

ADSORPTION OF HEAVY METAL Cr (VI) USING LOW COST ADSORBENTS

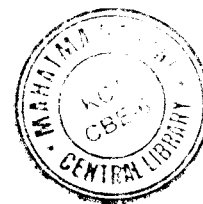
A PROJECT REPORT

Submitted by

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In partial fulfilment for the award of the degree

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APRIL 2009

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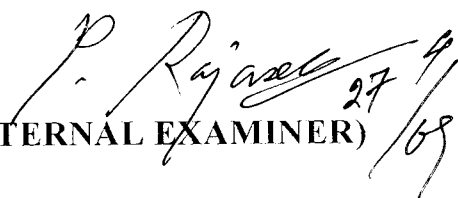
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DEDICATED TO

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ABSTRACT

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In developing countries where cost is often an important factor, many studies were done to determine the effectiveness and reliable factors in removing heavy metals from wastewaters using low cost adsorbent. This project study presents results pertaining to the adsorption studies carried out on chromium (VI) removal onto low cost adsorbents such as Almond leaves, peanut shells, egg shells and tile wastes using a simulated effluent. Influence of varying the conditions for removal of chromium (VI), such as the pH of the aqueous solution, the dosage of adsorbent, and the contact time with the adsorbent were investigated with each of the adsorbents mentioned by method of batch adsorption studies. The adsorption of Cr (VI) was found to be maximum at pH 3 and the removal efficiency was found to increase with the adsorbent dosage. Continuous adsorption using columns packed with the adsorbents were also investigated and reported. The results indicate that the low cost Almond leaves can be alternatively used to the commercially available adsorbents in the removal of hexavalent chromium, a known toxin from water and wastewater followed by the other adsorbents mentioned here that also showed appreciable removal efficiency. The isotherm studies of Langmuir and Freundlich indicated that almond leaves adsorbent was most effective, observed from their high correlation values. The pseudo first-order, pseudo second-order, second-order were used to analyze the kinetic data and the rate constants were evaluated. The kinetic adsorption data fitted the pseudo second-order kinetic model for almond leaves, peanut shells and egg shells whereas tile wastes followed a second-order.

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LIST OF ABBREVIATIONS

1,5- DPC	1, 5-diphenylcarbazide
MCS	Material control system
DI H ₂ O	De-ionised water
HPLC	High performance liquid chromatography
NIOSH	National Institute for Occupational Safety and Health
RHSD	Restriction of Hazardous Substances Directive

INTRODUCTION

CHAPTER 1

INTRODUCTION

1.1 TOXIC HEAVY METALS

Toxic metals are metals that form poisonous soluble compounds and have no biological role. Toxic metals sometimes imitate the action of an essential element in the body, interfering with the metabolic process to cause illness. Many metals, particularly heavy metals are toxic, but some heavy metals are essential and have a low toxicity. Toxic metals can bioaccumulate in the body and in the food chain causing deleterious effects. Therefore, a common characteristic of toxic metals is the chronic nature of their toxicity.

Toxic heavy metals are released into the environment from a number of industries such as mining, plating, dyeing, automobile manufacturing and metal processing. The presence of heavy metals in the environment has led to a number of environmental problems. In order to meet the water quality standards for most of countries and to prevent the widespread of diseases due to heavy metals, the concentration of heavy metals in wastewater must be controlled. Conventional physico-chemical treatment methods for removing heavy metals include precipitation, filtration, oxidation-reduction, ion exchange and membrane separation. However, when metals are dissolved in huge volumes at relatively low concentration, these methods become generally ineffective or expensive [Aderhold *et al.*, 1996; Blanco *et al.*, 1999; Lee and Suh., 2000; Eccles., 1995]. Therefore, there is a need for development of a low cost process to

remove heavy metals economically. Adsorption is one such effective technique for toxic metal removal from wastewater (Babu and Gupta., 2005).

1.2 LIST OF TOXIC HEAVY METALS

- Aluminium
- Cadmium
- Lead
- Mercury
- Thallium
- Vanadium
- Chromium
- Nickel
- Copper
- Iron

1.3 CHROMIUM

Chromium mainly exists in two states namely Cr (III) and Cr (VI). Cr (III) is an essential trace element, but chromium (VI) is a carcinogen. The toxicity of any metal depends on its ligands. Chromium is a natural constituent of the earth's crust and present in several oxidation states.

Trivalent chromium (Cr^{3+}) is naturally occurring, environmentally pervasive and a trace element in man and animals. Hexavalent chromium is generated anthropogenically from a number of commercial and industrial sources. Hexavalent Chromium (Cr^{6+}) readily penetrates

biological membranes and has been identified as an industrial toxic and cancer causing substance. Hexavalent chromium is a known inhalation irritant and associated with respiratory cancer and it is primarily associated with the chrome plating and anodizing process and emissions from chromate-treated cooling towers.

1.4 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).

1.5 EFFECTS OF CHROMIUM (VI)

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

Chromium (III) is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much chromium (III) can cause health effects as well, for instance skin rashes.

Hexavalent chromium is transported into cells via the sulfate transport mechanisms, taking advantage of the similarity of sulfate and chromate with respect to their structure and charge. Trivalent chromium, which is the more common variety of chromium compounds, is not transported into cells.

Inside the cell, Cr (VI) is reduced first to metastable pentavalent chromium Cr (V), then to trivalent chromium Cr (III). Trivalent chromium binds to proteins and creates haptens that trigger immune response. Once developed, chrome sensitivity can be persistent. In such cases, contact with chromate-dyed textiles or wearing of chromate-tanned leather shoes can cause or exacerbate contact dermatitis. Vitamin C and other reducing agents combine with chromate to give Cr (III) products inside the cell.

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

- Skin rashes
- Upset stomachs and ulcers
- Respiratory problems
- Weakened immune systems
- Kidney and liver damage
- Alteration of genetic material
- Lung cancer

The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in this product) is of low toxicity. The hexavalent form is toxic. Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions. Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch.

1.6 ADSORPTION

Adsorption is an effective technique for Cr (VI) removal from wastewater (Babu and Gupta., 2005). It is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms. 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. Recently, the removal of Cr (VI) from aqueous solution was studied by natural, low-cost materials such as sphagnum mass peat, saw dust, leaf mould, sugar beet pulp, bagasse, maize cob, biogas residual slurry, Fe (III)/Cr (III) hydroxide (Hu et al 2003) and Neem leaves (*Azadirachta indica*).

In the present study a non-conventional adsorbent from the leaves of the Almond leaves, powdered egg shells, powdered peanut shells, tile wastes were developed as adsorbents which was used for the removal of the toxic pollutant - Cr(VI) in aqueous medium. Adsorption capacity of these adsorbents were compared 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 these adsorbents was also evaluated.

1.7 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.

1.8 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).

1.9 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.

OBJECTIVES

CHAPTER 2

OBJECTIVES

The main objectives of this study are

- i. To investigate the Cr (VI) adsorption by low cost adsorbents.
- ii. To perform the batch and continuous study on adsorption of Cr (VI) from the stimulated effluent.
- iii. To study the influence of pH, adsorbent dose and initial chromium concentration on adsorption.
- iv. To determine appropriate adsorption isotherm and kinetics parameters of Cr (VI) adsorption.

LITERATURE REVIEW

CHAPTER 3

LITERATURE REVIEW



3.1 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 3^2 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).

3.2 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 removed up to 99.6% of the 1.5 mg/l of arsenic ion in synthetic water within the first 6 hours 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).

3.3 NEEM LEAVES AS ADSORBENT

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

environmental issues. 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).

3.4 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).

3.5 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 very well. The heat of biosorption was evaluated from the Langmuir isotherm equation, and the biosorption of lead, copper and cadmium was endothermic reaction (Young Kim *et al.*, 2005).

3.6 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).

3.7 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 industrial wastewaters has been investigated by 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).

3.8 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).

3.9 SAWDUST AS ADSORBENT

The purpose of this study conducted by Adouby is in the use of *Pterygota macrocarpa* sawdust as adsorbent 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).

3.10 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).

3.11 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).

3.12 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).

MATERIALS AND METHODS

CHAPTER 4

MATERIALS AND METHODS

4.1 ADSORBENT MATERIALS AND CHEMICALS

4.1.1 Adsorbent materials used

- Almond leaves
- Peanut shells
- Tile wastes and
- Egg shells.

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, 0.2N H₂SO₄, HCl, NaOH and distilled water were also used.

4.2 ADSORBENT PREPARATION

4.2.1 Peanut shells

Peanut (*Arachis hypogaea*) shells were collected and dried in sunlight for 7 days. They were ground to fine powder and sieved using a mesh size of 150µm.

4.2.2 Almond leaves

The Almond (*Terminalia catappa*) leaves were collected and dried in sunlight for 4 days. The ground powder was boiled in distilled water, filtered several times and dried again. The remaining moisture content was removed in hot air oven at 50°C for 2 days. It was sieved using 150µm sieve and the powder was stored.

4.2.3 Tile wastes

The waste tiles were collected from building construction sites within our college premises. It was then ground to fine powder using a jaw crusher and sieved using a 150µm sieve.

4.2.4 Egg shells

Egg shells were collected and soaked in 1% sodium hydroxide for 20 minutes and rinsed with distilled water. The moisture content was removed by keeping in a hot air oven at 50°C for an hour, powdered and sieved using 150µm sieve.

4.3 STOCK PREPARATION (Simulated effluent)

A stock solution (100mg/ml) of Cr (VI) was prepared by dissolving 2.8287 g of 99.9% $K_2Cr_2O_7$ in 1000ml of distilled water.

4.3.1 Preparation of Working Standard

The stock solution was diluted as required to obtain working standard solutions containing 20-100 mg/l of Cr (VI).

4.4 BATCH ADSORPTION STUDY

Batch adsorption experiments were conducted by agitating the flasks with each of the adsorbent and varying concentration of chromium solution (simulated effluent) from 20-100mg/l for a period of 8 hours at $30 \pm 10^{\circ}\text{C}$ in a mechanical shaker. Experiments were also carried out by varying the adsorbent dosage from 1g to 5g of all the adsorbents mentioned (Gupta *et al.*, 2005). 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 1-5 at an optimal simulated effluent concentration of 50mg/l with an adsorbent dosage of 2g for a time period of 8 hours. Adjustments to pH were made with HCl and NaOH (Nameni *et al.*, 2008).

4.6 EFFECT OF ADSORBENT DOSAGE ON INITIAL CONCENTRATION FOR 3 HOURS

To determine the effect of adsorbent dosage on adsorption, 100 ml of heavy metal solution of known concentration (50mg/ml) was added to, 1 to 5 g of adsorbent in a 150 ml conical flask and the mixture was stirred on a thermostat shaker bath for a contact time of 3 hours (Soon-An Ong *et al.*, 2007). Then, the solution was centrifuged at the speed of 6000

RPM, filtered, and then the supernatant was analyzed for Cr (VI) estimation by colorimetric method. [APPENDIX II]

4.7 CONTINUOUS ADSORPTION STUDY

The continuous adsorption of Cr (VI) was performed in a fixed-bed column packed with the various adsorbent materials. Inlet and outlet flow rate was measured. Solution at the outlet was collected for every 20 min interval and subjected to Cr (VI) estimation. [APPENDIX II]

4.8 ADSORPTION ISOTHERM

For adsorption isotherm study, 100 ml of heavy metal solution of known concentration (50mg/ml) was added to 5 g of all mentioned adsorbent materials in a 150 ml conical flask and the mixture was stirred on a thermostat shaker bath for a contact time of 8 hours. Then, the solution was centrifuged at 6000 rpm, filtered, and then the supernatant was analyzed for heavy metal Cr (VI) concentration by colorimetric method. [APPENDIX III]

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 0 and 180 min 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)

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

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). [APPENDIX III]

RESULTS AND DISCUSSION

CHAPTER 5

RESULTS AND DISCUSSION

5.1 STANDARD GRAPH CALIBRATION

Table 5.1 Estimation of Cr (VI)-COLORIMETRIC METHOD

REAGENTS	B	S1	S2	S3	S4	S5
Volume of working standard(ml)	-	20	40	60	80	100
Concentration of working standard (100mg/ml)	-	20	40	60	80	100
Volume of working sample(ml)	-	2	2	2	2	2
Volume of 0.2N H ₂ SO ₄ (ml)	5	5	5	5	5	5
Make up to 100ml with distilled water						
Kept at room temperature for 15 minutes						
Volume of 1,5- DPC reagent added(ml)	5	5	5	5	5	5
Kept at room temperature for an hour						
Absorbance at 540nm	0.00	.086	.196	.275	.369	.421

2ml of known standard Chromium solution sample was taken and 5ml of 0.2N Sulphuric acid was taken in a standard flask and made upto 100ml. After 15 minutes, 5 ml of 1,5- DPC was added and mixed well. The absorbance was measured at 540 nm using a Beckman BU 530 spectrophotometer after an incubation period of 1 hour. The standard graph was plotted by taking concentration along X axis and absorbance along Y axis. A straight line was obtained with a slope value of 0.0044 and R2 value of 0.9914 as shown in the fig 5.1.

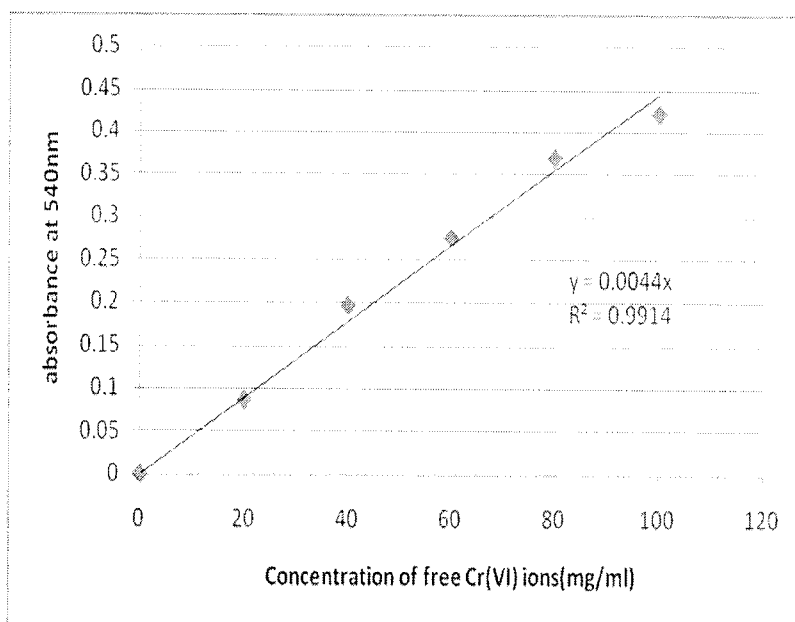


Fig 5.1 Standard graph for Cr (VI) estimation-Colorimetric Method

5.2 BATCH ADSORPTION STUDY

Table 5.2 Adsorption of Cr (VI) using tile waste after 8 hours

Adsorbent Dosage (g)	Initial concentration C_i (mg/ml)	Final concentration C_f (mg/ml)	q_e (mg/g)	%R
1	20	-	-	-
	40	-	-	-
	60	-	-	-
	80	-	-	-
	100	-	-	-
2	20	-	-	-
	40	-	-	-
	60	-	-	-
	80	-	-	-
	100	-	-	-
3	20	-	-	-
	40	-	-	-
	60	48	4	20.00
	80	71	3	11.25
	100	93	2.3	7.00

4	20	16	1.0	20.0
	40	33	1.75	7.50
	60	39	5.25	35.00
	80	63	4.25	21.25
	100	86	3.50	14.00
5	20	12	1.6	40.00
	40	26	2.8	35.00
	60	32	5.60	46.66
	80	48	6.40	40.00
	100	68	6.40	32.00

Table 5.3 Adsorption of Cr (VI) using egg shell after 8 hours

Adsorbent Dosage (g)	Initial concentration C_i(mg/ml)	Final concentration C_f(mg/ml)	q_e (mg/g)	%R
1	20	-	-	-
	40	-	-	-
	60	-	-	-
	80	-	-	-
	100	-	-	-

2	20	18	1.0	10.0
	40	35	2.5	12.5
	60	54	3.0	10.0
	80	68	6.0	15.0
	100	83	8.5	17.0
3	20	16	1.33	20.0
	40	28	4.0	30.0
	60	51	3.0	15.0
	80	65	5.0	18.75
	100	52	16.0	48.0
4	20	13	1.75	35.0
	40	21	4.75	47.5
	60	30	7.50	50.0
	80	51	7.25	36.25
	100	48	13.0	52
5	20	6	2.8	70
	40	11	5.8	72.5
	60	26	6.8	56.6
	80	44	7.2	45
	100	31	13.8	69

Table 5.4 Adsorption of Cr (VI) using peanut shell after 8 hours

Adsorbent Dosage (g)	Initial concentration C_i(mg/ml)	Final concentration C_f(mg/ml)	q_e (mg/g)	%R
1	20	-	-	-
	40	-	-	-
	60	-	-	-
	80	-	-	-
	100	-	-	-
2	20	20	-	-
	40	39	0.5	2.5
	60	44	8.0	26.67
	80	75	2.5	6.25
	100	92	4.0	8.0
3	20	17	1.0	15.0
	40	33	2.33	17.5
	60	39	7.0	35.0
	80	67	4.33	16.25
	100	81	6.33	19.0

4	20	13	1.75	35.0
	40	30	2.5	25.0
	60	27	8.25	55.0
	80	63	4.25	21.25
	100	71	7.25	29.00
5	20	0	4.0	100
	40	12	5.6	70.0
	60	17	8.6	71.67
	80	36	8.8	55.0
	100	41	11.8	59.0

Table 5.5 Adsorption of Cr (VI) using almond leaves after 8 hours

Adsorbent Dosage (g)	Initial concentration C_i(mg/ml)	Final concentration C_f(mg/ml)	q_e(mg/g)	%R
1	20	18	2.0	10
	40	32	8.0	20
	60	56	4.0	6.67
	80	74	6.0	7.5
	100	91	9.0	9.0

2	20	14	3.0	30.0
	40	26	7.0	35.0
	60	49	5.5	18.3
	80	69	5.5	13.75
	100	87	6.5	13.0
3	20	11	3.0	45.0
	40	21	6.33	47.5
	60	42	6.0	30.0
	80	59	7.0	26.25
	100	65	11.6	35.0
4	20	0	5.0	100
	40	0	10.0	100
	60	0	15.0	100
	80	2	19.5	61.25
	100	10	22.5	71.0
5	20	0	4.0	100
	40	0	8.0	100
	60	0	12.0	100
	80	0	16.0	100
	100	8	18.4	92

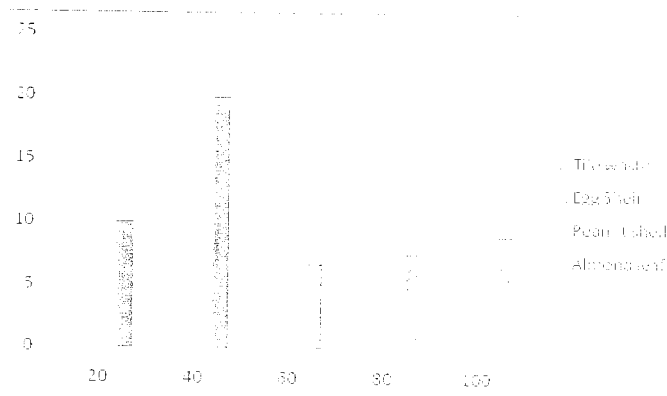
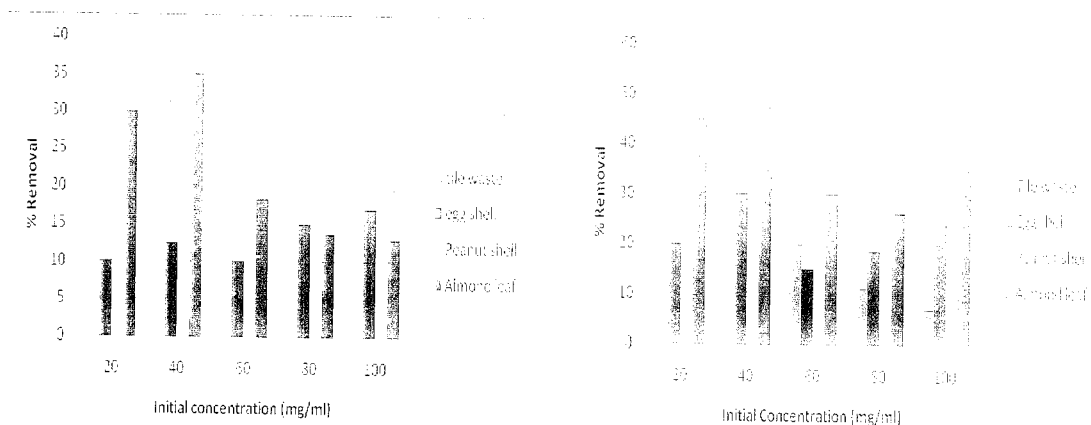


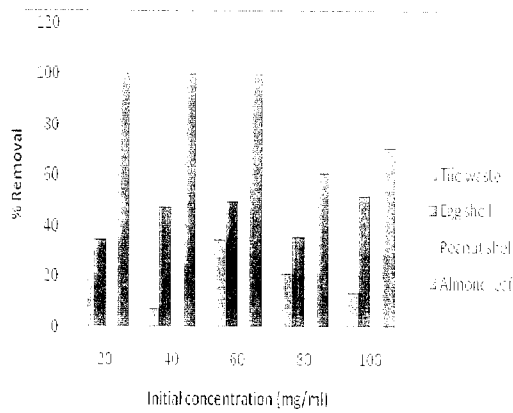
Fig 5.2 Plot for Initial concentration Vs % removal for almond leaves at an adsorbent dosage of 1g



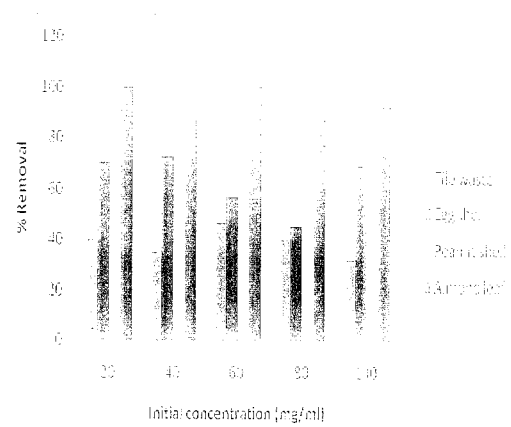
(a)

(b)

Fig 5.3 Plot for initial concentration Vs % removal at an adsorbent dosage of (a) 2g and (b) 3g.



(c)



(d)

Fig 5.4 Plot for initial concentration Vs % removal at an adsorbent dosage of (c) 4g and (d) 5g.

- The removal efficiency of the selected adsorbents increases with the increasing dosage levels of the adsorbents.
- The batch adsorption study result shows that almond leaves adsorbent showed effective removal of Cr (VI) even at a dosage level of 1g. Maximum adsorption occurs from 4g.
- Almond leaves showed complete removal of Cr (VI) and a maximum adsorption capacity (q_c) of 22.5mg/g
- Peanut shells, Tile wastes and Egg shells showed no removal of Cr (VI) at dosage level of 1g.
- Peanut shells has maximum adsorption capacity (q_c) of 11.8mg/g and 100% removal efficiency at adsorbent dosage of 5g.
- Tile wastes showed maximum removal efficiency (%R) of 46.66% at a dosage level of 5g and maximum adsorption capacity (q_c) of 6.40mg/g.

- Egg shell adsorbents showed maximum adsorption capacity (q_d) and removal efficiency (%R) of about 22.5mg/g and 72.5% respectively.

5.3 EFFECT OF pH

The optimum pH for maximum removal of Chromium (VI) was observed at pH 3.0 as shown in the fig 4.5. At pH 3.0, the maximum removal of Cr (VI) was seen for Almond leaves, followed by Peanut shells, Egg shells and Tile wastes.

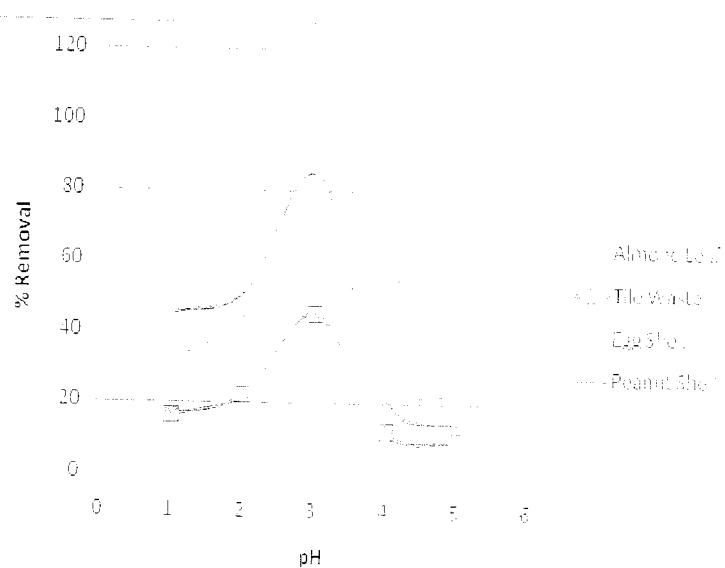


Fig 5.5 Effect of pH on % removal for an adsorbent dosage of 2g

5.4 EFFECT OF ADSORBENT DOSAGE ON INITIAL CONCENTRATION FOR 3 HOURS

Table 5.6 Adsorption using various dosage of egg shell powder

Adsorbent Dosage (g)	Initial Concentration (C_i) (mg/ml)	Final Concentration (C_f) (mg/ml)	q_e (mg/g)	R (%)
1	50	-	-	-
2	50	-	-	-
3	50	50	0	0
4	50	38	3	24
5	50	15	7	70

Table 5.7 Adsorption using various dosage of almond leaves powder

Adsorbent Dosage (g)	Initial Concentration (C_i) (mg/ml)	Final Concentration (C_f) (mg/ml)	q_e (mg/g)	R(%)
1	50	1.5	48.5	97
2	50	5	22.5	90
3	50	0	16.67	100
4	50	1.2	12.20	97.6
5	50	0	16.67	100

Table 5.8 Adsorption using various dosage of tile waste

Adsorbent Dosage (g)	Initial Concentration (C_i) (mg/ml)	Final Concentration (C_f) (mg/ml)	q_e (mg/g)	R(%)
1	50	-	-	-
2	50	-	-	-
3	50	-	-	-
4	50	50	0	0
5	50	38	3	24

Table 5.9 Adsorption using various dosage of peanut shell powder

Adsorbent Dosage (g)	Initial Concentration (C_i) (mg/ml)	Final Concentration (C_f) (mg/ml)	q_e (mg/g)	R(%)
1	50	-	-	-
2	50	42	4	16
3	50	2	16	96
4	50	22	7	56
5	50	0	10	100

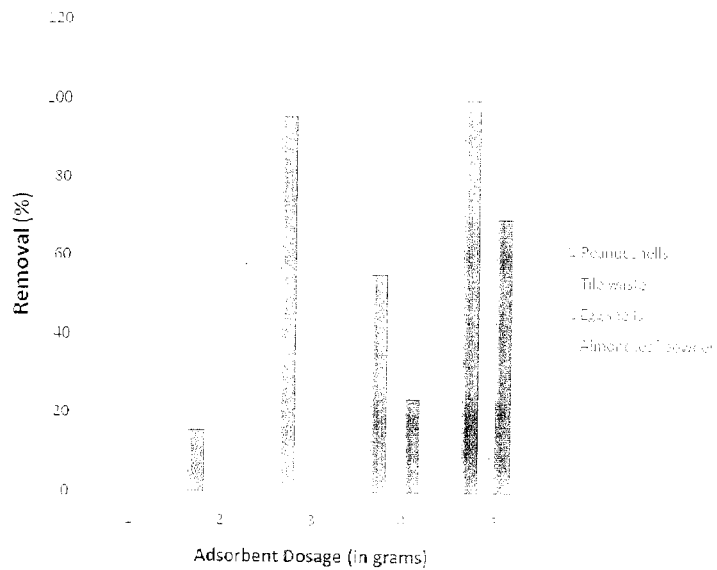


Fig 5.6 Effect of Adsorbent Dosage Vs % Removal

- Egg shells and Peanut shells showed a maximum removal of Cr (VI) at 5g after a treatment of 3 hours.
- Almond leaves showed maximum adsorption of Cr (VI) from 3g.
- Tile waste showed removal of Cr (VI) for an adsorbent feed of 5g whereas, no adsorption was observed at any other dosage levels.

5.5 CONTINUOUS ADSORPTION STUDY

Table 5.10 Continuous Adsorption Studies Using Peanut Shell, Almond Leaves , Tile Waste and Egg shell.

ADSORBENT	ALMOND LEAVES	EGG SHELL	PEANUT SHELL	TILE WASTE
Time (min)	Absorbance at 540 nm			
0	.009	.016	.009	.038
20	.012	.029	.048	.104
40	.013	.093	.114	.143
60	.019	.143	.165	.161
80	.020	.153	.179	.176
100	.029	.163	.198	.179
120	.031	.181	.233	.189
140	.038	.192	.236	.188
160	.036	.197	.235	.185
180	.033	.194	.239	.185



Fig 5.7 Absorbance Vs Time

From Fig 5.7 it is seen that the absorbance increases at time increases. The bed becomes saturated from 120 minutes and the concentration of Cr (VI) at the outlet attains a constant value.

5.6 EQUILIBRIUM TIME STUDY

Fig. 5.8 shows the time profiles of peanut shells, tile wastes, egg shells and almond leaves adsorption with Cr (VI) ions in aqueous solution. The adsorption of Cr (VI) was rapid in the first 1.5 h and followed by a slower rate of adsorption which adsorption appeared to have approached equilibrium.

Table 5.11 Equilibrium Time Study Using Peanut Shell, Almond Leaves , Tile Waste and Egg shell.

ADSORBENT	ALMOND LEAVES	EGG SHELL	PEANUT SHELL	TILE WASTE
Time (min)	x/m (mg/g)			
0	.01	0.2	.09	0.07
20	.01	0.3	0.5	0.4

40	.02	0.9	1.2	1.0
60	.09	1.5	1.7	1.4
80	.09	1.59	1.65	1.6
100	.29	2	1.67	1.75
120	.35	1.9	2.3	1.7
140	.36	-	2.44	1.9
160	.4	-	2.4	1.9
180	.033	-	2.4	1.9

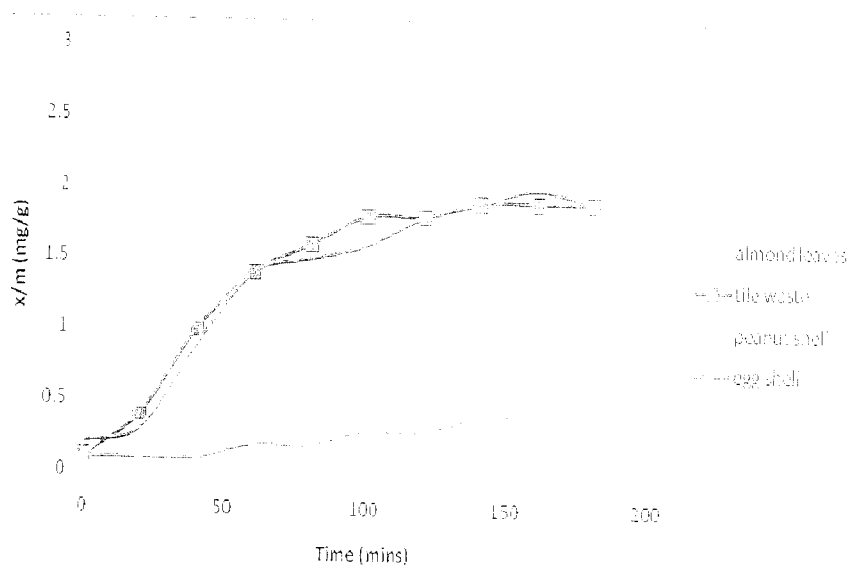


Fig 5.8 Contact time study for heavy metal Cr (VI) adsorption

5.7 ADSORPTION ISOTHERM

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

Table 5.12 Langmuir and Freundlich Isotherm

Almond leaves		Tile waste		Peanut shell		Egg Shell	
C_e (mg/l)	q_e (mg/g)	C_e (mg/l)	q_e (mg/g)	C_e (mg/l)	q_e (mg/g)	C_e (mg/l)	q_e (mg/g)
1	.18	.15	2.4	40	2	0.4	3
6	.4	.35	3.5	75	3	0.8	5
8	.48	.75	5.2	90	3.57	1.0	6
-	-	.85	5.9	-	-	1.3	7.9
-	-	-	-	-	-	1.4	8

5.7.1 Langmuir Isotherm

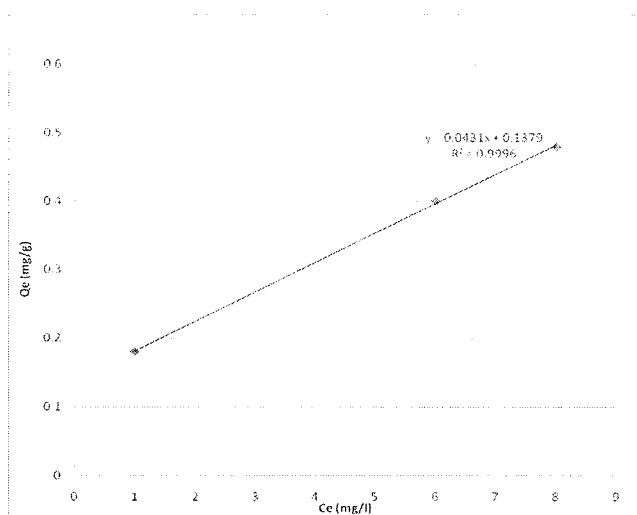


Fig 5.9 Langmuir plot for Cr (VI) Adsorption on Almond Leaf Adsorbent

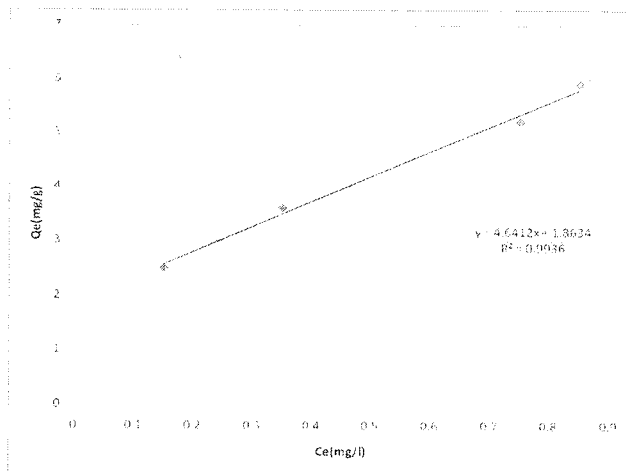


Fig 5.10 Langmuir Plot for Cr (VI) Adsorption on Tile waste Adsorbent

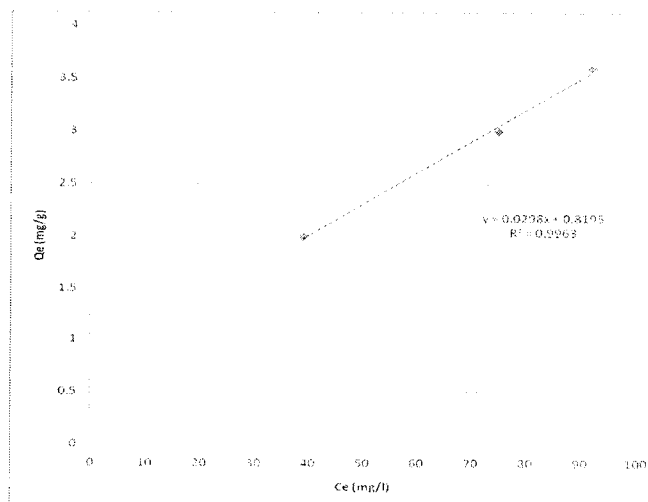


Fig 5.11 Langmuir Plot for Cr (VI) Adsorption on Peanut Shell Adsorbent

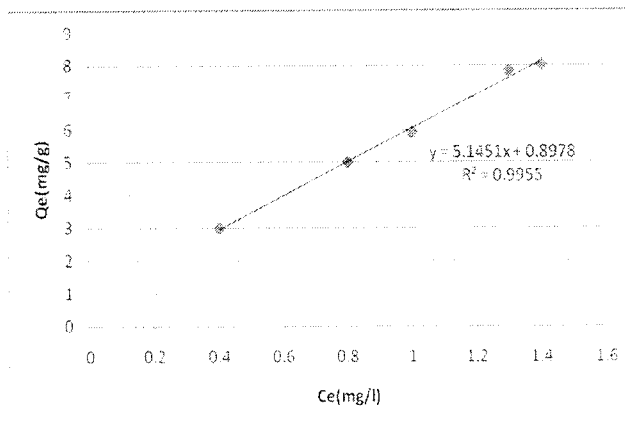


Fig 5.12 Langmuir Plot for Cr (VI) Adsorption on Egg Shell Adsorbent

Table 5.13 Langmuir Parameters

Adsorbent	Q_m (mg/g)	K_a	R^2
Peanut shells	1.221	27.5	0.996
Tile waste	0.536	0.401	0.993
Egg Shells	1.11	0.175	0.995
Almond Leaves	7.251	3.199	0.999

5.7.2 Freundlich Isotherm

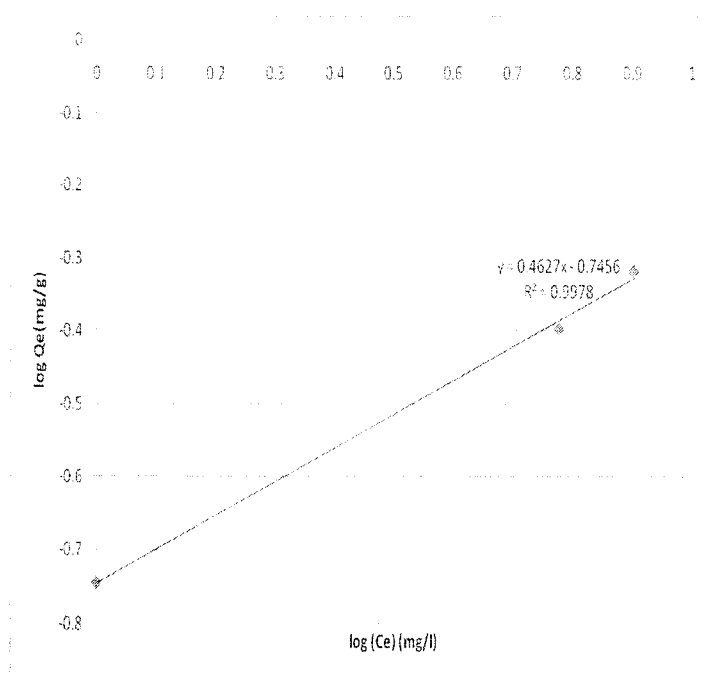


Fig 5.13 Freundlich Plot for Cr (VI) Adsorption on Almond Leaf Adsorbent

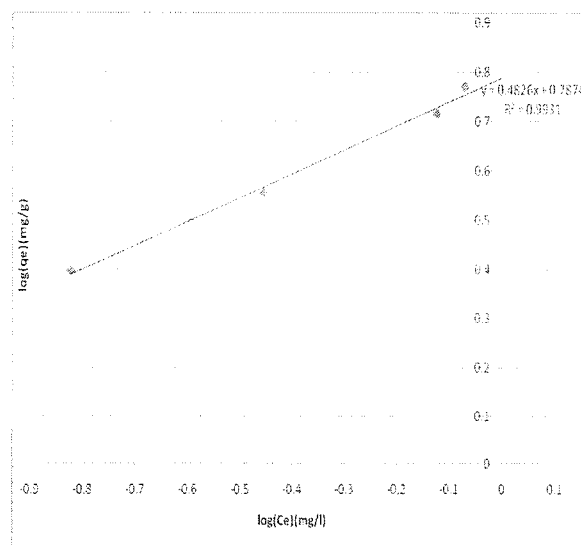


Fig 5.14 Freundlich Plot for Cr (VI) Adsorption on Tile Waste Adsorbent

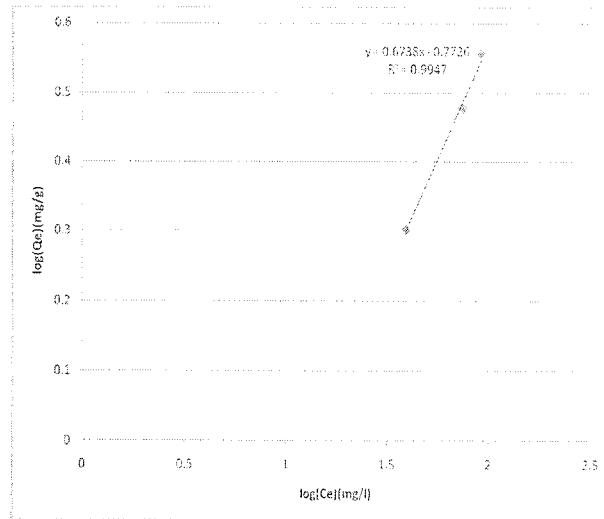


Fig 5.15 Freundlich Plot for Cr (VI) Adsorption Peanut Shell Adsorbent

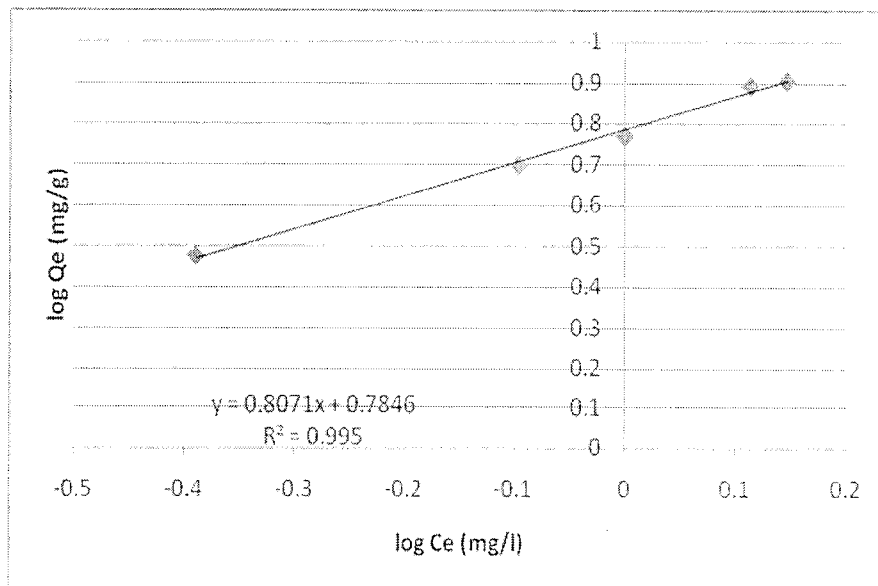


Fig 5.16 Freundlich Plot for Cr (VI) Adsorption Egg Shell Adsorbent

Table 5.14 Freundlich parameters

Adsorbent	K_F	1/n	R²
Peanut shells	0.772	0.673	0.994
Tile wastes	0.787	0.482	0.993
Egg Shells	0.784	0.807	0.995
Almond Leaves	0.745	0.462	0.997

- The Langmuir and Freundlich isotherm fits the data very well and the parameters were evaluated and presented in Table (5.13-5.14).
- Both the isotherm yielded maximum R² value for almond leaves.
- The equilibrium sorption capacity (q_m) for complete monolayer was found to be 1.221, 0.53, 1.11 and 7.25 mg/g and equilibrium sorption constant (K_a) was found to be 27.5, 0.4, 0.175 and 3.199 (l/mg) for Peanut shell, Tile waste, Egg shell and Almond leaves respectively from Langmuir isotherm data.
- The Freundlich parameter (1/n) for Peanut shell, Tile waste, Egg shell and Almond leaves was found to be 0.673, 0.482, 0.807, 0.462 respectively .
- As the values of 1/n < 1, it indicates favorable adsorption of Cr (VI) onto the adsorbents materials (Table 5.14).

5.8 ADSORPTION KINETICS

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

Table 5.15 q_e and q_t values

Time (min)	Almond leaves		Tile waste		Peanut shell		Egg Shell	
	q_e (mg/g)	q_t (mg/g)	q_e (mg/g)	q_t (mg/g)	q_e (mg/g)	q_t (mg/g)	q_e (mg/g)	q_t (mg/g)
20	12.4	8.5	2.44	1.40	6.98	5.43	4.43	1.95
40	12.4	9.43	2.44	1.83	6.98	5.74	4.43	2.54
60	12.4	10.41	2.44	2.00	6.98	6.38	4.43	2.98
80	12.4	11.47	2.44	2.18	6.98	6.59	4.43	3.19
100	12.4	11.9	2.44	2.22	6.98	7.02	4.43	3.48
120	-	-	-	-	-	-	4.43	3.83

Table 5.16 Kinetics study for Adsorbent Materials

Adsorbent	Tile			Egg shell			Peanut shell			Almond leaves		
	Log $q_e - q_t$	t/q_t	$1/(q_e - q_t)$	Log $q_e - q_t$	t/q_t	$1/(q_e - q_t)$	Log $q_e - q_t$	t/q_t	$1/(q_e - q_t)$	Log $q_e - q_t$	t/q_t	$1/(q_e - q_t)$
20	0.021	22.8	-0.95	0.32	45	-0.47	0.07	8.36	-0.66	0.49	12.3	-8.12
40	-0.25	53.3	-1.81	0.30	90.6	-0.5	-0.008	15.42	-0.98	0.32	21.3	-4.34
60	-0.52	83.8	-3.33	0.06	14.54	-0.86	-0.096	22.33	-1.5	-0.54	29.4	-5.88
80	-0.69	121	-5	-0.3	181.9	-3	-0.318	32.78	-2.08	-0.85	41	-8.12
100	-1.30	114	-5.6	-0.6	201.1	-4.5	-0.513	39	-2.7	-1.3	53.7	-13
120	-	-	-	-0.82	243	-6.66	-	-	-	-	-	-

Fig 5.17 Lagergren first order kinetics

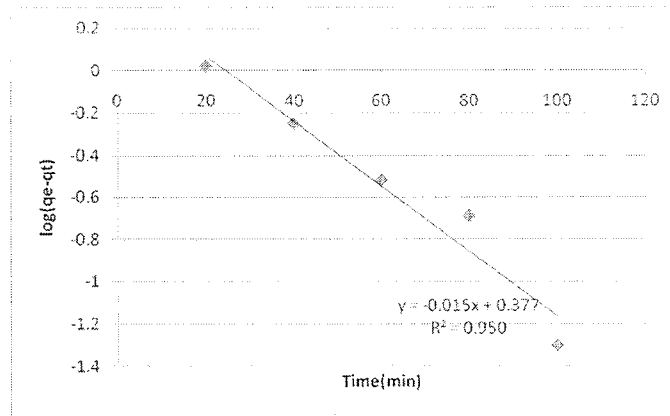


Fig 5.17 (a) Tile waste

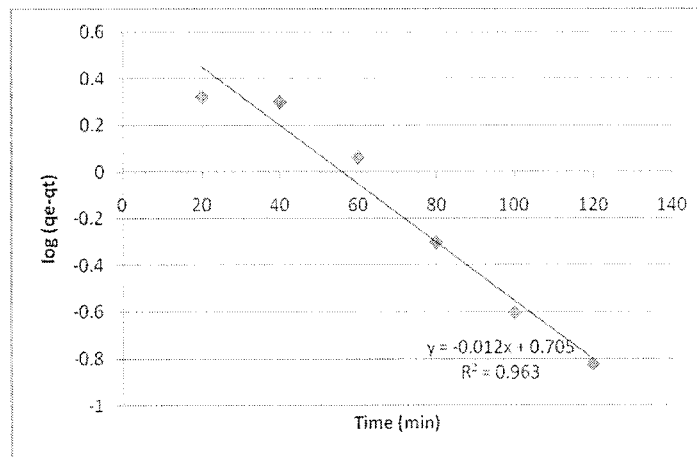


Fig 5.17 (b) Egg shell

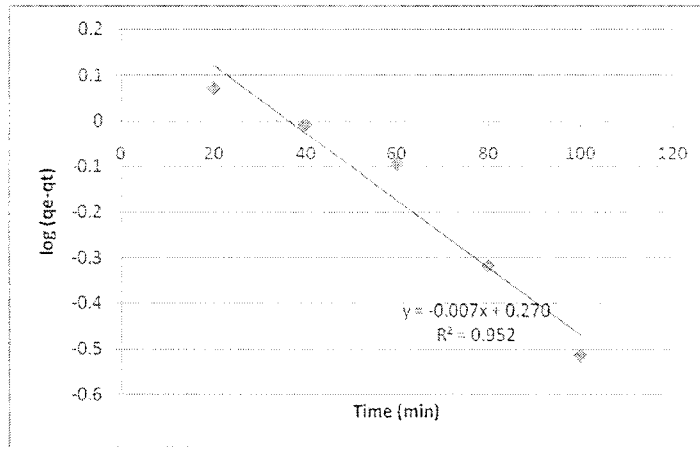


Fig 5.17 (c) Peanut shell

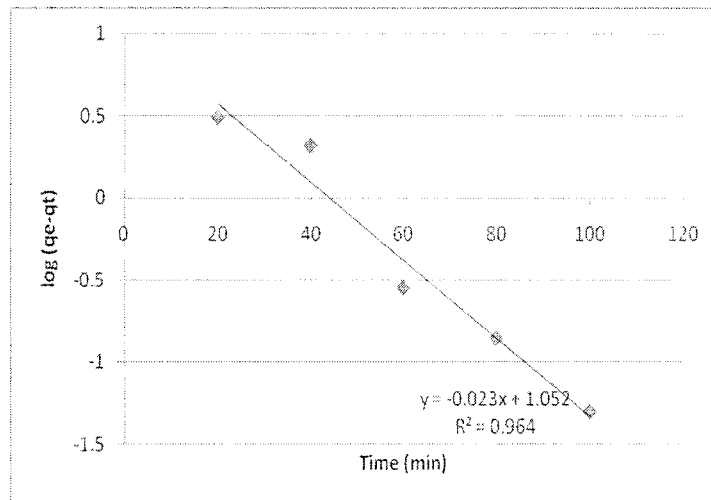


Fig 5.17 (d) Almond leaves

Fig 5.18 pseudo second order kinetics

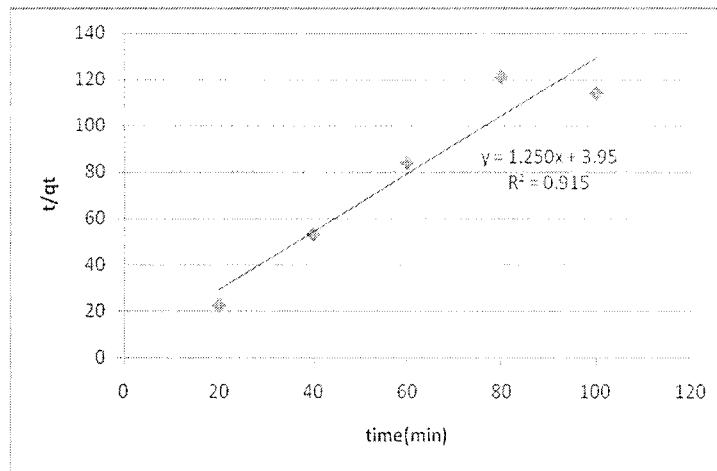


Fig 5.18 (a) Tile waste

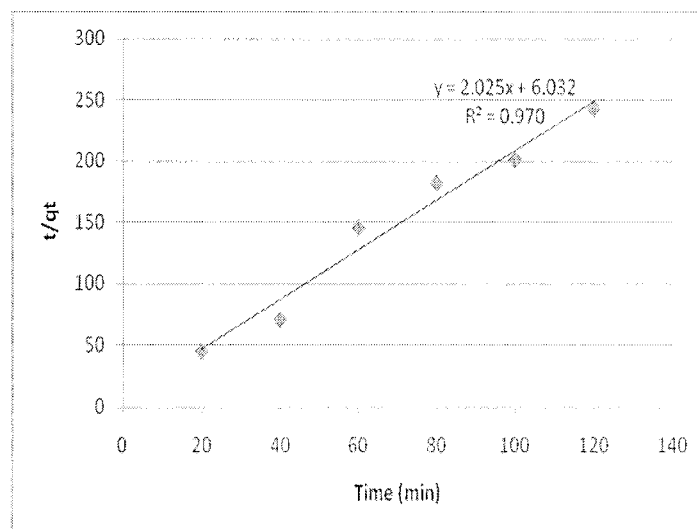


Fig 5.18 (b) egg shell

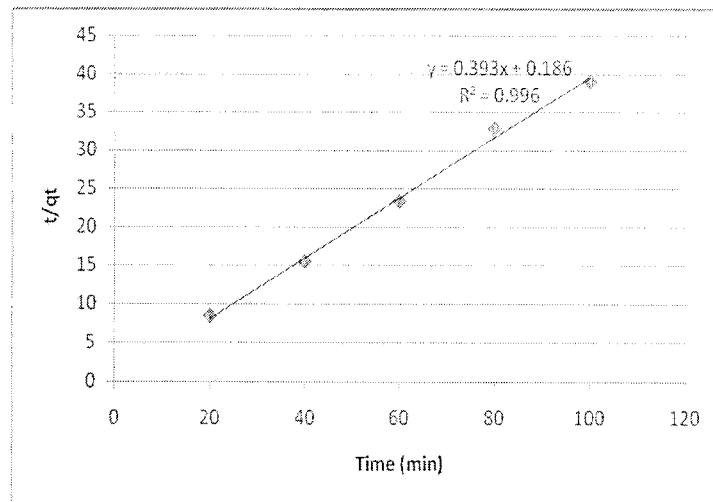


Fig 5.18 (c) Peanut shell

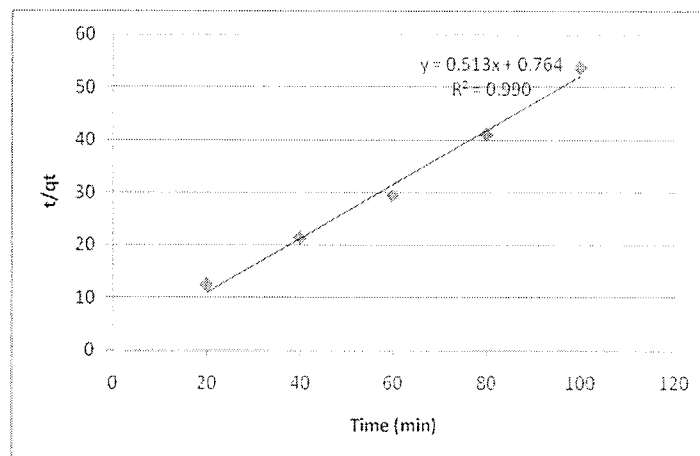


Fig 5.18 (d) Almond leaves

Fig 5.19 second order kinetics

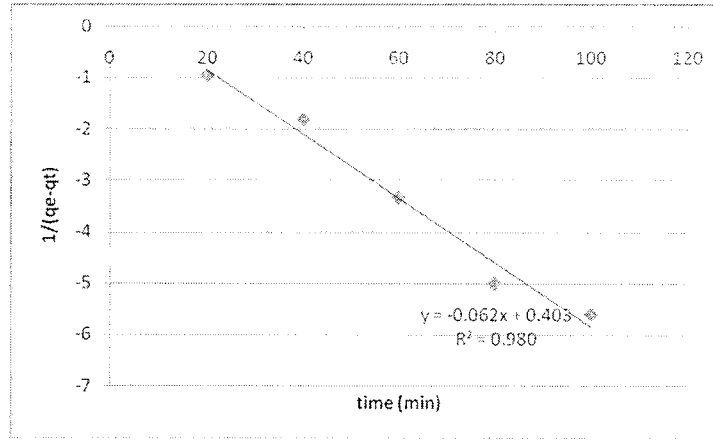


Fig 5.19 (a) Tile waste

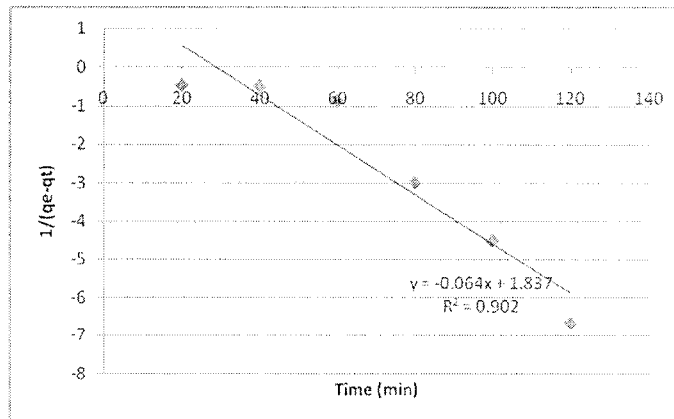


Fig 5.19 (b) Egg shell

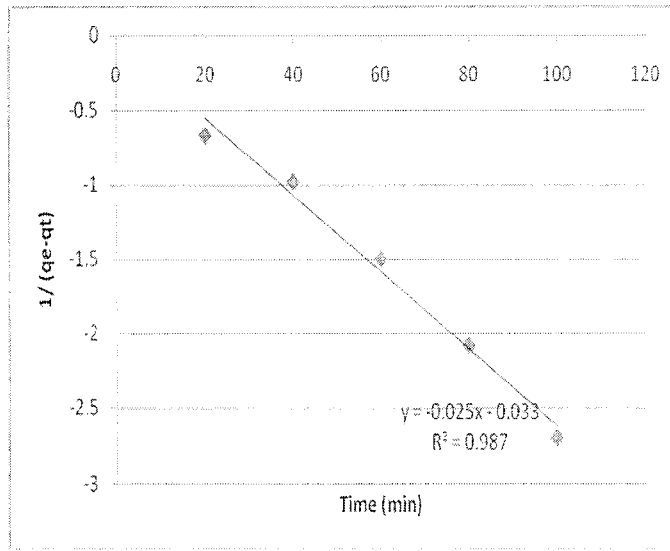


Fig 5.19 (c) peanut shell

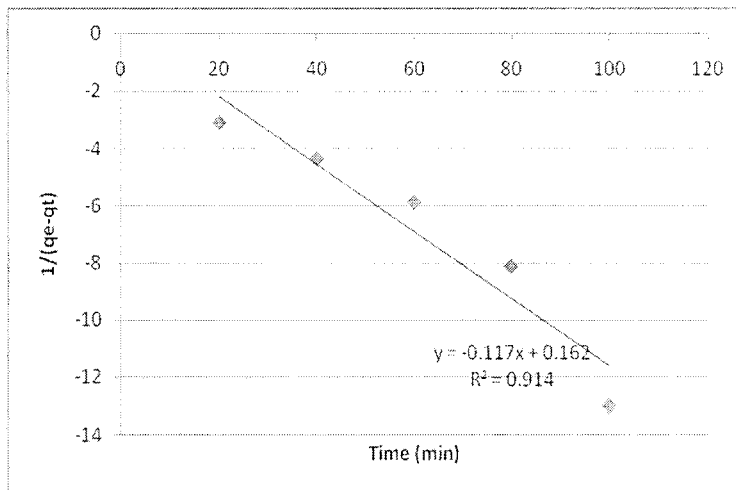


Fig 5.19 (d) almond leaves

Table 5.17 Lagergren first-order, pseudo-second order and second-order constants

Adsorbent	Lagergren		Pseudo second-order		Second-order	
	K_{ad} ($\times 10^{-2}$ min^{-1})	R^2	K' ($\times 10^{-2}$ g/mg min)	R^2	K (g/mg min)	R^2
Peanut Shells	1.6	0.952	0.833	0.996	0.025	0.987
Tile Wastes	3.45	0.950	0.396	0.915	0.062	0.980
Egg Shells	2.76	0.963	0.690	0.970	0.064	0.902
Almond Leaves	5.29	0.964	0.344	0.990	0.117	0.914

- The kinetic study was analysed and correlation coefficient values (R^2) of Egg shell, Peanut shell, and Almond leaves found to be 0.970, 0.996 and 0.990 respectively.
- The adsorbents other than Tile waste follow a pseudo-second order kinetics.
- Tile waste follows second-order kinetics indicated by the highest R^2 value (Table 5.17).

CONCLUSION

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. Few such low cost adsorbents generally available as wastes are the choice of materials in this study.

Following conclusions are drawn from the above discussed results

- All the adsorbents used can be obtained without excessive cost.
- Removal of Cr(VI) increases with increase of adsorbent dosage.
- The maximum adsorption of Cr(VI) took place at pH 3 for all the adsorbent materials.
- The removal efficiency of the selected adsorbents increases with the increasing dosage levels of the adsorbents.
- The batch adsorption study result shows that almond leaves adsorbent showed effective removal of Cr (VI) even at a dosage level of 1g. Maximum adsorption occurs from 4g. Peanut shells, Tile wastes and Egg shells showed no removal of Cr (VI) at dosage level of 1g.
- The adsorption process of Cr(VI) described by Langmuir isotherm and Freundlich isotherm model showed maximum correlation coefficient value for almond leaves.
- Kinetic study showed that almond leaves, peanut shells, egg shells followed pseudo-second order kinetics whereas tile waste followed second-order inferred by the values of correlation co-efficient.

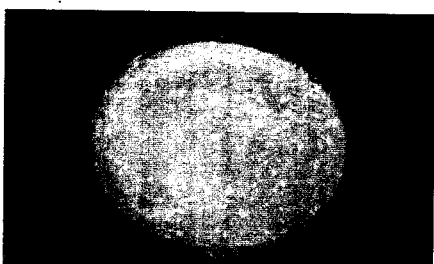
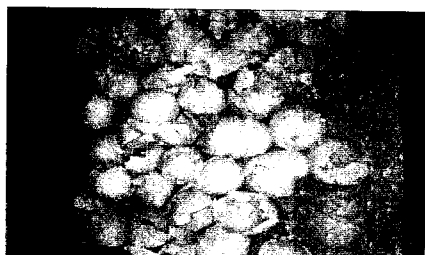
FUTURE PERSPECTIVES

- Adsorbents can be subjected to various chemical treatments before performing batch and continuous studies.
- Treatment using industrial effluent containing Cr (VI) .
- Analyze the results using atomic absorption spectroscopy (AAS).
- To adsorb heavy metal effluent containing Cr (VI) using the adsorbents and analyzing the data with various isotherms and kinetics.
- To find out the optimal contact time, adsorbent dosage and pH conditions.
- To apply the mentioned adsorbent materials for the removal of other toxic heavy metals like Pb, Cd, Zn, Fe etc. from effluents.

APPENDICES

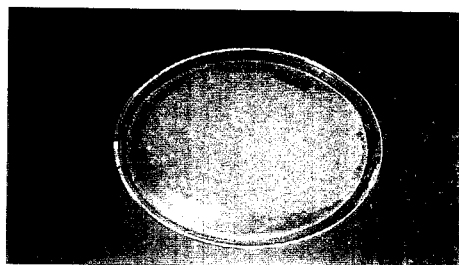
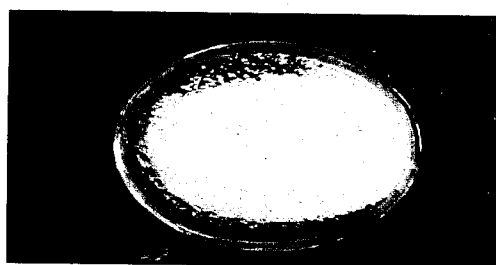
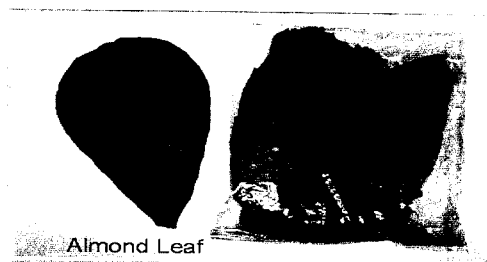
APPENDIX (I)

ADSORBENTS:



Egg Shell Adsorbent

Peanut Shell Adsorbent



Tile Waste Adsorbent

Almond Leaf Adsorbent

Fig I: Adsorbent Materials

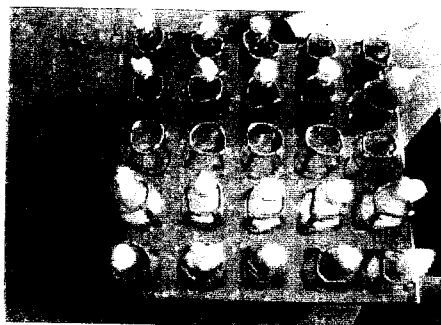


Fig II:

**Experiments carried out in a
mechanical shaker**

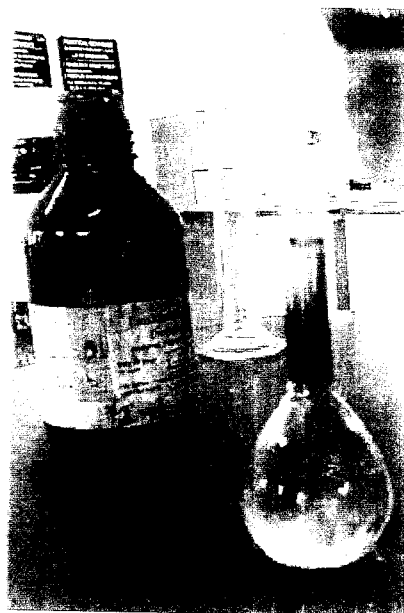


Fig IV:

**After 8 hours treatment ,
Pink colored complex is
formed after addition of DPC.**



Fig III:

Potassium Dichromate Standards.



Fig V:

Continuous Column

APPENDIX (II)

ESTIMATION OF CHROMIUM (VI) CONCENTRATION

Preparation of Stimulated Effluent

A stock solution (100mg/ml) of Cr (VI) was prepared by dissolving 2.8287 g of 99.9% $K_2Cr_2O_7$ in 1000ml of distilled water.

Molecular Weight of Chromium = 294.19

100 mg/ml of Chromium = $\frac{294.19}{51.99 \times 2} = 2.82g$ of 99.9% $K_2Cr_2O_7$ in 1000ml of distilled water.

Preparation of 1,5- DPC Complexing Agent

The classical method of Cr(VI) analysis for industrial hygiene use was colorimetry using 1,5-diphenylcarbazide (DPC) for colour development after acid extraction of the Cr (VI) from the sample. Dissolve 0.5 g 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 – Colorimetric Method

The working standard solutions with concentration ranging from 20-100 mg/l were prepared from the stock. Adsorbent feed was given and the experiment was carried out by agitating in a mechanical shaker for 8 hours. The concentration of free Cr (VI) ions was measured by reacting the solution with DPC reagent and a pink colored complex was formed. The absorbance was measured using a spectrophotometer at 540nm.

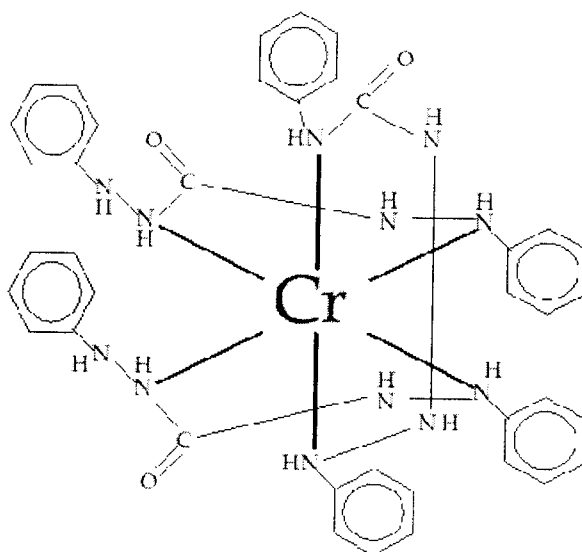


Fig VI: Interaction of free Cr (VI) with 1,5-DPC

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

REAGENTS	B	S1	S2	S3	S4	S5
Volume of working standard(ml)	-	20	40	60	80	100
Concentration of working standard (mg/ml)	-	20	40	60	80	100
Volume of working sample(ml)	-	2	2	2	2	2
Volume of 0.2N H ₂ SO ₄ (ml)	5	5	5	5	5	5
Make up to 100ml with distilled water						
Kept at room temperature for 15 minutes						
Volume of 1,5-DPC added(ml)	5	5	5	5	5	5
Kept at room temperature for an hour						
Measure Absorbance at 540nm						

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	$q_e = KC_e^{(1/n)}$	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:

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

where K_L is a dimensionless separation factor, C_o 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 pseudo 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 shown in Fig. 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 which derived from the pseudo second-order equation are shown in Table 5.17

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

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

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

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/l)

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

REFERENCES