ADSORPTIVE REMOVAL OF HEXAVALENT CHROMIUM (VI) FROM TANNERY WASTE WATER

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree

of

MASTER OF TECHNOLOGY

in

CHEMICAL ENGINEERING
(With Specialization in Industrial Pollution Abatement)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in this dissertation report entitled **"ADSORPTIVE REMOVAL OF HEXAVALENT CHROMIUM (VI) FROM TANNERY WATSE WATER"** in partial fulfilment of the requirements for the award of the degree of **MASTER OF TECHNOLOGY** in **CHEMICAL ENGINEERING** with specialization in "Industrial Pollution Abatement" submitted to the Department of Chemical Engineering, Indian Institute of Technology Roorkee, is an authentic record of my own work carried out during the period May 2013 to June 2014, under the supervision of **Dr. B. Prasad,** Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee. The matter embodied in this work has not been submitted for the award of any other degree.

Date:
Place: Roorkee

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CERTIFICATE

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

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ABSTRACT

In the present work, hexavalent chromium removal from tannery wastewater was investigated using a low cost activated carbon, carbonized and prepared from corncobs. Corncob based activated carbon (CAC) was characterized to understand the adsorption characteristics of chromium (VI) ions 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 400.006 m^2/g and 0.23 cm^3/g 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 ≈4.0 is found to be optimum for the removal of Cr(VI) from waste water by CAC at an optimum dose of 15 Kg/m^3. Optimum value of contact time is found as 5 hr. Various isotherm models were fitted for Cr(VI) removal. Freundlich model well fitted to Cr(VI) adsorption. Pseudo-second order kinetic model was well fitted for Cr(VI). Thermodynamic parameters represent the exothermic and spontaneous nature of adsorption

CHAPTER-1

INTRODUCTION

1.1 GENERAL

In the present day the industrialization and technology gives comfort life to human beings but in the other hand through these industrialization the problem of pollution increased day by day and possible accumulation of waste discharged in water, air and soil. In these industries one is tannery industry from many type of waste discharged in water, air and soil. From tannery industry many effluents are generate consisting of heavy metals like chlorides, chromium, total sulphide, sodium, boron, oil and grease. In these heavy metals chromium is very toxic in nature that's why it is necessary to reduce the amount of chromium from tannery waste water. There are two types of chromium present in the tannery waste water one is Cr(III) and second is Cr(VI). There are two oxidation state of chromium +6 and +3. It is mutagenic in +6 and bio element in +3 state (Oliveira et al., 2011).

Cr(III) is convoluted in hydrolysis behavior and produced mononuclear species, $Cr(OH)_4^-$, $Cr(OH)_2^+$, neutral compound $Cr(OH)_3^0$, and poly nuclear compound $Cr_2(OH)_2$ (Mohan et al., 2005). The hexavalent from of chromium is more toxic than trivalent. After hydrolysis of Cr(III) whatever generated stabilized by electron donor species (OH^-) while hydrolysis of Cr(VI) produced anions are hardly stabilized (Mohan et al., 2006).

Cr(III) is a necessary element for human as well as for other living organism for metabolism. Blood glucose level reduced by Cr(III) and also help transport of amino acid. Cr(III) also decrease the blood cholesterol and reduces the possibility of diabetes (Sarkar et al., 1984). Trivalent chromium ions are less toxic than hexavalent chromium due to their less mobility and less solubility in water. Due to high concentration of hexavalent chromium there are many disease causes like nausea, liver, respiratory system, and kidney damage, diarrhea (Mohan et al., 2006). The solubility of trivalent chromium in water is very less and mobility is also very less. Chromate and dichromate ions of Cr(VI) are very toxic in nature. Through oxygen rich conditions Cr(VI) converted into Cr(III).

Chromium effluent from tannery industry cannot discharged without removing it from tannery waste water. A minimal national standard (MINAS) is set by Central Pollution Control Board (CPCB), Delhi, India for Cr(VI) as .1 mg/l in the industrial discharge in the surface water. In the tannery industry high concentrated Cr(VI) 1500-2000 mg/l discharged into the sewage.

There are many treatment methods to remove Cr(VI) from waste water. Common methods like chemical coagulation (Song et al., 2003), through improved alkali hydrolysis (Mu et al., 2003), reverse osmosis membrane (Bodalo et al., 2005), biological treatment (El-sheikh et al., 2011), membrane treatment by nanofiltration (Cassano et al., 2002), electrochemical treatment (Costa and Botta, 2007) have used to the carrying away of hexavalent chromium from tannery waste water. Adsorption is also a treatment method to taking away of Cr(VI) from tannery wastewater.

1.2 ENVIRONMENT AND HEALTH EFFECT OF CHROMIUM

For living organism chromium is necessary nutrient as well as health. In nature chromium has two oxidation states. Oxidation state +6 Cr(VI) and +3 Cr(III). Cr(VI) is very harmful in nature and highly toxic comparison to Cr(III). In the other hand Cr(III) is good for health. The health effects of chromium are as follows:

- The range of oral toxicity for Cr(VI) is 60-160 µg/kg (Mohan et al., 2006).
- After reaching Cr(VI) in human blood it damages kidneys, blood cells, and liver.
- It causes allergic symptoms.
- It causes Chrome ulcer.

1.3 REGULATION AND GUIDELINE

The Central Pollution Control Board of India (CPCB) has set a standard value of the hexavalent chromium in the tannery waste water. The standard value is 0.1 mg/l after this limit the waste water shows harmful effect on human health and living organism. The standard value for total chromium is 2 mg/l is set by CPCB.

1.4 TANNERY INDUSTRY

The tanning is a process to transform of animal skins into leather which is a stable product. The structure of animal skin is very complex. There are three layers an outer layer, middle, lower layer. Leather produced from dermis which is the part of skin and is composed of bulky connective substance. That is bounded to the body by unfettered connective substance which contains elastin fibers and bundles collagen. The final tissue representing the under skin. In the managing of leather the subcutises are scrapping by the skin like a waste product and the substantial quantities of that are continuously being thrown away. However, this may be a origin of the manufacture of important commodity. In this procedure, the skin followed by a chemical treatment for a large numbers of inorganic and organic compound like synthetic and natural tannin (polyphenolic compound), surfactant, dyes, sulfonated oil, biocide, organic acid, acrylic resins and ammonium, Cr(III), sulfides salts, chlorides are employed (Lofrano et al., 2013).

Three main stages of the transformation of hides into leather first beamhouse, in which the hides are cleans and eliminate the leather which are more complex in nature second tanning; including; pretreated skins are transforming into the platform and third the finishing in which accompaniment the prime tanning some desired mechanical and physical properties like uniform colors, tensile strength, strong, elasticity, softness as well as its definite aspect of the presentation and the desired physical and mechanical properties. According to the skin process tanneries are classified into many stages i.e., first integrated tannery in which all the process have done to make finished leather from raw leather second wet-blue tannery in which wet blue chrome tanned leather is achieved from the tanned chrome leather third half finished leather in which to transform half finished leather we use wet-blue tanned leather and fourth is finishing tannery in which to transform finish leather we use crust leather. Production of finished leather, the tanning industry is a huge quantum of solid and liquid waste is generated adopted in the chemical and mechanical operation. The tanning process usually takes place in three different phases, i.e., firstly we prepare the raw material and tan it with tanning agents, like mineral/vegetable these tanning agents and post tanning to give color to finished leather. For transforming putrescibles collagen fibers into non-putrescibes leather matrix we used most tanning agent like chromium sulfate. Mechanical resistances of chrome tanned leather is highly impressive (Costa and Botta, 2007).

Tannery Industry is the world's oldest industry. From tannery industry many pollutants discharges like salinity, biological oxygen demand, chemical oxygen demand, total kjeldahl nitrogen, suspended solids, inorganic matter, ammonia, specific pollutants, dissolved and heavy metals etc. In tanning process a large amount of water used and of that water about 90% water discharged as effluent and some other type of waste also discharged like gaseous waste and solid. In the process of chrome tanning about 40% unused chromium discharged as effluent. Which is a very serious problem in the environment. In the country there is no effluent plant in the tannery industry and the owners of tannery industry is not taking interest to establish effluent treatment plant.

Table-1.1 Tannery industry effluent standard given by CPCB

EFFLUENTS	CONCENTRATION IN mg/l EXPECT pH
pH	6.5-9.0
BOD(3 days at 27^0C)	100
Suspended solids	100
Total chromium	2
Sulphides (S)	1
Grease and oil	10

Table-1.2 Leather industry effluent standard given by CPCB

Concentration in the effluent not to exceed milligrams per liter (except for pH and per cent sodium)

Parameter	Inland surface water	Public water	Land for irrigation	Marine coastal areas
Suspended solid	100	00	200	100
BOD 3 days at 27^0C	30	350	100	100
pH	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0
Chloride	1000	1000	600	-
Chromium Hexavalent	0.1	0.2	0.1	0.1
Total Sulphide	2.0	2.0	2.0	2.0
Sodium %	-	60	60	-
Boron	2.0	2.0	2.0	-
Oil and grease	10	20	10	20

1.4.1 PROCESS USED IN TANNERY INDUSTRY

There are two processes is used in tannery industry one is chemical and second is mechanical. The tanning operation is heart of the process in which inorganic or organic materials become bounded chemically to the protein structure of the skin and preserved it from deterioration. For making finished leather the process is divided into four groups of sub-processes: tanyard processes, beamhouse operation, finishing and retanning. However the product which we getting at the end for that product the tanning process is different and the amount of waste vary in a large range (Lofrano et al., 2013).

Beamhouse operation become after combing process i.e soaking, unhairing and liming, bating and deliming, degreasing, pickling. Traditionally more of tannery industries process all kind of leathers, thus starting from dehairing to retanning processes. However in some cases only pre-pickled leather is processed with a retanning process.

Vegetable tanning done by natural materials and that’s why this vegetable tanning is so eco friendly and suitable option to replace chromium because chromium is so toxic in nature. From vegetable tanning there are many kinds of leather made. However, vegetable tanning used in large loading of leathers which reduces its complexity to made distinct type of end products and there are also low resources availability. These vegetable tanned leathers are also known to be poorly biodegradable. The most important method of tanning is chrome tanning used to getting inexpensive leathers, light leathers of high bacterial resistance and thermal resistance, uses by tanning agent like basic chromium sulfate (Krishnamoorthy et al., 2012).

The processing of skins and hides into leather is a complicated procedure that requires a precise combination of many mechanical and chemical operations. There are mainly four process for production of leather. Those processes are pretanning, vegetable tanning, chrome tanning and finishing. In the pre-tanning there are four steps deliming, soaking, liming, bating, and unhairing. In vegetable tanning the process are degreasing, pickling, tanning, pressing and drying and in chrome tanning the process are degreasing, pickling, tanning, pressing and drying.

Soaking: In this process the skins and hides would be clean and remove the salts from the skin, and allow to reabsorb some lost water from the skins and to dissolve the some soluble proteins. Excess soaking can rob the hide of desirable substance and cause problems in liming (Cassano et al., 2002).

Unhairing: In this process we remove the hair of the skin which is presented at the animal hair. The skins are mixed in a mixture of water and lime, and transported in the another large vat, from this the hair loosens from the skin. Unhairing is done after soaking for this hair kept for 1 to 10 days and then removed mechanically from the skin (Saran et al., 2013).

Liming: Hair and epidermises are removed and a solution of limes and sodium sulphides are applied to soften and enhances hides for softness and flexibility has needed for upholsteries leather (Cassano et al., 2002).

Bating: Deliming hides and softness, suppleness and elasticity degree as the 'bated' is left in the bath. The enzymes act on proteins, which are used on the skin to achieve. It was a bright, classic finish strong enough to be classic crocodile skins as little bat (a matter of minutes) is required **(**Cabeza et al., 1998).

Deliming: It is strongly alkaline inevitably step into the skin of which is a partial neutralization. Deliming inflammation of the skin fibers can affect the position of the particular state. With ammonium salts and usually lasts about 12-14 hours. Movement of skins (such as paddle, to a lesser extent, or in revolving drums) to speed up the process but at this stage only the skins so the occasional paddling movement are very sensitive to friction (Lofrano et al., 2013).

Pickling: The synthetic skin tans (syntans) or with mineral tans are ready for bleaching and tanning treatments which have an acid bath. Classic skins for about two days, but can be marinated in a pit ossified bone dry skin to remove as much as possible to undergo a special pickling. This process takes several days and skins suspended in acid baths and is best done with gentle agitation view. Hydrochloric acid, usually together with other acids, salts and sometimes is used for crocodile skins (Lofrano et al., 2013).

Tanning: Plants with natural tans Tanned leather industry is still important. Use vegetable tannins and soft, full leather are easy to provide. With crocodile skin, however, the best results are achieved by using chromium salts. Chrome and leather tanning get more consistent results from batch to batch in order to improve the physical properties can be controlled with greater precision (Lofrano et al., 2013).

Drying: Drying the process to remove moisture evenly and should not be removed patch. Dry skin in preparation for dyeing and finishing "natural rind" and is known as the fall.

Finishing: Again, these processes and many types of leather skins like snake finish almost as many types of snakes. In fact, the tanneries are companies that specialize in the contract expires. After dyeing leather cut into a razor especially dry. The scale domed or a relief pattern (bombe effect) which is part of the lending process in classic skins. The dry shaving-what remains of osteoderms ossified skin should be careful to avoid demolition synthetic spices are perfect. Finally glazed in a special glazing machine. Best drum dyed leather caiman skins and other coatings strongly ossified rather than a polished smooth finish is treated. For the fans are very good leather, crocodile skin to create a special and long operation, but the best that could be clarified. The basic procedures are often above rinsing, washing, drying or partial drainage regular treatment, are separated by. This process can be repeated and can be used in the exceptional treatment. Needless to say, raw materials and work skills that should be worth the investment. Poor quality materials are tanned and finished properly (Lofrano et al., 2013).

1.5 OBJECTIVES

The study pertains to adsorptive removal of hexavalent chromium from tannery waste water by corncob based activated carbon with the following objectives:

- To prepare corncob based activated carbon.
- Characterization of corncob based activated carbon (CAC) using SEM, BET, FTIR and TGA.
- To determine the adsorption efficiency of CAC for hazardous chromium(VI).
- To study the effect of various parameters on the adsorption of Cr(VI) ion over CAC i.e., effect of contact time, pH, effect of adsorbent dose, effect of temperature.
- To determine the kinetic parameters which best fit the experimental adsorption process and
- To analyse the different isotherm models representing the adsorption process..

CHAPTER-2

LITERATURE REVIEW

Simeonova et al., (1996) investigated a method to convert this waste into useful products. The proposed treatment washing to remove inorganic salts, fat hydrolysis and separation of the insoluble residue with hot water and alkaline proteinase protein in a solution of the extraction involves the extraction of collagen. This results in the isolation of three parts: animal fat (total mass of the starting material (4-12%), hydrolyzed collagen glue (5-10%) and protein concentrate feed (1-3% yield). Up to 95 % of protein derived starting materials. Further purification of edible gelatin derived collagen fraction. The proposed method is applied to leather factories.

Cabeza et al., (1998) treated and recovered chromium remaining chrome cake with pure and tan hides, chrome shavings protein isolate designed to test a pilot plant. Because of high nitrogen content, the isolated collagen as a fertilizer and animal feed additives used in capacity. Gelatin cosmetics, adhesives, printing, photography, microencapsulation or even complete products for the leather industry has potential use as an additive.

Cassano et al., (2002) invested a nanofiltration (NF) process which is used for the finished tannins and water from the shower and wash them as tanning agent to recover and reuse, used to examine a nanofiltration. Chemical and physical analytical values measured on the recovered solution treated with skins tanned with standard solutions were very similar to those measured in control skins. According to the results obtained, a process plan is suggested. The water bath to recover and tired of tanning and a NF membrane purification/concentration by using the start, retentate solution tannin/non- tannin (T/NT) ratio to increase flexibility. Tired tested in a final volume of hair reduction factor was 5.25 T/NT ratio increased from 1.1 to 2.3 and the average permeate flux was 12.5 $l/m^2/h$. Profit environmental impact (COD reduction of global flows of up to 75%) reduction, wastewaters cleaning up the simplification of procedures, reduction of disposal costs, are in terms of chemicals and water savings.

Changdao et al., (2003) proposed a method which is a novel three-step treatment process CCLW. Gelatin extracted in the first stage production of the chemical for leather finishing agents have been modified. In the second phase proteins by chemical modification of different collagen hydrolysates are used as agents for retanning. The proposed three-stage procedure for treatment of possible CCLW provides a zero discharge process.

Song et al., (2003) investigated a treatment system that can effectively reduces the concentration of pollutants in tannery wastewater to environmentally acceptable levels and can significantly reduces the costs of effluent discharges. Aluminum sulfate and ferric chloride process was used as a coagulant. pH in the clotting process and improve the effectiveness of dosages of coagulants to remove organic matter , solids in suspension, and the same conditions chromium was studied and optimized. COD and chromium are removed mainly through setting: 38-46% removal of suspended solids, 12 mg/l at an initial concentration of chromium settled sewage disposal tanneries and 74-99%, 30-37% of the total COD removal can be obtained optimum pH (approximately 7.5) in the range (800 mg/1) by using the optimal dose of coagulant. It brings better results than aluminum sulphate, ferric chloride. Concentrations of chromium and chromium initial pH value of wastewater removal efficiency was a major influence. Low and high pH in the removal of chromium concentrations that produce a more effective result and a low pH, high concentrations of chromium did not increase the pollutant removal and they were not cheap. Centrifugation coagulation suspended solids (70%) combined with removal efficiency improvements. An additional 85-86% color removal, as indicated by a high level of explanation is reached.

Bodalo et al., (2005) describes a comparative study of six different reverse osmosis membranes, which were tested for their ability to reduces the salt content in the tertiary treatment after the removal of chromium salts and organic matter of effluent a pilot plant for industrial wastewater treatment the tanning industry to reach the established legal standards for safe disposal plant. The membranes were tested using a flat cell 3×10^{-3} m^2, where the concentrated current is recirculated to the feed tank.

Costa and Botta, (2007) done electrochemical treatment of tannery waste water using dimensionally stable anodes tin, Iridium, Ruthenium, and titanium-containing (DSA®). The electrodes were prepared by thermal decomposition of polymeric precursors. Electrolyses at room temperature, galvanostatic conditions was under. Oxide composition, current density, conductivity and flow effects were examined, and demonstrated current competence for electrolyses were calculated as a function of time. The results of the study, the total phenolic compounds and total organic carbon electrode (TOC) reduction in both materials, as well as UV-Vis absorbance led to that shown in the lower. Toxicity tests using Daphnia similis toxicity reduce electrical waste water treatment performed. Tannery wastewater using DSA®-type electrodes in electrochemical treatment, total phenolic compounds, TOC, absorbance, and can promote a reduction in toxicity since proved to be useful.

Jing-wei et al., (2007) done a experiment with low cell current (1A) and soluble electrode (mild steel electrode and the aluminum electrode) tannery wastewater by electrocoagulation. Compared with aluminum electrodes, mild steel electrodes with a removal efficiency of more than 90% were more effective to remove sulfide. But during the treatment process was produced black iron sulfides the typical velocity. Aluminum electrodes were effective to eliminate colority flow, sulfide removal efficiency was less than 12%. Two soluble electrode (mild steel and aluminum electrode) with removal of chemical oxygen demand, ammonia, total organic carbon, sulfide and colority was discussed in detail at the mechanism. Predominance of diffenent types of electrodes applied to the aluminum electrode at the end of the first tannery waste, elimination rates of chemical oxygen demand, ammonia, total organic carbon, sulphide and treated using mild steel electrodes, followed by colority filter respectively, the initial concentration was 2413.1 mg/L, 223.4 mg/L, 1000.4 mg/L, 112.3 mg/L and 256 times dilution, respectively 68.0%, 43.1%, 55.1%, 96.7% and 84.3%.

Carvalho et al., (2008) A Leather Industrial Co. emissions generated in a gaseous stream mimicking the operation was to treat a suspended growth bioreactor (SGB) works on. In the present main stream of gaseous volatile organic compounds (VOCs) 1-methoxy-2-propanol, 2,6-dimethyl 4-heptanone, 2-Butoxyethanol, including toluene and butylacetate. These VOCs able to degrade a microbial consortium had successfully enriched. SGB laboratory scale and with an 8-

hour cycle period was established with the shutdowns at the weekend and was operated for 210-D. With this period, SGB G 6.5 and 2.3*102 m^3 h^{-1} between the organic load (OL) was exposed. Most of the compounds were not detected at SGB store. 1.6*102 grams for an OLH1M3 SGB was fed the highest total VOC removal efficiency (RE) (99% CA) was observed.

Purkait et al., (2009) investigated leather treatment plant flow membrane based on experimental data and modeling examined. Two NF membrane (molecular weight 200 and 400 cut-offs (MWCO) are able to evaluate the performance. The experiments used a fixed batch cell. The use of RO membrane 400 MWCO operation followed by a joint operation of NF 200MWCO (membrane) of NF with a better choice than one that is celebrated operation. Batch experimental data after selecting the proper NF membrane, the membrane separation plan by conducting experiments using a cross flow cell is valid.

Kantarl and Yanik, (2010) study,activated carbon as raw material for production of a solid waste. For this purpose, activated carbon physical and chemical activation methods chromium and vegetable tanned leather shaving waste was produced. Acidity, total surface area, microporosity and mesoporosity of the extent of the surface properties of activated carbon including detailed analysis were presented. Production of activated carbon produced from waste vegetable tanned leather shaving chromium tanned leather shaving a high surface area and micropore volume of activated carbon is produced from waste. Adsorbent to remove water pollution as a potential application of activated carbon derived from vegetable tanned shavings phenol, methylene blue, and Cr (VI) has been checked.

Mandal et al., (2010) studied that thiobacillus ferrooxidans, Fenton's reagents , and combined treatment involving only the aerobic treatment of wastewater degradation studied by the leather industry oxidation sole treatment 69%, 72%, 88%, only 5%, 100% and T. ferrooxidans pH 2.5, FeSO4 16 g/L at 21 d of treatment, respectively, to an extent of 77%, 80%, 85%, 52%, 72%, 62% and COD removal efficiency up to 100% of delivered BOD at pH 2.5 and 30^0C, sulfide, chromium and color of Fenton's reagent treated samples subtract 350 and 470nm wavelength absorption was observed in the picture. The T.ferrooxidans may be the key factor for stimulating the biodegradation.

El-Sheikh et al., (2011) tannery wastewater up flow anaerobic sludge blanket to provide adequate treatment (UASB) using innovative low cost examined the possibility of applying biological treatment. Anaerobic treatment applications connecting two stage UASB reactors in the series, with volume of 94 l each five hydraulic retention time (HRT) lasted a year, producing the pilot, with 24 hours of the start of HRT use was assessed through each UASB reactor was then 18, 12, 8 and 5 hours in the end. 12 hours HRTs proposed procedure for the disposal of municipal sewers may be pre-treated tannery waste. The study of the efficiency of the system to predict the best fit equation.

Oliveira et al., (2011) prepared a wet blue leather waste activated carbon in aqueous media in the presence of hydrogen peroxide decomposition and oxidation of organics studied. Wet blue leather waste, the CO_2 flux under controlled pyrolysis, was transformed into chromium-containing activated carbon. CR microporous carbon with high surface area (889 m^2g^{-1}) to have shown. In addition, the carbon derived from wet blue leather were impregnated with chromium oxide nanoparticles. Chromium oxide on activated carbon nanodispersed, and the particle size was increased with activation time. In fact, in this work we obtained from waste leather combination of activated carbon adsorption and oxidation processes to remove methylene blue presents the observed higher.

Piccin et al., (2011) investigated an adsorbent in the removal of dyes from aqueous solution tannery to be an efficient and economical alternative has been proposed as a vegetable tanned leather and chromium in industrial waste reuse potential for works. A leather samples were characterized by water from wet finishing process. Aqueous solution of synthetic dye concentrations in the range of waste produced two types of wastes and leather (chromium and vegetable tanned) adsorption pH values were analyzed.

Krishnamurti et al., (2012) study, as an alternative to chrome-free tanning unnatural D-amino acids (D-AA) aldehyde (ALD) method based on green and sustainable or environmentally friendly tanning process, the approach has been attempted. Tanned leather, hydrothermal stability, mechanical properties and resistance to tanned leather in the collagenolytic activity of optically active D-AA the distribution, assessment of environmental friendly characteristics were investigated. Scanning electron microscopic (SEM) and atomic force microscopic (AFM) tanned leather surface morphology and roughness collagen matrix, respectively, indicate analyzes. Pressure and differential scanning calorimetric (DSC) tanned leather shrinkage temperature and denaturation temperature (Td) D-AA leather present in the matrix are related to the content of the analyzes show.

Lofrano et al., (2013) studied a state of the art treatment technologies and chemicals attempts to revise the global trends and advances for the Prevention of Pollution from tannery wastewater. The least measure progress, with a minimum of waste water according to the technology of production of leather and substitute chemicals, biological and chemical treatment processes that have been vigorously studied could be explained. Advanced Oxidation Technologies integrated with biological processes for the future prevention of the tanneries to implement the best solution would be to focus on the agenda of decision makers and water area.

Saran et al., (2013) studied about enzymatic completely beam house operation (dehairing and degreasing) and skins for leather industry standardized and protease of Bacillus licheniformis and Bacillus subtilis lipase hides. Due to its great importance and customized presentations of these enzymes protease and lipase in 36 hours of 34.91 IU/mL at 18 hours 4568 U/mL, resulting in a maximum yield was increased demand in a 300 L bioreactor. 100% of hides and skins enzymatic dehairing and degreasing (dehairing enzyme concentration of 5-10% to 2-5% (w/v) protease with a pH value of 8.0 and a temperature of 30-37^{0}C can be obtained at w/v) 8-12 within hours of lipase for degreasing. As observed for traditional crust leather hides processed enzymatically formed using dermal layer exhibited similar physical and tactile properties.

Chowdhury et al., (2013) study focused on waste characterization and physical and chemical treatment access by filtration and coagulation processes. Waste analysis results to basic pH of the raw wastewater, yellow, brown, were the shows, BOD_5, COD, TDS, TSS, TS and CR, Na, very high values of high concentrations of SO_4^{2-} and other organic and inorganic component. Sand stone and raw tannery waste disposal through the post after filtration, filters were treated with various doses of $FeCl_3$ waste. The major physico-chemical parameters for neutral pH showed the best removal efficiency study near 150 mg/L dose of the coagulant ($FeCl_3$) observed. The results of the analysis of physical and chemical parameters of the effluent discharged well below the permissible limits prescribed found that description. Study untreated tannery waste, dispose of coagulating with filtering and $FeCl_3$ will be treated by a joint process that shows.

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 sorbents Environmental friendly Efficient sorbent Versatile sorbent Easily regenerate	Nonporous adsorbent Variable in the pellet characteristics Highly pH-dependent Need chemical modification
3.	Starch based material	Renewable Economically attractive Easy to prepare Large swelling capacity in water Can remove vast range of pollutants Fast kinetics	Low surface area Need chemical activation Fouling problem
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	Non-selective Expensive Cost increases with quality High regeneration cost Quality depend on the type of carbon Need chemical activation

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	Fahim et al., 2006
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	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	Xavier et al., 2013
Activated carbon, SHT	69.1	3	3	30	Langmuir	Xavier et al., 2013
Activated carbon, CZ-105	40.4	3	3	30	Freundlich	Xavier et al., 2013
Activated carbon, CZ-130	44.9	3	3	30	Freundlich	Xavier et al., 2013

CHAPTER-3

ADSORPTION FUNDAMENTALS

3.1 GENERAL

Adsorption is the adhesion of ions, molecules, atoms, liquid or dissolved solids to a surface. Adsorption process called adsorbent material deposited on the surface of the substance (adsorbate) makes a film. This fluid is a liquid or solid substance is dissolved, which is similar to absorption. Sorption includes 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 needs. Adsorbents Generally, biodegradable, especially those that are not organic are used to reduce pollutants. The adsorption is driven by

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

Adsorbents are generally between 0.2 and 1 mm in diameter and thin, spherical pellets, moldings, monoliths or rods are used. Adsorbent high thermal stability, small pore diameter, high surface area, high adsorption capacity and the surface must have high abrasion resistance. There are three types of industrial adsorbents:

- 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

Select adsorbent depends on various parameters. In many cases, the pressure drop and the adsorption rate of all important process parameters, requires a degree of effectiveness. Almost every different applications require different set of priorities. For example, the need for purification of municipal water is low cost. With low cost activated carbon provides effective removal of high pollution. Adsorbents are a huge amount of variety available in the market, but it is very important to choose the right adsorbent. Select adsorbent is based on various parameters that affect the adsorption process.

Important parameters for selection of adsorbent are as follows:

Capacity
Selectivity
Regenerability
Kinetics
Compatibility

The high adsorption capacity of an adsorbent is the desired parameter. The adsorbate (g) per unit of mass is taken by the adsorbent on the surface of the material. The Capacity of the adsorbent depends of the temperatures, depending on the fluid phase concentration and other conditions. Generally, the adsorption capacity data, collected at different adsorbate concentrations at fixed temperature and the data are plotted as an isotherm. It also determines the amount of ships which states the required amount of adsorbent, the adsorption capacity is of paramount importance for working capital costs, and both are usually very important (El-Sherif et al., 2013).

Capacity is related to selectivity. Just another in a certain fluid concentration of selectivity that is the ratio of adsorbent capacity. Solution concentration goes to zero as the ratio usually leads to a constant value. The closest analogy Small price, big tool is the relative instability of that size. Key components leads to a very large selectivity which is not an ideal situation occurs more adsorbed (El-Sherif et al., 2013).

Adsorbent with uniform performance continuous adsorption cycle so that all applications can use, depending on regenerability of adsorbent. It should all adsorbable adsorbed pollutants that indicates relatively weak. Related to the energy required for regeneration of the adsorption heat, and the heat of adsorption at low values are desired (Piccin et al., 2011).

Intraparticle mass transfer kinetics is related to mass transfer resistance. The fixed bed adsorption process is very important because it will determine the timing cycle. Slow kinetics curve provides a distended, while the fast kinetics curve shows a sharp success. The effect of a distended curve or increase the cycle time can be destroyed in the end product by adding supplements. Kinetics also has been dubbed as the basis for adsorptive separation. Generally a slow diffusion of the adsorbate adsorption process is referred to as a loss (Mano et al., 2013).

Compatibility in adsorption various through indifference or biological contamination, the adsorbent can shorten the life of the various possible modes that include physical and chemical attack. For example, the binder, adsorbent, and working groups must be inert to the surface of the carrier and must not react with the real adsorbate or contaminants. Likewise, such as temperature, velocity, pressure, vibration and other operating conditions as adsorbent particles should not cause undue harm. This can also be caused by friction or crushing some standard methods for measuring them.

3.3 FACTORS AFFECTING ADSORPTION PROCESS

There are a lot of factor which affecting the adsorption process. Some of the factors which affecting adsorption process are following:

3.3.1 Surface area: Larger surface area, the greater will be the adsorbent on the adsorption of impurities. To interact with the adsorbent for the adsorbate is a large area and therefore large amount of adsorbate is attached inside the pore. In simple words we can say, larger size means a greater adsorption capacity and hence reduces the cost of working capital (Fahim et al., 2006).

3.3.2 Particle size: The small particle size and mass transfer inside the adsorbate to enter reduce internal diffusional resistance. The balance is easily available and almost complete adsorption capacity can be achieved by small particles. However, the waste water drop columns packed with adsorbent powder, packed beds of the adsorbent used is too high. Their removal should be followed by the addition of powdered carbon.

3.3.3 Residence time: Contact time will be longer and give more complete adsorption. However, the device size will be larger for longer residence time. The adsorbate with adsorbent big time enough time to react and therefore results in greater removal percent. But long contact time for the attachment of adsorbate on adsorbent should be the maximum time is not good for the adsorption process (Xavier et al., 2013).

3.3.4 Solubility of adsorbate in wastewater: High-soluble pollutants when compared with the slightly soluble in water pollutants is difficult to remove. Adsorbent surface so weak forces, attraction attached with water slightly soluble substances can easily break these weak bonds. Since water has a greater affinity for polar substances from polar to non- polar substance compounds are generally more easily removed. This substance is very similar to another substance, so it requires a lot of energy to separate them well- known fact. Therefore, we waste water pollutants with greater solubility, low adsorption will take place (Fahim et al., 2006).

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

3.3.6 Size of the molecules with respect to size of the pores: Adsorption process is totally depends on the pore size of the molecules. Large molecules can be difficult to enter the small pores. This independently from other causes, adsorbate can reduce the adsorption. As with the case of lignin, lignin removal adsorbent is suitable for the larger pores.

3.3.7 pH: With the degree of ionization is mainly influenced by the pH of the solution surface charge of adsorbent. Standards and working groups wastewater pH balance affects the dissociation kinetics of the reaction. Hydroxyl ions and hydrogen ions, therefore, changing the pH of the adsorption of other ions, are adsorbed quite strongly. Surface due to the accumulation of OH^- ions at high pH is more active for adsorption of cations, the surface because of the presence of H^+ ions that attract anions favorably at low pH (Sekaran et al., 1998).

3.3.8 Agitation speed: In batch experiments through agitation speed improve the removal efficiency. Between the adsorbent and the adsorbate ensures proper contact time. The less movement, the fluid film is rough around the particle. Adsorption process is controlled by mass transfer, then the transfer of particles of active sites for the film decreases. Through movement, the film thickness decreases and reduces the mass transfer resistance. Mass transfer resistance is very small, then the process is controlled by intra- particle intra- particle diffusion controlled process, the movement has no effect on the rate of adsorption.

3.3.9 Temperature: Temperature also affects the absorption of the adsorbate, but a particular range of temperatures to a limited extent. Normally exothermic adsorption process, the adsorption capacity (mg/g) increases with decreasing temperature. Adsorbent adsorption capacity reduction at high temperatures within the active sites may cause damage. Desorption of Adsorbed substances takes place at high temperatures. Since this condition is easily replicable it at room temperature is desirable to conduct the adsorption process (Sekaran et al., 1998).

3.4 ADSORPTION ISOTHERMS

When solution is agitated with a solid adsorbent in aqueous solution with a concentration of adsorbate phase getting shifted from solid phase to the liquid phase. Equal amounts of solute is finally being desorbed and adsorbed together unless this is known as adsorption equilibrium. Constant temperature adsorption process are illustrated by the equilibrium adsorption isotherm data. To design a heterogeneous reactor isotherm data is most important. There are many types of theoretical and empirical models are available to represent the different types of adsorption isotherms. Brunauer-Emmet Teller (BET), Langmuir, Redlich- Peterson (RP), Freundlich isotherm models, etc are usually used for dynamic equilibrium condition. Various types of equilibrium adsorption isotherms are followings:

3.4.1 LANGMUIR ISOTHERM

Langmuir isotherm equation is derived based on the assumption of the absorption of a solute from a liquid solution (Mohan et al., 2006).

- Surface has empathy in the direction of the solute existing in the solution.
- The adsorbent surfaces have a numbers of active sites where the adsorbate can be adsorbed.
- Formation of monolayer.

Equation of Langmuir isotherm is given by:

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

Where:

q_e (mg/g) =Mass of adsorbate at equilibrium condition.

Q_m (mg/g)= Mass of adsorbate required for mono layer.

K_A(mg/g)= Constant denotes to enthalpy of adsorption.

C_e (mg/g)= Adsorbate concentrations of solution at equilibrium condition.

3.4.2 FREUNDLICH ISOTHERM

In many process due to increasing expanse of adsorption process the amount of adsorption heat decreases. This decreasing graph of heat of adsorption is logarithmic, shows that adsorption active sites are distributed exponentially with the heat of adsorption. Such type of isotherm called Freundlich isotherm give by mathematically: (Oliveira et al., 2011)

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

Where

Q_e = Mass of adsorbate equilibrium condition

K_F = Freundlich constant

C_e = Equilibrium concentrations

n = Exponential constant

3.4.3 Tempkin isotherm:

Tempkin isotherm suitable for solute-adsorbent interaction. Tempkin isotherm assumes that (Oliveira et al., 2011):

(1) The heat of absorption of all the molecules/ions In the layer the heat of absorption of all the molecules decreases linearly with coverage of surface due to solute-adsorbent interactions

(2) Up to some maximum binding energy the adsorption is characterized by a equal distribution of bonding energies.

Tempkin isotherm equation is given by:

$$q_e = \frac{R * T}{b} \ln(K_T * C_e)$$

If we draw a plot between Qe vs Ce find a isotherm constant KT and b from the intercept and slop respectively.

3.5 ADSORPTION MECHANISM AND KINETICS

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

The adsorption behavior may be described by the following 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

According Lagergren pseudo first-order model the rate of change of solute with time is directly proportional to the difference in the equilibrium adsorption capacity and the amount of solute with time (Mohan et al., 2006).

General equation of this model is given by:

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

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}).
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

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

3.5.2 PSEUDO-SECOND ORDER MODEL

The pseudo second-order model is based on the sorption capacity of the solid phase. The general equation of this model is expressed as: (Mohan et al., 2006)

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

The linear form of above equation can be written as:

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

Where,

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

t = Contact time (min)

CHAPTER-4

EXPERIMENTAL WORK AND PROCEDURE

Present work is removal of hexavalent chromium from tannery waste water. Removal of hexavalent chromium is done with the help of activated carbon prepared by corncob.

4.1 PREPARATION OF CORNCOB BASED ACTIVATED CARBON (CAC):

The corncob was collected from market. Corncobs were washed with water to remove dirt and then cut into small pieces and dried into sunlight for 12 hours and after that further dried in hot air oven at 103°C 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: After well dried pieces of corncob crush into so small pieces and then put it in the grinder to prepare powder.

Step 2: After preparing the powder of corncob, mix 0.2N $ZnCl_2$ for activation

Step3: Prepared powder is ready for carbonization in the absence of oxygen for this we will use microprocessor programmable furnace.

Step 4: In microprocessor programmable furnace burn the prepared powder at 600°C for 2 hour.

Step 5: After 2 hour getting corncob based activated carbon.

4.2 CHARACTERIZATION OF CAC

4.2.1 PROXIMATE AND ULTIMATE ANALYSIS

Proximate analysis to determine fixed carbon, moisture content, ash content and volatile matter. For proximate analysis of corncob based activated carbon used Indian standard 1350 part I. From this analysis found essential component like carbon, hydrogen, nitrogen, oxygen and sulfur can also present.

4.2.2 BET SURFACE AREA

For determine the surface area of the corncob based activated carbon use Brunauer-Emmett-Teller (BET) and in the presence of N_2 adsorption isotherm using an ASAP 2020 micrometric instrument determine specific surface area.

4.2.3 SEM

For determine the morphology and porosity of the CAC use “FE-SEM Quanta 200 FEG, Netherlands”.

4.2.4 FTIR

FTIR analysis is used for finding the major functional groups involved in Cr(VI) removal. Firstly the CAC sample was mixed with KBr and after that we prepared pellet. FTIR of CAC is 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}. For finding out the spectra OMNIC software was used.

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 Analyser 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°C at the heating rate of 10°C/min under N_2 atmosphere.

4.3 CHEMICAL AND ANALYTICAL MEASUREMENT

All the chemicals used in the experiment process are analytical reagent (AR) group. For finding out the hexavalent chromium from the tannery waste water use flame atomic absorption spectrophotometer (AAS GBC Avanta, Australia) using air–acetylene burner at 425 nm wavelength. Before the analysis of hexavalent chromium the sample were diluted 10 times with the help of mili pore water. The calibration curve between absorbance and concentration gives a straight line.

4.4 SOURCE OF WASTE WATER

Tannery waste water collected from tannery industry kanpur city, U.P. India. Tannery waste water was filtered and kept at 15°C for further use. Tannery waste water is a major source of hexavalent chromium.

4.5 CALIBRATION CURVE

The calibration curve between absorbance and standard hexavalent chromium gives a straight line and the concentration range of standard solution is 5-30 mg/l. Standard solution prepared in the lab with the help of $K_2Cr_2O_7$ in the various concentration like 5, 10, 15, 20, 25 and 30 mg/l. The calibration curve is draw by flame atomic absorption spectrophotometer at wavelength of 425 nm. For adsorbate the concentration range is 5-30 mg/l.

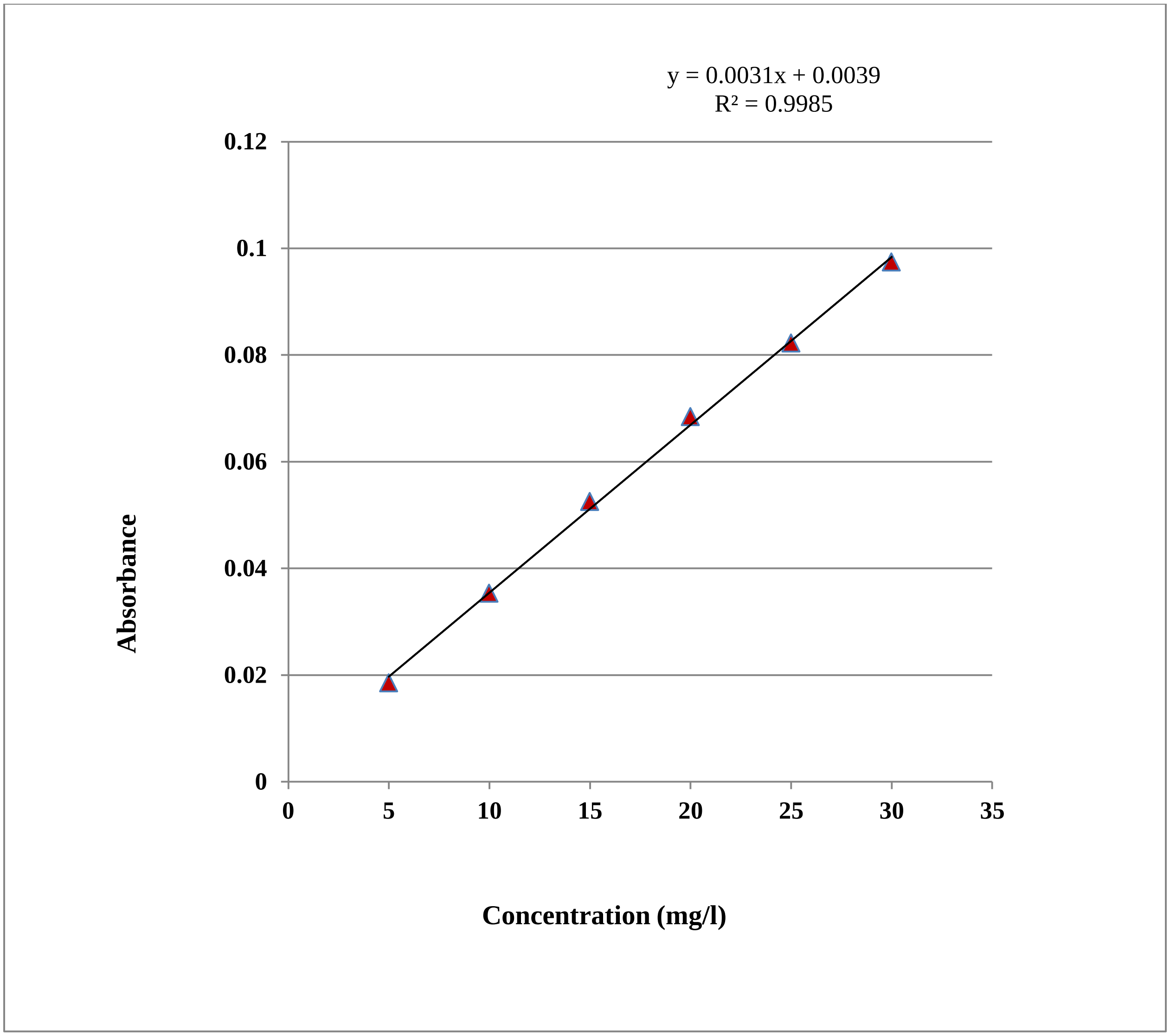

Figure 4.1 Calibration curve

4.6 CHEMICAL OXYGEN DEMAND

Chemical oxygen demand (COD) in industrial wastewater is considered as representing the level of pollution. How much oxygen required to oxidize the organic matter to CO_2 and H_2O know as chemical oxygen demand. The value of BOD always less than COD value including non-biodegradable and biodegradable compounds. The fact on COD works that many organic compounds strongly oxidize by strong oxidizing agents in the presence of strong acidic medium.
For COD measurement standard solution is prepared in the lab. The known amount of $K_2Cr_2O_7$ taking and mixed it with H_2SO_4.

4.7 BATCH ADSORPTION STUDIES

Batch adsorption studies different desired pH for different times, in different adsorbent dosage was carried out at different temperatures. First, take 100 ml of wastewater in 250 mL conical flask. After that maintain the pH of the sample at the desired dose of adsorbent and maintain the desired temperature then put the solution at 150 rpm in a shaker cum incubator at $25^{\circ}C$ for a certain time. The pH of the sample is adjusted by using 1N NAOH and 1N H_2SO_4. For the increasing the pH of the sample use NAOH and for decreasing pH of the sample use H_2SO_4. After completion of adsorption, the samples were filtered using Whatman filter paper and filtrates and to detect Cr(VI) use atomic adsorption spectrophotometer (GBC Avanta, Australia). Before analysis, all samples, put into a research centrifuge to remove suspended matter (Remi Instruments, Mumbai) 10,000 rpm for 30 minutes.

The percentage removal of metal ions by CAC and equilibrium adsorption uptake q_e (mg/g) in solid phase, were calculated using the following formula: (Tahir, 2006)

Metal ions removal (%) = $\frac{C_o - C_e}{C_o} \times 100$

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

$$q_e = \frac{(C_o - C_e)V}{W}$$

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

In different flask (250 ml) taking 100 ml of samples and maintain the pH of each flask at 2, 4, 6, 8 and 10 by adding 0.1N NAOH or 0.1N H_2SO_4 solution. After that in each flask put 10 g/l of CAC and the flask were krpt at 25°C for 2 hours. After completing 2 hours the sample were taken out from the shaker and centrifuged at 10,000 rpm for 30 minute.

ADSORBENT DOSE EFFECT

In the 100 ml of sample use different adsorbent dose from 1g/l to 20g/l but before adding adsorbent in the sample adjust the pH of each sample by using 0.1N NAOH and 0.1 H_2SO_4 and then samples were kept at 25°C for 2 hours in the incubater cum shaker. After that for analysis of hexavalent chromium use AAS.

TEMPERATURE EFFECT

In temperature effect the pH and dose of the sample kept constant and only temperature varied from 25°C to 50°C for the removal of Cr(VI) and COD.

CHAPTER-5

RESULTS AND DISCUSSION

5.1 CHARACTERIZATION OF CAC

There are many instruments and technique for the characterization of Corncob based activated carbon. The specific surface area, pore diameter and pore volume of the sample determined by using ASAP 2020 micrometric in the presence of liquid nitrogen and by Brunauer-Emmett-Teller (BET) method. FTIR used to determine the functional group act with the hexavalent chromium and find out the vibrational frequencies of the functional groups. Name of FTIR instrument is Nicolet 6700, USA spectrometer. FTIR is done before and after adsorption. Thermogravimetric analysis is done because of observation of the loss of weight with respect to temperature.

5.1.1 BET SURFACE AREA

The surface area of the Corncob based activated carbon was measured by N_2 adsorption isotherm using ASAP 2020 micrometric instrument and by Brunauer-Emmett-Teller (BET). The surface area of the CAC is determine 400.006 m^2/g by Brunauer-Emmett-Teller (BET) and micro area is determine almost 308.55 m^2/g and pore volume is determine almost 0.23 cm^3/g.

5.1.2 FTIR

The samples were scanned at resolution between 4000 and 500 cm^{-1}. Robust vibration peaks in between 3,900-5,00 cm^{-1} are separated as the vibrations of N-H and O-H functional groups. At 3871.55 cm^{-1} vibrations of O-H functional group can be seen in blank sample of activated carbon. At 3000 cm^{-1} shows very dominant vibrational nodes of the C-H functional group. At 3795.26 cm^{-1} found C-H stretching in blank CAC. The tip at 1617.50 cm^{-1} is caused due to the existence of C=C in aromatic rings and C=H stretching. There is a peak at 469.85 cm^{-1} because of stretch of C-N group. At 1390-1370 cm^{-1} vibrational frequency of uniform CH_3 occurs. The uniform CH_3 vibration occurs at 1099.55 cm^{-1}.

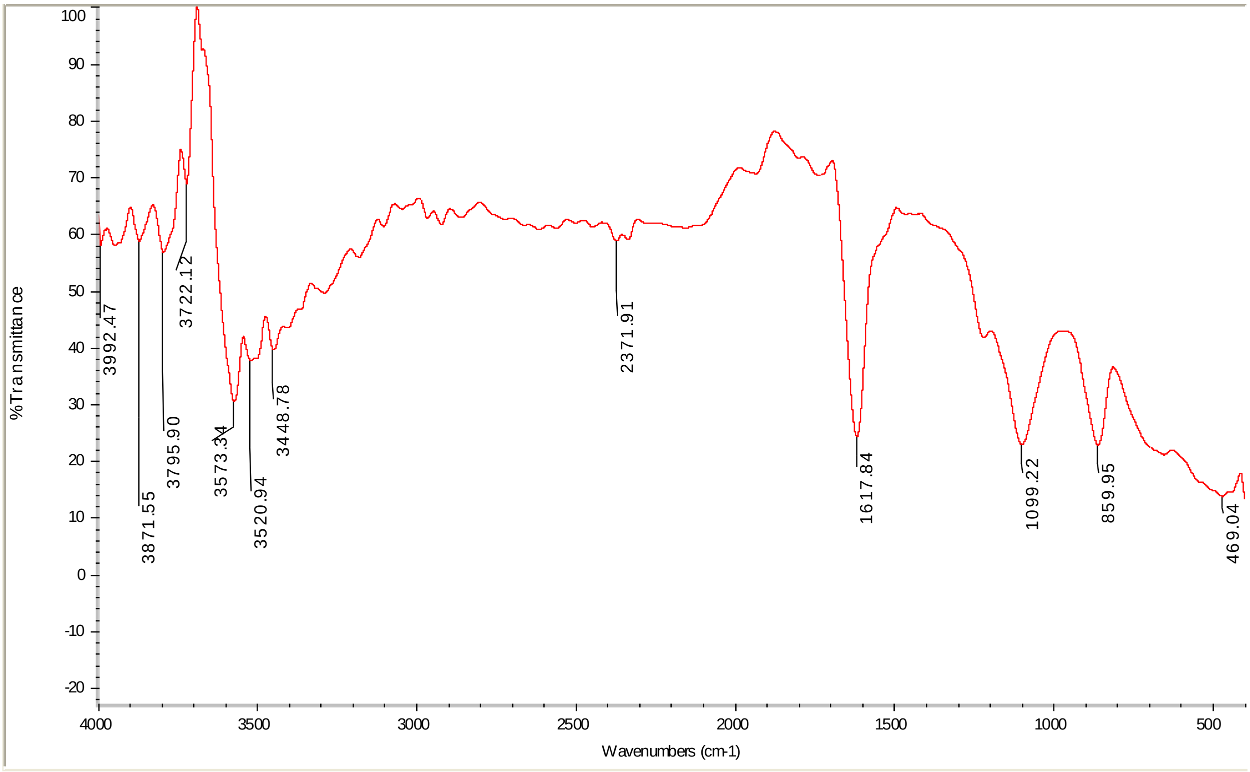

Figure 5.1 FTIR spectra of blank CAC

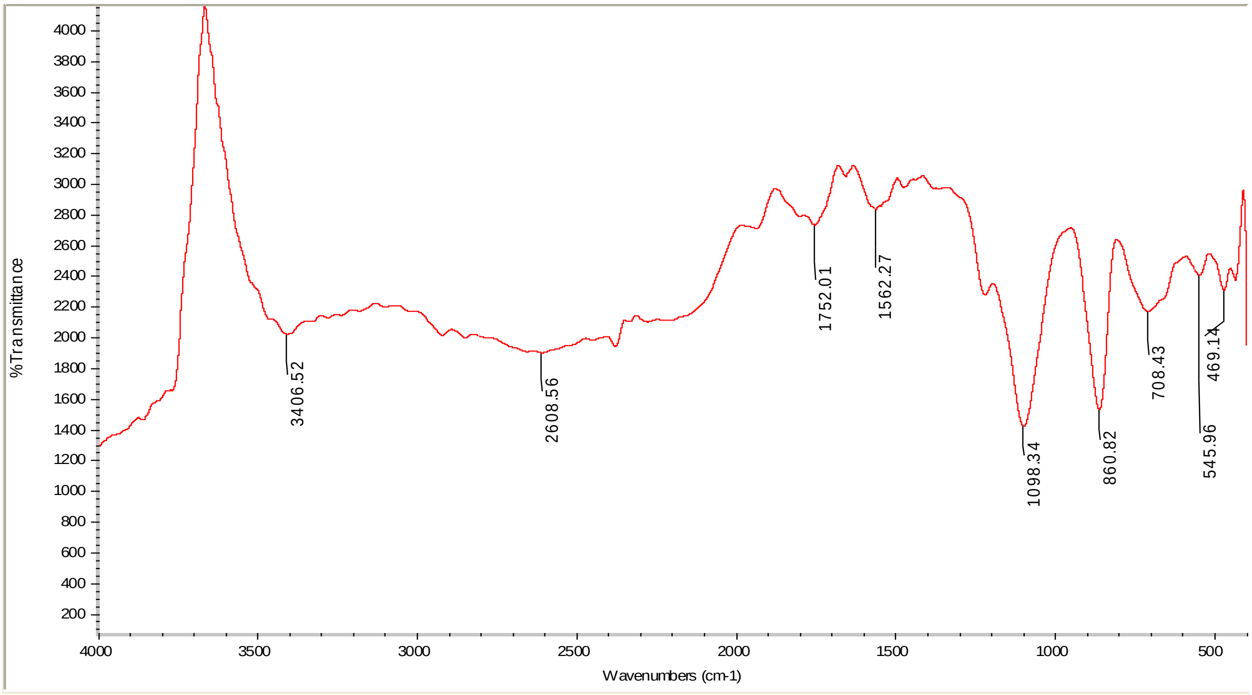

Figure 5.2 FTIR spectra of Cr(loaded) CAC

5.1.3 THERMOGRAVIMETRIC ANALYSIS OF CAC

Thermogravimetric analysis of CAC shows the variation of weight loss with respect to temperature. The TG curve for CAC shows that there is no weight loss at the room temperature and in increasing the temperature there is a weight loss. At 100°C there is a 19% weight loss like wise at 200°C weight loss in CAC is 27%. There are three different zones were found at different temperature first temperature range is 20 to 100°C second zone is 200 to 500°C and third zone is 500 to 1000°C.

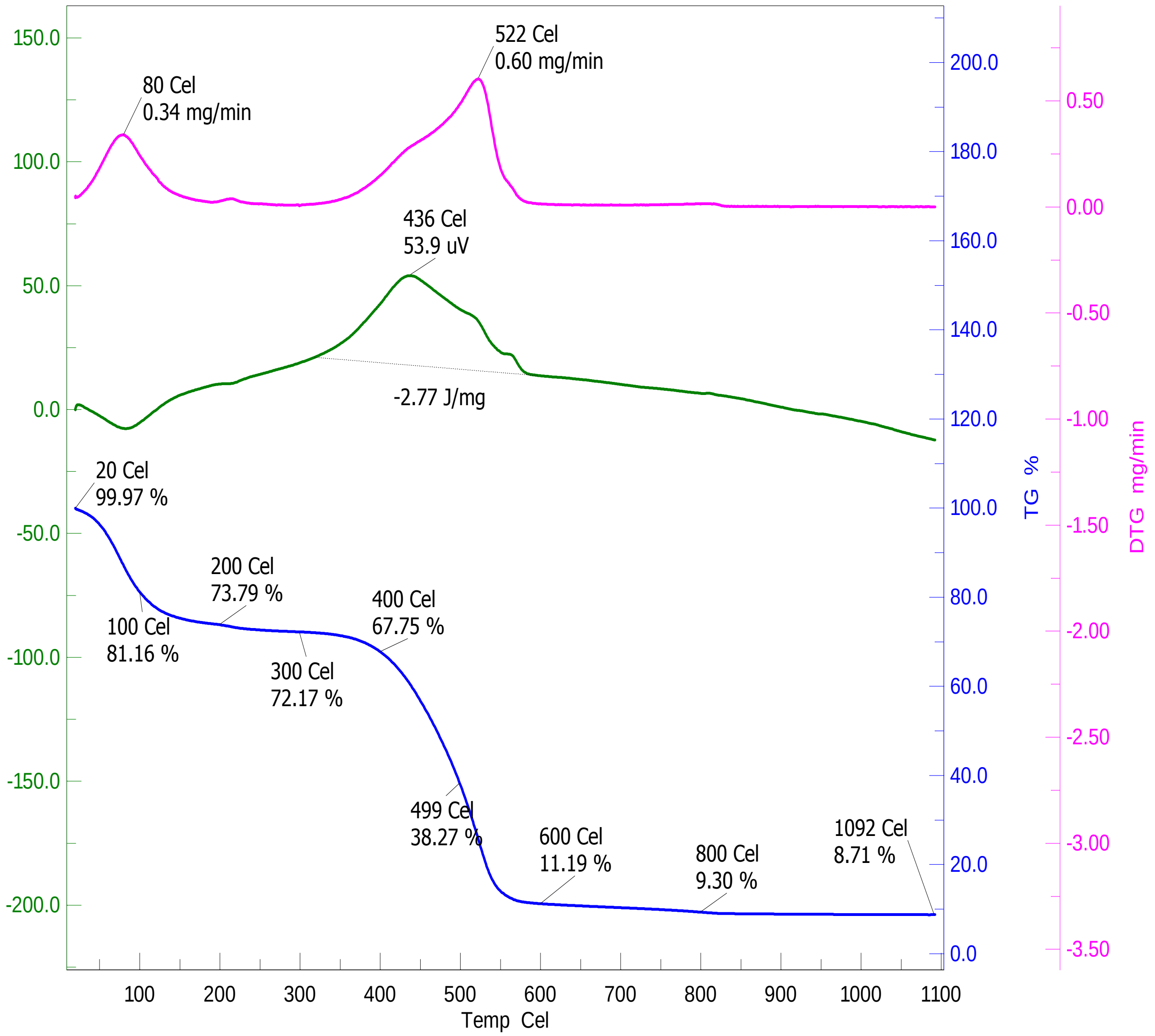

Figure 5.3 TG curve for CAC (Blank)

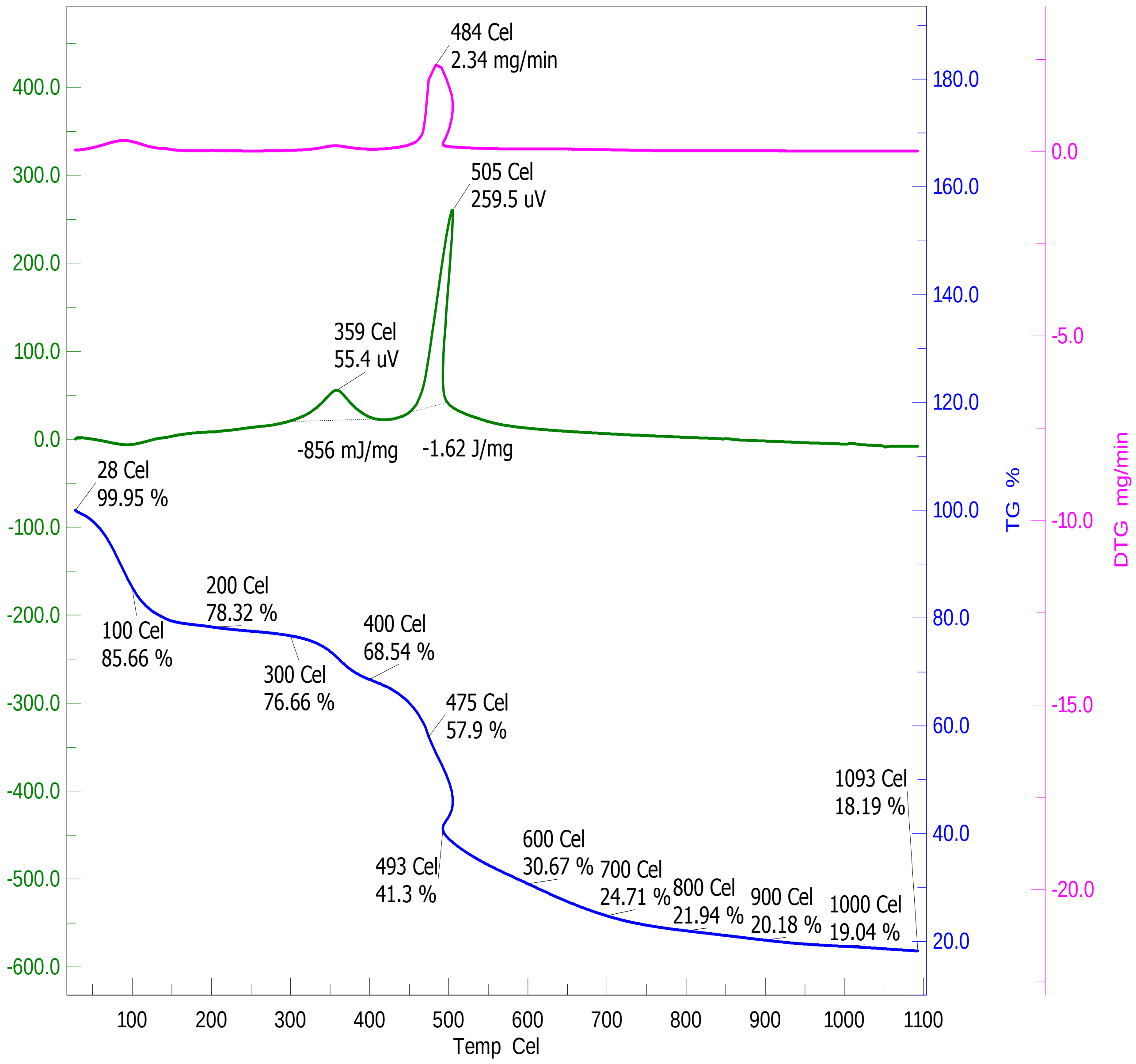

Figure 5.4 TG curve of CAC (after adsorption)

5.1.4 SCANNING ELECTRON MICROSCOPE (SEM)

Scanning electron micrograph (SEM) shows the morphological characteristics of CAC. The micrograph of CAC before adsorption is shown in the following figures.

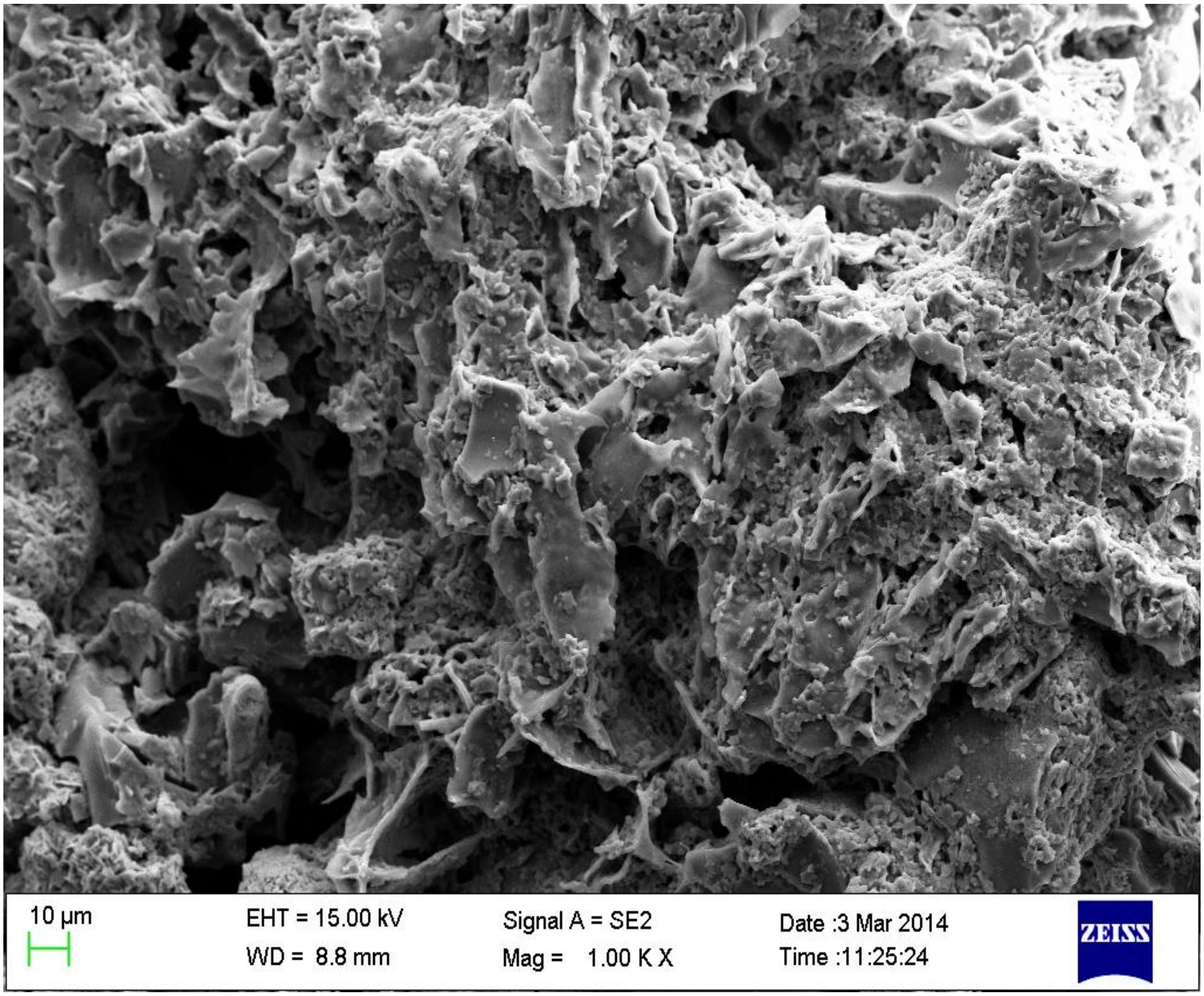

Figure 5.5 SEM image of CAC at 1000 X

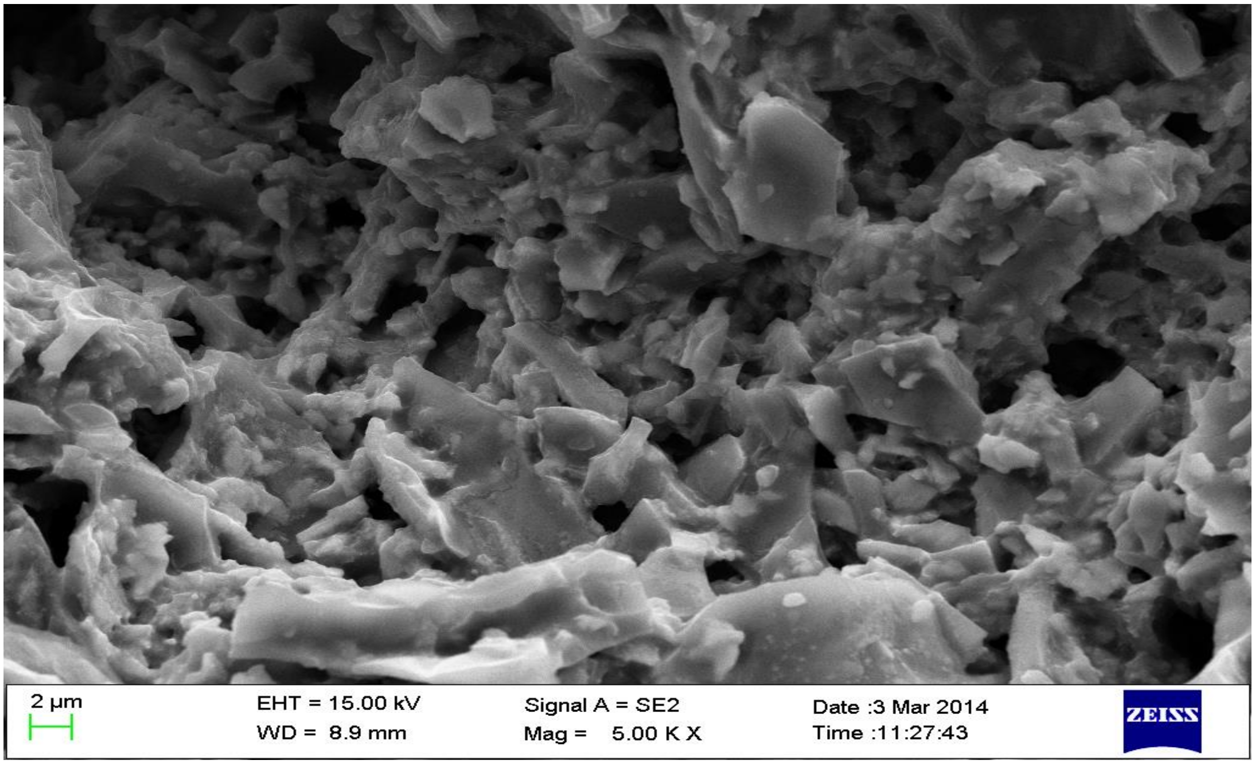

Figure 5.6 SEM image of CAC at 5000 X

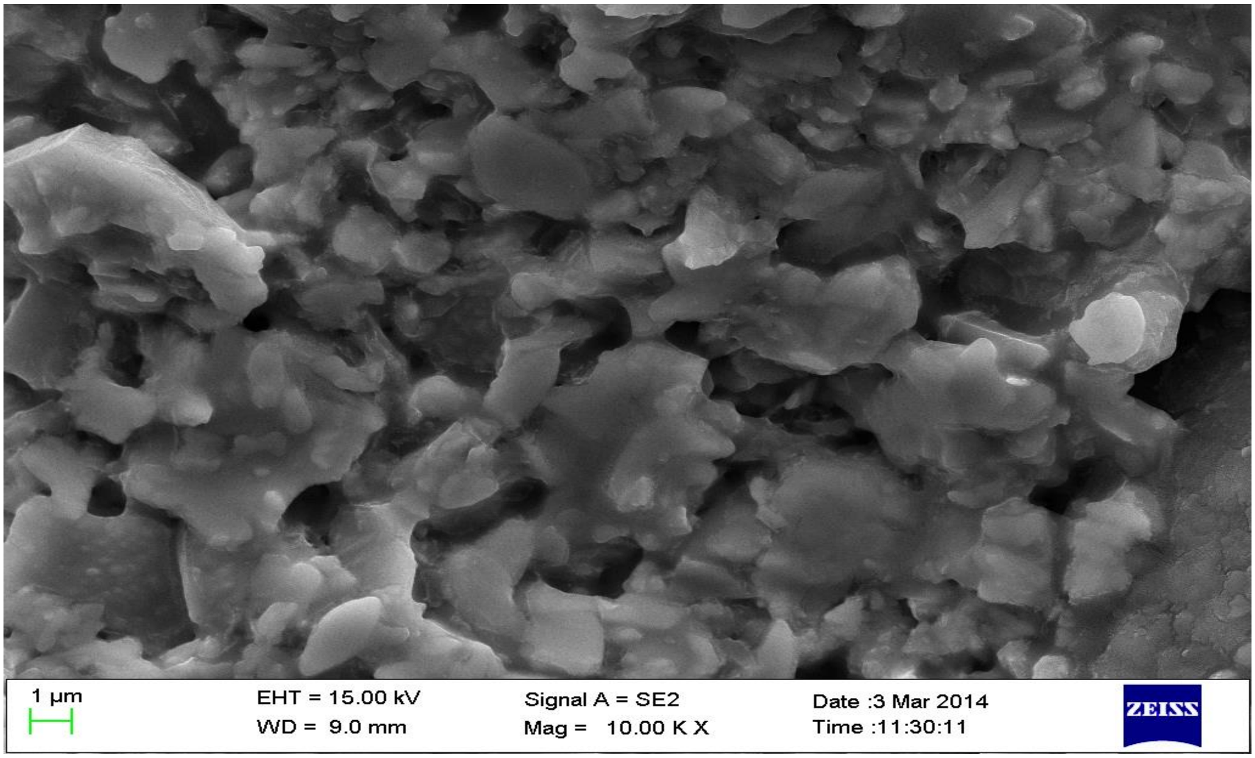

Figure 5.7 SEM image of CAC at 10000 X

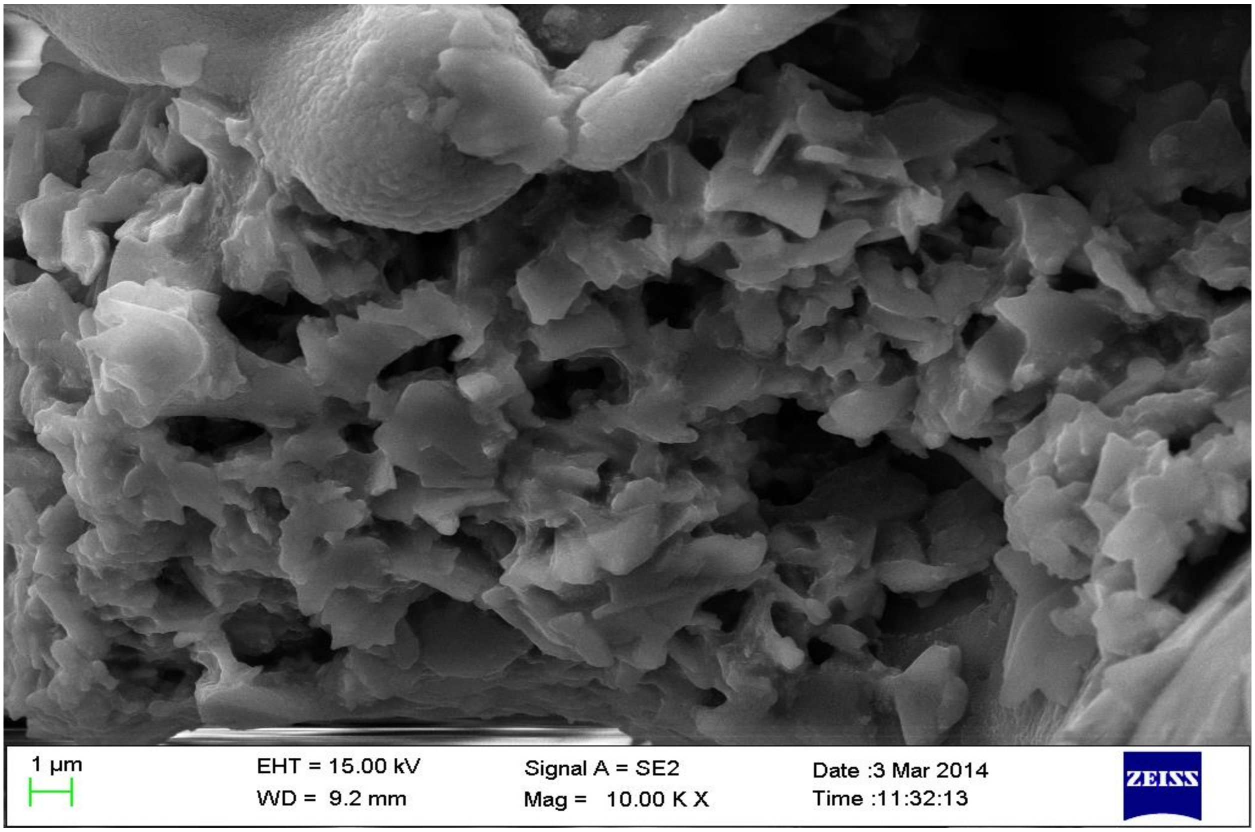

Figure 5.8 SEM images of CAC

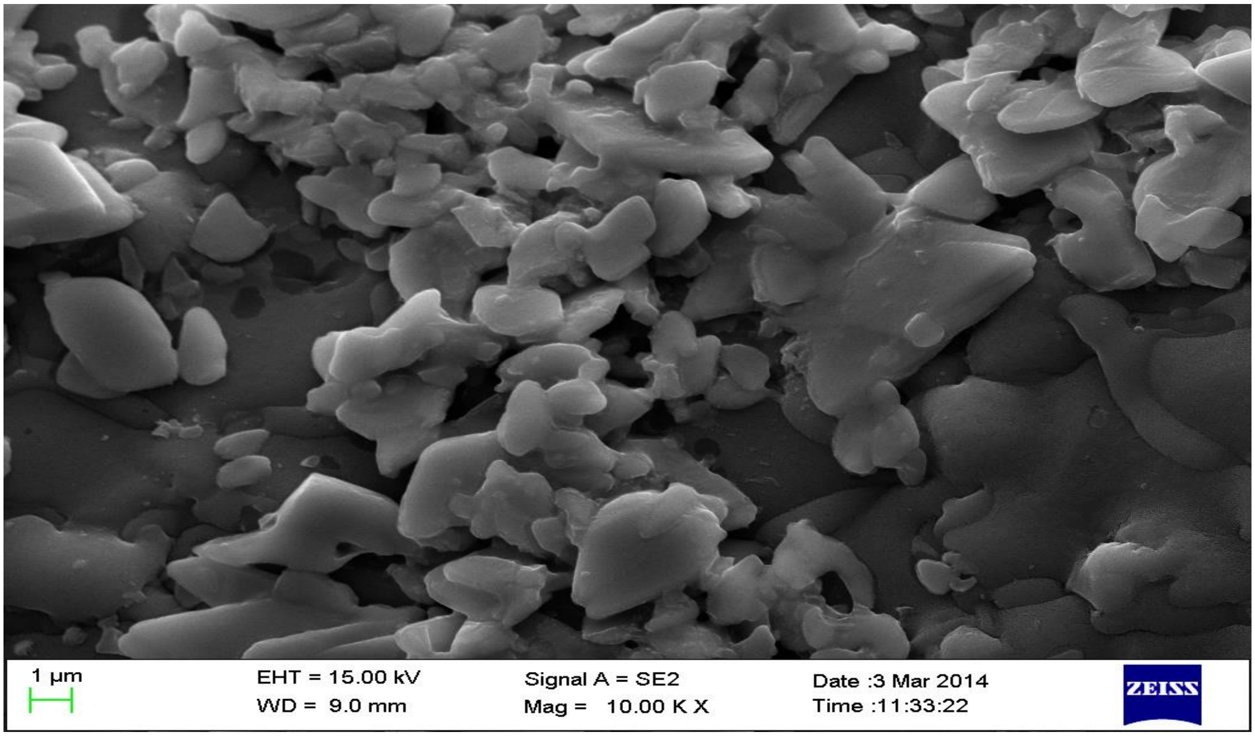

Figure 5.9 SEM images of CAC

5.1.5 EDAX

Through EDX analysis we can find out various types of elements like carbon, potassium, oxygen and sodium etc. After adsorption the EDX shows less % of oxygen.

Element	**Wt %**	**Atomic %**
C K	**26.51**	**64.91**
O K	**7.46**	**11.60**
CL K	**28.69**	**20.13**
Zn L	**31.99**	**12.17**

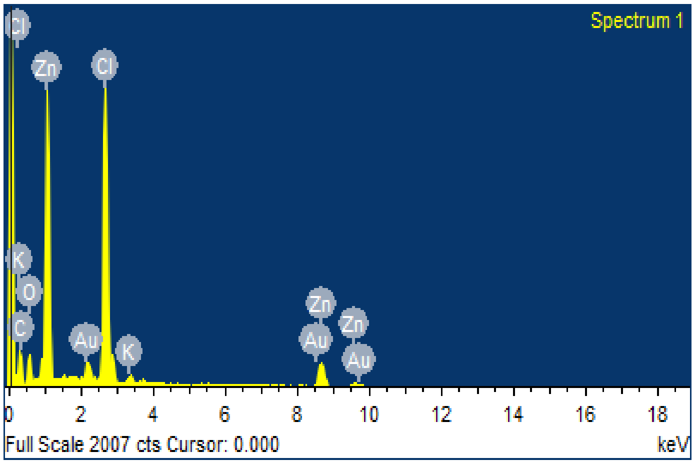

Figure 5.10 EDAX of CAC before adsorption

5.2 CHARACTERIZATION OF TANNERY WASTEWATER

Table 5.1 Various parameters of TANNERY wastewater are following:

S.No.	Parameter	Value
1	pH	3.6
2	Cr(VI) mg/l	1500
3	COD mg/l	4930
4	TDS mg/l	600
5	TSS mg/l	400
6	TOC mg/l	1040

5.3 EFFECT OF pH

The degree of ionization and charge of adsorbent of the solutes affected by pH of the solution. The hydrogen ion and hydroxyl ions are strongly adsorbed. If the sample is at lower pH the activated carbon surface adsorbs anions more because H^+ helps in the adsorption of anions and if the pH of the sample is high because of OH^- (Srivastava et al., 2005) the surface of adsorbent then become most effective for the adsorption. At the adsorbent surface there is a place where no charge is present in the presence of $pH_{pzc.}$ pH_{pzc} is a point where due to diffusion adsorption process takes place of metal ions in the macropore and micropore and electrostatic forces does not work also at this point.

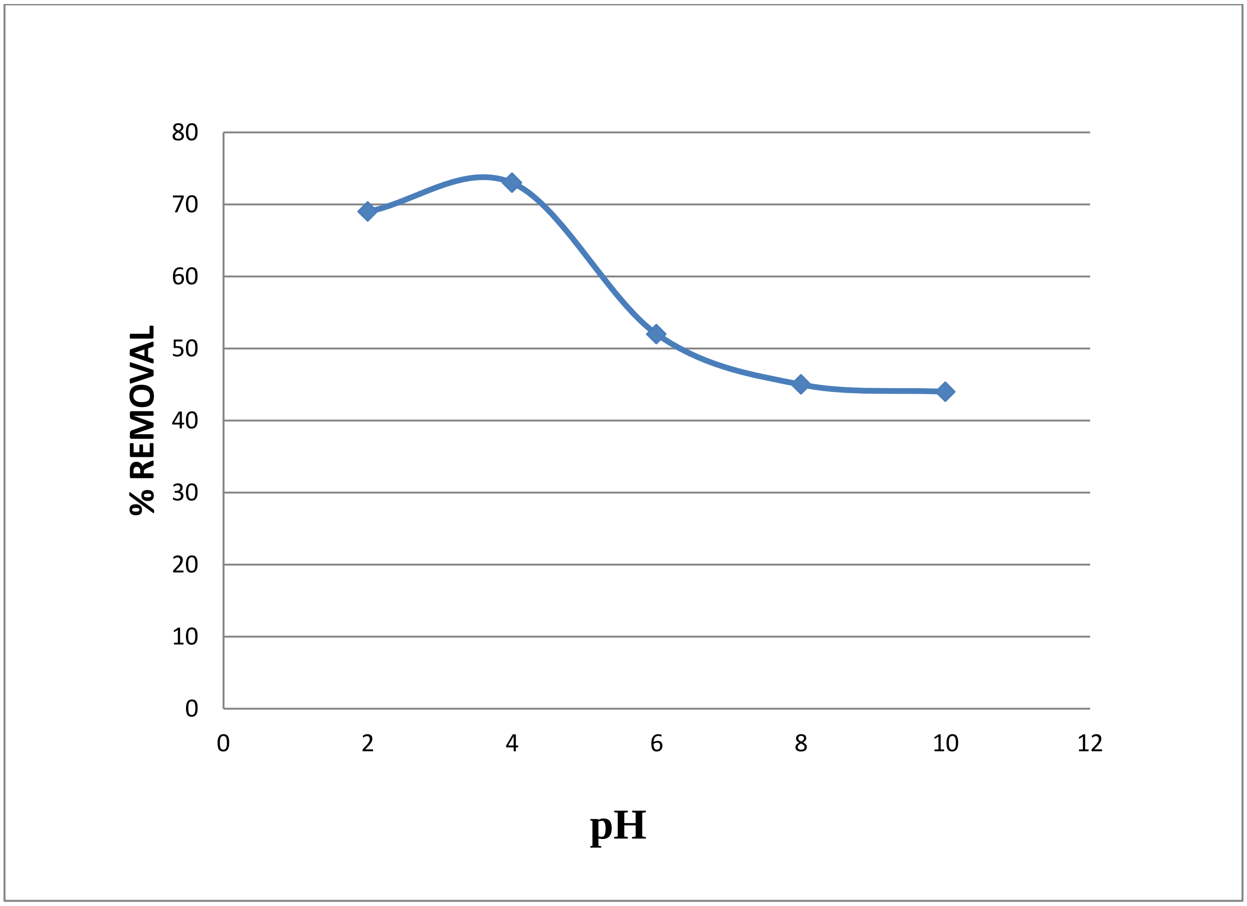

Figure 5.11 pH effect of Cr(VI) removal

5.4 EFFECT OF ADSORBENT DOSE

Effect of adsorbent dose is done by taking 1, 2, 3, 4, 5, 8, 10, 15 and 20 mg/l for hexavalent chromium. From the graph it is clear that on increasing the adsorbent dose the % removal is also increases and for a certain point it is constant. The maximum removal of the Cr(VI) at 15mg/l adsorbent dose this point is called optimum point of removal and at optimum point the % removal of Cr(VI) is about 87.

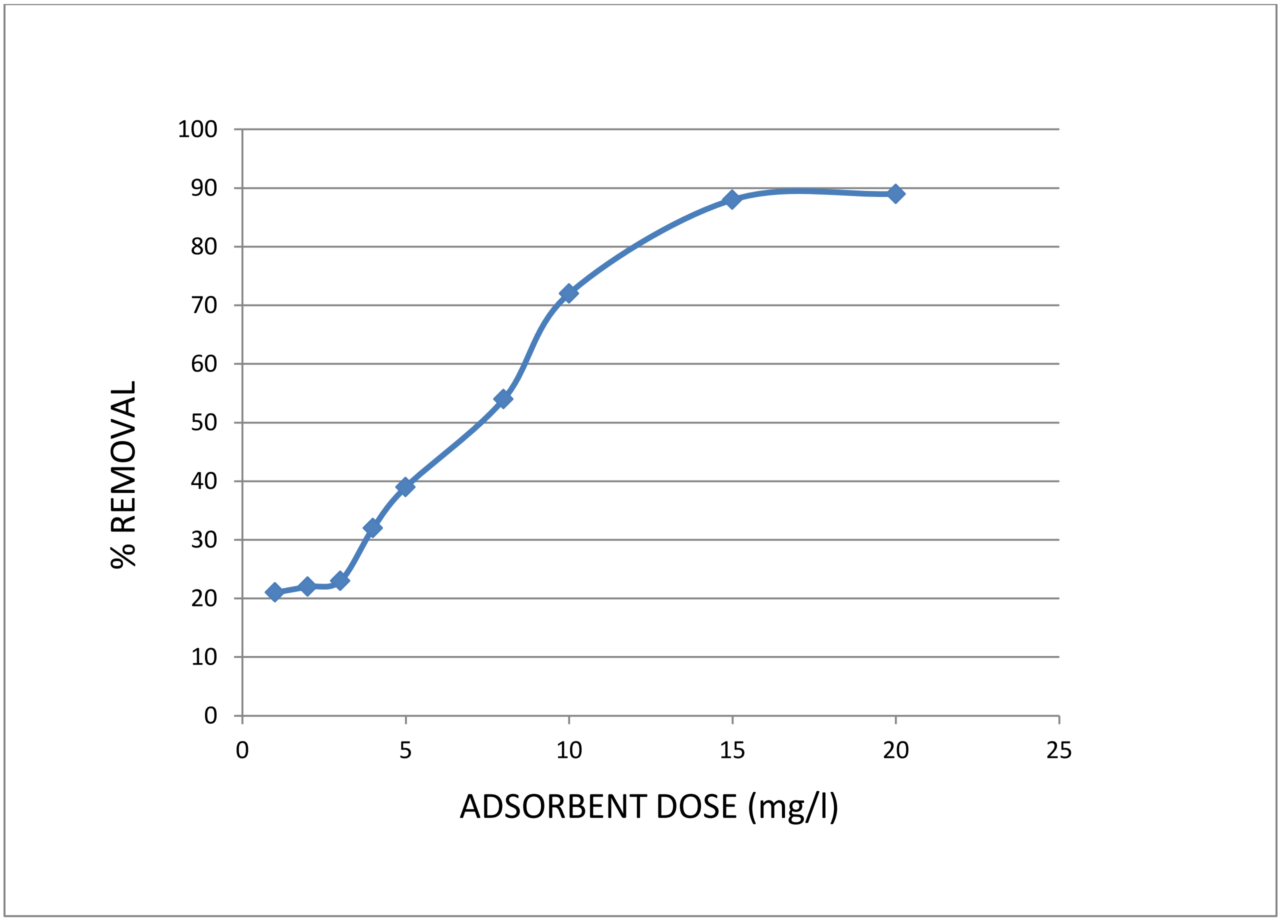

Figure 5.12 Effect of adsorbent dose on Cr(VI) removal

5.5 EFFECT OF CONTACT TIME

In adsorption process a point come where no more adsorption of activated carbon is possible this point is called equilibrium contact time. We have done adsorption process at different intervals for the optimum removal of hexavalent chromium. From the graph it shows that at increasing contact time the % removal of Cr(VI) is increases and reached a constant removal because due to again and again removal the ions of sample will be reduced and % removal is constant.

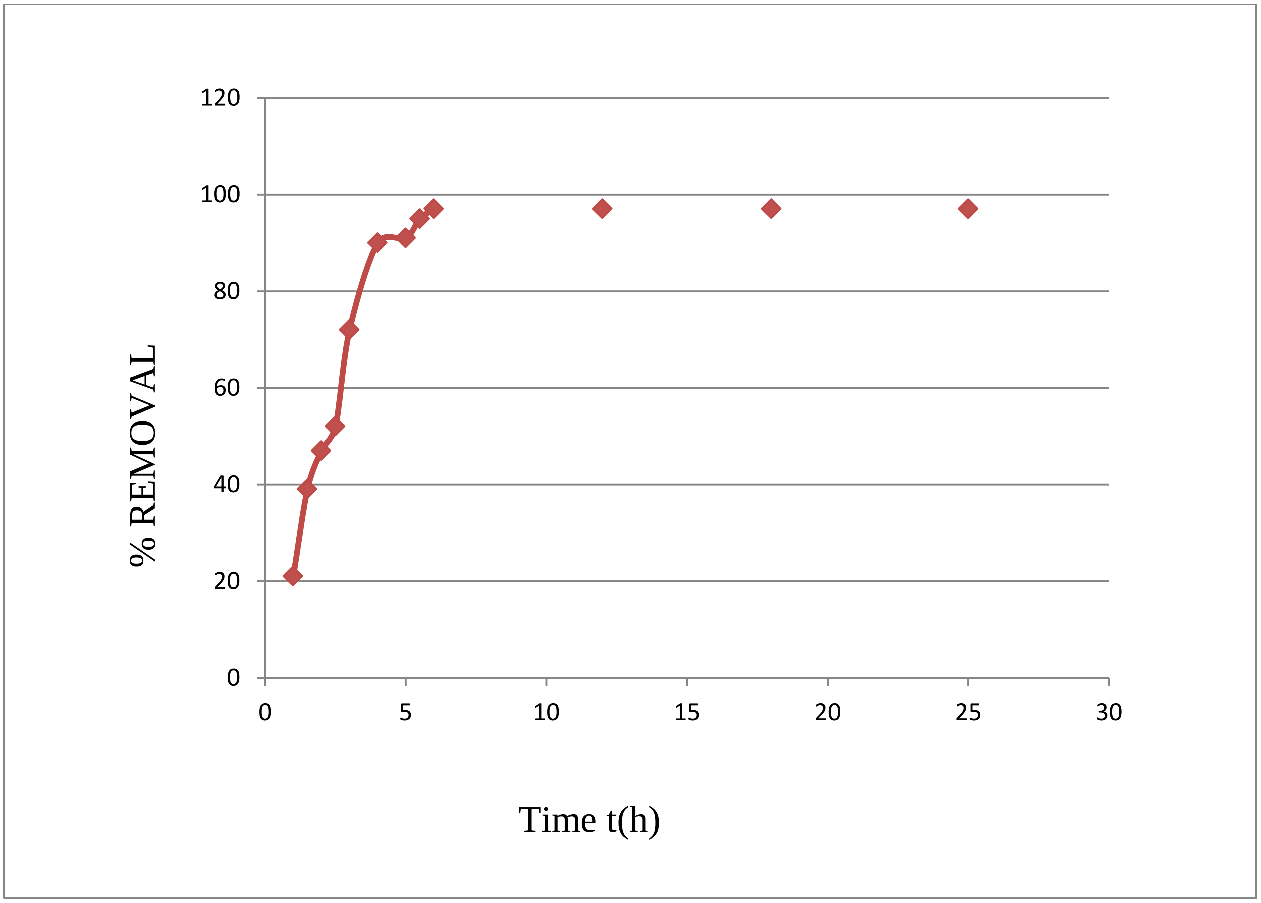

Figure 5.13 Effect of contact time for removal of Cr(VI)

5.6 KINETICS OF HEXAVALENT CHROMIUM

To determine the mechanism of adsorption like controlling step, potential rate, rate constant used pseudo first order, pseudo second order and intraparticle diffusion model. Firstly taken initial concentration of sample for hexavalent chromium and the value of pH kept constant. However the equilibrium does not achieved the sample can not used to determine the kinetics. From the experimental data we draw plot the graph of pseudo first order, second order and intraparticle diffusion model. For pseudo first order equation we draw a graph between t and log(qe-qt). for pseudo second order equation draw a graph between t and qt/t and intraparticle diffusion model draw a graph between t and qt.

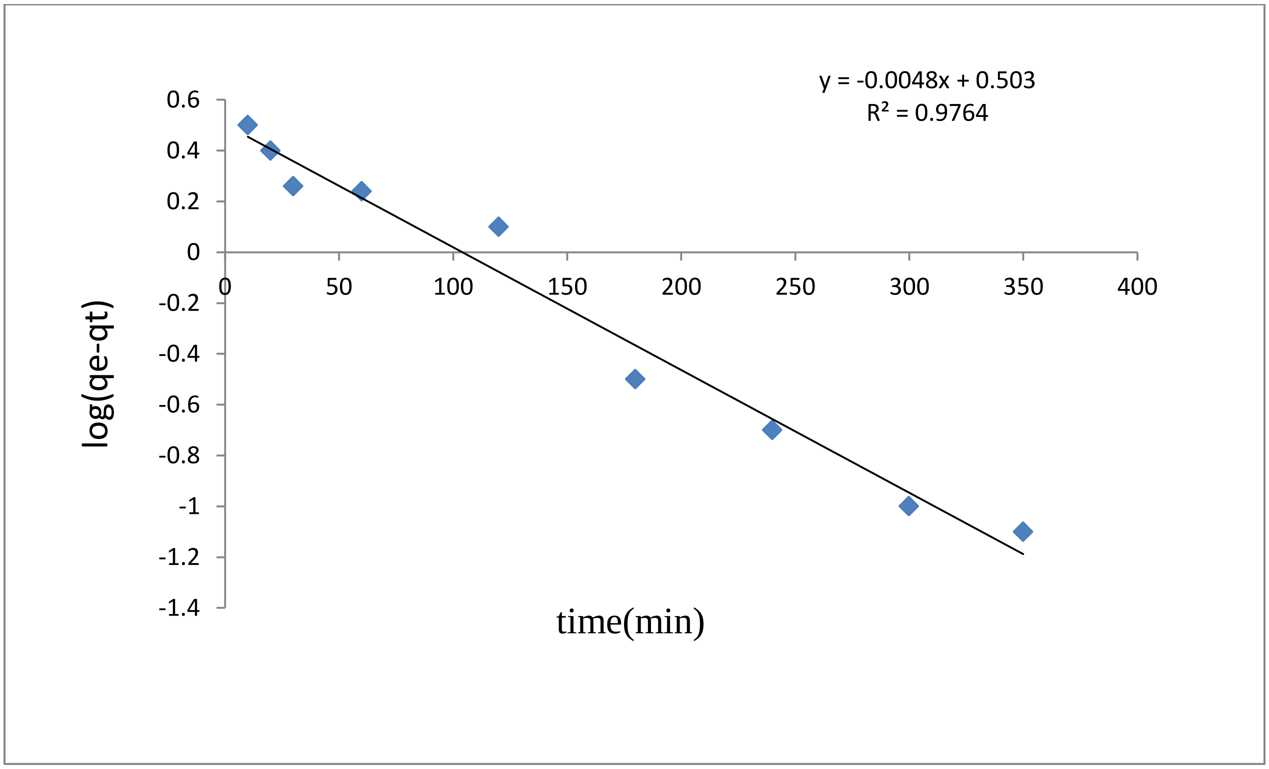

Figure 5.14 Pseudo first order plot for hexavalent chromium adsorption

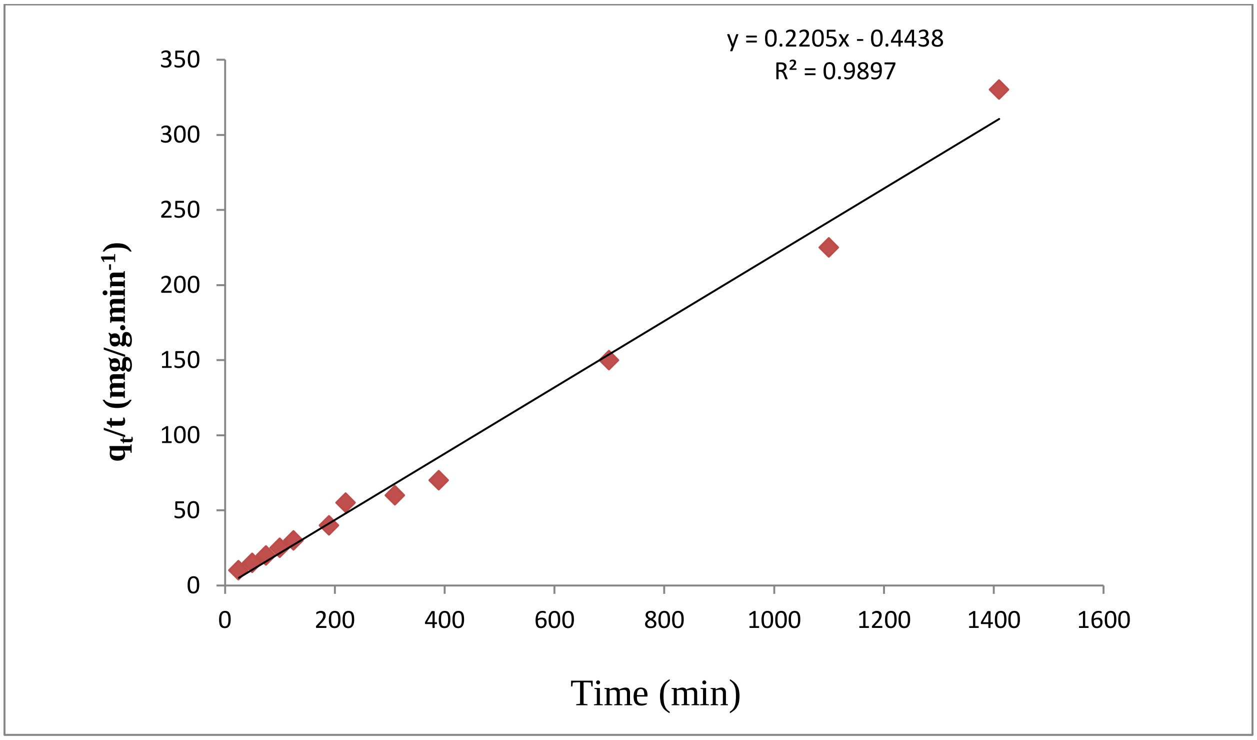

Figure 5.15 Pseudo second order plot for hexavalent chromium adsorption

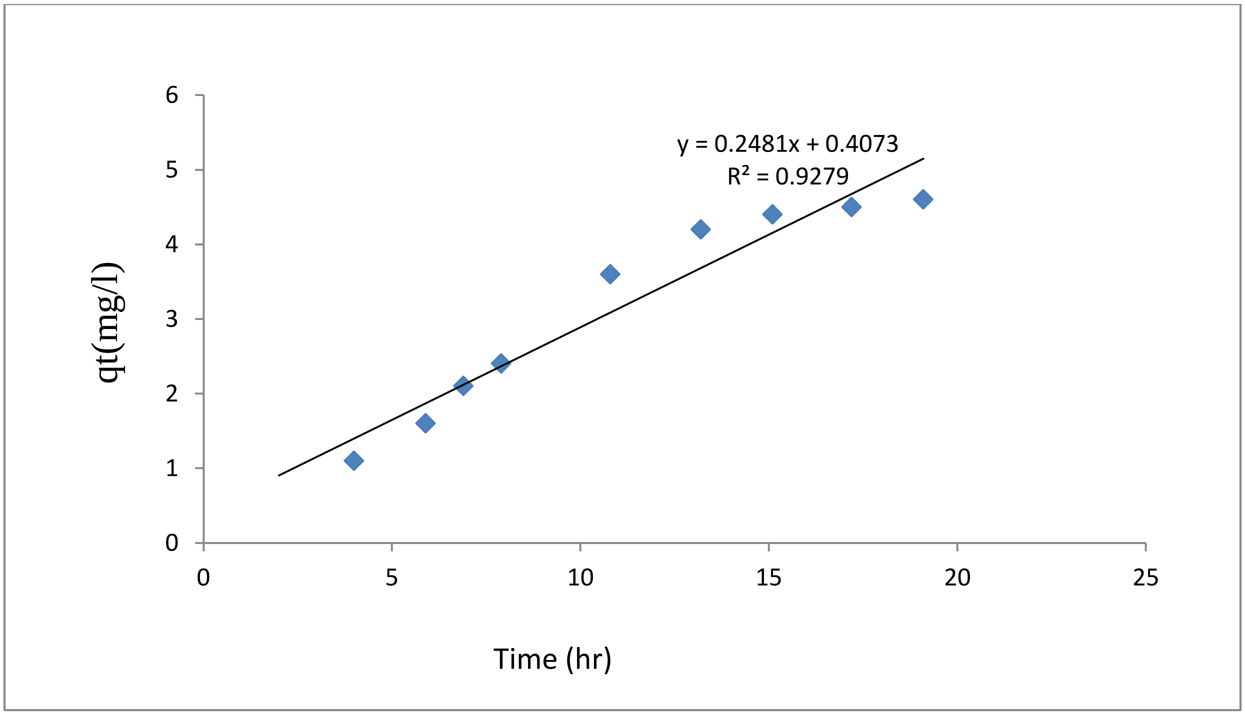

Figure 5.16 Intraparticle diffusion for hexavalent chromium adsorption

Table 5.2 Kinetic parameter for the adsorption of tannery waste water

Kinetic parameters	Cr(VI) removal
Pseudo first order	
K_1	0.0223
q_e	3.92
R^2	0.976
Pseudo second order	
K_2	0.00045
q_e	4.67
R^2	0.989
Intra particle diffusion	
K_{int}	0.23
I	0.5
R^2	0.927

5.7 ADSORPTION EQLIBRIUM ISOTHERM

We studied different isotherm models to attain equilibrium condition for adsorption. Langmuir, freundlich, Sips isotherm models, Redlich-Peterson model and Kobel-Corrigan model were used to determine equilibrium isotherms constants. From the above isotherms model we derived the equilibrium constants which given in table 5.4. Statistical indices were determined to know deviation from ideality are listed in table 5.3.

Table 5.3 Statistical indices for hexavalent chromium(VI)

Isotherm model	R^2	SSE	RMSE	SEP	NSD	ND
For Cr(VI) removal						
Freundlich isotherm model	0.986	44.134	3.004	30.45	25.56	11.87
Langmuir isotherm model	0.903	60.67	3.523	36.67	41.67	19.134
Redlich-Peterson model	0.997	64.78	3.78	37.87	43.67	18.97
Sips isotherm model	0.994	64.98	3.23	37.23	43.78	18.78
Kobel- Corrigan	0.991	67.65	3.53	37.45	44.78	18.56

5.8 ADSORPTION THERMODYNAMIC CONSTANTS

In the experiment of adsorption of hexavalent chromium various types of thermodynamic parameters are used. Experimental data were determined at various temperature (298K, 308K, 318K) with the help of different isotherms like Langmuir, Freundlich, Sips and Kobel-Corrigan, gibbs free energy, entropy and enthalpy was determined. From the experimental data the adsorption shows exothermic in nature and for exothermic low temperature favours. Negative value of ΔG shows decrease in Gibbs free energy.

Table 5.4 Thermodynamic parameters for different isotherms

Isotherms	**ΔH (kJ/mol)**	**ΔS (kJ mol^{-1} K^{-1})**	**ΔG(kJ/mol)**		
			T=298K	**T=308K**	**T=318K**
Freundlich	-10.34	-0.028	-2.678	-2.563	-2.563
Redlich-Peterson	-72.67	-0.234	-6.652	-2.367	-2.443
Sips	-18.65	-0.05342	-2.643	-2.752	-1.427
Kobel-Corrigan	-23.56	-0.00453	-2.356	-2.457	-1.642

CHAPTER-6

CONCLUSIONS

There are some conclusion which comes from my present study:

- For the removal of hexavalent chromium from the tannery industry using activated carbon based on corncob. For the activation using $ZnCl_2$ and H_3PO_4. $ZnCl_2$ gives better activation than H_3PO_4.
- The characterization of corncob based activated carbon is done by grade method. The results define the activated carbon is well prepared.
- The BET surface area of the CAC is found about 400.006 m^2/g. In kinetics model pseudo second order is given best fit than pseudo first order model.
- When increase in pH the % removal of hexavalent chromium decreases and with increases in adsorbent dose the % removal of hexavalent chromium is also increases.
- The optimum removal efficiency of Cr(VI) is found about 94.45%.

CHAPTER-7

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