ADSORPTIVE REMOVAL OF CHROMIUM (VI) FROM ELECTROPLATING WASTEWATER

A

DISSERTATION

Submitted in the partial fulfillment of the

Requirement for the award of the degree

Of

MASTER OF TECHNOLOGY

In

CHEMICAL ENGINEERING

(With Specialization in Industrial Pollution Abatement)

By

PRASHANT RAWAT

DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY, ROORKEE

ROORKEE-247667 (INDIA)

June-2013

CANDIDATE’S DECLARATION

I hereby declare that the work which is being presented by me in this dissertation report entitled “Adsorptive removal of chromium (VI) from electroplating wastewater ” submitted in partial fulfillment of the requirement for the award of the degree of, “**Master of Technology in Chemical Engineering**” with specialization in “**Industrial Pollution Abatement**”, and submitted to the Department of Chemical Engineering, Indian Institute of Technology, Roorkee, is an authentic record of the work carried out by me during the period June 2012 to June 2013, under the guidance of Dr. B. Prasad**,** professor of Chemical Engineering, Indian institute of Technology, Roorkee.

Date:

Place: IIT, Roorkee **Prashant Rawat**

CERTIFICATE

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

Dr. B. Prasad

Professor

Department of Chemical Engineering

Indian Institute of Technology Roorkee

Roorkee

ACKNOWLEDGEMENTS

I am greatly indebted to my guide **Dr. B. PRASAD**, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee for his kind support and guidance during the entire course of this work. His cooperation and in depth knowledge have made my work possible.

I am also thankful to **Dr. V.K. AGARWAL Prof and Head**, Department of Chemical Engineering and other staff members for their instant help in all kinds of work. I would like to thank my friends for their continuous support and enthusiastic help. Last but not least, it is owed to the blessings of my parents and God that I have come up with this work in due time.

Date:

Place: IIT Roorkee **(Prashant Rawat)**

CONTENTS

REFERENCES

LIST OF FIGURES

LIST OF TABLES

Abstract

In the present work, hexavalent chromium and COD removal from electroplating wastewater was investigated using a low cost activated carbon, which was carbonized and activated from corncobs. Corncob based activated carbon (CAC) was characterized to understand the adsorption characteristics of chromium (VI) ions on adsorption and its physiochemical properties. The particle size of CAC was in the range of 450-850 µm. Proximate and ultimate analysis of CAC showed the presence of high carbon content. BET surface area and pore volume were found 399.006 m^2g^{-1} and 0.23 cm^3g^{-1} respectively. The effect of parameters such as temperature (T), adsorbent dose (w), pH and contact time (t) on adsorption of chromium ions by CAC was investigated. The pH ≈3.0 is found to be optimum for the removal of Cr(VI) and COD from wastewater by CAC at an optimum dose of 15 Kg/m^3. Optimum value of contact time is found as 6 hr. Various isotherm models were fitted for Cr(VI) and COD removal. Freundlich model well fitted to Cr(VI) adsorption while Redlich-Peterson is found to be fit for COD removal. Pseudo-second order kinetic model was well fitted for both Cr(VI) and COD removal. Thermodynamic parameters represent the exothermic and spontaneous nature of adsorption.

CHAPTER-1

INTRODUCTION

1.1 GENERAL

The industrialization and technologies have comforted people's life but also resulted in increased environmental risk due to the possible accumulation of waste discharged in water, air and soil. The growth of industrial activity needs the manufacturing of materials, which are resistant to corrosion. Chrome and bronze plating are such methods to ensure longer durability of metallic equipment. Electroplating industries have potential to generate the effluent consisting of heavy metals like chromium, zinc, copper, cadmium etc. With increasing use of heavy metals in electroplating industry problem may arise of toxicity in environment to a great extent. Cost-effective method for purifying the wastewater is highly required.

Chrome plating is the most desirable in automobile parts, process equipment etc. for corrosion resistant. Chromium occurs in 1$^+$ to 6$^+$ oxidation states but Cr^{+1}, Cr^{+2}, Cr^{+4}, and Cr^{+5} are unstable and very less information about their hydrolysis (Mohan et al., 2006). The hydrolysis of chromium (III) is complex and generate species like CrOH^{2+}, Cr(OH)$_2^+$, Cr(OH)$_4^-$, neutral species Cr(OH)$_3^0$ and other species like Cr(OH)$_2$ and Cr(OH)$_4^{5+}$. Hydrolysis of chromium (VI) ions generates anionic as well as neutral species, mainly CrO$_4^{2-}$, HCrO$_4^{2-}$ and Cr2O$_7^{2-}$ (Mohan et al., 2005). Species generated by hydrolysis of Cr(III) generally stabilized by electron donor species (e.g. OH$^-$) while anions produced by hydrolysis of Cr(VI) are hardly stabilized. Chromium has beneficial as well as detrimental effect.

Cr(III) is an essential element needed for human and other living organism for metabolism. It reduces the blood glucose levels and help to transport of amino acids into the heart and liver. It has also been found to decrease blood cholesterol by reducing the concentration lipoproteins in the blood so it reduces the risk of diabetes (Sarkar et al., 1984). Hexavalent chromium ions are more toxic than trivalent chromium ions due to their high mobility and solubility in water. High concentration of Cr(VI) causes respiratory problem, nausea, liver and kidney damage, diarrhea disease, dermatitis and internal haemorrhage (Mohan et al., 2006). On the other hand, Cr(III) is less soluble in water, hence very less mobile. The most toxic forms of Cr(VI) ions are chromate and dichromate. The hexavalent form of chromium is rapidly reduced to trivalent chromium under oxygen rich conditions (Irwin et al., 1971).

Chromium bearing effluent from electroplating industry cannot be discharged without removing it from wastewater. The Central Pollution Control Board (CPCB), Delhi, India has set a minimal national standard (MINAS) for Cr(VI) as 0.1 mg/l in the industrial discharge into the surface water (CPCB 2012). In a typical chrome plating plant, high volume wastewater obtained from the washing unit, has high Cr(VI) concentration range of 1000-2000 mg/l. However low concentration wastewater emanating from the other sections of the range of 50-200 mg/l.

Several treatment methods have been developed to remove hexavalent chromium from wastewater. Common methods such as chemical precipitation (Paterson et al., 1975), membrane separation (Kozlowski et al., 2002), ultrafiltration (Ghosh et al., 2006), solvent extraction (Salazar et al., 1992), electro-chemical method (Heidmann et al., 2007), coagulation (Song et al., 2004), ion-exchange (Cavaco. et al., 2007) and reverse osmosis (Das et al., 2006) have been used for the removal of Cr(VI) from wastewater. Adsorption is also attractive treatment method for the removal of Cr(VI) from electroplating wastewater.

1.2 HEALTH AND THE ENVIRONMENT EFFECT OF CHROMIUM

Chromium (Cr) is considered an essential nutrient for living organism as well as health hazard due to its toxic nature. Chromium exists in nature more than one oxidation states. Specifically, Chromium in oxidation state +6, written as Cr(VI), is considered very harmful even in small intake quantity whereas Cr in oxidation state +3, written as Cr(III), is considered good for health in moderate quantity. The detrimental health effects of chromium are as follows:

- The detrimental oral toxicity for Cr(VI) ranges 50 to 150 µg/kg (Katz et al., 1992).
- As Cr(VI) reaches the blood stream, it damages kidneys, blood cells and the liver through oxidation reactions. Liver failure and haemolysis are the results of these damages (Dayan et al., 2001).
- Chromates are also the cause for allergic symptoms.
- “Chrome ulcer” may be cause by skin contact.

1.3 REASON FOR TOXICITY OF HEXAVALENT CHROMIUM

Hexavalent chromium is highly oxidizing agent. Cr(VI) form free radicals during reduction of hexavalent chromium to trivalent chromium inside the cell. Research on detrimental effect of chromium has focused on the fact that CrO_4^{2}- ions quickly pass through nuclear and cellular membrane by ion exchange process while Cr(III) pass at slow speed. This is due to the fact that Cr(III) hydrolyses smoothly at high pH to form insoluble hydroxide. In other words we can say Cr(III) ions are kinetically inert. Chromates ions entered in nuclear membrane are strongly reactive with DNA. It is thought that the reduction of Cr^{+6} to Cr^{+3}, produces free radicals which bind to DNA. These free radicals interfere with the DNA structure and may causes for acute diseases.

1.4 REGULATIONS AND GUIDELINES

The central pollution control board of India (CPCB) recommended the threshold limit for hexavalent chromium in potable water is 0.1 mg/l beyond this limit it shows harmful effect on flora and fauna. The CPCB also recommended the total chromium concentration should not more than 2 mg/l for potable water.

1.5 SOURCES OF HEXAVALENT CHROMIUM

Hexavalent chromium is being added by variety of sources into the environment. Chromium has good oxidation characteristics which makes it suitable for various applications, such as tannery industry uses chromium sulphate to harden the lather. Chromium compound are used in refractory material (for high temperature duty in blast furnace or cement kiln), wood preservative (from fungi, insect), synthetic ruby production, dye and pigment (lead chromate used for yellow colour) and metallurgy. All these industries generate large volume of wastewater containing hexavalent as well as trivalent chromium which should be treated before discharged into environment. Among these industries, metallurgy industry also known as electroplating industry alone generate huge amount of wastewater. Electroplating industry generally uses chromic acid for metal plating to enhance surface characteristic by improving anticorrosive property.

1.6 ELECTROPLATING INDUSTRY

Electroplating is an electro-deposition activity for producing a uniform coating, usually of metal, upon a surface by electric current [ASTM standard, 2003]. The coating on metal surface is usually for decorative or enhancing properties of the surface. The surface may be conductor or non-conductor. Coated metals are generally used for various industries like ship, automobile, machinery, defence and jewellerys. The heart of the electroplating industry is the electroplating unit. In the electroplating bath electric current is passed through a compartment consists of anode, cathode and electrolyte sample. In industrial electroplating, pre-treatment and post-treatment steps are generally required. The various steps used in electroplating industries are described as follows.

1.6.1 SURFACE PREPARATION

A variety of metal surface preparation processes including metal surface modification, surface cleaning, and rinsing are used for metal surface modification. A flow sheet of a electroplating unit, including surface treatment units and wastewater generation points are shown in Fig. 1. Surface pre-treatment is carried out to remove contaminants on the surface of the object. Therefore, surface pre-treatment is essential to ensure about the quality of product. Surface preparations consist of 3 basic steps including, metal surface cleaning, surface treatment, and rinsing. Large amount of Waste water generates in this step, but chromium contamination is very low. Acid washing, water washing, alkaline washing and polishing are the some basic steps which are used in surface preparation step.

1.6.2 SURFACE CLEANING

Surface cleaning methods are utilized to reduce metal damage during removal the dust and debris. Further surface cleaning method can be divided into two approaches, known as: chemical approach and mechanical approach.

Solvent Degreasing: Oils, grease of different types and waxes are main contaminants from solvent degreasing section. All such types of contaminants may be reduced by organic solvents or by vapour decreasing.

Chemical approaches: Chemical approach includes acid cleaning, solvent degreasing and alkaline cleaning.

Alkaline Cleaning: To remove dust and soil work pieces are immersed in the alkaline solutions. Different kind of electro-cleaning may referred as alkaline cleaning. In electro cleaning process, work piece can be cathode or anode. Due to electro cleaning of metal surface, gas generation (trace amount) at the surface of the metal may occur. No hexavalent containing wastewater generate in this unit.

1.6.3 ACID CLEANING: Acid cleaning used to remove heat-treats scale, oxide of compounds, and the lime solution. Sulphuric acid and hydrochloric acid are generally uses for acid cleaning. Efficient cleaning can be achieve by combining pickling with current.

1.6.4 MECHANICAL APPROACHE:

Mechanic approaches of metal surface include buffing polishing and some other process. Polishing is generally used to reduce small amount of metal by abrasive agents. After polishing the surface of metal, it found free to surface fault left by grinding. Buffing process is same as polishing process, but it uses fine abrasives agent to eliminate little amount of metals. By buffing process very fine and clean surface may be achieved.

1.6.5 SURFACE MODIFICATION TECHNIQUE

Uses of metal layer and hardening process are the changes create on the surface of metal due to the surface modification technique.

1.6.6 RINSING

In electroplating process, when metal pieces are shifted from one treating solution to another treating solution and after treatment when metal pieces leave the bath solution, it may carry some amount of the electrolyte solution. The solution attached to metal surface must be eliminated from the metal surface by washing before the metal pieces enter in to the next unit. After final treatment, metal pieces undergo rinsing or washing to eliminate residues of treating solution on metal surface.

Hexavalent chromium containing waste water mainly generate in rinsing or washing steps. The chromium bearing rinse water is further goes to wastewater treatment unit before discharge to water body. This step generate large amount of heavy metal bearing waste water which create environmental problem. A process flow diagram is shown in the following figure which shows the various steps in electroplating industry and as well as also indicate the waste water generation points.

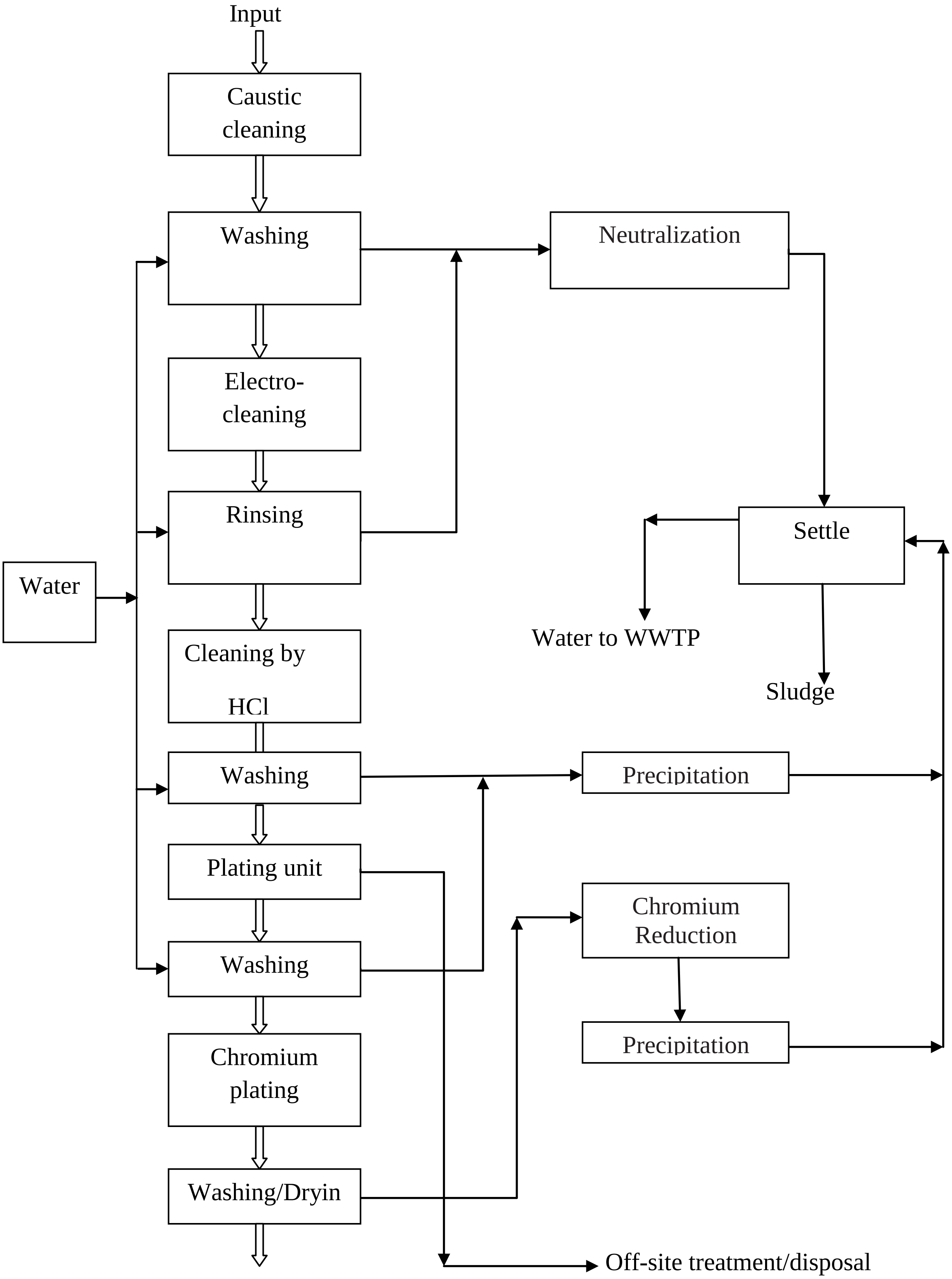


Figure 1.1: Process flow sheet of industrial electroplating unit

1.7 OBJECTIVES OF THESIS

Based on literature survey carried out, the objectives for the dissertation titled “Adsorptive removal of chromium(VI) from electroplating waste water” were as:

- Development of corncob based activated carbon.
- Characterization of corncob based activated carbon (CAC) to be carried out including SEM, BET, FTIR, TGA and point of zero charge.
- To determine the adsorption efficiency of CAC for hazardous chromium(VI) and COD.
- Examine the effect of various parameters on the adsorption of hexavalent chromium ion and COD over CAC i.e., effect of contact time, pH, effect of adsorbent dose, effect of temperature, effect of initial concentrations.
- To determine the kinetics which will fit the experimental adsorption process.
- To analyse the different isotherm models.
- Study the thermodynamic behaviour of adsorption process.
- Error analysis.

CHAPTER-2

LITERATURE REVIEW

2.1 PHYSICOCHEMICAL TECHNIQUES FOR TREATMENT OF WASTEWATER

There are many physicochemical processes have been used for the removal of chromium that are injurious to our biological cycle. Some of these techniques are chemical precipitation, adsorption, coagulation, oxidation, electro-chemical method, reverse osmosis, membrane separation, ultrafilteration, solvent extraction, floatation, sedimentation, soil flushing/washing, phytoremediation, dialysis/electrodialysis, chelation and ion-exchange. Most treatment methods remove chromium and COD effectively from chromium bearing waste water. However, remediation methods have some advantages and disadvantages. A number of review articles are being presented on removal of COD and Cr(VI) from electroplating waste water.

2.1.1 CHEMICAL PRECIPITATION

Chemical precipitation may be termed as the most used method for chromium removal. Reduction of Cr(VI) to Cr(III) may be used for removing the toxicity of Cr(VI) by chemical precipitation. Gheju et al., 2011 used scrap iron for the reduction of Cr(III) in a continuous experiment along with precipitation of cations according to:

$$2Cr_2O_7^{2-} + 6Fe^0 + 28H^+ \longrightarrow 4Cr^{3+} + 6Fe^{2+} + 14H_2O \tag{2.1}$$

The optimum pH range (7-8) was achieved with a 300 mg/l of caustic soda (NaOH) dose. Gould et al., 1982, reported that 1.33 mol of Fe^0 dissolved for each mol of Cr(VI) reduced. Fe^0 should be termed as the generator of eliminating agents.

Tadesse et al. (2005) investigated the elimination of Cr(III) from a tannery wastewater with lime in horizontal settling tanks. Integrated reactor (AIWPS) was also studied in the chromium removal by lime precipitation. Chemical precipitation by scrap iron, lime and lime plus caustic soda combination provided good chromium removal efficiency up to 98% . The main disadvantage in chemical precipitation method is the generation of large amount of sludge which requires proper disposal techniques. (Paterson et al.,1975).

2.1.2 ELECTROCHEMICAL METHOD

Chemical coagulation termed as efficient method for removing heavy metal from waste water but may create secondary pollutant by adding coagulant. Electrocoagulation uses no chemical as coagulating agents. Dermentzis et al., 2011, studied the working of electrocoagulation by iron electrodes to eliminate heavy metal from lab prepared solutions and effluent of electroplating industry.

Akbal et al. (2011) investigated the removal of chromium and nickel ions from electro-plating effluent by electrochemical method by using different electrode. They worked on several parameters such as pH, current density, influence of material (electrode), conductivity and effluent on removal performance. They found that the nickel reduction increased with increasing the different parameters (pH and current density). They compared removal efficiency of iron and aluminum electrode. They suggested that the electroplating process with Fe–Al electrode was found very effective at an electro-chemical current density of 10 mA/cm^2, a time of 20 min and a pH of 3.

Narayanan et al. (2009) studied the removal of Cr(VI) ions from wastewater (prepared in lab) in a electrocoagulation reactor (batch process) with Fe-Al electrode along with sorption. They worked on several parameters such as pH of solution, adsorbent concentration (g) and operating period (min). They found most effective removal pH was near 8 and current density in the range of 6.7-26.7 mA/cm^2. Electrocoagulation and then adsorption enhanced the removal efficiency.

Arroyo et al. (2009) studied the effect of chloride ions and pH on the elimination of Cr(VI) by batch experiment using iron plate electrode. They found that with the appearance of Cl^- ion electrode, dissolution of wastewater enhances due to the pitting corrosion. They also found that the Fe^{+3} formed during dissolution of anode which cause the reduction of Cr(VI) into Cr(III), which were precipitated with Fe^{3+} ions. They suggested that at highly acidic wastewater, the reduction of hexavalent chromium to trivalent chromium by ferrous ions (Fe^{+3}) was preferred, but the coagulation of Fe^{3+} and Cr(III) was much favored at the low acidic solution.

Golder et al. (2006) investigated the reduction of trivalent chromium from wastewater (synthetically prepared) in batch reactor with steel electrodes. Golder found that the only one step of process could eliminate the Cr^{3+} ions from 1000 to of 2 mg/l. Sludge generation in this method constitute a environmental risk.

Rana et al. (2004) experimentally studied the electrochemical removal of Cr(VI) from aqueous solution by electrode (carbon). In their study they investigated the effect of various parameters including concentration 2–8 (mg/l), pH (2–7), and charge on chromium removal. They experimentally found that the chromium ions removal significantly increases at low pH and at high current density. The hexavalent chromium reduction in wastewater up to 98.5% was achieved at high current (0.8 Ah) and low pH condition. They investigated the effect of parameter such wastewater concentration, pH and electric current on the % removal was evaluated by using Box–Behnken model. Box–Behnken model was applied to optimize the parameters to maximize the Cr-removal.

2.1.3 REVERSE OSMOSIS

Covarrubias et at. (2008) studied the reduction of toxic contamination in the wastewater from aqueous solution by zeolite membranes using reverse osmosis process. Faujasite membrane was synthesize by ZSM-2 seeds and coated with silica. Experimentally they found that the chromium ions undergo ion exchange with Na^+ ions in the membrane until saturation achieved.

Liu et al. (2008) evaluated the performance of different nanofiltration and reverse osmosis membranes in treating the toxic metal wastewater from metallurgical industry. They compared the wastewater flux of membrane with theoretical calculation using mass transfer models, and observed good consistency. They found a high rejection rate of metal ions up to 95% and a low chemical oxygen demand value of 10 mg/l. They observed that the purified water by reverse osmosis desalination satisfied the State Reutilization Qualification.

Das et al. (2005) studied the reuse of heavy metal (total Cr) from the electroplating wastewater by using nano-filtration along with reverse osmosis. Studies were carried out by rectangular reactor. They found flux improvement while they use wire for turbulent generation. They evaluated various parameters as chromium ions (concentration), chemical oxygen demand, biological oxygen demand, total solid, pH and TDS. They observed the retention of chromium was 98.8–99.7% for reverse osmosis.

Ozaki et al. (2002) evaluated the working of reverse osmosis reactor for separating copper, Ni and Cr(VI) from bulk solution. Various parameters such as pH operating pressure, feed concentration and effect of other ions were also studied.

Johnston (1975) investigated the selective rejection of various heavy metals by reverse osmosis membranes. He found that the series of membranes showed the NaCl rejection level of from 26 to 91%. He observed the selectivity pattern of divalent metals and suggested that the ion-water interaction rather than ion-membrane interactions are the controlling factors in the cation rejections by the membranes. He experimentally found that the partial molal free energies and the entropies of the ions in the solution adequately represent these controlling factors.

Although chromium ions reduction by membrane, using reverse osmosis process gives the high removal percentage but membranes used for reverse osmosis process are very costly which are not economical feasible for industrial activity. Membranes used in heavy metal reduction are easily degraded by contamination and have short life span.

2.1.4 ION EXCHANGE

In ion exchange process synthetic ion exchange resin is used to remove selective pollutant from the waste water. These resins are specific in nature, generally termed as cation and anion ion exchange resin.

Gode et al. (2003) Rengaraj et al., 2003, misra et al., 2003, Cavaco et al., 2007 and Shi et al., 2009 are the researchers who worked on reduction of chromium ion by ion exchange resign. Ion exchange resin shows better remediation efficiency but resins are expensive compared to other methods and regeneration of resin frequently required to provide good potential for metal ions removal.

Rengaraj et al. (2001) investigated the performance of IRN77 cation exchange resins in the batch experiments for removal of chromium. Several parameters such as pH of solution, contact time, doses of resin were studied. During their study they found the reversible uptake of Cr(VI) ions and, thus ion exchange have good potential for removal/recovery of Cr(VI).

2.2 CHROMIUM REMOVAL BASED ON ADSORPTION

Chen et al. (2012) investigated the removal of chromium by adsorption using corn stalk as adsorbent. The adsorption experiment was carried out in continuous fixed-bed column to remove the chromium. They evaluated the effect of various parameters like flow rate, bed depths, influent solution pH and influent Cr(VI) concentrations were investigated and experimental result found that the adsorption capacity increases with increasing bed depth, while decreases with increasing the flow rate and inlet concentration. They found that the column adsorption process execute better result at lower flow rate and lower inlet Cr(VI) concentration. The adsorption capacity (mg/g) of Cr(VI) onto corn stalk highly dependent on the solution pH. To determine the breakthrough curves researchers applied the Thomas, Yoon–Nelson and Adams–Bohart models under various experimental conditions of the fixed-bed column. Their result showed that curve fitting of Yoon–Nelson and Thomas models were good with the experimental data.

Othman et al. (2012) prepared Activated carbon by peanut shell followed by activation (chemical) with potassium hydroxide for the reduction of chromium ions from wastewater. They characterized the prepared adsorbent using the BET surface area test to understand micropore surface area, pore structure and average pore diameter. Average pore diameter, BET surface area, pore volume and micropore surface area were determined by nitrogen adsorption at -196 ^{0}C. They also investigated the effects of pH, initial metal concentration, contact time and temperature on adsorption of Cr(VI). Experimental data showed that chromium ions adsorption from waste water samples followed the first and second order kinetics models.

Niladri et al. (2012) developed the highly effective glycine doped polypyrrole adsorbent for efficient Cr(VI) removal. They prepared glycine doped polypyrrole adsorbent using in situ polymerization method of pyrrole monomer for Cr(VI) reduction. They prepared adsorbent by dissolving 1.0 g of glycine in 90 mL of distilled water at normal temperature in a 50 mL flask. The pH of this solution was 5.03. They characterized the adsorbent using FTIR and XRD to confirm the doping of glycine. They carried out the adsorption isotherm study and found the Langmuir isotherm model with best fit and also have highest adsorption capacity of 217.39–232.55 μg/mg at 25 to 45 ^{0}C. They also conducted the desorption experiment to understand the regeneration feasibility of polypyrrole-glycine based activated carbon and found that it can be regenerate and recycled for 3 runs with loss of removal percentage.

Kumar et al. (2012) prepared prawn shell based activated carbon for the quick remediation of chromium from laboratory based wastewater. They prepared the adsorbent by collecting of prawn shells and then washed with water and dried in sun light. About 25 g of dried prawn shell was chemically treated with 20 ml of sulfuric acid (98 % v/v) to make slurry and then dried at 103 ^{0}C in oven. They characterized the prepared activated carbon by XRD, SEM and FTIR to understand characteristic of adsorbent. They used RSM to optimize the various process parameters for the maximum chromium ion removal. Adsorption of chromium on prawn shell based activated carbon followed both Freundlich as well as Langmuir isotherms and obeyed second-order kinetics.

Machida et al. (2012) studied the reduction of cadmium ion using mesoporous silica as well as activated carbon. They investigated the role of surface functionality on mesoporous silica and carbonaceous substance for adsorption of cadmium ions using different mesoporous silica and activated carbon. They experimentally found that the silica surfaces were mainly functionalized by mercapto- and mono-amino-group. Based on the experimental results, they predicted that the surface functional groups rather than silica structure and carbon seemed to play a principle role for cadmium ions adsorption.

Boparai et al. (2011) investigated the thermodynamics and kinetics of cadmium reduction by adsorption onto nano iron particles. They predicted the nano zero valent iron as an effecient adsorbent for reduction of different pollutants. In this study iron particles were utilized to investigate the remediation of cadmium ions in the range of 25 to 450 mg/l. They investigated the effect of temperature on kinetics and equilibrium of cadmium adsorption on nano iron particles. They found the highest adsorption capacity of adsorbent for Cd^{2+} ions, 769.2 mg/g at 25 ^{0}C.

Ali et al. (2011) investigated the utilization of carbon nanotube to remediate Cr(VI) ions from synthetic waste water. This research examined the effect of the various conditions including the pH, initial concentration, doses and agitation speed. They prepared activated carbon from palm kernel shell and activated by acid treatment to diminish inorganic impurities. They carried out characterization of nanotubes by using FESEM and XRD. The performance of the carbon nanotubes and the activated carbon was investigated as potential adsorbent. Experimentally this study found the highest adsorption capacity as 9 mg/g by using adsorbent (carbon nanotube) while adsorption study was carried out in the batch adsorption experiment.

Xu et al. (2011) investigated the fundamental behavior of amine-cross linked wheat straw and its adsorption mechanisms such as isotherm study and kinetics for phosphate and Cr(VI) removal from wastewater. The physicochemical change between wheat straw and amine-cross linked wheat straw were investigated by elemental content, BET surface area and zeta potential analysis. In this research the regeneration capacities for Cr(VI) loaded activated carbon and phosphate-loaded activated carbon was found as 74.8% and 98.1% respectively.

Gupta et al. (2011) prepared a magnetic adsorbent by carbon nanotubes and iron oxide. The characterization of prepared adsorbent was carried out by X-ray diffraction to understand crystalline structure of adsorbent, FESEM for morphology and FTIR for functional group. FESEM images showed that the iron oxide was attached to the carbon nanotubes. The adsorption capacity of the carbon nanotubes were tested in fixed bed and batch modes. They experimentally found that the composites showed a better adsorption capacity to that of adsorbent. Experimental data represented the reduction of chromium ion by adsorbent is highly dependent on agitation speed, and pH in batch experiment while on the bed thickness and flow rate in case of fixed bed experiment. The main advantage of the composites was that it can be used as adsorbing agent for impurities in effluent.

Gupta et al. (2010) studied the reduction of Cr(VI) from wastewater (synthetically prepared) using a low cost waste material which is a waste of fertilizer industry. In this research work carbon slurry was used to prepare efficient adsorbing agent for reduction of Cr(VI) from system solution. Further slurry was activated, characterized, and then used for the adsorptive reduction of metals. They carried out the batch experiments to investigate the effect of pH, temperature, adsorbent dose, contact time and concentration on adsorption process. The highest adsorption was at 303 K temperature, 2 pH, 70 min and 4.0 gl^{-1} of dose. Maximum adsorption capacity (mg/g) of solute removal on activated carbon (carbon slurry) was found to be 15.24 mg/g at 100 mg/l of Cr(VI) concentration. Both Freundlich and Langmuir isotherm models were used to fit adsorption equilibrium data and found good fit. They investigated the thermodynamic behavior which indicates that the adsorption of metal on activated carbon (carbon slurry) was spontaneous, feasible and exothermic under the standard conditions. 5% HNO_3 acid was used to recover the metals from the used adsorbent effectively.

Kauspediene et al. (2010) compared the removal efficiency of chromium complex dye from aqueous solution using the activated carbon and Macronet . Evaluation was carried out under different experimental conditions such as temperature, pH and initial dye concentration. They experimentally found that the effectiveness of macronet polymer for the Chromium removal, relatively higher than that of activated carbon in both neutral and acidic solutions. To evaluate the adsorption kinetics and to determine the constants of kinetics two theoretical models (intraparticle diffusion and pseudo-second-order-reaction) were studied by researchers. Both sorption systems best fitted to the pseudo-second-order kinetic model with a higher rate constant value for dye-MN 200 in acidic media at temperature of 20 ^{0}C when compared with that of the dye activated carbon. They discovered, the rate of chromium dye adsorbed on adsorbents was highly based on film diffusion and intraparticle diffusion.

Wei et al. (2009) studied the reduction of chromium ions from waste liquid by Fe-Ni oxides. Sedimentation process was investigated for adsorption and separation of chromium ions on the Iron-nickel oxide which have magnetic properties. The experimental data was fitted using Freundlich and Dubinin-Kaganer-Radushkevich (DKR) isotherm equation for synthesis wastewater. They used FTIR analysis to know about functional group present in adsorbent before and after adsorption. The researcher found the adsorption capacity (maximum) of Cr(VI), nearly 30 µg/mg at 5 pH, and adsorption capacity reduces by increasing TDS of wastewater. They evaluated the sorption energies E about 10310-21321 J/mol which was derived at different TDS. In this research the recycle of used adsorbent was carried out by using the 0.1mol/L of caustic solution.

Aydin et al. (2009) used the chitosan (biologically produced polymer) as adsorbent which was prepared from chitson flake and activated by acid treatment for removal of chromium. In this study researchers were investigated the optimization of Cr (VI) adsorption upon chitosan by using Surface response methodology (SRM). They also evaluated the variety of process characteristic such as initial Cr (VI) concentration, pH and adsorbent dose in this research work. They studied the effects of these factors in the ranges of 1.5-9.5, 1.8-24.2 mg/ml and 15–95 mg/l, respectively. 20 experimental run were carried out with 3 replication of each to predict variance analysis of data obtained from quadratic model. They attained experimentally a maximum of 92.9% chromium removal at pH 3 with 13 g/l of chitosan dose. They calculated the mean free energy of adsorption (E) as 167 J/mol, which indicates the physical adsorption occurring on the surface of adsorbent due to weak van der Waals forces.

Acharya et al. (2009) investigated the adsorptive reduction of chromium ions on activated carbon which were prepared from tamarind wood (low cost adsorbent) and activated with zinc chloride to increase porosity. In this research work, study was conducted in the range of 10mg/l to 50 mgl^{-1} of C_0 and at temperature (T) in the range of 10 to 50 ^{0}C. Adsorption equilibrium data were fitted well by the researchers with highest adsorption capacity (mg/g) of 28.019 µg/mg. In their research they found that the rates of adsorption of Cr(VI) ions fitted the pseudo-second-order kinetics with good correlation factor rather than of pseudo first order kinetics. They found that the rate of chromium ions uptake was by film diffusion, pore diff usion and particle diffusion. Various thermodynamic parameters, such as ΔH^0, ΔG^0 and ΔS^0 were also evaluated and found the feasibility of adsorption process for Chromium remediation by low cost adsorbent.

Fouladi et al. (2009) prepared adsorbent using low-cost activated carbon, derived from nut shells, and further modified by chemical activation have been used as alternative for the current expensive methods of removing cadmium ions from waste waters. The performance of the adsorbent to remove cadmium using different kind of activated carbon such as: commercial activated carbon, prepared activated carbon, and the sulfurized ones were investigated. They prepared, treated with sulphur and characterized the carbon and then used it for the removal of Cd^{2+}. Samples were then characterized and tested to understand the mechanism of adsorption of cadmium ion. They also evaluated the effect of some parameters such as: initial concentration of metal, contact time and pH were examined

Mohan et al., (2006) developed various agriculture based activated carbon different feedstock(coconut shell).. Prepared activated carbon was characterized, and utilized it for the reduction of hexavalent chromium from wastewater. They systematically studied the chromium (VI) adsorption kinetics and equilibrium low-cost agricultural based activated carbons and also by commercially available activated carbon. Batch adsorption study was carried out at various parameters such as solution pH, adsorbent particles size, ambient temperatures, and adsorbent doses (g/l). The Freundlich and Langmuir models were fitted at constant temperature and the experimental data found reasonable. The experimental data showed that Langmuir model found well fitted compared to Freundlich isotherm. It also found that the data were good fitted with the nonlinear model than the linear. They also conducted kinetic studies to understand the effects of initial adsorbate concentration, temperature, solid to liquid ratio and adsorbent particle size. They found that the reduction of Cr(VI) follows "pseudo-second-order" rate model. To establish the mechanism different process parameters such as the entropy (S), diffusion coefficient and activation energy were also evaluated.

Suksabye et al. (2006) used coir pith to prepare adsorbent. Coir pith consists a healthy percentage of lignin which is better for metal ions (Cr(VI)) removal from effluent by changing the parameters such as pH of solution, dose, temperature (T) and contact time. They found maximum reduction of chromium at 2% dosage(wt/v), particle size less than 75 µm, system pH 2, at initial chromium ions concentration 1647 mg/l and an contact time of 18 hours. They evaluated the isotherm model for adsorbent and found Langmuir model fitted well. They experimentally found the maximum chromium ions adsorption capacity (mg/g) of adsorbent at 60 ^{0}C was 317.65 mg/g. They also studied the thermodynamic parameters which indicate an endothermic process. These researchers carried out the sorption experiment of hexavalent chromium on adsorbent and X-rays absorption which indicated that mostly chromium ion bound on the adsorbent was in the form of trivalent chromium because Cr(VI) adsorbed on the adsorbent surface was easily reduced to Cr(III). Functional groups were determined by FTIR spectrometry analysis. FTIR spectrum of chromium loaded adsorbent indicates the involvement of the different groups in the process of chromium reduction.

Srivastava et al. (2005) used rice husk ash (RHA) a low cost adsorbent for removal of heavy metals (Cd(II), Ni, Zn) from synthetically prepared wastewater. They characterized the rice husk ash for physic-chemical properties and mechanism of metal ions adsorption. During characterization they found the average particle size, ash content, Bulk density and the heating value of RHA as 150.47 µm, 104.9 g/l and 9680 KJ/kg respectively. The BET surface area and average pore diameter was 36.44 m^2/g and 42.603A^0 respectively. FTIR spectrum was evaluated to determine functional group on the surface of RHA. The presence of Si–O–Si, –OH, –C–OH and silicon-hydrogen groups on Adsorbent surface enhance a good amount of metal ion adsorption capacity. They experimentally found that cation exchange capacity on RHA surface was due to the presence of polar groups on the RHA surface. Batch experiments were carried out for removal of heavy metals from wastewater. They found optimum initial pH of system approximately 6 for individual cation at an optimum dose of 10 g/l. They studied the kinetics of adsorption which indicated that the equilibrium achieved in 5 hours. They found the pseudo-second-order kinetics model fitted well for experimental data. They also determined the diffusion coefficient for adsorptive removal of metals onto the RHA in the order of 10 to13 m^2/s.

.

Table 2.1 Advantages and disadvantages of different sorbents for chromium removal

S. No.	Sorbents	Advantages	Disadvantages
1	Ion-exchange resin	Good physicochemical characterization Highly selectivity towards aromatic Effective adsorbent Good surface area No loss during Regeneration	Expensive Sensitive to the particle Specific to pollutant Highly pH-dependent
2	Chitosan-based material	Low cost sorbent Environmental friendly Efficient sorbent Versatile sorbent Easily regenerate	Nonporous adsorbent Variability in the bead characteristics Highly pH-dependent Requires chemical modification Less affinity for basic dyes
3	Starch based material	Renewable Economically attractive Easy to prepare High swelling capacity in water Can remove wide range of pollutants Fast kinetics	Low surface area Requires chemical activation Fouling problem

S. No.	Sorbents	Advantages	Disadvantages
4	Activated carbon	Most effective sorbent Very high surface areas High capacity Porous adsorbent High rate of adsorption Fast kinetics Wide range of pollutants can be treated High percentage removal	Non-selective Expensive Cost increases with quality High regeneration cost Quality depend on the type of carbon Requires chemical activation Regeneration results in a loss of the carbon Not effective for hydrophilic substance

Advantages and disadvantages of various sorbent used for pollutant reduction from aqueous solution are listed in above table. Depending upon literature review carried out, the activated carbon is preferred for further experimental procedure for chromium ion removal using adsorption process. The history of using activated carbon as adsorbent is very long. Coal was firstly used as sorbent to remediate impurity from water and since then too many modifications have been seen to enhance the quality of activated carbon.

Table 2.2 Comparison of low cost activated carbons for hexavalent chromium removal

Adsorbents	Adsorption capacity (mg/g)	Contact time (h)	pH	Temperature (K)	Model fitted well	References
Chitosan	102	2	3	25	Langmuir	Aydin et al., 2009
Micellar compound	17.85	2	3	30	Freundlich	Sadaoui et al., 2009
Carbon slurry	15.24	1	2	30	Freundlich	Gupta et al., 2010
Peanut shell	8.24	20	4	25	Freundlich	Othman et al., 2012
Tamarind wood	28.09	0.75	6	30	Langmuir	Acharya et al., 2009
Raw dolomite	10.01	96	2	20	Freundlich	Albadarin et al., 2012
Heat treated algae	30.20	24	2	25	Langmuir	Arica et al., 2005
Beech sawdust	16.1	4	1	25	Langmuir	Acar et al., 2004
Ion exchange resin 1200H	84	2	4	25	Langmuir	Petruzzelli et al., 1995
Ion exchange resin 1500H	188.7	4	3.8	25	Langmuir	Petruzzelli et al., 1995
Ion exchange resin IRN97H	58.1	4	3.8	25	Langmuir	Petruzzelli et al., 1995
Activated carbon, GA-3	101.4	3	3	30	Langmuir	Hu et al., 2003
Activated carbon, SHT	69.1	3	3	30	Langmuir	Hu et al., 2003
Activated carbon, CZ-105	40.4	3	3	30	Freundlich	Hu et al., 2003
Activated carbon, CZ-130	44.9	3	3	30	Freundlich	Hu et al., 2003

CHAPTER-3

ADSORPTION FUNDAMENTALS

3.1 GENERAL

Adsorption is the adhesion of ions, molecules, atoms, liquid or dissolved solids to a surface. Adsorption process makes a film of the substances (adsorbate) which accumulate on the surface of the material called adsorbent. It is similar to absorption, in which a fluid is dissolved by a liquid or solid matter. Sorption encompasses both adsorption and desorption processes. It is a surface phenomenon. Adsorption occurs naturally but so many modifications have been made by researchers to meet industrial requirement. Adsorbents are generally used to reduce organic pollutant, especially those that are not biodegradable. The adsorption may be driven by

- Weak attraction force among atoms and molecules (Vanderwaals)
- Short range strong metallic forces

Adsorbents are generally used in the form of granular, spherical pellets, moldings, monoliths or rods with diameters between 0.2 and 1 mm. Adsorbent must have high thermal stability, small pore diameters, high surface area, high surface capacity and high abrasion resistance for adsorption. Most industrial adsorbents fall into these three categories:

- Polymer based compound- polymer matrix contains polar or non-polar functional group.
- Carbon based compound- such as activated carbon and graphite.
- Oxygen based compound- such as silica gel and graphite.

3.2 PARAMETERS FOR SELECTION OF ADSORBENT

Selection of adsorbent depends on various parameters. All process requires a degree of effectiveness, in many cases the pressure drop and adsorption rate are important parameters. Activated carbon offers low cost as well as high effective removal of pollutants. A large amount of various adsorbents are available in the market but it is very important to choose right adsorbent. Selection of adsorbent is based on various parameters which affect the adsorption process.

Important parameters for selection of adsorbent are as follows:

- Capacity
- Selectivity
- Regenerability
- Kinetics
- compatibility

High **Adsorption capacity** is the most desirable parameter of an adsorbent. It is the mass of solute (mg) adsorbed by the adsorbent on the surface, with 1 gram of adsorbent used. Capacity highly depends on the system temperature, concentration and other conditions. Generally adsorption capacity data are gathered at various adsorbate concentrations, fixed temperature and the data are plotted as an isotherm. Adsorption capacity is highly important because it determines the working cost of adsorption process. It determines the volume of the reactor which is much significant for economy of adsorption process.

Selectivity is related to the capacity. The selectivity simply is the ratio of the capacity of one adsorbing agent to other one at a fixed concentration. Selectivity usually tends to a constant at low concentration. The analogy to selectivity is the relative volatility.

All continuous adsorption applications depend on **regenerability** of adsorbent, so that the adsorbent can use in cycles with uniform performance. This indicates that the each adsorbable pollutant must be relatively weakly adsorbed. The heat of adsorption related to the energy required for regeneration, and low values of heat of adsorption are desirable.

Mass transfer kinetics is a term related to intraparticle mass transfer resistance. It is quite important because it fixed the cycle time for fixed bed adsorption process. Fast kinetics shows a sharp breakthrough curve while slow kinetics provides a distended curve. The effect of a distended curve may be eliminating by increasing the cycle time or adding dose at the product end. Kinetics has even been termed as the basis of adsorptive separations. Most common example is the separation of nitrogen from air using carbon molecular sieve, which relies on fast diffusion of oxygen compared to the nitrogen. Normally slow diffusion of any adsorbate is termed as a disadvantage to adsorption process.

Compatibility includes various possible modes of physical and chemical attack that could shorten the life of the adsorbent, by the means of attrition or biological fouling. For example, the binder, adsorbent, and surface functional groups should be inert to the carrier and should not irreversibly react with the adsorbate or contaminants. Likewise, other operating conditions such as temperature, velocity, vibration and pressure should not cause undue harm to the adsorbent particles. This could happen by abrasion or crushing and there are some standard methods for measuring those.

3.3 FACTORS AFFECTING ADSORPTION PROCESS

There are a number of factors that interfere with the adsorption process. The most important factors affecting adsorption are as follows:

3.3.1 Surface area of adsorbent: Larger the surface area, greater will be the adsorption of impurities on adsorbent. This provides a large area for adsorbate to interact with the adsorbent and hence larger amount of adsorbate get attached within the pore. In simple word we can say, larger sizes imply a greater adsorption capacity and hence reduces the working capital cost.

3.3.2 Particle size: Smaller particle sizes reduce mass transfer and internal diffusional resistance to the penetration of the adsorbate inside the pore. Equilibrium is easily attained and almost full adsorption capability can be achieved by smaller particles. However, wastewater drop across columns, packed with powdered adsorbent is too high for use of this adsorbent in packed beds. Addition of powdered carbon must be followed by their removal.

3.3.3 Residence time: The longer the contact time the more adsorption will be accomplish. However, the equipment size will be larger for longer residence time. Larger time gives enough time for the adsorbate to react with the adsorbent and hence results in greater removal percentage. But long contact time is not good for adsorption process there should be optimum time for attachment of adsorbate on the adsorbent.

3.3.4 Solubility of adsorbate in wastewater: High soluble pollutant is hard to remove when compared with slightly soluble pollutant in water. Slightly soluble substance attached with water by weak forces hence, attraction by adsorbent surface may break these weak bonds easily. Non-polar substances generally more easily removed than polar compounds since the polar substances have a greater affinity for water. It is well known fact that if a substance has much affinity for another substance, then it requires a lot of energy to separate them. Hence, we may say that greater the solubility of pollutant with wastewater, lesser will the adsorption will take place.

3.3.5 Affinity of the solute for the carbon: it is a fact that the surface of activated carbon is slightly polar. Hence non-polar compounds show high affinity to the carbon surface while polar ions show repulsive effect on adsorbent surface.

3.3.6 Size of the molecules with respect to size of the pores: Pore size plays important role in adsorption process. Large molecules may be difficult to enter in small pores. This may reduce adsorption of adsorbate, independently of other causes. As with the case with lignin, adsorbent having larger pores is suitable for lignin removal.

3.3.7 The pH: The degree of ionization as well as surface charge of the adsorbent mainly affected by pH of the solution. The pH of wastewater affects the equilibrium parameters and reaction kinetics due to the dissociation of functional groups. The hydroxyl ions and hydrogen ion are adsorbed quite strongly and, therefore, the adsorption of other ions is altered by the pH. It is a general consideration that the surface attract anions favorably at lower pH due to presence of H^+ ions, while, the surface is more active for the adsorption of cations at higher pH due to accumulation of OH^- ions (Srivastava et al., 2005).

3.3.8 Agitation speed: In batch experiments agitation speed improve the removal efficiency of impurity. This ensures proper contact time between the adsorbent and the adsorbate. At lower agitation, the fluid film around the particle is thicker. If adsorption process is controlled by mass transfer then transfer of particles to the active sites decreases due to this film. By the means of agitation, the thickness of this film decreases and reduces the mass transfer resistance. When mass transfer resistance is very small then process governs by intra particle diffusion. Solution does not affect by the extent of agitation and hence for intra particle diffusion controlled process, agitation has no effect on the rate of adsorption.

3.3.9 Temperature: Temperature also affects the absorption of adsorbate, but to a limited extent under a particular range of temperature. Adsorption is normally exothermic process, so adsorption capacity (mg/g) increases with decrease in temperature. Reduction in adsorption capacity at higher temperature may be due to the damage of active sites within the adsorbent. Desorption of adsorbed substance also takes place at high temperature. Hence it is desirable to conduct adsorption process at room temperature since this condition is easily replicable.

3.4 ADSORPTION ISOTHERMS

When a solution is agitated with a solid adsorbent, molecules/ions of adsorbate get shifted from the fluid to the solid phase until the concentration of adsorbate in aqueous solution as well as in the adsorbent are in equilibrium. When equal amounts of solute eventually are being desorbed and adsorbed simultaneously then this is known as adsorption equilibrium. In adsorption process the equilibrium data at constant temperature are illustrated by adsorption isotherm. Isotherm study is important for the design of heterogeneous reactors to purify the wastewater. Many empirical and theoretical models have been proposed to represent the different types of adsorption isotherms. Brunauer-Emmet-Teller (BET), Langmuir, Redlich-Peterson (R-P), Freundlich etc. are commonly used isotherm models for reporting the dynamic equilibrium condition. Various isotherm equations used for the adsorption study are given below:

3.4.1 LANGMUIR ISOTHERM

Langmuir derived the isotherm equation on basis of assumption for the absorption of a solute from a liquid solution.

- Surface has affinity towards the solute present in the solution.
- The adsorbent surface has a number of active sites where the adsorbate can be adsorbed.
- Monolayer adsorption.

Numerically Langmuir isotherm equation can be written as:

$$q_e = \frac{Q_m K_A C_e}{1 + K_A C_e} \tag{3.1}$$

Where,

Q_e (mg/g) = Mass of adsorbate adsorbed per unit mass of adsorbent at equilibrium condition.
Q_m (mg/g) = Mass of adsorbate adsorbed per unit mass of adsorbent required for mono layer.
C_e(mg/l) = Adsorbate concentrations of solution at equilibrium condition.
K_A = Constant related to enthalpy of adsorption.

3.4.2 FREUNDLICH ISOTHERM

In many instances the heat of adsorption decreases with increasing extent of adsorption process. This decline in heat of adsorption is logarithmic, suggesting that adsorption active sites are distributed exponentially with the heat of adsorption. This type of isotherm does not show an adsorption limit when coverage is enough to fill a mono layer. The equation that show such type of isotherm is called Freundlich isotherm which mathematically given as

$$q_e = K_F C_e^{1/n} \tag{3.2}$$

Where,

Q_e = Mass of adsorbate adsorbed per unit mass of adsorbent at equilibrium condition

K_F = Freundlich constant

C_e = Equilibrium concentrations

n = Exponential constant

3.5 ADSORPTION MECHANISM AND KINETICS

Kinetic study for a given system is probably the most important factor in adsorption process design. Various kinetic models have been presented to describe the reaction order of adsorption process based on concentration. These include pseudo-first-order and pseudo-second-order, bangham model and intra-particle diffusion model to study the kinetic behavior of adsorption process.

The adsorption dynamic behavior can be described by the following three steps:

- Transport of adsorbate from bulk solution through liquid film to adsorbent surface;
- Adsorbate diffusion into the pore of adsorbent except for a small quantity of sorption on external surface;
- Adsorption of Adsorbate on interior surfaces of capillary spaces and pores of adsorbent.

3.5.1 PSEUDO-FIRST ORDER MODEL

Lagergren pseudo first-order model assumes that the rate of change of solute uptake with time is directly proportional to the difference in the equilibrium adsorption capacity and the amount of solute uptake with time.

The general form of this model is expressed as

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad (3.4)$$

Where,

q_t is the mass of adsorbate per mass of adsorbent used at time t (mg/g).

q_e is the adsorption capacity at equilibrium (mg/g).

K_1 is the rate constant of adsorption $(\min^{-1})$.

t is the contact time (min).

After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the equation becomes,

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \qquad (3.5)$$

Value of adsorption rate constant (K_1) is determined by the plot of $\log(q_e - q_t)$ vs time. From the slope and the intercept the values of K_1 and q_e are calculated respectively.

3.5.2 PSEUDO-SECOND ORDER MODEL

The pseudo second-order model is based on the sorption capacity of the solid phase. The general form of this model is given by:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{3.6}$$

The linear form of above equation can be written as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{3.7}$$

Where,

K_2 = Pseudo-second order rate constant [g / (mg) (min)].

t = Contact time (min)

3.5.3 INTRA-PARTICLE DIFFUSION STUDY

In many adsorption cases Weber-Morris found that, adsorbate uptakes varies proportionally with $t^{1/2}$ rather than residence time t (Alkan et al., 2007). Weber-Morris model is used to explain intra-particle diffusion. Diffusional model proposed by Weber-Morris mathematically written as:

$$q_t = k_{int} t^{1/2} + I \tag{3.8}$$

Where, k_{int} is the intra-particle diffusion rate constant (mg g^{-1} $min^{-1/2}$), q_t is the adsorption capacity (mg/g) and I is the intercept (mg g^{-1}). According to above equation, a plot of q_t versus $t^{1/2}$ should be a straight line with a intercept I and slope k_{int} for diffusion model. It is evident that if intra-particle diffusion is the only rate-limiting step in the adsorption process then q_t versus $t^{1/2}$ plot should go through origin. The deviation of the straight lines from the origin may be due to the difference in the mass transfer rate during the initial and final stages of adsorption (Mall et al., 2005).

3.5.4 BANGHAM'S KINETIC EQUATION

Slow steps occurred in adsorption study were further analyzed using Bangham's equation (Aharoni et al., 1979). Bangham's model mathematically expressed as:

$$\log\left(\log\left(\frac{C_0}{C_0 - q_t m}\right)\right) = \log\left(\frac{C_0 m}{2.303V}\right) + \alpha \log(t) \tag{3.9}$$

Where, m is the mass of adsorbent used per liter of solution (g/l), α (<1) and k_0 (g) are constants, V is the volume of solution (l).

3.6 ESTIMATION OF THERMODYNAMIC PARAMETERS

Thermodynamic parameters such as Gibbs free energy change ΔG^0 (kJ/mol) generally estimated using classical Vant's Hoff equation at different temperatures (298 K, 308 K, 318 K, 328 K):

$$\Delta G^0_{ads} = -RT \ln K_{ads} \tag{3.10}$$

Where K_{ads} is the equilibrium constant of interaction between the solute and the adsorbent surface, R is the universal gas constant (R=8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (Kelvin). The Gibbs free energy also related to the heat of adsorption (ΔH^0) and change in entropy (ΔS^0) at a constant temperature, which may be given by the equation:

$$\Delta G^0_{ads} = \Delta H^0 - T\Delta S^0 \tag{3.11}$$

The previous two relations give the equation:

$$\ln K_{ads} = \frac{\Delta G^0_{ads}}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R}\left(\frac{1}{T}\right) \tag{3.12}$$

Where ΔH^0 (kJ/mol) is the change in enthalpy and ΔS^0 (kJ mol^{-1} K^{-1}) is the change in entropy. Thus ΔH^0 and ΔS^0 can be determined by the slope and intercept of linear Vant's Hoff plot (ln K_{ads} versus (1/T)) respectively. Where m is the amount of adsorbent (g/L), C_e is concentration of metal ion solution at equilibrium (mg/L), q_e is the amount of metal ion at equilibrium in unit mass of adsorbent (mg/g), q_e/C_e is called the adsorption affinity. ΔH^o, ΔS^o and ΔG^o are changes in enthalpy (KJ mol^{-1}), entropy (J mol^{-1} K^{-1}) and free energy (KJ mol^{-1}), respectively.

3.7 MODEL VALIDATION

In order to investigate the goodness of the fit of the experimental values and the prediction accuracy of the models utilized in this work, the following statistical indices are employed for hexavalent chromium adsorption system.

The sum of the squares of the error (SSE): The function will result in the estimated isotherm parameters providing a better fit at the higher end of the liquid-phase concentration. This is due to the fact that magnitude of the errors and hence the square of the errors will increase as solution concentration increase (Allen et al., 2004):

$$\text{SSE} = \sum\left(q_{e,exp} - q_{e,cal}\right)^2 \tag{3.13}$$

Root mean squares of error (RMSE): It is a frequently measure of the differences between values predicted by a model or an estimator and the values actually observed. It is a good measure of accuracy.

$$\text{RMSE} = \sqrt{\frac{\sum\left(q_{e,exp} - q_{e,cal}\right)}{N}} \tag{3.14}$$

Standard error of prediction (SEP): The SEP is the standard deviation of differences between the predicted and reference values for a set of samples (). The formula of SEP is given below.

$$\text{SEP} = \frac{\text{RMSE}}{\sum\left(q_{e,exp}/N\right)} \times 100 \tag{3.15}$$

Normalized standard deviation (NSD): The calculation of NSD can be achieved by using following formula:

$$\text{NSD} = \sqrt{\frac{\sum\left[\left(q_{e,exp} - q_{e,cal}\right)/q_{e,exp}\right]^2}{N}} \times 100 \tag{3.16}$$

Normalized deviation (ND): The formula for the calculation of ND is given below:

$$\text{ND} = \sum\left|\frac{\left(q_{e,exp} - q_{e,cal}\right)}{q_{e,exp}}\right| \times \frac{100}{N} \tag{3.17}$$

Where, $q_{e,exp}$ is the experimental value of adsorption capacity $q_{e,}$ while $q_{e,cal}$ is the predicted value of q_e by models and N is the number of data points in the experimental run.

CHAPTER-4

EXPERIMENTAL WORK AND PROCEDURE

Present investigation was carried out to remove hexavalent chromium and COD from wastewater of the electroplating industry. Removal of hexavalent chromium and COD was carried out with the help of activated carbon prepared by corncob. In this chapter, experimental setup and procedure used for present study are being described.

4.1 PREPARATION OF CORNCOB BASED ACTIVATED CARBON (CAC):

The corncob was collected from Rama agro mill located nearby Roorkee, India. Corncobs were washed with water to remove dirt and then cut into small pieces of 0.5-1 cm. size and dried into sunlight for 12 hours and after that further dried in hot air oven at 103^0C for four hour. The activated carbon was then prepared by thermal as well as chemical activation process. Carbonization and activation step may be written as:

Step 1: First step is carbonizations step in which small pieces of corncobs were put into muffle furnace and the furnace temperature increased up to 450 ^{0}C for four hour.

Step 2: After carbonization step char/corncob ratio obtained. Now char was crushed and sieved by screen analysis to a uniform size ranging from 850 to 2000 µm.

Step 3: This powder well mixed with sodium hydroxide in glass beaker with weight ratio of NaOH/char equal to 3 and impregnated for two hour.

Step 4: The impregnated char was put in hot air oven at 103 ^{0}C for overnight to remove water.

Step 5: Now dried impregnated char again carbonized in muffle furnace at 600 ^{0}C, and kept at this temperature for two hour.

Step 6: The resultant carbon was again washed several times to remove leachable component attached to CAC and to adjust pH in the range of 6-8 with distilled water. It was further dried at 110^0C in an oven for 6 hours. Finally, the dried corncob based activated carbon (CAC) was sieved to get the particle-size ranging from 450 to 850 µm.

4.2 CHARACTERIZATION OF CAC

4.2.1 PROXIMATE AND ULTIMATE ANALYSIS

Proximate analysis was used to determine moisture content, fixed carbon, volatile matter and ash content. Indian standard 1350 part I was used to perform proximate analysis of corncob based activated carbon. Any organic matter basically composed of essential component (element) like carbon, oxygen, hydrogen and nitrogen. Trace amount of sulfur may also present. Ultimate analysis was used to find out the composition of these essential elements. Indian standard 1350 part VI was followed for ultimate analysis.

4.2.2 BET SURFACE AREA ANALYSIS

Brunauer-Emmett-Teller (BET) analyzer was used to determine the surface area of corncob based activated carbon (CAC). The specific surface area of the CAC was investigated by N_2 adsorption isotherm using an ASAP 2020 micrometric instrument.

4.2.3 SEM

For the present study, “FE-SEM Quanta 200 FEG, Netherlands” instrument was used to observe the surface texture of the CAC and to get qualitative idea about the morphology and porosity of the CAC.

4.2.4 FTIR

FTIR analysis was performed to find the major functional groups involved in Cr(VI) and COD removal. The CAC sample was mixed with KBr and pellet was prepared. FTIR of CAC was done before and after adsorption. The FTIR spectra were recorded using a Nicolet 6700 FTIR apparatus. The sample was scanned at resolution between 4000 and 500 cm^{-1}. OMNIC software was used to find out the spectra.

4.2.5 THERMOGRAVIMETRIC ANALYSIS:

To determine the chemical and physical properties of the prepared CAC, TGA analysis has been carried out by using “EXSTAR TG/DTA 6300, PerkinElmer, Japan” a Thermogravimetric Analyzer with simultaneous measuring of derivatives thermogravimetry (DTG), differential thermal analysis (DTA) and thermogravimetry (TG) curves. Samples of 10-11 mg were heated from room temperature to 1000 ^{0}C at the heating rate of 10 ^{0}C/min under N_2 atmosphere. The temperature of decomposition and melting were measured as the temperature of corresponding endothermic maximum point.

4.2.6 POINT OF ZERO CHARGE

It is important to find out the point of zero charge (pH_{PZC}) to understand the adsorption mechanism. We know that adsorption of cations is favoured at pH greater than the pH_{PZC}, while anions is favoured at pH lower than the pH_{PZC}. The adsorption of anions shifts towards higher values, while the adsorption of cations shifts towards lower value. Solid addition method was carried out to determine the point of zero charge of CAC [Balistrieri et al., 1981]. To determine pH_{PZC}, $NaNO_3$ solution of known concentration was prepared by dissolving known amount of sodium nitrate pellets into a 500 ml conical flask. 45 ml of sodium nitrate solution was then transferred into a series of flask (100 ml). The initial pH (pH_0) of the various flask were roughly adjusted from 2-12 by adding either 0.1N H_2SO_4 or sodium hydroxide solution. The initial pH values of each flask were accurately noted. Thereafter one gram of CAC was added to each flask and capped properly. Then flasks were shaked and allowed to equilibrate for 2 days. After 48 h, the final pH of the each solution was noted. The difference between the initial (pH_0) and final pH (pH_f) values ($\delta pH = pH_0 - pH_f$) was plotted against the initial pH (pH_0) values. The point of intersection of the resulting curve at which δpH is zero gave the point of zero charge. This procedure was repeated for different concentrations of $NaNO_3$ (Srivastava et al., 2006).

4.3 SOURCE OF WASTEWATER

Electroplating waste water was collected from S K udhyog (Automobile part’s plating) Agra city, U.P. India. Wastewater was filtered and stored at 5 ^{0}C for further use. S K udhyog a small scale electroplating industry uses chromic acid for chrome plating which is source of hexavalent chromium.

4.4 CHEMICAL AND ANALYTICAL MEASUREMENT

Chemicals utilized in the present study were of analytical reagent (AR) grade. Chemical oxygen demand was measured using UV–visible spectrophotometer (HACH, DR 5000, USA) and digestion unit (DRB 200, HACH, USA). Dissolved hexavalent chromium was determined by flame atomic absorption spectrophotometer (AAS GBC Avanta, Australia) using air–acetylene burner at 425.4 nm wavelength. Before the analysis, the sample was diluted to the suitable concentration range (2-20 mg/l) with distilled water. After adsorption samples were filtered using Whatman (40 µm) filter paper and the filtrates after suitable dilutions, were analysed. The calibration curve of absorbance versus Cr(VI) concentration showed a straight line in the concentration range of 5-20 mg/l. pH of samples were maintained by adding NaOH or H_2SO_4 as per requirement.

4.5 CALIBRATION CURVE

The calibration curve of absorbance versus standard Cr(VI) solution concentration showed a linear variation in the concentration range of 0-20 mg/l. Standard solution (analytical grade, purity > 99%) of hexavalent chromium was procured from market. Standard solution of concentration 5, 10, 15 and 20 were prepared by diluting procured stock solution. The calibration of adsorbate (Cr(VI)) was carried out by flame atomic absorption spectrophotometer at wavelength of 425.4 nm. The concentration range was taken 5-20 mg/l of adsorbate. The calibration curve was obtained between standard concentration of Cr(VI) and corresponding absorbance.

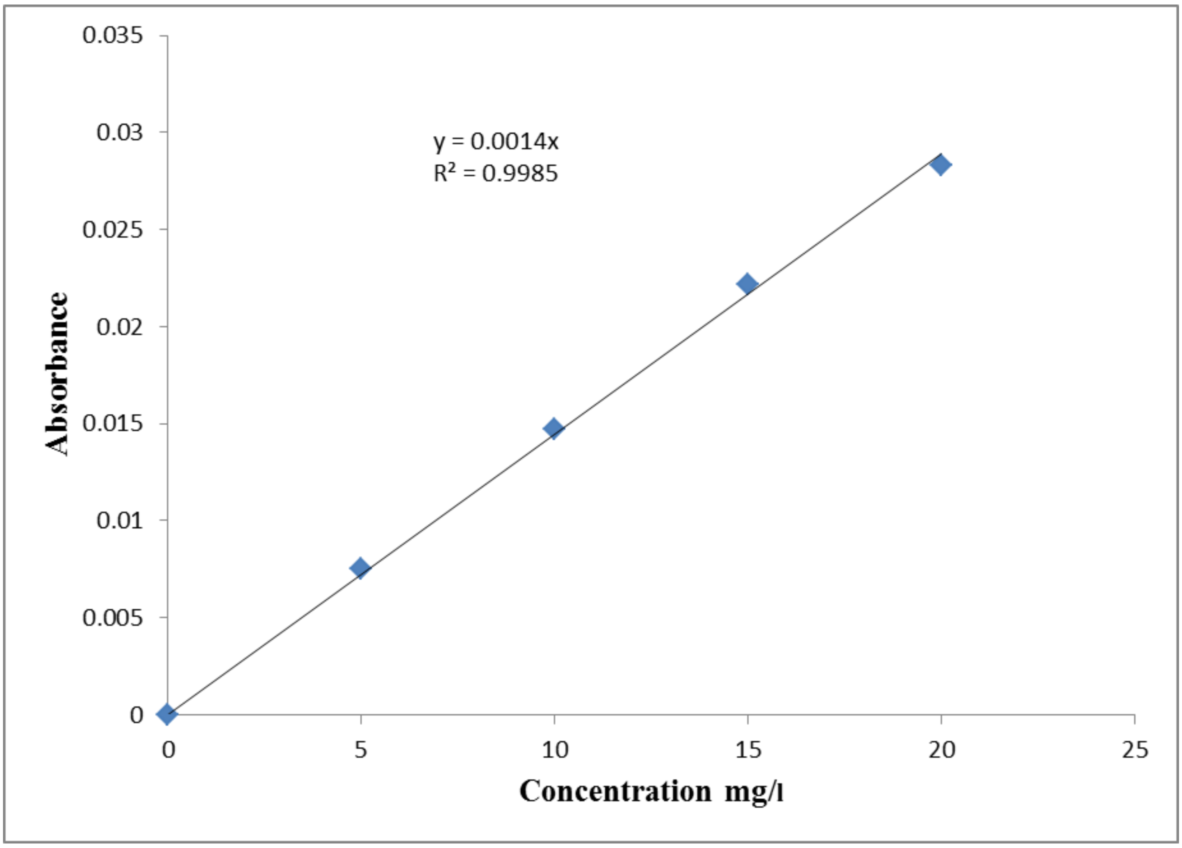


Figure 4.1: Calibration curve

4.6 CHEMICAL OXYGEN DEMAND

The chemical oxygen demand (COD) is considered as the representation of pollution level in industrial wastewater. COD value is the measurement of total oxygen required to oxidize the organic matter to CO_2 and H_2O. COD value is always greater than BOD because COD value include oxidation of biodegradable as well as non-biodegradable substances. The COD measurement is based on the fact that mostly organic compounds can be completely oxidized by strong oxidizing agents in the acidic medium. Standard solutions were prepared for COD measurement. A fixed amount of $K_2Cr_2O_7$ was mixed with appropriate amount of H_2SO_4. Prepared solution marked as solution (1). To prepare solution (2), calculated amount of Ag_2SO_4 was mixed with appropriate amount of H_2SO_4. For COD measurement, we took 1.5 ml of solution (1), 3.5 ml of solution (2) and 3 ml of diluted wastewater and then mixed them to COD vials. After proper mixing vial were put in digester for 2 hr at 150 ^{0}C. Thereafter we measured COD by COD meter.

4.7 BATCH ADSORPTION STUDIES

Batch adsorption studies were carried out at different desired pH, for different time, different adsorbent dose and at different temperature. First of all, 100 ml of wastewater was taken in the 250 ml of conical flask. Then solution was maintained at desired pH, with desired adsorbent dose, at a particular temperature and for a definite time in a shaker cum incubator at 150 rpm maintained temperature and at 25 ^{0}C. The initial pH (pH_0) of the adsorbate solution was adjusted using 0.1N H_2SO_4 or 0.1N NaOH aqueous solution. After completion of adsorption, the samples were filtered using whatman filter paper (40 µm) and filtrates were analyzed by Atomic adsorption Spectrophotometer (GBC Avanta, Australia) for Cr(VI) detection. Before the analysis, the samples were centrifuged at 10,000 rpm for 30 min using a Research Centrifuge (Remi Instruments, Mumbai) to remove all the suspended matter.

The percentage removal of metal ions by CAC and equilibrium adsorption uptake q_e (mg/g) in solid phase, were calculated using the following relationships:

$$\text{Metal ions removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

Amount of adsorbed metal ions per gram of solid (adsorption capacity)

$$q_e = \frac{(C_0 - C_e)V}{w}$$

Where,

C_0 = Initial metal ion concentration (mg/l)

C_e = Equilibrium metal ion concentration (mg/l)

V = Volume of the solution (l)

W = Mass of the CAC (g)

4.8 STUDY OF VARIOUS EFFECTS ON ADSORPTION

The pH EFFECT

100 ml of the samples were taken in different flasks (250 ml). Thereafter pH of the samples in each flask was maintained at 2, 3, 4, 5, 7, 8 and 9 by adding 0.1N H_2SO_4 or 0.1N NaOH solution. There after each flask were loaded with 10 g/l of CAC and the flasks were kept at 25^0C for two hours. After two hours flasks were taken out and the samples were centrifuged at 10,000 rpm for 30 min. Then samples were analyzed by AAS instrument.

ADSORBENT DOSE EFFECT

Different amounts of adsorbents from 1g/l to 20 g/l were added to 100 ml of sample. Before adding adsorbent pH of each sample was maintained at the optimum level. After that samples were kept for 2 hours at 25^0C in an incubator cum shaker. The analysis for Cr(VI) and COD were achieved by above given methods.

TEMPERATURE EFFECT

Here pH and dose were kept constant as obtained earlier. Temperature was varied from 25^0C to 45^0C. Rest of the process for Cr(VI) and COD was same.

4.9 KINETICS STUDY FOR Cr(VI) AND COD REMOVAL

The samples were kept in duplicate for 15, 30, 45, 60, 120, 180, 240, 300, 360, 720, 1080 and 1440 min in shaker cum incubator at 25^0C. Other parameters were kept constant. Then samples were analyzed for Cr(VI) and COD removal.

CHAPTER-5

RESULT AND DISCUSSION

5.1 PROXIMATE AND ULTIMATE ANALYSIS OF CORNCOB

Result of proximate and ultimate analysis shows that a good amount of carbon is present in the corncob which makes this a potential raw material for activated carbon preparation. Values of proximate and ultimate analysis are given in the following table:

Table 5.1 Proximate and ultimate analysis of corncob

Proximate analysis (% ash free basis)	
Moisture content %	14.5
Volatile matter %	68.7
Fixed carbon %	16.8
Ultimate analysis	
Carbon	44.26
Hydrogen	1.915
Nitrogen	0.228
Sulphur	0.01

5.2 THERMOGRAVIMETRIC (TG) ANALYSIS FOR CORNCOB

The TG curve for corncob shows that there is no loss in weight at room temperature. At 100^0C loss in weight of corncob is 5.5% corresponding to the moisture content. Three different zones were found at different temperature ranges (1st zone- 27 to 200^0C, 2nd zone- 200 to 500^0C, 3rd zone – 500 to 1000^0C) for corncob. In first zone loss in weight of corncob is 6.6% due to the loss of bound moisture. Corncob does not show any endothermic transition in the first zone which indicates the lack of any phase change during oxidation [Ng et al., 2002]. The weight loss ~64.10% occurred in the second zone. The exothermic peak for corncob was found between 200 ^{0}C and 400 ^{0}C shows the degradation of sample by oxidation due to the loss of volatile matter and carbonaceous compound. On degradation it produced

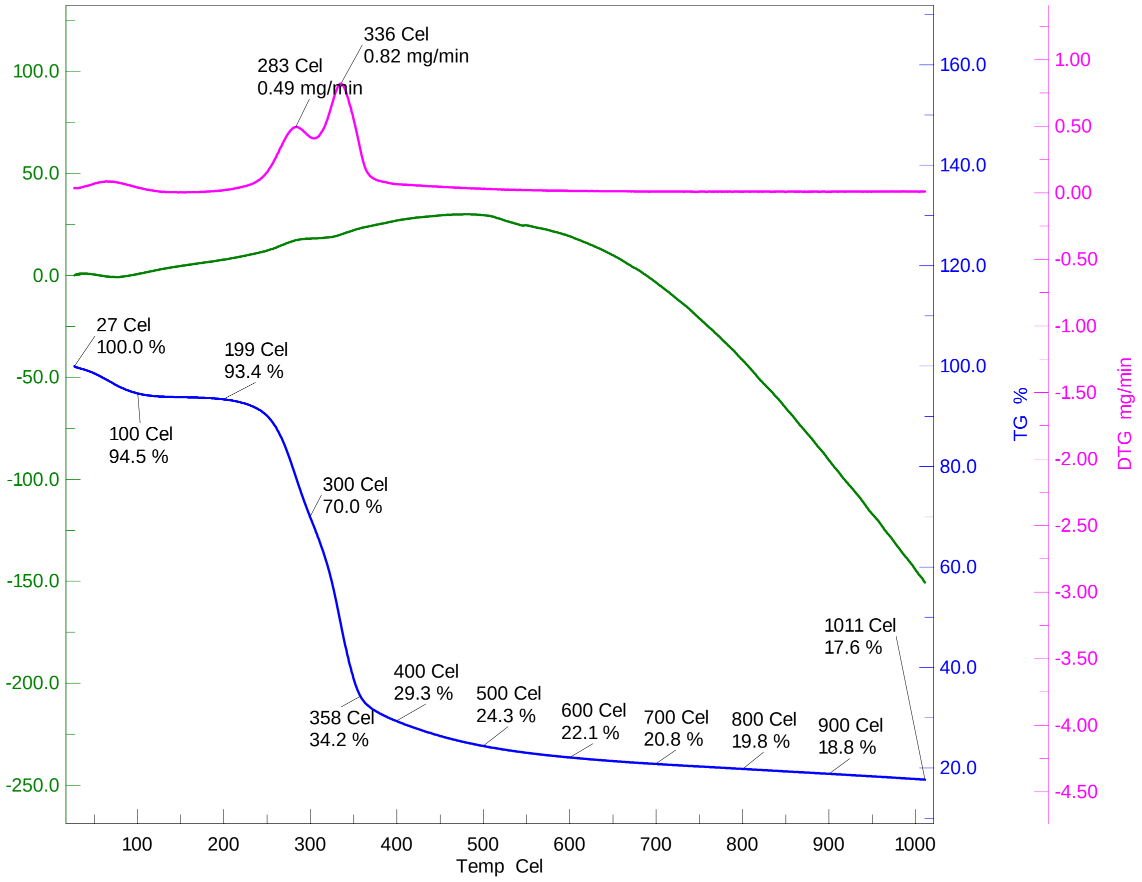


Figure 5.1 TG curve for corncob

5.3 CHARACTERIZATION OF CAC

Various techniques and instruments were used for the characterization of Corncob based activated carbon. Indian standard 1350 part I and IV was used to perform proximate and ultimate analysis of CAC respectively. The pore volume, specific surface area and pore diameter of the sample were determined by N_2 adsorption isotherm using ASAP 2020 micrometric instrument and by Brunauer-Emmett-Teller (BET) method. FTIR instrument was used to find out the vibrational frequencies of the functional groups present in the adsorbents. FTIR, Nicolet 6700, USA spectrometer was utilized to find out the various type of functional groups on the adsorbents surface before as well as after adsorption. Thermogravimetric analysis of the adsorbents (EXSTAR TG/DTA 6300, PerkinElmer, Japan) was carried out to observe the loss of weight of adsorbent as well as corncob with change in temperature.

5.3.1 BET SURFACE AREA

The specific surface area of the CAC was measured by N_2 adsorption isotherm using ASAP 2020 micrometric instrument and by Brunauer-Emmett-Teller (BET) method. The micro-pore area of the CAC was 307.55 m^2/g. The pore volume of CAC was 0.23cm^3/g. The BJH Adsorption average pore diameter (4V/A) and BJH Desorption average pore diameter were 31.741 A^0 and 29.999 A^0 respectively. Properties of corncob based activated are listed in table 5.2 as follows:

Table 5.2 Properties of corncob based activated carbon (CAC)

S.NO.	Properties	Value
1	BET Surface Area (m^2/g)	399.066
2	Total pore volume (cm^3/g)	0.230426
3	Point of zero charge (pH)	6.5
4	Moisture content (wt %)	9.32
5	Volatile matter (wt %)	24.77
6	Fixed carbon (wt %)	37.62
7	Ash content (wt %)	28.29
8	Average pore diameter (A^0)	23.0965
9	Particle size (µm)	450-850
10	Carbon (wt %)	81.86
11	Hydrogen (wt %)	0.35
12	Nitrogen (wt %)	0.308
13	Sulphur (wt %)	0.037

5.3.2 Point of zero charge

The value of point of zero charge obtained at the intersection of the initial pH with the $\delta pH = 0$ line. Point of zero charge represents the point at which pH of solution neither favours cations nor anions. At all concentrations of $NaNO_3$, the point of zero charge lies at the initial pH value of 6.5.

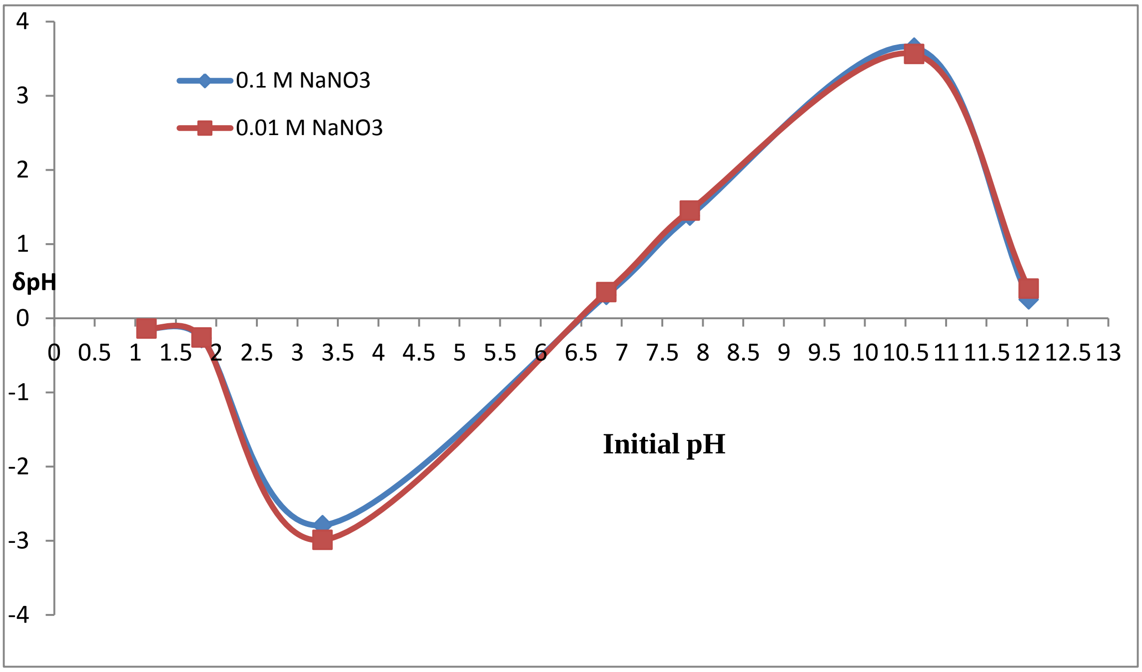


Fig 5.2 Point of zero charge of CAC

5.3.3 FTIR

The samples were scanned at resolution between 4000 and 500 cm^{-1}. Strong vibration peaks in between 3,500-3,000 cm^{-1} are demarcated as the vibrations of O-H and N-H functional groups. O-H stretching vibrations can be seen at 3434.61 cm^{-1} in blank CAC. The most important vibrational modes are the C-H stretching around 3000 cm^{-1}. C-H stretching found at 2923.26 cm^{-1} in blank CAC. The peak at 1569.50 cm^{-1} is caused due to the presence of C=C in aromatic rings and C=H stretching. Due to stretch of C-N there is a peak at 1061.85 cm^{-1}. The symmetric CH_3 vibration occurs at 1390-1370 cm^{-1}. The symmetric CH_3 vibration found at 1383.55 cm^{-1}. The new band at 1456.19 cm^{-1} attributed to CH_3 asymmetric deformation vibration due to Cr(VI) loading. From the above analysis it could be concluded that oxygen and nitrogen atoms play a major role in adsorption of Cr(VI).

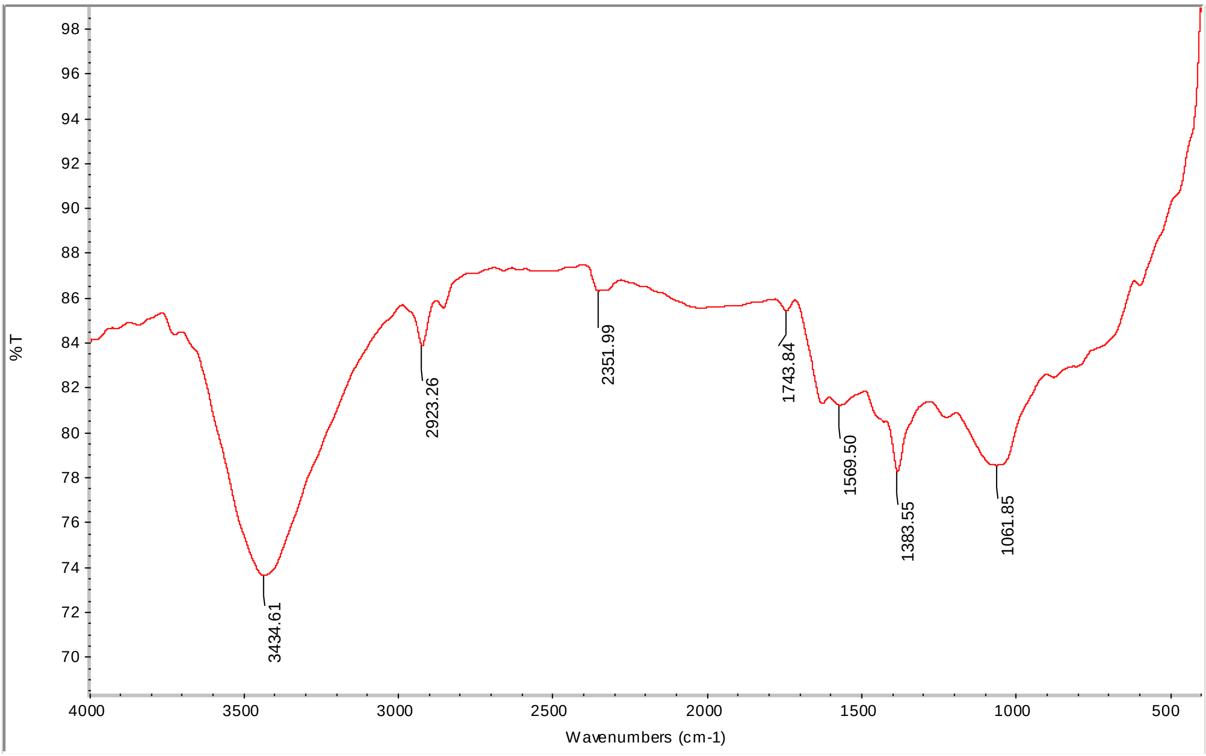


Fig 5.3 FTIR spectra of blank CAC

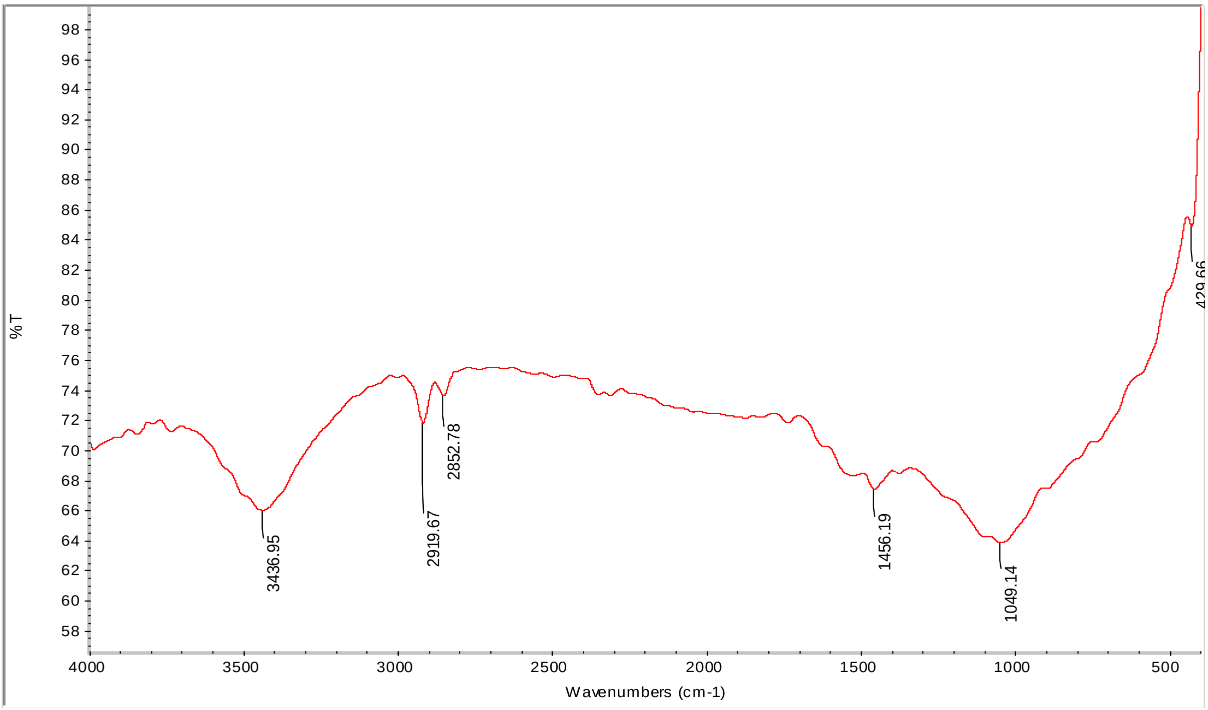


Fig 5.4 FTIR spectra of Cr(VI) loaded CAC

5.3.4 THERMOGRAVIMETRIC ANALYSIS OF CAC:

Thermal stability of CAC is directly dependent on the decomposition temperature of its various oxides and functional groups. The TG curve for corncob based activated carbon shows that there was no loss in weight at room temperature. At 100^0C loss in weight of CAC was 7.77% corresponding to the moisture content. Three different zones were found at different temperature ranges (1^{st} zone- 27 to 200^0C, 2^{nd} zone- 200 to 500^0C, 3^{rd} zone – 500 to 1000^0C) for CAC. In first zone loss in weight of corncob is 8.68% due to the loss of bound moisture while other zones did not show appreciable amount of weight loss.

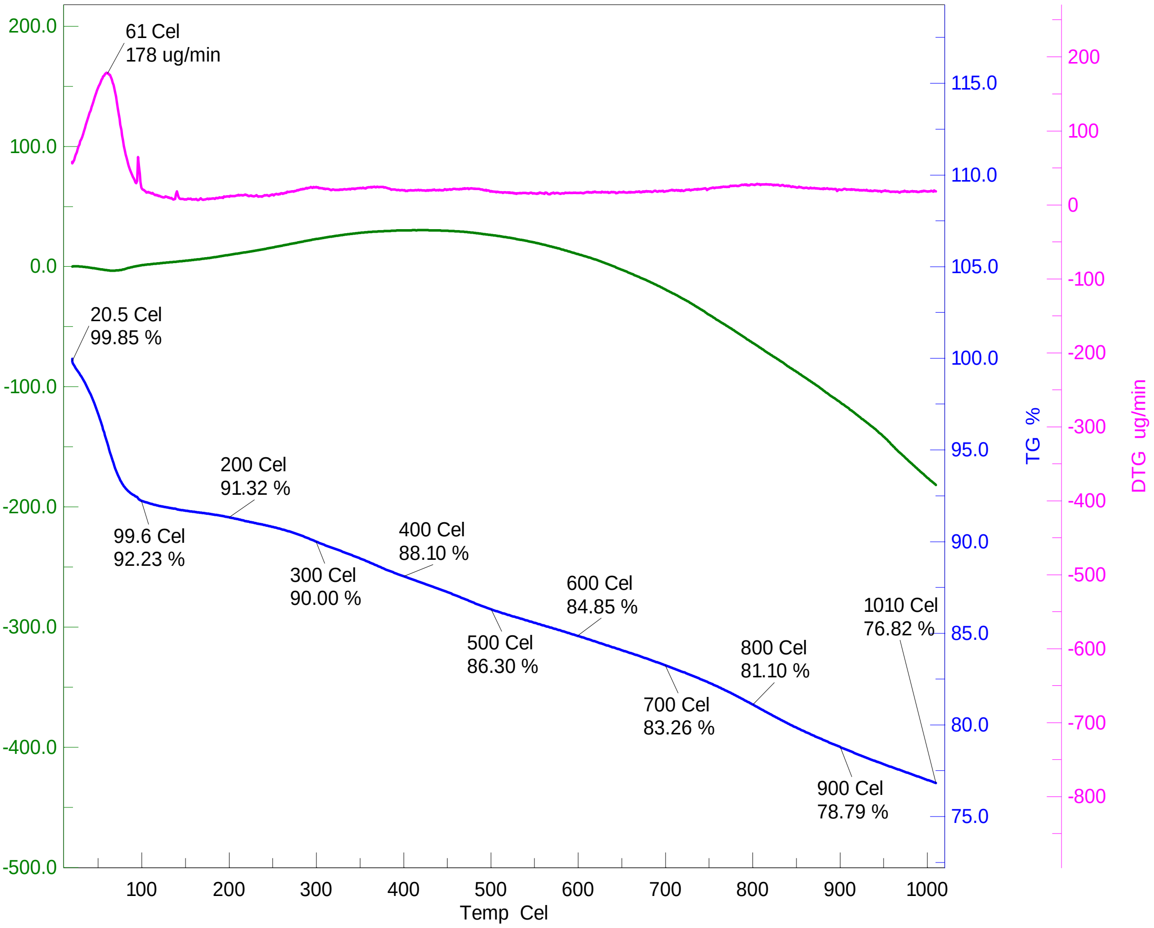


Fig 5.5 Thermogravimetric curve of CAC (before adsorption)

5.3.5 SCANNING ELECTRON MICROSCOPE (SEM)

Scanning electron micrograph (SEM) showed the morphological characteristics of CAC. The micrographs of CAC before adsorption are shown in the following figures. The SEM micrograph shows porous and irregular surface for CAC which indicate that surface is ideal for adsorption.

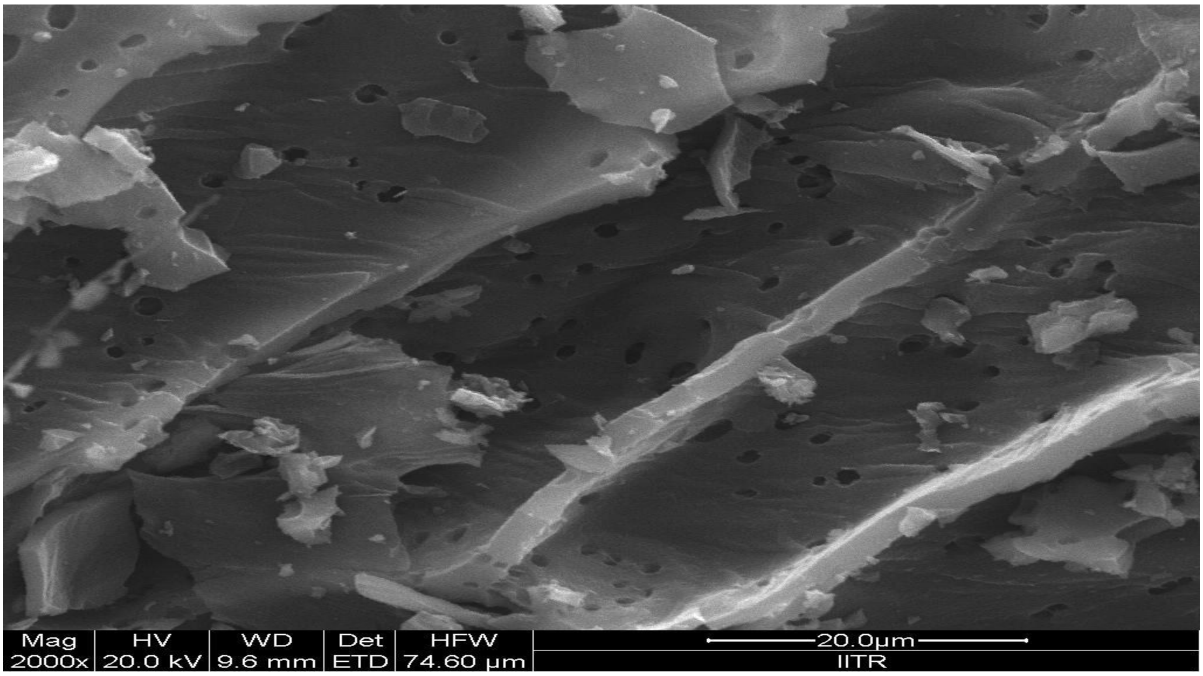


Figure 5.6: SEM image of CAC at 2000 X

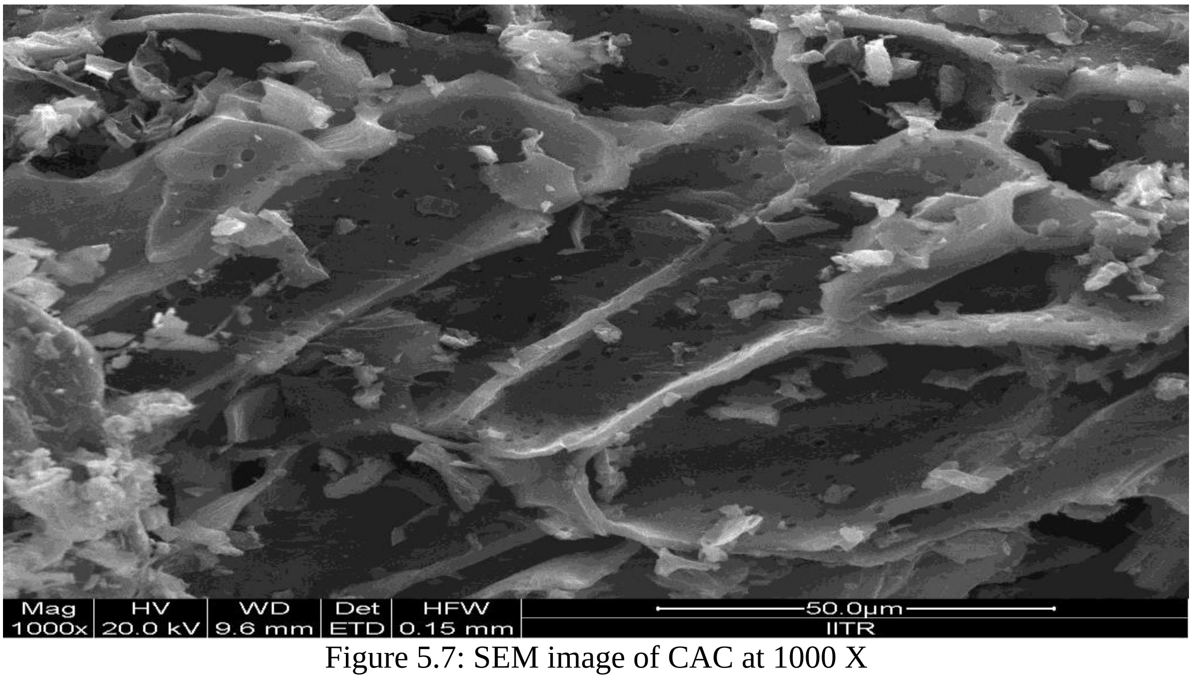


Figure 5.7: SEM image of CAC at 1000 X

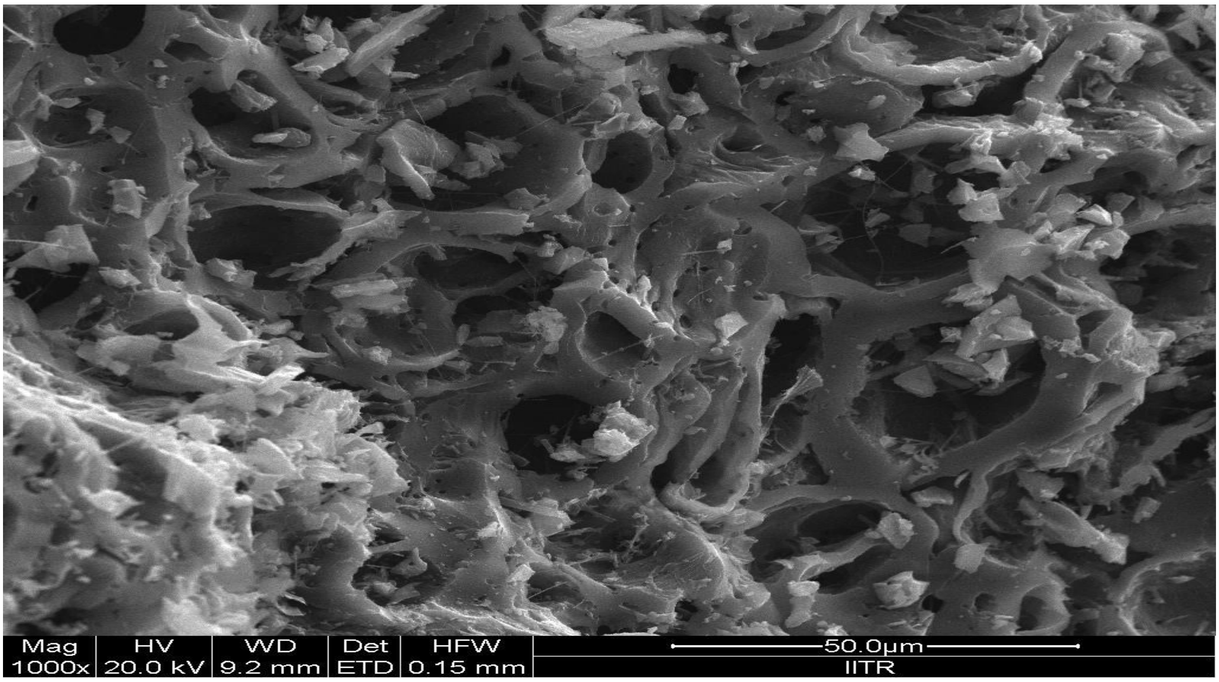


Fig.5.8 SEM images of CAC

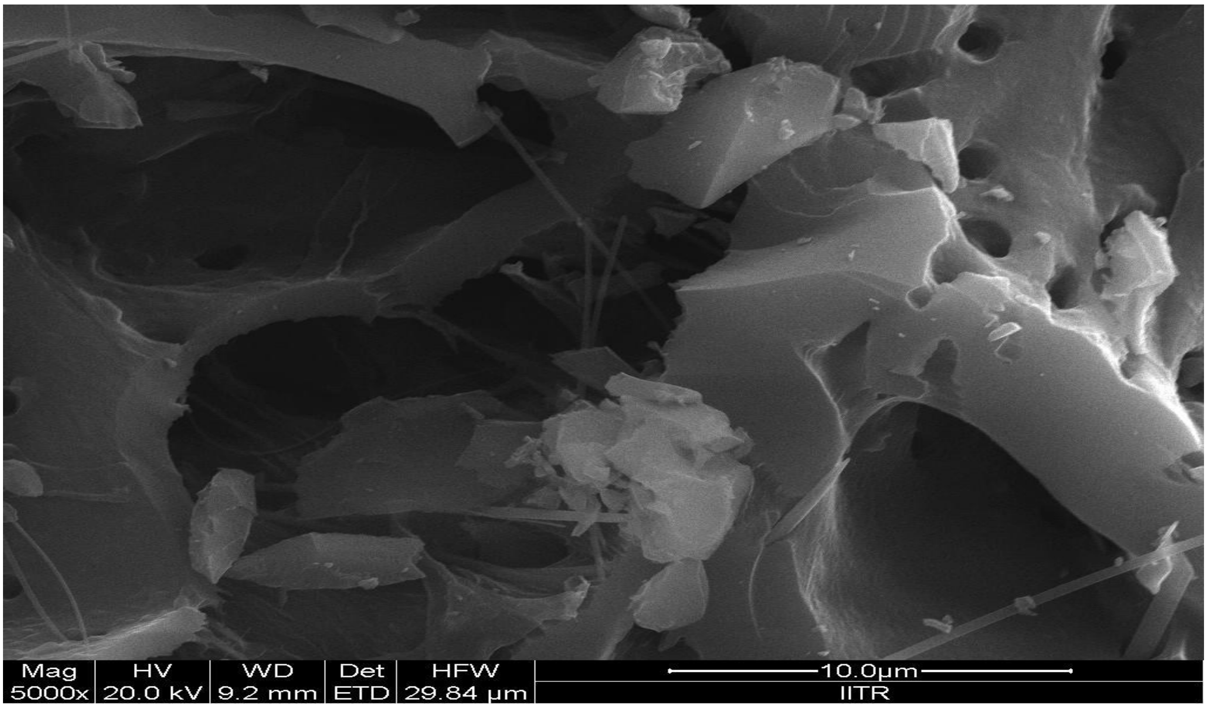


Figure 5.9: SEM image of CAC at 5000 X

Activation with caustic mainly develops pores of large diameter of the order 10 µm. The majority of pores present in CAC are in the category of macropores. Macropores are favourable for the removal of metal ions, since it requires large pore structure for penetration of metal ions.

5.3.6 EDAX

The EDAX analysis of CAC before and after adsorption is shown in fig 5.10 and fig 5.11 respectively. The EDAX analysis of virgin CAC shows the presence of various elements such as carbon, oxygen, sodium, potassium etc. The EDAX analysis of adsorbed CAC shows the similar pattern but less percentage of oxygen was observed. EDAX analysis after adsorption showed the chromium ions present in the pore of CAC. EDAX analysis of CAC also indicates the presence of sulphur and chlorine adsorbed by CAC.

Element	Wt%	Atomic%
C K	86.23	89.8
O K	11.75	9.19
Na K	1.57	0.85
K K	4.45	0.14

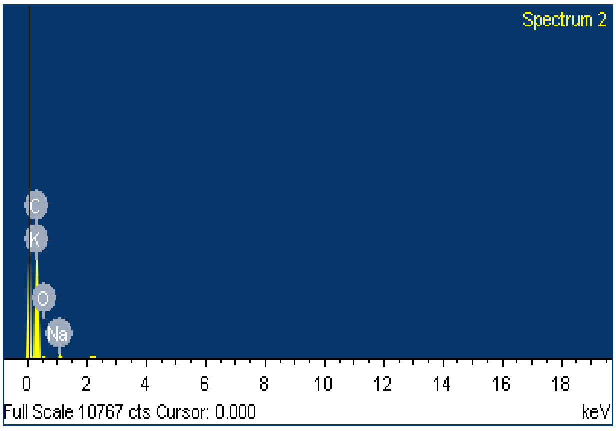


Figure 5.10: EDAX of CAC before adsorption

Element	Weight%	Atomic%
C K	88.69	91.77
O K	10.12	7.70
Na K	0.50	0.16
S K	0.17	0.14
Cl K	0.19	0.14
Cr K	0.33	0.08

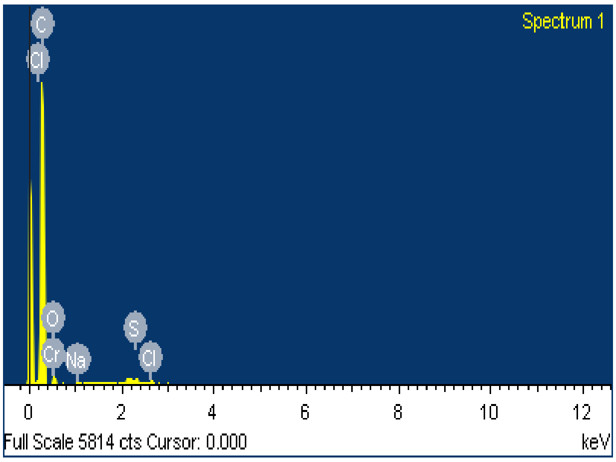


Figure 5.11: EDAX of CAC after adsorption at optimum conditions

5.4 CHARACTERIZATION OF ELECTROPLATING WASTEWATER

Table 5.3: Various parameters of electroplating wastewater

S. No.	Parameter	Value
1	pH	4.5
2	Cr(VI) (mg/l)	1080
3	COD (mg/l)	1836
4	TDS (mg/l)	1443
5	TSS (mg/l)	285
7	Fe(mg/l)	89
8	TS (mg/l)	1728

5.5 EFFECT OF pH

The surface charge of the adsorbent as well as the degree of ionization of the solutes present in the solution mainly affected by pH of the solution. The hydroxyl ions and hydrogen ions are strongly adsorbed and, therefore, the adsorption of metal ions is affected by the pH of the solution. It is a well-known fact that the surface adsorbs anions most favorably at lower pH due to presence of H^+ ions, whereas, the adsorbent surface is more active for the adsorption of cations at higher pH due to presence of OH^- ions (Srivastava et al., 2005). The pH_{pzc} is the point where adsorbent surface has no charge. At pH_{pzc} point, adsorption process is governed by diffusion of metal ions into micropore and macropore alone. At this point electrostatic forces do not play significant role. The experimental value of CAC is found to be 6.5. Hexavalent chromium present in aqueous solution is mainly in the form of chromate ($HCrO_4^-$) or dichromate ions ($Cr_2O_7^-$), which is electron-donor group. Hence, at a pH value lower than pH_{pzc} of CAC, the surface of CAC is positively charged attracting chromate ($HCrO_4^-$) and dichromate ions ($Cr_2O_7^-$) onto its surface. Hence, we can conclude that acidic solution would be ideal for adsorption onto CAC. The adsorption by CAC was studied over a pH range of 2-9 at 25^0C and the studies were carried out for 2 hour at 150 rpm. The adsorbent dose was kept at 10 g/l. The effect of pH is shown in the following figure. From figure we can justify the theoretical explanation with experimental observation for Cr(VI) and COD removal. For Cr(VI), we observe that as pH is varied from 2 to 10, the removal of Cr(VI) firstly increase to a maximum value at 3 pH and then gradually decreases. Compare to pH value 3, low metal ion removal at 2 pH value was found due to repulsive force caused by the large amount of hydrogen ions. Quite similar result was obtained for COD removal. Optimum pH was obtained as 3 for further experiments.

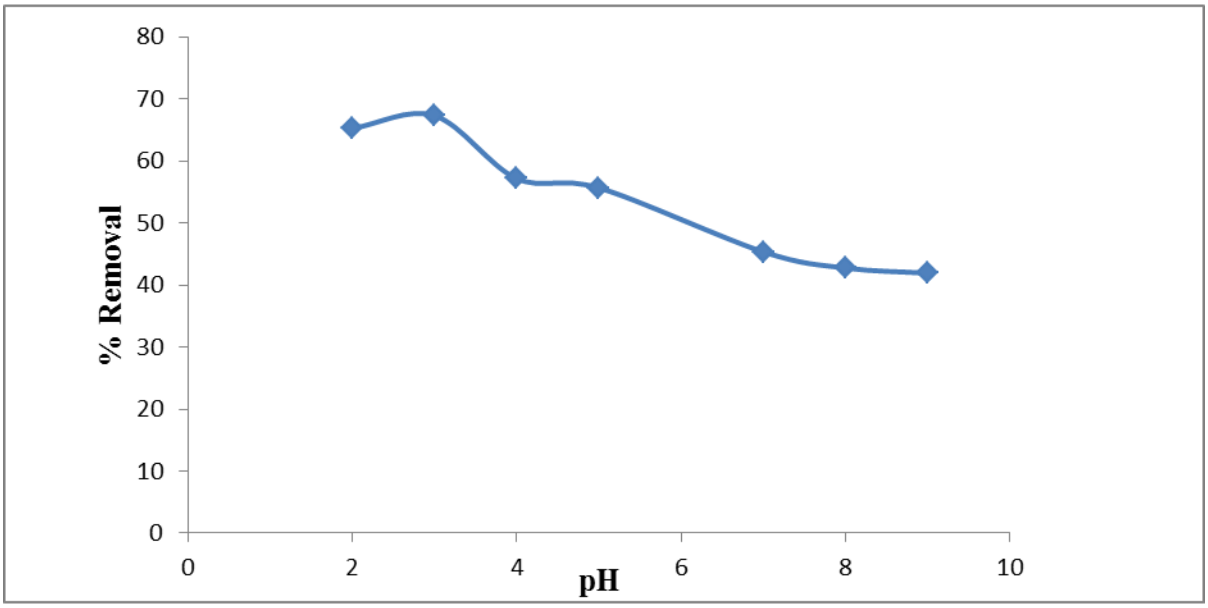


Figure 5.12: pH effect on Cr(VI) removal

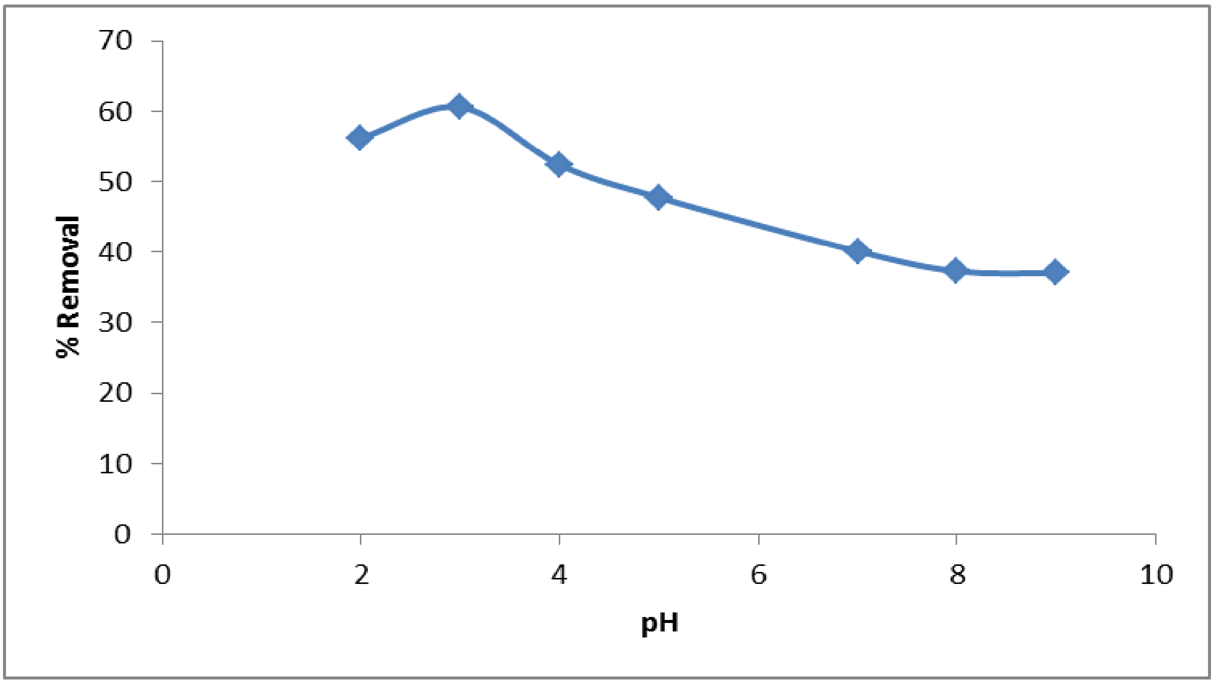


Figure 5.13: pH effect on COD removal

5.6 EFFECT OF ADSORBENT DOSE

Effect of adsorbent dose was estimated by using doses, 1, 2, 3, 4, 5, 8, 10, 15 and 20 for Cr(VI) and COD removal. The effect of adsorbent dose on Cr(VI) and COD removal is shown in figure 5.12 and 5.13 respectively. It is found that on increasing CAC dose, the percentage removal for Cr(VI) ions increases gradually up to a certain limit and then it reached a constant value. The Optimum CAC dose for the removal of metal ion is obtained as 15 g/l. The maximum removal Cr(VI) at optimum dose was obtained as 88.28 %. It can be explained by the fact that on increasing adsorbent dose, the surface area also increases due to the increase in the number of active sites. This consequently results in more removal of metal ions from wastewater. But after a certain limit all the active sites are occupied by the metal adsorbed, hence no more Cr(VI) removal achieved after certain limit (threshold limit).

5.7 EFFECT OF CONTACT TIME

The time at which the adsorption of CAC reaches a saturation limit, this time is termed as equilibrium contact time. At different intervals, the percentage removal of Cr(VI) and COD were examined. The effect of contact time on the removal of Cr(VI) and COD by CAC for m = 15 g/l, COD = 122 mg/l and C_0 = 72 mg/l are shown in figure. This figure shows the rapid adsorption by CAC in the first 15 min, and thereafter, the adsorption rate decreases gradually. The residual Cr(VI) concentration was 10% after 3 h, 2.91% after 6 h, 2.82% after 12 h, and 2.75% after 18 h of contact time. The difference in Cr(VI) removal at 6 and 18 h was <0.25% of the 18 h removal value hence, a steady-state approximation was assumed and a quasi-equilibrium condition was accepted at t = 6 h and further experiments were conducted only at t = 6 h [Lataye et al., 2006]. Contact time for COD removal was also found 6 h.

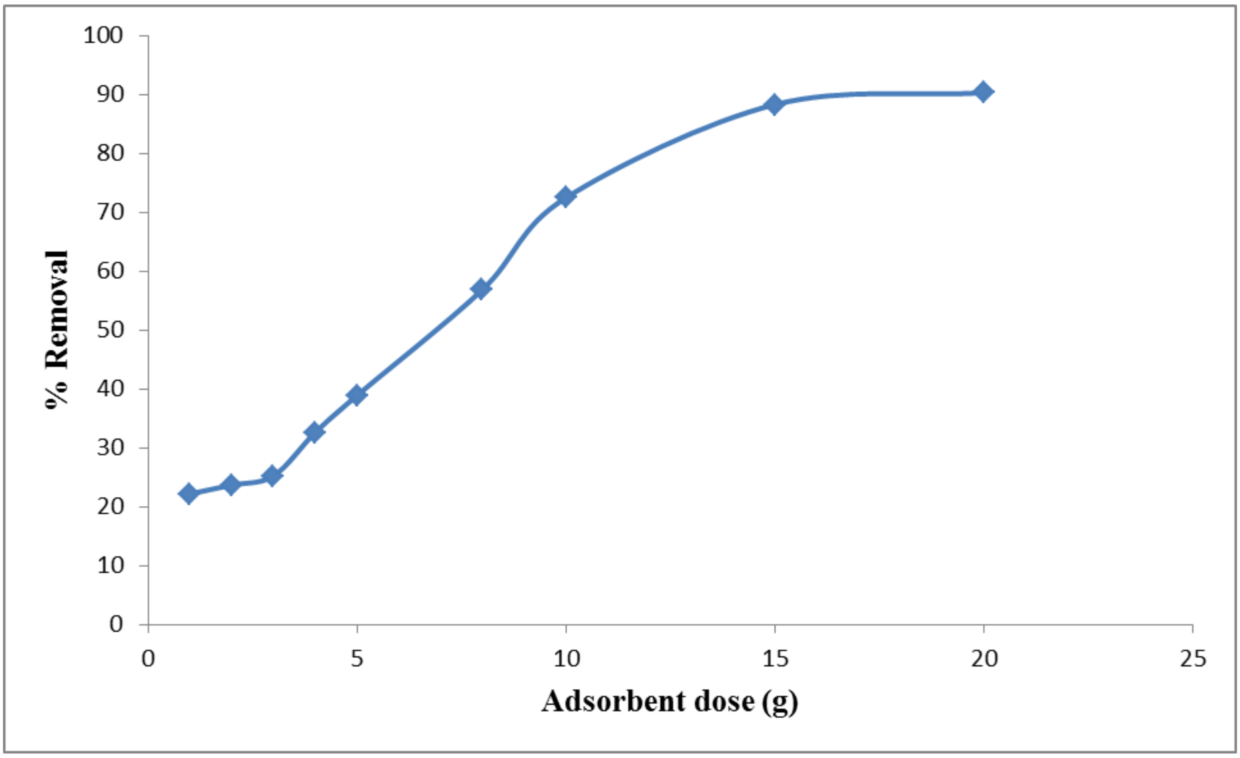


Figure 5.14: Effect of adsorbent dose on chromium(VI) removal

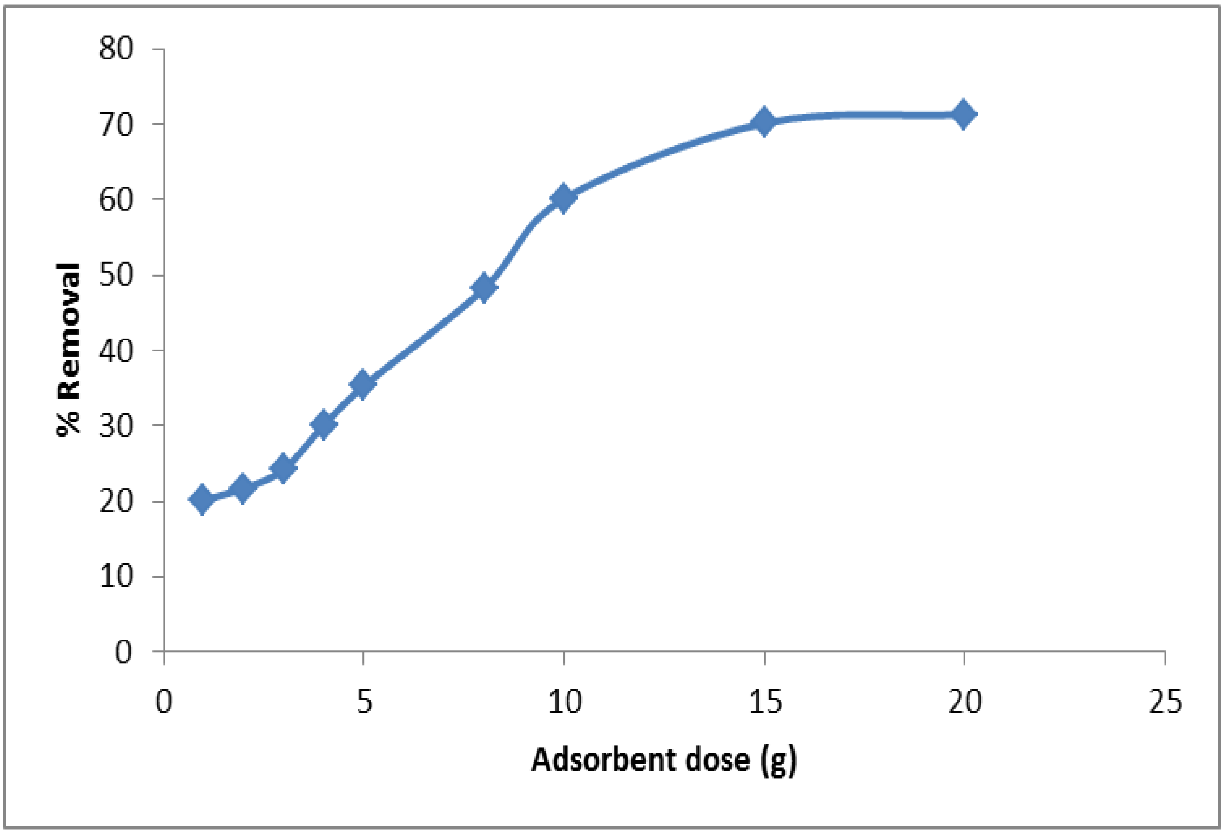


Figure 5.15: Effect of adsorbent dose on COD removal

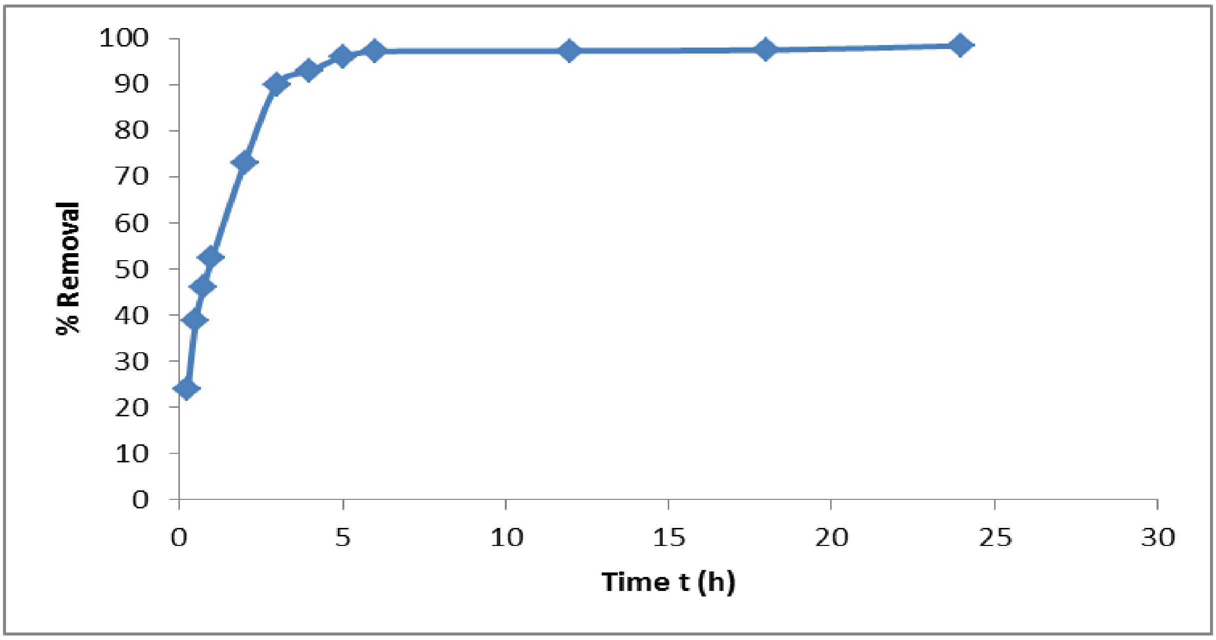


Figure 5.16: Effect of contact time on Cr(VI) removal

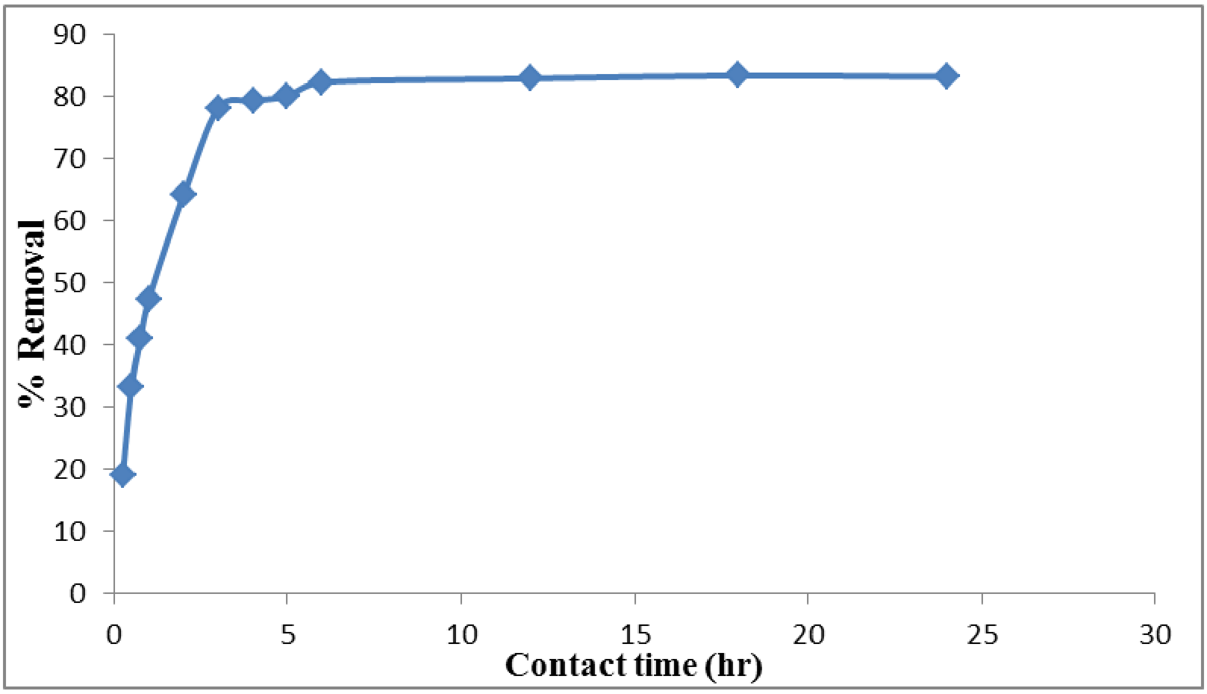


Figure 5.17: Effect of contact time on COD removal

5.8 EFFECT OF INITIAL CONCENTRATION AND TEMPERATURE

The effect of initial concentration on the removal of Cr(VI) by CAC adsorbents is shown in following figure 5.18. From the figure 5.18, we can conclude that the amount of Cr(VI) adsorbed increases with the increase in initial concentration, while percentage of Cr(VI) removal decreased with the increase in initial concentration. Adsorption capacity of Cr(VI) removal increased with the increase in initial metal ion concentration due to reduction in the resistance. So we can conclude that adsorption rate increases due to improvement in the driving force. The percent removal of Cr(VI) with CAC was studied by varying initial concentration from 72-360 mg/l (72, 136, 216, 288, and 360) and keeping adsorbent dose (15 g/l), stirring speed (150 rpm), pH (3.0) and contact time (6 hr) constant. Temperature was also varied (298 K, 308 K, and 318 K) keeping other parameters constant. Higher concentrations of chromium ions were used to study the maximum adsorption capacity q_e (mg/g) of the adsorbents [Mohanty et al., 2006]. From the figure 5.18 it is evident that hexavalent chromium removal follows exothermic adsorption process which means on increasing temperature, percentage removal of Cr(VI) decrease. Adsorption process gave maximum percentage removal at 298 K.

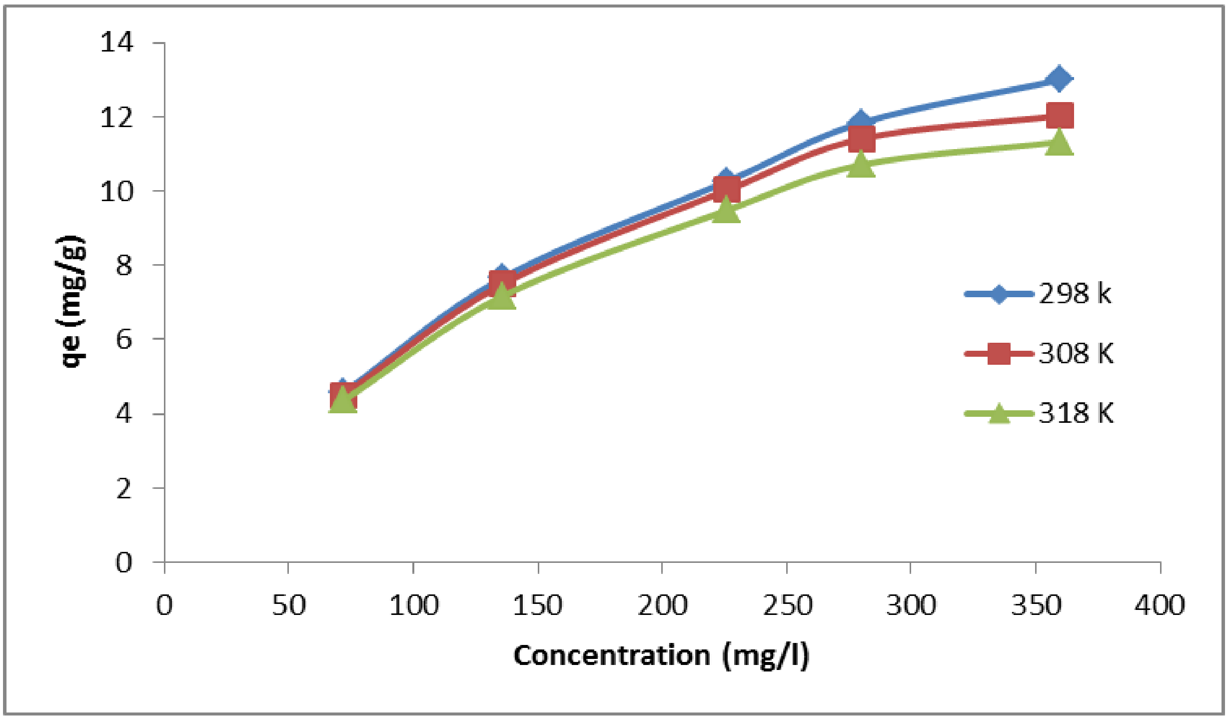


Figure 5.18: Effect of concentration and temperature on Cr(VI) removal

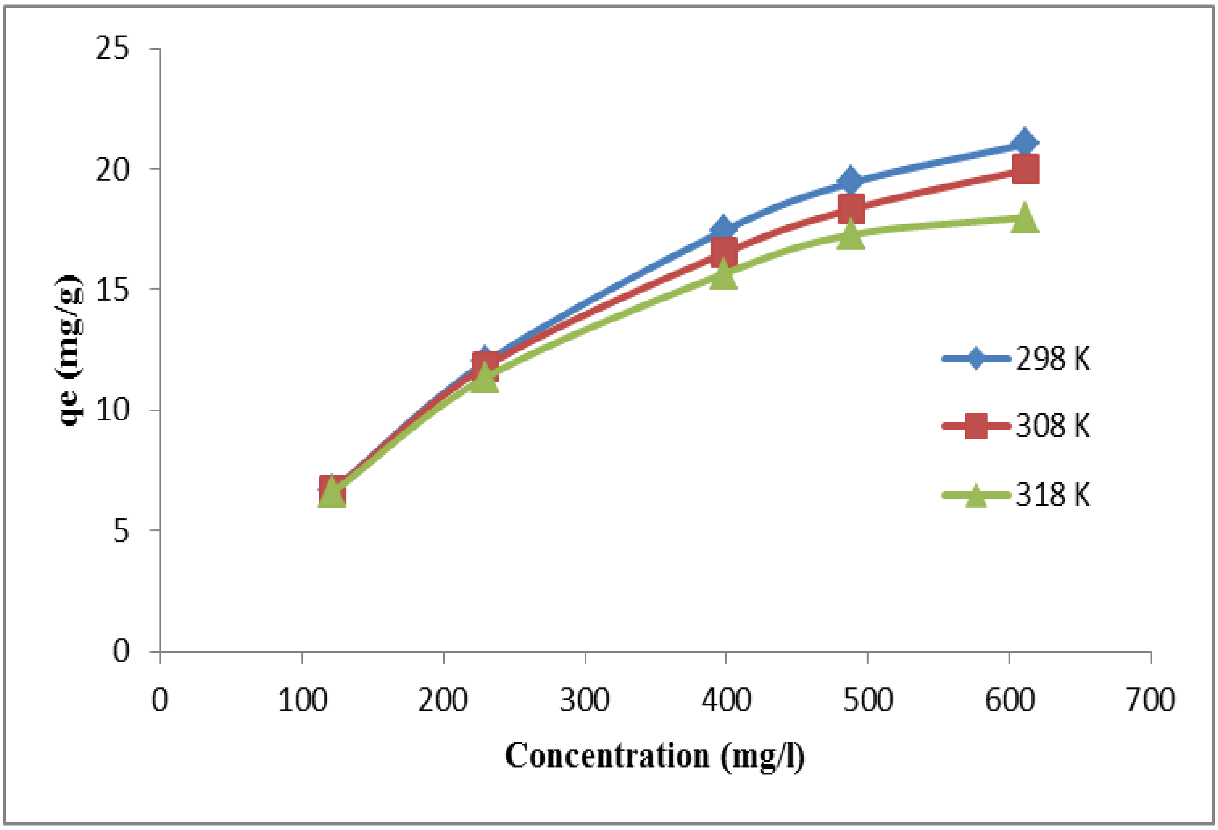
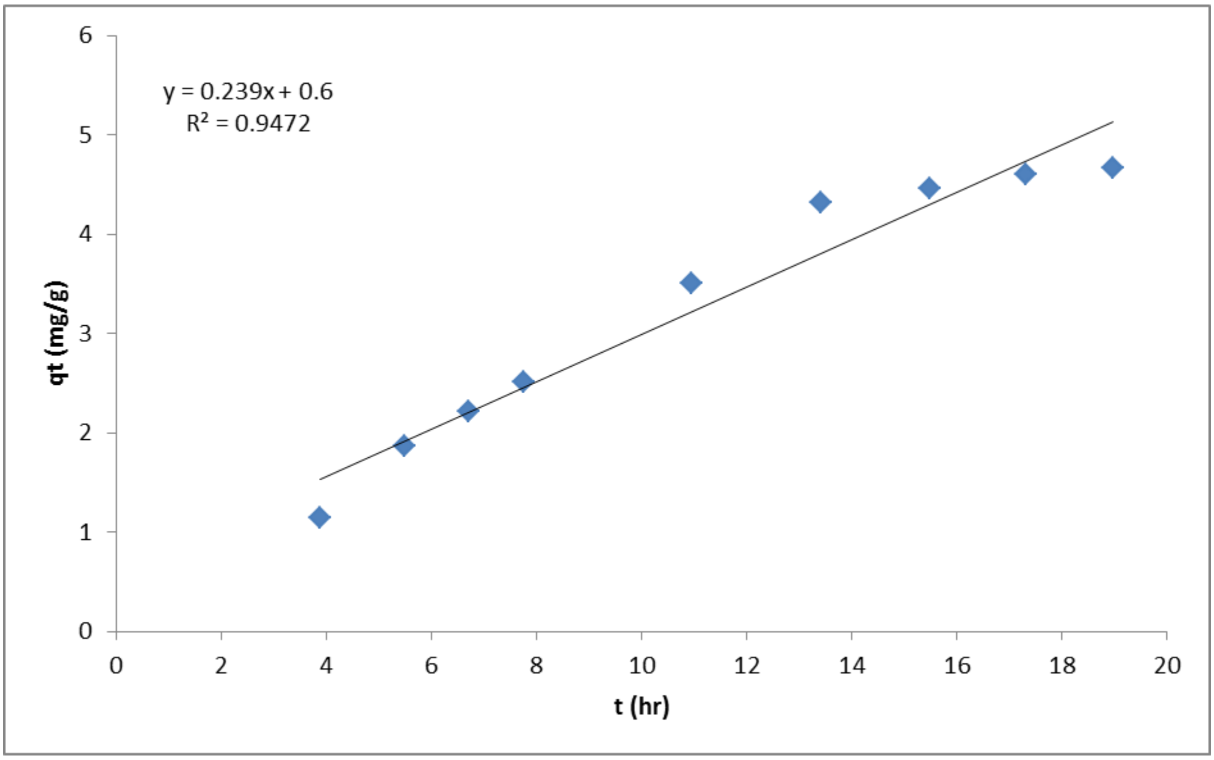


Figure: 5.19 Effect of initial concentration and temperature on COD removal

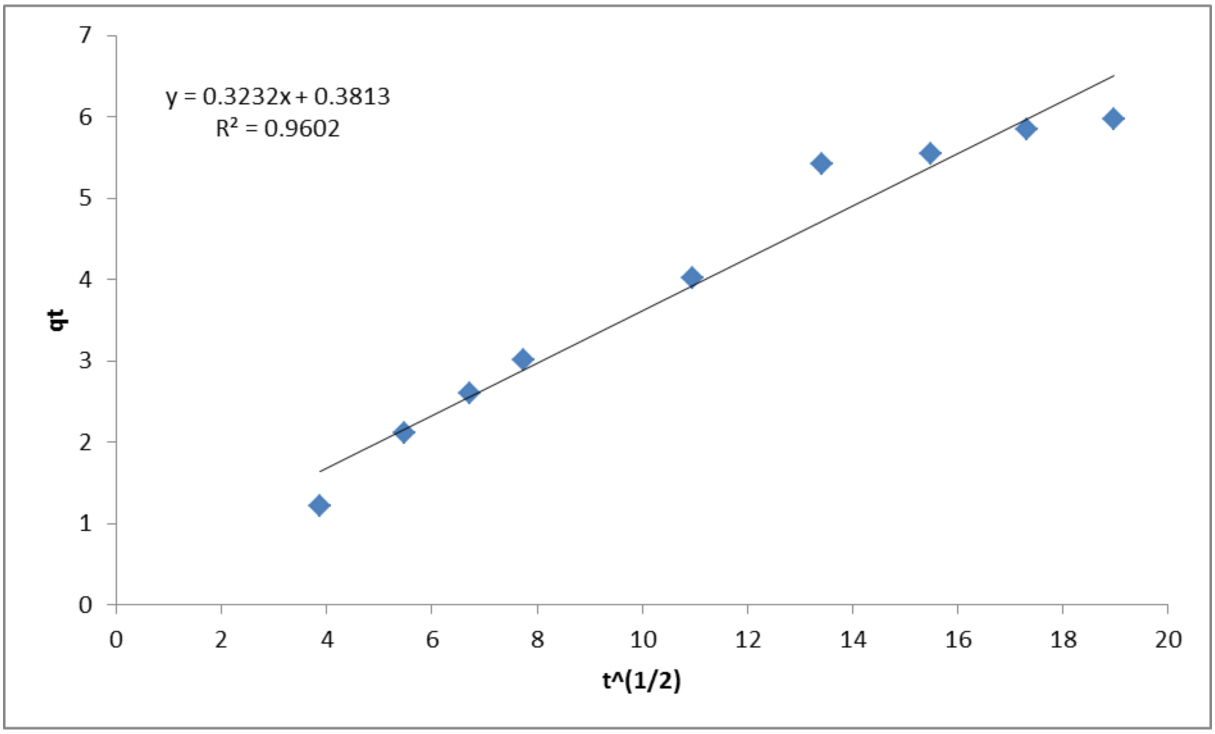
5.9 KINETICS OF Cr(VI) AND COD REMOVAL

For the purpose of determining the mechanism of adsorption, particularly the potential rate controlling step, the transient behavior of the chromium metal ion adsorption process was analysed using the pseudo-first order, pseudo-second order, intraparticle diffusion model and Bangham's equation. Initial concentration of 72 mg/l was used for Cr(VI) and COD removal, while optimized value of pH was kept fixed. The samples were collected at specified intervals till equilibrium was achieved. The experimental data obtained was used to plot the three graphs as per equation (3.5), (3.7) and (3.8) to evaluate the predictive capabilities of pseudo first order, pseudo second order and intra-particle diffusion respectively. According to Equation 3.8, a plot of q_t versus $t^{1/2}$ should be a straight line with intercept I and slope k_{int} for Weber-Morris's intra-particle diffusion model. If intra-particle diffusion is the only rate-limiting step in the adsorption mechanism then q_t versus $t^{1/2}$ plot should go through origin, but in this research work plot does not go through origin because of other diffusion such as film diffusion may also prevailing here. Figure 5.17 presents a plot of q_t versus $t^{1/2}$ for CAC. The value of I (Table 5.4) gives an idea about the thickness of the boundary layer effect (Kannan et al., 2001). The deviation of the straight lines from the origin may be due to the difference in the rate of mass transfer during the initial and final stages of adsorption (Mall et al., 2005). The values of k_{int} and I obtained from the plot listed in Table (5.4).

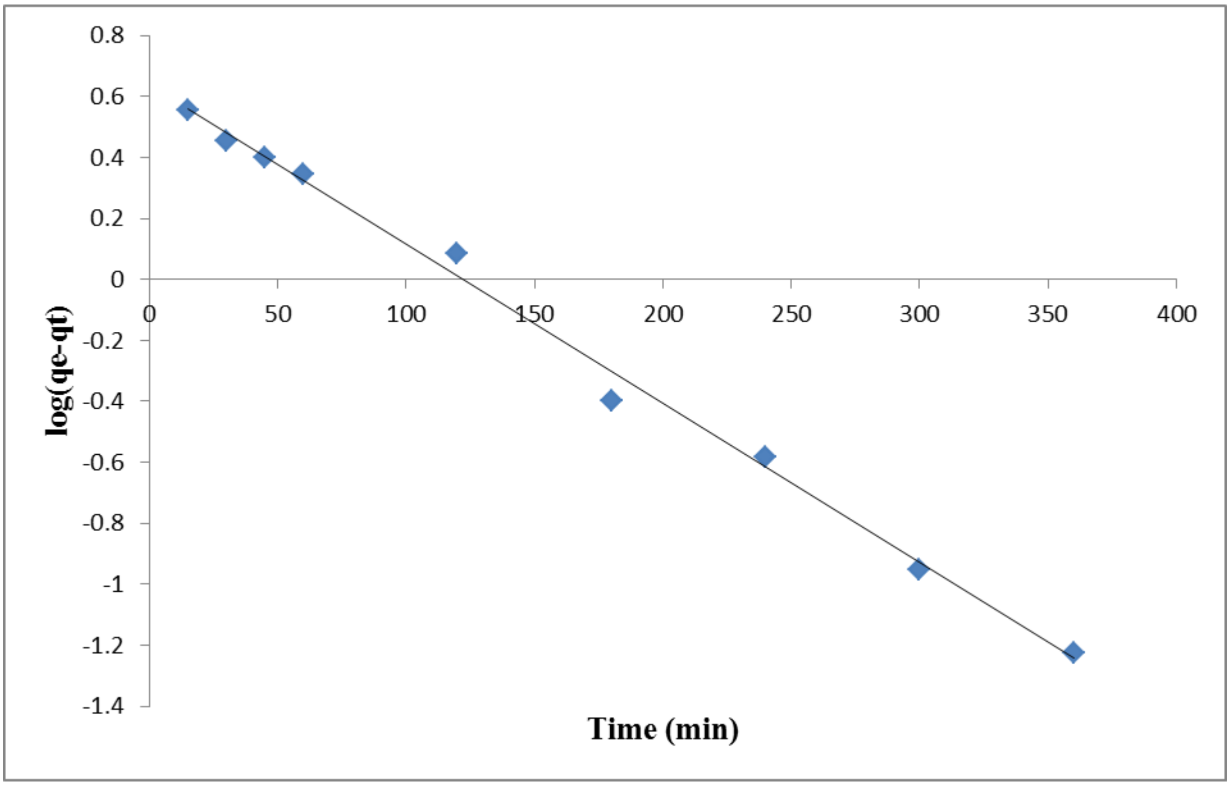
It is observed that the experimental data do not fit with pseudo first order kinetics properly giving a non-linear plot and low correlation coefficient R^2 value as compared to pseudo second order kinetics. Thus plot obtained from pseudo second order kinetics fitting for Cr(VI) and COD removal are shown in figure 5.23 and 5.24 respectively. Pseudo second order kinetics gave a high correlation coefficient R^2 of the order 0.999 for Cr(VI) which indicates that adsorption complies with pseudo-second order kinetics. The kinetics parameters for all kinetic models are tabulated in table 5.4. From table it can be seen that the rate constant k_2 for pseudo-second order model is very low for Cr(VI) as well as COD removal. Adsorption capacity is high for pseudo-second order model which justify the best fitting model for hexavalent chromium adsorption.



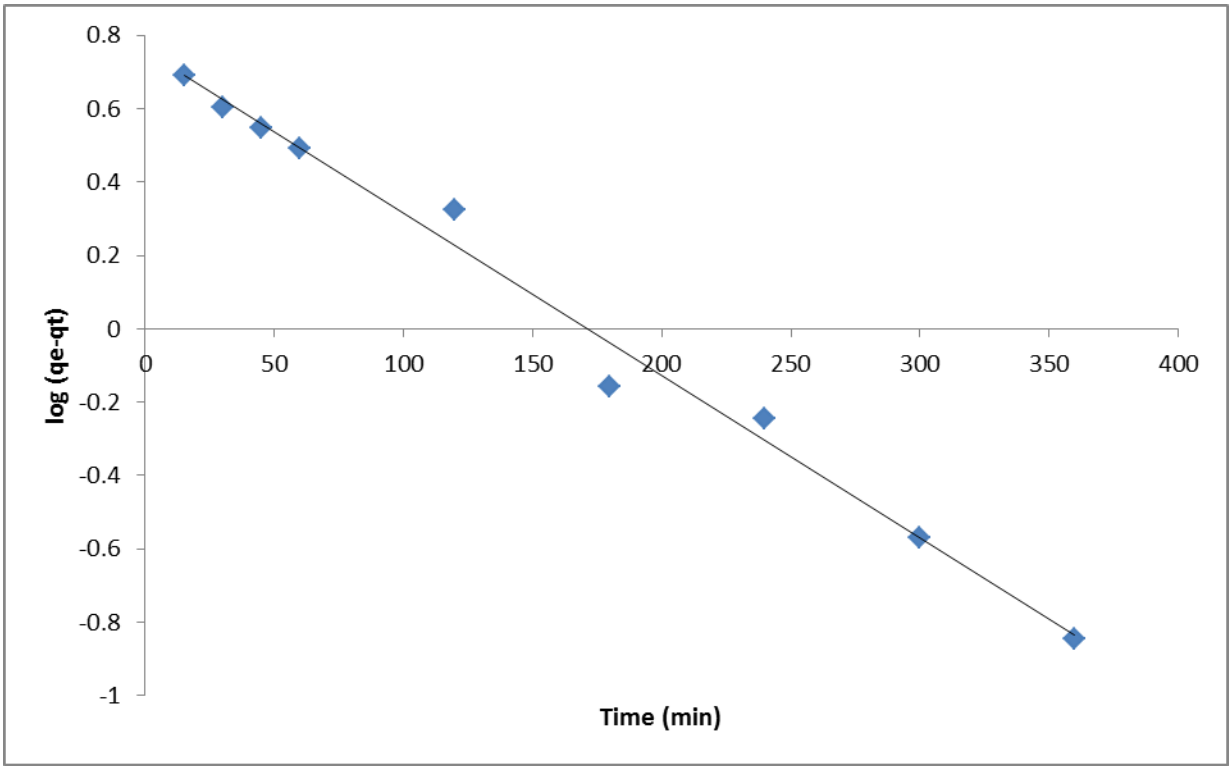
. Figure 5.20: Intraparticle diffusion for Cr(VI) adsorption on CAC



. Figure 5.21: Intraparticle diffusion for COD removal by CAC



. Figure 5.22: Pseudo first order plot for Cr(VI) adsorption on CAC



. Figure 5.23: Pseudo first order plot for COD removal by CAC

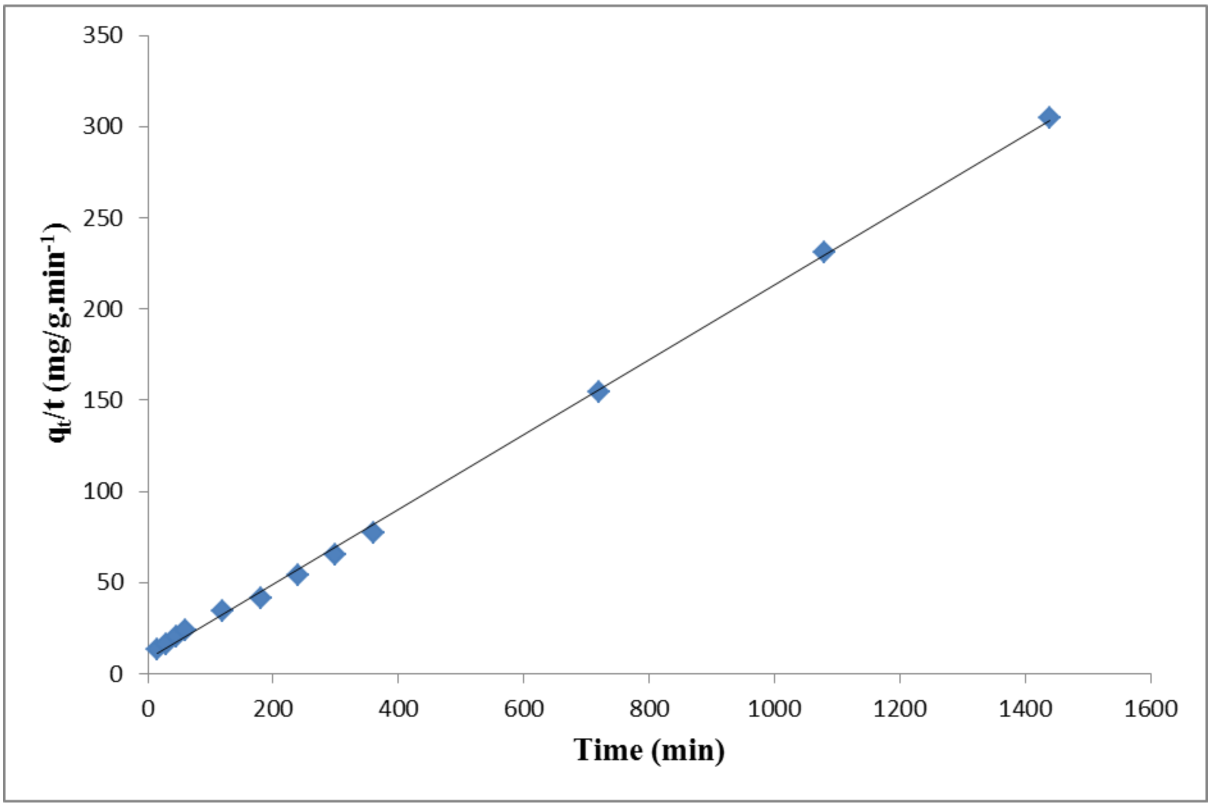


Figure 5.24: Pseudo-second order plot for adsorption of Cr(VI) on CAC

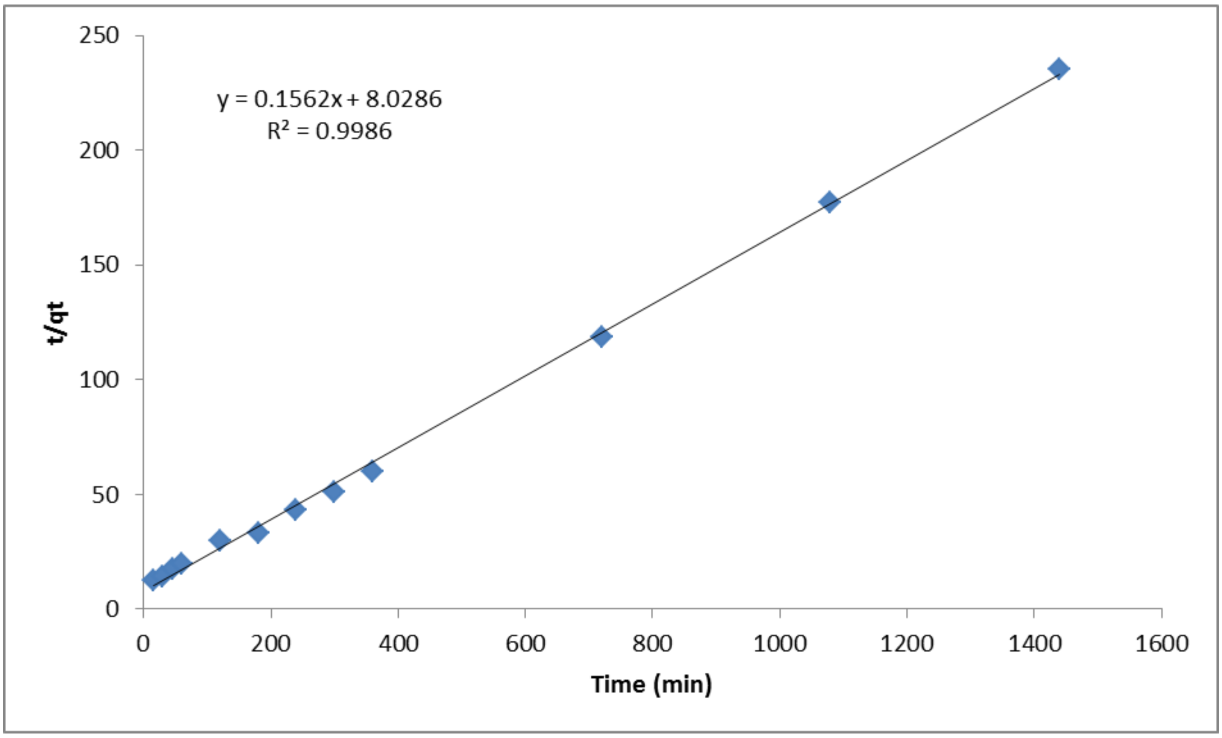


Figure 5.25: Pseudo-second order plot for COD removal by CAC

Table 5.4 Kinetic parameters for the adsorption of electroplating wastewater

Kinetic Parameters	**Cr(VI) removal**	**COD removal**
Pseudo-first order		
k_1	0.0119	0.0101
q_e	4.32	5.704
R^2	0.9951	0.9891
Pseudo-second order		
k_2	0.00054	0.0003
q_e	4.87	6.402
R^2	0.999	0.9986
Intra-particle diffusion		
k_{int}	0.24	0.3232
I	0.6	0.3813
R^2	0.9472	0.9602
Elovich model		
b	0.97	1.51
k_0	1.4478	2.0139
R^2	0.8773	0.9562

5.10 ADSORPTION EQUILIBRIUM ISOTHERM

Different isotherm models were studied for adsorption equilibrium condition. Freundlich, Langmuir, Redlich-peterson model, Sips isotherm model and Kobel-corrigan isotherm models were used to determine equilibrium isotherm constants. The equilibrium constants derived from above isotherm models for Cr(VI) and COD removal are listed in Table 5.6 and 5.7 respectively. Constants listed in table 5.6 and 5.7 indicates that experimental data were fitted well for Freundlich isotherm for Cr(VI) removal while Langmuir isotherm model for COD removal respectively. Statistical indices were determined to know deviation from ideality (error in experimental work) are listed in table 5.5.

Table 5.5: Statistical indices for chromium (VI) and COD removal

Isotherm model	**R^2**	**SSE**	**RMSE**	**SEP**	**NSD**	**ND**
For Cr(VI) removal						
Freundlich isotherm model	0.996	45.163	3.005	31.741	26.684	11.933
Langmuir isotherm model	0.914	63.504	3.563	37.638	40.576	18.146
Redlich-peterson model	0.996	65.227	3.611	38.145	42.80	19.144
Sips isotherm model	0.990	65.561	3.621	38.243	44.504	19.902
Kobel-corrigan	0.996	68.150	3.691	38.99	43.102	19.276
For COD removal						
Freundlich isotherm model	0.968	5.082	1.0082	6.725	6.632	2.966
Langmuir isotherm model	0.981	5.653	1.062	6.871	9.036	4.041
Redlich-peterson model	0.967	6.694	1.157	7.718	11.7687	5.263
Sips isotherm model	0.968	6.898	1.174	7.834	12.508	5.594
Kobel-corrigan	0.947	12.87	1.604	10.37	10.927	4.886

Table 5.6 Adsorption equilibrium isotherm constants for hexavalent chromium

Adsorption Isotherm Model	**Model equation**	**Parameters**
Freundlich Adsorption Isotherm	$q_e = K_F C_e^{1/n}$	$K_F = 3.34$ n = 3.741495 $R^2 = 0.996227$
Langmuir Adsorption Isotherm	$q_e = \frac{Q_m K_A C_e}{1 + K_A C_e}$	$Q_m = 12.68175$ $K_A = 0.103554$ $R^2 = 0.91384$
Sips Adsorption Isotherm	$q_e = \frac{q_m^s\, a C_e^n}{1 + a C_e^n}$	$q_m^s = 0.034893$ a = 3.355226 n = 0.294655 $R^2 = 0.9891$
Koble-Corrigan Adsorption Isotherm	$q_e = \frac{A C_e^n}{1 + B C_e^n}$	A = 3.35522606 B = 0.034893 n = 0.294655 $R^2 = 0.9925$
Redlich-Peterson equation	$q_e = \frac{K C_e}{1 + a C_e^b}$	K = 12.323 a = 3.30539 b = 0.753472 $R^2 = 0.9827$

Table 5.7 Adsorption equilibrium isotherm constants for COD removal

Adsorption Isotherm Model	**Model equation**	**Parameters**
Freundlich Adsorption Isotherm	$q_e = K_F C_e^{1/n}$	$K_F = 2.85$ $n = 3.11$ $R^2 = 0.966$
Langmuir Adsorption Isotherm	$q_e = \frac{Q_m K_A C_e}{1 + K_A C_e}$	$Q_m = 18.34$ $K_A = 0.030$ $R^2 = 0.996$
Sips Adsorption Isotherm	$q_e = \frac{q_m^s \, a C_e^n}{1 + a C_e^n}$	$q_m^s = 0.019$ $a = 1.516$ $n = 0.019$ $R^2 = 0.9531$
Koble-Corrigan Adsorption Isotherm	$q_e = \frac{A C_e^n}{1 + B C_e^n}$	$A = 0.0599$ $B = 0.0037$ $n = 1.6945$ $R^2 = 0.9478$
Redlich-Peterson equation	$q_e = \frac{K C_e}{1 + a C_e^b}$	$K = 0.815$ $a = 0.0867$ $b = 0.8848$ $R^2 = 0.995$

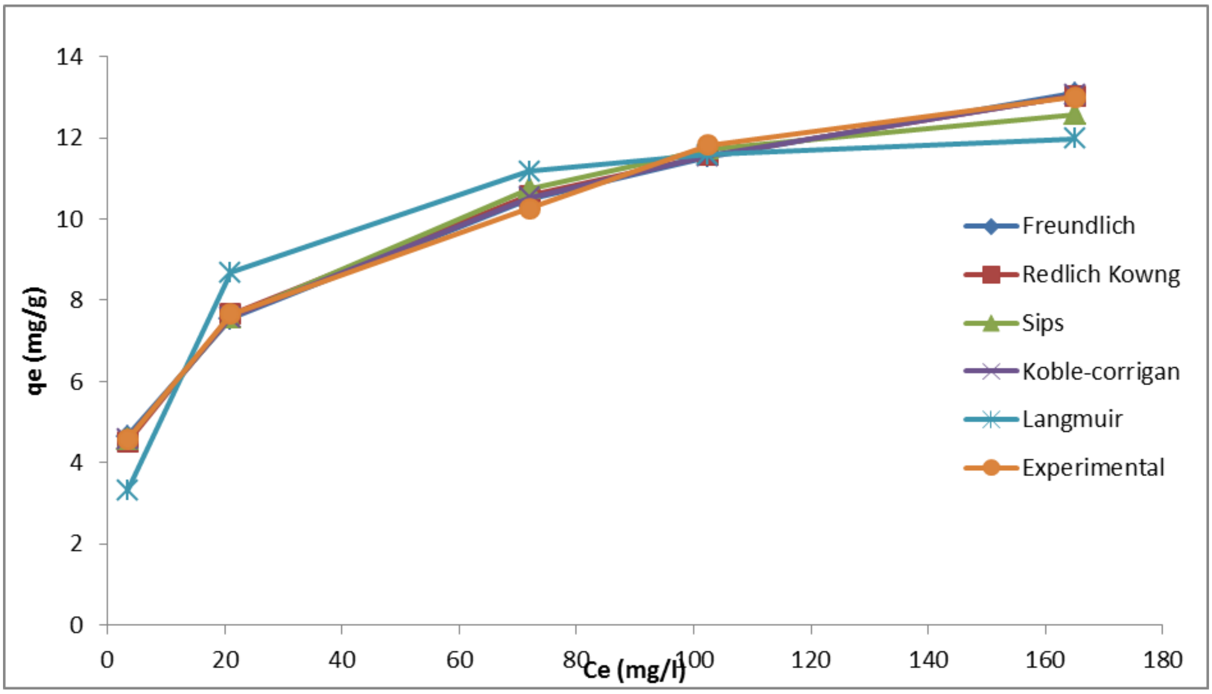


Figure 5.26: Comparison of various isotherm models for Cr(VI) removal

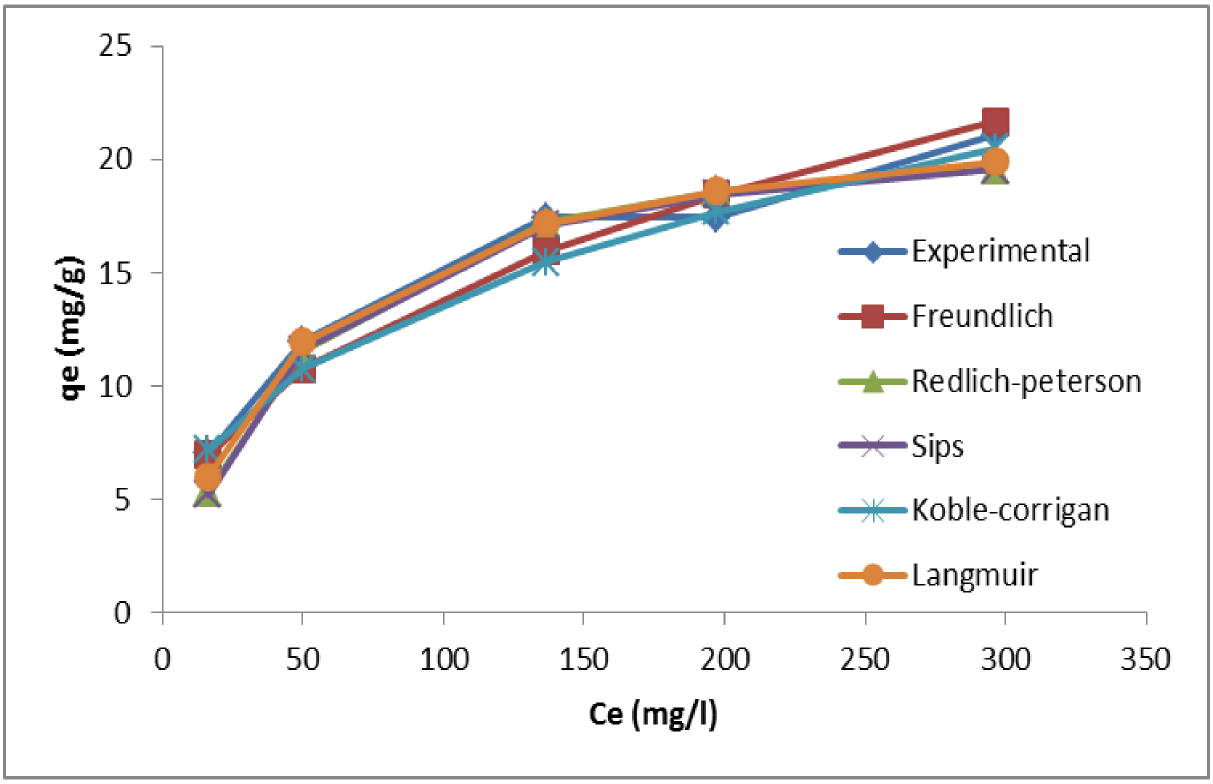


Figure 5.27: Comparison of various isotherm models for COD removal

5.11 ADSORPTION THERMODYNAMIC CONSTANTS

Various thermodynamic parameters was studied for adsorption of Cr(VI) on CAC. Experimental data were determined at various temperatures (298 K, 308 K, 318 K) with the help of different isotherms (e.g. Freundlich, Redlich-Peterson, Sips, Koble-corrigan and toth), enthalpy, entropy and Gibb's free energy was determined. For our experimental data thermodynamic parameters show the exothermic and spontaneous nature of adsorption process which indicates that adsorption process is favoured at low temperature. Negative values of enthalpy (Table 5.8) insure the exothermic nature of adsorption. Adsorption process showed complex mechanism because it is neither fully chemical sorption process nor fully physical process. Negative value of ΔG^0 indicates the decrease in Gibbs energy and feasibility and spontaneity of adsorption process.

Table 5.8 Thermodynamic parameters of various isotherm models for Cr(VI) removal

Isotherms	**ΔH^0 (kJ/mol)**	**ΔS^0 (kJ mol^{-1} K^{-1})**	**ΔG^0 (kJ/mol)**		
			T = 298 K	**T = 308 K**	**T = 318 K**
Freundlich	-11.47	-0.028	-2.7779	-2.4225	-2.4729
Redlich-Peterson	-73.1274	-0.2245	-6.2223	-3.9253	-1.73327
Sips	-19.29679	-0.054477	-2.99915	-2.67656	-1.89977
Koble-corrrigan	-24.76824	-0.072618	-2.9915	-2.67656	-1.52894
Toth	-3.837909	-0.002475	-3.09243	-3.09249	-3.04183

5.12 DISPOSAL OF CAC

After adsorption pores of adsorbent fill by pollutant contained in wastewater and it is not reliable for further use. In present study loaded adsorbent has some chromium ions attached to its pores; hence proper disposal technique should be applied. Recycling of loaded CAC may be possible by chemically or thermally regeneration method but it is less feasible because of its high cost. The oxidation behavior of loaded CAC was investigated by thermogravimetry instrument in oxidizing environment. The thermal degradation of loaded CAC was shown by differential thermal analysis (DTA), thermal gravimetric analysis (TGA) and differential thermal gravimetric (DTG) analysis.

The curves of DTG, TGA and DTA are shown in figure 5.25. The TG curve shows 5.57% loss of moisture and volatile matter evolution from 200 ^{0}C to 500 ^{0}C for loaded CAC. CAC was activated at 600 ^{0}C; hence it showed very low weight loss up to that temperature. The weight loss about 9.03% was found between 400 ^{0}C to 1010 ^{0}C for loaded CAC. Loaded CAC showed total weight loss of about 17.24%. Heating value of blank CAC was estimated as 22.36 MJ/Kg. Loaded CAC may be dried and further can be used for heating purpose. Ash may be used to make fire bricks or may blend with cement mixture (Kushwaha et al., 2010)

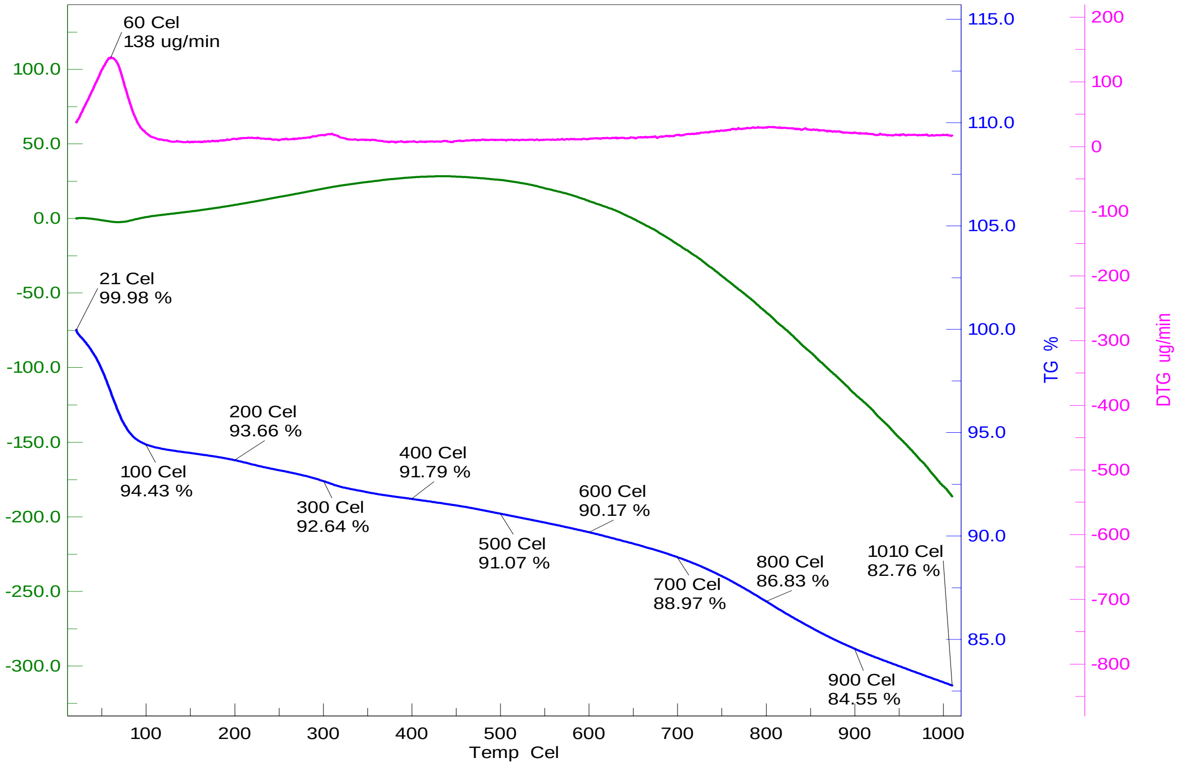


Figure 5.28: TG/DTA/DTG curve for loaded CAC

CHAPTER-6

CONCLUSION

The following conclusions are made from the present study:

- Batch adsorption studies have been carried out for the removal of Cr(VI) and COD using corncob based activated carbon. The carbonization and activation of corncobs are done by 0.1N NaOH solution. NaOH has showed better result (high surface area with low cost) compare to KOH solution.
- The characterization of CAC was done by standard methods. The result obtained from characterization suggests that the prepared CAC has a well-defined pore with majority of macropores, giving advantage for present study.
- BET surface area was found to be 399.006 m^2/g. Some kinetic models were appropriate for the present experimental data. Pseudo-second order model followed best fit in comparison of pseudo-first order and intra-particle diffusion model.
- The adsorption of Cr(VI) and removal of COD found high dependent on solution pH, contact time, Adsorbent dose and temperature. In the present study, percentage removal decreases with increase in pH value and removal increases with increase in adsorbent dose. The adsorption of chromium ions and COD removal were observed maximum at pH of 3, and 15 g/l of adsorbent dose.
- The maximum removal efficiency of chromium ions and COD were found to be 95.27% and 82.28 % respectively.

CAC prepared by low cost agricultural waste showed good potential for chromium ion and COD removal. Corncobs are easily available in any part of India at negligible cost, which makes it the potential raw material for preparation of activated carbon. Since the removal efficiencies of Cr(VI) and COD removal are satisfactory, it is concluded that CAC is an effective and efficient alternative adsorbent for hexavalent chromium and COD removal from electroplating waste water.

REFERENCES

1) A.K. Golder, A.N. Samanta, S. Ray, “Removal of trivalent chromium by electrocoagulation”, Journal of Hazardous Materials 196 (2011) 131– 138
2) Acharya Jyotikusum, Sahub J.N., Sahoob B.K., Mohanty C.R., B.C. Meikapb B.C., “Removal of chromium(VI) from wastewater by activated carbon developed from Tamarind wood activated with zinc chloride”, Chemical Engineering Journal 150 (2009) 25–39
3) AL-Othman Z.A., Ali R., Naushad Mu., “Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: Adsorption kinetics, equilibrium and thermodynamic studies”, Chemical Engineering Journal 184 (2012) 238– 247.
4) Atieh Muataz Ali, “Removal of Chromium (VI) from polluted water using carbon nanotubes supported with activated carbon” Procedia Environmental Sciences 4 (2011) 281–293.
5) Ballav Niladri, Arjun Maity, Mishra Shivani B., “High efficient removal of chromium(VI) using glycine doped polypyrrole adsorbent from aqueous solution”, Chemical Engineering Journal 198–199 (2012) 536–546
6) C. Covarrubias, R. Garcia, R. Arriagada, J. Yanez, H. Rammanan, Z. Lai, M. Tsapatsis, “Removal of trivalent chromium contaminant from aqueous media using FAU-type zeolite membranes”, journal of membrane science 312 (2008) 163-173
7) Cavaco S.A., S. Fernandes, M.M. Quina, L.M. Ferriera, “Removal of chromium from electroplating industry effluents by ion exchange resins”, Journal of Hazardous Materials, 144, p. 634-638. 2007.
8) Central Pollution Control Board (CPCB), Pollution control acts, rules and notifications issued thereunder, March 2012.
9) Chandan Das, Piyush Patel, Sirshendu De, Sunando Das Gupta, “Treatment of tanning effluent using nanofiltration followed by reverse osmosis”, Separation and Purification Technology 50 (2006) 291–299
10) Chen Suhong, Qinyan Yue, Baoyu Gao, Qian Li, Xing Xu, Kaifang Fu, “Adsorption of hexavalent chromium from aqueous solution by modified corn stalk: A fixed-bed column study”, Bioresource Technology 113 (2012) 114–120

11) Das C., P. Patel, S. D., S. Das Gupta. “Treatment of tanning effluent using nano filtration followed by reverse osmosis”, Separation and Purification Technology, 50, p. 293-299, 2006

12) Dinesh M., Charles U., & Pittman J., “Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water”. Journal of Hazardous Materials, 137 (2006), 762–811

13) E. Tütem, R. Apak, C. F. Ünal, Wat. Res. 8 (1998) 2315 - 2324.

14) F. Gode, E. Pehlivan, “A comparative study of two chelating ion-exchange resins for the removal of chromium(III) from”, Journal of Hazardous Materials B100 (2003) 231–243

15) F.N. Acar, E. Malkoc, “The removal of chromium(VI) from aqueous solutions by Fagus orientalis”, Bioresour. Technol. 94 (1) (2004) 13–15

16) Feini LIU, Guoliang ZHANG, Qin MENG, Hongzi zhang, “Performance of Nanofiltration and reverse osmosis membrane in metal effluent treatment”, Chinese Journal of Chemical Engineering, Volume 16, Issue 3, June 2008, Pages 441-445

17) Feryal Akbal, Selva Camci, “Copper, chromium and nickel removal from metal plating wastewater by electrocoagulation”, Desalination, Volume 269, Issues 1–3, 15 March 2011, Pages 214-222

18) G Ghos, P.K. Bhattacharya, “Hexavalent chromium ion removal through micellar enhanced ultrafiltration”, Chem. Eng. J. 119 (1) (2006) 45–53

19) Gupta V.K., Agarwal Shilpi, Tawfik A. Saleh, “Chromium removal by combining the magnetic properties of iron oxide with adsorption properties of carbon nanotubes”, water research 45 (2011) 2207 -2212

20) Gupta Vinod K., Rastogi Arshi, Nayak Arunima, “Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material”, Journal of Colloid and Interface Science 342 (2010) 135–141

21) H. Kirk Johnston, “Reverse osmosis reduction of heavy metal cations”, Desalination, Volume 16, Issue 2, April 1975, Pages 205-224

22) Hardiljeet K. Boparai, Meera Joseph, Denis M. O’Carroll, “Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles”, Journal of Hazardous Materials 186 (2011) 458–465

23) Heidmann I., Wolfgang C., “Removal of Cr(VI) from model wastewaters by electrocoagulation with Fe electrodes” Separation and Purification Technology 61 (2008) 15–21.

24) Hiroaki Ozaki, Kusumakar Sharma, Wilasinee Saktaywin, “Performance of an ultra-low-pressure reverse osmosis membrane (ULPROM) for separating heavy metal: effects of interference parameters”, Desalination 144 (2002) 287-294

25) I. Tadesse , S.A. Isoaho, F.B. Green, J.A. Puhakka, “Lime enhanced chromium removal in advanced integrated wastewater pond system”, Bioresource Technology 97 (2006) 529–534.

26) Indian Standard-1350 Part-1, 1984, Methods of Test for Coal and Coke: Proximate analysis (Second Revision), Bureau of Indian Standards, New Delhi.

27) Indian Standard-1350, Part–IV/Sec 1, 1974, Methods of Test for Coal and Coke: Ultimate Analysis: Determination of Carbon and Hydrogen, Bureau of Indian Standards, New Delhi.

28) Irwin R.J., M.V.N. Mouwerik, L. Stevens, M.D. Seese, W. Basham, Environmental Contaminants Encyclopedia Chromium(VI) (Hexavalent Chromium) Entry, National Park Service Water Resources Divisions, Fort Collins, CO, 1971.

29) J. P. Gould, The kinetics of hexavalent chromium reduction by metallic iron, Water Res. 16 (1982) 871–877.

30) J.W. Paterson, “Wastewater Treatment Technology”, Ann Arbour Science, Michigan, 1975, pp. 43–58.

31) Jai Prakash Kushwaha, Vimal Chandra Srivastava, Indra Deo Mall, “Treatment of dairy wastewater by commercial activated carbon and bagasse fly ash: Parametric, kinetic and equilibrium modelling, disposal studies”, Bioresource Technology 101 (2010) 3474–3483.

32) K. dermentzis1, A. christoforidis, “removal of hexavalent chromium from electroplating wastewater by electrocoagulation with iron electrodes”, Global NEST Journal, Vol 13, No 4, pp 412-418, 2011

33) Kauspediene D., E. Kazlauskiene, A. Gefeniene, R. Binkiene, ”Comparison of the efficiency of activated carbon and neutral polymeric adsorbent in removal of chromium complex dye from aqueous solutions” Journal of Hazardous Materials 179 (2010) 933–939

34) Kozlowski C.A., W. Walkowiak, “Removal of chromium(VI) from aqueoussolutions by polymer inclusion membranes”, Water Res. 36 (2002) 4870–4876.

35) Linsen Wei, Gang Yang, Ren Wang, Wei Ma., “Selective adsorption and separation of chromium (VI) on the magnetic iron-nickel oxide from waste nickel liquid”, Journal of Hazardous Materials 164 (2009) 1159–1163

36) M. Gheju, I. Balcu, “Removal of chromium from Cr(VI) polluted wastewaters by reduction with scrap iron and subsequent precipitation of resulted cations”, Journal of Hazardous Materials 196 (2011) 131– 138.

37) M.G. Arroyo, V. Perez-Herranz, M.T. Montanes, J. Garcia-Anton, J.L. Guinon, “Effect of pH and chloride concentration on the removal of hexavalent chromium in a batch electrocoagulation reactor”, journal of Hazardous Materials, Volume 169, Issues 1–3, 30 September 2009, Pages 1127-1133

38) M.Y. Arıca, I˙. Tu¨zu¨n, E. Yalc¸ın, O¨ . I˙nce, G. Bayramog˘lu, “Utilisation of native, heat and acid-treated microalgae Chlamydomonas reinhardtii preparations for biosorption of Cr(VI) ions”, Process Biochem. 40 (7) (2005) 2351–2358

39) Mall, I.D., Srivastava, V.C., Agarwal, N.K., “Removal of orange-G and methyl violet dyes by adsorption onto bagasse fly ash – kinetic study and equilibrium isotherm analyses”. Dyes Pigment 69 (2006), 210–223.

40) Mohan D., K.P. Singh, V.K. Singh, Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth, Ind. Eng. Chem. Res. 44 (2005) 1027–1042.

41) Mohan D., K.P. Singh, V.K. Singh, Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth, J. Hazard. Mater. 135 (2006) 280–295.

42) Motoi Machidaa, Babak Fotoohia, Yoshimasa Amamo, Tomonori Ohbad, Hirofumi Kanohd, Louis Merciera., “Cadmium(II) adsorption using functional mesoporous silica and activated carbon”, Journal of Hazardous Materials 221– 222 (2012) 220–227

43) N. Vivek Narayanan, M. Ganesan, “Use of adsorption using granular activated carbon (GAC) for the enhancement of removal of chromium from synthetic wastewater by electrocoagulation”, Journal of Hazardous Materials, Volume 161, Issue 1, 15 January 2009, Pages 575-580

44) P. Rana, N. Mohan, C. Rajagopal, “Electrochemical removal of chromium from wastewater by using carbon aerogel electrode”, Water Research, Volume 38, Issue 12, July 2004, Pages 2811-2820

45) Parinda Suksabye, Paitip Thiravetyan, Woranan Nakbanpote, Supanee Chayabutra, “Chromium removal from electroplating wastewater by coir pith”, Journal of Hazardous Materials 141 (2007) 637–644

46) Paterson J. W., Wastewater Treatment Technology, Ann Arbour Science, Michigan, 1975, pp. 43–58.
47) R.K. Misra, S.K. Jain, P.K. Khatri, “Iminodiacetic acid functionalized cation exchange resin for adsorptive removal of Cr(VI), Cd(II), Ni(II) and Pb(II) from their aqueous solutions”, Journal of Hazardous Materials 185 (2011) 1508–1512
48) S. J. Allen, G. Mckay, J. F. Porter, “Adsorption isotherm models for basic dye adsorption by peat in single and binary component system”, journal of colloid and interface Science, 280 (2004) 322-333.
49) S. Rengaraj, C.K. Joo, Y. Kim, J. Yi, “Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H”, J. Hazard. Mater. 102 (2/3) (2003) 257–275
50) S. Rengaraj, Cheol Kyun Joo, Younghun Kim, Jongheop Yi, “Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H”, Journal of Hazardous Materials B102 (2003) 257–275
51) S. Rengaraj, Kyeong-Ho Yeon, Seung-Hyeon Moon, “Removal of chromium from water and wastewater by ion exchange resins”, Journal of Hazardous Materials B87 (2001) 273–287
52) Sadaoui Z., Hemidouche S., Allalou O., “Removal of hexavalent chromium from aqueous solutions by micellar compounds”,Desalination 249 (2009) 768–773
53) Salazar E., M.I. Ortiz, A.M. Urtiaga, Equilibrium, Kinetics of Cr(V1) extraction with Aliquat 336, Ind. Eng. Chem. Res. 31 (1992) 1516–1522.
54) Sarkar R., “General and Inorganic chemistry Part I and Part II”’, New central Book Agency (Pvt.) Ltd., Kolkata, 1984.
55) Sofia A. Cavaco, Sandra Fernandes, Margarida M. Quina, Lic´ınio M. Ferreira, “Removal of chromium from electroplating industry effluents by ion exchange resins”, Journal of Hazardous Materials 144 (2007) 634–638
56) Song Z., C.J. Williams, R.G.J. Edyvean, “Treatment of tannery wastewater by chemical coagulation”, Desalination 164, p. 249-259, 2004
57) Taihong Shi, ZhuochaoWanga, Yang Liub, Shiguo Jia, Du Changminga, “Removal of hexavalent chromium from aqueous solutions by D301, D314 and D354 anion-exchange resins”, Journal of Hazardous Materials 161 (2009) 900–906
58) Vimal Chandra Srivastava, Indra Deo Mall, Indra Mani Mishra, “Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA”, Journal of Hazardous Materials B134 (2006) 257–267

59) Xing Xu, Bao-Yu Gao, Xin Tan, Qin-Yan Yue, Qian-Qian Zhong, Qian Li, “Characteristics of amine-crosslinked wheat straw and its adsorption mechanisms for phosphate and chromium (VI) removal from aqueous solution”, Carbohydrate Polymers 84 (2011) 1054- 1060

60) Yasar Andelib, Aydin, Nuran, DeveciAksoy., “Adsorption of chromium on chitosan: Optimization, kinetics and Thermodynamics”, Chemical Engineering Journal 151, (2009), 188–194

61) Z. Hu, L. Lei, Y. Li, Y. Ni, “Chromium adsorption on high-performance activated carbons from aqueous solution”, Sep. Purif. Technol. 31 (1) (2003) 13–18