REMOVAL OF CHROMIUM FROM ELECTRO WASTEWATER BY ADSORPTION

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Industrial Pollution Abatement)

By

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CANDIDATE'S DECLARATION

I hereby certify that the work, which is being presented in the dissertation entitled **"REMOVAL OF CHROMIUM FROM ELECTROPLATING WASTEWATER BY ADSORPTION"** in partial fulfillment of the requirement for the award of the degree Master of Technology in Chemical Engineering with specialization in **Industrial Pollution Abatement (IPA)**, and submitted in the **Department of Chemical Engineering of Indian Institute of Technology Roorkee**, under the kind guidance of **Dr. B Prasad**, Assistant Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

The matter presented in this dissertation has not been submitted by me for the award of any other degree of this or any other Institute / University.

Place: Roorkee

Date: 28 th June, 2005

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

Chromium waste discharged from industries may consist of chromium in hexavalent and trivalent forms. These industries are aluminum anodizing and metal cleaning, chrome tanning, dyes manufacturing, electroplating etc. Hexavalent form believed to be more toxic and is known to be carcinogenic. The need for treatment of industrial wastewater for hexavalent chromium removal prior to discharge to water ways is a big problem even today. Central Pollution Control Board (CPCB) and Bureau of Indian Standards (BIS) have the given the tolerance limits of various parameters for the wastewater of different industries.

At present many methods are available for removal of chromium from waste water such as ion exchange, precipitation, membrane separation, reverse osmosis, adsorption, etc.; but adsorption by activated carbon still continues to be most widely used process because of its safe, environment friendly and easy process.

The Cr(VI) adsorption experiments were carried out to analyze the influence of adsorbent dose, pH, initial Cr(VI) concentration, carbon-solution time and temperature, on the efficiency of Cr(VI) retention by activated carbons.

The equilibrium data could be described well by Langmuir and Freundlich isotherm equations. A separation factor was used to judge the favorable adsorption. Thermodynamic parameters such as Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) were also calculated.

Characteristics of the activated carbon are done by XRD, SEM process and by proximate and ultimate analysis. The extent of adsorption and reduction processes depends on the porous texture, nature and preparation procedure of activated carbons.

CONTENTS

NOMENCLATURE

a_R	R-P isotherm constant, l/mg
C_o	Initial concentration of adsorbate, mg/l
C_e	Concentration of adsorbate solution at equilibrium, mg/l
C_S	Concentration of solute at saturation of all layers
h	Initial sorption rate, mg/g min
k_{id}	The intra-particle diffusion rate constant
k_s	The rate constant of pseudo-second-order model, g/mg min
k_f	The rate constant of pseudo-first-order model, min^{-1}
K	Adsorption rate constant, min^{-1}
K_A	Constant related to enthalpy of adsorption
K_F	Freundlich isotherm constant, $(mg\ g^{-1})\ (mg\ l^{-1})^{-1/n}$
K_B	Constant related to energy of adsorption
K_R	R-P isotherm constant, l/g
K_T	The equilibrium binding constant, l/mg
n	Freundlich isotherm constant
Q	Mass of solute adsorbed / mass of adsorbent
Q_m	Mass of solute adsorbed / mass of adsorbent for complete monolayer
Q_e	Adsorption capacity in equilibrium, mg/g
Q_t	Amount of adsorbate adsorbed at time t, mg/g
R_L	Separation factor
β	Exponent lies between 1 and 0
ΔG^0	Gibbs free energy, kJ/mol
ΔH^0	Enthalpy, kJ/mol
ΔS^0	Entropy changes, J/mol/K

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CHAPTER 1

INTRODUCTION

1.1 GENERAL

Metal finishing industries are one of the largest users of many toxic chemicals in the world. Electroplating industry alone is the second largest end user of nickel and nickel compounds, the third largest end user of cadmium and cadmium compounds, and the user of a substantial amount of chromium.

Many industries like automotive, electronics, aerospace, hardware, jewelry, heavy equipment, appliances, tires and telecommunication, use metal electroplating in their manufacturing processes (Shreeram and Ramasami, 2001).

1.2 MARKET SERVED BY METAL FINISHERS

Metal plating is important and necessary for surface finishing and life prolonged due to resistance to corrosion and wear. It also enhances electrical properties, to form and shape compounds, and to enhance the bonding of adhesives or organic coating. Overall, metal finishing alters the surface of metal products to enhance (Legg et al., 1996):

- Corrosion resistance
- Wear resistance
- Electrical conductivity
- Electrical resistance
- Reflectivity and appearance (e.g., brightness or color)
- Torque tolerance
- Solderability
- Tarnish resistance
- Chemical resistance
- Hardness

Metal finishing uses a variety of materials and processes to clean, etch, and plate metallic and non-metallic surfaces to have work-piece of desirable surface characteristics.

Electrolytic plating, electro-less plating, and chemical and electrochemical conversion processes are typical in their use. The typical supporting processes can include degreasing, cleaning, pickling, etching, and/or polishing.

Some of the materials used in metal finishing are solvents and surfactants for cleaning, acid and bases for etching and solutions of metal salts for plating the finish onto the substrate.

1.3 CHEMISTRY OF CHROMIUM

Chromium is a naturally occurring element found in rocks, animals, plants, soil, and in volcanic dust and gases. Chromium exists in every one of the oxidation states from -(II) to +(VI), but only the valencies of (0), (II), (III) and (VI) are common. The most common forms are chromium(0), trivalent [or chromium(III)], and hexavalent [or chromium(VI)]. Physical and Chemical Properties of Chromium and Compounds is given in table 1.1 (Chen et al., 2002).

Table 1.1: Physical and Chemical Properties of Chromium and Compounds

	Molecular weight	Color	Physical state	Melting point	Boiling point	Density, g/cm
Chromium(0)	51.996	Steel-gray	Solid	1,857 EC	2,672 EC	7.20 (28 EC)
Chromium(III)acetate, monohydrate	247.15	Gray-green orbluish-green	Solid	No data	No data	No data
Chromium(III)-nitrate,nonahydrate	400.15	Purple or violet	Solid	60 EC	Decomposes at 100 EC	No data
Chromium(III)chloride	158.36	Violet or purple	Solid	1,150 EC	Sublimes at 1,300 EC	2.76 (15 EC)
Chromium(III) chloride, hexahydrate	266.45	Violet	Solid	83 EC	No data	1.76

Ferrochromite(Chromium(III))	223.84	Brown-black	Solid	No data	No data	4.97 (20 EC)
Chromium(III)oxide	151.99	Green	Solid	2,266 EC	4,000 EC	5.21
Chromium(III)phosphate	146.97	Gray-brown to blackd	Solid	>1,800 EC	No data	2.94 (32.5 EC)
Chromium(III)sulfate	392.16	Violet or red	Solid	No data	No data	3.012
Sodium chromite (Chromium(III))	106.98	No data	No data	No data	No data	No data
Chromium(IV)oxide	83.99	Brown-black	Solid	Decomposes at 300 EC	Not applicable	No data
Ammoniumdichromate (Chromium(VI))	252.06	Orange	Solid	Decomposes at 170 EC	Not applicable	2.15 (25 EC)
Potassium dichromate (Chromium(VI))	294.18	Red	Solid	398 EC	Decomposes at 500 EC	2.676 (25 EC)
Sodium chromate (Chromium(VI))	161.97	Yellow	Solid	792 EC	No data	2.710–2.736

The metal chromium, which is the chromium(0) form, is a steel-gray solid with a high melting point. It is used mainly for making steel and other alloys. The naturally occurring mineral chromite in the chromium(III) form is used as brick lining for high-temperature industrial furnaces, for making metals and alloys (mixtures of metals), and chemical compounds. Chromium compounds, mostly in chromium(III) and chromium(VI) forms, produced by the chemical industry are used for chrome plating, the manufacture of dyes and pigments, leather tanning, and wood preserving (Chua, 1998).

Cr(III) adsorbs strongly to the soil surface, does not leach out into the ground water and does not significant increases the chromium content of plants. Cr(VI) can leach out easily into the deeper soil layers, so it can cause ground and surface water contamination. Cr(VI) can reduce to Cr(III) only in the top layer of soil and the rate of reduction depends on the pH and humid acid content of the soil. Comparison between Cr(VI) and Cr(III) is shown in Table 1.2.

Table 1.2: Comparison between Cr(VI) and Cr(III)

Cr(VI)	Cr(III)
Exists in oxidizing environments	Exists in reducing environments
the PEL is an 10-hour time-weighted average (TWA) of 1 µg Cr(VI)/m^3	the PEL is an 8-hour time-weighted average (TWA) of 500 µg Cr/m^3
Mobile in soil	Strong adsorption onto solids
Soluble as chromate from pH, 2-14	Soluble when pH<3.6
Toxic; carcinogen, mutagen	Less toxic
Easily leach out into the ground water	Does not leach out into the ground water

(Source:http://www.atsdr.cdc.gov/HEC/CSEM/chromium/standards_regulations.html#Standards)

1.4 SOURCES OF CHROMIUM

Occupational sources of chromium exposure may occur in the following industries (agency, 2002):

- Stainless steel welding [chromium (VI)]
- Chromate production [chromium (VI)]
- Chrome plating [chromium (VI)]
- Ferrochrome industry [chromium (III) and chromium (VI)]
- Chrome pigments [chromium (III) and chromium (VI)]
- Leather tanning [chromium (VI)]

Examples of other occupations that may involve chromium exposure include (agency, 2002):

- Painter [chromium (III) and chromium (VI)]
- Worker involved in the maintenance and servicing of copying machines, and the disposal of some toner powders from copying machines [chromium (VI)]
- Battery makers [chromium (VI)]
- Candle makers [chromium (III) and chromium (VI)]

- Dye makers [chromium (III)]
- Printers [chromium (III) and chromium (VI)]
- Rubber makers [chromium (III) and chromium (VI)]
- Cement workers [chromium (III) and chromium (VI)]

1.5 HEALTH EFFECTS

Chromium (III) is an essential nutrient that helps the body use sugar, protein, and fat. An intake of 50 to 200 μg of chromium (III) per day is recommended for adults. Without chromium (III) in the diet, the body loses its ability to use sugars, proteins, and fats properly, which may result in weight loss or decreased growth, improper function of the nervous system, and a diabetic-like condition (Gulland et al., 2003).

Breathing in high levels (greater than $2\mu g/m^3$) of chromium (VI) can cause irritation to the nose, such as runny nose, sneezing, itching, nosebleeds, ulcers, and holes in the nasal septum (Chen et al., 2002). These effects have primarily occurred in factory workers who make or use chromium (VI) for several months to many years. Long-term exposure to chromium has been associated with lung cancer in workers exposed to levels in air that were 100 to 1000 times higher than those found in the natural environment.

The department of Health and Human Services determined that certain chromium (VI) compounds (calcium chromate, chromium trioxide, lead chromate, sodium dichromate, strontium chromate, and zinc chromate) are known carcinogens.

1.6 TOLERANCE LIMITS OF CHROMIUM

The allowable chromium concentrations for various purposes specified by various regulating agencies are as follows:

For public water supplies chromium in the hexavalent from should not exceed 0.05 mg/l and preferably should be absent entirely (CPCB, 2004).

For agriculture tolerance of chromium and chromate ions varies with the plants species. More sensitive plants are adversely affected by concentrations of 5 mg/l (EPA. 2004).

Dissolved chromium in natural and man made water is given in Table 1.3. Allowable concentration in farmstead waters is 0.05 mg/l (Prokisch et al., 1998).

Maximum allowable concentration in stream is 1 mg/l [Table 1.4]. Maximum permissible concentration of chromium in specific water in undetectable [Table 1.5].

A world health organization standard for potable water for chromium is 0.05 mg/l concentration [Table 1.6].

According to IS 2296-1974, potable streams containing in excess to 0.05 mg/l are considered objectionable for domestic water supplies and bathing places.

According to IS 7968-1974, the tolerance limit for hexavalent chromium in public sewers is 2.0 mg/l and into marine 1.0 mg/l.

According to IS 7968-1976, amount of chromium which can be tolerated in irrigation water is 5.0 mg/l for continuous use and 20.0 mg/l for short term use in fine textures soil. Tolerance limit of chromium for industrial effluents discharged into marine coastal areas is 1.0 mg/l. To prevent injury to the treatment plants, chromium limits is set around 0.05 mg/l.

Table 1.3: Dissolved chromium in natural and man-made waters (Jadhao, 2001)

Type of Water	Chromium concentration (nmol/l)	
	Typical	**Range**
Seawater	3	0.1-16
Interstitial Water (marine sediments)	-	1.0-6.0
River	10	0-2200
Lake	-	<2-33
Groundwater	<20	10-4000
Polluted water	-	960-27,000
Tap water	8	0-700

Table 1.4: Suggested maximum concentrations allowable in streams (Jadhao, 2001)

Metal	Concentration
Lead	0-0.5 mg/l
Copper, Zinc	ILL appropriate to hardness
Cadmium	0-0.1mg/l
Nickel	5 mg/l
Chromium	1 mg/l

Table 1.5: Maximum permissible concentration of specific water (Jadhao, 2001)

Constituents	Maximum permissible concentration (mg/l)
Lead (as pb)	0.1
Selenium (as Se)	0.05
Fluoride (as F)	1.0
Arsenic (as As)	1.0
Chromium (as Cr)	Undetectable
Cyanides	Undetectable
Copper (as Cu)	1.0
Iron (as Fe)	0.2
Magnesium (as Mn)	0.2
Zinc (as Za)	5.0
Phenolics	Nil
	Desirable criteria, ppm
Magnesium (as Mg)	125
Chlorides (as Cl)	250
Sulfate (as SO_4)	250
Nitrates (as N)	2-5
Nitrates (as NO_2)	9-22

Table1.6: World Health Organization standards for potable water (Jadhao, 2001)

Constitute	Criterion	
Lead (as pb)	0.1 mg/l	
Selenium (as Se)	0.05 mg/l	
Arsenic (as As)	0.2 mg/l	
Chromium (as Cr^{+4})	0.05 mg/l	
Cyanide (as CN^-)	0.01 mg/l	
	Permissible	**Excessive**
Total solids	500 mg/l	1,500 mg/l
Color	5 units	50 units
Turbidity	5 units	25 units
Taste	Unobjectionable	------
Odor	Unobjectionable	------
Iron (Fe)	0.3 mg/l	------
Manganese (Mn)	0.1 mg/l	0.5 mg/l
Copper (Cu)	1.0 mg/l	1.5 mg/l
Zinc (Zn)	5.0	15 mg/l
Calcium (Ca)	75 mg/l	200 mg/l
Magnesium (Mg)	50 mg/l	150 mg/l
Sulfate (SO_4)	200 mg/l	400 mg/l
Chloride (Cl)	200 mg/l	600 mg/l
pH	7.0-8.5	(6.5 or) 9.2
(Mg + Na) SO_4	500 mg/l	1,000 mg/l
Phenolics	0.01 mg/l	0.002 mg/l
α emitters	10^{-9} e/ml	------

1.7 ACTIVATED CARBON AS AN ADSORBENT

Over the past few decades investigation of the adsorption process on activated carbon has confirmed their great potential for industrial wastewater purification from toxic and heavy metals. Activated carbon has been used to remove Cr(VI) (Kim, 1977;

Axuma and Hitomi, 1972; Yoshida et al., 1977; Nagasaki, 1974). The kinetics and thermodynamics of the Cr(VI) adsorption on novel activated carbon has been studied (Lybchik el al., 2004).

1.8 CLEAN-UP TECHNOLOGY

Chromium present in the water body can be cleaned-up by following techniques:

(a) **Reduction:** The standard reduction treatment technique is to lower the waste stream pH to 2.0-3.0 with sulfuric acid and convert the Cr(VI) to Cr(III) with a chemical reducing agent such as sulfur dioxide, sodium bisulfite, metabisulfite or hydrosulfite, or ferrous sulfate. The Cr(III) is then removed, usually by hydroxide precipitation. The reduction of hexavalent to trivalent chromium is not completely effective, and the amount of residual nonreduced hexavalent chromium depends upon the allowable time of reaction, pH of the reaction mixture, and concentration and type of reducing agent employed.

(b) **Ion-exchange:** The ion exchange process is reported to be economical for chromium recovery and elimination of waste discharge. Cation exchange can be applied to remove trivalent chromium and anion exchange resin is exhausted it is regenerated (usually with sodium hydroxide) and sodium chromate is eluted from the ion exchange resin. The eluted sodium chromate can be passed to cation exchange resin to recover purified chromic acid at concentration as high as 6%. If chromic acid is not recovered, the concentrated waste yielded by the resin regeneration process must be treated. This may be accomplished by reduction to trivalent chromium, followed by precipitation. Treatment by ion exchange produced reusable water which may provide an economic benefit when water costs are high.

Advantages

(i) relatively inexpensive.

(ii) commercial products available.

(iii) tried and tested in industrial applications.

(iv) capable of clean up to ppb level.

(v) can be easily used in conjugation with other techniques (e.g. precipitation) as part of an integrated waste treatment.

(vi) can be applied to many flow types : intermittent, continuous relatively large volume.

Disadvantages

(i) can not handle large concentration of metals.

(ii) matrix easily fouled by solids and some organics.

(iii) taditional ion-exchange is generally not selective.

(iv) exhausted exchange must usually be disposed of as toxic waste.

(v) matrices can be decompose over time.

(vi) performance is sensitive to effluent pH.

(vii) large volume effluents require very large ion exchange columns.

(c) **Electrochemical reduction:** An electrochemical process similar to the cementation process, but employing an imposed DC electrical potential and consumed iron electrodes, has been reported to achieve chromate reduction from 3.5 mg/l to below 0.05 mg/l in cooling tower blow down, treating 0.036 MGD (Srivatava et al., 2003). Electric current applied to the electrodes results in the release of ferrous ions into solution. These ferrous ions then reduce the Cr(VI) to yield trivalent chromium ions. Both this process and the cementation process produce some excess sludge solids upon precipitation of trivalent chromium, as a result of the soluble iron released in the electrochemical reactions. One source had reported fourfold increase in dry sludge solids (Adhoum et al., 2004).

(d) **Evaporative recovery:** This process consists of evaporating metal-plating rinse water, to drive off the water as vapor and thus concentrated the chromic acid for recovery and reuse. Evaporative recovery and reuse are appropriate for almost all process reuse water systems, with the exception of those which chemically deteriorate with use. In evaporative recovery, all nonvolatile constituents of the waste water are retained in the concentrated product. In practice, this has been a major disadvantage of evaporative recovery, since the build up of impurities can result in defective plating practices.

(e) **Precipitation:** The oldest and most frequently used method for removal of trivalent chromium from wastewater is as precipitation. Research on the efficient of various alkali such as sodium hydroxide, sodium carbonate, sodium hydrogen carbonate, calcium carbonate, basic magnesium carbonate and magnesium oxide, showed that chromium in tanning liquors can be converted into denser precipitation when less soluble precipitation are used.

Precipitation is by far the most common method for dealing with metals containing waste. The theory is simple. Some metal salts are very insoluble, precipitation generate these insoluble salts in the waste stream by the addition of an appropriate counter anion, the precipitation is then filtered off

$$MX_n(aq) + NY_n(aq) \rightarrow NX_n(aq) + MX_n(s)$$

The anion Y is usually hydroxide (oil), sulfide (S^{-2}) or carbonate (CO_3^{-2}) and M is usually an alkali metal or alkaline earth. Broadly speaking the effectiveness of a particular precipitation for a particular toxic metal N can be estimated by looking up the solubility product of the precipitation metal salt NY_n. The lower the solubility product the more effective is the precipitation.

Advantages

(i) cheap.

(ii) long history of successful.

(iii) does not require large expenditure in new plant.

(iv) capable of treating a wide range of metal contaminates.

(v) under the correct conditions can give excellent removal of metals.

Disadvantage

(i) acidic effluent are difficult to treat.

(ii) non-selective: it gives a high water content sludge containing a cocktail of toxic and nontoxic metals. The sludge has to be landfilled at some times larger cost.

(iii) The presence of other salts, organic complexing agents and solvent can severaly compromise the precipitation efficiency.

(iv) can not be used to treat low concentrations of metals.

1.9 OBJECTIVE OF STUDY

In this project work, the aim is to conduct experiments which will be helpful for gathering some useful information regarding the use of adsorption for the removal of chromium from the electroplating wastewater. Here I have used activated carbon as an adsorbent at various parameters.

The aims and objectives of the work are as follows:

- Synthetic wastewater solutions of Cr(VI) of desired concentrations (10–300 mg/l) were prepared by dissolving accurately weighed quantity of $K_2Cr_2O_7$ (AR grade) in distilled water. Physical, chemical and biological characteristics of these wastewaters determined.

Parameters to be studied:

1. The removal of Chromium from electroplating wastewater using adsorption technique in batch system using activated carbon as adsorbent.
2. The effect of following parameters on chromium removal from wastewater
   (1) Effect of adsorbent dose.
   (2) Effect of pH.
   (3) Effect of initial concentration of adsorbate.
   (4) Effect of time.
   (5) Effect of temperature.
3. Study the removal of chromium using Lagergren, rate constant.
4. Study of thermodynamic adsorption parameters, ΔG^0, ΔH^0 and ΔS^0.

CHAPTER 2

ELECTROPLATING PROCESS AND EFFLUENT TREATMENT

2.1 GENERAL

Metal plating and/or finishing generally encompasses one or more of the following unit operation: cleaning, surface treatment, electroplating, electroless plating and rinsing.

The chemical solutions or bath used in these operational have a limited life and must be replaced to maintain the desired concentration of ingredients to give proper coating or finish. These solutions, as well as the rinse waters, are the primary sources of waste from metal plating and finishing operations.

Wastewater characteristics are dependent on the bath or solution from which it originated and the type(s) of metal being treated by the bath. Wastes are typically alkaline or acidic in nature and may contain one or more toxic heavy metals.

2.2 INDUSTRY DESCRIPTION AND PRACTICES

Electroplating involves the depositions of a thin protective layer (usually metallic) onto a prepared surface of metal, using electrochemical processes. The process involves pretreatment (cleaning, degreasing, and other preparation steps), plating, rinsing, passivating, and drying. The cleaning and pretreatment stages involve a variety of solvents (often chlorinated hydrocarbons, whose use is discouraged) and surface stripping agents including caustic soda and a range of strong acids, depending on the metal surface to be plated. The use of halogenated hydrocarbons for degreasing is not necessary as water based systems are available. In the plating process, the object to be plated is usually used as the cathode in an electrolytic bath. There are three main types of plating solutions: are acid or alkaline solutions and may contain complexing agents such as cyanides.

2.2.1 Surface Treatments

Surface treatment of a metal part is performed to render the part more corrosion-resistant or make it more amenable to other coating operations by altering the outer layer.

As a result of the electrochemical reaction of hexavalent chromium with a metallic surface in the presence of certain anions or activators, a complex film of chromium compound is observed on the surface. Chromate conversion coating are generally applied to aluminum, cadmium, copper, magnesium, silver, and zinc metal surfaces to impart corrosion resistance.

2.2.2 Electroplating

The electroplating of various metals such as brass, bronze, cadmium, chromium, copper, gold, indium, iron, lead, nickel, nickel-iron, palladium and zinc onto the surface of other conductive base materials is most common plating process. Metals are reduced on the conductive part (the cathode) from an electrolyte solution by the application of an electric current. Electroplating baths can be acidic or alkaline and generally require some heating and/or agitation.

2.2.3 Electroless Plating

The plating or chemical reduction of soluble metal ions onto a base substrate in the presence of a catalyst, reducing agent(s), complexing agent(s), and stabilizer(s), without the use of electrical current, is referred to as electroless plating. Electroless plating requires specific aqueous metal concentrations as well as temperature and pH levels. Electroless plating can be performed on non-metal as well as metal substrates.

2.2.4 Rinse Water

The rinsing of material before or after plating or coating operation is necessary to remove any plating bath solution that may be left sticking on the material. Water used in rinsing can consist of deionized, demineralized, or tap water, depending on what the finishing operation will tolerate. Rinsing operations produce the largest volumes of wastes from metal plating or finishing operations. Rinse waters ultimately become contaminated to varying degrees with whatever bath chemistry is left on the material. Depending on the type of rinsing scheme, rinse water can contain concentrations of heavy metals. There are several types of rinsing schemes that can be used in metal plating and finishing operations. Production specifications and quality control may limit the use of only one or two of the schemes. Some of the rinsing operations have advantages over the others in regard to water conservation and waste minimization.

2.3 TREATMENT OF EFFLUENT

Plating shop effluents consist of acids, alkalies, cyanides, hexavalent chromium and traces of metals like Cd, Cu, Ni, Ag and Sn. The effluent discharged is controlled within the limits as per IS: 2490.

2.3.1 The Chrome System

The chrome containing wastewater requires a separate treatment procedure to detoxify the Cr^{6+}. This wastewater is sent to one of two collection tanks, similar to those used in the acid/alkali system. The pH of the water is lowered to 2 or 3 by addition of sulfuric acid; sodium bisulfite then is used to reduce Cr^{6+} to Cr^{3+}. Lime or sodium hydroxide returns the pH to 8.0-8.5

$3NaHSO_3$ + $2H_2CrO_4$ + $2H_2SO_4$ (pH 2.0)
(Sodium bisulfite) (Chromic acid) (Sulfuric acid)

→ $Cr_2(SO_4)_3$ + $5H_2O$ + $3NaHSO_4$
(Chromic sulfate) (Water) (Sodium bisulfate)

The water flows to the sludge lagoon to remove the solids, and the supernatant is combined with that of the acid/alkali system and treated by the demineralization/neutralization tank and by clarifier of the general rinse system, and then is discharged to the river or some water body.

2.4 WASTE CHARACTERISTICS

Any or all of the substances used in electroplating (such as acidic solutions, toxic metals, solvents, and cyanides) can be found in the wastewater, either via rinsing of the product or due to spillage and dumping of process baths. The solvents and vapors from hot plating baths result in elevated levels of volatile organic compounds (VOCs) and in some cases, volatile metal compounds (when may contain chromates). Approximately 30 percent of the solvents and degreasing agents used can be released as VOCs when baths are not regenerated.

The mixing of cyanide and acidic wastewaters can generate lethal hydrogen cyanide gas and this must be avoided. The overall wastewater stream is typically extremely variable (1 liter to 500 liters per square meter of surface plated) but usually high in heavy metals (including cadmium, chrome, lead, copper, zinc, and nickel), cyanides, fluorides, and oil and grease, all of which are process dependent. Air emissions may contain toxic organics (such as trichloroethylene and trichloroethane).

Cleaning or changing of process tanks and the treatment of wastewaters can generate substantial quantities of wet sludge containing high levels of toxic organics and/or metals. The characteristics of chrome plating industrial effluent are given in table 2.1.

Table 2.1: Characteristics of chrome plating industrial effluent (Selvaraj et al., 2003)

Parameter	Value
Turbidity (NTU)	23.0
Total solids (mg/l)	4240.0
Conductivity (ms/cm)	16.4
COD (mg/l)	120.0
Chloride (mg/l)	704.0
Sodium (mg/l)	780.0
Total chromium (mg/l)	29.5
Cr(VI) (mg/l)	28.2

2.5 POLLUTION PREVENTION AND CONTROL

Plating involves different combinations of a wide variety of processes and there are many opportunities to improve upon the traditional practices in the industry. The following improvements should be implemented where possible:

2.5.1 Changes in Process

- Replace cadmium with high quality corrosion resistant zinc plating. Use cyanide-free systems for zinc plating where appropriate. In those cases where cadmium plating is necessary, use bright chloride, high alkaline baths or other alternatives. However, alternate complexing agents to cyanides may cause problems in wastewater treatment for they may result in the release of heavy metals.
- Use trivalent chrome instead of hexavalent chrome: acceptance of the change in finish needs to be promoted.
- Give preference to water-based surface cleaning agents, where feasible, instead of organic cleaning agents, some of which are considered toxic.
- Regenerate acids and other process ingredients, whenever feasible.

2.5.2 Reduction in Drag-out and Wastage

- Minimize drag-out by effective draining of bath solutions from the plated part by measures such as making drain holes in bucket type pieces, if necessary.
- Allow dripping time of at least 10 to 20 seconds before rinsing.
- Use fog spraying of parts while dripping.
- Maintain the density, viscosity, and temperature of the baths to minimize dragouts.
- Place recovery tanks before the rinse tanks (which then provide make-up for the process tanks). The recovery tank provides for static rinsing with high dragout recovery.

2.5.3 Minimizing Water Consumption in Rinsing Systems

It is possible to design rinsing systems to achieve 50-99% reduction of traditional water usage. Testing is required to determine the optimum method for any specific process but proven approaches include:

- Agitation of rinse water or work pieces to increase rinsing efficiency.
- Multiple countercurrent rinses.
- Spray rinses (especially for barrel loads).

2.5.4 Management of Process Solutions

- Recycle process baths after concentration and filtration. Spent bath solutions should be sent for recovery and regeneration of plating chemicals, not discharged into wastewater treatment units.
- Recycle rinse waters (after filtration).
- Regularly analyze and regenerate process solutions to maximize useful life.
- Clean racks between baths to minimize contamination.
- Cover degreasing baths containing chlorinated solvents when not in operation to reduce losses. Spent solvents should be sent to solvent recyclers and the residue from solvent recovery properly managed (e.g., blending with fuel and burning in a combustion unit with proper controls for toxic metals).

2.5.5 Target Pollution Loads

A key parameter is the water use in each process and systems should be designed to reduce water use. Where electroplating is routinely performed on objects with known surface area in a production unit, water consumption of no more than 1.3 liters per squence meter plated (L/m^2) for rack plating and 10 L/m^2 of surface area plated for drum plating should be achieved. The recommended pollution prevention and control measures can achieve the following target levels:

- Cadmium plating should be avoided. In cases where there are no feasible alternatives, a maximum cadmium load in the waste of 0.3 grams for every kilogram (kg) of cadmium processed is recommended (Cushnie, 1997).
- At least 90% of the solvent emissions to air must be recovered by the use of an air pollution control system such as a carbon filter.
- Ozone depleting solvents (such as chlorofluorocarbons and trichloroethane) are not to be used in the process.

2.6 TREATMENT TECHNOLOGIES

Segregation of waste streams is essential due to the dangerous reactions which can occur: strong acid/caustic reactions can generate boiling and splashing of corrosive liquids; acids can react with cyanides and generate lethal hydrogen cyanide gas. In addition, segregated streams that are concentrated are easier to treat.

2.6.1 Air Emissions

Exhaust hoods and good ventilation systems protect the working environment but the exhaust streams should be treated to reduce VOCs (using carbon filters which enable the reuse of solvents) and heavy metals to acceptable levels before venting to the atmosphere. Acid mists and vapors should be scrubbed with water before venting. In some cases, VOC levels of the vapors are reduced by combustion (and energy recovery) after scrubbing adsorption, or other treatment methods.

2.6.2 Liquid Effluents

Cyanide destruction, flow equalization and neutralization, and metals removal are required, as a minimum, for electroplating plants. Individual design is necessary to address the characteristics of any specific plant but there are a number of common treatment steps. For small facilities, the possibility of sharing a common wastewater treatment plant should be considered. Cyanide destruction must be carried out upstream of the other treatment processes. If hexavalent chrome (Cr^{+6}) occurs in the wastewater, then this is also usually pretreated to reduce it to a trivalent form using a reducing agent (such as a sulfide) followed by precipitation and sedimentation/filtration.

The main treatment processes are equalization, pH adjustment for precipitation, flocculation, and sedimentation/filtration. The optimum pH for metal precipitation is usually in the range of 8.5-11 but this depends on the mixture of metals present. The presence of significant levels of oil and grease may affect the effectiveness of the metal precipitation process. Hence, the level of oil and grease affects the choice of treatment options and the treatment sequence. It is preferred that the degreasing baths be treated separately. Flocculating agents are sometimes used to facilitate the filtration of suspended solids. Pilot testing and treatability studies may be necessary. Final adjustment of pH and further polishing of the effluent may also be required. Modern wastewater treatment systems use ion exchange, membrane filtration, and evaporation to reduce the release of toxics and the quantity of effluent that needs to be discharged. These can be designed to have a closed system with a minor bleed stream.

2.6.3 Solid and Hazardous Wastes

Treatment sludge contains high levels of metals and these should normally be managed as hazardous waste or sent for metals recovery. Electrolytical methods may be used to recover metals. Sludge is usually thickened, dewatered, and stabilized using chemical agents (such as lime) before disposal which must be in an approved and controlled landfill. High costs of proper sludge disposal are likely to become an increasing incentive for waste minimization.

2.7 EMISSION GUIDELINES

Emission levels for the design and operation of each project must be established through the Environmental Assessment (EA) process, based on country legislation and the Pollution Prevention and Abatement Handbook as applied to local conditions. The emission levels selected must be justified in the EA and acceptable to MIGA.

The following guidelines present emission levels normally acceptable to the World Bank Group in making decisions regarding provision of World Bank Group assistance, including MIGA guarantees; any deviations from these levels must be described in the project documentation.

The guidelines are expressed as concentrations to facilitate monitoring. Dilution of air emissions or effluents to achieve these guidelines is unacceptable.

All of the maximum levels should be achieved for at least 95% of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours.

2.7.1 Air Emissions

A 90% recovery of the quantity of VOCs released from the process is required.

2.7.2 Liquid Effluents

Electroplating plants should use closed systems where feasible or attain the following effluent levels. Table 2.2 shows the maximum allowable limit of heavy metals discharge from the electroplating industries.

Table 2.2: Maximum allowable limit of heavy metals discharge from the electroplating industries according to CPCB

Parameter	Unit	Limitation Values		
		A	B	C
Temperature	°C	40	40	45
pH value		6 - 9	5,5 - 9	5 - 9
BOD_5 (20°C)	mg/l	20	50	100
COD	mg/l	50	100	400
Suspended solids	mg/l	50	100	200
Arsenic	mg/l	0.05	0.1	0.5
Cadmium	mg/l	0.01	0.02	0.5
Lead	mg/l	0.1	0.5	1
Residual Chlorine	mg/l	1	2	2
Chromium (VI)	mg/l	0.05	0.1	0.5
Chromium (III)	mg/l	0.2	1	2
Mineral oil and fat	mg/l	ND	1	5
Animal-vegetable fat and oil	mg/l	5	10	30
Copper	mg/l	0.2	1	5
Zinc	mg/l	1	2	5
Manganese	mg/l	0.2	1	5
Nickel	mg/l	0.2	1	2
Organic phosphorous	mg/l	0.2	0.5	1
Total phosphorous	mg/l	4	6	8
Iron	mg/l	1	5	10
Mercury	mg/l	0.005	0.005	0.01
Total nitrogen	mg/l	30	60	60
Ammonia (as N)	mg/l	0.1	1	10
Cyanide	mg/l	0.05	0.1	0.2
Sulfide	mg/l	0.2	0.5	1
Fluoride	mg/l	1	2	5

Column A may be discharged into the water bodies using for sources of domestic water supply.

Column B is discharged only into the water bodies using for navigation. irrigation purposes or for bathing, aquatic breeding and cultivation, etc.

Column C is discharged only into specific water bodies permitted by authority agencies.

2.7.3 Sludge

Wherever possible, generation of sludge should be minimized. Sludge must be and stabilized, and should be disposed of in an approved secure landfill. Leachates from stabilized sludge should not contain toxics at levels higher than those indicated for liquid effluents. Where feasible, sludge may be re-used provided toxics are not released to the environment.

2.8 MONITORING AND REPORTING

Equipment to continuously monitor pH should be installed to provide an indication of overall treatment reliability. For larger plants (with discharges of more than 10,000 liters per day), the effluent should be sampled daily for all parameters except metals. Sampling of metals should be carried out at least monthly and when there are process changes. For smaller plants (having discharges of less than 10,000 liters per day), monthly monitoring of all parameters except pH may be acceptable. Frequent sampling may be required during start-up and upset conditions.

Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken. Records of monitoring results should be kept in an acceptable format. These should be reported to the responsible authorities and relevant parties, as required, and provided to MIGA if requested.

2.9 KEY ISSUES

The following box summarizes the key production and control practices that will lead to compliance with emission guidelines:

- Use cyanide free systems.
- Avoid cadmium plating.
- Use trivalent chrome instead of hexavalent chrome.
- Prefer water-based surface cleaning agents where feasible, instead of organic cleaning agents, some of which are considered toxic.
- Minimize drag out.
- Use countercurrent rinsing systems and/or recycle rinse waters to the process after treatment.
- Regenerate and recycle process baths and rinse waters after treatment.
- Recycle solvent collected from air pollution control systems.
- Send spent solvents for recovery.
- Do not use ozone depleting substances.
- Manage sludge as hazardous waste. Reuse sludge to the extent feasible, provided toxics are not released to the environment

CHAPTER 3

LITERATURE REVIEW

3.1 SOURCES OF CHROMIUM POLLUTION

The main sources from which metal pollution of the environment oriented are

(a) Geological weathering of rocks and sediments, a naturally occurring process.

(b) Industrial processing of ores and mineral

(c) Use of metals and metal compounds in various industries. These are anthropogenic sources of metal pollution.

(d) Leaching of metals from garbage and solid waste dumps. It is again the results of man's activity and is the principle source of ground water contamination. Main source of chromium in wastewater is industrial manufacturing and utilization process. Chromium is primarily used in plating industry, as a component of alloy metal, chrome tanning and wood impregnation industries (Trivedy, 1998). Chromium occurs in aqueous systems as both the trivalent and the hexavalent ions. Chromium is present in industries wastes primarily in the hexavalent form, as (CrO_4^{-2}) and dichromate ($Cr_2O_7^{-2}$) (Patterson, 1985).

3.1.1 Municipal Wastewater

The wastes that comprise municipal sewage are of four principle origins: domestic sewage, industrial wastes, surface runoff and groundwater. Industrial wastes or wastes from the material processing operations of manufacturing are frequently discharge into sewage system and therefore, comprise a portion of municipal sewage; chromium occurs in particulate state in municipal waste waters with 97% to 99% dissolved fraction in hexavalent form (Gurnham, 1955).

3.1.2 Industrial Wastes

Hexavalent chromium is one of the important industrial metal toxicants. Chromium compounds are added to cooling water to inhibit corrosion. They are employed in the manufacture of inks and industrial dyes and paint pigments, as well as in chrome tanning, aluminium anodizing, and other metal cleaning, pre-plating and electroplating operations. Chromates are also contained in some preservative for meat packing, brewery, distillery and fire retardant chemicals used in wood preservation treatment. Automobile parts manufacturers are one of the largest producers of chromium in the chromic acid bath and rinse water in such metal plating operations.

Use of chromates in cooling water system is wide spread and blow down from the cooling system can constitute a significant chromium containing wastewater. Hexavalent chromium treatment normally involves reduction to the trivalent form, prior to removing the chromium from the industrial waste. Thus trivalent chromium in industrial effluents may result from one step of the waste treatment process itself, that of chemical reduction of hexavalent chromium. Industries which employ trivalent chromium directly in manufacturing processes include glass, ceramics, photography, inorganic pigments (including anodizing compounds), textile dye, and animal-glue manufacture.

The electrolysis of chromium metal yields only trivalent chromium due to the process design, and an effluent chromium level of 1964 mg/l in the furnace scrubber water have been reported. Municipal refuse incinerator scrubber water was reported to contain 25 mg/l trivalent chromium and only 0.5 mg/l hexavalent chromium.

Kura Bhaskar et al. (1998) give hexavalent chromium exposure levels resulting from shipyard welding, which is also the source of water pollution.

Prasad et al. (1999) studied evaluation of heavy metals in ground water near mining area and development of heavy pollution index.

3.2 EFFECT OF CHROMIUM ON ENVIRONMENT

Chromium has oxidation states varying Cr^{-2} to Cr^{+6}, but the hexavalent form of chromium is the most harmful among all the forms and its toxicity keeps on increasing with its solubility in the water.

Genatoxic Effects

Genatoxic effect includes induction of tumors, anomalies of embryonic development and mutations genotoxicity is an important part of general environment toxicity. The principles of genetic toxicity and short term tests for mutagens and carcinogens are briefly reviewed. The genotoxicity of chromium compounds is discussed and hypotheses for the genotoxic actions are presented.

Chromium is peculiar, because its low common oxidations states, chromium(VI) and chromium(III), differ markedly in a number of their biological properties. In water chromium(III) exists at pH values less than four as the aquo cation $[Cr(H_2O)_6]^{3+}$, or at sufficiently high chloride concentration as $[Cr(H_2O)_4Cl_2]^+$. At physiological pH values and in basic medium polymeric rather insoluble hydroxo complexes, $[Cr(H_2O)_m(OH)_{6-m}]^{m-3}$, are formed that are unable to cross cell membranes. In solutions of chromium(VI), chromate ions, CrO_4^{2-}, predominate at physiological and basic pH values, whereas the dichromate ion, $Cr_2O_7^{2-}$, is favored under acidic conditions. Chromate and dichromate ions are strong oxidizing agents. Chromate ions easily cross cell membranes. Chromium(III) can not be oxidized to chromium(VI) by biological systems. Chromium(III) is devoid of cytotoxic and genotoxic activity. Chromium(VI) is easily reduced to chromium(III) inside and outside a cell. Extra cellular reduction abolishes the cytotoxicity and genotoxicity of chromium(VI). Intra cellular reduction of chromium(VI) is then sequested, or in the nucleus, whereas chromium(VI) may interact with genetic materials for instance, with nucleophilic sites in DNA such as the nitrogen and oxygen atoms of the cyclic bases negatively chared oxygen atoms of phosphate groups.

Chromium(VI) compounds, unlike most other metal compounds, are actively transported through cell membrances and thus can reach genetic targets. Consequently, the genotoxic effects of chromium have been studied with a varity of short term tests covering the entire range of genotoxic damages. The results indicate that chromium(VI) is an active genotoxic agent in intact cell systems, whereas chromium(III) is inactive. Chromium(III) gives a positive mutagenic response only when tested invitro on purified DNA. Chromium(VI) gives contradictory results under these conditions.

The mechanisms of chromium genotoxicity derived from short tests explain also some features of chromium carcinogenicity such as the site tumors on experimental animals and exposed humans. Cell extracts and microsomes markedly in their ability to prevent the mutagenicity of chromium(VI). Erythrocytes, liver microsomes and gastric juice agents with good preventive abilities are also the major sites for in-vitro reduction of chromium(VI).

Lung and muscles do not reduce chromium(VI), are unable to prevent the mutagenic effects of chromium(VI), and are preferred targets for the induction of tumors.

The effects of Cr(III) and Cr(VI) compounds on renal and hepatic respiratory enzymes and metabolites of a freshwater fish, Anabas scandas were studied Reddy et al. (1992). In a subschronic exposure of 30 days, both forms of chromium inhibited the activities of lactate dehydrogense, whereas the hexavalent form induced greater effects. The levels of pyruvate and lactate are not exacted dehydrogenase activity.

3.3 TREATMENT TECHNOLOGIES

Removal of chromium or reduction of chromium(VI) to chromium(III) involve various technique as follows (Gode and Pehlivan, 2004) :

(i) Precipitation
(ii) Ion Exchange
(iii) Extraction
(iv) Electrochemical Reduction
(v) Reverse Osmosis
(vi) Biological Treatment
(vii) Adsorption

Adsorption technique, now a days is becoming more important than other techniques. Out of many adsorption techniques, biological treatment is the cheapest and more efficient of all. Various techniques which are carried up till now is discussed in two main groups.

(i) Precipitation

Few works pertaining to this class with some of the precipitation are discussed below:

by the Ferrite process: Mehmet et al. (2004) studied that an efficient Cr(III) removal (about 100%) in the solution from the Cr(VI) reduction process utilising sodium sulphite as reducing agent was achieved when the solution was treated at pH 9 and 50 °C for 60 min in the presence of Fe^{2+}/Cr^{3+} weight ratio of 16. For the other Cr(III) solution prepared from Cr(VI) reduction by ferrous sulphate, a Fe^{2+}/Cr^{3+} weight ratio of 17.9 at the same conditions was found to produce complete removal of Cr(III).

by Copper Smelting Slag: Kiyak et al. (1999) evaluated the extent of reduction is dependent on the amounts of acid and reductant, contact time, Cr(VI) concentration, temperature of the solution and particle size of CSS. When twice the amount of acid required with respect to Cr(VI) was used, Cr(VI) in 100 ml solution (100 mg/l) was completely reduced in a contact period less than 5 min by a 10 g/l dosage of CSS. Reduction efficiency increased with increase in temperature of solution, showing that the process is endothermic. Reduced chromium, and iron and other metals dissolved from CSS were effectively precipitated by using NaOH or calcinated carbonatation sludge from sugar plant.

by NaOH: Guo et al. (2005) shows that effectively removed Cr^{3+} from the aqueous phase with a removal of higher than 99% and a recovery of ~60%. The substitution of NaOH with CaO or MgO resulted increased the Cr recovery ratio from 60% to 80%. The best alkali was a mixture of CaO and MgO (4:1, by weight) to balance the cost and performance. COD and SS were removed in the process via sweeping by the precipitate with removal percentages of 47.6% and 86.3%, respectively.

by Streptomyces griseus: Laxman et al. (2002) shows that a strain of Streptomyces griseus was found to grow and reduce highly toxic Cr^{6+} to less toxic Cr^{3+} from media containing 5–60 ppm of Cr^{6+}. The concentration of Cr^{3+} increased with simultaneous decrease in Cr^{6+} during growth with complete conversion in 3–4 days.

by Steel Wool: Tumen et al. (1997) invested the reduction of Cr(VI) by steel wool and the precipitation of reduced chromium by CaCO3 powder and NaOH solution in continuous and batch systems, respectively. Optimum result was found at Cr(III) conc 494 mg/l; iron conc. 572 mg/l; initial pH 1.74; shaking time, 30 min; temperature, 25°C.

by Alkaline Tailings: Fonseca et al. (1997) described chromium precipitation from spent tanning liquors using industrial alkaline tailings and removal efficiencies are compared with those obtained with traditional chemicals as NaOH, CaO and MgO: (i) using steelmaking dusts at dosages up to 70 gl^{-1} residual Cr remains >3.7 mgl^{-1}. Moreover Cr and mainly Pb are partially leached by the spent tanning liquor, therefore limiting the use of this industrial residue as Cr precipitant; (ii) a dosage of 80 g l^{-1} (dry basis) of chemical sludge from a water treatment plant results in a removal efficiency of 99.97% Cr and residual Cr<2mgl^{-1} under experimental conditions that include stirring at 100 rpm for 1 h and settling for 23 h.

(ii) Ion Exchange

by IERECHROM process: Tiravanti et al. (1996) utilizes a weak cation (carboxylic) ion exchange resin and allows for recovery and reuse of 90% of high purity (> 99%) chromium from other interfering metals such as Fe and Al present in the spent tanning baths. The process is based on the acid leaching of the sludges and on treating the leachate by a weak base anion resin.

by 1200H, 1500H and IRN97H: Rengaraj et al. (2003) described the removal of chromium from aqueous solution by an ion exchange resins 1200H, 1500H and IRN97H remarkable increase in sorption capacity for chromium, compared to other adsorbents. The adsorption process, which is pH dependent show maximum removal of chromium in the pH range 2–6 for an initial chromium concentration of 10 mg/l.

by zeolite NaX: Barros et al. (2004) carried out experiments in continuous and batch systems at 30 °C. The batch isotherm evidenced an irreversible shape with a maximum chromium uptake of 3.61 meq/g. The column experiments were carried out at pH = 3.5, with a flow rate of 9 ml/min and an average particle size of 0.180 mm. The dynamic system provided a distinct ion-exchange mechanism, which generated a favorable isotherm with a chromium uptake of 3.27 meq/g.

by heat-activated bauxite: Erdem et al. (2004) studied to increase the Cr(VI) adsorption capacity of bauxite, heat treatment method was tested. Although heating provides an enhanced adsorption, the heat-activated bauxite was found to be a weak adsorbent for Cr(VI). The maximum adsorption yield (64.9%) was obtained at the conditions of pH 2, activated bauxite dosage of 20 g/l, contact time of 180 min, for the initial Cr(VI) concentration of 10 mg/l and temperature of 20 °C by using the bauxite sample heated at 600 °C.

by SB-6407, AFN and ACM: Esengul et al. (2002) deals with the transport of hexavalent chromium through SB-6407, AFN and ACM anion-exchange membranes in contact with different salt solutions. The effect of salt solutions on the transport of chromium(VI) was investigated. The effect of salt solutions was observed at different sequences and the transport efficiencies of the membranes was found to be in the order SB-6407>AFN>ACM.

(iii) Extraction

by Quaternary Ammonium Compounds: Shiue et al. (1997) investigated the chromium(VI) from aqueous solution of 0.1M ionic strength by trioctylmethlammonium compounds (Aliquat 336) in a mixture of kerosene and xylene. Experiments results showed that hydrogen chromate ion ($HCrO^{4-}$) is the major extractable species of Cr(VI) at pH 3.53-3.75, expressd by the mechanism $R_3CH_3NNO_3 + HCrO^{-4} = R_3CH_3NHCrO_4 + NO^{3-}$.

by Tetrabutyl Ammonium Bromide: Venkateswaran et al. (2004) evaluated the extraction of hexavalent chromium (Cr) from aqueous solutions by tetrabutyl ammonium bromide (TBAB) salt in dichloromethane. The results indicated that the maximum extraction efficiency of Cr(VI) was at pH 1 ± 0.1 and no significant loss in volume of dichloromethane and retains the same extracting ability even after five extraction cycles.

by Cyanine dyes: Balogh et al. (2000) studied the solvent extraction of chromium(VI) ion associates with symmetric cyanine dyes including the heterocyclic radicals of 1,3,3-trimethyl-3N-indoline, benzooxazol, benzothiazol and quinoline by means of spectrophotometric method. The extraction of chromium is the highest during extraction from the sulphuric acid medium in the range 0.05–03 M H_2SO_4. It was found that the Cr(VI):Cl:R molar ratio is 1:1:1.

by Cyanex 272: Lanagan et al. (2002) investigated the solvent extraction behavior of chromium with Cyanex 272. The effects of various experimental variables such as the metal oxidation state, pH, presence of anions such as nitrate, chloride, sulphate and acetate including the conditions of extraction relevant to the separation of nickel and cobalt directly from the partially neutralized. The nature and forms of the extracted species are inferred from slope analysis and UV–VIS spectroscopy data.

by Cupferron: Shen et al. (2001) studied on a three-step process for the separation of Cr(III) from interfering element metals(Al, Fe, Ca, Mg, and Zn) present in the acid extract (leachate) of tannery sludge. The removal efficiency of Cr(III), Ca, and Mg were

99.6, 12.7, and 4.9%. After all three steps, the molar percentages of Al, Ca, Cr, Fe, Mg, and Zn in the precipitate formed at pH 7.0 and 21°C in a typical case were 2.94, 0.055, 95.649, 0.302, 1.013, and 0.041, respectively.

by sodium hypochlorite: Kazi et al.(2001) studied on insoluble chromated copper arsenate (CCA) wood preservative form sludges when the hexavalent chromium component is reduced by wood extractives, wood particles and preservative additives in the solution. It is having a multi-stage recycling process whereby approximately 97% of the CCA components are recovered from the sludge. It involves extraction with sodium hypochlorite to remove and oxidize chromium (more than 90%) and extract most of the arsenic (approx. 80%) followed by extraction of the copper and remaining arsenic and chromium with phosphoric acid.

(iv) Electrochemical Reduction

Cristobal et al. (2005) studies on chromium nitride—CrN—coatings that have emerged as an alternative in machining applications, low deposition temperature, excellent wear resistance and good corrosion resistance. In this work a stripping method based on electrochemical techniques has been developed to strip chromium nitride coatings in an oxidising alkaline solution process. The complete removal of the chromium nitride layer is indicated by a sudden rise in the potential in time, which allows simple control of the stripping process.

Gao et al. (2004) designed a combined electrocoagulation and electroflotation process to reduce Cr^{6+} to Cr^{3+} first and then to remove the total Cr from wastewater to a value below 0.5 mg/L. The two-stage electroflotation arrangement can separate the solids from the wastewater to a value of less than 3 mg/l with total Cr less than 0.5 mg/l. The optimal conditions for the treatment are: charge loading about 2.5 Faradays/m^3 water, pH value in the coagulation unit is 5–8, residence time required is about 1.2 h.

Sawada et al. (2003) removed the chromate anions from the soil to the anodic reservoir by the moving force of electromigration. The process provides for an efficient removal of anionic chemicals from contaminated soils. In this process, the chromate anions that accumulate in the anodic reservoir are simultaneously eliminated by using a column packed adsorbent.

Adhoum et al. (2004) investigated the performance of electrocoagulation, with aluminium sacrificial anode, in the treatment of metal ions (Cu^{2+}, Zn^{2+} and Cr(VI)) containing wastewater. Results obtained with synthetic wastewater revealed that the most effective removal capacities of studied metals could be achieved when the pH was kept between 4 and 8, retention time 20 min, current density 0.8–4.8Adm^{-2}. The electrode and electricity consumptions were found to be 1 g l^{-1} and 32 A h l^{-1}, respectively.

(v) Reverse Osmosis

Cassanol et al. (1996) described the use of pressure-driven membrane processes integrated with conventional precipitation/dissolution operations in order to reduce chromium content in waste water from elimination/reduction of organic lipolytic components, metals and other impurities that accompany the chromium recovered by traditional processes. The process permits also the reuse of the permeate from the nanofiltration in the pickling phase, considering the high content of chlorides in me solution.

Drioli et al (1997) showed that many operations can be improved integrating them with membrane operations. The steps studied in this work were: enzymatic skins unhairing, degreasing of pickled sheepskins and chromium tanning; furthermore, the recovery and reuse of salts contained in the solution coming from chromium (III) precipitation were studied. The obtained results realize a reduction in environmental impact, a simplification of depuration processes of waste water, an easy reuse of sludge, a decrease of disposal costs and a saving of chemicals and water.

Shaalan et al. (2001) studied on leather tanning processing involves treatment of skin in chrome baths where the percentage exhaustion of chromium salts is usually in the range of 60-70%. In this, parameters governing the separation of protein/fat mix by ultrafiltration are obtained by analysis of published results on separation of proteins by ultrafiltration. The parameters for the concentration of chromium by nanofiltration are also deduced. A simulation model based on the resistance model and involving material balance and energy requirements for the ultrafiltration/nanofiltration scheme has been developed.

(vi) Biological Treatment

Chen et al. (1998) conducted he review to describe the microbial reduction of hexavalent chromium in general and biological treatment of Cr(VI) containing wastes particle. Several micro organism, however, have been found to be able to resist and or reduce Cr(VI) concentrations. The microbial Cr(VI) reduction activities are either plasmid or membrane associated phenomena. Factors affecting microbial Cr(VI) reduction, inducting biomass concentration, initial Cr(VI) level, carbon source, pH and temperature, oxidation-reduction potential, organism and metal cations are discussed.

Kratochvil et al. (1998) removal of trivalent and hexavalent chromium by seaweed biosorbent. Protonated or Ca from sargassium seaweed biomass gets bound up to 40 mg/l of Cr(III) by ion exchange at pH 4. An ion exchange model assuming that the only species taken up by the biomass was $Cr(OH)^{+2}$, successfully represents data for Cr(III). The maximum uptake of Cr(VI) to Cr(III) reduction was explained.

Low et al. (1997) studied the potential of the biomass of nonliving water hyarinth roots Eichharnia crassipes, as a biosorbent for Cr(VI) from synthetic solution and electroplating waste under batch conditions. Various factors affecting sorption of chromium were studied. They include effect of pH, initial concentration, dosage, agitation rate, temperature and the presence of other anions.

Al-Ashes et al. (1996) treated canda meal for its ability to adsorb Cr(III) from solution. It was noticed that a decrease in the Cr concentration. An increase of the metal ions adsorbed more metals when the metal concentrations in the solutions were higher.

Aksu et al. (1999) also investigated simultaneous biosorption of copper(III) and chromium(VI) on drived Chloral Vulgaris from binary metal mixtures. It is application of multicomponent adsorption isotherms. They investigated the effects of pH and single and dual-metal ion concentration on the equilibrium uptakes. It was observed that the equilibrium uptakes of chromium(VI) ion were changed due to the biosorption pH and the presence of the other metal ions.

Qimimg et al. (1999) studied heavy metal uptake capacities of common marine macro algal biomass. Biosorption of heavy metals is an effective technology for the treatment of industrial wastewater. The results indicated that he biomass of the marine algae is suitable for the development of efficient biosorbents for the removal.

Tobin et al. (1998) used mucor biosorbent for chromium removal from tanning effluent. *Mucor mesh biomass was found to be an effective biosorbent for the removal of* chromium. In comparative studied with ion exchange resins, the mucor biomass demonstrated chromium biosorption levels that correspond closely to those of commercial staongly acidic resin while pH behaviour mirrored that of the weakly acidic resins in solutions.

Andre et al. (1996) studied heavy metal removal using bioprocess technology. Sulfate reducing bacteria convert sulfate to H_2S. The H_2S reacts with the dissolved metals to from insoluble metal sulfite precipates. Sulfite oxidizing bacteria convert excess H_2S to elemental sulfur. SO2 can be removed from flue gas using a scrubber technology and the two biological steps.

Chui et al. (1996) studied on removal and recovery of copper(VI), chromium(III) and nickel(III) solution using crude shrimp chitin packed in small columns. The strip chitin demonstrated remarkable Cu(II) and Cr(III) collecting ability of over 95% and 96%, respectively, comparable to the best metal chelating biopolymer chitosan, whose Cu(III) and Cr(III) removal ability under the same conditions were 98% and 99% respectively.

Santiago et al. (1993) studied resting cells of Agrobacterium radiobacter EPS grown on glucose, maltose, lactose, mannitol or glycerol 0.5 mm chromate. However, resting cells of strain EPS-016 grown on glutamate or succinate did not reduce chromate. The ability of washed cells to reduce chromate was correlated with their redox potential.

Jackson et al. (1997) studied immobilized microbial reactor for the bio transformation of Cr(VI). Out of an bacterial isolated from soil contaminated with effluents from electroplating wastewater, Bacillus coagulans exhibited the maximum Cr(VI) reduction potential. Experimental result demonstrated that near complete removal of Cr(VI) was achieved in the reactor with an initial Cr(VI) concentration of 26 mg/l in 24 hours.

(vii) Adsorption

Manganese di oxide: Datal et al (1996) studied adsorption OF Cr(III) by electrolytic manganese do oxide, which has been followed between pH 2-5. The adsorption isotherm all fitted a simple Langmuir adsorption equation quit well. The amount of metal ion adsorbed increased with pH for lead and copper ion. For both thallium and chromium a significant drop in adsorption between pH 3 and 4 was observed.

Poly Pyrrole: Senthuchlven et al (1996) elaborated on an earlier communication from the laboratory that described a new approach to the electro chemical remediation of Cr(VI) based on the use of a conducting polymer, namely poly-pyrrole.

Alataree et al (1998) studied reduction of Cr(VI0 by polypyrrole deposted on different carbon substrats. This work focuses on the reduction of Cr(VI) ions in aqueous media by poly pyrrole deposits on porous, high area three dimensional carbon electrodes.

Smectite: Volzone et al. (1995) studied adsorption of Cr(III) on a Smectite from a tanning wastewater. Similarly adsorption of sodium chloride and sulphate were analyzed. Testes were carried out with solutions with a Cr(III) content ranging between 0.62-31.20 nmol/l. The method used to develop this work covered the characterization of solution and of the Smetite before and after each tests. The Langmuir equation was used in order to quantify the Cr(III) adsorption.

by IRN77 and SKN1: Yeon et al. (2001) evaluated the performance of IRN77 and SKN1 cation exchange resins in the removal of chromium from aqueous solutions. It was found that more than 95% removal was achieved under optimal conditions. The adsorption capacity (k) for chromium calculated from the Freundlich adsorption isothermwas found to be 35.38 and 46.34 mg/g for IRN77 and SKN1 resins, respectively.

Bentanite: Khan et al. (1995) evaluated the sorption of Cr(III), CR(VI) and Ag(I) from aqueous solutions on bentanite by batch technique. The sorption of Cr(III) and Ag(I) on bentonite is exothermic in nature while Cr(VI) is an endothermic process.

Activated Carbon: Muthukumaran et al. (1995) shows that the chemically activated coconut shell carbon [CSC(HT)] is superior to F-400 and CH(H) for the removal of Cr(VI) from plating waste.

Ploy (acrylic acid) gels: Heitz et al. (1999) studied the ability of cross linked poly (acrylic acid) to retain chromium species as a function of pH. In contrast, a very fast desorption was observed when retention occurs via adsorption at the surface of the polymer gel.

Thiourea: Maxcy et al. (1998) studied the reduction of chromium(VI) to Cr(III) by thiourea. A study was undertaken to develop a kinetic model for the reduction reaction.

Potassium Sulfate Crystals: Guzman et al. (1998) studied adsorption isotherms of chromium(III), a crystal growth suppressor, on the surface of potassium sulfate crystal powder suspended in saturated solution at 45°C at different constant pH (equals 2.5, 3,4 and 5). The higher the pH, the largest amount of chromium(III) was adsorbed.

Alginate Beads: Araujo et al. (1997) studied the applicability of Cr(III) removal from aqueous solutions using calcium alginate beads. The equilibrium isotherms were plotted at two temperatures. The relationship between the chromium sorbed and the calcium released was determined as well as the effect of alginate amount and initial pH on the equilibrium results was shown.

Carbon: Chin-Pao et al. (1975) investigated the effect of some partinenated factors on the removal of chromium from diluted aqueous solution by calcinated coke. A semi quantitative model governing the attachment of chromium species onto the carbon surface is presented. Removal efficiency by various solids in a controlled or otherwise identical condition also is compared.

Hydrotalcite: Manju et al. (1999) evaluated the sorbent power hydrotalcite $[Mg_3Al(OH)_8]2CO_3xH_2O$ for Cr(VI) from water solution. The adsorption behaviour of Cr(VI) was investigated at different initial concentration of adsorbate, contact time, pH, temperature and adsorbent dose by batch equilibrium technique.

Sawdust: Use of sawdust, a waste product from wood processing industry has been explored herein Mathur et al. (1986). The results show significant removal by combination of physical adsorption and solids phase reaction. The kinetics and equilibrium capacities have been work out.

Lignite Coal: Kannan et al. (1991) studied removal of chromium(VI) by adsorption lignite coal. A method for removal of Cr(VI) from effluents by adsorption process on lignite coal is developed. In order to understand the adsorption behaviour and adsorption potential of coal a number of batch experiments were conducted on adsorbent adsorbate system at various pH (1-6) with different amounts of adsorbent. The result illustrates that, the adsorption is maximum around pH 2 and the lignite coal has a greater adsorption potential around pH 2.

Bituminuous Coal: Nagesh et al. (1989) developed a method for removal of Cr from water by adsorption; it is maximum at pH 2 and reduction is also at pH 2. At pH More than 7 the removal of chromium very less.

Hematite: Singh et al. (1993) studied the ability of hematite to remove Cr(VI) from aqueous solution, at different concentrations, temperatures and pH. The maximum removal (97%) was observed at 40°C. The equilibrium data obey the Langmuir isotherm for the present system. An empirical equation has been developed to predict equilibrium adsorption capacity from knowledge of equilibrium adsorbate concentration.

Activated Sludge: Srivastava et al. (1997) generated the blast furnace waste in steel plants converted into a low cost adsorbent. The resulting activated sludge has been characterized and used for the removal of lead and chromium. The uptake of lead is found to be greater than that of chromium. Adsorption on activated sludge follows both Freundich and Langmuir models.

Flyash: Dasmahapatra et al. (1996) studied on separation of Cr(VI) from an aqueous solution by flyash. It is observed that the percent removal of Cr(VI) by flyash is affected by its concentration in aqueous solution, temperature, particle size and pH. Better separation is obtained at acidic pH and at higher temperature.

Trivedy et al. (1998) investigated efficiency of flyash for removal of Cr(VI).

TiO_2: Hongxiang et al. (1998) studied adsorption of the Cr(VI) ion into TiO_2. This study not only provides information on the removal of heavy metal ions from polluted aqueous solution, but is also useful for further investigation of the photocatalytic decontamination of the Cr(VI) ion.

Hydrogen Sulfide: Pettine et al. (1998) measured the influenced of an extanded set of metals on the reduction rate of Cr(VI) with H_2S in NaCl solution. The metals studied, caused large increases in the reduction rates at micromolar concentrations.

Zeolite: Tahir et al. (1998) measured the concentration of potencially toxic chromium metal ions in sediments and waste samples from selected tanneries by atomic absorption spectrophotometry after digestion with nitric acid. The results suggest that natural aluminosolicates such as Zeolite -3A can be utilized as low cost ion exchange for various other heavy metals.

Biskup et al. (1998) determined relationships between corrected selectivity coefficient and fraction of the exchanged cadmium ions in both the solid and liquid phase at equilibrium of the exchange processes between cadmium ions from solution and sodium ions from zeolite at different total ion concentrations and temperatures.

FeS: Watson et al. (1995) described experiment to investigate the properties of an ion sulfide material produced by sulphate reducing micro organisms when they are grown with a substrate containing appreciable ion.

Acrylamide/Malic acid: Saraydin et al. (1995) studied acrylamide-malic acid hydrogels in the form of rod, prepared by gamma radiation. They have been used for adsorption of some heavy metal.

Sediment particles: Huang et al. (1997) studied theoretically and experimentally the sorption of heavy metal on sediment particles. The sorption processes of heavy pollutants on sediment particle can be described by Langmuir model.

Biogas Residual Slurry: Yamuna et al. (1994) investigated the ability of waste biogas residual slurry (BRS) to remove Cr (VI) from aqueous solutions. The adsorption followed first order rate expression. The equilibrium data fit well into Langmuir and Freundlich isotherms. Adsorption was maximum at an initial pH of 1.51. Temperature studies showed that the adsorption process was endothermic in nature.

Maple Sawdust: Batch adsorption studies have been carried out by Dorris et al. (2002). An empirical relationship has been obtained to predict the percentage chromium(VI) removal at any time for known values of sorbent and initial sorbate concentration. In pH range of 1–2, there is little or no adsorption. The percent adsorption increases in the pH range of 3–10, showing the maximum adsorption at pH 5.

Wine processing waste sludge: Liu et al. (2003) Wine processing waste sludge has been shown to be an effective adsorbent for the adsorption of Cr(III) from aqueous solution. The sludge has been characterized by scanning electron microscopy (SEM) and energy dispersive X-rays (EDX). The calculated thermodynamic parameters, ΔH^0 and ΔS^0, are 1.95 kJ/mol and 27.16 J/molK, respectively. The ΔG^0 values range from −5.98 to −6.79 J/mol, which shows the physical adsorption properties of the sludge.

Soya cake: Daneshvar et al. (2002) observed a high efficiency for adsorption of chromium at pH < 1. The favorable temperature for adsorption was found to be 20 °C.

Experimentally, the best time was 1h and with increasing soya cake mass up to 30 g, the adsorption efficiency was increased. Dissolution of LiCl in the experimental solutions, increased the efficiency of adsorption, however, this effect was not observed in the case of KCl.

Casurina equisetifolia leaves: Rangnathan et al. (1999) Casurina equisetifolia leaves were carbonised and activated after treatment with sulphuric acid (1:1), phosphate salt (10%) or zinc chloride (25%), at different temperatures. Desorption studies show that 65-80% of adsorbed chromium could be desorbed by alkali followed by acid treatments.

iron (III) hydroxide-loaded sugar beet pulp: Altundogan et al. (2004) investigated a composite adsorbent was prepared from sugar beet pulp by loading with iron (III) hydroxide and its Cr(VI) removal properties from aqueous solutions. Maximum total chromium-removal efficiency of PSFH was 83.1% at the final pH of 4.4 for the conditions of 10 mg l^{-1} Cr(VI) concentration, 120 min contact time and 25 °C. Also, it was found that the reduction of Cr(VI) occurred during the sorption process is an important issue.

Heat-activated bauxite: Erdem et al. (2004) studied on heat-activated bauxite. However, the heat-activated bauxite was found to be a weak adsorbent for Cr(VI). The maximum adsorption yield (64.9%) was obtained at the conditions of pH 2, activated bauxite dosage of 20 g l^{-1}, contact time of 180 min, for the initial Cr(VI) concentration of 10 mg l^{-1} and temperature of 20 °C by using the bauxite sample heated at 600 °C.

Fe-modified steam exploded wheat straw: Chun et al. (2003) investigated the removal of hexavalent chromium, Cr(VI), from aqueous solution by a novel materials, Fe-modified steam exploded wheat straw(Fe-SEWS), in batch studies. The highest removal efficiency was 96.84 and 96.00%, respectively. Adsorbed Cr(VI) can be recovered by desorbing and the desorption rate reached 87–90%.

Turkish brown coals: Gode et al. (2004) evaluated the effects of adsorbent dose, initial sorbate concentration and contact time on the adsorption of Cr(III) by Isparta-Yalvac-Yarikkaya (YK) and Kasikara (KK) brown coals. The maximum equilibrium uptake was 0.05 mmol of Cr(III)/g for KK, and 0.26 mmol of Cr(III)/g for YK, respectively, at a pH of 4.5. More than 90% of chromium(III) was removed by KK and YK from an aqueous solution after 60 min.

Bacterial strain (NRC-BT-2): Rabbani et al. (2005) Biosorption of Cr^{3+} has been investigated by 17 various bacterial strains isolated from Ramsar warm springs, Iran. The effect of initial concentration of the metal solution in the range of 10–250 ppm has been studied, and the maximum removal occurs in 10 ppm, in pH 4 and 1 h of contact time (100%). Sodium acid, high temperature and g-ray did not affect the biosorption. Presence of the other cations such as Ni^{2+}, Zn^{2+}, Cu^{2+} and Pb^{2+}, reduce removal efficiency. Desorption of Cr from biomass by nitric acid was revealed in 31.45% of biosorbed chromium.

CHAPTER 4

ADSORPTION FUNDAMENTALS

4.1 BASIC CONCEPTS

When two phases, at least one of which is liquid or gas, come into contact, the composition of these phases close to the phase boundary will differ from the composition observed in regions distant from the boundary i.e. within the bulk of the phases. This will occur even through the phases may be in equilibrium. This increase in concentration in the region where the phases are in mutual contact relative to the concentration in the bulk of the phase is called "adsorption". Conversely, a concentration decrease may be observed in, for example, solution of electrolyte. This phenomenon is called negative adsorption. The phase in the surface of which a substance in the other phase accumulates is termed the adsorbent and the adsorbed substance is called "adsorbate".

Penetration of particles of one phase deep into the other phase, resembling dissolution to some extent is called adsorption. This process may also be accompanied by adsorption, if the particles are irregularly distributed around the phase boundary the majority being concentrated close to the phase boundary. In cases where the absorption is combined with adsorption the process involved is most often called sorption.

Adsorption is said to be mono molecular when only one layer of particles (molecules, atoms or dissociated fragments) is involved, when adsorbate concentration may vary over a large distance from the phase boundary the multi-molecular adsorption is involved.

Adsorption may be either physical or chemical. The latter is also known as chemisorption, depending on what process cause the adsorption. In physical adsorption the electron cloud of the substance adsorbed interacts as a whole within the adsorbent and only its polarization occurs. In chemisorption, on the other hand, electron transfer and sharing of electrons (formation of a new molecular orbital) takes place between the adsorbate and the adsorbent as in the case of normal chemical compounds. Different thermal effects accompany these two types of adsorption. When adsorbed particles are able to migrate along adsorbent surface, mobile adsorption is involved. When migration does not occur, adsorption is said to be immobile. Sometimes catalyst is also used.

Physical adsorption is independent of the nature of adsorbent surface, covering surfaces of rather different chemical character with roughly equal numbers of layers at the same pressure. At temperature close to the boiling point of the adsorbate, physical adsorption is reversible. The molecules do not dissociate on physical adsorption. Physical adsorption takes place without any activation energy and its rate should always be proportional to the first order of pressure. A comparison between physical adsorption and chemical adsorption is given in Table 4.1

Table 4.1: Comparison of Physical and Chemical Adsorption

Sl. No.	Physical Adsorption	Chemical Adsorption
1	Heat of adsorption = 5 kcal/mole	Heat of adsorption = 20-100 kcal/mole
2	Adsorption only at temp less than the boiling point of the adsorbate	Adsorption can occur even at higher temperature
3	No activation energy involved in the adsorption process	Adsorption energy may be involved
4	Mono and multi layer adsorption	Almost monolayer adsorption
5	Quantity adsorbed per unit mass is high i.e. entire surface is participating	Quantity adsorbed per unit mass is low i.e. only active surface sites are important
6	Extent of adsorption depends upon the properties of adsorbent	Extent of adsorption depends on both adsorbent and adsorbate
7	Rate of adsorption controlled by resistance mass transfer	Rate of adsorption controlled by resistance reaction

4.2 ADSORPTION PRACTICES

The practical application of the adsorption process for the removal of heavy metal from water or waste water is accomplished by contacting either in a batch type contact unit operation or a continuous flow system.

Adsorption systems are run either on batch or on continuous basis following tests give a brief account of both types of systems as in practice.

4.2.1 Batch Adsorption Systems

In a batch adsorption process the adsorbent is mixed with the solution to be treated in a suitable reaction vessel for the stipulated period of time, which depends on the kinetics of adsorption. Agitation is generally provided to ensure proper contact of the two phases. After the equilibrium is attained the adsorbent is separated from the liquid through any of the methods available like filtration, centrifugation or setting. The adsorbent can be regenerated and reused depending upon the cases.

4.2.2 Continuous Adsorption Systems

In continuous flow systems the solution to be treated is passed through a bed of adsorbent, which is fixed, moving or fluidized state. These columns may be used in several stages if necessary. Continuous counter current columns are generally not used for wastewater treatment due to operational problems. Fluidized beds have higher operating costs. In certain cases the column may also function as filter bed retaining suspended solids entering.with the feed.

4.3 INTRA-PARTICLE DIFFUSION PROCESS

The rate of adsorption is determined by the rate of transfer of the adsorbate from the bulk solution to the adsorption sites. This process can be broken conceptually into a series of consecutive steps

1. Diffusion of adsorbate across a stationary solvent film surrounding each adsorption.
2. Diffusion through the pores to the immediate vicinity of the internal adsorbent surface.
3. Adsorption at an appropriate site.

It is assumed that the third step occurs very rapidly in comparison to the second step. If the system is agitated vigorously, the exterior diffusion film around the adsorbent will be very thin, offering negligible resistance to diffusion. So, it can be assumed that the main resistance to adsorption shall lie in the pore diffusion step. Weber and Morris while referring to the rate limiting step of organic materials uptake by granulated activated carbon in the rapidly mixed batch system propose the term "intra-particles transport" which comprises of surface diffusion and molecular diffusion. Several researches have shown that surface diffusion is the dominant mechanism and is the rate determining step. A function relational common to most of the treatments of intra-particle transport is that the uptake varies almost proportionally with square root of time.

4.4 ADSORBATE EQULIBRA

Adsorbate molecules are simultaneously adsorbed and desorbed from the adsorbent surface. At equilibrium the rate of adsorption equals that of desorption. The equilibrium is of dynamic nature in the sense that the state of equilibrium changes with the change in the several parameters. Equilibrium behavior is best described by isotherms of adsorption. As the name indicates an isotherm is a plot of amount of solute adsorbed per unit amount of adsorbent against the corresponding equilibrium concentration in the solution phase, temperature remaining constant. Vital conclusion can be drawn from these isotherms, which are useful in designing of adsorption systems.

A number of isotherms equations have been proposed like Frenundich, Langmuir, Brunnauer-Emment-Teller (BET), Redich-Peterson, Toth, and Radke-Prausnitz etc. out of these the Frenundlich and Langmuir isotherm equations have been widely used by many researches. These two equations have satisfied the data for various organic contaminants conventional or conventional adsorbents.

4.5 LANGMUIR ISOTHERMS

Langmuir isotherms have been on the following assumptions:

1. Only mono layer adsorption is possible.
2. Adsorbent surface is uniform in terms of energy of adsorption.
3. Adsorbed molecules do not interact with each other.
4. Adsorbed molecules do not migrate on the adsorbent surface.

Langmuir isotherm is given as:

$$Q = \frac{Q_m K_A C}{1 + K_A C}$$

where

Q = mass of solute adsorbed / mass of adsorbent.

Q_m = mass of solute adsorbed / mass of adsorbent for complete monolayer.

C = concentration of solute in solution, mass/volume

K_A = constant related to enthalpy of adsorption.

The Langmuir isotherm can be rearranged to the following linear forms:

$$\frac{C_e}{Q_e} = \frac{1}{K_A Q_m} + \frac{C_e}{Q_m}$$

$$\frac{1}{Q_e} = \left(\frac{1}{K_A Q_m}\right)\frac{1}{C_e} + \frac{1}{Q_m}$$

4.6 FREUNDLICH ADSORPTION ISOTHERMS

Freundlich developed an empirical equation for the adsorption isotherm (Freundlich et al 1938)

$$Q_e = K_F C_e^{1/n}$$

Where K_F and n are the constants and n is greater than one. By taking logarithm of both sides, this equation is converted into a linear form:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e$$

where

Q_e = adsorption capacity in equilibrium, mg/g

C_e = concentration of solute in solution in equilibrium, mg/l

The Freundlich equation is most useful for dilute solutions over small concentration ranges. It is frequently applied to the adsorption of impurities from a liquid solution on to the activated carbon.

4.7 BRUNAUER-EMMETT-TELLER (BET) ADSORPTION ISOTHERM (BRUNAUER ET AL., 1938)

The BET equation model assumptions are:

1. Adsorbed molecules do not migrate on the surface.
2. Enthalpy of adsorption is constant for all molecules in a given layer.
3. All molecules in layers need not be completed before the next one stats.

For the adsorption from a liquid solution, the BET equation the form is:

$$Q = \frac{Q_m K_B C}{(C_S - C)[1 + (K_B - 1)(C/C_S)]}$$

Where

C_S = concentration of solute at saturation of all layers

K_B = constant related to energy of adsorption.

The BET equation can be rearranged to a linear form.

4.8 FACTORS CONTROLLING ADSORPTION

The amount adsorbed by an adsorbent from the adsorbate solution is influenced by a number of factors as given below.

1. Nature of adsorbent

Both the physical state and chemical nature of adsorbent is important. Adsorbate differs in their specified area affinity for adsorbate. Adsorption capacity is directly proportional to the particle size diameter whereas for porous substances particle size effects the rate of adsorption. For substance like granular activated carbon the breaking of large particle to form smaller ones open up previously sealed channel making more surfaces accessible to adsorbent.

Pores may be characterized according to the sizes. Macropores have specific areas in the range of 0.5 to 2 m^2/ g. Through their contribution to the total adsorption is inappreciable, they play vital role in making the internal parts of the particle available for the adsorption. Pores having the specific area in the range of 20-40 m^2/g are known as transitional pores and adsorb relatively large molecules or particles of colloidal nature for micropores the concept of specific area is not important, as the mechanism of adsorption is one of the volume filling rather than the layer to layer filling for macro and transitional pores.

2. pH of solution

The surface of the adsorbents charge as well as the degree of ionization is effected by the pH of solution. Since the hydrogen and hydroxyl ions are adsorbed readily on the adsorbent surface the adsorption of the other molecules and ions is effected by the pH of the solution. It is common observation of other molecules and ions is effected by the pH. Adsorption of various anionic and cationic species on such adsorbents has been explained on the basis of the competitive adsorption of H^+ and OH^- ions with adsorbates. It is common observation that the surface adsorbs anion favorably at lower pH due to presence of H^+ ions, whereas, the surface active for the adsorption of cations at higher pH due to the deposition of OH^- ions.

3. Contact time

In physical adsorption, most of the adsorbate species are adsorbed on the adsorbent surface with in an initial contact time. The uptake of adsorbate is fast in the initial stages of the contact period and becomes slow near equilibrium. In physical adsorption most of the adsorbate species are adsorbate within a short interval of contact time. However strong chemical binding of adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Available adsorption results reveal that the uptake of adsorbate species are fast at the initial stages of the contact period, and thereafter it becomes slow near equilibrium. In between these two stages of uptakes, the rate of adsorption is found to be nearly constant. This may be due to the fact that a large number of active sites are available for adsorption at the initial stage and the rate of adsorption is a function of available vacant sites concentration. With the lapse of time, available surface site concentration goes down and the repulsion between the solute molecules on the solid and bulk phases decreases the adsorbate removal rate.

4. Initial concentration

A given mass of adsorbent can adsorb only a fixed amount of adsorbate. So the initial concentration of adsorbate solution is very important. The amount of adsorbed decreases with the increasing adsorbate concentration as the resistance to the uptake to the solution from solution of the adsorbate decreases with increasing solute concentration. The rate of adsorption increases because of increasing driving forces.

5. Temperature

Temperature dependence of adsorption is of complex nature. Adsorption is generally exothermic in the nature and the extent and the rate of adsorption in most cases decreases with increasing temperature. This trend may be explained on the basis of rapid increases in the rate of desorption or alternatively explained on the basis of Le-Chatelier's principle. Some of the adsorption studies show increased adsorption with increasing temperature. This increase in adsorption is mainly due to increases in number of adsorption sites caused by breaking of some of the internal bonds near the edge of the of the active surface sites of the adsorbents.

6. Degree of agitation

Agitation in batch adsorption is important to insure proper contact between the adsorbent and the solution. At lower speeds the stationary fluid film around the particle is thicker and the process is external mass transfer controlled. With the increases in agitation this film decreases in the thickness and the resistance to mass transfer to this film is reduced and after a certain time this process becomes intra-particle diffusion controlled. Whatever is the extent of agitation, the solution inside the pores remains unaffected and hence, for intra-particle mass transfer controlled process agitation has no effect on the rate of adsorption.

CHAPTER 5

EXPERIMENTAL PROGRAMME

5.1 GENERAL

Batch study has been carried out for the removal of chromium(VI) from synthetic wastewater as well as industrial wastewater using Activated Carbon (AC) as an adsorbent. Laboratory grade activated carbon was used in the study.

5.2 CHARACTERIZATION OF ADSORBENT

The physico-chemical characteristics of the activated carbon were determined using standard procedures as detailed below:

5.2.1 Proximate Analysis

Proximate analysis of the activated carbon was carried out using the procedure as per IS 1350 (Part -I):1984.

5.2.2 Density

The bulk density of activated carbon was determined using MAC make bulk density meter.

5.2.3 X-Ray Diffraction Analysis

X-Ray diffraction analysis of activated carbon was carried out by using Phillips (Holland) diffraction unit (Model PW1140/90) available in the institute instrumentation center.

5.2.4 Scanning Electron Microscope (SEM)

SEM analysis of activated carbon was carried out by using LEO 435 VP scanning electron microscope available in the institute instrumentation center.

5.2.5 Ultimate or CHN Analysis

The ultimate analysis was performed on finely ground and oven-dried activated carbon to determine the weight fractions of carbon, hydrogen and nitrogen. The Perkin Elmer CHN elemental analyzer available in the department of chemistry was used in the study.

5.3 ADSORBATE

Synthetic wastewater solutions of Cr(VI) of desired concentrations (10–300mg/l) were prepared by dissolving accurately weighed quantity of $K_2Cr_2O_7$ (AR grade) in distilled water. Industrial wastewater samples were obtained from chromium electroplating plant of a small scale unit working in the industrial area of Roorkee town.

5.3.1 Analytical Measurements

Concentration of Cr(VI) is determined by Atomic Adsorption Spectroscopy, GBC Avanta instrument. Standard solutions of Cr(VI) was taken and their absorbance was determined by AAS at different concentrations. The linearity of calibration curves indicates applicability of the Lambert-Beer's Law.

Calibration curves for Chromium(VI) is given in Fig. 5.1 and calibration data is given in Table 5.1.

Table 5.1: Calibration Data

Concentration (mg/l)	0	2	5	10	15
Absorbence	0.0037	0.088	0.1813	0.329	0.5288

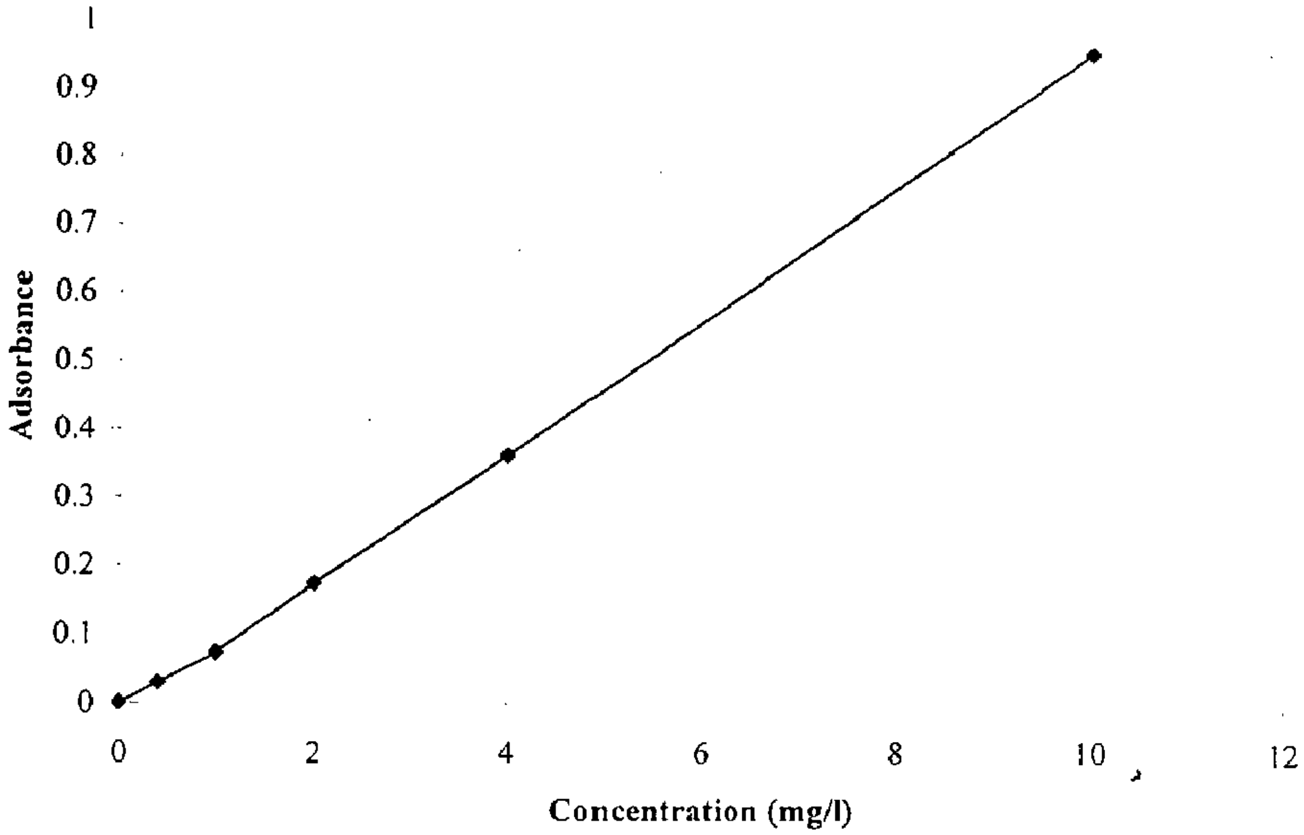

Fig. 5.1: Calibration curve

5.4 ANALYSIS OF TYPICAL ELECTROPLATING PLANT WASTES

The analysis of metals was carried out by atomic absorption spectroscopy.

5.5 BATCH ADSORPTION EXPERIMENTS

In order to study the effect of different parameters like adsorbent dose, initial concentration, pH, contact time, temperature effect etc., batch experiments were conducted. For each experimental run, 50 ml of synthetic wastewater of known metal concentration was taken with known amount of AC in a 100 ml stoppered conical flask. These samples were agitated in a temperature controlled shaking water bath. The temperature was maintained at 25 ± 1 °C. Samples were withdrawn at appropriate time intervals. The filtrate solution was analyzed for remaining metal concentration by AAS.

For adsorption isotherms, metal solutions of known concentration were agitated with different known amount of AC till equilibrium was achieved. For optimum amount of adsorbent per unit mass adsorbate [Cr(VI)] in 50 ml synthetic wastewater were agitated separately with different AC doses till equilibrium was attained. To see the effect of temperature for the adsorption of metal from solution by AC, experiments were also conducted at 30 ± 1 °C and 35 ± 1 °C.

CHAPTER 6

RESULTS AND DISCUSSION

6.1 GENERAL

The detailed discussion on the results of the experiments conducted is given in this chapter. These results include

- Characterization of wastewater from chromium electroplating unit.
- Characterization of Activated Carbon (AC).
- Batch adsorption studies.
- Adsorption of Chromium effluents by activated carbon.

6.2 CHARACTERIZATION OF INDUSTRIAL WASTE

Experiments on wastewater samples from electroplating were carried out in current study. These wastes were characterized for their pH, turbidity, total solids, suspended solids, hardness, total dissolved solids and initial metal concentration. The effluents are in the basic pH range and have very high metal concentration. Suspended solids form the majority of the total solids.

6.3 CHARACTERIZATION OF ACTIVATED CARBON

Laboratory grade activated carbon, obtained from m/s Wishwani chemical suppliers, was used as adsorbent in the present investigation. Particle size analysis, proximate analysis, and ultimate analysis were carried out for physico-chemical characteristics. Morphological characteristics are given through scanning electron microscope analysis.

The physico-chemical characteristics of AC are given in Tables 6.1 and 6.2. The scanning electron micrograph of AC is given in Fig. 6.1. It is seen that AC particles are fibrous and linear in nature. There are holes at the end and in between the particles.

X-ray diffraction pattern of AC is shown in Fig. 6.2. From the XRD pattern, major components identified in AC are SiO_2, and tridymite. Diffraction peaks corresponding to crystalline carbon were not observed in AC. The other peaks indicate the presence of Fe_2O_3, MgO and CaO. The broad peak in AC is due to presence of silica. Activated carbon is generally described as an amorphous form of graphite with a random structure of graphite plates; having highly porous structure with a range of cracks and crevices reaching molecular dimensions.

6.4 BATCH ADSORPTION STUDIES

In order to study the effect of different parameters the batch studies are most suitable. Batch adsorption experiments were carried out in 100 ml stoppered conical flask for removal of heavy metals from synthetic solutions of individual metal ions solutions of known concentrations. The effect of solution pH (2.0–10.0), contact time (0–240 min), initial metal concentration (10.0–300.0 mg/l), AC dose (2–28 g/l) and temperature (25^0C-35 ^{0}C) were studied.

6.4.1 Effect of Adsorbent Dose

Effect of activated carbon dose for the removal of Cr (VI) from 50-150 mg/l metal solutions each at temperature of 25 ^{0}C for contact time of 4 hr and pH (2 and 3) is shown in Figs. 6.3 and 6.4. Table 6.3 presents the chromium removal at different pH. Figs. 6.3 and 6.4 reveal that the percent removal of chromium increases as adsorbent concentration from 0.1 to 2.5 gm per 50 ml solution, while removal per unit mass of adsorbent increases with the decreases in adsorbent concentration. For larger concentrations of adsorbents the adsorption sites are larger and the chromium atoms have to travel considerable distance in order to reach these sites. Thus it is found the percent removal of chromium at adsorbent concentrations larger than 20 g l^{-1} remains almost unchanged. Further in all the cases equilibrium was found to be attained more rapidly at lower concentrations.

6.4.2 Effect of pH

The effect of pH on the degree of metal removal Cr(VI) ions presented in Fig. 6.5. Table 6.4 depicts the parametric values at different levels. In these experiments, the AC loading was 1.2 g in 50 ml of solution containing 50-150 mg/l each of Cr(VI) at 25 ^{0}C.

The contact time was 4 hr to attain equilibrium, as discussed earlier. In all cases adsorption of chromium decreases with increase in pH. Upto pH 7 the decrease in adsorption is gradual, which however drops drastically for pH>7. The maximum removal of chromium was found at 3 pH.

Panday et al. (1986) have shown that the presence of oxides of alumina, calcium and silicon in the AC develop charge in contact with water according to pH of the solution as follows:

$$\text{M–OH} \longrightarrow \text{OH–M–OH} \longrightarrow \text{O}^- \text{–M–OH}^-$$

Except silica, all other oxides possess positive charge for the pH range of interest because zero point charge (pH_{ZPC}) of SiO_2 is 2.2 (Panday et al., 1986). A positive charge develops on the surface of the oxides of AC in an acidic medium due to aqua complex formation of the oxides present as follows:

$$\text{–MO} + \text{H–OH} \xrightarrow{H^+} \text{M–OH}^{2+} + \text{OH}^-$$

Lowering of chromium adsorption at low pH is due to the fact that surface charge, thus, developed is not suitable for chromium adsorption. For pH below 6, a significant electrostatic repulsion exists between the positively charged surface of the adsorbent and cationic metal ions. Besides this, a higher concentration of H^+ in the solution competes with Cr(VI) for adsorption sites, resulting in the reduced uptake of metal ions.

As the pH of the system increased, the number of positively charged sites decreased and the number of negatively charged sites increased on the surface of AC as shown in equations given below.

$$\text{–MOH} + \text{OH}^- \longrightarrow \text{–MO}^- + H_2O$$

$$\text{–MO}^- + \text{Cr} \longrightarrow \text{–M–O–Cr}$$

A negatively charged surface site on the AC favours the adsorption of cationic metal ions due to electrostatic attraction.

At lower pH values, there is decrease in ionization of chromium ions favouring adsorption on the adsorbents. The adsorbents have greater affinity for neutral molecules than for charged ions. As pH increases, the adsorption suddenly drops indicating greater ionization of the molecules and less affinity to adsorbents.

6.4.3 Effect of Contact Time and Initial Concentration

Figs. 6.6 and 6.7 shows the percentage removal of Cr(VI) solutions of 10-80 mg/l initial concentrations at pH 3, temp 25 °C at different contact time by AC for 1.2 g per 50 ml. In table 6.5 and 6.6 removal of chromium at different initial concentration and contact time are given. The contact time curves show that initially the removal is very rapid in first 30 minutes, then the adsorption rate gradually decreases and the removal reaches equilibrium in around 180 minutes. It is also seen that the time required to attain equilibrium is dependent on the initial concentration of chromium. For the same concentration, the percent removal of chromium increases with increases in contact time till equilibrium attained in 180 minutes. The curves are single, smooth and continuous leading to saturation. These curves indicate the possible monolayer coverage of metal on the surface of AC (Wong and Yu, 1999; Inbraj and Sulochna, 2002).

A given mass of adsorbent can adsorb only a fixed amount of adsorbate. So the initial concentration of adsorbate solution is important. From Fig. 6.6, it is evident that the percent adsorption was decreased with increase in initial metal concentration. Though the percentage removal decreased with increase in initial metal concentration but the actual amount of Cr(VI) adsorbed per unit mass of AC increased with increase in initial metal concentration in test solution. This was because of the decrease in resistance for the uptake of solute from solution with increase in metal concentration.

6.4.4 Effect of temperature

The adsorption studies were carried out at three different temperatures, 25, 30 and 35 ^{0}C. Fig. 6.8 presents the result of the experiments for the metal ions of Cr(VI), since the adsorption is decreasing at higher temperatures therefore Cr(VI) adsorption on activated carbon is endothermic in nature. The decrease in adsorption with increase in temperature may be explained on the basis of rapid increase in the rate of desorption of the adsorbed species from the surface of the adsorbent. However, an alternative approach for explaining the decrease in adsorption with the rise in temperature may be drawn forms Chatelier's Principle. A low amount of a solute adsorbed with the size in solution temperature may also be explained due to the fact solubility of almost all compounds in water decreases with increasing solution temperature, thereby decreasing the adsorption capacity.

6.5 ADSORPTION KINETIC STUDY

There are various models available to explain the kinetics of the adsorption. In order to investigate the adsorption processes of Cr(VI) on activated carbon, three kinetic models viz. pseudo-first-order model, pseudo-second-order model and intra-particle diffusion model were used.

6.5.1 Pseudo-First-Order and Pseudo-Second-Order Model

Lagergren rate equation is one of the most widely used sorption rate equations for the adsorption.

The pseudo-first-order equation is

$$\frac{dQ_t}{dt} = k_f(Q_e - Q_t) \tag{6.1}$$

Where Q_t is the amount of adsorbate adsorbed at time t (mg/g), Q_e is the adsorption capacity in equilibrium (mg/g), k_f is the rate constant of pseudo-first-order model (min^{-1}), and t is the time (minute). After definite integration by applying the initial conditions at t=0, Q_t=0 and at t=t, $Q_t = Q_t$, the equation becomes (Mohan and Singh, 2002, Yan et al., 2003):

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_f}{2.303} t \tag{6.2}$$

The plot of log ($Q_e - Q_t$) against t for Cr(VI) is shown in Fig. 6.9. The straight-line plot shows the validity of this model. Tables 6.8 gives the value of adsorption rate constant (k_f) of Cr(VI) with AC. These values indicate that the adsorption rate was very fast at the beginning of adsorption.

The pseudo-second-order model can be represented in the following form:

$$\frac{dQ_t}{dt} = k_S(Q_e - Q_t)^2 \tag{6.3}$$

where, k_S is the rate constant of pseudo-second-order model (in g/mg min). After integrating eq. (6.3) for boundary conditions at t=0, Q_t=0 and at t=t, $Q_t=Q_t$, the following form of equation can be obtained:

$$\frac{t}{Q_t}=\frac{1}{k_S Q_e^2}+\frac{1}{Q_e}t \tag{6.4}$$

the initial sorption rate, h (mg/g min), as t → 0 can be defined as

$$h=k_S Q_e^2 \tag{6.5}$$

The initial sorption rate (h), the equilibrium adsorption capacity (Q_e). and the pseudo-second order constant k_S can be determined from the plot of t/Q_t versus t. Fig. 6.10 shows the results obtained for chromium. Calculated correlation coefficients both linear and non-linear for pseudo-first-order model and pseudo-second-order model by using regression procedure for Cr(VI) adsorption on AC are shown in Table 6.8.

Since correlations coefficients were found to be more close to unity for pseudo-second order model than first order, therefore sorption reaction was better approximated by pseudo-second-order kinetics model. The k_s and h values as calculated from the figure are also listed in Table 6.8.

6.5.2 Intra-particle Diffusion Model

An empirically found functional relationship, common to the most adsorption processes, is that the uptake varies almost proportionally with $t^{1/2}$, the Weber-Morris plot, rather than with the contact time t.

$$Q_t=k_{id}t^{1/2}+C \tag{6.6}$$

where k_{id} is the intra-particle diffusion rate constant. Fig. 6.11 shows the results obtained for Cr(VI). Values of intercept C give the idea about the thickness of boundary layer. The deviation of straight line from the origin (Fig. 6.11) may be due to difference in the initial and final stages of adsorption. Further such deviation of straight line from the origin indicates the pore diffusion is not the sole- rate-controlling step.

From Fig. 6.11, it may be seen that there are two separate regions-the initial portion is attributed to bulk diffusion and liner portion to intra-particle diffusion. The values of k_{id} as obtained from the intercepts of straight lines are listed in Table 6.8. Again it may be that both film and pore diffusion was involved in the removal process to different extent. The values of intra-particle diffusion rate parameters are given in Table 6.8.

6.6 ADSORPTION ISOTHERM EQUATIONS

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations have been used to describe the equilibrium nature of adsorption. Some of these equations are Freundlich, Langmuir, Redlich-Peterson, Radko-Praunitz and Toth equations. Out of these Freundlich and Langmuir isotherm equations are widely used by researchers in the field of environmental engineering.

6.6.1 Freundlich and Langmuir Isotherm

Linearised form of Freundlich and Langmuir isotherm equations are given as

$$\ln Q_e = \ln K_F + \frac{1}{n}\ln C_e \quad \text{(Linear form)} \qquad (6.7)$$

$$\frac{C_e}{Q_e} = \frac{1}{K_A Q_m} + \frac{C_e}{Q_m} \qquad \text{(Linear form)} \qquad (6.8)$$

Fig. 6.12 shows the Freundlich isotherm plots (ln Q_e vs ln C_e) for Cr(VI) at 25, 30, 35 ^{0}C. Langmuir isotherm plot (C_e/Q_e vs C_e) are shown in Fig. 6.13 for Cr(VI) adsorption on AC.

Freundlich and Langmuir isotherm parameter along with linear and non-linear correlation coefficients are given in Table 6.9. At all temperatures, Langmuir isotherm represents a better fit of the experimental data then Freundlich isotherm equation. The essential characteristics of a Langmuir isotherm can be expressed in trems of a dimensionless factor, R_L, which describes the type of pattern and is defined as $R_L = 1/(1 + K_A C_i)$ (where C_i is initial concentration and K_A is Langmuir constant) indicates the nature of adsorption as (Rao et al., 2002)

If $R_L > 1$	Unfavourable
$R_L = 1$	Linear

$0 < R_L < 1$ Favourable

$R_L = 0$ Irreversible

The values of R_L for Cr(VI) is also given in Table 6.9. The value of R_L is found to be less than 1 for both the metals, so adsorption using AC is favorable. The values of 1/n were also found to be less than 1. So, it again proves adsorption to be favourable.

6.6.2 Redlich-Peterson isotherm

Redlich and Peterson (1959) model combines elements from both the Langmuir and Freundlich equation and the mechanism of adsorption is a hybrid and does not follow ideal monolayer adsorption. The Redlich-Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. The R–P equation is a combination of the Langmuir and Freundlich models. It approaches the Freundlich model at high concentration and is in accord with the low concentration limit of the Langmuir equation. Furthermore, the R–P equation incorporates three parameters into an empirical isotherm, and therefore, can be applied either in homogenous or heterogeneous systems due to the high versatility of the equation.

It can be described as follows:

$$Q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \qquad (6.9)$$

where K_R is R–P isotherm constant (L/g), a_R is R–P isotherm constant (L/mg) and β is the exponent which lies between 1 and 0, where β=1

$$Q_e = \frac{K_R C_e}{1 + a_R C_e} \qquad (6.10)$$

It becomes a Langmuir equation. Where β=0

$$Q_e = \frac{K_R C_e}{1 + a_R} \qquad (6.11)$$

i.e. the Henry's Law equation

Eq. (6.11) can be converted to a linear form by taking logarithms:

$$\ln\left(K_R \frac{C_e}{Q_e} - 1\right) = \ln a_R + \beta \ln C_e \qquad (6.12)$$

Plotting the left-hand side of equation (6.12) against ln C_e to obtain the isotherm constants is not applicable because of the three unknowns, a_R, K_R and β. Therefore, a minimization procedure was adopted to solve equation (6.12) by maximizing the correlation coefficient between the theoretical data for Q_e predicted from equation (6.12) and experimental data.

Therefore, the parameters of the equations were determined by minimising the distance between the experimental data points and the theoretical model predictions with the solver add-in function of the Microsoft excel. Fig. 6.14 shows the R-P isotherm plot. The R-P isotherm parameters and the correlation coefficients, R^2, for the R-P isotherms are listed in Tables 6.9. The correlation coefficients are significantly higher than both the Langmuir and Freundlich values for Cr(VI) adsorption on AC. The Redlich Peterson is certainly the best-fit isotherm equation of the three isotherm studied so far.

6.7 THERMODYNAMIC STUDY

Thermodynamic data such as adsorption energy can be obtained from Langmuir and Tempkin equation,

$$-\Delta G^0_{ads} = RT\ln(K_L) \tag{6.13}$$

where K is Langmuir or Tempkin constant. For the Langmuir isotherm, the Gibbs free energy of adsorption for Cr(VI) was –6.9827, -7.2182, -7.5127kJ/mol at 25, 30 and 35 ^{0}C, respectively by Langmuir constant.

6.7.1 Tempkin Isotherm

Tempkin isotherm contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases with coverage due to adsorbate – adsorbate interactions, and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (Tempkin and Pyzher, 1940, Kim et al. 2004). The Tempkin isotherm is represented by following equation:

$$Q_e = \frac{RT}{b}\ln(K_T C_e) \tag{6.14}$$

Eq.(6.14) can be expressed in its linear form as:

$$Q_e = B_1 \ln K_T + B_1 \ln C_e \tag{6.15}$$

where $$B_1 = \frac{RT}{b} \tag{6.16}$$

The adsorption data can be analyzed according to Eq. 6.15. A plot of Q_e versus $\ln C_e$ enables the determination of the isotherm constants K_T and B_1. K_T is the equilibrium binding constant (l/mg) corresponding to the maximum binding energy and constant B_1 is related to the heat of adsorption.

6.7.2 Kinetic Study

The thermodynamic parameters such as Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and (ΔS^0) were calculated by using the following equations, and the values of thermodynamic parameters are given in Table 6.10 (Mohan et al., 2002);

$$-\Delta G^0_{ads} = RT\ln(K_L) \tag{6.17}$$

$$\ln(K_L) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{6.18}$$

where T is temperature in the Kelvin (K), R is the universal gas constant (1.987 cal/mol K), and K_L is the Langmuir adsorption constant. ΔH^0 and ΔS^0 can be obtained from the slope and intercept of Van't Hoff plots of $\ln K_L$ vs 1/T. the calculated thermodynamics constants are listed in Table 6.11.

All negative valve of ΔG^0 show that the adsorption process is spontaneous with a high preference of Cr(VI) for the sludge. Jaycok and Parfitt reported that physical adsorption is in range 0 to -19.67 kJ/mol, and chemical adsorption is in range -79.50 to 397.48 kJ/mol.

The range of ΔG^0 values in the studies are range from -6.9827 to -7.5127 kJ/mol, which are in the range of physical adsorption. The calculated ΔH^0 value was 4.792 kJ/mol. The positive value suggests an endothermic reaction for the adsorption process, for which similar results had been obtained in the studies of Langmuir isothermal equation and separation factor.

The value of the entropy changes (ΔS^0) was found to be 27.691 J/mol/K. A positive value shows a higher randomness tendency at the sludge/solution interface during the adsorption of Cr(VI) on the sludge. Based on thermodynamics, negative ΔG^0 value and positive ΔH^0 and ΔS^0 values give a spontaneous process at high temperature.

Table 6.1: Characteristics of Activated Carbon

Proximate Analysis		Physical Properties	Ultimate Analysis	
Moisture %	0.31	Bulk density (kg m^{-3}) 650.82	C %	92.2
Ash %	2.67		H %	2.0
Volatile matter %	7.72		S %	0.2
Fixed carbon %	89.30		N %	0.5

Table 6.2: Particle size analysis of Activated Carbon

Sieve size (μm)	% weight
>600	5.547
600-500	18.770
500-425	9.650
425-355	15.335
355-250	22.482
250-212	8.307
212-180	3.519
180-150	12.995
<150	3.389

Table 6.3: Chromium Removal at different dose

	2 pH			3 pH		
Dose (g/50 ml)	% Removal at 50 (mg/l)	% Removal at 100 (mg/l)	% Removal at 150 (mg/l)	% Removal at 50 (mg/l)	% Removal at 100 (mg/l)	% Removal at 150 (mg/l)
0.1	22	21.27	20	22.12	21.39	20.2
0.2	41.12	40.82	39.21	41.89	41.38	39.99
0.3	62.9	61.62	60.03	63.89	62.62	61.62
0.4	76	75.72	74.22	77.12	76.99	75.72
0.5	87.99	87.9	86.01	88.25	88.89	86.99
1	95.77	93.83	92	97.35	93.83	92
1.3	95.89	93.86	92.99	97.45	93.84	92
1.6	95.89	93.99	92.98	97.46	93.89	92
2	96.12	93.99	93	97.49	93.99	91.4
2.5	96.67	94	93.02	97.53	94	91

Table 6.4: Chromium Removal at different pH

pH	% Removal at 50 (mg/l)	% Removal at 100 (mg/l)	% Removal at 150 (mg/l)	% Removal at 200 (mg/l)	% Removal at 250 (mg/l)	% Removal at 300 (mg/l)
1.5	89.59	88.26	87.63	86	84.98	83.32
2	92.82	90.69	89.75	88.82	87.36	86.19
3	95.66	93.03	91.19	90.09	88.38	85.01
4	93.93	91.01	89.18	87.27	86.49	81.39
5	89.82	88.2	85.3	84.37	82.82	77.79
6	80.59	77.4	74.22	70.83	68.37	65.04
7	73.83	72.57	68	63.59	61.9	59.99
8	64.71	62.06	55.92	52.99	49.31	47.83
9	47.6	45.57	44.01	41.6	40.27	38.63
10	42.6	41.1	38.5	37.5	35.7	33.4

Table 6.5: Chromium Removal at different concentration

Concentration (mg/l)	10	20	30	40	50	60	70	80
Removal %	98.76	97.71	97.24	96.62	95.1	94	93.89	92.53

Table 6.6: Chromium Removal at different Time

Time (min)	% Removal at 10 (mg/l)	% Removal at 20 (mg/l)	% Removal at 30 (mg/l)	% Removal at 40 (mg/l)
0	0	0	0	0
5	33.97	33.09	33.25	32.82
15	57.39	56.31	55.82	54.22
30	72	71.38	71.09	70.68
45	80.2	79.26	79.99	79
60	84.09	83.95	83.94	83.2
180	94	93.38	93.95	93.73
240	96.89	96.11	96	94
300	97.27	97	96.24	95.2
360	98.71	97.39	96.73	95.78

Table 6.7: Chromium Removal at different Temperature

Concentration (mg/l)	% Removal at 25°C	% Removal at 30°C	% Removal at 35 °C
10	99.01	98.89	98.82
20	98.37	98.35	98.5
30	98.12	97.99	96.98
40	94.01	93.78	94.39
50	88.19	87.63	85.24

Table 6.8: Kinetic parameters for the removal of Chromium by AC (pH= 3, T= 25 °C, C_o= 10, 20, 30 and 40 mg/l and dose = 20 g l^{-1})

Pseudo-first-order

C_o mg l^{-1}	$Q_{e,exp}$ (mg g-1)	$Q_{e,calc}$ (mg g^{-1})	k_f (min^{-1})	R^2 (linear)	R^2 (non-linear)
10	0.368385	0.5093	0.16121	0.9729	-0.94942
20	0.744077	0.7051	0.0170422	0.978	-0.96378
30	1.138962	0.8565	0.0165816	0.9826	-0.98229
40	1.498308	0.9782	0.016127	0.9848	-.0.98862

Pseudo-second-order

C_o mg l^{-1}	$Q_{e,calc}$ (mg g^{-1})	h (mg g^{-1} min^{-1})	k_S (g mg^{-1} min^{-1})	R^2 (linear)	R^2 (non-linear)
10	0.3759	0.3759	19.60	0.9939	0.99989
20	0.7616	0.7616	2.4799	0.9939	0.99982
30	1.1521	1.1521	0.66911	0.9934	0.99998
40	1.5297	1.5297	0.29118	0.9989	0.99978

Intra-particle diffusion

C_o mg l^{-1}	k_{id} (mg g^{-1} $min^{-1/2}$)	C_1 (mg g^{-1})	R_1^2 (linear)	R_2^2 (non-linear)
10	0.0355	0.0613	0.9871	0.95323
20	0.071	0.1289	0.9960	0.98689
30	0.1045	0.2119	0.9993	0.99336
40	0.141	0.2624	0.9844	0.97363

C_o mg l^{-1}	k_{id2} (mg g^{-1} $min^{-1/2}$)	C_2 (mg g^{-1})	R_2^2 (linear)	R_2^2 (non-linear)
10	0.0015	0.3394	0.9767	0.98829
20	0.0036	0.6771	0.8936	0.94858
30	0.0091	0.967	0.9356	0.96619
40	0.0109	1.2981	0.9892	0.98839

Table 6.9: Isotherm parameters for removal of Chromium by AC (pH= 3, T= 25 °C, 30 °C and 35 °C, *t*= 300 *min*, C_o= 10-50 *mg/l*, *dose* = 20 *g* l^{-1},)

Freundlich constants

T °C	K_F ((mg g^{-1}) (mgl^{-1})$^{-1/n}$)	$1/n$	R_1^2 (linear)	R_2^2 (non-linear)
25	1.4796	0.3357	0.9734	0.984348
30	1.2464	0.3674	0.925	0.975214
35	1.1929	0.3678	0.9483	0.992144

Langmuir constants

T°C	K_A (l mg^{-1})	Q_m (mgg^{-1})	R_L	R_1^2 (linear)	R_2^2 (non-linear)
25	0.07824	2.4361	0.24	0.9965	0.991348
30	0.08110	2.3267	0.23	0.9986	0.999107
35	0.12061	2.3009	0.17	0.9981	0.999291

Redlich-Peterson constants

T°C	K_R (l g^{-1})	a_R(l mg^{-1})$^{1/\beta}$	β	R_1^2 (linear)	R_2^2 (non-linear)
25	7.5	0.8909	3.0137	0.9948	0.991230
30	6.00	0.9581	2.3324	0.9968	0.992882
35	5.21	0.9982	1.9507	0.9982	0.994341

Temkin constants

T°C	K_T (l mg^{-1})	B_1	R_1^2 (linear)	R_2^2 (non-linear)
25	37.5247	0.4296	0.9904	0.994411
30	27.8093	0.4355	0.9959	0.961259
35	25.9886	0.4308	0.9709	0.974196

Table 6.10: Thermodynamic parameters for the removal of chromium by AC

Thermodynamic Properties					
	ΔG^0_{ads} (kJ/mol)			ΔH^0 (kJ/mol)	ΔS^0 (J/mol/K)
	25 °C	30 °C	35 °C		
Langmuir	-6.9827	-7.2182	-7.5127	4.792	27.691
Freundlich	-10.7127	-12.7129	-12.0071	3.539	32.719
R-P	-8.5787	-11.1278	-10.7123	3.924	30.812

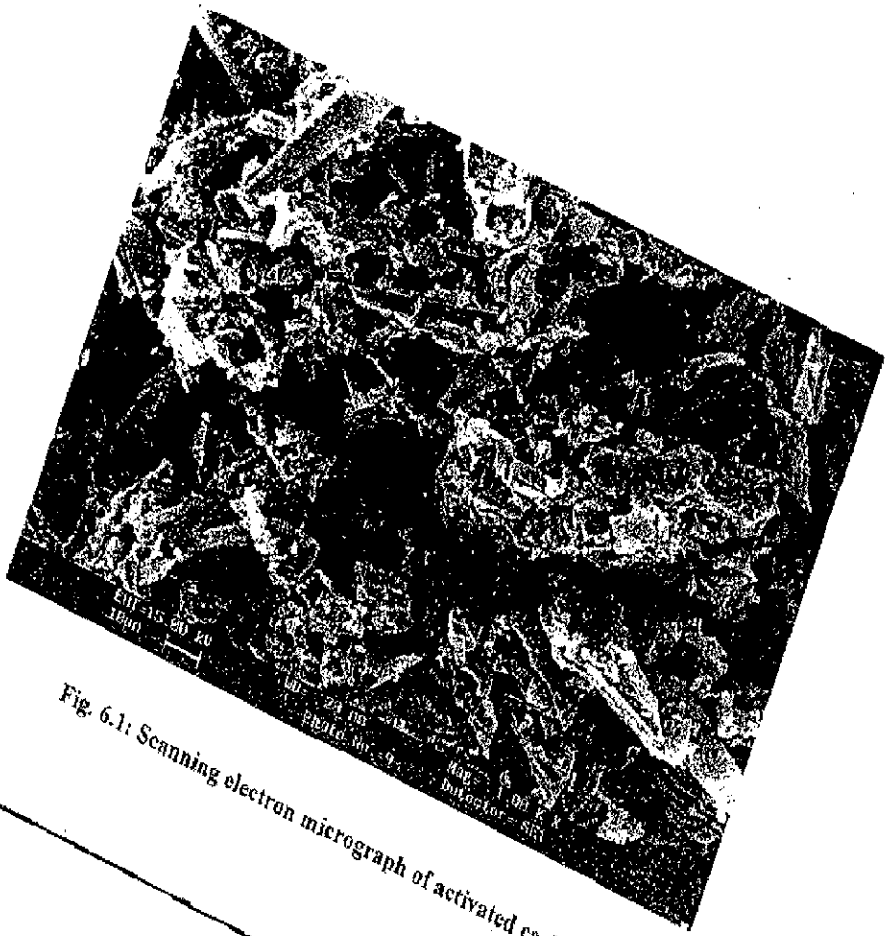

Fig. 6.1: Scanning electron micrograph of activated carbon

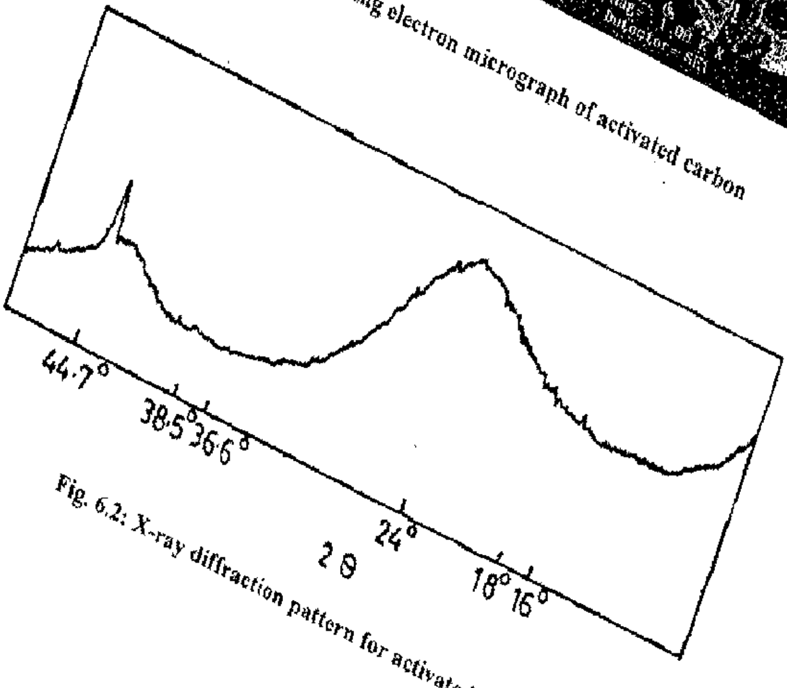

Fig. 6.2: X-ray diffraction pattern for activated carbon

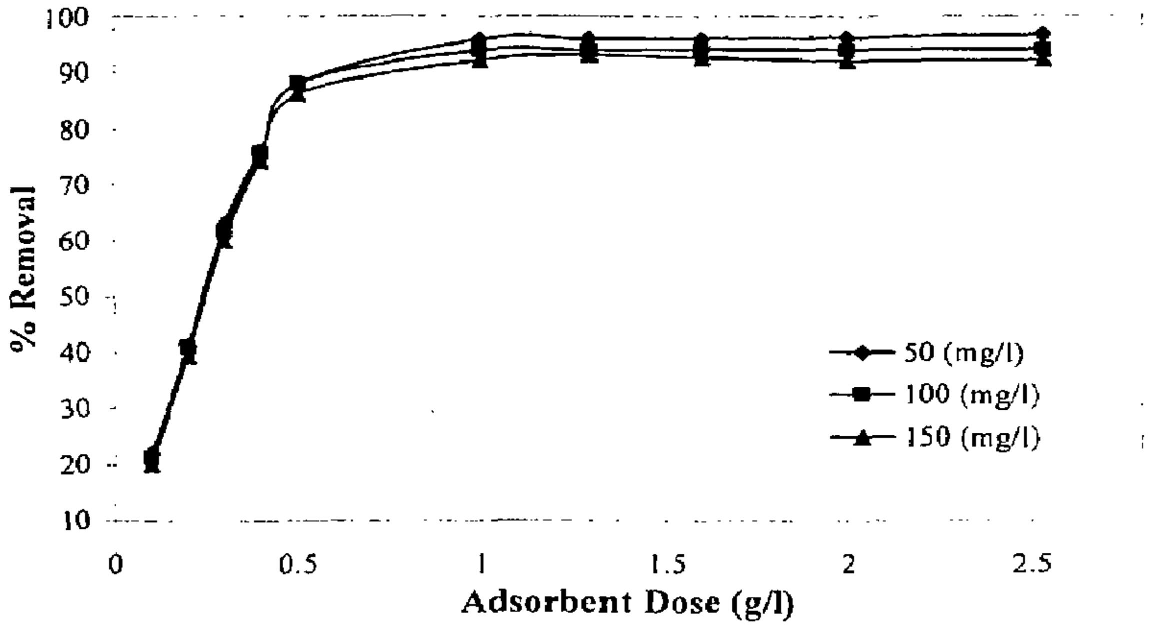

Fig. 6.3: Effect of adsorbent dosage on the adsorption of Cr(VI) by AC (pH= 2, T= 25 °C, t= 300 min, C_o= 10 mg/l)

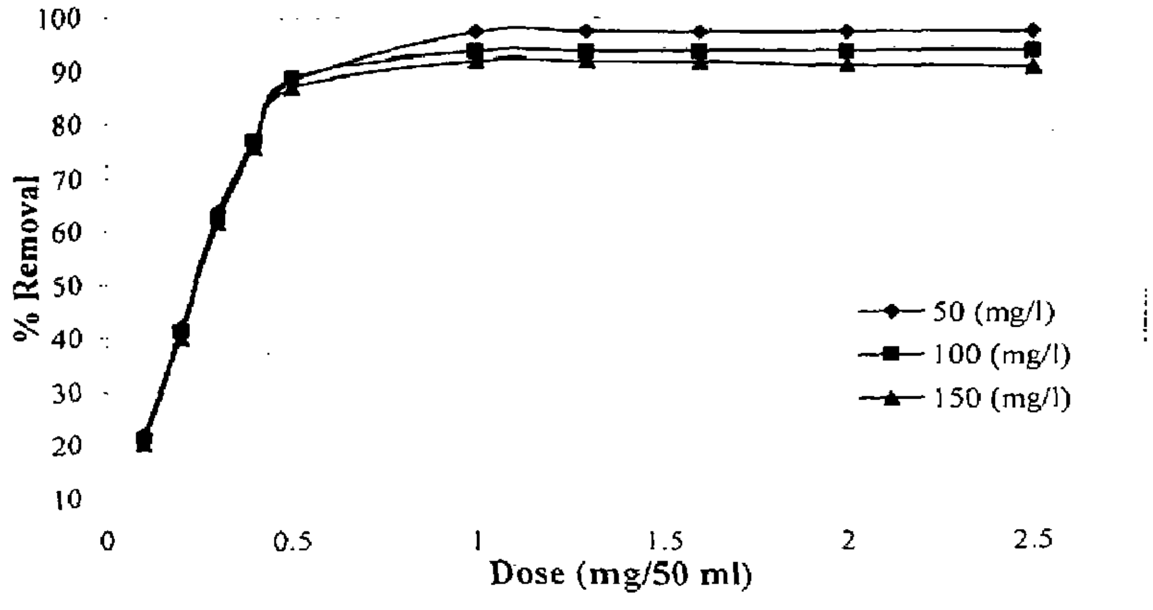

Fig. 6.4: Effect of adsorbent dosage on the adsorption of Cr(VI) by AC (pH= 3, T= 25 °C, t= 300 min, C_o= 10 mg/l)

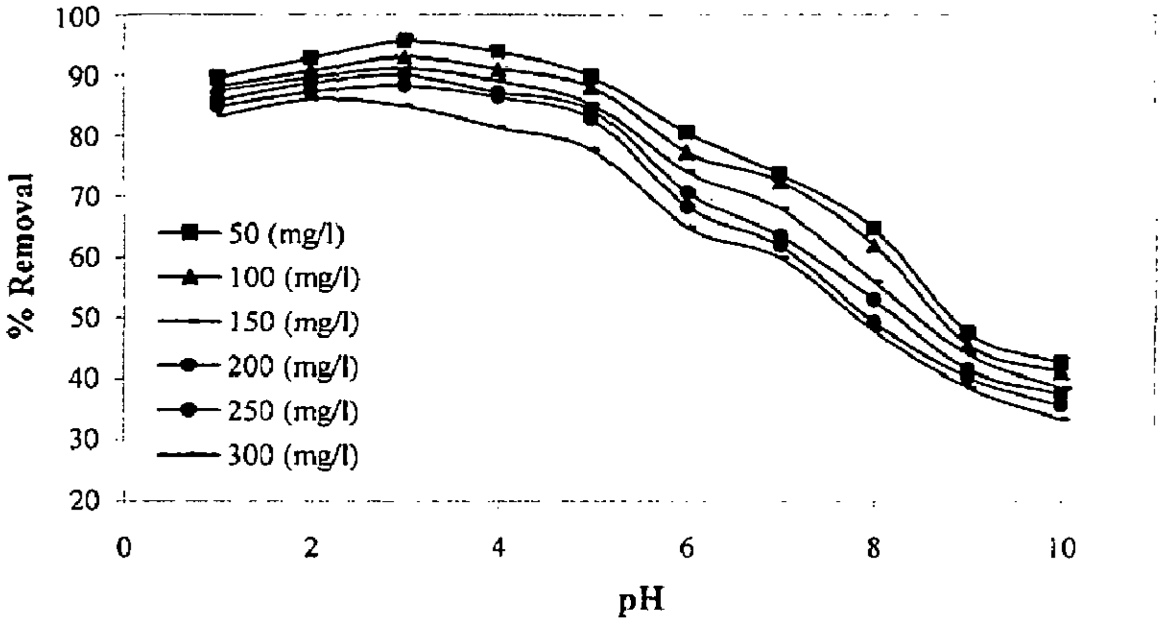

Fig. 6.5: Effect of pH on the adsorption of Cr(VI) by AC (Dose= 1.3 mg, T= 25 °C, t= 300 min, C_o= 10 mg/l)

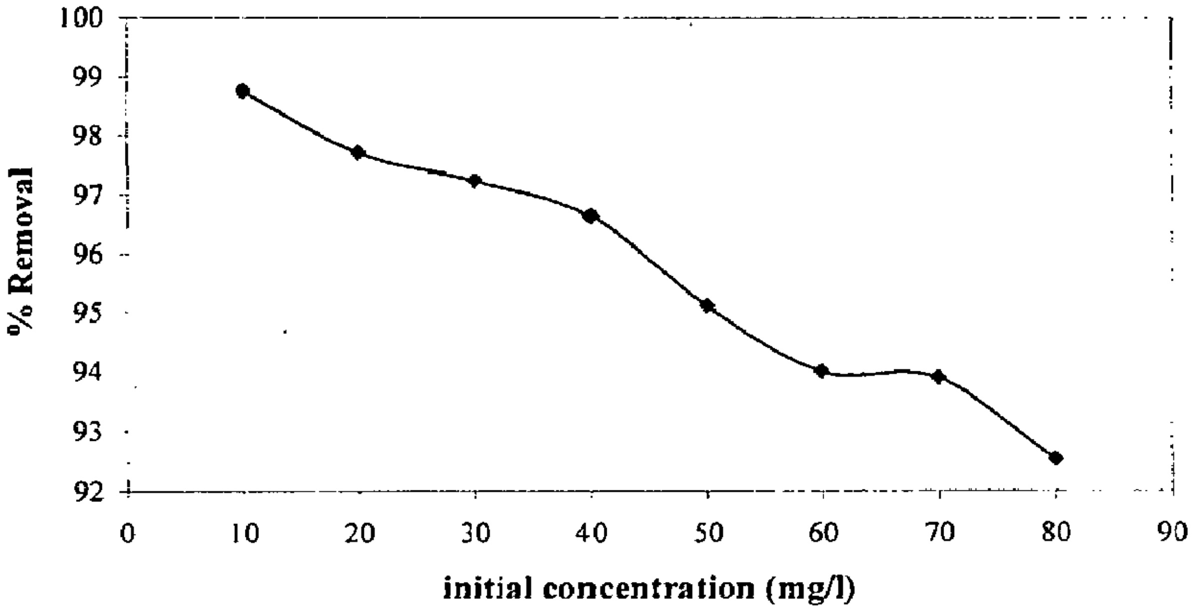

Fig. 6.6: Effect of initial concentration on the adsorption of Cr(VI) by AC (Dose = 1.3 mg, pH = 3, T = 25 °C, t = 300 min)

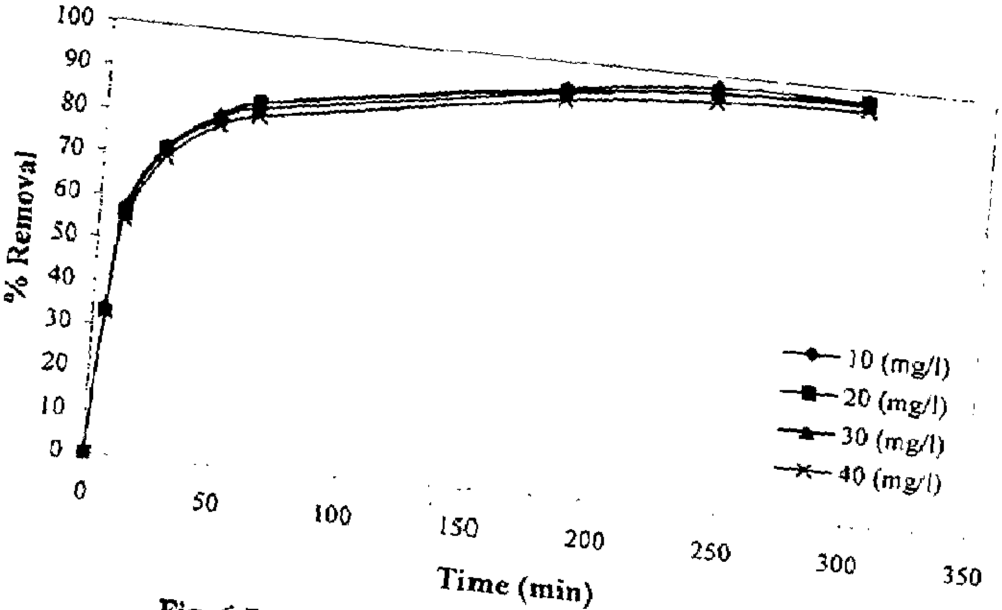

Fig. 6.7: Effect of initial time on the adsorption of Cr(VI) by AC (Dose = 1.3 mg, pH = 3, T = 25 °C)

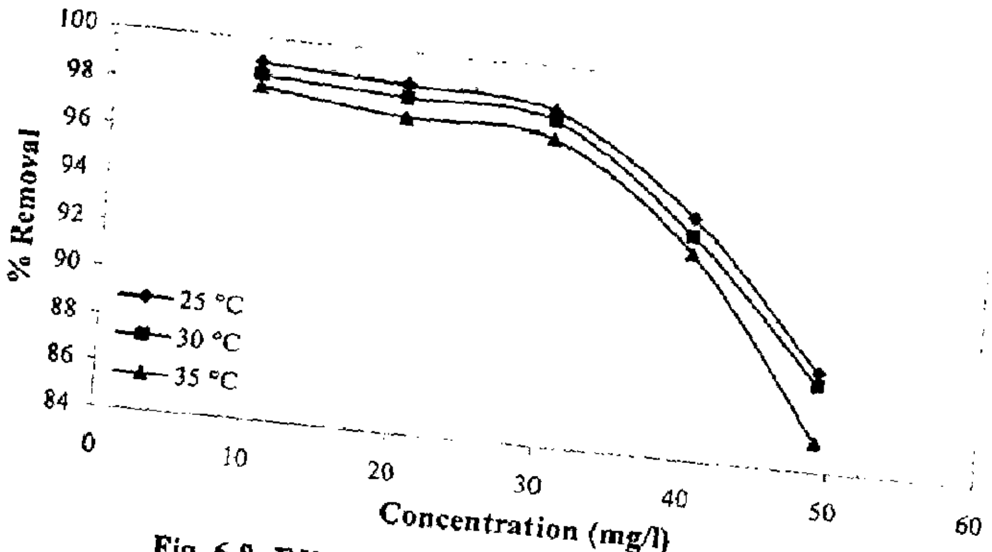

Fig. 6.8: Effect of temperature on the adsorption of Cr(VI) by AC (Dose = 1.3 mg, pH = 3, t = 300 min)

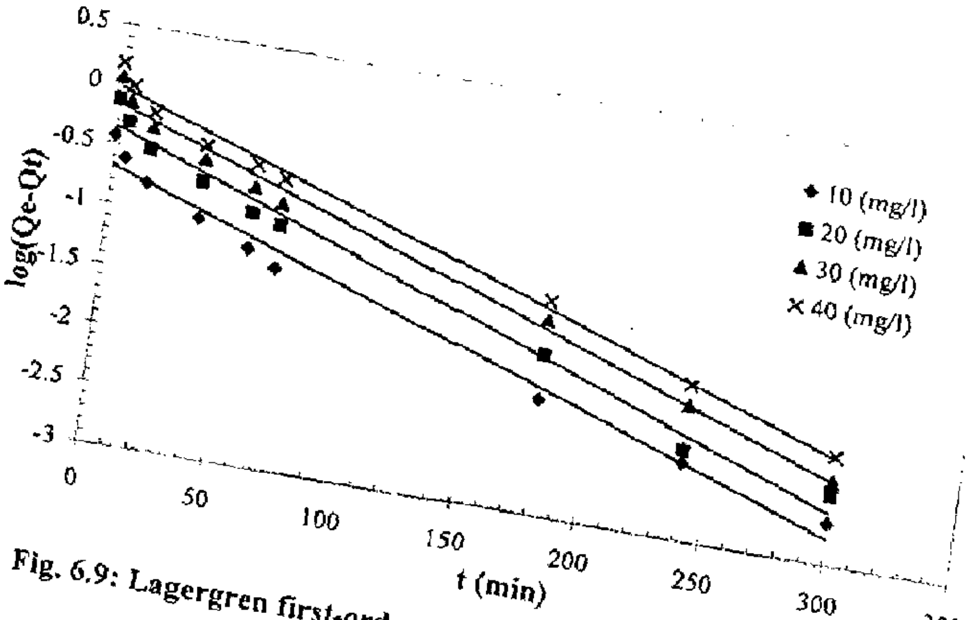

Fig. 6.9: Lagergren first-order kinetic plots (pH=3, Dose= 1.3 mg, T=25 °C)

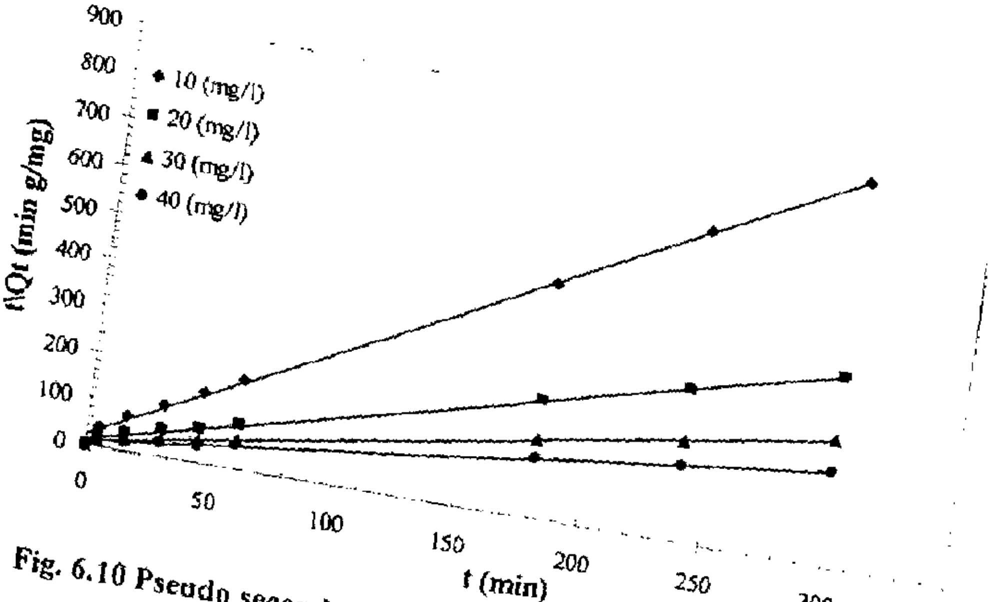

Fig. 6.10 Pseudo second-order kinetic plots (pH=3, Dose= 1.3 mg, T=25 °C)

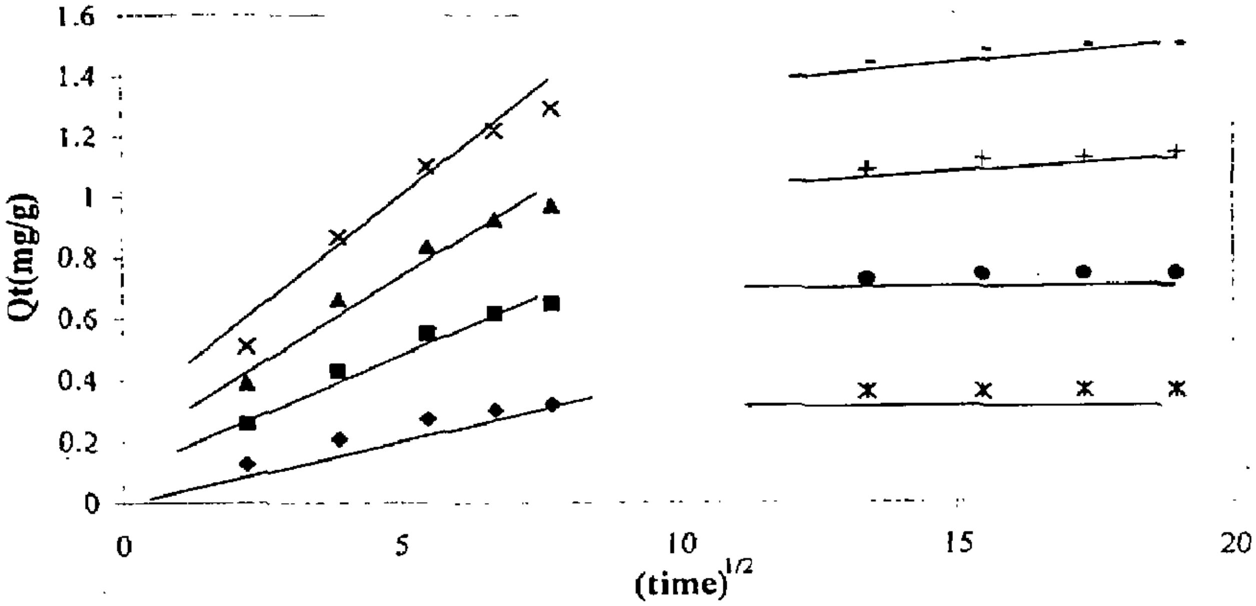

Fig. 6.11: Weber and Morris intra-particle diffusion plots (pH=3, Dose= 1.3 mg, T=25 °C)

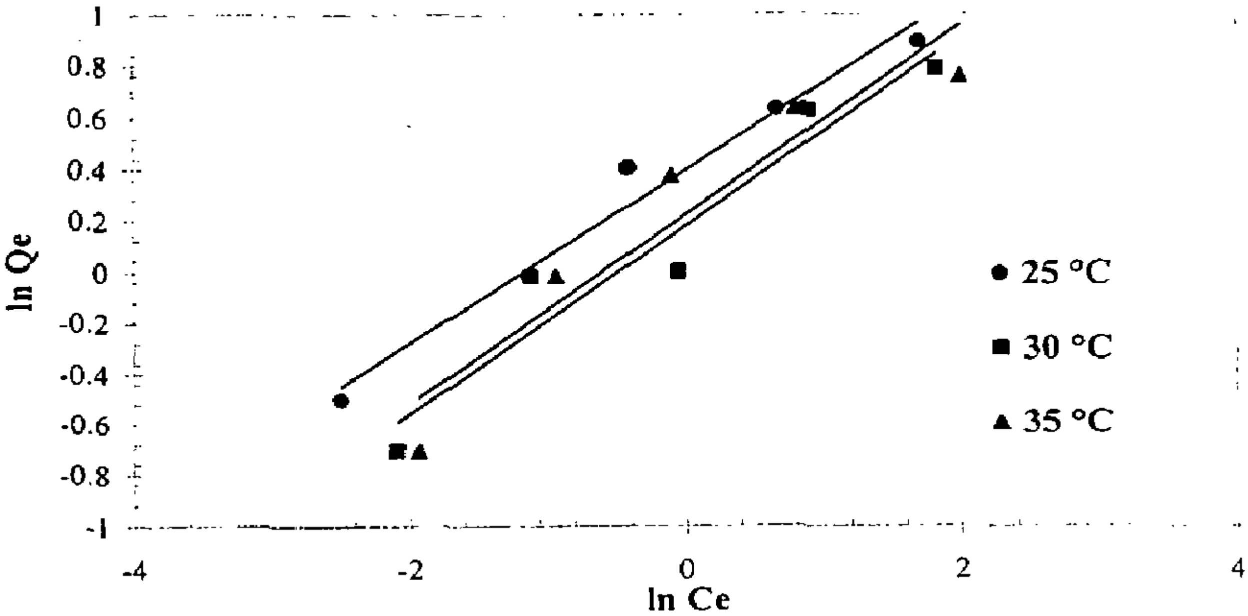

Fig. 6.12: Freundlich Isotherm plots (pH=3, Dose= 1.3 mg, t=300 min)

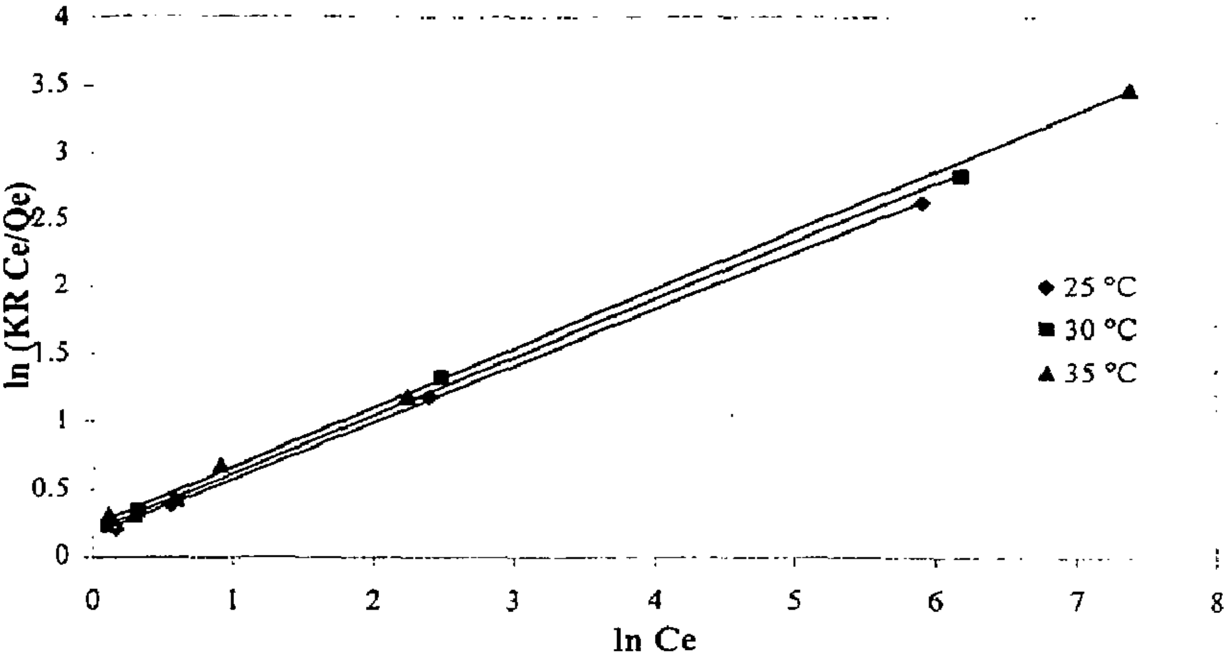

Fig. 6.13: Langmuir Isotherm plots (pH=3, Dose = 1.3 mg, t=300 min).

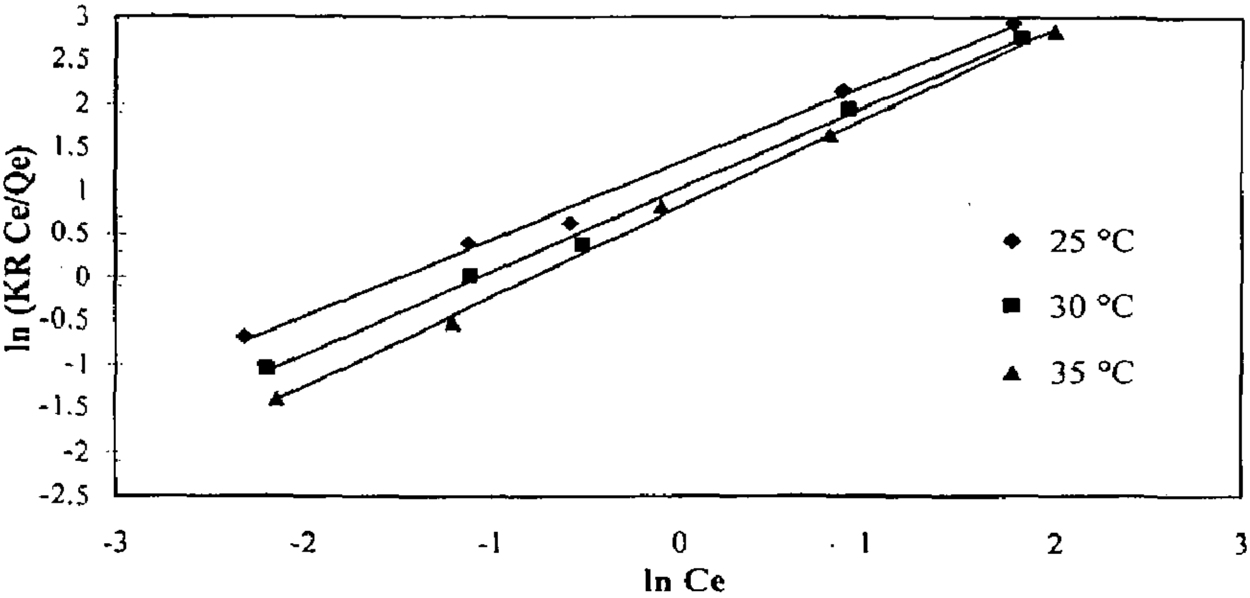

Fig. 6.14: Redlich-Peterson Isotherm plot (pH=3, Dose = 1.3 mg, t=300 min)

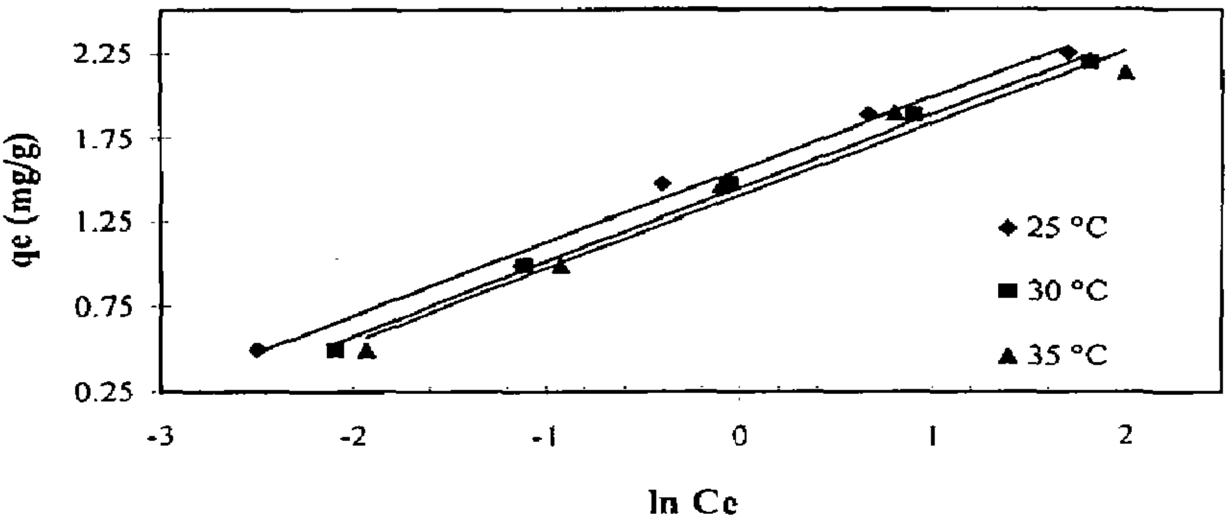

Fig. 6.15: Temkin isotherm plots (pH=3, Dose = 1.3 mg, t=300 min)

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

The following major conclusions drawn from the present work and study are given below:

1. Bulk density of activated carbon was found to be 650.82 Kg m^{-3}, fixed carbon: 89.30%, which shows excellent adsorptive characteristics of activated carbon for the removal of Cr(VI) from aqueous solution.
2. Percent removal of chromium increase in adsorbent concentration upto 20 mg/l after that removal percent remains constant, while removal per unit weight of adsorbent increases with the decrease in adsorbent concentration.
3. Adsorption of chromium compounds increases with reduction in pH. Reduction in adsorption at high pH is possibly due to increased solubility of chromium compounds. Percent removal of Cr (VI) is maximum at 3 pH.
4. Effect on initial chromium concentration on the activated carbon shows that for any contact time the percent removal decreases with increase in initial concentrations of chromium.
5. Adsorption of Cr(VI) onto AC increases with time and reaches equilibrium in 300 min. Rate of adsorption of Cr(VI) is fast initially decreases with increase in time
6. Adsorption of Cr(VI) onto AC increase with decrease in temperature indicating exothermic nature of the process.
7. Freundlich, Langmuir, Redlich-Peterson and separation factor equations follow the equilibrium adsorption data very well.
8. Weber-Morris plot reveals that the intra-particle transport (pore diffusion) is the rate-controlling step.
9. Kinetic study shows that Cr(VI) adsorption on activated carbon follows the second order kinetics, which was useful for design purposes.
10. The thermodynamic adsorption parameters, ΔH^0 and ΔS^0 are 4.792 kJ/mol and 27.691 J/mol/K, respectively.

7.2 RECOMMENDATIONS

1. AC shown the good adsorbent for synthetic Cr(VI) wastewater, it can also be suitable for used in the industrial wastewater treatment.
2. Costing of the adsorption based on industrial scale treatment system should be carried out to popularize the adsorption technique with activated carbon. As AC is easily available in developing countries.
3. Activated carbon should be characterized for physical-chemical parameters and surface characteristics to arrive at average values for use in design.
4. Column studies can be done to see the effect of bed height, flow rate and concentration of adsorbate.
5. It could also be tested for removal of other metals.

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APPENDIX - A

Table A-1: Lagergren Plot for removal of Chromium for different initial concentrations (pH = 3, T = 25 °C, Dose = 20 g/l)

Sl. No.	Time (min)	Log (Q_e-Q_t)	Log (Q_e-Q_t)	Log (Q_e-Q_t)	Log (Q_e-Q_t)
		10 mg/l	**20mg/l**	**30 mg/l**	**40 mg/l**
1.	0	-0.4337	-0.12838	0.056509	0.175601
2.	5	-0.61591	-0.31131	-0.12668	-0.0047
3.	15	-0.7963	-0.50211	-0.32169	-0.19928
4.	30	-1.0153	-0.70503	-0.51118	-0.39777
5.	45	-1.19018	-0.89019	-0.67045	-0.55452
6.	60	-1.31529	-1.00707	-0.7729	-0.68451
7.	180	-2.10322	-1.6699	-1.26483	-1.20977
8.	240	-2.16455	-2.25062	-1.67778	-1.7057
9.	300	-2.65155	-2.42375	-1.77949	-2.22185

Table A-2: Pseudo second order kinetic Plot for removal of Chromium for different initial Concentrations (pH = 3, T = 25 °C, Dose = 20 g/l)

Sl. No.	Time (min)	t/Q_t	t/Q_t	t/Q_t	t/Q_t
		10 mg/l	**20mg/l**	**30mg/l**	**40 mg/l**
1.	0	0	0	0	0
2.	5	39.60999	19.54887	12.75635	9.821698
3.	15	71.92918	34.93372	22.65203	17.31486
4.	30	110.3565	54.86004	36.11111	27.31858
5.	45	148.1013	73.13414	48.62843	36.90386
6.	60	187.5	92.92352	61.83851	46.45622
7.	180	499.3065	249.0687	165.9574	125.2945
8.	240	663.8298	325	214.6764	162.314
9.	300	819.3277	405.2369	267.2972	201.0309

Table A-3: Weber Morris Plot for removal of Chromium for different initial concentrations (pH = 3, T = 25 °C, Dose = 20 g/l)

Sl. No.	$T^{1/2}$ $(\text{min})^{0.5}$	Q (mg/g) 10 mg/l	Q (mg/g) 20mg/l	Q (mg/g) 30mg/l	Q (mg/g) 40 mg/l
1.	0	0	0	0	0
2.	2.236068	0.126231	0.255769	0.391962	0.509077
3.	3.872983	0.208538	0.429385	0.662192	0.866308
4.	5.477226	0.271846	0.546846	0.830769	1.098154
5.	6.708204	0.303846	0.615308	0.925385	1.219385
6.	7.745967	0.32	0.645692	0.970269	1.291538
7.	13.41641	0.3605	0.722692	1.084615	1.436615
8.	15.49193	0.361538	0.738462	1.117962	1.478615
9.	17.32051	0.366154	0.740308	1.122346	1.492308

Table A-4: Freundlich isotherm for removal of Chromium at different temperatures (pH = 3, t = 300 min, Dose = 20 g/l)

Sl. No.	25 °C		30 °C		35 °C	
	ln Q_e	ln C_e	ln Q_e	ln C_e	ln Q_e	ln C_e
1.	-0.503096	-2.496237	-0.70430924	-2.09463	-0.70501735	-1.9342
2.	-0.0164343	-1.120857	-0.01663764	-1.108662	-0.01511363	-0.9235
3.	0.405	-0.40584	.3.598	-0.04727	0.37479969	-0.098716
4.	0.6313781	0.67389	0.62892860	0.911479	0.63541213	0.80826
5.	0.8906412	1.70622	0.78424395	1.822127	0.75659135	1.9987736

Table A-5: Langmuir isotherm for removal of Chromium at different temperatures

(pH = 3, t = 300 min, Dose = 20 g/l)

Sl. No.	25 °C		30 °C		35 °C	
	C_e/Q_e	C_e	C_e/Q_e	C_e	C_e/Q_e	C_e
1.	0.2000242	0.099	0.2244919	0.111	0.2388181	0.118
2.	0.3314019	0.326	0.3355363	0.33	0.3045685	0.3
3.	0.3832042	0.564	0.4102459	0.603	0.6228088	0.906
4.	1.2743325	2.396	1.3265089	2.488	1.1886852	2.244
5.	2.6222301	5.905	2.8232341	6.185	3.4631628	7.38

Table A-6: Tempkin adsorption isotherm for removal of Chromium at different temperatures (pH = 3, t = 300 min, Dose = 20 g/l)

Sl. No.	25 °C		30 °C		35 °C	
	Q_e (mg/g)	ln C_e	Q_e (mg/g)	ln C_e	Q_e (mg/g)	ln C_e
1.	*0.49494*	*-2.496237*	*0.49445*	*-2.09463*	*0.4941*	*-1.9342*
2.	0.9837	-1.1208579	0.9835	-1.1086626	0.985	-0.9235
3.	1.46985	-0.40584	1.4718	-0.04727	1.4547	-0.098716
4.	1.8802	0.67389	1.8756	0.9114792	1.8878	0.80826
5.	2.2519	1.70622	2.19075	1.822127	2.131	1.9987736

Table A-7: Redlich-Peterson adsorption isotherm for removal of Chromium at different temperatures (pH = 3, t = 300 min, Dose = 20 g/l)

Sl. No.	25 °C		30 °C		35 °C	
	ln(KR*C_e/Q_e - 1)	ln C_e	ln(KR*C_e/Q_e - 1)	ln C_e	ln(KR*C_e/Q_e - 1)	ln C_e
1.	-0.6927836	-2.312635	-1.0585713	-2.1982251	-1.4095955	-2.137070
2.	0.39576076	-1.120857	0.0131315	-1.1086626	-0.5330678	-1.203972
3.	0.62809215	-0.572701	0.37944665	-0.5058381	0.80863157	-0.098716
4.	2.14680738	0.873800	1.94004342	0.9114792	1.64732121	0.80826
5.	2.92674257	1.775799	2.7687943	1.822127	2.83574416	1.9987736