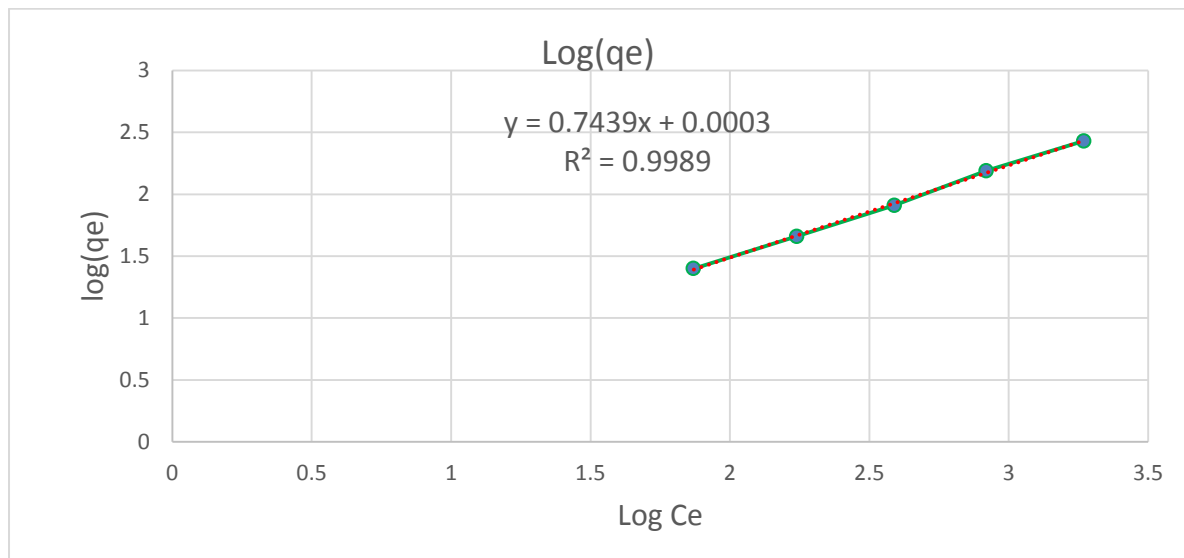
Fig. 5.2.6 Freundlich isotherm in case of newspaper.

Table 5.2.7 Freundlich isotherm variables in case of newspaper.

Log Ce	Log (qe)
1.87	1.40
2.24	1.66
2.59	1.91
2.92	2.19
3.27	2.43

5.2.2.2 Langmuir isotherm

The Langmuir isothermal equation is

Ce/qe = 1/ Qeb+ Ce/Qe

Where 'Ce' is the equilibrium concentration and 'qe' is the amount of adsorbate adsorbed per gram of adsorbent at equilibrium (mg/g), 'Q_e' and 'b' are Langmuir constants related to the sorption capacity and intensity respectively.
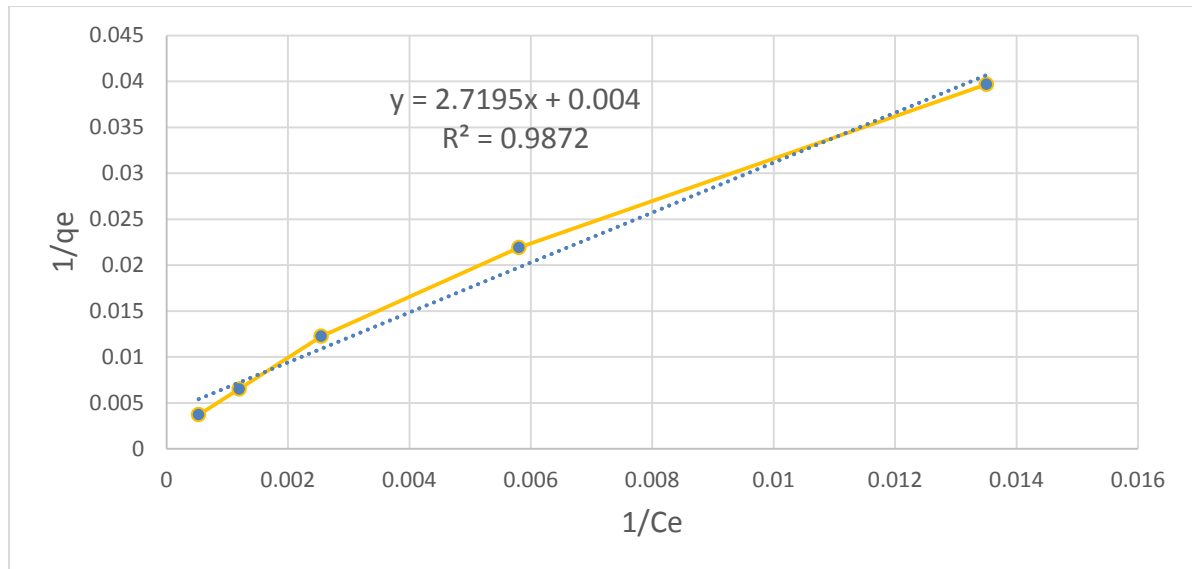
Fig. 5.2.7 Langmuir isotherm in case of newspaper.

Table 5.2.8 Langmuir isotherm variables in case of newspaper.

1/Ce	1/qe
0.00053	0.00372
0.00120	0.00651
0.00255	0.01225
0.00581	0.02192
0.01351	0.03968

5.2.3 Pseudo first order kinetics

In order to find the adsorption kinetic of heavy metal ions, the kinetic parameters for the adsorption process were studied for contact times ranging from 30 to 540 min by monitoring the removal percentage of the Cr (III). The data were then regressed against the Lagergren equation which represents a first order kinetics equation (Namasivayam and Yamuna, 1995).

$$\log (qe - qt) = \log qe - (K_1 / 2.303)t$$

The correlation coefficient and rate constants were calculated and were given in Table 5.2.9. From the table it is observed that the correlation coefficients are in good agreement with the pseudo first order kinetics.

$y = -0.0047x + 1.1944$
$R^2 = 0.9887$
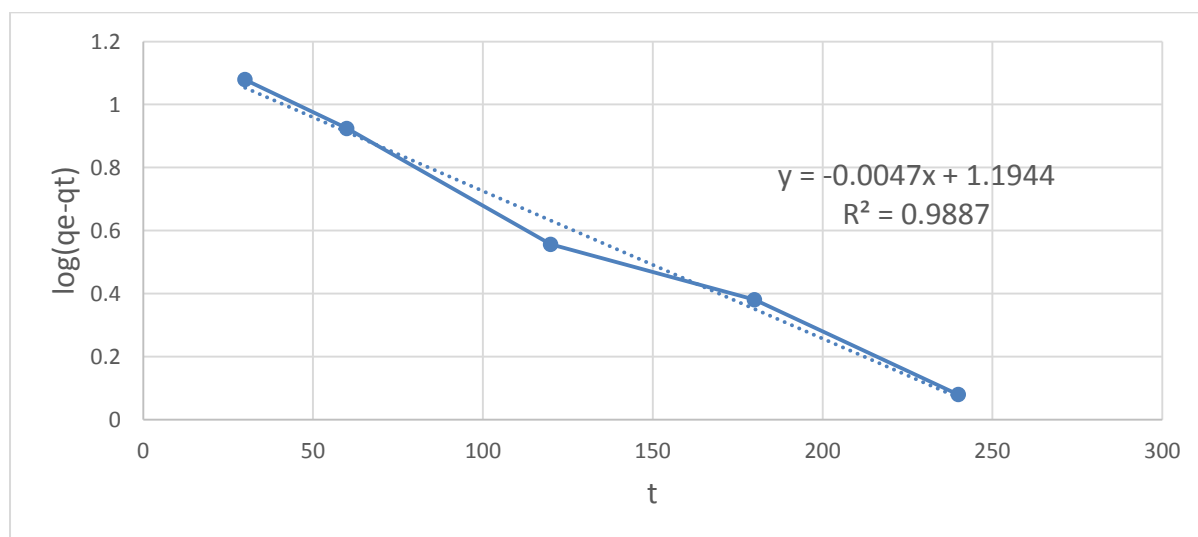
Fig. 5.2.8 Kinetic variables in case of newspaper.

Table 5.2.9 Kinetic variables in case of newspaper .

t (min)	log (qe-qt)
30	1.0791
60	0.9242
120	0.5563
180	0.3802
240	0.0791

where, qt is the metal uptake per unit weight of adsorbent (µg /g) at time t, qe is the metal uptake per unit weight of adsorbent (µg /g) at equilibrium, and k_1 (min^{-1}) is the rate constant of the pseudo-first-order (Argun et al., 2006). The slopes and intercepts of these curves were used to determine the values of K_1 as well as the equilibrium capacity (qe).

5.2.4 Desorption

Recovery of the adsorbed material and regeneration of the adsorbent are also important aspects of wastewater treatment. Attempts were made to desorb chromium (III) from the ground newspaper surface with various eluents, such as hydrochloric, sulfuric and nitric acid solutions and base solutions containing sodium hydroxide and potassium hydroxide. For each experiment, after adsorption, 100mL of desorption solution was added to the adsorbent and was shaking for two hours. The results are presented in Table 5.2.10. The present work showed that effective desorption was obtained with alkaline solutions. These phenomena are consistent with the results observed for the effect of pH. Potassium hydroxide solution was useful for the desorption of chromium from the surface of newspaper and the desorption efficiencies with 0.5M of KOH was 89%.
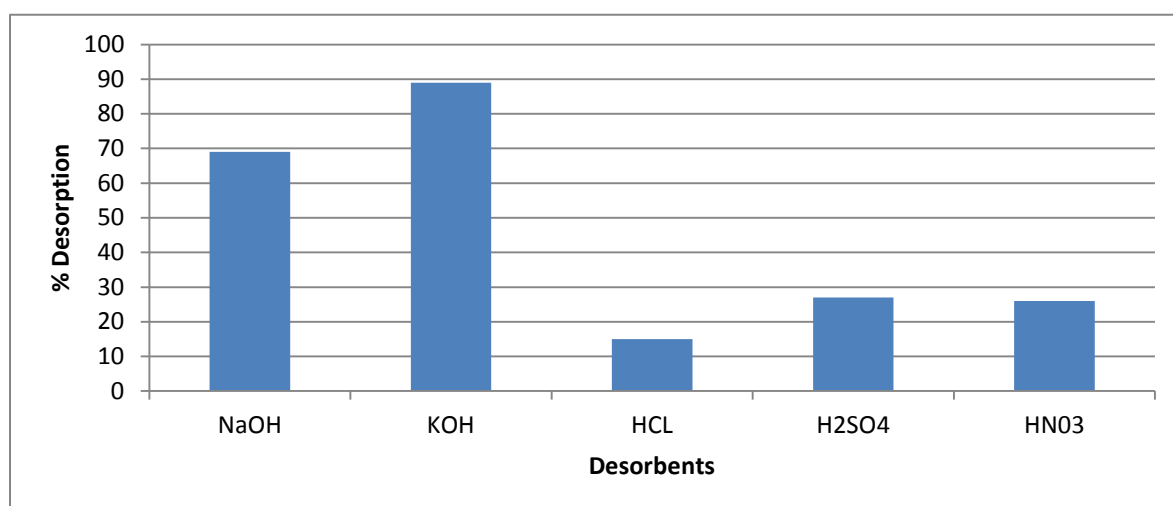
Fig.5.2.9 Desorption of newspaper powder using different desorbents (shaking time-2 hours, con. 0.5M).

Table 5.2.10 Desorption in case of newspaper using different desorbents (shaking time-2 hours, con. 0.5M).

Desorbent	Desorption (%)
NaOH	69
KOH	89
HCL	15
H_2SO_4	27
HNO_3	26

5.2.5 Relevance of the developed treatment method

Tanning industries are one of the main economic activities in Bangladesh. It has been well documented that waste water discharged from tanneries without appropriate treatment results in detrimental effects on the ecosystem. No ecotoxicity evaluation of any aquatic environment in Bangladesh has been conducted so far.

In this study Chromium analysis were carried out from water samples obtained from two sampling points: S1-Near Samina Tannery Khal, Hazaribag, where different effluents of tanneries are flowing and S2-effluent discharging site on the river Buriganga at Rayer Bazer patrol pump, in the Hazaribagh tannery area of Dhaka City, Bangladesh. The concentrations of chromium in the samples were 7.3 mg/L and 3.67 mg/L. The treatment results are presented in Table 5.2.11. Although 25 g of adsorbent was applied in the treatment, the concentrations of chromium in the treated sample water could be 823 µg /L and 441 µg /L. The desorption efficiencies with 100mL of 0.5M KOH were 100%. From the present results, the chromium was successfully removed from practical chromium contaminated water and adsorbed chromium could be recovered from the surface of newspaper.

Fig.5.2.10 Tannery effluent at Hazaribag, Dhaka, Bangladesh.

Table 5.2.11 Removal and desorption of chromium from tannery wastewater.

Factor	Sample 1	Sample 2
pH	10	7.5
Initial Cr conc. (ug/L)	7300	3670
Final Cr conc. (ug/L)	823	441
Removal (%)	88.73	87.98
Desorption (%)	100	100

5.3 Results Discussion for packaging box (corrugated box)

5.3.1 Parameters for optimization of the process

5.3.1.1 Effect of adsorbent dose on chromium adsorption

At this stage, the experiments were done under the conditions with pH of 1.5 and variable adsorbent doses (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 g/100 mL). The effect of adsorbent doses on the adsorption of chromium by packaging box was presented in Fig. 5.3.1. As illustrated in Fig. 5.3.1 the increase in percentage adsorption with the increase in adsorbent dose might be due to the increased number of free surface available, which caused increased number of adsorbate molecules to adsorb. The decrease in uptake might be due to the larger surface area at higher dose which remained free for adsorption at equilibrium. Chromium removal efficiency increased with increase in adsorbent dose, since contact surface of adsorbent particles increased and then availability of more binding sites for adsorption (Garg et al., 2004).
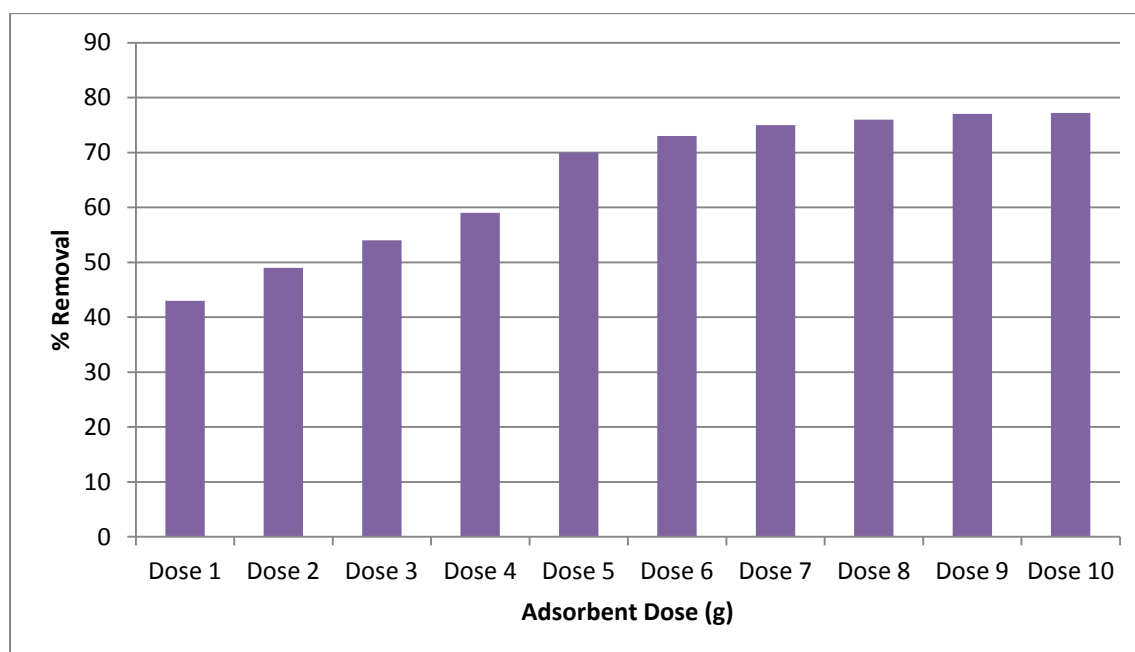
Fig. 5.3.1 Effect of adsorbent dosage on Cr (III) adsorption (contact time 120 min, initial concentration 200 μg /L, initial pH 1.5 of Cr (III) solution in the case packaging box.

Table 5.3.1 Effect of adsorbent dosage on percentage (%) removal of Cr (III) ions for aqueous solutions (contact time 120 min, initial concentration 200 µg /L, initial pH 1.5 of Cr (III) solution.

Adsorbent dosage (g)	Cr (III) removal (%)
1	43
2	49
3	54
4	59
5	70
6	73
7	75
8	76
9	77
10	77.2

5.3.1.2 Effect of contact time on chromium adsorption

In order to find out the equilibrium contact time, experiments were carried out for 9 h. From the experimental data it was observed that percentage adsorption increased with increase in contact time up to 7 h and after that it attained a stationary phase. From Fig. 5.3.2, it is observed that initially the adsorption rate was fast followed by a slower rate. Further, the plots between times vs. percentage adsorption were smooth and continuous suggesting the possible monolayer adsorption of Cr (III) on the surface of adsorbent. As optimum adsorption was achieved in 2 h, rests of the experiments were carried out for 2 h time.

In this stage, all of the parameters except contact time, including temperature (25 °C), adsorbent dose (5 g/100 ml), pH (1.5), initial chromium concentration (200 µg /L) and agitation speed (60 rpm), were kept constant. There was no significant change in equilibrium concentration after 420 min up to 480 min and after 420 min the adsorption phase reached to equilibrium. During the initial stage of sorption, a large number of vacant surface sites are available for adsorption. After a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the adsorbate molecules on the solid surface and in the bulk phase. Besides, the metal ions are adsorbed into the meso-pores that get almost saturated during the initial stage of adsorption.

Thus the driving force for the mass transfer between the bulk liquid phase and the solid phase decreases with the passage of time. Further, the metal ions have to transverse further and deeper into the pores encountering much larger resistance (Srivastava et al., 2006). This results the slowing down of the adsorption during the later phase.
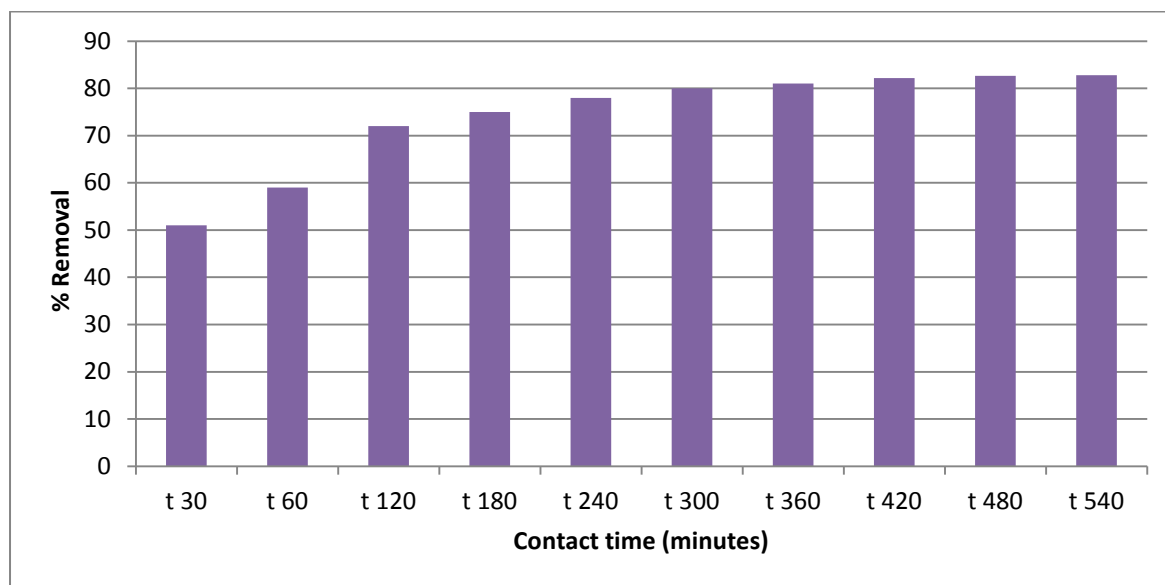
Fig. 5.3.2 Effect of contact time on Cr (III) adsorption (initial concentration 200 µg /L, initial pH 1.5, adsorbent dose 5 g /100 ml, rotation speed 60 rpm).

Table 5.3.2 Effect of contact time on Cr (III) adsorption (initial concentration 200 µg /L, initial pH 1.5, adsorbent dose 5 g/100 ml, rotation speed 60 rpm).

Contact time (min)	Chromium (III) removal (%)
30	51
60	59
120	72
180	75
240	78
300	80
360	81
420	82.2
480	82.63
540	82.81

5.3.1.3 Effect of pH on chromium adsorption

Adsorption experiments were performed at different pH values (1.5, 2.0, 3.0, 4.0, 6.0, 8.0, 10.0, and 12.0). From Fig. 5.3.3, it is observed that the percentage of adsorption increased from 66 to 82 percent at a pH from 1.5 to 3 then decrease the percent adsorption with the increase of pH up to 12. The increase in percentage adsorption as well as uptake at lower pH could be well explained by protonation properties of the adsorbent. At low pH values, i.e., higher hydrogen ion concentration, the negative charge at the surface of internal pore were neutralized and some more new adsorption sites were developed which provided a positive charge for anionic Cr (III) complex to get adsorbed on the surface. Again it is observed that the final pH of the solution was always greater than the initial pH of the solution, which confirmed the neutralization of H^+ ions with the negative charge at the surface and envelopment of more H^+ ions in formation of positively charged surface. As a result, the concentration of H^+ ions decreased in the solution and hence the pH of the solution increased. Many authors also reported similar results (Yu et al., 2003). From the adsorption uptake at both higher and lower pH (12 and 1.5) it is concluded that the adsorbent can be used for the treatment of Cr (III) contaminated Tannery water at lower pH.

Fig. 5.3.3 Effect of pH on Cr (III) adsorption (contact time 120 min, initial concentration 200 µg /L, adsorbent dose 5g/100 ml).

Table 5.3.3 Effect of pH on Cr (III) adsorption (contact time 120 min, initial concentration 200 µg /L, adsorbent dose 5 g/100 ml).

pH value	Chromium (III) removal (%)
1.5	66
2	71
3	82
4	78
6	72
8	68
10	56
12	43

5.3.1.4 Effect of initial chromium concentration on Cr (III) adsorption

The percentage adsorption with different adsorbate concentrations was studied by varying Cr (III) concentration from 200 ppb to 3200 ppb keeping adsorbent dose at (5 g/100 mL), stirring speed (60 rpm), pH (1.5), and temperature (25^0 C) constant. Fig. 5.3.4 shows the effect of initial adsobate concentration. It was observed that the percentage of adsorption decreased with the increase of adsorbate concentration. This may be due to the fact that at a fixed adsorbent dose, the number of active adsorption sites to accommodate the adsorbate ions remained unchanged while with higher adsorbate concentrations, the adsorbate ions to be accommodated increased. Thus, the loading was faster with higher initial concentrations of adsorbate.
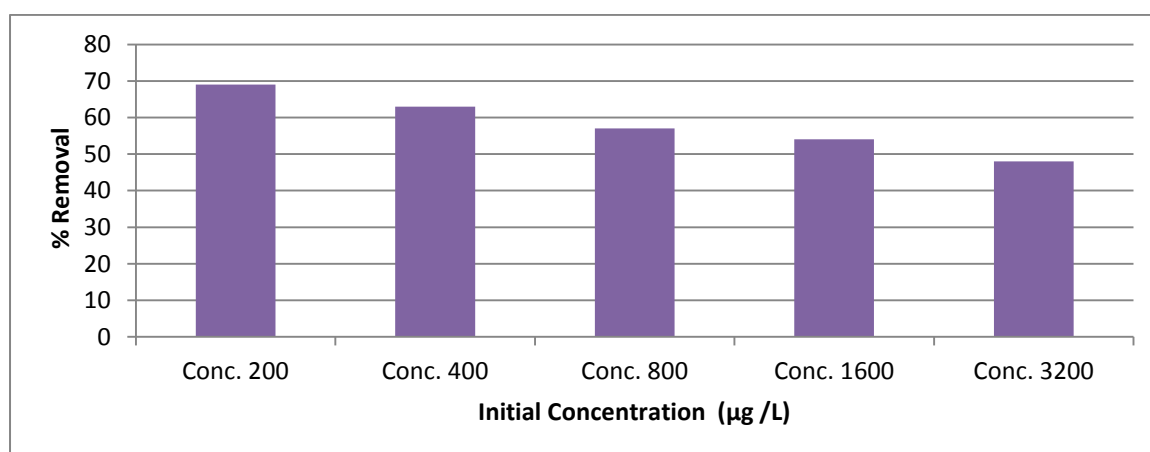
Fig. 5.3.4 Effect of initial chromium concentration on adsorption (contact time 120 min, initial pH 1.5, adsorbent dose 5 g/100 ml, rotation speed 60 rpm)   .

Table 5.3.4 Effect of initial chromium concentration on adsorption (contact time 120 min, initial pH 1.5, adsorbent dose 5 g/100 ml and rotation speed 60 rpm).

Initial concentration (µg /L)	Chromium (III) removal (%)
200	69
400	63
800	57
1600	54
3200	48

5.3.1.5 Effect of particle size of adsorbent

Batch adsorption experiments were carried out for the removal of chromium from aqueous solution using five different particle sizes (0.074, 0.125, 0.177, 0.42, 0.841 mm). The results are shown in Figure 5.3.5. With decreasing particle size, the removal increased from 67 to 83%. Munaf and Zein (1997) reported that, when the size of the adsorbent particles increased, the adsorption of metal ions decreased. Similar trends have been reported by Wong et al. (2003). These phenomena might be due to the fact that the smaller particles offer comparatively larger surface areas and greater numbers of adsorption sites compare to larger particles.
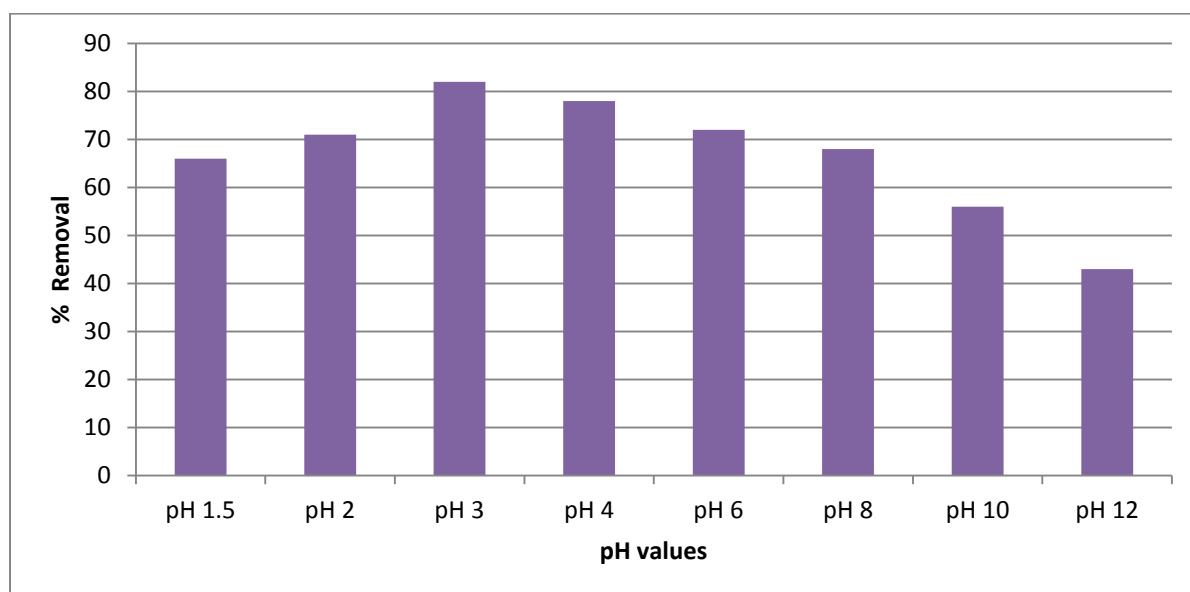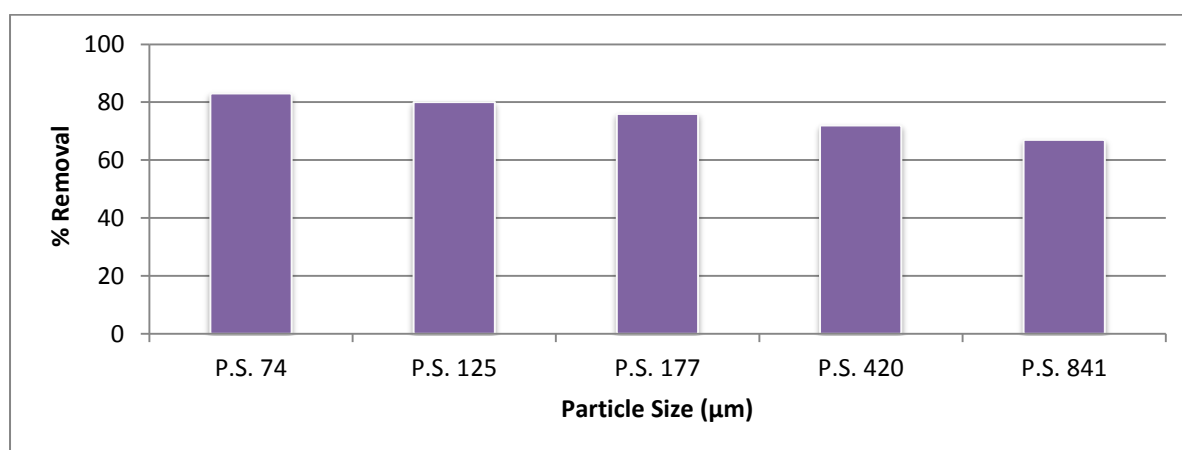

Fig. 5.3.5 Effect of particle size on Cr (III) adsorption (contact time 120 min, initial concentration 200 µg /L, adsorbent dose 5 g/100 ml, pH 1.5).

Table 5.3.5 Effect of particle size on Cr (III) adsorption (contact time 120 min, initial concentration 200 µg /L, adsorbent dose 5 g/100 ml, and pH 1.5).

Particle size (mesh no.)	Particle size (mm)	Particle size (um)	Chromium (III) removal (%)
200	0.074	74	83
120	0.125	125	80
80	0.177	177	76
40	0.42	420	72
20	0.841	841	67

5.3.2 Adsorption isotherms

At a fixed initial concentration of the adsorbate (200 µg /L), the adsorbent dose was varied. Different adsorption isotherms were tested for the adsorption process.

It was found that the data fitted well into the linearized Freundlich adsorption isotherm, whose mathematical expression is Log q_e = logk + 1/n logc. The plot of log q_e vs. log (Ce) in Fig. 5.3.6 shows a linear curve and hence the adsorption obeys the Freundlich adsorption isotherm.

The Langmuir adsorption isotherm whose mathematical expression is given in equation was applied for the equilibrium adsorption data and was plotted in Fig. 5.3.7. The linear plot of 1/q_e vs. '1/Ce' shows that the adsorption obeys the Langmuir adsorption isotherm also.

Table 5.3.6 Isotherm equations (Bulut and Baysal, 2006; Argun et al., 2006).

Isotherm name	Isotherm equation	Parameters
Langmuir	$q_e = \dfrac{0.b.Ce}{1+b.Ce}$	C_e: the equilibrium concentration (mg/L)
		q_e: the amount adsorbed per amount of adsorbent at the equilibrium (mg/g)
		0 (mg/g) and b (L/mg): the Langmuir constant related to the maximum sorption capacity and energy of adsorption, respectively.
Freundlich	$q_e = KC_e\ 1/n$	K (mg/g): an indicator of the adsorption capacity.
		1/n (mg/L) : adsorption intensity
		K : constant related to the adsorption energy (mol^2/KJ^2)

5.3.2.1 Freundlich isotherm

Freundlich isothermal equation is

Log q_e = logk + 1/n logc

where 'qe' is equilibrium adsorption capacity (mg/g), 'Ce is the equilibrium concentration of the adsorbate in solution, 'K' and 'n' are constants related to the adsorption process such as adsorption capacity and intensity respectively.
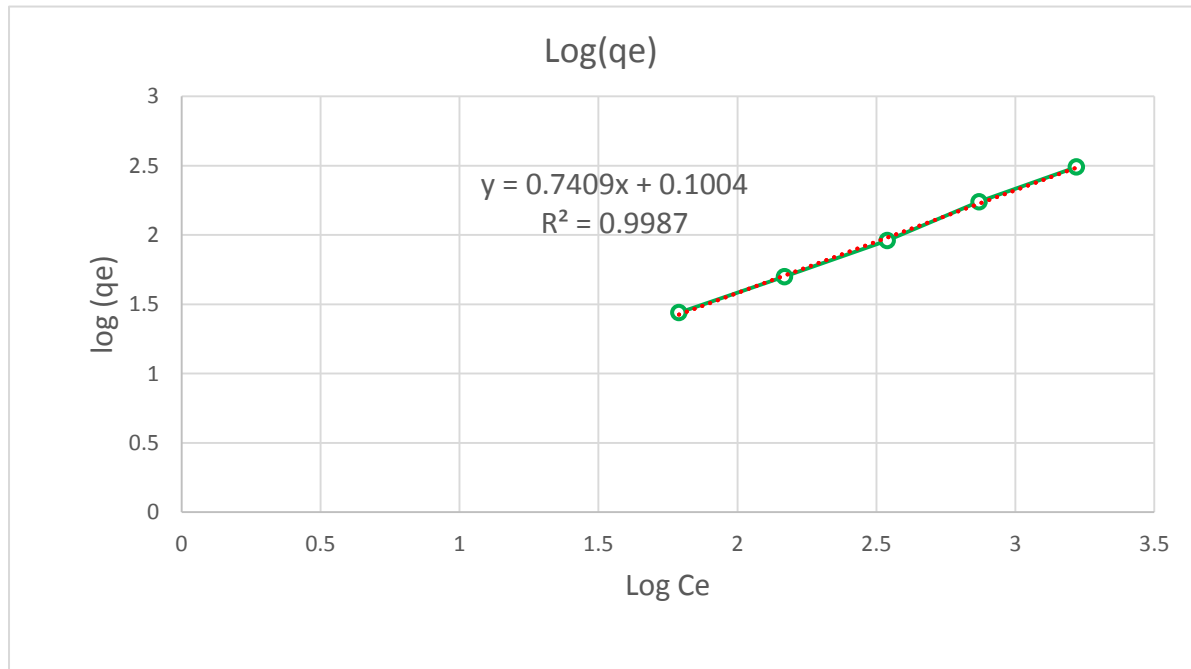
Fig. 5.3.6 Freundlich isotherm in case of packaging box.

Table 5.3.7 Freundlich isotherm variables in case of packaging box.

log Ce	log (qe)
1.79	1.44
2.17	1.70
2.54	1.96
2.87	2.24
3.22	2.49

5.3.2.2 Langmuir isotherm

The Langmuir isothermal equation is

Ce/qe $= 1/ Qeb+ Ce/Qe$

Where 'Ce' is the equilibrium concentration and 'qe' is the amount of adsorbate adsorbed per gram of adsorbent at equilibrium (mg/g), 'Q_e' and 'b' are Langmuir constants related to the sorption capacity and intensity respectively.
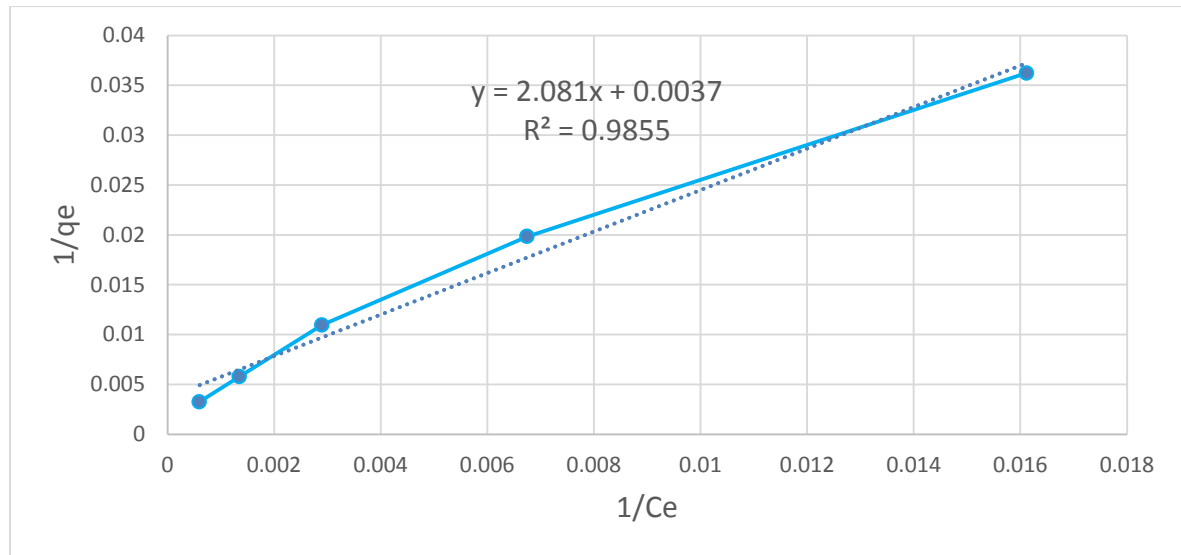
Fig. 5.3.7 Langmuir isotherm in case of packaging box.

Table 5.3.8 Langmuir isotherm variables in case of packaging box.

1/Ce	1/qe
0.00060	0.00325
0.00135	0.00578
0.00290	0.01096
0.00675	0.01984
0.01612	0.03623

5.3.3 Pseudo first order kinetics

In order to find the adsorption kinetic of heavy metal ions, the kinetic parameters for the adsorption process were studied for contact times ranging from 30 to 540 min by monitoring the removal percentage of the Cr (III). The data were then regressed against the Lagergren equation, which represents a first order kinetics equation (Namasivayam and Yamuna, 1995).

$$\log (q_e - q_t) = \log qe - (K_1/2.303)t$$

The correlation coefficient and rate constants were calculated and were given in Table 5.3.9. From the table it is observed that the correlation coefficients are in good agreement with the pseudo first order kinetics.
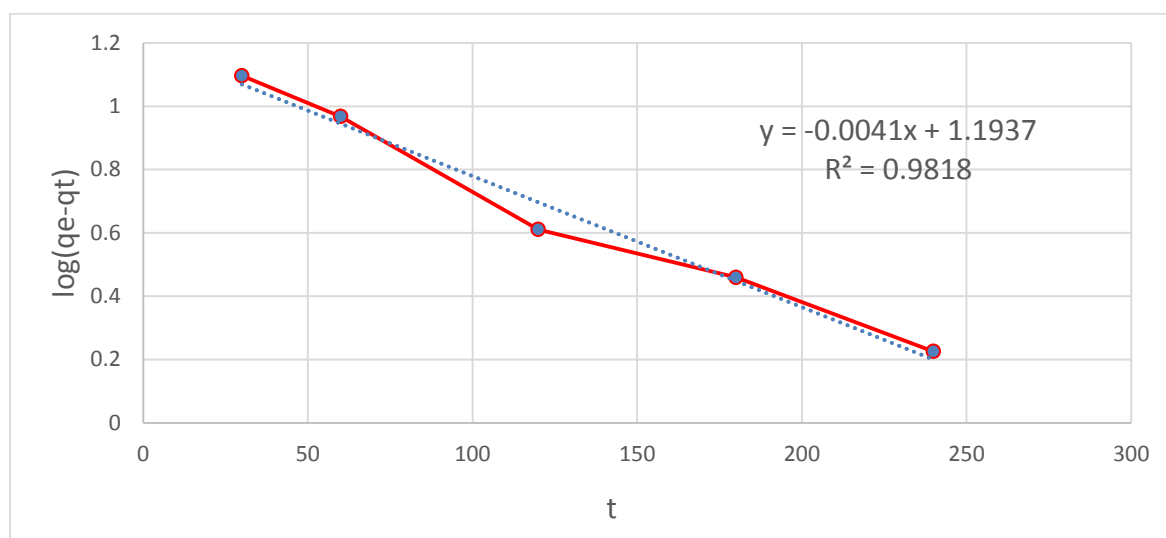
Fig. 5.3.8 Kinetic variables in case of packaging box.

Table 5.3.9 Kinetic variables in case of packaging box.

t (min)	Log (qe-qt)
30	1.0962
60	0.9675
120	0.6106
180	0.4593
240	0.2253

where, qt is the metal uptake per unit weight of adsorbent (ug/g) at time t, qe is the metal uptake per unit weight of adsorbent (ug /g) at equilibrium, and k_1 (min^{-1}) is the rate constant of the pseudo-first-order (Argun et al., 2006). The slopes and intercepts of these curves were used to determine the values of K_1, as well as the equilibrium capacity (qe).

5.3.4 Desorption

Recovery of the adsorbed material and regeneration of the adsorbent are also important aspects of wastewater treatment. Attempts were made to desorb chromium (III) from the ground packaging box surface with various eluents, such as hydrochloric, sulfuric and nitric acid solutions and base solutions containing sodium hydroxide and potassium hydroxide. For each experiment, after adsorption, 100mL of desorption solution was added to the adsorbent and was shaking for two hours. The results are presented in Table 5.3.10. The present work showed that effective desorption was obtained with alkaline solutions. These phenomena are consistent with the results observed for the effect of pH. Potassium hydroxide solution was useful for the desorption of chromium from the surface of packaging box and the desorption efficiencies with 0.5M of KOH was 93%.
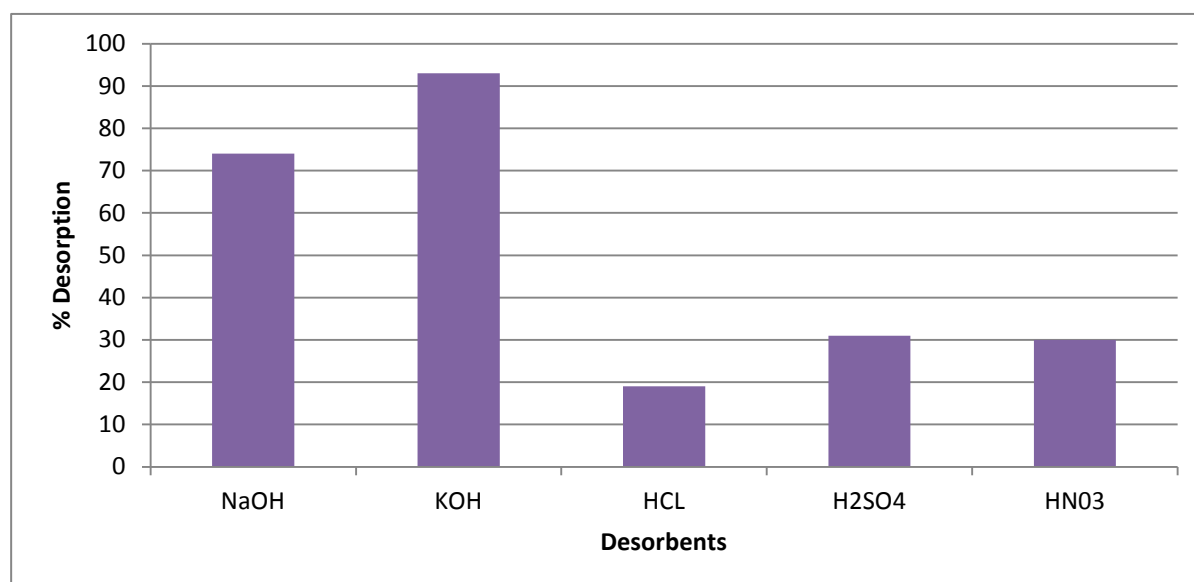
Fig.5.3.9 Desorption of packaging box powder using different desorbents (shaking time-2 hours, con. 0.5M).

Table 5.3.10 Desorption in case of packaging Box using different desorbents (shaking time-2 hours, con. 0.5M).

Desorbent	Desorption (%)
NaOH	74
KOH	93
HCL	19
H_2SO_4	31
HNO_3	30

5.3.5 Relevance of the developed treatment method

Tanning industries are one of the main economic activities in Bangladesh. It has been well documented that waste water discharged from tanneries without appropriate treatment results in detrimental effects on the ecosystem. No ecotoxicity evaluation of any aquatic environment in Bangladesh has been conducted so far. In this study Chromium analysis were carried out from water samples obtained from two sampling points: S1-Near Samina Tannery Khal, Hazaribug, where different effluents of tanneries are flowing and S2-Effluent discharging site on the river Buriganga at Rayer Bazer patrol pump, in the Hazaribagh tannery area of Dhaka City, Bangladesh.

The concentrations of chromium in the samples were 7.3 mg/L and 3.67 mg/L. The treatment results are presented in Table 5.3.11. Although 25 g of adsorbent was applied in the treatment, concentrations of chromium in the treated sample water could be lower to 587 µg /L and 363 µg /L. The desorption efficiencies with 100 mL of 0.5M KOH were 100%.

From the present results, the chromium was successfully removed from practical chromium contaminated water and adsorbed chromium could be recovered from the surface of packaging box.

Fig. 5.3.10 Tannery effluent flowing to the river Buriganga from Hazaribag, Dhaka, Bangladesh.

Table 5.3.11 Removal and desorption of chromium from tannery wastewater.

Factor	Sample 1	Sample 2
pH	10	7.5
Initial Cr conc (µg /L)	7300	3670
Final Cr conc (µg /L)	587	363
Removal (%)	91.96	90.11
Desorption (%)	100	100

CHAPTER 6

CONCLUSION

6.1 Conclusion

The experimental results show that newspaper and packaging box (corrugated box) are excellent alternative for the removal of Cr (III) from aqueous solution. The adsorption of Cr (III) was dependent on pH, particle sizes, contact time, adsorbent dose and initial chromium concentration. It was observed that the best efficiency of absorption of Cr (III) by newspaper is at a condition of pH 4, adsorption time 2 hours, adsorbent amount 5 g/100 ml solution of 200 ppm Cr (III) solution and that for packaging box is at a condition of pH 3, adsorption time 2 hours, adsorbent amount 5g/100 ml solution of 200 ppm Cr (III) solution. Both Langmuir and Freundlich isotherms were followed by the adsorption of Cr (III). The kinetic analysis of the study showed that the adsorption of Cr (III) ions onto ground newspaper and packaging box could be well described with the pseudo-first order kinetic model. The desorption experiments show that the metal can be desorbed after adsorption and Cr (III) can be recovered. Based on the results of this research, Newspaper and Packaging box can be considered as available, low cost, environmental friendly and effective adsorbent for removal of chromium from tannery waste water.

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