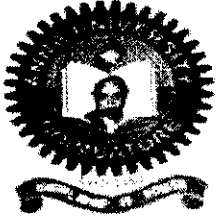
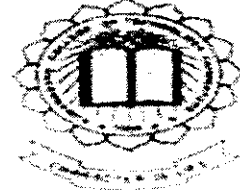


P-3409



**REMOVAL OF Cr (VI)
FROM ELECTROPLATING
EFFLUENT**



A PROJECT REPORT

Submitted by

**ANNAKKILI M (0710204005)
BRINDHA C (0710204007)
DAKSHNA PRIYA B (0710204008)
LEELAVATHI T (0710204022)**

*in partial fulfillment for the award of the degree
of*

BACHELOR OF TECHNOLOGY

In
BIOTECHNOLOGY

KUMARAGURU COLLEGE OF TECHNOLOGY

(An autonomous institution affiliated to Anna University, Coimbatore)

COIMBATORE – 641 049

APRIL 2011

KUMARAGURU COLLEGE OF TECHNOLOGY

COIMBATORE 641049

BONAFIDE CERTIFICATE

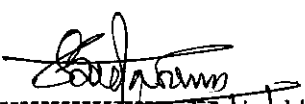
Certified that this project report “REMOVAL OF Cr (VI) FROM ELECTROPLATING EFFLUENT” is the bonafide work of ANNAKKILI M (0710204005), BRINDHA C (0710204007), DAKSHNA PRIYA B (0710204008) and LEELAVATHI T (07010207022) who carried out the project work under my supervision.


SUPERVISOR

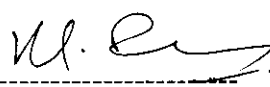
Mr. S.SENTHIL KUMAR
Assistant Professor (SRG)
Department of Biotechnology
Kumaraguru College of Technology
Coimbatore - 641049


HEAD OF THE DEPARTMENT

Dr. S. SADASIVAM
DEAN (Biotechnology)
Department of Biotechnology
Kumaraguru College Of Technology
Coimbatore - 641049



Internal Examiner



External Examiner

ACKNOWLEDGEMENT

*With our deepest sense of gratitude, we extend our heartfelt thanks to **Mr.Senthil Kumar. S**, Assistant Professor (SRG) , Department of Biotechnology, Kumaraguru college of Technology, for his relentless support, guidance, creative ideas and patient effort for the successful completion of the project.*

Our sincere thanks to **Dr. S. Sadasivam**, DEAN, Department of Biotechnology, Kumaraguru College of Technology. His gracious and ungrudging guidance all through our project work is highly acknowledged with gratitude.

We are happy to thank **Mr. M. Shanmugaprakash**, Assistant Professor(SRG), Department of Biotechnology, Kumaraguru College of Technology for his unsolicited and timely help encouragement without any hesitation.

We would like to heartily thank our review panel members **Dr. J.Aravind**, Assistant Professor (SRG) and **Mr. Manimaran D.R**, Assistant Professor (SRG), Department of Biotechnology, for their valuable ideas and guidance during the project work.

With our deepest sense of gratitude we thank **Mr. S.Ramasamy** , non-teaching staff, Department of Biotechnology, Kumaraguru College of Technology for his timely help and relentless support.

We wish to extend our thanks to all **Teaching and Non-Teaching** staff members of the Department of Biotechnology for their kind and patient help throughout the project work.


Our sincere thanks to Department of Environmental Engineering Lab,

Department of Civil Engineering, Kumaraguru College of Technology for their timely help to analyse the samples.

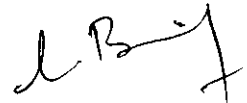
We wish to extend our thanks to Department of Chemistry and Department of Metallurgy, PSG College Of Technology ,Coimbatore and SITRA, Coimbatore to spend for us to analyse the samples in FTIR, SEM and AAS.

We thank all our friends who physically and emotionally helped us to bring out the work successfully.

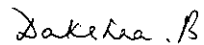
Finally, we wish to express our deep sense of gratitude to our beloved parents and family members for their constant encouragement and love, without whose inspiration this study would not have seen the dawn of day.



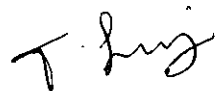
[Annakkili M]



[Brindha C]



[Dakshna Priya B]



[Leelavathi T]

TABLE OF CONTENTS

| CHAPTER NO. | TITLE | PAGE NO. |
|-------------|-------------------------------------|----------|
| | CERTIFICATE | II |
| | ACKNOWLEDGEMENT | III |
| | TABLE OF CONTENTS | V |
| | ABSTRACT | VII |
| | LIST OF TABLES | VIII |
| | LIST OF FIGURES | IX |
| | LIST OF NOMENCLATURE | XI |
| | INTRODUCTION | 1 |
| 1 | Electroplating industry | 1 |
| 1.1 | Toxic heavy metals | 1 |
| 1.2 | List of toxic metals | 2 |
| 1.3 | Chromium | 3 |
| 1.4 | Hexavalent Chromium | 3 |
| 1.5 | Effects Of Chromium (VI) | 4 |
| 1.6 | Adsorption | 4 |
| 1.7 | Adsorbents | 5 |
| 1.8 | Isotherm | 6 |
| 1.9 | Advantages Of Adsorption | 7 |
| 1.10 | OBJECTIVES | 8 |
| 2. | LITERATURE REVIEW | 9 |
| 3. | Dead fungal species as Adsorbents | 9 |
| 3.1 | Heat activated bauxite as Adsorbent | 9 |
| 3.2 | Peanut shells as adsorbent | 10 |
| 3.3 | Egg shells as adsorbent | 10 |
| 3.4 | Neem Leaves as Adsorbent | 11 |
| 3.5 | Pyrolyzed Wastes as Adsorbent | 12 |
| 3.6 | Brewery Biomass as Adsorbent | 12 |
| 3.7 | Rice Husk as Adsorbent | 13 |
| 3.8 | Tea Waste as Low Cost Adsorbent | 13 |
| 3.9 | Wheat Bran as Adsorbent | 14 |
| 3.10 | Sawdust as Adsorbent | 14 |
| 3.11 | Brazilian Pine-Fruit Shell As | 14 |
| 3.12 | Adsorbent | 15 |
| 3.13 | Green Alga (Oedogonium Hatei) From | 15 |

| | | |
|-------|---|----|
| | Aqueous Solutions as Adsorbents | 15 |
| 3.14 | Cyanobacteria as a Biosorbent | 15 |
| 3.15 | Water plant as a biosorbent | 16 |
| 4. | MATERIALS AND METHODS | 17 |
| 4.1 | Adsorbent materials and Chemicals | 17 |
| 4.1.1 | Adsorbent Materials used | 17 |
| 4.1.2 | Chemicals | 17 |
| 4.2 | Adsorbent Preparation | 17 |
| 4.2.1 | Papaya leaf stem | 17 |
| 4.3 | Stock Preparation | 17 |
| 4.4 | Batch Adsorption Study | 17 |
| 4.5 | Effect of pH | 18 |
| 4.6 | Effect of Adsorbent dosage at pH 2 | 18 |
| 4.7 | Effect of contact time at pH 2 and 2.5g adsorbent | 18 |
| 4.8 | Adsorption Isotherm | 18 |
| 4.8.1 | Langmuir Adsorption Isotherm | 19 |
| 4.8.2 | Freundlich Adsorption Isother | 19 |
| 4.9 | Adsorption Kinetics | 19 |
| 5. | RESULTS AND DISCUSSION | 21 |
| 5.1 | Standard Graph Calibration | 21 |
| 5.2 | Batch Adsorption Study Effect of pH | 22 |
| 5.3 | Effect of Adsorbent Dosage at pH 2 after 24 hours | 24 |
| 5.4 | Effect of contact time at pH 2 and 2.5g of adsorbent | 25 |
| 5.5 | Effluent at different dilutions | 26 |
| 5.6 | Adsorption Isotherm | 27 |
| 5.6.1 | Langmuir Isotherm | 27 |
| 5.6.2 | Freundlich Isotherm | 28 |
| 5.7 | Adsorption Kinetics | 29 |
| 5.8 | FTIR Analysis of the adsorbent | 34 |
| 5.9 | SEM Analysis of the adsorbent | 40 |
| | CONCLUSION | |
| | APPENDICES | |
| | REFERENCES | |

ABSTRACT

Chrome plating is used in electroplating industry. It releases Cr (VI) which can strongly attach to the soil and only a small amount can dissolve in water and move deeper in the soil to underground water. It causes many hazardous effects. Chromium can be removed from the effluents by employing many biosorbents. The aim of this work is to evaluate the efficiency of papaya leaf stem powder in reducing the level of chromium in electroplating effluent. Adsorption experiments were carried out using batch process. It was found that, at room temperature the optimized pH for the reduction of chromium content was found to be pH 2.0. At pH 2, when comparing different concentrations of papaya powder, the maximum reduction was obtained using 2.5g and the optimum contact time was found to be 20hours. Then the isotherms were drawn and the correlation coefficients were calculated. The kinetics study was also done and found that the reaction follows pseudo second order kinetics. FTIR and SEM analysis were done for the adsorbent.

LIST OF TABLES

| TABLE NO. | TITLE | PAGE NO. |
|-----------|---|----------|
| 5.1 | Estimation of Cr (VI) Spectrophotometric Method | 21 |
| 5.2 | Adsorption of Cr(VI) at different pH and 1g of adsorbent after 24 hours | 23 |
| 5.3 | Adsorption of Cr(VI) at pH 2 after 24 hours | 24 |
| 5.4 | Adsorption of Cr(VI) at pH 2 with 2.5g of adsorbent at different contact time | 25 |
| 5.5 | Adsorption of Cr(VI) at different dilutions | 27 |
| 5.6.1 | Langmuir Isotherm | 28 |
| 5.6.2 | Freundlich Isotherm | 29 |
| 5.7.1 | Lagergren first-order kinetics | 30 |
| 5.7.2 | Pseudo-second order kinetics | 31 |
| 5.7.3 | Second order kinetics | 33 |
| 5.8.1 | FTIR Analysis before adsorption | 34 |
| 5.8.2 | FTIR Analysis after adsorption | 37 |
| I | Estimation of Cr (VI) free ions –Spectrophotometric Method | 49 |
| II | Isotherm Equations | 51 |

LIST OF FIGURES

| FIGURE NO | TITLE | PAGE NO |
|-----------|--|---------|
| 5.1 | Standard graph for Cr(VI) estimation – Spectrophotometric Method | 22 |
| 5.2 | Plot for removal (%) Vs pH | 23 |
| 5.3 | Plot for removal (%) Vs Dosage of papaya powder | 25 |
| 5.4 | Plot for removal (%) Vs Time | 26 |
| 5.5 | Concentration of Cr(VI) Vs Dilutions | 27 |
| 5.6.1 | Langmuir isotherm | 28 |
| 5.6.2 | Freundlich isotherm | 29 |
| 5.7.1 | Lagergren first order kinetics | 31 |
| 5.7.2 | Pseudo second order kinetics | 32 |
| 5.7.3 | Second order kinetics | 33 |
| 5.8.1 | FTIR Analysis before adsorption | 36 |
| 5.8.2 | FTIR Analysis after adsorption | 39 |

| | | |
|--------------|---|-----------|
| 5.9.1 | SEM Analysis before adsorption | 40 |
| 5.9.2 | SEM Analysis after adsorption | 41 |
| I | Adsorbent | 43 |
| II | Experiments carried out in mechanical shaker | 43 |
| III | Raw effluent | 43 |
| IV | Treated effluent with different dosages | 44 |
| V | Treated effluent at different pH | 45 |
| VI | Treated effluent at different contact time | 46 |
| VII | Treated effluent at different dilutions | 47 |
| VIII | Interaction of free Cr(VI) with 1,5-DPC | 49 |

LIST OF NOMENCLATURE

C_e = Concentration of Cr(VI) at equilibrium (mg/L)

q_e = Amount of Cr(VI) adsorbed by the adsorbent (mg/g)

q_m = Maximum adsorption capacity (mg/g)

K_F = Freundlich constant (mg/g)

n = Freundlich constant (L/mg)

K_{ad} = Lagergren rate constant (l/min)

K' = Pseudo second-order rate constant (g/mg.min)

K = Pseudo second order rate constant (g/mg min)

q_t = Amount of heavy metal adsorbed per unit mass of adsorbent (mg/g)

K_L = Dimensionless separation factor

C_0 = Initial concentration (mg/ml)

C_i = Initial Concentration (mg/ml)

C_f = Final Concentration (mg/ml)

M = Mass of the adsorbent (g)

V = Volume of solution (ml)

K_a = Langmuir constant (l/mg)

%R = Removal Efficiency

CHAPTER 1

INTRODUCTION

1.1 ELECTROPLATING INDUSTRY

Electroplating is a plating process in which metal ions in a solution are moved by an electric field to coat an electrode. The process uses electrical current to reduce cations of a desired material from a solution and coat a conductive object with a thin layer of the material, such as a metal. Electroplating is primarily used for depositing a layer of material to bestow a desired property (e.g., abrasion and wear resistance, corrosion protection, lubricity, aesthetic qualities, etc.) to a surface that otherwise lacks that property. Another application uses electroplating to build up thickness on undersized parts. Chrome plating, often referred to simply as chrome, is a technique of electroplating a thin layer of chromium onto a metal object. The chromed layer can be decorative, provide corrosion resistance, ease cleaning procedures, or increase surface hardness. It releases Cr (VI) which can strongly attach to the soil and only a small amount can dissolve in water and move deeper in the soil to underground water. It causes many hazardous effects. The sample for this study was taken from the electroplating industry in Coimbatore.

1.2 TOXIC HEAVY METALS

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted.

Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater.

Pollution of water due to presence of certain heavy metal ions is a severe socio-environmental problem caused by the discharge of industrial wastewater. In view of their toxicity, non-biodegradability and persistent nature, their removal becomes an absolute necessary. Chromium is one of the major pollutants in the environment and is frequently present in wastewaters from various industrial units. Several conventional physical and chemical treatment techniques may be used for the removal of chromium. However, such processes are not only expensive and highly energy intensive, but also lead to production of harmful by-products and end-products, the ultimate disposal of which again causes secondary pollution. The potential application of microorganisms as biosorbent for the removal of chromium has been recognized as an alternative to the existing conventional physico-chemical methods [Sen and Dastidar. 2010]. The aim of the present study is to review the removal of chromium from wastewater using powdered leaf stem of papaya, which has been studied as potential chromium biosorbents.

1.3 LIST OF TOXIC HEAVY METALS

- Aluminium
- Cadmium
- Lead
- Mercury

- Vanadium
- Chromium
- Nickel
- Copper
- Iron

1.4 CHROMIUM

Chromium mainly exists in two states namely Cr (III) and Cr (VI). There is good evidence from the clinic and the laboratory that Cr[VI] is the ion responsible for most of the toxic actions, although much of the underlying molecular damage may be due to its intracellular reduction to the even more highly reactive and short-lived chemical species Cr[III] and Cr[V]. Exposure to Cr[VI] can result in various point mutations in DNA and to chromosomal damage, as well as to oxidative changes in proteins and to adduct formation

1.5 HEXAVALENT CHROMIUM

Metals in an oxidation state abnormal to the body may also become toxic. Hexavalent chromium refers to chemical compounds that contain the element chromium in the +6 oxidation state. Virtually all chromium ore is processed via conversion to sodium dichromate. Approximately 136,000,000 kilograms (300,000,000 lb) of hexavalent chromium was produced in 1985. Other hexavalent chromium compounds are chromium trioxide and various salts of chromate and dichromate. Hexavalent chromium is used for the production of stainless steel, textile dyes, wood preservation, leather tanning, and as anti-corrosion and conversion coatings as well as a variety of niche uses.

Hexavalent chromium is recognized as a human carcinogen via inhalation. Workers in many different occupations are exposed to hexavalent chromium. Problematic exposure is known to occur among workers who handle chromate containing products as well as those who arc-weld stainless steel. Within the European Union, the use of hexavalent chromium in

electronic equipment is largely prohibited by the Restriction of Hazardous Substances Directive (RHSD).

1.6 EFFECTS OF CHROMIUM (VI)

Numerous industrial applications raised chromium to a very important economic element. At the same time, with the development of its uses, the adverse effects of chromium compounds in human health were being defined. Trivalent chromium is an essential trace element in humans and in animals. Chromium as pure metal has no adverse effect. Little toxic effect is attributed to trivalent chromium when present in very large quantities. Both acute and chronic toxicity of chromium are mainly caused by hexavalent compounds. The most important toxic effects, after contact, inhalation, or ingestion of hexavalent chromium compounds are the following: dermatitis, allergic and eczematous skin reactions, skin and mucous membrane ulcerations, perforation of the nasal septum, allergic asthmatic reactions, bronchial carcinomas, gastro-enteritis, hepatocellular deficiency, and renal oligo anuric deficiency. Prevention of occupational risks, biological monitoring of workers, and treatment of poisoning are also reported.

Three mechanisms have been proposed to describe the genotoxicity of chromium (VI). The first mechanism includes highly reactive hydroxyl radicals and other reactive radicals which are by products of the reduction of chromium (VI) to chromium (III). The second process includes the direct binding of chromium (V), produced by reduction in the cell, and chromium(IV) compounds to the DNA. The last mechanism attributed the genotoxicity to the binding to the DNA of the end product of the chromium(III) reduction.

1.7 ADSORPTION

The presence of toxic heavy metals such as chromium (VI) contaminants in aqueous streams, arising from the discharge of untreated metal containing effluents into water bodies is one of the most important environmental problems. Adsorption is one of the effective techniques for chromium (VI) removal from wastewater [Babu and Gupta., 2005]. Because of their high surface area and high porous character, activated carbons have been considered as potential adsorbents for Cr (VI) [Jianlong et al., 2000]. The use of commercial activated carbon is not suitable for developing countries because of its high cost. Therefore,

there is a need to produce low cost adsorbent for Cr (VI) removal from cheaper and readily available materials which can be used economically on large scale. The removal of chromium using various low-cost adsorbents has been investigated. Wool, sawdust, pine needles, almond shells, charcoal and cactus leaves have been used as adsorbents [Dakiky et al., 2002].

In the present study a non-conventional adsorbent was obtained by powdering leaf stems of papaya and was used for the removal of the toxic pollutant - Cr(VI) from electroplating effluent. Adsorption capacity of this adsorbent was studied and reported in the literature. The parameters investigated in the present study included pH, contact time, initial Cr (VI) concentration and adsorbent dosage. The kinetics of Cr (VI) adsorption on this adsorbent was also evaluated.

1.8 ADSORBENTS

Adsorbents are used usually in the form of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm. They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption. The adsorbents must also have a distinct pore structure which enables fast transport of the gaseous vapours.

Most industrial adsorbents fall into one of three classes:

- Oxygen-containing compounds – Are typically hydrophilic and polar, including materials such as silica gel and zeolites.
- Carbon-based compounds – Are typically hydrophobic and non-polar, including materials such as activated carbon and graphite.
- Polymer-based compounds - Are polar or non-polar functional groups in a porous polymer matrix.

The main disadvantages of the above adsorbents are that they are expensive and also they pose a threat to the environment. The use of low cost adsorbents like sugarcane baggase, dried leaves, rice husks, sawdust, maize and corn cob, biogas residual slurry, brewery biomass etc. are widely studied.

1.9 ISOTHERM

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials.

The first mathematical fit to an isotherm was published by Freundlich and Küster (1894) and is a purely an empirical formula for gaseous adsorbates,

$$q_e = KC_e(1/n)$$

Where k and n are empirical constants for each adsorbent-adsorbate pair at a given temperature. The function has an asymptotic maximum as pressure increases without bound. As the temperature increases, the constants k and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface.

Langmuir published a new model isotherm for gases adsorbed on solids, which retained his name. It is a semi-empirical isotherm derived from a proposed kinetic mechanism. It is based on four assumptions:

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.
2. Adsorbed molecules do not interact.
3. All adsorption occurs through the same mechanism.
4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

The isotherm equation is given by

$$q_e = (\theta \cdot b \cdot C_e) / (1 + b \cdot C_e)$$

Where C_e the equilibrium concentration (mg/l), q_e the amount adsorbed per amount of adsorbent at the equilibrium (mg/g), θ (mg/g) and b (l/mg) the Langmuir constants related to

the maximum sorption capacity and energy of adsorption, respectively (Bulut and Baysal., 2006).

1.10 ADVANTAGES OF ADSORPTION

- More effective.
- Less expensive.
- Ease to handle high volume.
- Capacity to handle even low metal concentration.
- Feasible alternative for removing heavy metals from effluents.

CHAPTER 2

OBJECTIVES

The main objectives of this study are

- I. To investigate the Cr (VI) adsorption by papaya leaf stem.
- II. To perform the batch study on adsorption of Cr (VI) from the electroplating effluent.
- III. To study the influence of pH, adsorbent dose and contact time on adsorption.
- IV. To determine appropriate adsorption isotherm and kinetics parameters of Cr (VI) adsorption.

CHAPTER 3

LITERATURE REVIEW

3.1 DEAD FUNGAL SPECIES AS BIOSORBENTS

R. oryzae, *S. cerevisiae*, *P. chrysogenum* and *A. niger* were used as the biosorbents for the reduction of Cr(VI). To screen the efficient biomass, 5 g/l of dead fungal biomass of four species were contacted with 50 mg/l of Cr(VI) at pH 2. To find the effects of the pH, a pH of 1, 2, 3 and 4 were used and to find the effect of the initial Cr(VI) concentration, concentrations of 25, 50, 100 and 200 mg/l were used. To find the effect of biomass concentration on the Cr(VI) removal, biomass concentrations of 1, 2.5, 5 and 10 g/l were employed. The removal rate of Cr(VI) increased with a decrease in pH or with increases in Cr(VI) concentration and biomass concentration. The removal capacity of Cr(VI) for 24 hours of contact time increased in the order *R. nigricans* > *R. arrhizus* > *A. oryzae* > *A. niger*. These results lead to the conclusion that the *Rhizopus* species is most efficient fungal biomass for Cr(VI) removal (Park *et al.*, 2004).

3.2 HEAT ACTIVATED BAUXITE AS ADSORBENT

1 g of HAB sample was contacted with the 50 cm³ chromate solutions containing 10 mg/l Cr(VI) with the initial pH values varying from 2 to 9 for 60 min. The HAB dosages of 5–40 g/l were studied for a concentration of 10 mg/l Cr(VI) by adjusting the initial pH to 2 and varying the contact time from 5 to 120 min and thus the effect of contact time on Cr(VI) adsorption onto HAB was also examined. The reduction of Cr(VI) by HAB is maximum at pH 2. And the adsorbent dosage more than 20g/l does not exhibit an enhanced removal of Cr(VI). Cr(VI) adsorption efficiencies were found to be 61.3%, 47.0% and 27.8% at 20, 35 and 45 °C respectively. The decreases in Cr(VI) adsorption by increasing the temperature was found. (Erdem *et al.*, 2004).

3.3 PEANUT SHELLS AS ADSORBENT

The use of agricultural products and by-products has been widely investigated as a replacement for current costly methods of removing heavy metals from water and wastewater. Some of the agricultural materials can be effectively used as a low-cost sorbent. Modification of agricultural by-product could enhance their natural capacity and add value to the by-product (Upendra Kumar., 2006).

Peanut (*Arachis hypogaea*) shells were modified by combinations of treatments following a 3² factorial design. Treatments consisted of either no wash, water wash or base wash followed by no modification or modification with 0.6M citric acid or 0.6M phosphoric acid. The nine samples were evaluated for their uptake of five metal ions (Cd (II), Cu (II), Ni (II), Pb (II) and Zn (II)) from solution. The percent of metal ions adsorbed per gram of adsorbent was significantly increased by each of the acid treatments, average values ranged from 19 to 34% compared with non-acid treated samples at 5.7%. The percent of metal ions adsorbed for base-washed samples were higher than water-washed or unwashed shells. Interaction between wash and acid treatment was not significant for most of the experimental conditions used. In solutions containing multiple metal ions, citric acid samples were found to be most effective and selective for Cu (II) compared with Cd (II), Ni (II), and Zn (II). In general, phosphoric acid-modified shells removed the most metals from solution for the experimental samples and were more effective in removing Cd (II) and Zn (II) than two of the three commercial resins. Acid-modified peanut shells are promising as metal ion adsorbents (Wafwoya *et al.*, 1999).

3.4 EGG SHELLS AS ADSORBENT

The batch removal of arsenic from aqueous solution using low-cost adsorbent (powdered egg shell) under the influences of initial arsenic ion concentrations (0.50 to 1.50 mg/l), pH (3.2 to 11.5) and particle size of eggshells (63 to 150 μm) were investigated. Eggshells were collected, washed with distilled water, air dried, ground into powder and sieved into different sieve sizes using British standard sieve. Adsorption isotherms and dynamics of arsenic onto PES were studied. The study revealed that there was a slight reduction in the rate of adsorption of arsenic ion onto the larger particle size, but adsorption capacity and parameters were unaffected. Powdered eggshell with particle size of 63 μm

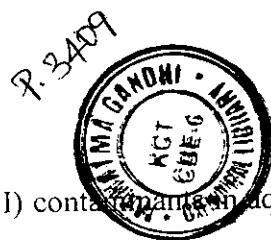
but decreased to 98.4% and 97.4% when the powdered eggshell particle sizes were increased to 75 and 150 μm respectively. The pH optimum for arsenic removal was 7.2. The adsorption isotherms and adsorption dynamic kinetic studied through the use of graphical method revealed that Freundlich activated sludge adsorption and pseudo second-order kinetic models correlate significantly with the experimental data with correlation coefficient of not less than 0.964 (Oke *et al.*, 2007).

Heavy metals have been used in many industries for colouration purpose. Textile industry is one of the prominent polluters releasing high concentrated effluent into the surrounding environment. Dyes contain carcinogenic materials which can pose serious hazards to aquatic life and end users of the water. Therefore, it is important to remove these pollutants from wastewater before their final disposal. This study investigates the potential of egg shell powder as a low cost adsorbent for heavy metal removal. The adsorption was carried out to study different initial methylene blue concentration using batch technique. Data were analyzed using Langmuir and Freundlich isotherm models (Ghani *et al.*, 2007).

The research carried out by Arunlertaree to investigate the removal of lead from battery manufacturing wastewater by egg shells. The effect of operating parameters i.e., initial pH, contact time, types of egg shell and dose of egg shell were investigated. The characteristics and chemical compositions of egg shells were also investigated and experimental samples were analyzed using AAS, then the data was statistically processed using least significant difference at a 95% confidence level ($p < 0.05$). The results indicated that the optimum pH for lead removal using 4 types of egg shell was at pH 6, but at this pH final concentration of lead was too low for study of adsorption isotherm. Therefore, unadjusted pH wastewater was used with an initial lead concentration of about 2.365 mg/l, initial pH of 1.35-1.45. Unadjusted pH wastewater decreased the use of expensive chemical reagent for adjusting pH and reduced chemical residues in the environment due to basic properties of egg shell which immediately increased the pH of solution. The optimum dose of egg shell was 1.0 g/100 ml of wastewater with a contact time of 90 minutes (Arunlertaree *et al.*, 2007).

3.5 NEEM LEAVES AS ADSORBENT

The presence of toxic heavy metals such as Cr (VI) containing in aqueous streams, arising from the discharge of untreated metal containing effluents into water bodies, is one of



Adsorption is one of the effective techniques for Cr

(VI) removal from wastewater. Batch adsorption studies demonstrate that the activated neem (*Azadirachta indica*) leaves has a significant capacity for adsorption of Cr (VI) from aqueous solution. The parameters are investigated in this study included contact time, adsorbent dosage, initial Cr (VI) concentration and pH. The adsorption process of Cr (VI) are tested with Langmuir and Freundlich isotherm models. Application of the Langmuir isotherm to the systems yielded maximum adsorption capacity of 10 mg/g at solution pH of 7. The adsorption of Cr (VI) was found to be maximum at low pH (1-3) (Gupta *et al.*, 2005).

3.6 PYROLYZED WASTE AS ADSORBENT

Heavy metals are present in abundance naturally and enter the water cycle through a variety of geochemical processes. Many metals are added to water by industrial processes. Disposal of untreated wastes, surface run-off and highway run-off also cause metal pollution of surface water (Marquies *et al.*, 1976).

The possibility of using pyrolyzed wastes produced in already working incineration plants, as adsorbents for waste water treatment, was studied. Showing very poor adsorption properties, they were improved by steam activation technique used in the conventional activated carbon manufacturing. It is concluded that various organic waste materials can be converted to carbonaceous final products with a character similar to activated carbon. Their adsorption properties and pore size distribution are determined by the structure of the starting material. Adsorption tests with model waste waters confirmed that adsorption properties are strongly influenced by the character of the surface. The adsorption capacity of these samples can be utilized for the treatment of strongly polluted industrial waste waters. Considering that the raw material 'needed' to manufacture these adsorbent is produced permanently and the adsorbents do not have to be regenerated, it might be worthwhile using these kinds of adsorbents in the primary treatment of industrial waste waters (Bóta *et al.*, 2005).

3.7 BREWERY BIOMASS AS ADSORBENT

Biosorption of lead, copper and cadmium by waste brewery yeast has been studied. The adsorption capacity for lead, copper and cadmium on the biomass increased with the increasing temperature and the maximum uptakes were 0.465 mmolPb/g (96.4 mg/g), 0.769 mmolCu/g (48.9 mg/g) and 0.127 mmolCd/g (14.3 mg/g) at 308 K. The Langmuir isotherm, favorable type, and the pseudo second-order kinetic model represent our experimental data

the biosorption of lead, copper and cadmium was endothermic reaction (Young Kim *et al.*, 2005).

3.8 RICE HUSK AS ADSORBENT

The adsorption behavior of Cu (II) and Cd (II) ions onto rice husk and modified rice husk by Soon-An Ong. The adsorption of the heavy metal ions over both the adsorbents was found to follow Langmuir and Freundlich adsorption isotherm models. It was observed that the adsorption capacity of rice husk increased after treated with nitric acid. The pseudo first-order, pseudo second-order, second order and intra-particle diffusion models were used to analyze the kinetic data and the rate constants were evaluated. The preliminary study show that the RH and MRH can be used effectively in the removal of Cu (II) and Cd (II) from aqueous solution through adsorption. The equilibrium data was fitted very well with Freundlich and Langmuir isotherm models. The values of Langmuir and Freundlich constants indicate favorable conditions for adsorption and the adsorption capacity of RH improved after treated with nitric acid. The pseudo second-order model provided the best description for the experimental data obtained compared to first order Lagergren and second order kinetic models as shown in the correlation coefficients (Ong *et al.*, 2007).

3.9 TEA WASTE AS LOW COST ADSORBENT

Batch experiments were conducted to determine the factors affecting adsorption of Pb and turbidity removal. Heavy metals contents in the sample solution were analyzed by Flame Atomic Absorption Spectrophotometry (AAS) while turbidity meter is used to determine turbidity removal. As the results, 96.4 % of ions Pb removed using tea waste compared to only 10.5 % ions Pb removed. This is to shows that tea waste is capable of binding appreciable amounts of Pb from aqueous solutions. Besides, tea waste is able to removed 59.73 % of turbidity of the synthetic wastewater. The adsorption capacity was highest at solution pH range 5–6. Therefore, it is proven that the tea waste can be used as alternative adsorbent to remove heavy metals and turbidity presence in the water and reduce cost of material (Sabrina *et al.*, 2008).

In the study carried out by Hossein Mahvi removal of cadmium, lead and nickel from

aqueous solution using tea waste as a natural adsorbent. The

research is a bench scale experimental type and analyses have performed by using different amounts of adsorbent in solutions with 5 different concentrations of each metal and also in a mixed combination. Besides, the effect of various amounts of tea waste used in adsorption efficiency experiments has been investigated. Results indicate that the removal efficiency is highest for lead and is minimum for cadmium. About 94 and 100% lead removal were achieved by using 0.5 and 1.5g adsorbent for solutions having concentrations of 5 and 10 mg/L Pb. Whereas, 1.5g tea waste can treat nickel solution of 5 mg/L concentration with an efficiency of not more than 85.7%. For cadmium, the efficiency was only 77.2% in the same conditions. On the other hand, for mixtures of metals and by applying 0.5 g tea waste, we considered a 3.5% decrease in lead removal efficiency and a 13.2% decrease in nickel adsorption for a mixed solution of 5 mg/l (Mahvi *et al.*, 2005).

3.10 WHEAT BRAN AS ADSORBENT

Adsorption of chromium (VI) ions on wheat bran has been studied through using batch adsorption techniques. The main objectives of this study are to investigate the chromium adsorption from aqueous solution by wheat bran, study the influence of contact time, pH, adsorbent dose & initial chromium concentration on adsorption process performance and to determine appropriate adsorption isotherm and kinetics parameters of chromium (VI) adsorption on wheat bran. The results of this study showed that adsorption of chromium by wheat bran reached to equilibrium after 60 min and after that a little change of chromium removal efficiency was observed. Higher chromium adsorption was observed at lower pH, and maximum chromium removal (87.8 %) obtained at pH of 2. The adsorption of chromium by wheat bran decreased at the higher initial chromium concentration and lower adsorbent doses. The obtained results showed that the adsorption of chromium (VI) by wheat bran follows Langmuir isotherm equation with a correlation coefficient equal to 0.997. In addition, the kinetics of the adsorption process follows the pseudo second-order kinetics model with a rate constant value of 0.131 g/mg.min The results indicate that wheat bran can be employed as a low cost alternative to commercial adsorbents in the removal of chromium (VI) from water and waste water (Nameni *et al.*, 2008).

3.11 SAWDUST AS ADSORBENT

The purpose of this study conducted by Adouby is in the use of *Pterygota* wood dust for lead and copper into aqueous acid solutions. The results

showed that the rate of removal is better for particle sizes lower than 0.5mm, in the metal solutions at pH 3. The Langmuir, Freundlich and Temkin isotherms studies were allowed to determine the maximum capacity of adsorption of the sawdust; it is 115.61 and 24.02 mg g⁻¹ for the lead and copper removal, respectively. This study also showed that the metal ions removal is accompanied by a releasing of K⁺, Ca²⁺ and Mg²⁺ in the metal solutions. This could constitute a way of valorization of the sawdust, a main waste of the wood industry (Adouby *et al.*, 2007).

3.12 BRAZILIAN PINE-FRUIT SHELL AS ADSORBENT

The Brazilian pine-fruit shell (*Araucaria angustifolia*) is a food residue, that was used as biosorbent for the removal of non-hydrolyzed reactive red 194 (NRR) and hydrolyzed reactive red 194 (HRR) forms from aqueous solutions. Chemical treatment of Brazilian pine-fruit shell (PW), with chromium (Cr-PW), with acid (A-PW), and with acid followed by chromium (Cr-A-PW) were also tested as alternative biosorbents for the removal of NRR and HRR from aqueous effluents. It was observed that the treatment of the Brazilian pine-fruit shell with chromium (Cr-PW and Cr-A-PW) led to a remarkable increase in the specific surface area and average porous volume of these biosorbents when compared to unmodified Brazilian pine-fruit shell (PW) (Rastogi *et al.*, 2002).

3.13 GREEN ALGA (*Oedogonium hatei*) FROM AQUEOUS SOLUTIONS AS ADSORBENTS

The hexavalent chromium, Cr(VI), biosorption by raw and acid-treated *Oedogonium hatei* were studied from aqueous solutions. Thermodynamic parameters showed that the adsorption of Cr(VI) onto algal biomass was feasible, spontaneous and endothermic under studied conditions (Gupta *et al.*, 2004).

3.14 CYANOBACTERIA AS A BIOSORBENT

Cyanobacteria as a biosorbent for mercuric ion was investigated by Cain. The biosorption of Hg²⁺ by two strains of cyanobacteria, *Spirulina platensis* and *Aphanothece flocculosa*, was studied under a batch stirred reaction system. Essential process parameters, including pH, biomass concentration, initial metal concentration, and presence of co-ions were shown to influence the Hg²⁺ uptake (Cain *et al.*, 2007).

3.15 WATER PLANT AS A BIOSORBENT

Eichhornia crassipes as a biosorbents for the reduction of hexavalent chromium, Cr(VI). The pH was varied from 2.0 to 6.0 at 30°C for 8 hours in the batch reactor. The initial concentration of Cr(VI) was 10 mg/l. And it was reduced to 6 mg/g at pH 6.0. (Sen *et al.*, 2010).

CHAPTER 4

MATERIALS AND METHODS

4.1 ADSORBENT MATERIALS AND CHEMICALS

4.1.1 Adsorbent materials used

- Papaya leaf stem

4.1.2 Chemicals

All the chemicals used were of analytical reagent grade were used without any further purification. Potassium dichromate (salt) was purchased from Qualigens Fine Chemicals (Mumbai). 1,5-diphenylcarbazide, Acetone, 98% H_2SO_4 , HCl, NaOH and distilled water were also used.

4.2 ADSORBENT PREPARATION

4.2.1 Papaya leaf stem

Papaya leaf stems were collected and dried in sunlight for 3 days. They were ground to fine powder and sieved using a mesh size of 250 μ m

4.3 STOCK PREPARATION

A stock solution was prepared by dissolving 10ml of raw electroplating effluent is made upto 1000ml with distilled water.

4.4 BATCH ADSORPTION STUDY

Batch adsorption experiments were conducted by agitating the flasks with the adsorbent. The contact time of the adsorbent was varied from 2 hours to 24 hours in an orbital shaker. Experiments were also carried out by varying the adsorbent dosage from 0.5g to 5g of all the adsorbents mentioned (Gupta *et al.*, 2005). The pH of the effluent was varied from 1 to 10. The concentration of free chromium (VI) ions in the effluent after treatment was

determined spectrophotometrically from the purple colour developed with 1,5-DPC in acidic solution. [APPENDIX II]

4.5 EFFECT OF pH

The adsorption of Cr (VI) from aqueous solution is dependent on the pH of the solution, which affects the surface charge of the adsorbent. It was therefore important to study the effect of pH on the adsorption of Cr (VI). The effect of the pH of the suspending medium on metal removal efficiency was studied by performing equilibrium sorption tests at different pH values ranging from pH 1-10 with an adsorbent dosage of 1g for a time period of 24 hours. The effluent was filtered and the concentration of free chromium (VI) ions in the effluent was determined spectrophotometrically from the purple colour developed with 1,5-DPC in acidic solution. [APPENDIX II] Adjustments to pH were made with HCl and NaOH (Nameni *et al.*, 2008).

4.6 EFFECT OF ADSORBENT DOSAGE AT pH 2

To determine the effect of adsorbent dosage on adsorption, 100 ml of heavy metal solution at pH 2 was added to, 1 to 5 g of adsorbent in a 150 ml conical flask and the mixture was stirred on an orbital shaker for a contact time of 24 hours (Soon-An Ong *et al.*, 2007). The effluent was filtered and the concentration of free chromium (VI) ions in the effluent was determined spectrophotometrically from the purple colour developed with 1,5-DPC in acidic solution. [APPENDIX II]

4.7 EFFECT OF CONTACT TIME AT pH 2 AND 2.5g ADSORBENT

To determine the effect of contact time on adsorption, 100 ml of heavy metal solution at pH 2 was added to, 2.5g of adsorbent in a 150 ml conical flask and the mixture was stirred on an orbital shaker for different contact times -2 to 24 hours (Soon-An Ong *et al.*, 2007). The effluent was filtered and the concentration of free chromium (VI) ions in the effluent was determined spectrophotometrically from the purple colour developed with 1,5-DPC in acidic solution. [APPENDIX II]

4.8 ADSORPTION ISOTHERM

For adsorption isotherm study, 100 ml of heavy metal solution was added to 2.5g of

adsorbent in a 150 ml conical flask and the mixture was stirred on an orbital shaker for a

contact time of 20 hours. Then, the solution was filtered and the concentration of free chromium (VI) ions in the effluent was determined spectrophotometrically from the purple colour developed with 1,5-DPC in acidic solution. [APPENDIX II]

4.8.1 Langmuir Adsorption Isotherm

The linear form of Langmuir isotherm is given by the following equation:

$$C_e/q_e = 1/(q_m K_a) + C_e/q_m \quad (1)$$

Where q_e is the amount adsorbed per unit mass of adsorbent (mg/g), C_e the equilibrium concentration of the adsorbate (mg/l), q_m the equilibrium sorption capacity for complete monolayer (mg/g) and K_a the sorption equilibrium constant (l/mg). When C_e/q_e was plotted against C_e , a straight line with slope $1/(K_a q_m)$ and an intercept of $1/q_m$ were obtained.

4.8.2 Freundlich Adsorption Isotherm

The linear form of Freundlich isotherm is given by the following equation:

$$\log q_e = 1/n \log C_e + K_f$$

Where q_e is the amount adsorbed per unit mass of adsorbent (mg/g), C_e the equilibrium concentration of the adsorbate (mg/l). K and n are the Freundlich constants. When $\log q_e$ was plotted against C_e , a straight line with slope $1/n$ and an intercept of K_f was obtained.

4.9 ADSORPTION KINETICS

In order to define the adsorption kinetics of heavy metal ions, the kinetic parameters for the adsorption process were studied for contact times ranging between 2 and 24 hours by monitoring the percent removal of the heavy metal Cr (VI) by the adsorbent. The data obtained was analyzed with the Lagergren first-order, pseudo second-order and second order kinetic models as shown below:

Lagergren first-order model (Lagergren, 1898)

$$\log (q_e - q_t) = \log q_e - K_{ad}t/2.303$$

Pseudo second-order model (Ho, 1995; Ho & Mckay, 2000)

Lagergren second order model (Lagergren, 1898)

$$1/(q_e - q_t) = 1/q_e - Kt$$

Where q_t is the amount of heavy metal adsorbed per unit mass of adsorbent (mg/g) at time t (min), q_e the amount of heavy metal adsorbed per unit mass of adsorbent (mg/g) at equilibrium, K_{ad} the Lagergren rate constant (l/min), K' the pseudo second-order rate constant (g/mg.min) and K the second order rate constant (g/mg min). [APPENDIX III]

CHAPTER 5

RESULTS AND DISCUSSION

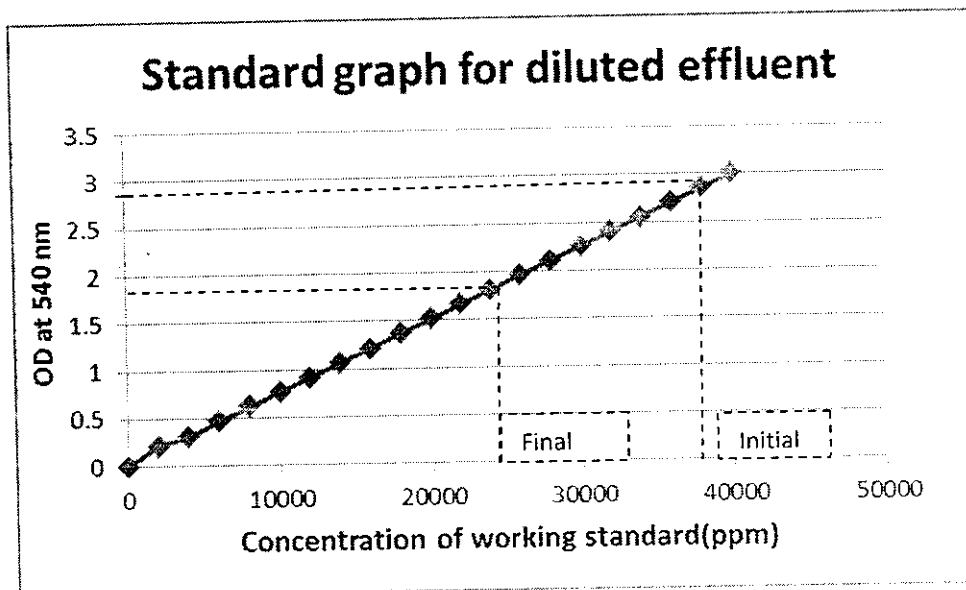
TABLE 5.1: STANDARD GRAPH CALIBRATION- Spectrophotometric method

| Reagents | B | S1 | S2 | S3 | S4 | S5 | T1 |
|--|---|-------|-------|-------|-------|-------|-------|
| 1.Volume of standard Cr solution(ml) | 0 | 1 | 2 | 3 | 4 | 5 | - |
| 2.Concentration of standard Cr solution(ppm) | - | 2000 | 4000 | 6000 | 8000 | 10000 | - |
| 3.Volume of effluent(ml) | - | - | - | - | - | - | 1 |
| 4.Volume of diluted 98% H ₂ SO ₄ (1:5 dilution with d.H ₂ O) (ml) | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 5.Volume of distilled water(ml) | 8 | 7 | 6 | 5 | 4 | 2 | 7 |
| 6.Volume of DPC(ml) | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 7.Absorbance at 540 nm | 0 | 0.207 | 0.306 | 0.469 | 0.611 | 0.769 | 0.370 |

1ml of known standard Chromium solution sample was taken and 1ml of 98% Sulphuric acid (1:5 dilution with distilled water) was added and made upto 10ml with distilled water. 1ml of 1,5- DPC was added and mixed well. The absorbance was measured at 540 nm using a Beckman BU 530 spectrophotometer. The standard graph was plotted by

taking concentration along X axis and absorbance along Y axis. A straight line was obtained as shown in the fig 5.1.

Fig 5.1 Standard graph for Cr (VI) estimation- Spectrophotometric method



5.2 BATCH ADSORPTION STUDY

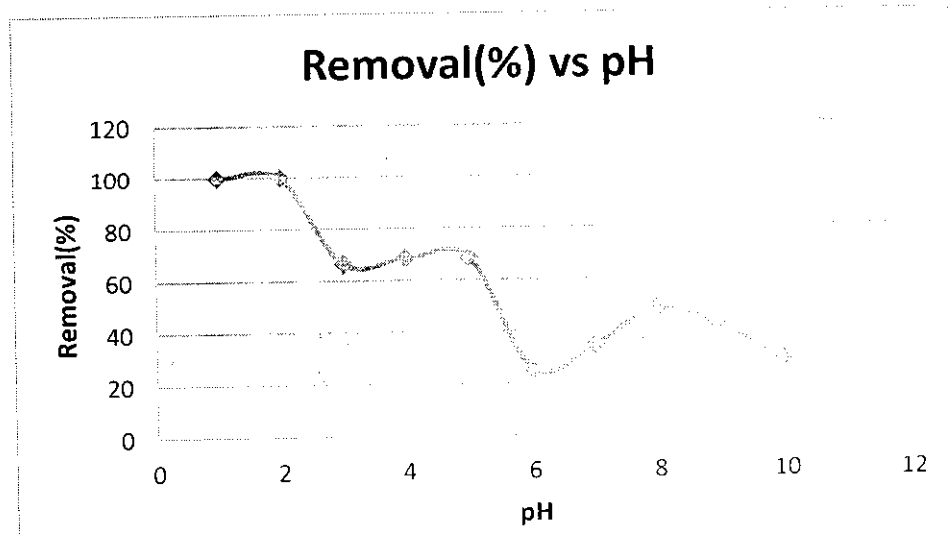
EFFECT OF pH

The optimum pH for maximum removal of Chromium (VI) was observed at pH 2.0 as shown in the fig 5.2. At pH 2.0, the maximum removal of Cr (VI) was seen in 1g of the adsorbent.

Table 5.2 Adsorption of Cr (VI) at different pH and 1g of adsorbent after 24 hours

| pH | Initial Conc Ci(mg/ml) | Final Conc Ce(mg/ml) | %R |
|----|---------------------------|-------------------------|--------|
| 1 | 38400 | 60.32 | 99.843 |
| 2 | 38400 | 5.76 | 99.985 |
| 3 | 38400 | 12891.648 | 66.428 |
| 4 | 38400 | 12178.56 | 68.285 |
| 5 | 38400 | 12013.824 | 68.714 |
| 6 | 38400 | 26000 | 25.29 |
| 7 | 38400 | 22800 | 34.48 |
| 8 | 38400 | 18000 | 48.27 |
| 9 | 38400 | 20400 | 41.37 |
| 10 | 38400 | 24800 | 28.74 |

Fig 5.2 Effect of pH vs removal (%)



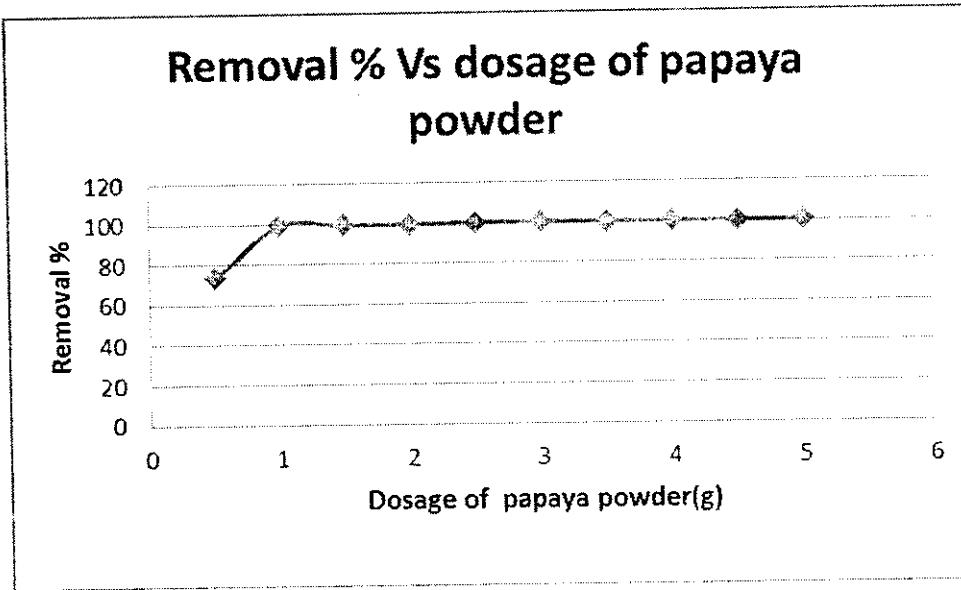
5.3 EFFECT OF ADSORBENT DOSAGE AT pH 2 AFTER 24 HOURS

The optimum dosage of the adsorbent was found to be 2.5g at optimized pH 2 after 24hours as shown in fig 5.3. The colour of the treated effluent was greatly reduced.

Table 5.3 Adsorption of Cr(VI) at pH 2 in different dosages of adsorbent after 24 hours

| Adsorbent Dosage | Initial Conc C _i (mg/ml) | Final Conc C _e (mg/ml) | q _e ×10 ⁻⁵ (mg/g) | %R |
|------------------|--|--------------------------------------|---|-------|
| 0.5 | 38400 | 10400 | 5600000 | 72.91 |
| 1.0 | 38400 | 4000 | 3826400 | 99.10 |
| 1.5 | 38400 | 4000 | 2550933 | 99.10 |
| 2.0 | 38400 | 4000 | 1913200 | 99.30 |
| 2.5 | 38400 | 68 | 1533280 | 99.98 |
| 3.0 | 38400 | 68 | 1277733 | 99.98 |
| 3.5 | 38400 | 68 | 1095200 | 99.98 |
| 4.0 | 38400 | 68 | 958300 | 99.98 |
| 4.5 | 38400 | 68 | 851822 | 99.98 |
| 5.0 | 38400 | 68 | 766640 | 99.98 |

Fig 5.3 Effect of dosage vs removal (%)



5.4 EFFECT OF CONTACT TIME AT pH 2 AND 2.5 g OF ADSORBENT

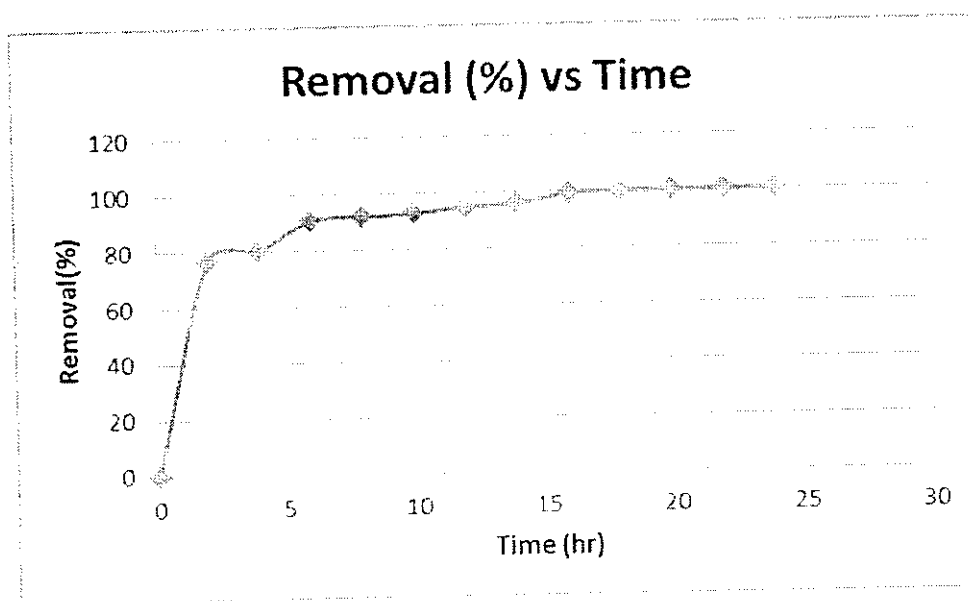
The optimum contact time for maximum reduction of Cr(VI) at optimied pH 2 with optimized dosage 2.5 g of adsorbent was found to be 20 hours as shown in fig5.4

Table5.4 Adsorption of Cr(VI) at pH 2 with 2.5g of adsorbent at different contact time

| Time(hr) | Initial Conc Ci(mg/ml) | Final Conc Ce(mg/ml) | qt(mg/g) | %R |
|----------|---------------------------|-------------------------|----------|-------|
| 0 | 38400 | 38400 | 0 | 0 |
| 2 | 38400 | 9000 | 1176000 | 76.56 |
| 4 | 38400 | 7600 | 1232000 | 80.20 |
| 6 | 38400 | 3600 | 1392000 | 90.63 |
| 8 | 38400 | 3200 | 1408000 | 91.67 |

| | | | | |
|----|-------|------|---------|-------|
| 10 | 38400 | 2800 | 1424000 | 92.79 |
| 12 | 38400 | 2000 | 1456000 | 94.79 |
| 14 | 38400 | 1600 | 1472000 | 95.84 |
| 16 | 38400 | 400 | 1520000 | 98.95 |
| 18 | 38400 | 85 | 1532600 | 99.77 |
| 20 | 38400 | 68 | 1533280 | 99.82 |
| 22 | 38400 | 68 | 1533280 | 99.82 |
| 24 | 38400 | 68 | 1533280 | 99.82 |

Fig5.4 Effect of Time vs removal (%)



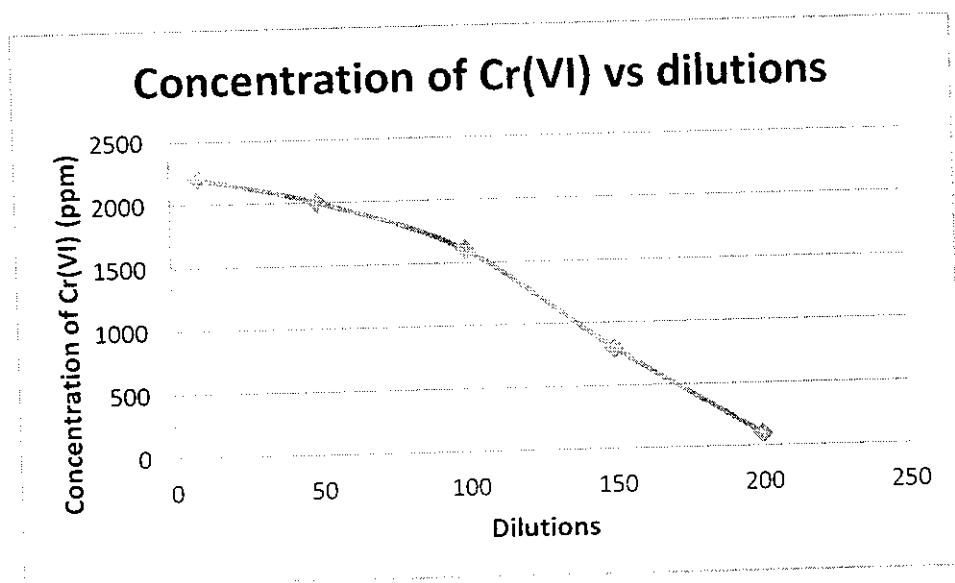
5.5 EFFLUENT AT DIFFERENT DILUTIONS

The effluent is diluted in different dilutions – 1:10, 1:50, 1:100, 1:150 and 1:200. The effluent is made to the optimized pH 2 and added with optimized dosage of 2.5 g of the adsorbent and placed in the shaker for 20 hours.

Table 5.5 Adsorption of Cr(VI) at different dilutions

| Dilutions | Concentration of Cr (VI) (ppm) |
|------------------|---|
| 10 | 2200 |
| 50 | 2000 |
| 100 | 1600 |
| 150 | 800 |
| 200 | 100 |

Fig 5.5 Concentration of Cr(VI) vs dilutions



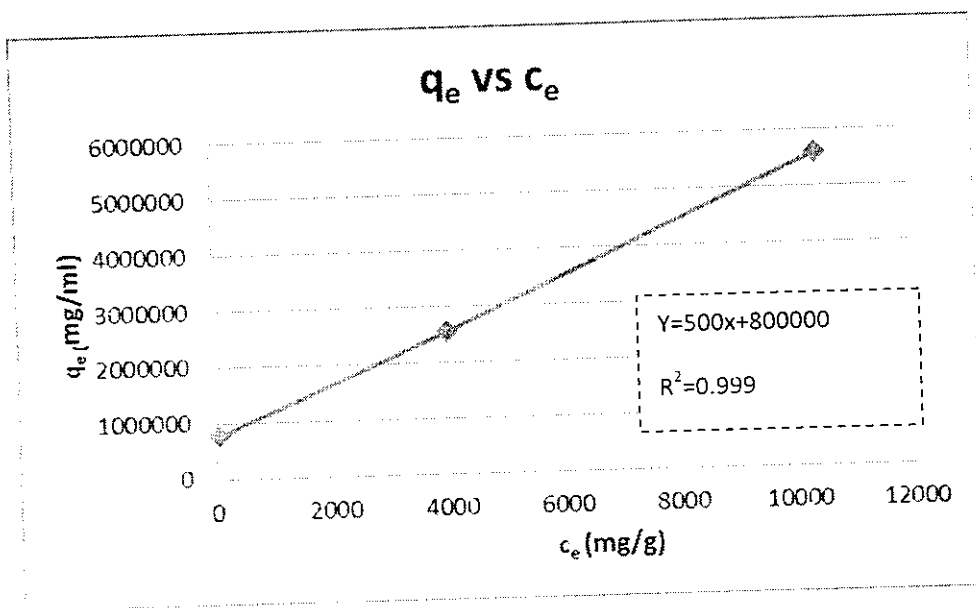
5.6 ADSORPTION ISOTHERM

The results obtained on the adsorption of Cr (VI) were analyzed by the well-known models given by Freundlich and Langmuir.

Table 5.6.1 Langmuir Isotherm

| q_e (mg/g) | C_e(mg/ml) |
|---------------------------------------|-----------------------------|
| 5600000 | 10400 |
| 2550933 | 4000 |
| 766640 | 68 |

Fig5.6.1 Langmuir Isotherm



From the graph(fig 5.6.1) Langmuir constants were found to be ,

The equilibrium sorption capacity for complete monolayer $q_m = 2 \times 10^{-3}$ (mg/g)

The sorption equilibrium constant $k_a = 6.25 \times 10^{-4}$ /mg

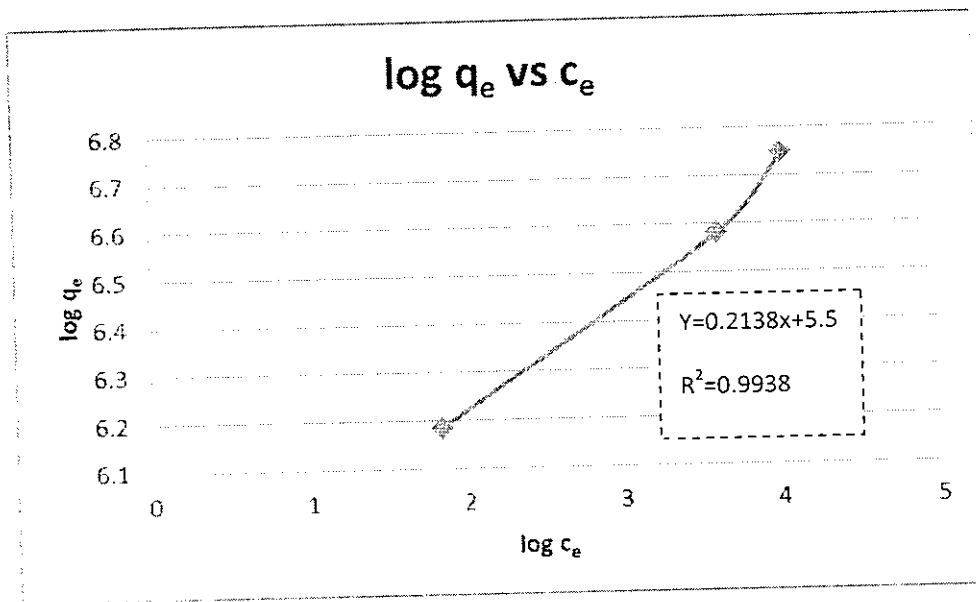
The correlation coefficient $R^2 = 0.999$

The adsorption factor $k = 0.04$ which indicates the favourable adsorption of Cr(VI)

Table 5.6.2 Freundlich isotherm

| Log q_e | Log c_e |
|-----------|-----------|
| 6.748 | 4.017 |
| 6.582 | 3.602 |
| 6.185 | 1.83 |

Fig 5.6.2 Freundlich isotherm



From the graph(fig 5.6.2) Freundlich constants were found to be

$n=4.677$ and $k_f=316227.76$

The correlation coefficient $R^2=0.9938$

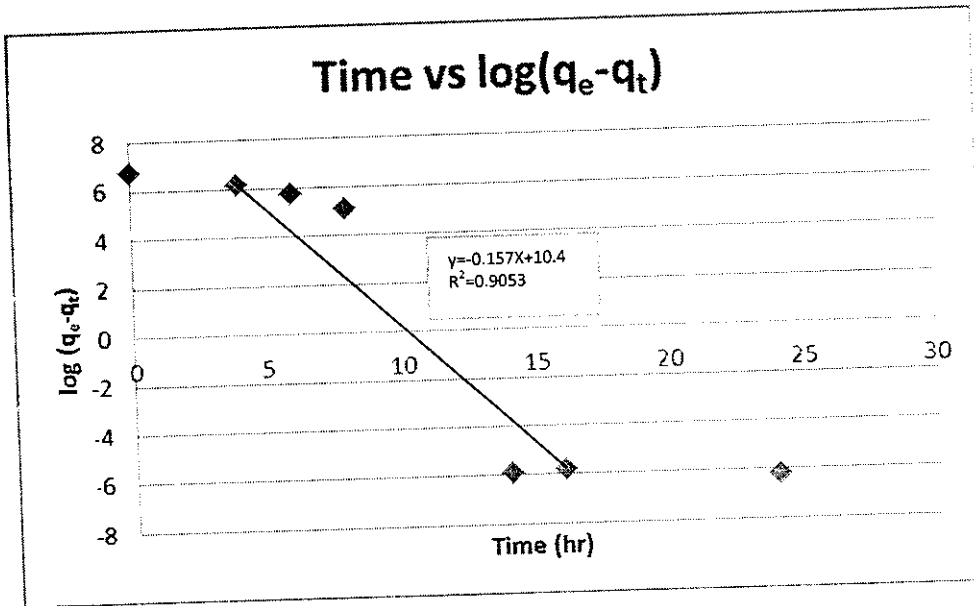
5.7 ADSORPTION KINETICS

The data obtained was analyzed with the Lagergren first-order, pseudo second-order and second order kinetic models as shown below:

Table 5.7.1 Lagergren first-order kinetics

| Time(hr) | Log (qe-qt) |
|----------|-------------|
| 0 | 6.74 |
| 4 | 6.12 |
| 6 | 5.71 |
| 8 | -5.09 |
| 14 | -5.91 |
| 16 | -5.84 |
| 24 | -6.18 |

Fig 5.7.1 Lagergren first-order kinetics



From the graph (fig5.7.1)

The Lagergren rate constant $K_{ad} = 0.3615$ /min

The amount of heavy metal adsorbed per unit mass of adsorbent at equilibrium, q_e
 $= 2.51 \times 10^{10}$ mg/g

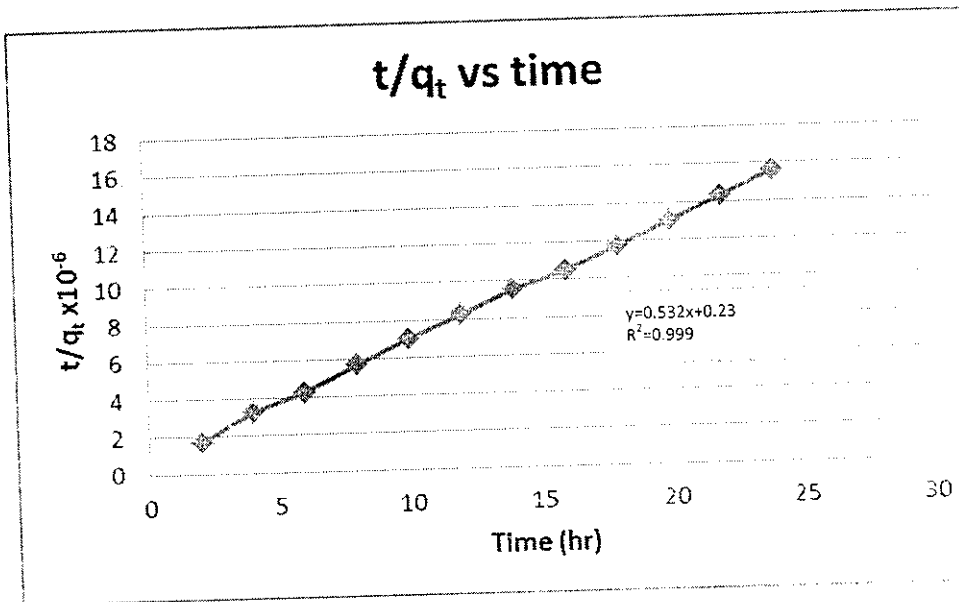
The correlation coefficient $R^2 = 0.9053$

Table 5.7.2 Pseudo second-order kinetics

| Time(hr) | $(t/ q_t) \times 10^{-6}$ |
|----------|---------------------------|
| 0 | 0 |
| 2 | 1.700 |
| 4 | 3.246 |
| 6 | 4.310 |
| 8 | 5.681 |
| 10 | 7.022 |

| | |
|----|-------|
| 12 | 8.241 |
| 14 | 9.51 |
| 16 | 1.052 |
| 18 | 1.174 |
| 20 | 1.304 |
| 22 | 1.434 |
| 24 | 1.565 |

Fig5.7.2 Pseudo second-order kinetics



From the graph (fig5.7.2)

The pseudo second-order rate constant $K' = 1.232 \text{ g/mg.min}$

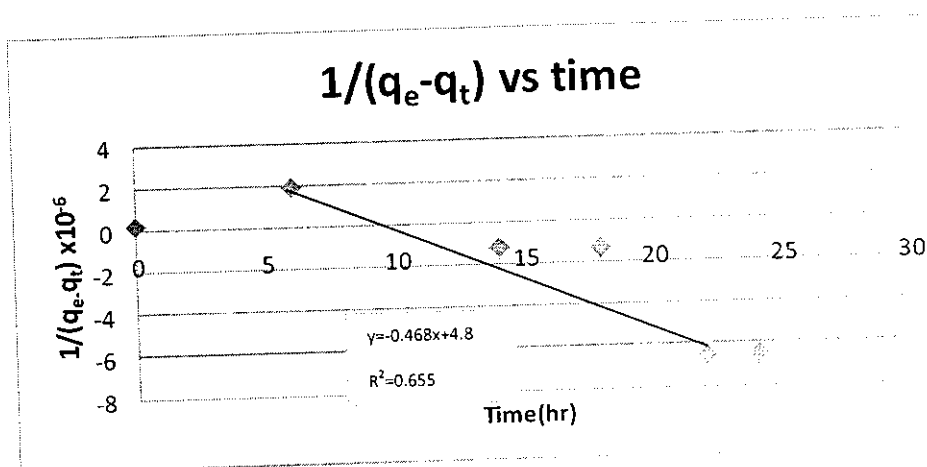
The amount of heavy metal adsorbed per unit mass of adsorbent at equilibrium, q_e
 $= 1.879 \text{ mg/g}$

The correlation coefficient $R^2 = 0.999$

Table 5.7.3 Second order kinetics

| Time(hr) | 1/(q _e -q _t) |
|----------|-------------------------------------|
| 0 | 0.178 |
| 6 | 1.91 |
| 10 | -6.83 |
| 14 | -1.22 |
| 18 | -1.3 |
| 22 | -6.52 |
| 24 | -6.52 |

Fig 5.7.3 Second order kinetics



From the graph (fig5.7.3)

The second order rate constant $k = 0.468 \text{g/mg min.}$

The amount of heavy metal adsorbed per unit mass of adsorbent at equilibrium, $q_e = 0.208 \text{mg/g.}$ The correlation coefficient $R^2 = -0.655.$

5.8 FTIR ANALYSIS OF THE ADSORBENT

The powdered papaya leaf stem was analysed using Fourier Transform Infra Red spectroscopy. The functional groups of the adsorbent before adsorption and after adsorption were analysed and seen the difference.

Table 5.8.1 FTIR Analysis Before adsorption

| Wave number | Range | Group | Vibration | Type |
|-------------|----------------|---------------|-----------------|----------------|
| 3421.83 | 3350 \pm 150 | Stretch | OH | OH Stretch |
| 3402.54 | 3000 \pm 500 | Stretch | COOH | Anti symmetric |
| 2924.18 | 2926 \pm 10 | Stretch | CH ₂ | Anti symmetric |
| 2856.67 | 2853 \pm 10 | Stretch | CH ₂ | Symmetric |
| 2360.95 | 2500 \pm 300 | Overtone | COOH | Bands |
| 2332.02 | 2500 \pm 300 | Overtone | COOH | Bands |
| 1734.06 | 1755 \pm 15 | Stretch | O=C-O-O=C | Anti symmetric |
| 1624.12 | 1615 \pm 15 | Bend | NH ₂ | Scissoring |
| 1419.66 | 1424 \pm 25 | Bend/Stretch | COOH | Combination |
| 1384.94 | 1395 \pm 10 | Bend | CH=O | C-H |
| 1319.35 | 1400 \pm 100 | Bend | OH | Broad |
| 1259.56 | 1250 \pm 50 | Stretch/ Bend | COOH | Combination |

| | | | | |
|---------|---------------|---------|------------------|----------------------------------|
| 1105.56 | 1125 \pm 25 | Stretch | C-O-C-C | Anti symmetrically coupled |
| 1055.10 | 1050 \pm 25 | Stretch | C-O-C-C | Anti symmetrically coupled |
| 1035.81 | 1050 \pm 25 | Stretch | C-O-C-C | Anti symmetrically coupled |
| 898.86 | 909 | Bend | =CH ₂ | Out of plane |
| 779.27 | 797 | Wag | NH ₂ | Band |

Fig 5.8.1 FTIR Analysis Before adsorption

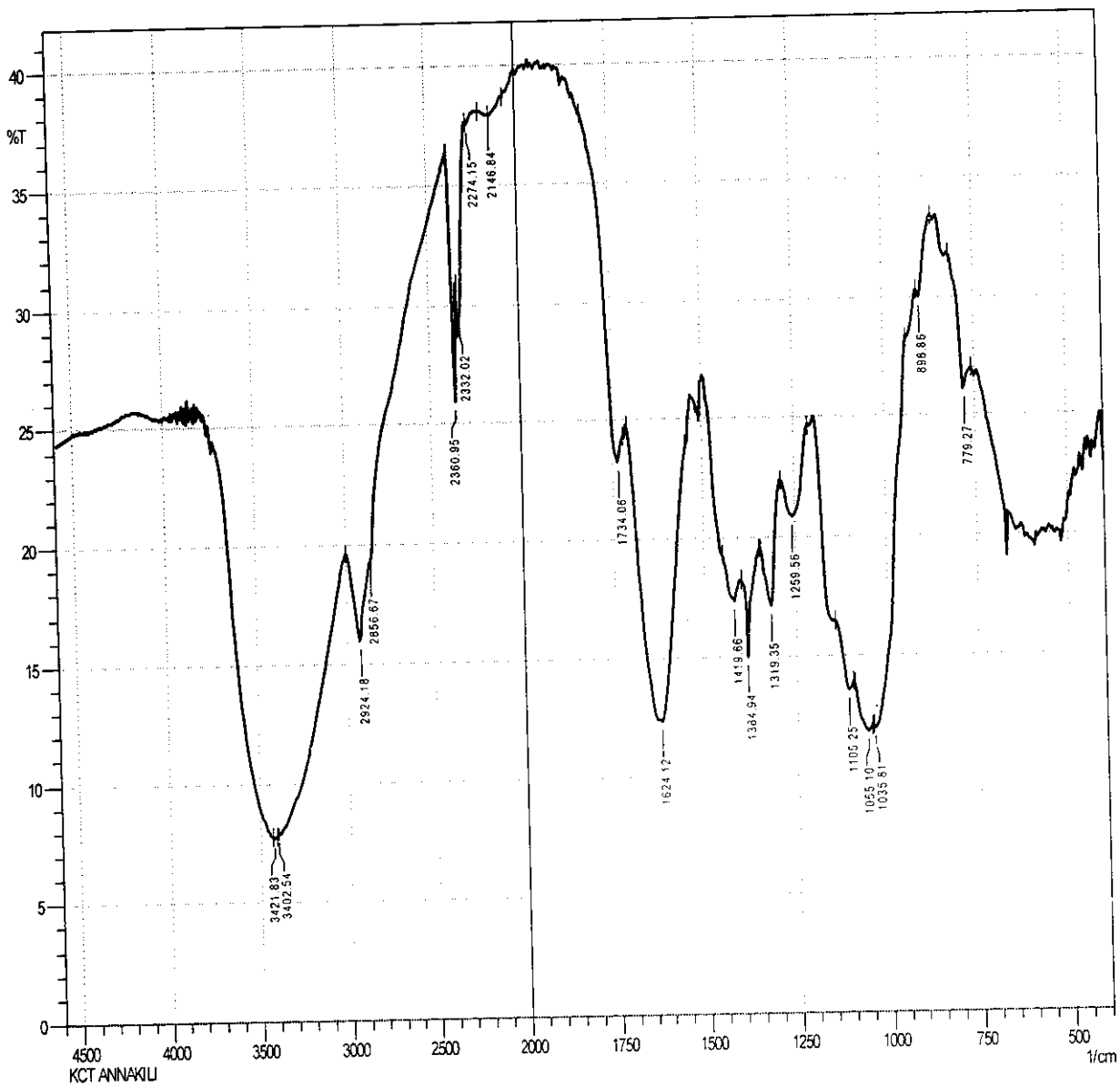
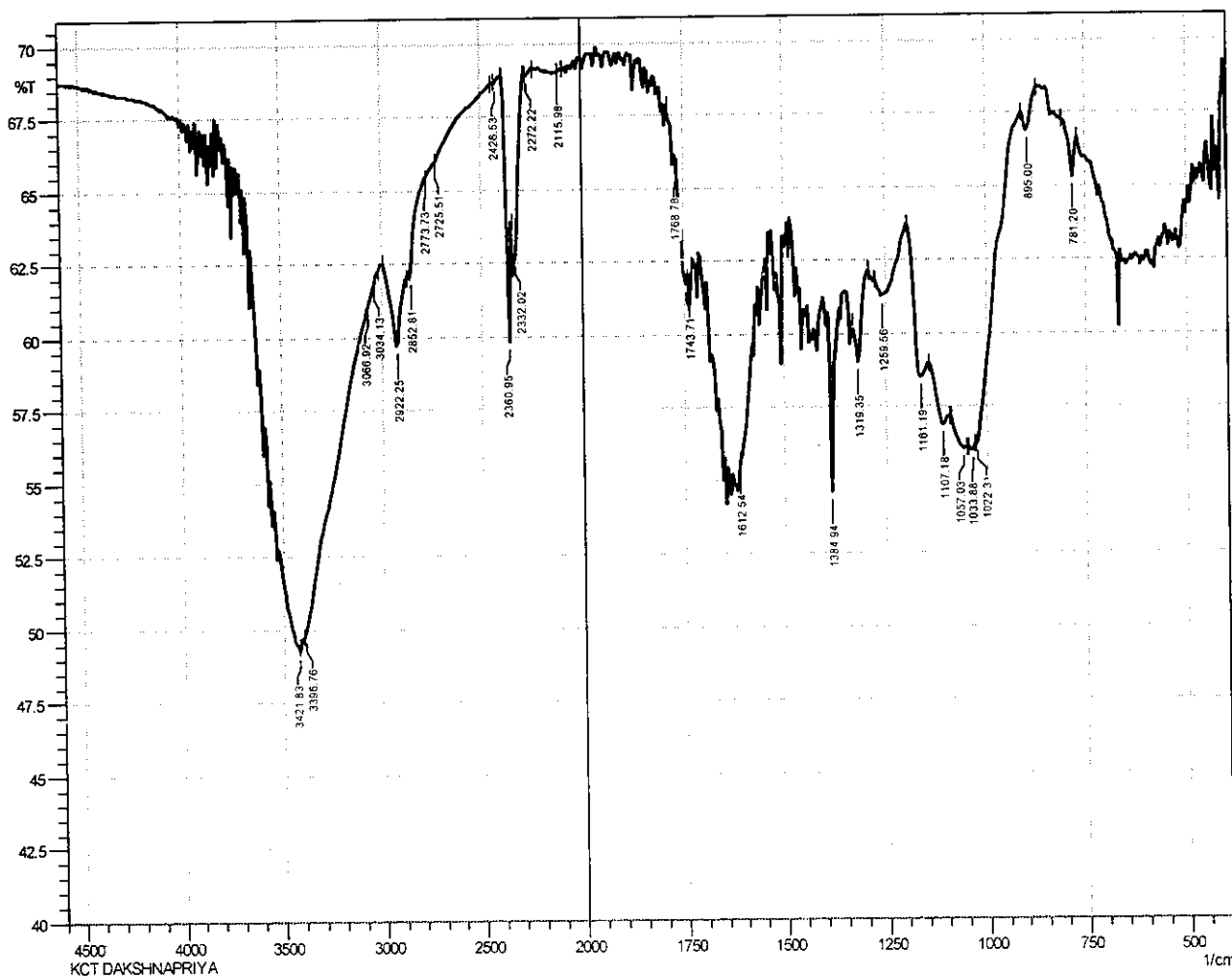


Table 5.8.2 FTIR Analysis After adsorption

| Wave number | Range | Group | Vibration | Type |
|-------------|----------------|------------------------------------|-----------|------------------------------|
| 3421.83 | 3350 \pm 150 | OH | Stretch | OH Stretch |
| 3396.76 | 3350 \pm 50 | OH | Stretch | OH Stretch |
| 3066.92 | 3050 \pm 50 | C(SP ²)H (Aromatic) | Stretch | Aromatic (or) unsaturated |
| 3034.13 | 3050 \pm 50 | C(SP ²)H (Aromatic) | Stretch | Aromatic (or) unsaturated |
| 2922.25 | 2929 \pm 10 | CH ₂ | Stretch | Anti Symmetric |
| 2852.81 | 2853 \pm 10 | CH ₂ | Stretch | Symmetric |
| 2773.73 | 2500 \pm 300 | COOH | Overtone | Bands |
| 2725.51 | 2500 \pm 300 | COOH | Overtone | Bands |
| 2426.53 | 2500 \pm 300 | COOH | Overtone | Bands |
| 2360.95 | 2500 \pm 300 | COOH | Overtone | Bands |
| 2332.02 | 2500 \pm 300 | COOH | Overtone | Bands |
| 2272.22 | 2500 \pm 300 | COOH | Overtone | Bands |
| 2115.98 | 2500 \pm 300 | COOH | Overtone | Bands |
| 1768.78 | 1755 \pm 15 | O=C-O-C=O | Stretch | Anti Symmetric |
| 1743.71 | 1615 \pm 15 | O=C-O-C=O | Stretch | Anti Symmetric |
| 1612.54 | 1395 \pm 10 | NH ₂ | Bend | Scissoring |
| 1384.94 | 1250 \pm 10 | CH=O | Bend | C-H |

| | | | | |
|---------|---------------|------------------|---------------|----------------------------|
| 1319.35 | 1250 \pm 50 | COOH | Stretch/ Bend | Combination |
| 1259.56 | 1250 \pm 50 | COOH | Stretch/ | Combination |
| 1161.19 | 1190 \pm 30 | O-C(O)-C | Stretch | O-C-C |
| 1107.18 | 1125 \pm 25 | C-O to C-C | Stretch | Anti symmetrically coupled |
| 1057.03 | 1050 \pm 25 | C-O to C-C | Stretch | Anti symmetrically coupled |
| 1033.38 | 1050 \pm 25 | C-O to C-C | Stretch | Anti symmetrically coupled |
| 1022.31 | 1050 \pm 25 | C-O to C-C | Stretch | Anti symmetrically coupled |
| 895.00 | 909 | =CH ₂ | Bend | Out of plane |
| 781.20 | 797 | NH ₂ | Wag | Band |

Fig 5.8.2 FTIR Analysis After adsorption



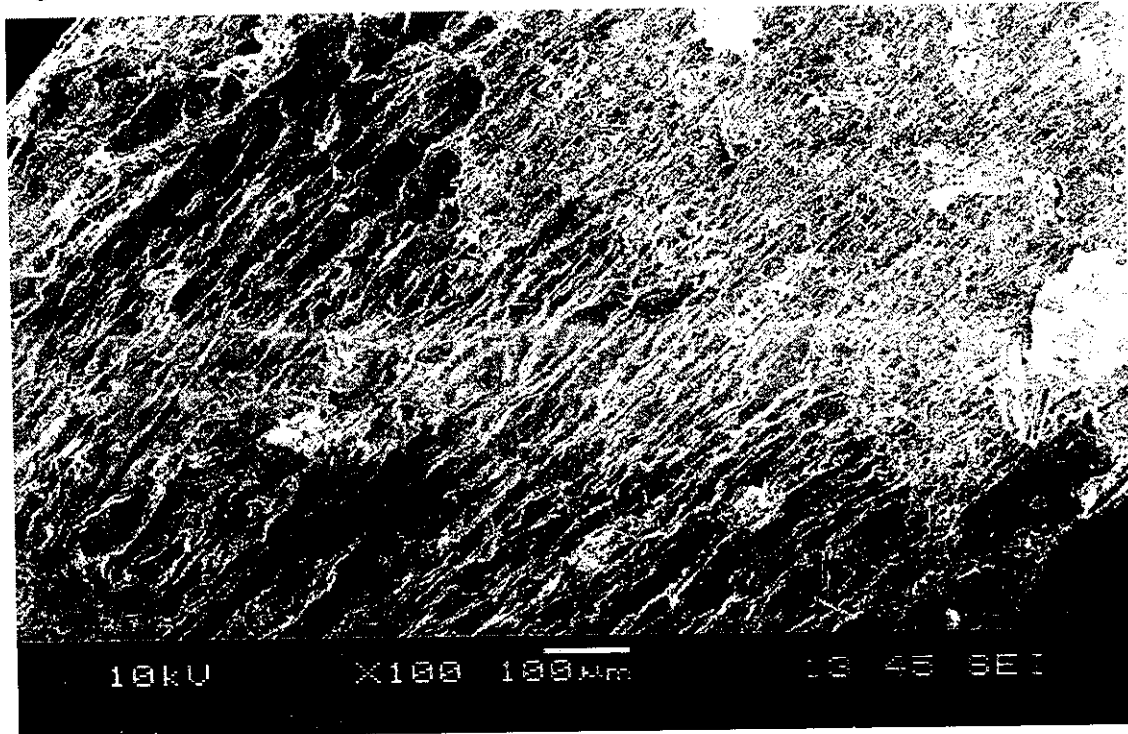
5.9 SEM ANALYSIS OF THE ADSORBENT

The powdered papaya leaf stem was analysed using Scanning electron microscopy. Structure of the adsorbent before adsorption and after adsorption were analysed and seen the difference.

Fig 5.9.1 Before adsorption



Fig 5.9.2 After adsorption



CONCLUSION

The use of low-cost adsorbents may contribute to the sustainability of the surrounding environment. Undoubtedly low-cost adsorbents offer a lot of promising benefits for commercial purpose in the future. Such a low cost adsorbent is the choice of material in this study.

Following conclusions are drawn from the above discussed results

- The adsorbent used can be obtained without excessive cost.
- Removal of Cr(VI) increases with increase of adsorbent dosage and it is optimized at 2.5g.
- The maximum adsorption of Cr(VI) took place at pH 2.
- The reduction of Cr(VI) is maximum at the contact time of 20 hours.
- The adsorption process of Cr(VI) described by Langmuir isotherm and Freundlich isotherm model showed maximum correlation co-efficient value .
- The rate constants and the amount of Cr(VI) adsorbed were found by the kinetic study.
- It follows the pseudo second order kinetics.
- FTIR analysis was performed for the adsorbent to see the functional groups before and after the adsorption
- SEM analysis was performed for the adsorbent to see the structure before and after the adsorption
- Adsorbents can be subjected to various chemical treatments before performing batch studies.
- To apply the mentioned adsorbent materials for the removal of other toxic heavy metals like Pb, Cd, Zn, Fe etc. from effluents.
- Continuous studies can be done from this optimal pH, dosage of the adsorbent and the contact time.
- Batch and continuous process can be carried out at different temperatures.

APPENDIX (I)

Fig I ADSORBENT-Powdered papaya leaf stem

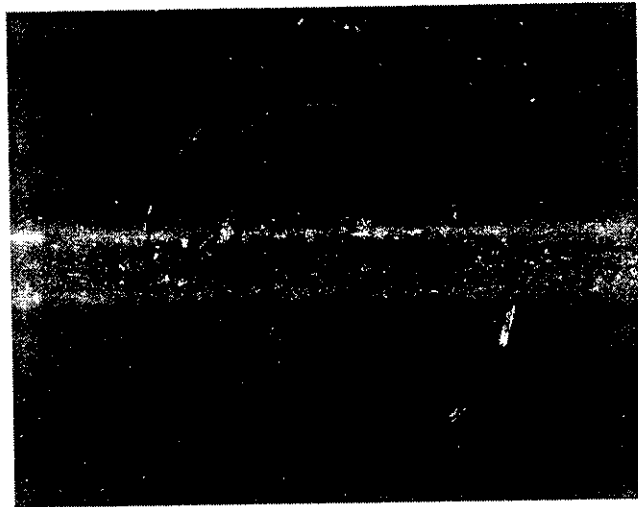


Fig II

Experiments carried out in a mechanical shaker

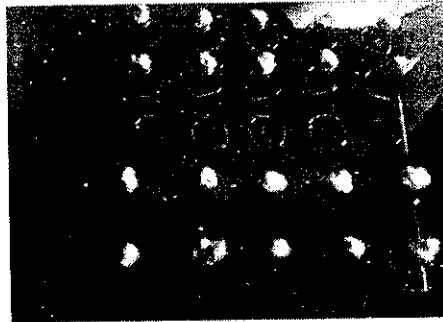


Fig III Raw effluent



Fig IV Treated effluent with different dosages

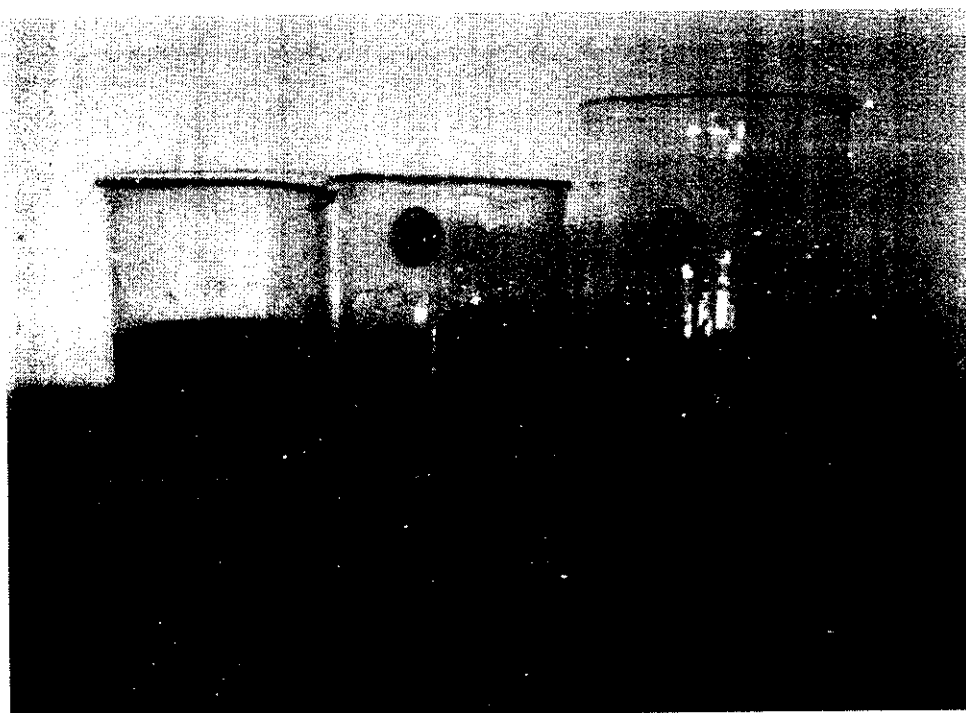
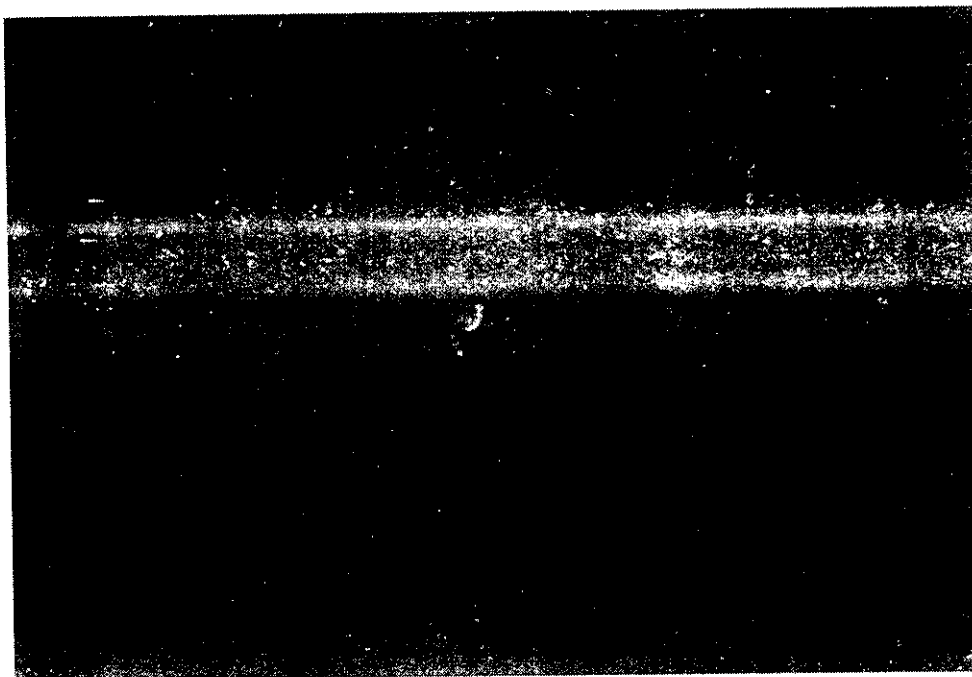


Fig V Treated effluent at different pH

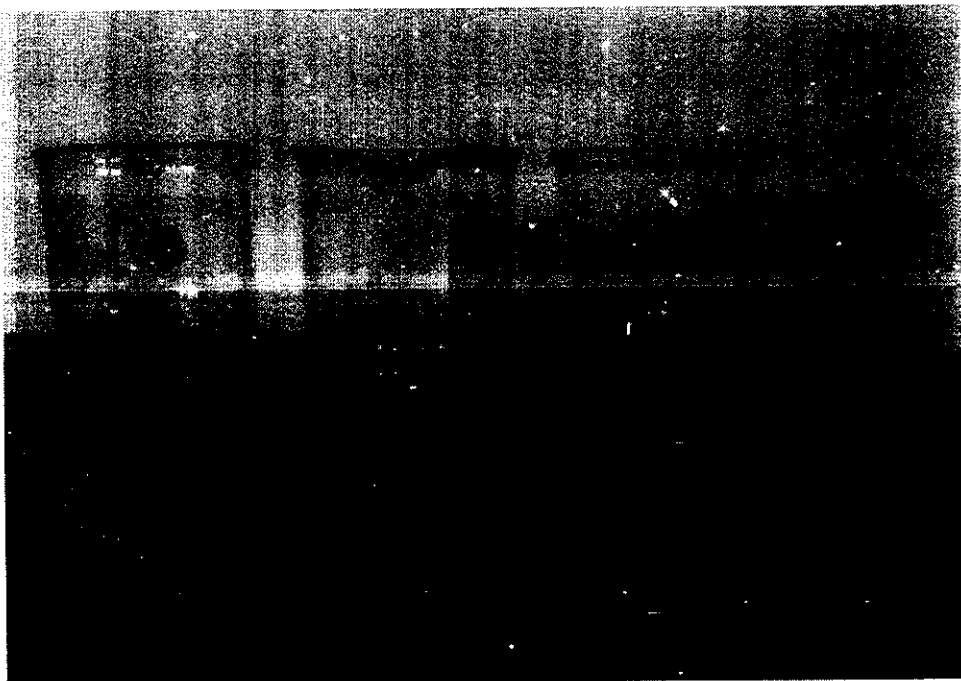
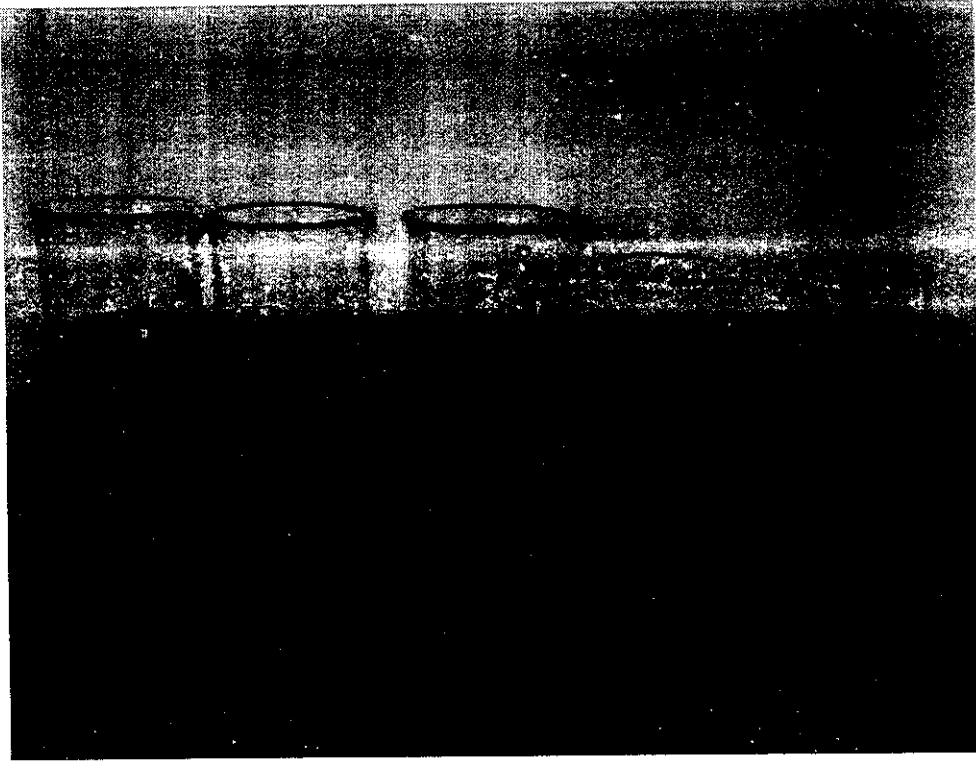
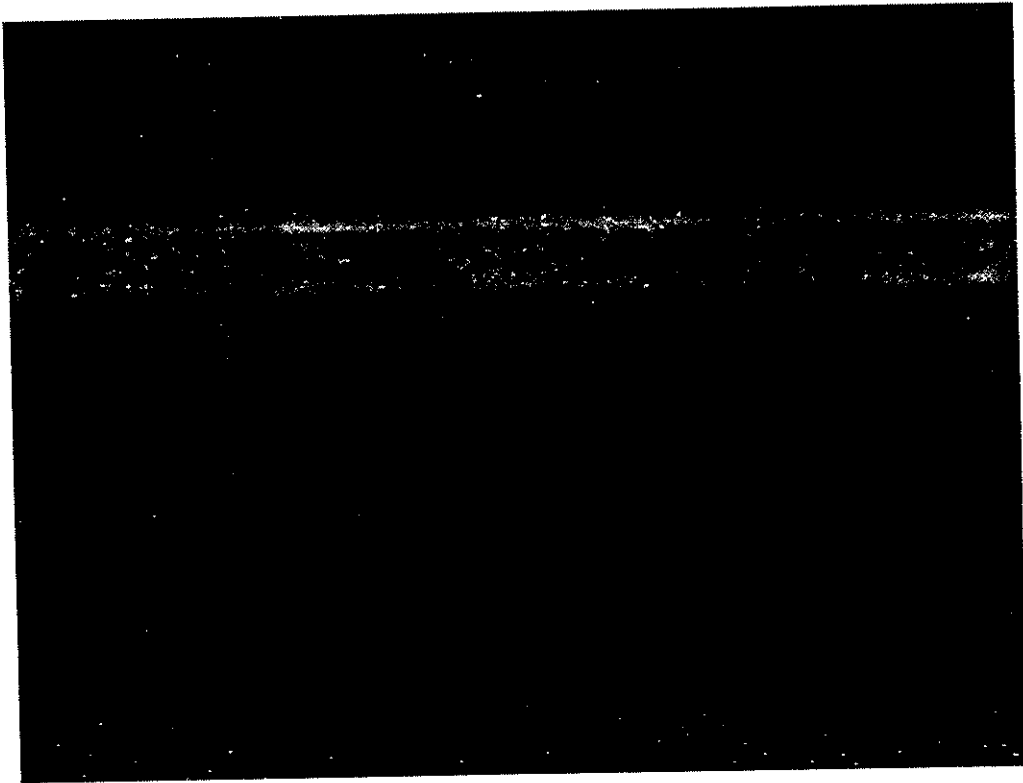


Fig VI Treated effluent at different contact time



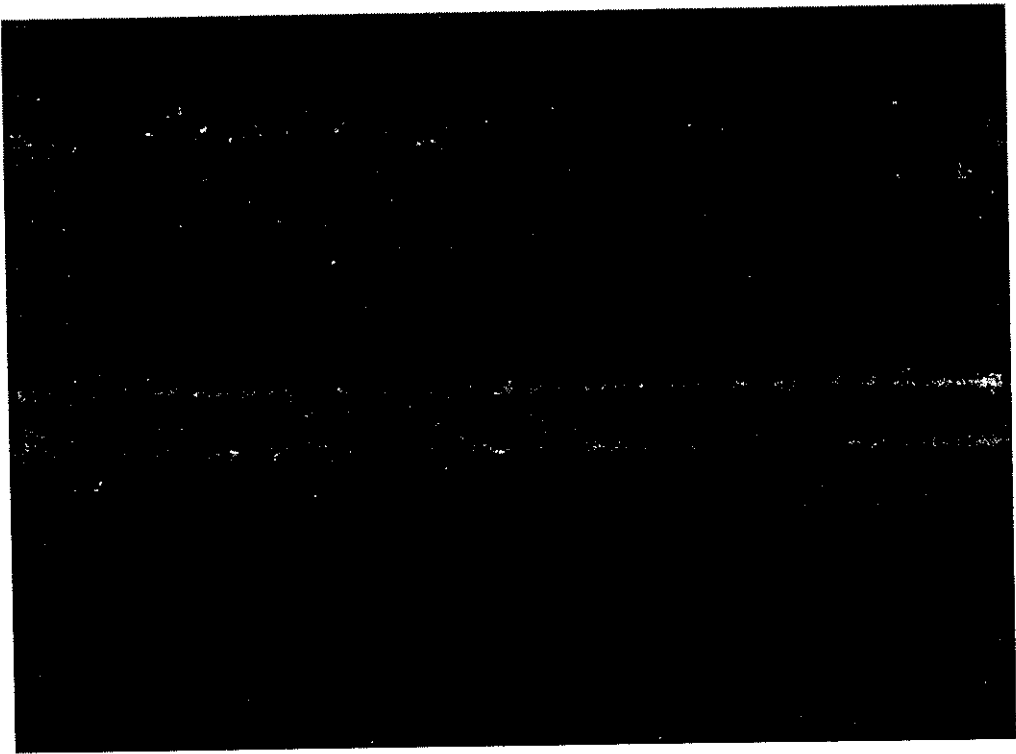
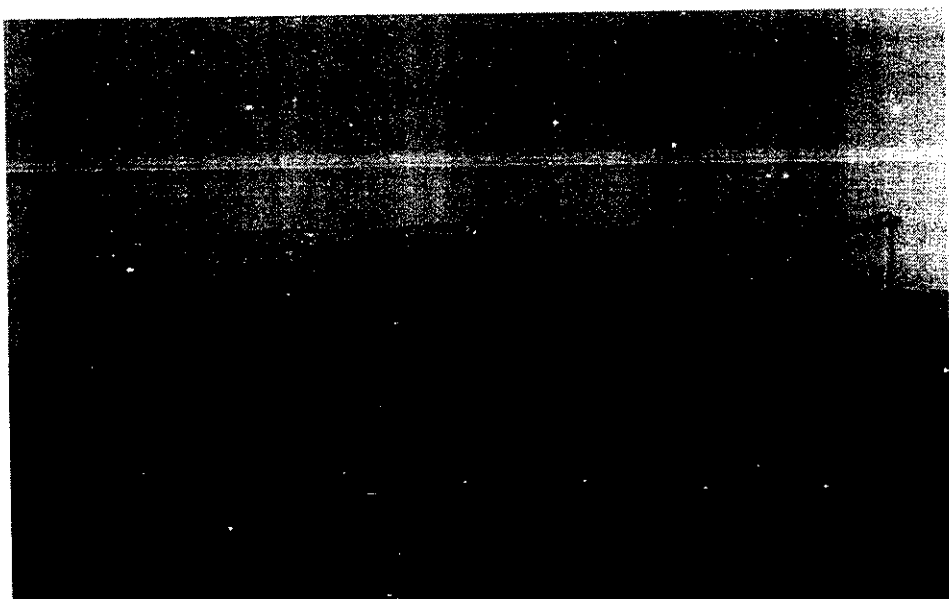


Fig VII Treated effluent at different dilutions



APPENDIX (II)

ESTIMATION OF CHROMIUM (VI) CONCENTRATION

STOCK PREPARATION

A stock solution was prepared by dissolving 10ml of raw electroplating effluent is made upto 1000ml with distilled water.

Preparation of 1,5- DPC Complexing Agent

The classical method of Cr(VI) analysis for industrial hygiene use was spectrometry using 1,5-diphenylcarbazide (DPC) for colour development after acid extraction of the Cr (VI) from the sample. Dissolve 0.5g of DPC in 100 ml of HPLC grade CH_3COCH_3 and add 28 ml of 98% H_2SO_4 to about 500 ml of distilled H_2O . Make additions very, very slowly, with mixing, and allow to cool. Mix the solutions carefully and dilute, with stirring, in a 1litre volumetric flask with distilled H_2O . Cool solution to room temperature. The reaction of the DPC with Cr (VI) will be incomplete if this solution is warm. Transfer the solution to the 1litre brown bottle and store in a cool dark place as the solution is sensitive to light. The solution is stable for up to 3 days but should only be prepared as it is used, 1litre at a time. The sensitivity of the method is dependent on the freshness of the DPC solution (NIOSH Manual of Analytical Methods).

Estimation of Free Chromium (VI) Ions – Spectrometric Method

. Adsorbent feed was given to the diluted effluent (1:100 dilution) and the experiment was carried out by agitating in a mechanical shaker for 24 hours. The concentration of free Cr (VI) ions was measured by reacting the solution with 1,5-DPC reagent and a pink colored complex was formed. The absorbance was measured using a spectrophotometer at 540nm.

Fig VIII: Interaction of free Cr (VI) with 1,5-DPC

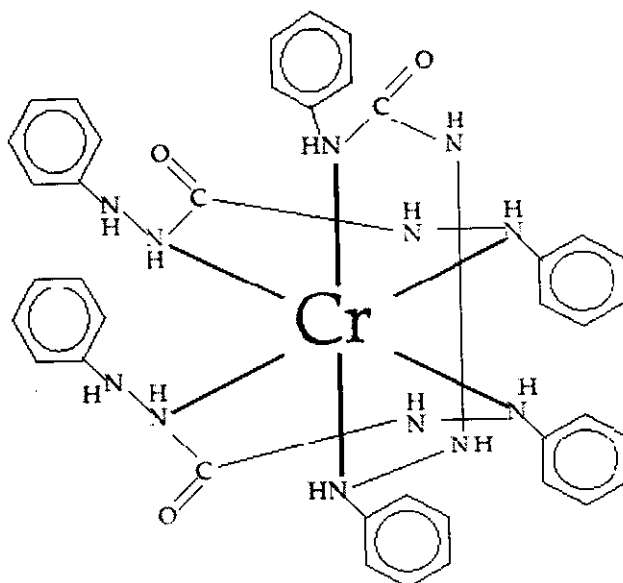


Table I: Estimation of chromium (VI) free ions – Spectrometric Method

| Reagents | B | S1 | S2 | S3 | S4 | S5 | T1 |
|--|---|------|------|------|------|-------|----|
| 1. Volume of standard Cr solution(ml) | 0 | 1 | 2 | 3 | 4 | 5 | - |
| 2. Concentration of standard Cr solution(ml) | - | 2000 | 4000 | 6000 | 8000 | 10000 | - |
| 3. Volume of effluent(ml) | - | - | - | - | - | - | 1 |

| | | | | | | | |
|--|---|-------|-------|-------|-------|-------|-------|
| 4. Volume of diluted 98% H ₂ SO ₄ (ml) 1:5 dilution with d.H ₂ O | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 5. Volume of distilled water(ml) | 8 | 7 | 6 | 5 | 4 | 2 | 7 |
| 6. Volume of DPC(ml) | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 7. Absorbance at 540 nm | 0 | 0.207 | 0.306 | 0.469 | 0.611 | 0.769 | 0.370 |

CALCULATION FOR BATCH ADSORPTION STUDY

- Adsorption capacities (q_e):

$$q_e = (C_i - C_e) / M * V$$

where

C_i – Initial Concentration (mg/ml)

C_f – Final Concentration (mg/ml)

M – Mass of the adsorbent (g)

V – Volume of solution (ml)

- Removal Efficiency of the adsorbent:

$$R(\%) = (C_i - C_e) / C_i * 100$$

where

C_i – Initial Concentration (mg/ml)

C_f – Final Concentration (mg/ml)

APPENDIX (III)

ISOTHERM AND KINETICS

ADSORPTION ISOTHERM

The distribution of metal ions between the liquid phase and the solid phase can be described by several isotherm models such as Langmuir and Freundlich. The isotherm equations of these models are summarized in the table below. The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. However, the Freundlich model assumes that the uptake of metal ions occurs on a heterogeneous surface by monolayer adsorption (Bulut and Baysal., 2006). In order to find the most appropriate model for the chromium adsorption, the data were fitted to both these isotherm models.

Table II: Isotherm Equations (Bulut and Baysal., 2006)

| Isotherm name | Isotherm Equation | Parameters |
|----------------------|--|--|
| Langmuir | $q_e = (\theta \cdot b \cdot C_e) / (1 + b \cdot C_e)$ | C_e : the equilibrium concentration(mg/l) q_e : the amount adsorbed per amount of adsorbent at the equilibrium(mg/g) θ : (mg/g) and b (l/mg): the Langmuir constants related to the maximum sorption capacity and energy of adsorption, respectively. |
| Freundlich | $q_e = K C_e^{(1/n)}$ | K (mg/g) : an indicator of the adsorption capacity. $(1/n)$ (mg/l): adsorption intensity. |

LANGMUIR ADSORPTION ISOTHERM

The Langmuir adsorption isotherm describes quantitatively the build up of a layer of molecules on an adsorbent surface as a function of the concentration of the adsorbed material in the liquid in which it is in contact. In a modified form it can also describe a bi-layer deposition. The shape of the isotherm (assuming the (x) axis represents the concentration of adsorbing material in the contacting liquid) is a gradual positive curve that flattens to a constant value. It often represents an initial surface adsorption followed by a condensation effect resulting from extremely strong solute-solute interaction.

The linear form of Langmuir isotherm is given by the following equation:

$$C_e/q_e = 1/(q_m K_a) + C_e/q_m \quad (1)$$

Where q_e is the amount adsorbed per unit mass of adsorbent (mg/g), C_e the equilibrium concentration of the adsorbate (mg/l), q_m the equilibrium sorption capacity for complete monolayer (mg/g) and K_a the sorption equilibrium constant (l/mg). When C_e/q_e was plotted against C_e , a straight line with slope $1/(K_a q_m)$ and an intercept of $1/q_m$ were obtained

According to Hall et al., (1966), the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_L which is defined by the following relationship:

$$K_L = 1/(1 + K_a C_0)$$

where K_L is a dimensionless separation factor, C_0 the initial concentration (mg/l), K_a the Langmuir constant (l/mg). The parameter K_L indicates the shape of the isotherm and nature of the adsorption process (Soon-An Ong et al., 2007).

[$K_L > 1$: Unfavorable; $K_L = 1$: Linear; $0 < K_L < 1$: Favorable; $K_L = 0$: Irreversible].

The value of K_L obtained was in between 0 and 1 indicating the favorable adsorption of Cr (VI).

FREUNDLICH ADSORPTION ISOTHERM

An adsorption isotherm is a curve relating the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact. The Freundlich isotherm curves in the opposite way of Langmuir isotherm and is exponential in form. It often represents an initial surface adsorption followed by a condensation effect resulting from extremely strong solute-solute interaction. The Freundlich isotherm (Freundlich, 1906) is the earliest known relationship describing the sorption equation. This fairly satisfactory empirical isotherm can be used for non-ideal sorption that involves heterogeneous sorption.

The linear form of Freundlich isotherm is given by the following equation:

$$\log(q_e) = 1/n \log(C_e) + \log(K_F)$$

Where q_e is the amount adsorbed per unit mass of adsorbent (mg/g), C_e the equilibrium concentration of the adsorbate (mg/l), K_F and n are Freundlich equilibrium coefficients.

$$\text{Slope} = 1/n$$

$$\text{Intercept} = \log K_F$$

ADSORPTION KINETICS

Lagergren first-order model (Lagergren, 1898):

$$\log(q_e - q_t) = \log q_e - K_{ad}t/2.303$$

Pseudo second-order model (Ho, 1995; Ho & Mckay, 2000):

$$t/q_t = 1/(K'q_e^2) + t/q_e$$

Lagergren second order model (Lagergren, 1898):

$$1/(q_e - q_t) = 1/q_e - Kt$$

Where q_t is the amount of heavy metal adsorbed per unit mass of adsorbent (mg/g) at time

t (min), q_e the amount of heavy metal adsorbed per unit mass of adsorbent (mg/g) at

equilibrium, K_{ad} the Lagergren rate constant (l/min), K' the pseudo second-order rate constant (g/mg.min) and K the second order rate constant (g/mg min). Linear plots of $\log (q_e - q_t)$ versus t , t/q_t versus t and $1/(q_e - q_t)$ versus t are drawn. The values of amount of adsorption equilibrium, q_e , Lagergren rate constant, K_{ad} , pseudo second order rate constant K' , pseudo second order rate constant, K , calculated amount of adsorption equilibrium, q_e , c , and the correlation coefficient, R^2 are calculated.

Linear plot of $\log (q_e - q_t)$ versus t

$$\text{Slope} = -K_{ad}/2.303$$

$$\text{Intercept} = \log q_e$$

Linear plot t/q_t versus t

$$\text{Slope} = 1/q_e$$

$$\text{Intercept} = 1/q_e^2 K'$$

Linear plot $1/(q_e - q_t)$ versus t

$$\text{Slope} = -K$$

$$\text{Intercept} = 1/q_e$$

REFERENCES

1. Abell, M.T. and Carlberg, J.R. (1974). 'A Simple Reliable Method for the Determination of Airborne Hexavalent Chromium', *Am. Ind. Hyg. Assoc. J.*, vol. 35, pp229-235.
2. Argun, M.E., *et al* (2006). 'Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics', *J. Hazard. Mater.*, vol.141 No.1,pp 77-85.
3. Babu, B.V. and Gupta,S. (2005). 'Modelling and Simulation of Fixed Bed Adsorption Column: Effect of Velocity Variation', *J. Eng. & Technol.*, vol. 1 No.1, pp. 60-66.
4. Baral, S. S., *et al* (2006). 'Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust', *Biochem. Eng. J.*,vol. 31 No.3, pp. 216-222.
5. Bishnoi, N. R., *et al* (2004). 'Adsorption of Cr(VI) on activated rice husk carbon and activated alumina', *Bioresource Technol.*, vol. 91 No. 3, pp 305-307
6. Bulut, Y and Baysal, Z. (2006). 'Removal of Pb(II) from wastewater using wheat bran', *J. Env. Mng.*, vol. 78 No. 2, pp.107-113.
7. Erdem M., *et al* (2004) 'Removal of hexavalent chromium by using heat-activated bauxite', *Minerals Engineering* (2004)., vol. 17 pp. 1045-1052
8. Guo, X.Y., *et al*(2008). 'Adsorption of metal ions on lignin', *J. Hazard. Mater.*,vol.151, pp.134-142.
9. Hemrajani, S.N and Narwani,C.S.(1967). *J. Indian Chem. Soc.*, vol. 44,pp. 704.

10. Hu, Z., Lei, L., Li, Y and Ni, Y. (2003). 'Chromium adsorption on high-performance activated carbons from aqueous solution', *Separation and Purification Technol.*, vol. 31, pp. 13-18.
11. Jianlong, W., Xinmin, Z and Yi, Q.(2000). 'Removal of Cr (VI) from Aqueous Solution by Macroporous Resion Adsorption', *J. Env. Sci. Health*, vol. 35 No.7, pp. 1211-1230.
12. Ko, D. C. K., Porter, J. F and McKay, G. (2000).*Chem. Eng. Sci.*, vol. 55,pp. 5819-5829.
13. Cabatingan, K.L and Agapay , C.R. *et al.*(2001). *Ind. Eng. Chem. Res.*, vol. 40, pp.2302.
14. Low, K. S., Lee, C. K., Wong, S. Y and Tang, P. L.(2000). *Environ. Technol.*, vol. 21, pp.1239-1244.
15. Mukherjee, S., Kumar, S., Misra, A.K. and Fan, M. (2007). 'Removal of phenol from water environment by activated carbon bagasse ash and wood charcoal,' *Chem. Eng. J.*, vol.129, pp.133-142.
16. Namasivayam, C .and Yamuna, R. T., (1995). 'Adsorption of chromium (VI) by a low-cost adsorbent: biogas residual slurry.', *Chemosphere*, vol. 30 No. 3, pp. 561-578.
17. NIOSH (1975) Criteria for a Recommended Standard.' Occupational Exposure to Chromium (VI) Cincinnati, OH: U.S. Department of Health, Education, and Welfare, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication', pp.76-129.

18. NIOSH/OSHA (1981) Occupational Health Guidelines for Chemical Hazards. 'Occupational Health Guidelines for Chromic Acid and Chromates, U.S. Department of Health and Human Services (NIOSH) Publication', pp. 81-123.
19. Park, D., Yun, Y.S and Park, J.M. (2004). 'Reduction of hexavalent chromium with the brown seaweed *Ecklonia* biomass', *Environ. Sci. Technol.*, vol. 38, pp. 4860-4864.
20. Park, D., et al (2004). 'Use of dead fungal biomass for the detoxification of hexavalent chromium: screening and kinetics', *Process Biochemistry* (2005) vol. 40 pp. 2559-2565
21. Qaiser, S., et al (2007) ,Heavy metal uptake by agro based waste materials, *Electronic J. Biotech*'.vol. 10, pp.409-416.
22. Sarin, V., Pant, K. K., (2006). 'Removal of chromium from industrial waste by using eucalyptus bark', *Bioresource Technol.*, vol. 97 No.1, pp. 15-20.
23. Selvaraj, K., et al (2003). 'Removal of hexavalent chromium using distillery sludge', *Biores Technol.*, vol.89, pp. 207-211.
24. Sen, M., and Dastidar, M (2010). 'Chromium removal using various biosorbents', *Iran. J. Environ. Health. Sci. Eng.*, 2010, Vol. 7, No. 3, pp. 182-190
25. Sharma, A. and Bhattacharyya, K. G. (2004). 'Adsorption of Chromium (VI) on *Azadirachta indica* (Neem) Leaf Powder, *Adsorption*', vol. 10, pp. 327-338.
26. Thomsen, E. and R.M. Stern(1979). 'A Simple Analytical Technique for the Determination of Hexavalent Chromium in Welding Fumes and Other Complex Matrices'. *Scand. J. of Work, Environ. and Health*, vol. 5, pp. 386-403.

27. Tunali, S., *et al* (2006). 'Removal of lead and copper ions from aqueous solutions by bacterial strain isolated from soil', *Chem. Eng. J.*, vol. 115, pp. 203–211.
28. Veglio, F., *et al* (2000). *Ind. Eng. Chem. Res.*, vol. 39, pp. 2480.
29. Weston, A. and Murthy, M.(1996). 'Synthesis of Fullerenes: An Effort to Optimize Process Parameters, Carbon', vol. 34, pp. 1267-1274.
30. Yu, J., *et al* (2007). 'Cystine-modified biomass for Cd(II) and Pb(II) biosorption,' *J. of Hazard. Mater.*, vol.143, pp. 277-284.