TREATMENT OF DYEING WASTEWATER

A DISSERTATION

Submitted in partial fulfillment of the

requirements for the award of the degree

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INTEGRATED DUAL DEGREE

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CHEMICAL ENGINEERING

(With specialization in Hydrocarbon Engineering)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled **"Treatment of Dyeing Wastewater"** in the partial fulfillment for the requirements of the award of the Integrated Dual Degree (Bachelor of Technology & Master of Technology) in Chemical Engineering with specialization in "Hydrocarbon Engineering", submitted in the Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, is an authentic record of my own work carried out during the period from June 2012 to June 2013 under supervision of **Dr. Shri Chand**, Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

I have not submitted the matter, embodied in this dissertation for the award of any other degree.

Date: June, 2013
Place: Roorkee

(Stanzin Wangyal)

CERTIFICATE

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

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STANZIN WANGYAL

ABSTRACT

Corn cob was obtained from local vendors and it was activated by chemical activation method to examine the removal of COD and colour from dyeing wastewater by ACC. The adsorbent prepared was characterized by BET, FTIR, XRD, SEM/XRD and TGA/DTA analysis. The surface area of the adsorbent was 165.349 m^2/g and a pore volume of $0.1056m^2/g$. The FTIR spectra showed that it contained carboxylic groups, aliphatic compounds and alcohols while no sharp distinct were observed in XRD pattern suggesting that it was amorphous in structure. The wastewater was obtained from a textile mill and characterized after procurement. Two stage batch adsorptions were carried out. First the effect of various parameters such as pH, temperature, adsorbent dosage and time were examined. The optimum conditions were found out to be, pH=3, adsorbent dosage=0.6g/100ml of wastewater, time=3.5 hours and temperature=15°C. Four different isotherms models were used and it was found that Redlich-Peterson isotherm was the best fitting model for both colour and COD. The removal in first stage was 76.9 % and 81.3 % for COD and colour respectively. After the second stage the removal was found out to be 93.76 % and 96.19 % for COD and colour respectively. Since the prepared adsorbent was cheaper than commercially available adsorbents and it brought down the COD and colour level in the wastewater within the norms set by CPCB, it was concluded to be a good alternative.

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NOMENCLATURE

a	Sips constant
b	affinity; langmuir isotherm constant
C_o	intial concentration of adsorbate in the solution (mg/l)
C_t	concentration of adsorbate at time=t (mg/l)
C_e	concentration of adsorbate at equilibrium (mg/l)
k	Freundlich constant $(mg/g)(l/mg)^{1/n}$
n	constant in Sips and Freundlich
q_e	adsorbate adsorbed per gram of the adsorbent at equilibrium condition (mg/g)
K_r	Redlich constant
Q_o	maximum amount of adsorbate adsorbed
t	time (min)
W_0	weight of adsorbent precursor before activation (g)
W_1	weight of the adsorbent obtained after preparation (g)
R^2	correlation coefficient

Abbreviations

COD	Chemical oxygen demand
BOD	Biological oxygen demand
TWW	Textile wastewater
ACC	Activated corn cob
TOC	Total organic carbon
IC	Inorganic Carbon

CHAPTER 1

INTRODUCTION

The textile industry of India is among the largest textile industries in the world. After the liberalization in 1991 the textile industry has seen unprecedented growth. Therefore it has a notable share in its contribution towards the economy and also has one of the largest employment base in India. According to a report on the Indian textile industry 27 % of the Foreign Exchange Reserve that our country makes is obtained through textile exports. Its share in the Industrial production of the country is 14 % and contribution towards the GDP is 3%. This industry generates approximately 3.5 crore jobs. It can be divided further into various categories such as the woolen, synthetic and cotton etc., i.e. the naming relies upon the nature of the fibre that is used. In the chronological sequence, cotton comes first.

1.1 DYEING IN TEXTILE INDUSTRY

Among all the industries in India, the textile industry is one of the largest water consuming industry along with Thermal industry and Paper and Pulp industry. Dyeing, one of the most prominent feature of the industry also consumes lots of water. A dye is basically a coloured substance which is mixed with water and then used to impart colour to the fibre. The operation is generally carried along with a mordant which helps the dye particles to attach itself on the fibre. To produce 1 kilogram of finished textile, around 34.5 gallons of water is consumed (Kocabas et al., 2009). Being a water intensive industry, the generation of wastewater is also huge which comes mostly from the dyeing and finishing processes. The amount of total different commercial dyes that are present in the market is around one tenth of a lakh, and the global production of these dyes pigments per annum goes up to 7.1×10^5 tons. Out of the dyes produced, 7×10^4 to 1.05×10^4 tons of dyes are discharged as effluents along with the wastewater during the dyeing process (Kuberan et al., 2011). Dyes can be broadly distinguished into various categories. Based on the chemical structure of chromophoric group, synthetic dyes are classified as azo dyes, anthraquinone dyes, triarylmethane dyes, etc. They can be also categorized on the basis of the method implied in the dyeing process, for e.g. acid dyes, basic dyes, vat dyes, etc. Azo dyes are mostly used in industries as they as their share is more than 50% in the usage of all the dyes.

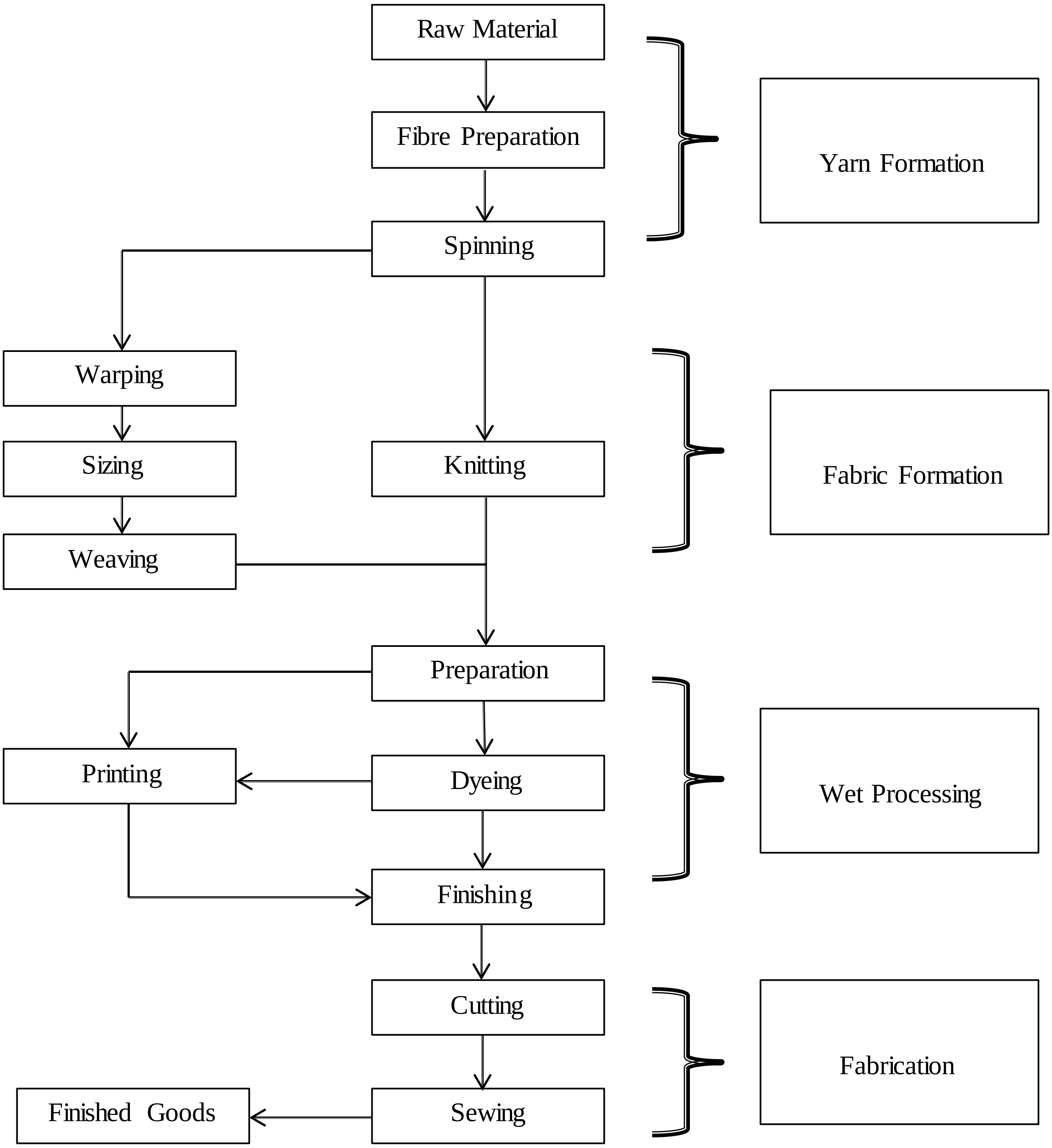

Figure 1.1 Stages in Textile Processing

The figure above represents a typical step by step process that occurs in the textile industry. The raw material is obtained and its fibre is processed then they go further spinning and knitting. After that it is sent for preparation and dyeing and finishing, and for printing if required. This section is called the wet processing unit this section consumes a lot of water and subsequently produces a lot of wastewater.

The wastewater that comes out of the textile mills are densely coloured as they contain the residues of dyes, have high COD (Chemical Oxygen Demand) and BOD (Biological oxygen Demand) content. They also contain hard degradation material. This wastewater is generally discharged into adjacent or neighbouring water bodies or land. If this wastewater is discharged without treatment it can cause various problems. For instance as the wastewater is densely coloured, it blocks the sunlight that falls into the water bodies which is necessary to maintain the ecological balance in the water body or the stream. On top of that quite a lot of dyes are toxic and may directly affect the aquatic life in the water body, their high BOD and COD also affects the dissolved oxygen content of the water body drastically. Table 1 shows the most commonly used fabrics in the industry and the corresponding dyes used to dye the fabric

Table 1.1 Categories of fibres used and their respective dyes

The variety of Fibre	**Commonly Used Dyes**
Cellulose fiber	Direct, Reactive, Vat, Sulfide and Azo dyes
Wool	Acid Dyes
Silk	Direct Dyes, Acid Dyes
Polyester	Azo Dyes, Disperse Dyes
Polyester-Cotton	Disperse / Vat dyes, Disperse / Insoluble dye
Poly acrylonitrile fiber-wool	Cationic dyes, Disperse dyes
Vinlyon	Direct dyes, Vat dyes, Sulfur dyes, Acid dyes

1.2 STANDARDS FOR DYEING WASTEWATER

As mentioned before the textile wastewater is not suitable for discharge into the water bodies or land without treatment of the same. Therefore various countries have set certain norms for the discharged wastewater. The standards set are different in different countries. In India, the job of setting the standards falls under the purview of Central Pollution Control Board (CPCB). CPCB is a statutory organisation and was formed in September, 1974. It sets standards for various Industries like petroleum oil refinery, thermal power plants, sugar industry, fertilizer industry, paper and pulp industry etc. in India. The standards that have been set for the dyeing and textile industries are displayed in Table 2 on the next page. For dyeing industry the colour content, organic pollutants (shown by COD content) and heavy metal ions are of important consideration. Therefore any plant that discharges dyeing wastewater must treat it so that it meets the norms shown in the table.

Table 1.2 CPCB standards for discharged wastewater from dyeing industry

S.No.	Parameter	Standard
1	pH	6-8.5
2	Suspended Solids	100 mg/l
3	COD	250 mg/l
4	BOD 3 days, 27°C	100 mg/l
5	Colour	400 Hazen Unit
7	Temperature	Shall not exceed 5°C above the ambient temperature of water in the receiving body
8	Mercury(as Hg)	0.01 mg/l
9	Chromium(as Cr^{6+})	0.1 mg/l
10	Total Chromium(as Cr)	2 mg/l
11	Copper(as Cu)	3 mg/l
12	Zinc(as Zn)	5 mg/l
13	Nickel(as Ni)	3 mg/l
14	Lead(as Pb)	0.1 mg/l
15	Manganese(as Mn)	2 mg/l
16	Cadmium(as Cd)	2 mg/l
17	Chloride	1000 mg/l
18	Sulphate	1000 mg/l
19	Phenolic Compounds(as C_6H_5OH)	1.0 mg/l
20	Oil and Grease	10 mg/l

1.3 WASTEWATER TREATMENT METHODS

1.3.1 CONVENTIONAL PROCEDURE

In the conventional procedure for the treatment of wastewater in plants the wastewater goes for preliminary treatment followed by primary treatment, secondary treatment and then finally the tertiary treatment.

Preliminary Treatment The objective of preliminary treatment is to remove the large suspended/floating materials so that subsequent operations can be carried out smoothly. In primary treatment the aim is to remove settleable solids and floating substances. The former is done by sedimentation and the latter by skimming.

Secondary treatment It aims at further removal of residual organics and the solids that are dissolved/suspended generally by methods such as biological treatment, suspended sludge, activated sludge, trickling filters etc.

Tertiary treatment Finally the tertiary treatment is done when particular constituent is not removed and also further improves the standard of the wastewater before discharging and may consist specialised methods like adsorption etc.

1.3.2 SPECIFIC METHODS FOR TEXTILE WASTEWATER TREATMENT

Textile Industry also implies a wide range of water treatment processes. The process implied should be economic and efficient. Some of the most common methods are described in brief below

1.3.2.1 Biological Methods

It is done by simply allowing nature to follow its course as the microorganisms in the water break down the pollutants and reduce the BOD of wastewater. Activated sludge process can oxidise nine tenth of the oxidizable substance present in the water (Pala and Tokat, 2002). Although they are not so efficient in reducing the COD of dyeing wastewater because the biodegradability of the synthetic dyes is not good.

1.3.2.2 Ozone Process

Ozone is being used a lot to treat wastewater accompanied with photo sensitive reaction or oxidizing agents like hydrogen peroxide. It is very efficient in colour reduction, but the COD content is not reduced in the same proportion as they do in adsorption processes (All`egre et al., 2006).

1.3.2.3 Electrochemical Treatment

As the name suggests the process involves electrolytic cells. The wastewater is made to flow through the cell which consists of electrodes made of iron (Lin and Peng, 1994)). Its limitation is that after some time it forms a soft bed of iron oxide.

1.3.2.4 Coagulation-Flocculation Method

This treatment works very well for colloidal solutions. As a result it is oftenly used to remove insoluble dyes (Merzouk et al., 2011). But it is not so efficient in removing the soluble dyes. Also the sludge formed has to be treated and it is not so economic.

1.3.2.5 Membrane Separation Process

It is a physical process and as the name suggests has a permeable membrane. The wastewater is treated and the pollutant and water are separated through the membrane. In this process permeate is the substance that goes through the membrane and retenate is the one that stays behind. There are many specialised processes such as microfiltration, ultrafiltration and reverse osmosis. But one of the most common problems that occur during this process is the fouling of the membrane (Drews, 2010). This impacts the flux.

Another process that is implemented is adsorption (used in this thesis) which is explained properly in the next section

1.4 ADSORPTION

Adsorption is primarily a separation process. Molecules from one phase are transferred to the other phase and they are attached on to the surface of other medium. It can occur from gas to solid (adsorption of N_2 on SiO_2) or from liquid to solid (adsorption of dyes on activated carbon). The molecules which are deposited onto the surface are called adsorbate and the substance on which it is adsorbed is called the adsorbent. This process is widely implemented in the wastewater treatment process, mostly as tertiary treatment. It is an attractive option as it is easy to implement, costs less relatively than other processes and does not react further with the toxic pollutants and hence has very less environmental impact.

Adsorbents are also selective towards certain compounds and hence are more suited for those processes, for example phenols are selectively adsorbed on various adsorbents like Acticarbone SA1817, Kastell S-112 etc. (Soto et al, 2011). They have been reported to be very effective in the removal of various dyes as they efficiently reduce the colour from the TWW and they cost less (Gil et al., 2011)

Sorption includes both adsorption and absorption under its umbrella, however they are different processes as the former is a surface phenomenon while in the latter the whole volume of the phase is involved. Adsorption is basically classified on the basis of the type of bonding between the adsorbent and the adsorbate. They are

1.4.1 PHYSISORPTION (PHYSICAL ADSORPTION)

This type of adsorption generally has weak force of attractions between the adsorbate and adsorbent. The adsorbate settled onto the surface is attached to the surface of adsorbent by Van der Waals forces. In comparison with chemical bonds these forces are weak. As there are no chemical bonds, therefore new compounds are not formed. This is one of the advantages of physisorption as some important chemicals and dyes can be retained. Physisorptoin is generally and exothermic process and requires no activation energy. They can also change the surface conductivity and hence are implemented to use as sensors (Dai and Yuan, 2012).It is not confined to monolayer formation, multilayer formation can also occur.

1.4.2 CHEMISORPTION

Unlike physisorption, in chemisorption the molecules attaches itself on the adsorbent through chemical bonds and they are stronger. This process is generally not reversible therefore it tough to retain the adsorbent in this case. This process is confined to monolayer formation.

1.4.3 POSITIVE AND NEGATIVE ADSORPTION

These are defined on the basis of solute concentration in solution after the process. In positive adsorption, the solute molecules are binded to the adsorbent surface and eventually their concentration in the solution decreases. This is not always true and sometimes the solvent is adsorbed. Therefore the concentration of the solute in the solution increases, hence it is called negative adsorption.

1.5 ADSORBENTS

They come in various forms such as in powder or granules and in different shapes and sizes such as pellets and rods. It is desired that the adsorbent should be able to withstand high temperatures and it should be able to hold abrasion. Small pore diameter is also a desired quality. They generally have high surface area per unit weight therefore offering more sites for adsorbates.

1.5.1 CRITERIA FOR SELECTING ADSORBENT

Different plants and wastewaters have different requirement. The mode of adsorption employed also changes according to better integration with the plant processes or maybe for better removal results. There are various parameters that are considered before selecting the adsorbent and they are discussed briefly below.

Loading is basically the amount that an adsorbent can take on its surface. It is expressed in terms of mass per unit mass (mg/g). It is a function of the concentration of adsorbate in the solution and temperature.

Selectivity is also another parameter. It is useful when we want to remove a particular pollutant. It is not necessary that adsorbents selectivity towards a particular compound makes it better or worse since we can use that selectivity to increase its concentration in a solution where other one or more solutes are present.

Regenerabilty of an adsorbent is also considered if the modus operandi selected is cyclic. Good regenerabilty means an adsorbent can perform more uniformally and efficientally during its respective turn is each consecutive cycle. Regeneration is only feasible for physically adsorbed adsorbates as they are weakly linked. Regeneration is done by varous processes for e.g. Pressure swing.

Cost it can be different with time and also from person to person selling it for the same material. There are low cost adsorbents and costly adsorbents also which are usually not indigenous.

1.5.2 MODES OF ADSORBENT PREPARATION

Basically there are two different ways to prepare adsorbent from carbonaceous compound and they are physical and chemical activation method.

1.5.2.1 Physical activation

The precursor is transformed into activated carbons using gases at high temperature. This process is usually carried out by using one or a combination of the following processes:

Carbonization: Material carbonaceous in nature are pyrolyzed at temperatures in the range 873 K–900 K, without the presence of oxygen (usually in inert atmosphere with gases like Ar or N_2)

Activation/Oxidation: Now the material is introduced to oxidizing environment (CO_2, O_2 or steam) at temperatures above 523K, usually in the temperature range of 873 K–1473 K.

For example the raw material involved here can be high carbon containing materials like pine (Nowicki and Pietrzak, 2010).

1.5.2.2 Chemical activation

Before carbonization, the adsorbent precursor is impregnated with certain chemicals. The chemical is usually an acid, strong base, or a salt (phosphoric acid, potassium hydroxide, sodium hydroxide). Afterwards, the precursor is carbonized at lower temperatures (523 K–1172 K). It is believed that the carbonization / activation step proceeds simultaneously with the chemical activation. Biomass precursors like Andalucia can be used for this process (Castilla et al., 2001).

Chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material.

1.5.3 ADSORBENT TYPES

They are broadly classified as organic and inorganic adsorbents. The typical inorganic adsorbents are alumina, silica and zeolites. The most common forms of organic adsorbents are fly ash, activated carbon, polymers etc. As activated carbon was used in this thesis it will be discussed briefly,

1.5.3.1 Activated Carbon

They are full of pores and surface area per unit mass is very high and can go as high as 1158 m^2/g (Karakaş et al., 2004) generally are non-crystalline in structure made up of graphite layer and are non-polar. They can be loaded with various metals so as to make them more selective towards a particular compound, for example activated carbon loaded with bentonite is a very good Hydrogen adsorbent (Thanh et al., 2005). They are usually produced from carbonaceous materials like coal, peat, nutshells etc. and adsorbents prepared from biomass are generally cheap (Taya et al., 2009). Its preparation has already been discussed in the earlier section. Generally they are very cheap and it is one of the reasons they favoured over other adsorbents. A good activated carbon has following properties

1) High carbon content

2) Low inorganic matter

3) High density and sufficient volatile content

4) Inexpensive precursor

1.6 ISOTHERMS

The adsorptions processes that occur are studied through isotherms. An isotherm basically gives a mathematical relation between the amount of adsorbate on the adsorbent and adsorbates concentration in the solution, at given temperature. If the adsorbent and the adsorbate are kept in contact for a long time and equilibrium is reached between the adsorbate in the mediums i.e the adsorbent and the solution. At this point the solutes are being adsorbed and at the same time they are being desorbed from the surface of the adsorbent. The equilibrium relationship is studied by isotherms. Therefore we can say that an isotherm is a curve relating equilibrium concentration of solute on the surface of adsorbent q_e, and the concentration in the solution C_e, with which it is in contact. q_e is usually expressed in mg/g and C_e in mg/l.

There are many isotherms that predict the nature of adsorption like Freundlich, Langmuir, Temkin, Henry's law etc. Some are empirical relationships and while some are theoretical. The isotherms used are discussed in detail below

1.6.1 Langmuir Isotherm

It was given by Irving Langmuir. It is widely used due because it not that complex and fits a lot of experimental adsorption curves. Its features are given on the next page

1. It assumes that there is monolayer coverage (Mourao et al., 2006) on the surface of the adsorbent.

2. It assumes a particular equilibrium model

3. All the active sites that are available for adsorption are equally probable

4. A second order reaction

It is mathematical equation is as follows

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

q_e = ratio of adsorbate adsorbed per unit amount of adsorbent

C_e = adsorbate concentration in solution

K_A = constant related to enthalpy of adsorption

q_m = adsorbate required for monolayer formation at equilibrium, per unit amount of adsorbent

1.6.2 Freundlich Isotherm

This isotherm was proposed by Freundlich in 1906.It is an empirical co relation and it is expressed as

$$q_e = K_F C_e^{\frac{1}{n}}$$

K_F = constant which indicates the adsorption capacity

1/n = constant which measures the adsorption intensity (Carvalho et al., 2007)

These constants are system specific.

1.6.3 Redlich Peterson

Redlich Peterson isotherm incorporates both the Freundlich and Langmuir isotherm. The mechanism of adsorption according to this isotherm is a mixed version of both the above mentioned isotherms. Unlike Langmuir isotherm, R-P isotherm doesn’t assume a monolayer formation. At high concentration it behaves like Freundlich and like Langmuir for the opposite. Also the equation of this isotherm has three parameters; hence it can be applied for systems having more than one solute or adsorbates and for the same reason a lot of papers have stated that they are more precise than Langmuir and Freundlich isotherms (Wu et al., 2010). The relationship is given as follows

$$q_e = \frac{K_R C_e}{1 + a_B C_e^{\beta}}$$

1.6.4 Sips Isotherm

IT was proposed by Sips and its equation is

$$q_e = \frac{K_s C_e^{\beta_S}}{1 + a_s C_e^{\beta_S}}$$

This is an empirical relationship and the β_S is the Sips constant.

1.7 MOTIVATION

In the current scenario in industries, water is being consumed a lot and there are many processes that are water intensive. Our country is facing shortage of water in many areas and it has become a very precious resource for us today. Given the unreliable nature of monsoon we cannot rely on the rainy season too. Although our planet is 70% water and the rest land, only a small 2% of the total water quantity exists as fresh water. Therefore it is imperative that we use the water judiciously and reuse it as much as possible.

Also agricultural remains that are left after procuring the desired product from the crop/fruit are discarded as waste and not utilized. These wastes are generally high in carbon content and a very good precursor for preparation of activated carbon. Therefore these wastes can be used to treat the wastewater therefore utilizing agricultural waste and ipso facto save water, maintain the eco balance of water bodies and the aesthetic of surroundings.

1.8 OBJECTIVES OF DISSERTATION

- Preparing an adsorbent from corn cob, which is an agricultural waste, by chemical activation method

- To characterize the activated corn cob adsorbent produced by various characterization methods. BET to analyse the surface, SEM to study the surface morphology, XRD to analyse the crystal structure, FTIR to determine the presence of functional groups and TGA for the analysis of content with the increase in temperature.

- Characterize the TWW obtained from the textile mill

- Use the prepared ACC for colour and COD removal of TWW.

- Find out the effect of variables that affect the adsorption of colour and COD like initial pH, contact time, dosage of ACC and temperature and conduct adsorption in series if necessary for more removal of COD and colour

- To study the various isotherm curves and find the best fit with curve for colour and COD

- To ensure that colour and COD removal falls within the standard set by CPCB.

CHAPTER 2

LITERATURE REVIEW

This chapter is divided into two sections; the first section contains the literature review that pertains to preparation of activated carbon from agricultural wastes and other biomass. The second section contains the literature review on the treatment of wastewater containing colour, COD and in some reviews synthetic wastewater containing a particular dye or mixture of dyes.

2.1 LITERATURE REVIEW ON ADSORBENT PREPARATION

Tsai et al. (1998) prepared adsorbent from corn cob and characterized it. They used the method of chemical activation on corn cob. Zinc Chloride ($ZnCl_2$) used as the chemical for activation of the biomass. They studied the effects of various process variables that affect the adsorbent. Impregnation ratio, time for soaking the biomass and the activation temperature were taken into consideration. The $ZnCl_2$/corn cob ratio, i.e. the impregnation ratio was concluded to be the most important factor. At higher impregnation ratio lesser micropores were formed relatively. The optimum temperature was found out to be 500°C and time was 0.5 hour. They characterized the adsorbents by analysing the BET surface area, micropore surface area and the percentage of micropore.

Petrov et al. (2000) characterized the adsorbent prepared from furfural. Sulphuric acid (H_2SO_4) was used to for the activation process. They prepared different samples by impregnating the furfural with various concentration of sulphuric acid to obtain the polymer precursor. It was found that increasing the concentration of sulphuric acid leads extra polymerization. Effect of activation temperature was also studied. The sample activated with air had a BET surface area of 480 m^2/g at 400°C which was the highest among all the temperature considered, while the sample activated with steam at 750°C had the surface area of 1100 m^2/g. FTIR spectroscopy showed that different types of oxygen-containing groups of acidic character (carboxyl groups, carboxyl groups in lactone-like binding, phenolic hydroxyl and carbonyl groups) and different chemical properties are present on the surface of carbon oxidized with air. The water vapour activated sample mostly consisted of oxygen containing groups with basic character. The proximate and ultimate anlaysis was alsod done and they showed negligible ash and sulphur content.

Tsai et al. (2001) conducted an experiment to study adsorbent prepared from corn cob. They used KOH/K_2CO_3 to impregnate the corn cob for chemical activation. The temperature was varied from 400°C to 800°C as the step for physical activation. The contact time for the chemicals was kept 1 hour. The adsorbent properties were then examined BET surface area and total pore volume. Best results were obtained at 800°C thus establishing the conclusion that higher temperature led to better results. Its characteristics were analysed with respect to the commercially available adsorbents and it was suggested that they can be considered as an alternative as they had less environmental impact.

Ahmad and Hameed (2011) used bamboo wastes as the biomass precursor to prepare the adsorbent. Phosphoric acid ($H_3PO_{4)}$ was used for chemical activation. They observed the effects that the changes in parameters caused. They varied three parameters i.e. the weight percentage of H_3PO_4 used (in the water solution), the temperature of activation and the time for which the adsorbent was exposed to high temperature. They developed models to check the how the mentioned variables affected the COD removal of wastewater from cotton textile mill. The best results were obtained when the temperature was 558°C for 2.23 hours and the impregnation ratio was 5.14.The surface was analysed through BET and FTIR. Colour removal was 93.2 % while COD removal was 73 %.

Ahmedna et al. (2000) worked on making granular activated carbon from two types of materials. The classification of the materials was done on the basis of density and hardness. The first group contained soft materials with a low density such as bagasse, rice husk etc. The activated carbon from these sources was activated by physical processes. The other kind of material was harder and denser and activated via chemical techniques. The prepared adsorbents were used in experiments and were characterized on a variety of parameters including and not limited to bulk density, ash content, conductivity and colour removal characteristics. It was concluded by the authors that the type of binder and activation method play a key role in determining the properties of the activated carbon. Sugarcane based activated carbon was found optimum for removal of colour in sugar industry.

Tsai et al. (2003) prepared adsorbent from the filter mud from the sugarcane industry. They varied the temperature while preparing the adsorbent form 873 K to 1073 K as they used thermal activation method. Because of the change various temperature that was selected for the process, its effect was studied on the surface morphology and chemical properties. They found that it had pores in the range of .002 µm to .050 µm. They surface area for the adsorbents prepared was observed to be between 56 m^2/g-131.8 m^2/g. The area of the prewashed sample was found out to be more than those that were not washed. They concluded that the wastes can be used to remove contaminants that were not inorganic.

Örkün et al. (2012) prepared various adsorbent samples from *Corylus avellana* nut shell as the production of nuts of the same left behind a lot of waste material. They made changes to the temperature and the time for which it was exposed to that temperature. They also studied the effect of various impregnation ratios during the chemical activation step by phosphoric acid. They concluded that the optimum temperature was 673 K for the adsorbent characteristics and various concentration of the acid used can be used to obtain desired pores spacing and size.

Soleimani and Kaghazchi (2008) used *Prunus armeniaca* stones as the precursor in this paper by the authors. It was used to recover gold from wastewater. They conducted various runs by varying factors that affect the adsorption and found that only 2 % remained in the wastewater and the rest was adsorbed after 180 minutes. The gold could also be retained from the adsorbent and they suggested it could be an alternative for the commercially available AC.

Alves et al. (2013) used *Zea mays* to prepare adsorbent for the removal of compounds in water solution resulting from the synthesis of protein. Thermo-chemical activation method was used in this paper. The equilibrium time was achieved at 180 minutes and apart from Langmuir and Fruendlich Isotherm binary LCM model was also used. They concluded they prepared adsorbent was efficient.

2.2 LITERATURE REVIEW ON ADSORPTION OF WASTEWATER

Mahmoodi et al. (2011) conducted various runs on diffrent dyes. According to them, in a review paper pine cone was not used to treat dye coloured wastewater hence they chose this adsorbent. They characterised the outer surface of the adsorbent by Electron Microscopy and spectra obtained from FTIR. The factors that affect the process were changed such as the dosage of pine cone, pH, temperature and initial concentration in the experiments. They used various kinetics models and experimental data complied with the pseudo-second order kinetics. The maximum removal occurred at lower range of pH values and at pH 2 it showed maximum removal. The isotherm plots were also matched and AG25 and AG26 showed best results with Langmuir. The AB7 dye complied with the Freundlich isotherm.

Armagan et al. (2004) focused their experimental study on zeolite found in Turkey. The main purpose was to find the efficacy of this particular type of available zeolite in removing colour from dyeing waste water from textile mills. Three types of dyes indicative of industrial grade pollutant were used for lab scale experiments. Hydrophilic properties influenced the removal of dyes to a large extent. It was found that amine group attachment on the surface of these natural zeolites increases its adsorption efficiency to a great extent, which is very low in natural state, rendering the use without modification unfeasible.

Kang et al. (2009) studied the removal of three types of dyes in single and multicomponent systems. The latter included binary and ternary mixture of these dyes. A particular adsorbent EPIDMA/bentonite was used for the work. In the single component system, it was found that model based on Langmuir isotherm fits the adsorption data well. Kinetics of amount of adsorbate adsorbed, follows pseudo second order kinetic model. Effect of changing various parameters on colour removal and kinetics was also a part of the study.

Kargi and Ozmıhcı (2005) focused their experiments and work to study the removal of dye from wastewater. The authors have analysed the use of powdered activated sludge and contrasted it with activated carbon, especially by comparing outlet colour removal in the experiments. The efficiency and the extent to which the removal is successfully carried out is studied as a function of loading rate and other input parameters. The experimental data were also fitted using three models and Langmuir type of model was found to be best suited for the current study on the basis of minimum root mean square error. The colour removal performance of activated sludge was found comparable to activated carbon adsorbent. Different optimum conditions were evaluated and studied however the activated sludge is preferred.

Hameed et al. (2009) used *Ananas comosus* stem as the precursor to prepare the adsorbent which is found in huge amounts in Malaysia. They synthesized the wastewater with MB dye and studied its removal with the prepared adsorbent. Their experiments were conducted at 303 K and parameters such as the dosage of adsorbent, the concentration at the start of experiment etc. were changed. The obtained readings were fitted into various isotherm plots and it fit well with Langmuir with and adsorption capacity of 119 mg/g. Pseudo second order explained the kinetic data better than first.

Ahmad and Hameed (2009) obtained wastewater from a textile mill in Malaysia. *Bambuseae* waste was collected and used for preparing adsorbent. It was used to study its effect on COD and colour removal of the wastewater obtained. The surface area of the adsorbent was 987.13 m^2/g and they found out that the best removal occurred in more acidic medium whilst the equilibrium time was 600 minutes. The treated wastewater met the requirements set by the Malaysian Environment Quality.

Gong et al., (2005) investigated how various functional groups like (-COOH, -OH and $-NH_2$) behaved with various dyes. Different functional groups behave differently during adsorption. They used peanut hull and made changes relating each functional group on different adsorbents. Six different dyes were used in this study. They found that –COOH groups inhibited the adsorption of acid dyes and but was instrumental for adsorption of basic dyes. The hydroxyl group did not show inclination of any sorts towards any dye and was an important group. The amide had negligible effect on adsorption of the dyes.

Naas et al. (2010) made adsorbent, for which date pit was the biomass precursor. They used it to abate the COD level in the refinery wastewater. Various adsorption runs were carried out and it was found to be endothermic in nature. The results were compared with a BDH-AC, a costlier commercially available adsorbent. They concluded that the adsorbent prepared from date pit was a viable option as it was cheaper and there was not much difference between the performances of the adsorbents.

Parande et al. 2009 used adsorbents from various biomass sources and compared their results in the removal of COD. The wastewater was obtained from sugar mill and used for the various runs. They varied the dosage from .1 g/litre to .8 g/ litre and time was varied from .5 hour to 4 hour. They observed the maximum removal when at the neutral pH. Among the chosen adsorbents the best result was demonstrated by metakaolin.

Gupta and Suhas (2009) did a comprehensive review on the cheap adsorbents that were available and stressed that since the available activated carbon in the market are costly, the cheaper alternative was viable as they had quick kinetics and could hold adsorbates in high proportions. They concluded that further studies should be conducted on the mechanism of functional groups during adsorption.

CHAPTER 3

MATERIALS AND METHODS

3.1 WASTEWATER CHARACTERIZATION

The wastewater that was used for the experiments was obtained from a textile mill. The textile mill is located in Ghaziabad, Uttar Pradesh. 10 litres of wastewater was procured, brought to the lab and stored at a temperature of 4°C so that the values of COD and other parameters do not change. Below is the image of the wastewater obtained.

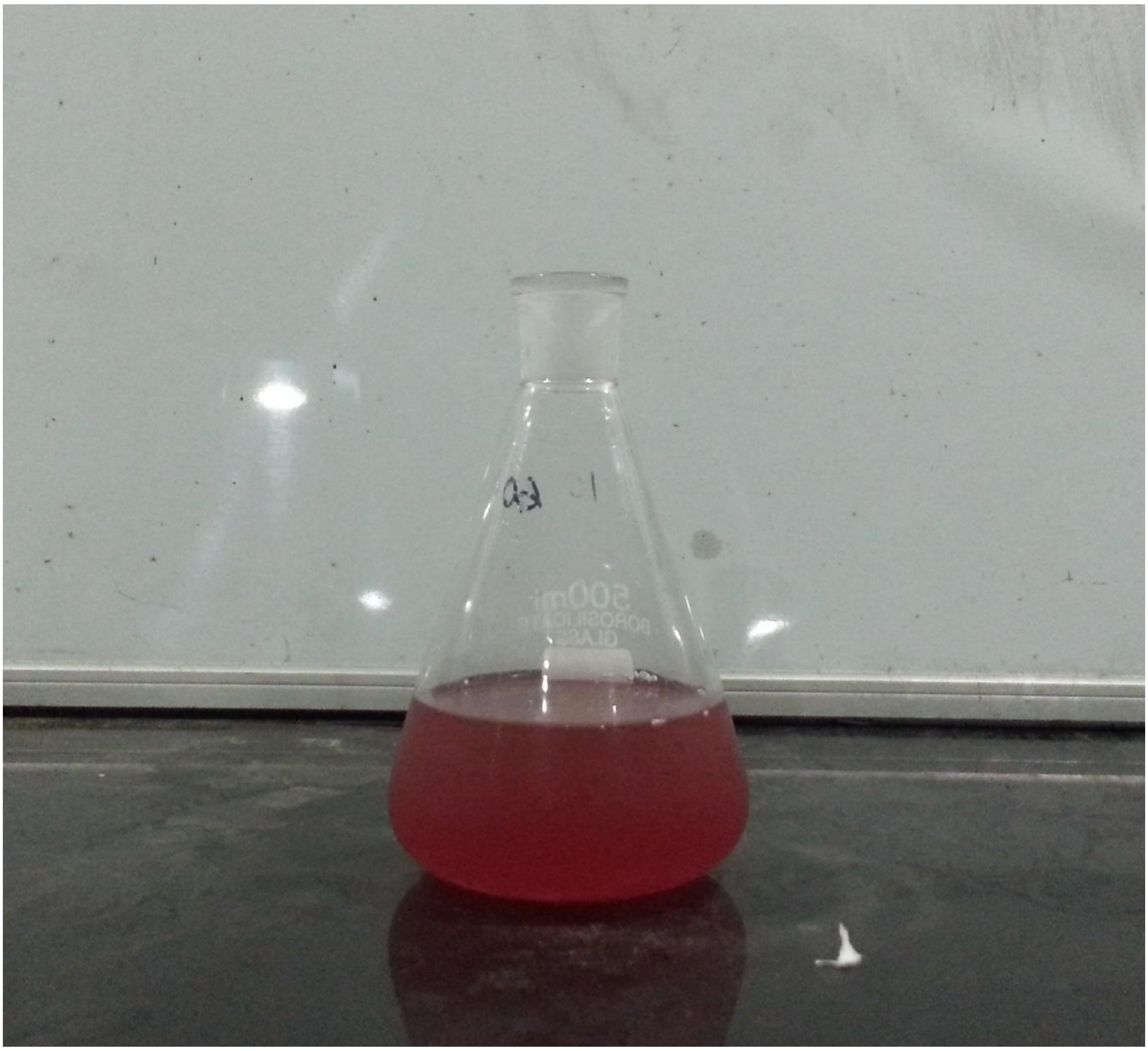

Figure 3.1 A sample of the wastewater

The wastewater obtained was pink in colour and a few suspended solid particles were visible to the naked eye. The data obtained after characterization of the wastewater are given below.

Table 3.1 Characterization of Dyeing Wastewater

S.No.	Parameter	Value
1	COD	1043 mg/l
2	Colour	1786 Pt Co
3	TOC	597.3 mg/l
4	pH	6.7
5	Inorganic Carbon (IC)	110.3 mg/l

3.2 ADSORBENT PREPARATION

Corn, binomial name: *Zea mays* were initially grown in the American region. It slowly spread across the world because it has the ability to grow in different kinds of climate. According to the Food and Agriculture Organization of the United Nations India was the sixth largest producer of the corn in 2009 with an annual production of 17.3 million tonnes. Among the Indian states Uttarakhand produces corn along with the nearby states such as UP, Haryana and Punjab (UP being one of the major corn producing states). After stripping the kernels off, what remains is the central part of corn that is the corn cob. It cannot be consumed and it is discarded away as waste. Therefore these kinds of agricultural wastes which have high carbon content can be used to produce cheap adsorbents. Corn cob was obtained from local vendors and then washed properly and then it was dried. Then it was crushed in the rotary mill so as to reduce its size. After it was reduced to smaller size (shown in Fig 3.2), the method of chemical activation was implied prepare the adsorbent. It was prepared by chemical activation method. Phosphoric acid (H_3PO_4) was used for impregnation.

Step 1- First a diluted solution of phosphoric acid was prepared (50 wt. %).

Step 2- In the activation step the corn cob was impregnated with the prepared solution in the ratio of 50 g of corn cob in 180 ml of the solution.

Step 3-It was stirred for 1 hour continuously and then kept at 110°C for 4 hours. The impregnated sample was washed with distilled water several times

Step 4- It was carbonized by keeping it in a muffle furnace at a temperature of 450°C for 4 hours.

Step 5- The Sample obtained was soaked in a solution of sodium bicarbonate ($NaHCO_{3)}$ to remove the excess acid in the sample.

Step 6-The sample was separated from the solution with the help of filter paper and then it was washed with distilled water till a constant pH of 4.6 was obtained.

Step 7- Finally it was kept in a hot air oven at 110°C and grinded.

The images below show the corn cob prior to the activation and carbonisation and after it.

Fig 3.2 Corn cob prior to chemical activation

Fig 3.3 Activated corn cob, final product

3.3 CHARACTERIZATION OF CORN COB ADSORBENTS

The prepared adsorbent was then characterized by various methods that are discussed below.

3.3.1 BET SURFACE AREA ANALYSIS

BET analysis was done to find out the surface area of an adsorbent. The moisture of the adsorbent was removed first before the analysis. The principle is to use a particular gas as an adsorbate and calculate the surface area by the volume of gas adsorbed. Nitrogen gas was used for this method. The surface area was analysed by using Chemisorb 2720 model manufactured by Micrometrics, USA. The software used was Chemisoft TPx.

3.3.2 X-RAY DIFFRACTION (XRD)

This characterization is based on Bragg's law ($n\lambda=2d\sin\theta$). It was done to determine the crystal structure of the activated corn cob. It also determines the various properties of small crystalline structures present in it. It was carried out using Bruker AXS diffractometer. Ni was the filter media and Cu was used as the target. The K radiation was set at .1542 nm. The scanning angle was varied from 10 to 90 degrees.

3.3.3 SPECTRO ELECTRON MICROSCOPY (SEM)

It is an electron microscope that shows the surface of the sample at very high magnification (can examine samples at micrometre and nanometre scale) on a connected screen. This characterization was done to determine activated corn cob's surface arrangement of physical features in a particular area and the morphology. It was done using LEO 435 VP (England) and EDX (Energy Dispersive X ray spectrometer) was done by QUANTA 200 FEG. Before the samples are studied they are coated with gold so as to improve the surface conductivity of the same. The equipment used for this purpose was Edward S150.

3.3.4 FOURIER TRANSFORM INFRARED ANALYSIS (FTIR)

This characterization is done to find out various functional groups that the adsorbent possesses. The sample is first kept in the oven at 110°C and then given for characterization. The characterization was done using NICOLET AVTAR 370, USA model. Press disk method was implied for this characterization and the pellets were synthesized by using an equal ratio of activated corn cob in potassium bromide.

3.3.5 THERMOGRAVIMETRIC ANALYSIS (TGA)

If any substance is heated its characteristics changes, the physical and chemical characteristics vary as we increase the temperature. This analysis is done to see the various changes that occur at different temperature ranges. The equipment used for TGA of activated corn cob was Pyris Diamond, Perkin Elmer Inc. USA) and the graphs for differential thermal analysis (DTA), thermogravimetry (TG) and derivatives thermogravimetry (DTG) were obtained at the same time. The adsorbent weighing about .010 g were heated from 323 K to 1223 K at a steady rate of 283 K/min.

3.3.6 YIELD OF ACC

It is defined by the following formula

$$\frac{(W_1 - W_2)}{(W_1)} \text{X } 100$$

W_1 = mass of the precursor or material used for preparing the adsorbent

W_2 = mass of the prepared adsorbent after the final step

3.4 PROCEDURE

3.4.1 EXPERIMENTAL PROCEDURE

Batch adsorption runs were carried out in 250 ml borosil flasks. For every run, 100 ml of TWW was used and a particular quantity of prepared adsorbent was added to it. Initially the adsorbent dosage was varied from 0.1g to 0.8 g. When using the batch adsorption in series, the flasks were taken out after a stipulated time and then the adsorbent was separated with filter paper, the parameters were measured and the adsorbents were again introduced and readings were obtained using the same procedure.

For finding out the equilibrium time flasks were taken out from the incubator at particular time intervals of 0.5 hours starting from 0.5, 1 to 7 hours. There was a time interval of 3 hours between the last two runs.

While optimizing the pH, first of all the pH scale instrument was calibrated with pH buffer capsules of pH 4, 7 and 9. The content of each capsules were mixed with 100 ml of water and the solutions of corresponding pH were obtained. The runs were taken at various pH of 2, 3, 4, 6, 8, 10 and 12. The pH of TWW was changed with a diluted solutions of sodium hydroxide (NaOH) and H_2SO_4 of various concentrations so that there was a maximum change of 3% in the total volume of TWW in the flask. The NaOH solution was prepared by dissolving the NaOH pellets in distilled water and the H_2SO_4 solution was prepared by mixing conc. H_2SO_4 of 97% purity in distilled water.

All these runs were carried out in an orbital shaking incubator set at the speed of 120 rpm. Initially the runs were conducted at a temperature of 30°C and after optimization various runs at 15ºC and 45°C were taken at varying initial concentrations of 20%, 40%, 60%, 80% and 100 %. Before taking the readings of the treated TWW with the activated carbon, the adsorbent and was separated from it with the help of filter papers and then it was centrifuged at 6500 rpm for 18 minutes so as to separate any dissolved solid present in it.The percentage removal was determined by the following equation

$$Y = \frac{(C_o - C_t)}{(C_o)} X\ 100$$

C_o = initial concentration of the solution

C_t = concentration of the solution at time t

3.4.2 METHODS OF MEASURING COLOUR AND COD

The COD was measured using method no. 5220 mentioned in the American Public Health Association standards. The principle behind the functioning of the instrument is that it measures the amount of dichromate ions from $K_2Cr_2O_7$ which is reduced to the chromic ion $Cr^{3+.}$ The dichromate ion shows maximum absorbance at 600 Å, at 400 Å the value is almost zero, and it is the vice versa for chromic ion. Therefore this contrasting behaviour allows for the measurement of reduction of dichromate ion.

First the 3 ml of the sample to be examined was added to the COD vial, then 1.5 ml of $K_2Cr_2O_7$ solution was added followed by 3.5 ml of $AgSO_4$ solution. The order of addition is not important. The vials were kept in the digester preheated to 423 K for two hours. After that the vials are allowed to cool down to the room temperature and their reading was taken in the COD meter. First the reference point is set as zero with a blank sample containing the mentioned chemicals above and instead of the sample distilled water is added.

The colour was measured directly with a colorimeter. First the vial provided with the meter was filled with distilled water and the reference point was set, then the sample to be examined were filled in other similar vials and their colour was obtained in Pt/Co scale

3.5 EQUIPMENTS USED

For the various runs carried out, the following instruments were used to measure the values

- COD of the samples were measured by Aqua lytic COD vario.
- The COD vial digester used was Aqua lytic AL38 SC digester.
- Colour was measured with Ion specific meter HI-93727 (HANNA instruments)
- pH was measured by pH/Ion 510 Eutech Instruments
- The runs were carried out in REMI orbital shaker incubator

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 CHARACTERIZATION OF CORN COB ADSORBENT

4.1.1 BET

The prepared corn cob adsorbent was again washed properly and then kept in a hot air oven for moisture removal and then given for BET analysis. 0.202 g of the sample was used for the analysis and it was found that it had a surface area equivalent to 165.349 m^2/g and a pore volume of 0.1056m^2/g.

4.1.2 SEM/EDX

The SEM and EDX analysis was also done and different images were obtained at various magnification. At the scale of 10 micrometre some pores were visible but they were not so distinct in nature. The elemental analysis showed that it contained high amount of Carbon and oxygen, Phosphor was also present in a very small proportion. Its presence can be attributed to the fact that Phosphoric acid was used for chemical activation. The composition is shown in the Table 4.1(a). The SEM and EDX of adsorbent after it was used to treat the TWW were also done. The images showed very different surface morphology and there were no visible pores on the same scale of 10 micrometre (Figure 4.1(b)). The difference can be attributed to the deposition of dyes on the surface of the adsorbent hence changing the surface topography of the adsorbent. The elemental analysis showed presence of new elements Sodium and Chlorine and an increased carbon percentage. (Fig. 4.2(a) and (b)).

4.1.3 FTIR

FTIR of the ACC was done before and after the adsorption and is shown in Fig 4.3(a) and (b). The spectra showed spikes in the curve at 1747.63 cm^{-1} which indicates the presence of carboxylic groups. They have higher boiling point than the corresponding alkane grouips and it is even higher than alcohols because the acid pair molecules are held by two hydrogen bonds. The sharp curve at 1432 cm^{-1} and 1234.09 cm^{-1} is indicative of C-O stretching. The curves at around 3000 cm^{-1} suggests the presence of aliphatic compounds and the curve at 2923.27 cm^{-1} indicates CH_2 absorption and presence of aliphatic compounds. The peak at 1375.39 cm^{-1} corresponds to the symmetric CH_3 vibration. The spike at 1234.09 cm^{-1}

confirms the presence of t-butyl group and primary alcohol group is confirmed by the spike 1047.19 cm^{-1}. The curve at 469.57 cm^{-1} indicates the presence of Si-H bond. Therefore the FTIR spectra show the presence of carboxylic acid with C-O stretching and aliphatic compounds with CH_2 absorption and alcohol. The FTIR spectra of ACC after adsorption was similar but it showed the presence of inorganic phosphate compounds as there were two strong bands around 1000 cm^{-1} and 550 cm^{-1} and the typical water at around 3428.20 cm^{-1} and 1621.55 cm^{-1} were also present.

4.1.4 XRD

XRD analysis of the adsorbent was done and the graph obtained is shown in Fig4.4 (a). The graph did not have distinct sharp peaks which meant that the adsorbent was amorphous in nature and not crystalline. The small peaks corresponded to quartz, graphite pentacene and methanol and the sample after adsorption showed martensite and suessite along with graphite.

4.1.5 TGA/DTA

The fig shows the TGA/DTA graph of the adsorbent before and after use is shown in Fig. 4.5 (a) and (b). The temperature range was from 26.4°C to 1196°C and the air flow was set at 200ml/min. The weight loss in first phase, that is from 27°C to 100°C showed a weight loss of 12.68 %. This is primarily due to the removal of the moisture from the sample. After that there was a steady weight loss. From 100°C to 400°C there was total loss of 15.48 % of weight and the rate of weight loss was more. In this temperature range the weight loss primarily occurs from the carbonaceous content of the material and primarily carbon monoxide is produced. From 400°C there is sudden steep decline in the curve and there is spike in the DTA curve which suggests a sudden combustion process. The heat of reaction was -8.46 J/mg. From 400°C to 600°C there was a steeper decline in the curve and no significant loss of weight occurred. At 1196°C there was total loss of 84.68 %. For the adsorbent the curve was almost similar except that there was a steady weight loss in the zone of 600°C to 800°C and the peak observed in the DTA curve was at 700°C. The enthalpy change was -1.61 J/mg. The maximum rate of loss of weight for ACC before use was 2.90 mg/min at 444°C and for ACC after use was .41 mg/min 742 °C.

4.1.6YIELD

The yield of the adsorbent was found out to be 24.718%.

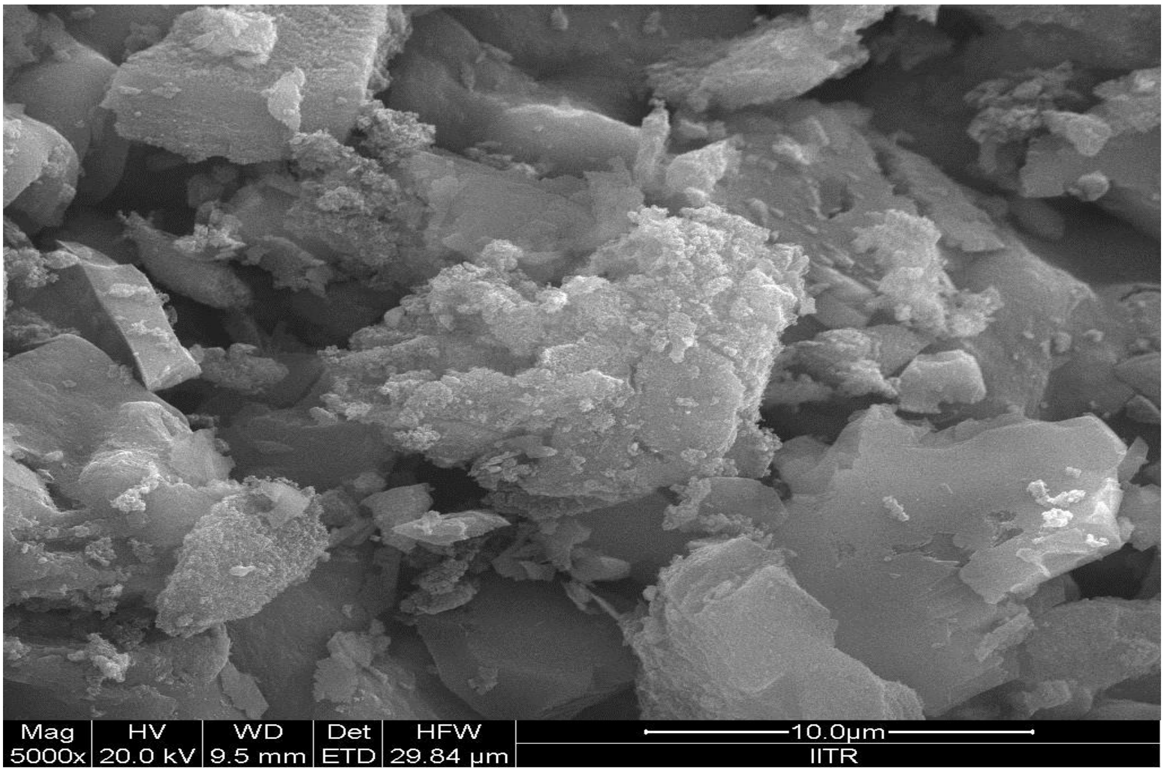

Fig 4.1(a) SEM of ACC before use

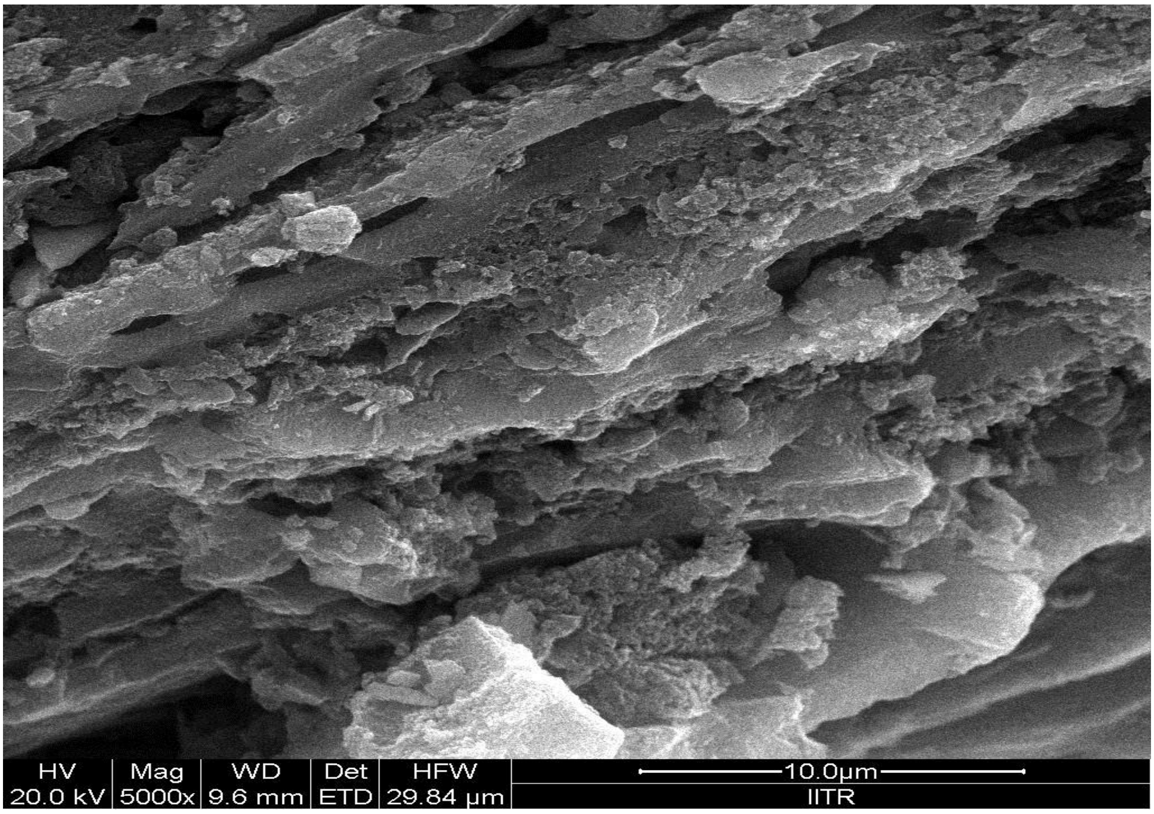

Fig. 4.1 (b) SEM of ACC after treating TWW

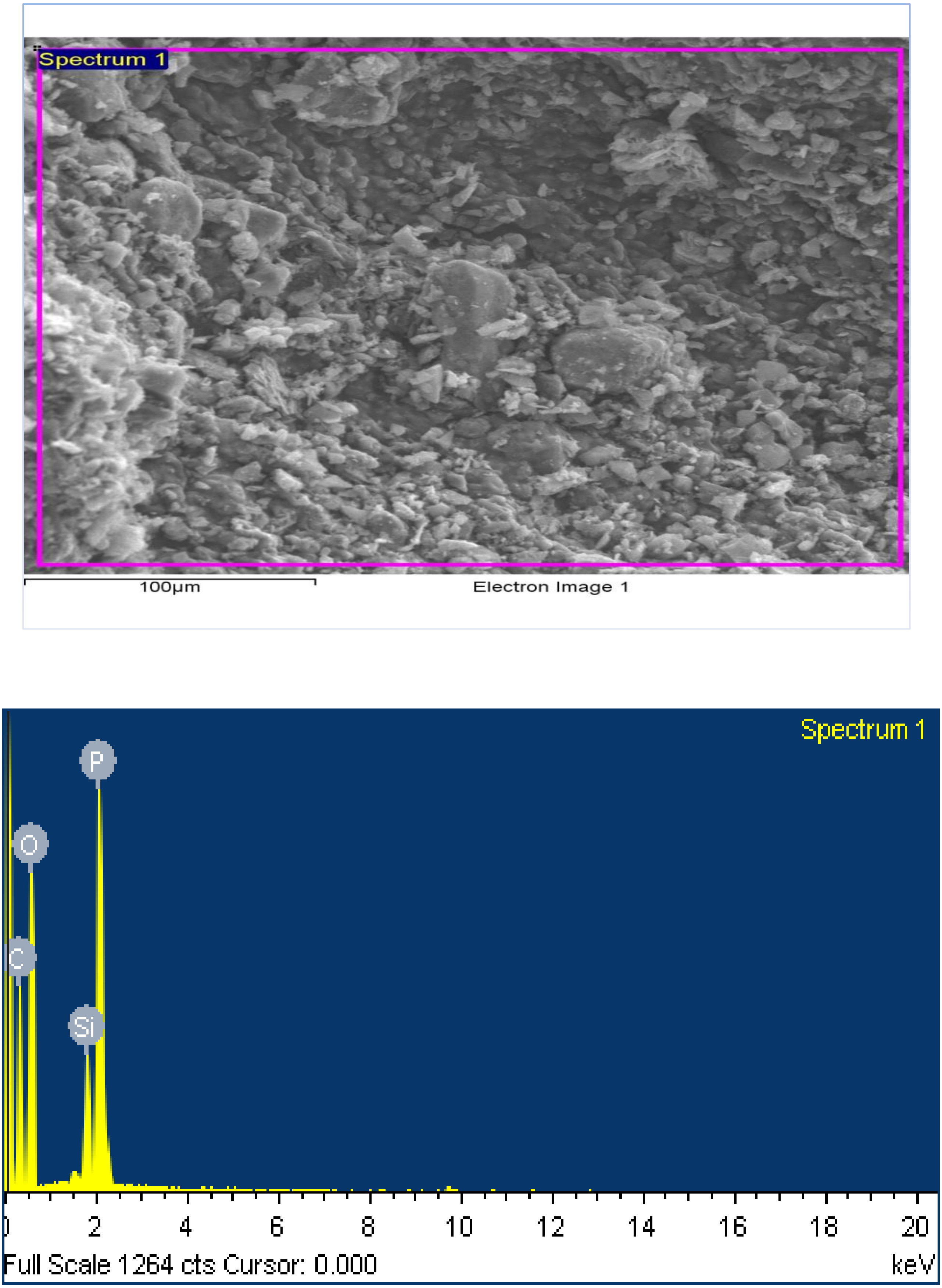

Fig 4.2 (a) EDX analysis of ACC before use

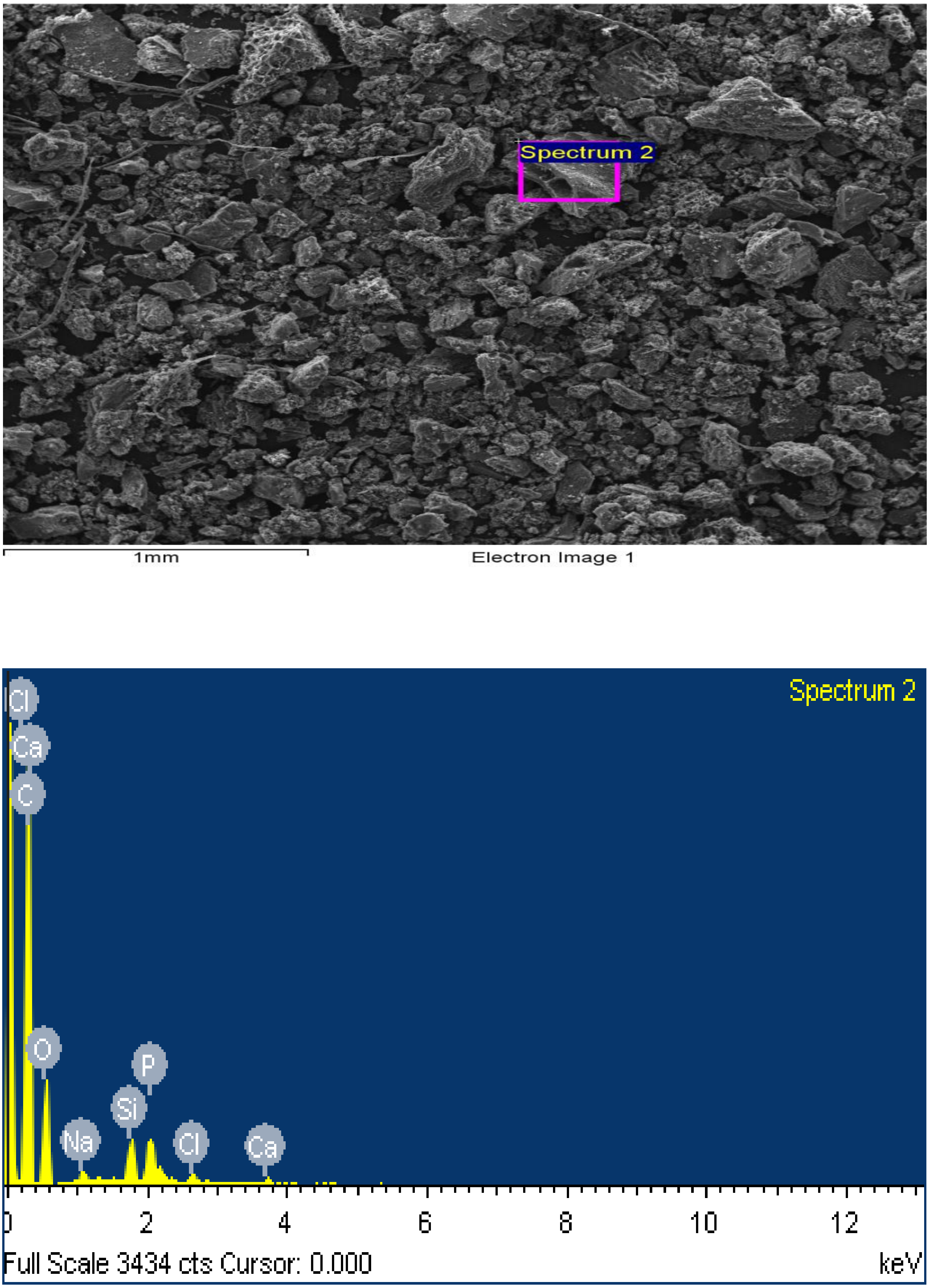

Fig 4.2 (b) EDX analysis of ACC after use

Table 4.1(a) EDX of ACC before use

Element	**Weight %**	**Atomic %**
CK	42.65	52.74
OK	43.70	40.57
SiK	2.88	1.52
PK	10.76	5.16

Table 4.1(b) EDX of ACC after use

Element	**Weight %**	**Atomic %**
CK	66.17	73.39
OK	29.77	24.79
NaK	0.48	0.28
SiK	1.35	0.64
PK	1.50	0.65
ClK	0.43	0.16
CaK	0.30	0.10

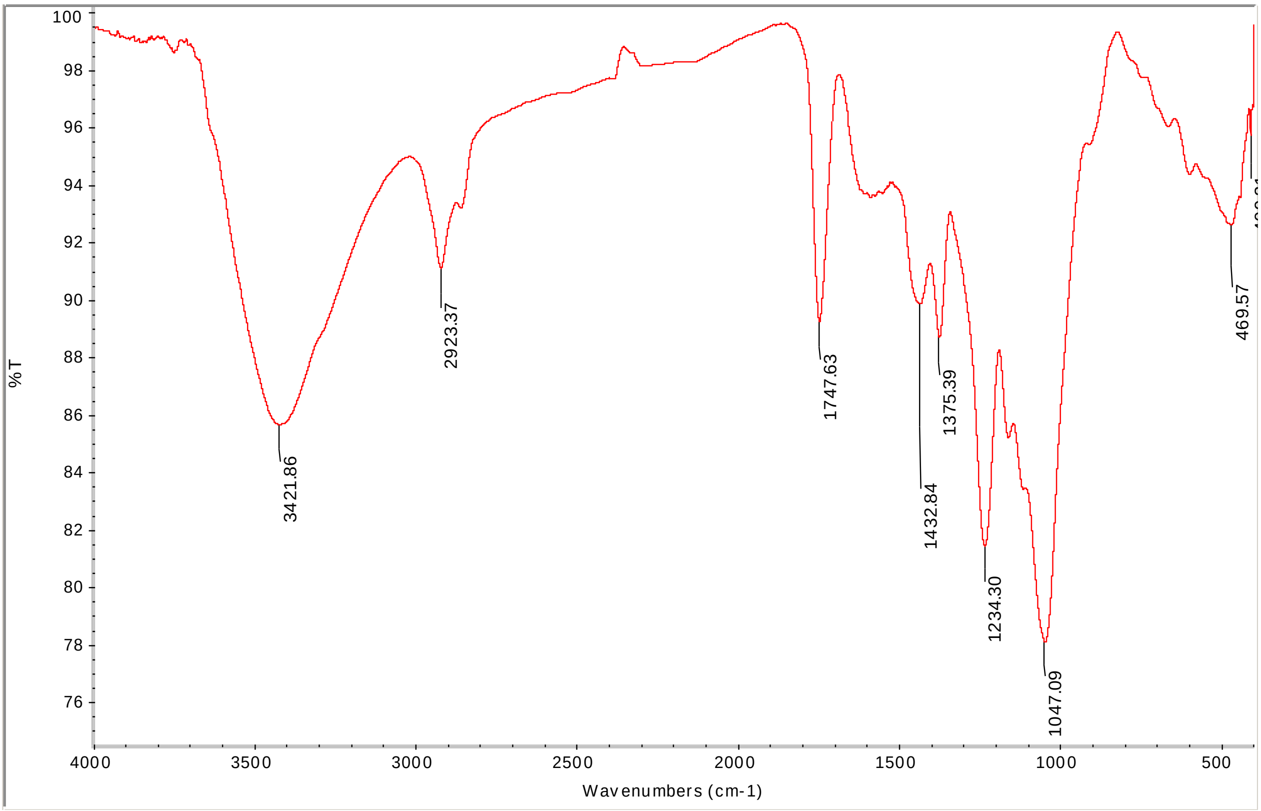

Fig 4.3(a) FTIR spectra of ACC before adsorption

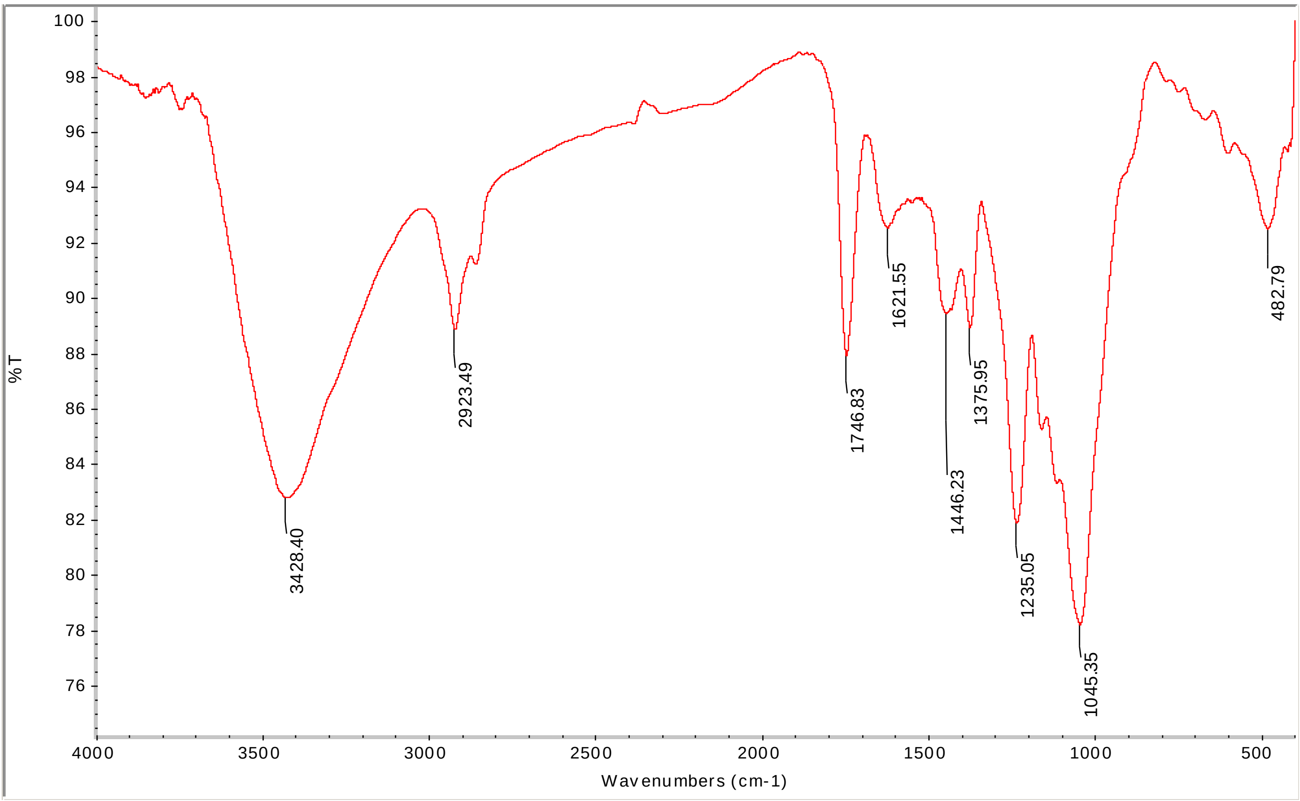

Fig 4.3(a) FTIR spectra ACC after adsorption

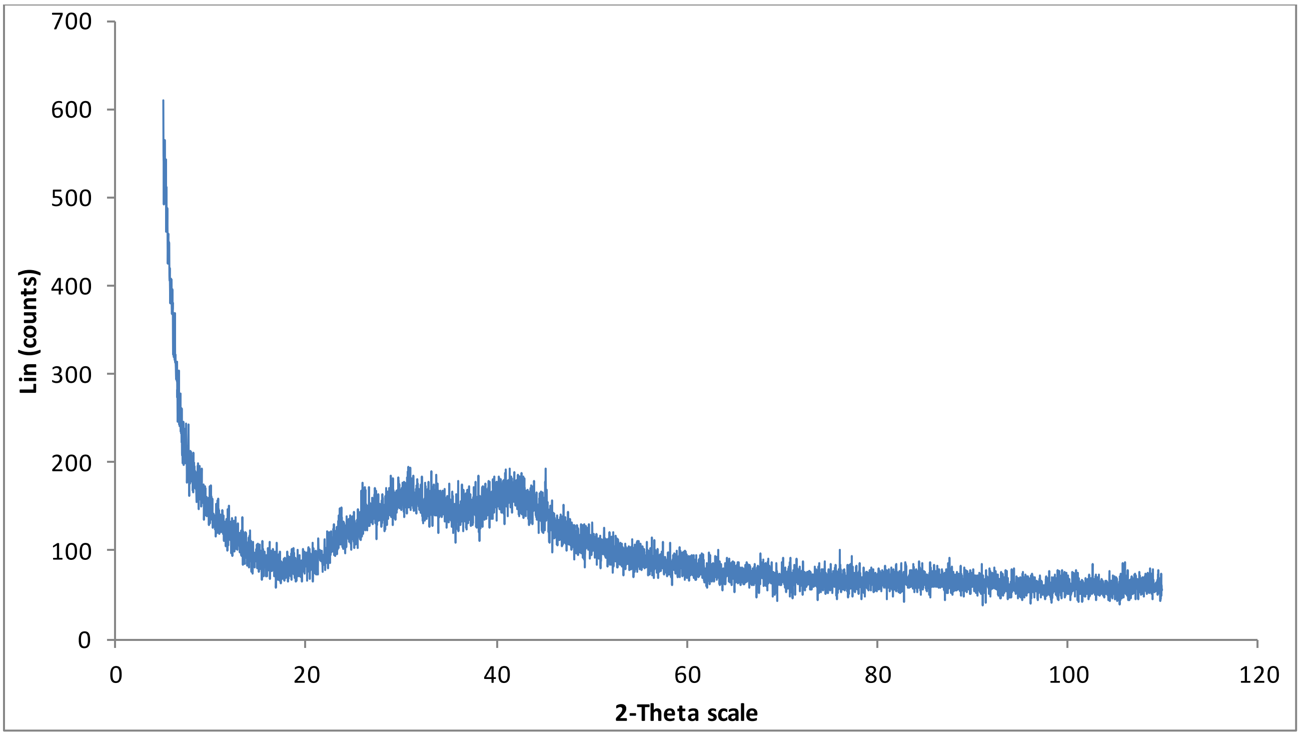

Figure 4.4(a) XRD pattern of ACC before use

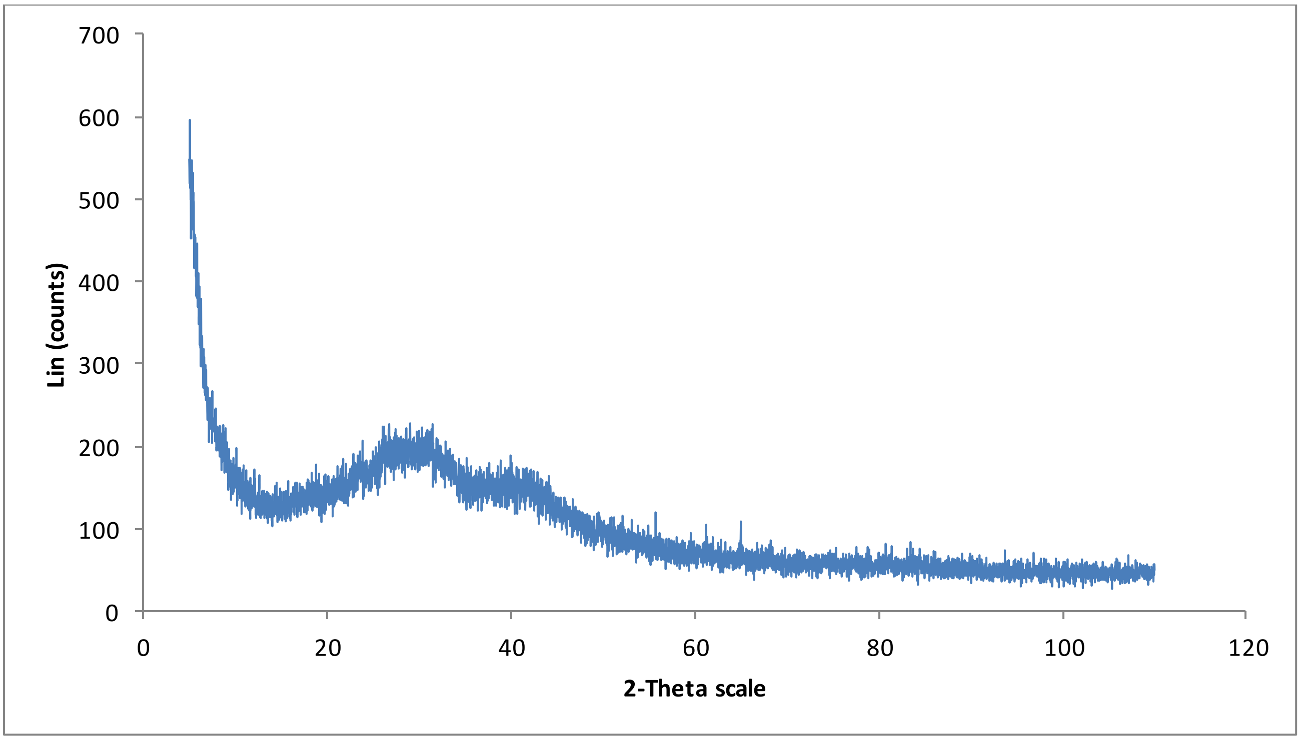

Figure 4.4(b) XRD pattern for ACC after use

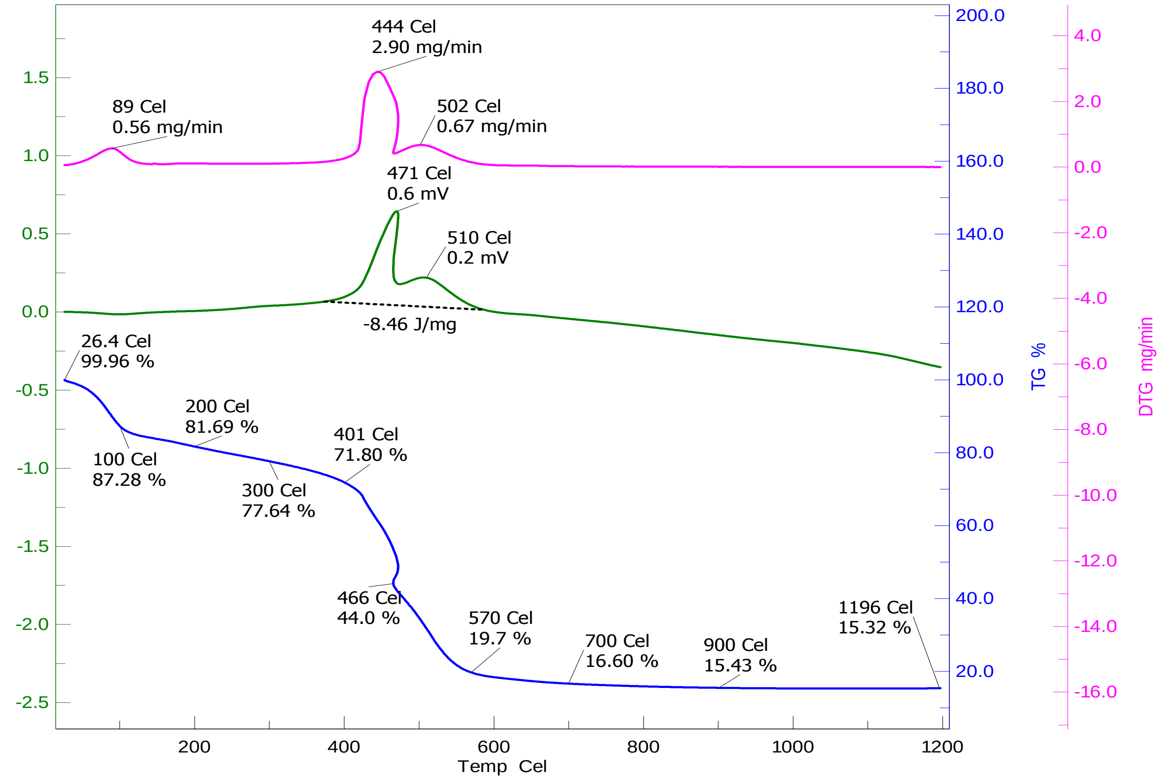

Figure 4.5(a) TGA/DTA analysis of ACC before use

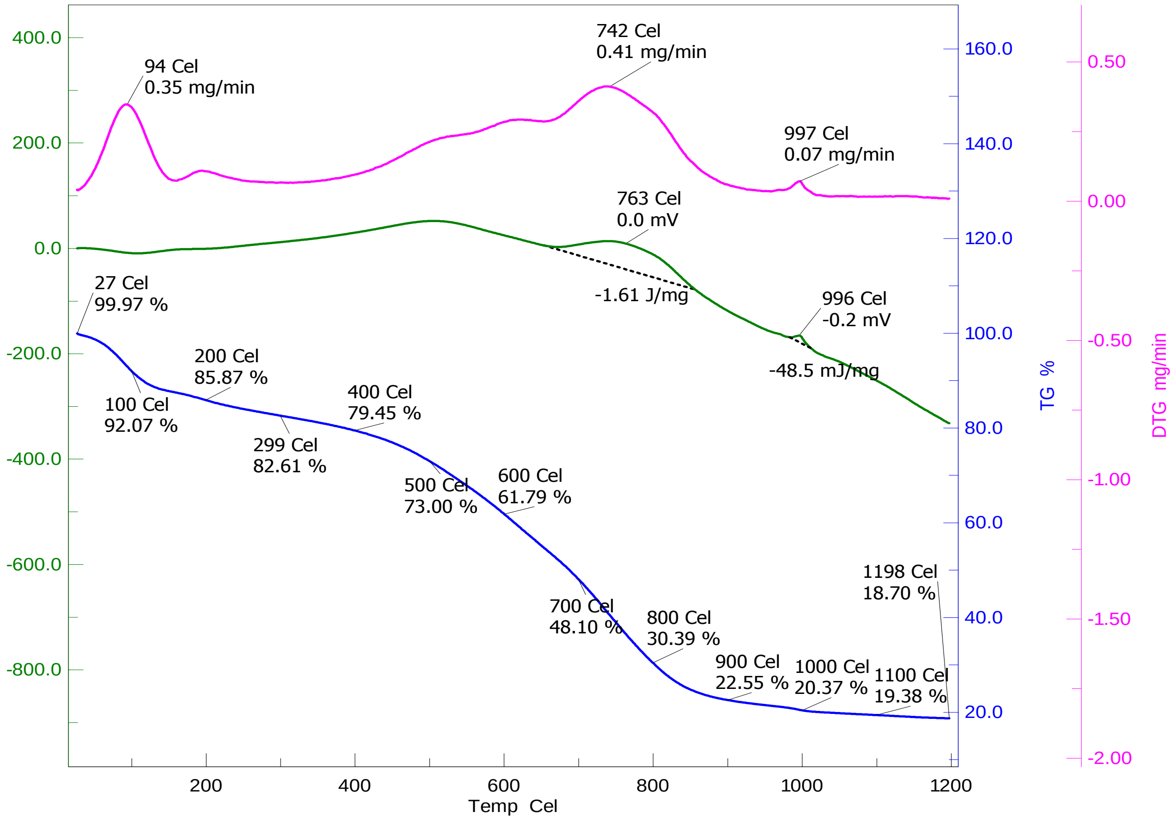

Figure 4.5(b) TGA/DTA analysis of ACC after use

4.2 EFFECT OF ACC DOSAGE

First of all the adsorbent dosage was varied. The runs were taken by varying the dosage from 0.1g, 0.2g, 0.3g and up to 0.8 g per 100 ml of TWW. 8 flasks were taken and introduced with various dose of adsorbent. The concentration of TWW was not changed and the temperature was set at 30°C for the run and the speed of motor was set to 120 rpm. It was kept in the orbital shaker for 10 hours. By increasing the dosage the percentage removal of COD and colour also increased at rapid rate initially. The reason for it is the availability of more sites for adsorption for the solutes in the solution. After increasing dosage from 0.4 g the relative increase in percentage removal was less than the increment of dosage at initial values. After 0.6 g the removal % stagnated and there was no further significant increase in the % removal of colour and COD. The graph of adsorbent dosage with contact time is plotted in Fig. 6.6. The % removal of colour was more than that of COD for all the readings. Thus the optimum dosage was selected as 0.6g.

4.3 EFFECT OF RUN TIME

After optimizing the adsorbent, runs were carried out to find the equilibrium time. The contact time was varied as 0.5 h, 1h, 1.5h, 2h, 2.5h, 3h, 3.5h, 4h, 4.5h, and 7 hours. The flasks were taken out at a constant time interval of 30 minutes except for the last reading and the temperature was set at 30°C and pH. The percentage removal increased initially and after 3.5 hours there was not a considerable increase in the % removal of colour and COD. The graph is plotted in Fig 6.7.After a certain time the adsorbate is not able to attach itself as all the active sites are filled up. Even increased agitation duration with the shaker, as there is relatively less space available and as surface tension of adsorbate decreases there is a decrease in driving force for adsorption.

4.4 EFFECT OF pH

After optimizing the dosage and run time, runs were carried out to find the optimum pH for the removal of colour and COD. Runs were taken at a pH value of 2, 3, 4, 6, 8, 10 and 12. At lower pH values it was found that the removal was high and it decreased as the pH value increased. The graph for the pH variance and % removal is plotted in Fig 6.8**.** At pH=3, maximum removal in COD and colour was obtained. The value of pH of the solution at the start of the run is very important. The pH value affects the degree of ionization of solutes present in the TWW and hence it changes the equilibrium properties of the process. At lower pH negatively charged ions are adsorbed more easily because of the presence of Hydrogen ions and higher pH favours the adsorption of positively charged ions. The runs were carried out for 3.5 hours with and adsorbent dosage of 0.6g/100ml at a temperature of 30°C.

4.5 TEMPERATURE EFFECT

After optimizing the pH at 3, dosage at 0.6g and the time at 3.5 hours, the effect of temperature was examined. The runs were taken at temperatures of 15°C, 30°C, 45°C and 60°C. Better removal was observed at lower temperature as adsorption is a process that emits heat and therefore is more favourable at lower temperatures. The best removal was obtained at 15°C and the graphs are plotted in the second Fig 6.9

4.6 TREATMENT OF TWW BY SERIES ADSOPRTION

After treating it with adsorbents with various dosages, it was taken out from incubator and its readings were recorded. Adsorbent was separated and the same dose of adsorbent was introduced in the respective flasks. It was done to further remove the remaining COD and colour. They showed the same trend, as discussed in section 4.1 but the % removal at respective dosages were comparatively higher this time. It is plotted in Fig 6.10.

4.7 ADSORPTION ISOTHERMS

Readings were taken at a constant temperature and various initial concentration of the TWW. Curve fitting tool in MATLAB was used to determine the values of constants and the value of R^2. The curve was fitted into of Freundlich, Langmuir, Redlich Peterson and Sips isotherm. The following datas were obtained

Table 4.2 Isotherm parameters for the removal of COD by ACC

Isotherms	**Parameters**	**Temperature (°C)**		
		15	**30**	**45**
Langmuir $q_e = \frac{Q_o b C_e}{1 + b C_e}$	Q_o	238.2	263	273.6
	b (mg/g)	0.005951	0.003892	0.002935
	R^2	0.958	0.9526	0.9265
Freundlich $q_e = K_F C_e^{1/n}$	K_F (L/mg)	5.257	3.386	2.53
	n	1.657	1.511	1.447
	R^2	0.9143	0.9202	0.8977

Redlich-Peterson $q_e = \frac{K_R C_e}{1+a_R C_e^g}$	a_R (L/mg)	3.675x10^{-9}	7.372x10^{-9}	1.397x10^{-8}
	K_R (L/mg)	0.9343	0.657	0.5346
	g	3.472	3.151	2.938
	R^2	0.9969	0.9445	0.9151
Sips $q_e = \frac{K_s C_e^{\beta_S}}{1+a_s C_e^{\beta_S}}$	K_S	0.07177	0.04781	0.01769
	a_S (mg/g)	0.000464	0.0003054	0.000118
	β_S	1.765	1.743	1.877
	R^2	0.9885	0.9788	0.9564

Table 4.3 Isotherm parameters for the removal of colour by ACC

Isotherms	**Parameters**	**Temperature (°C)**		
		15	**30**	**45**
Langmuir $q_e = \frac{Q_o b C_e}{1+bC_e}$	Q_o	482.3	649.8	621
	b (mg/g)	0.003145	0.001699	0.001546
	R^2	0.991	0.9668	0.9675
Freundlich $q_e = K_F C_e^{1/n}$	K_F (L/mg)	5.371	2.802	2.539
	n	1.509	1.309	1.316
	R^2	0.9718	0.9498	0.9498
Redlich-Peterson $q_e = \frac{K_R C_e}{1+a_R C_e^g}$	a_R (L/mg)	2.424x10^{-6}	1.036x10^{-8}	1.162x10^{-8}
	K_R (L/mg)	1.172	0.9247	0.8032
	g	2.142	2.962	2.889
	R^2	0.9984	0.987	0.9883
Sips $q_e = \frac{K_s C_e^{\beta_S}}{1+a_s C_e^{\beta_S}}$	K_S	0.401	0.0517	0.03601
	a_S (mg/g)	0.001176	0.0001634	0.0001194
	β_S	1.319	1.681	1.712
	R^2	0.9965	0.9853	0.9875

It is clear from the values of R^2 obtained that the Sips and Redlich-Peterson model fits are better than Langmuir and Freundlich models. The best fit for COD was the Redlich Peterson with a value of 0.9969 while for the colour plots too, the best fit was Redlich-Peterson model with an R^2 value of 0.9984. The plots are given in Fig 6.11 and 6.12.

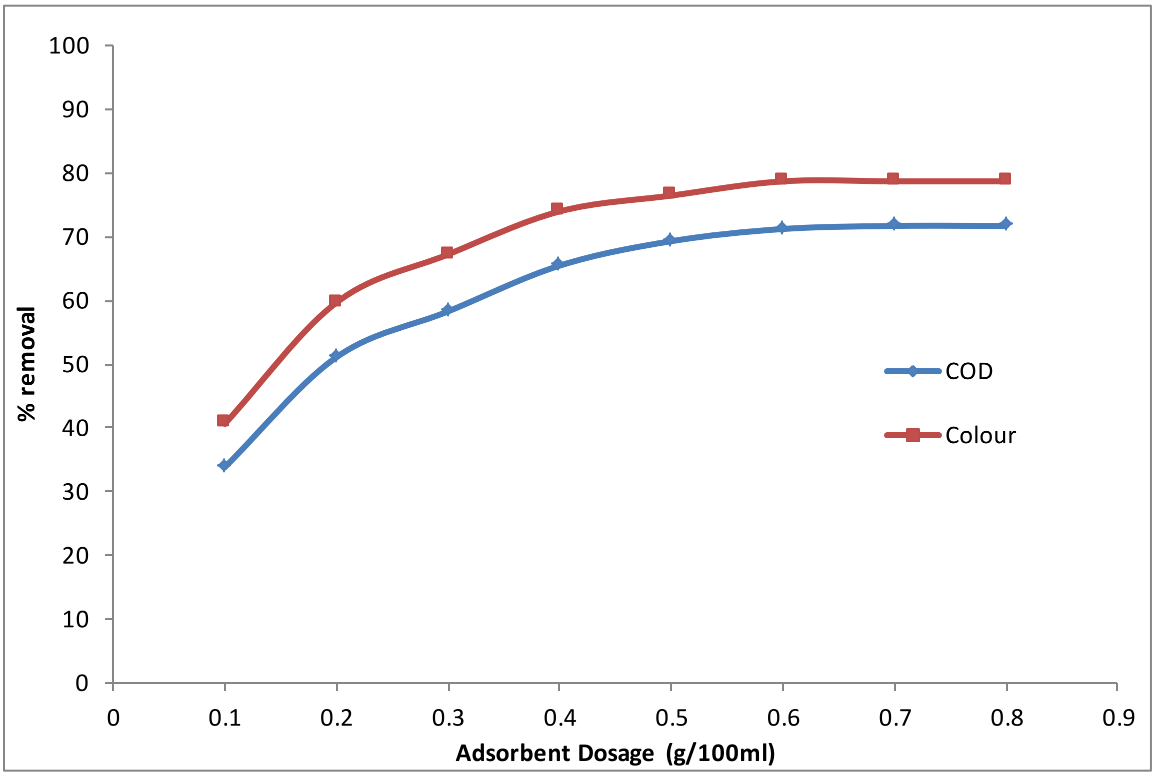

Fig 4.6 % removal of COD and colour at 30°C with varying dosage

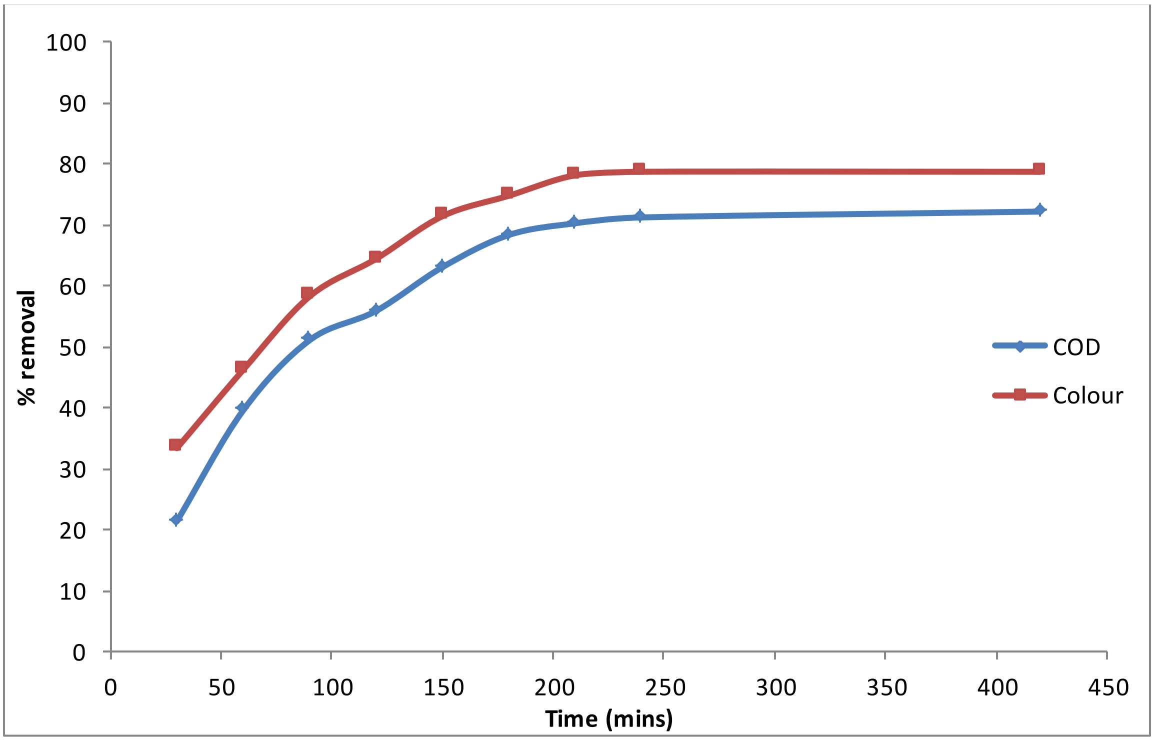

Fig 4.7 % removal of COD and colour at 30°C, and dosage of 0.6g/100ml adsorbent dosage with time

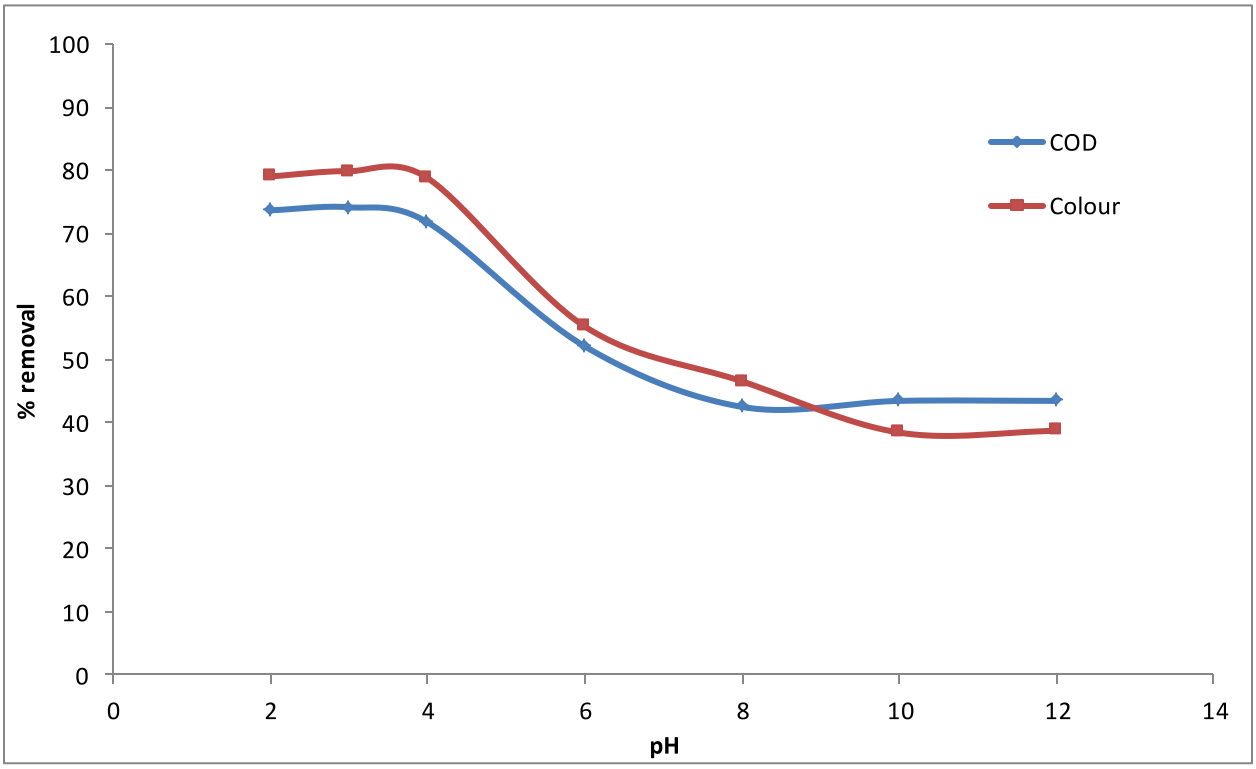

Fig 4.8 % removal of COD and colour at 30°C, and dosage of 0.6g/100ml with varying pH

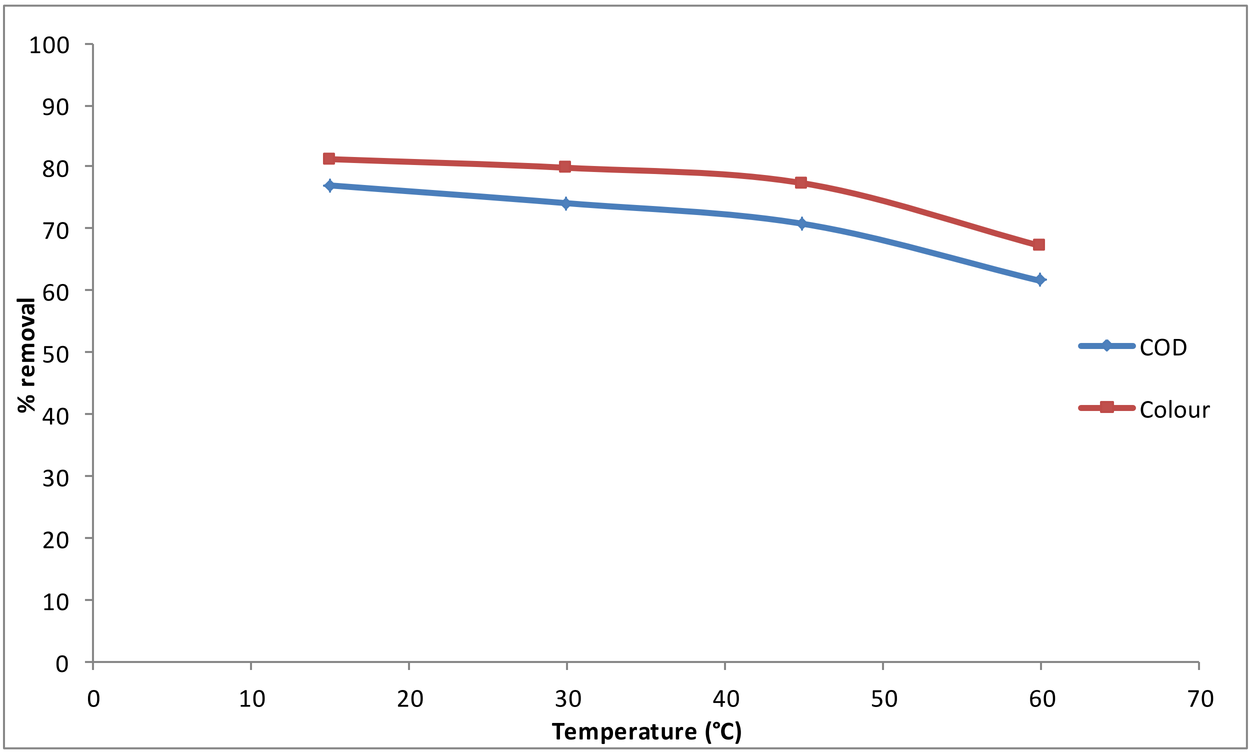

Fig 4.9 % removal of colour and COD at 0.6g/100ml pH=3 and time=3.5 with varying temperature

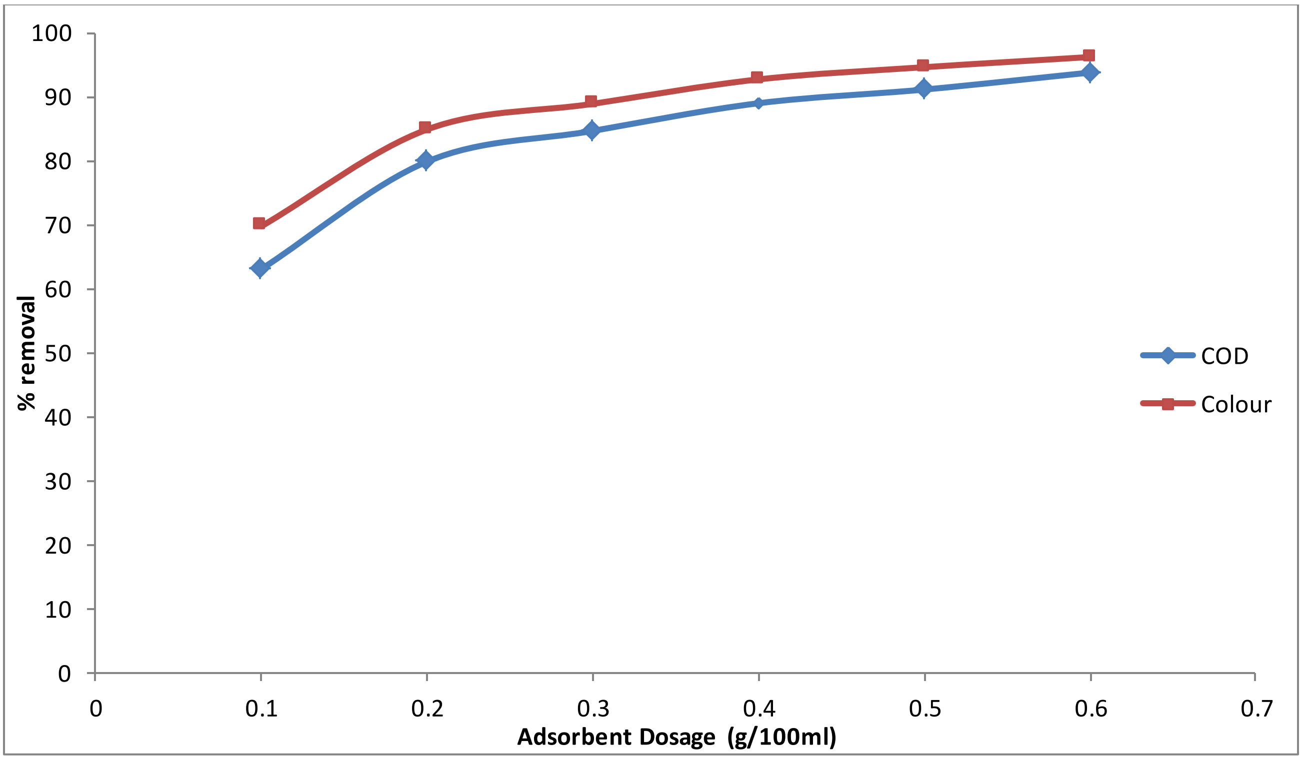

Fig 4.10 % removal in the second stage of batch adsorption for COD and colour

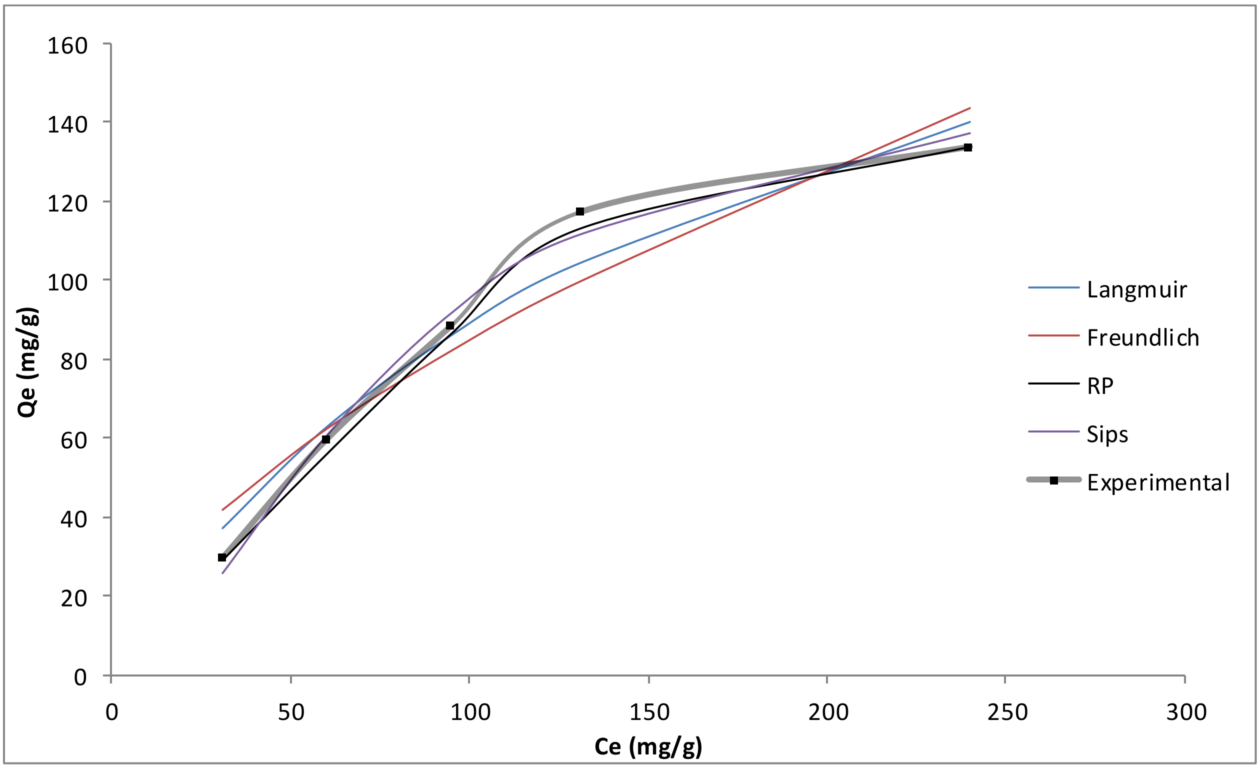

Fig 4.11 Isotherm plots for COD removal at 15°C

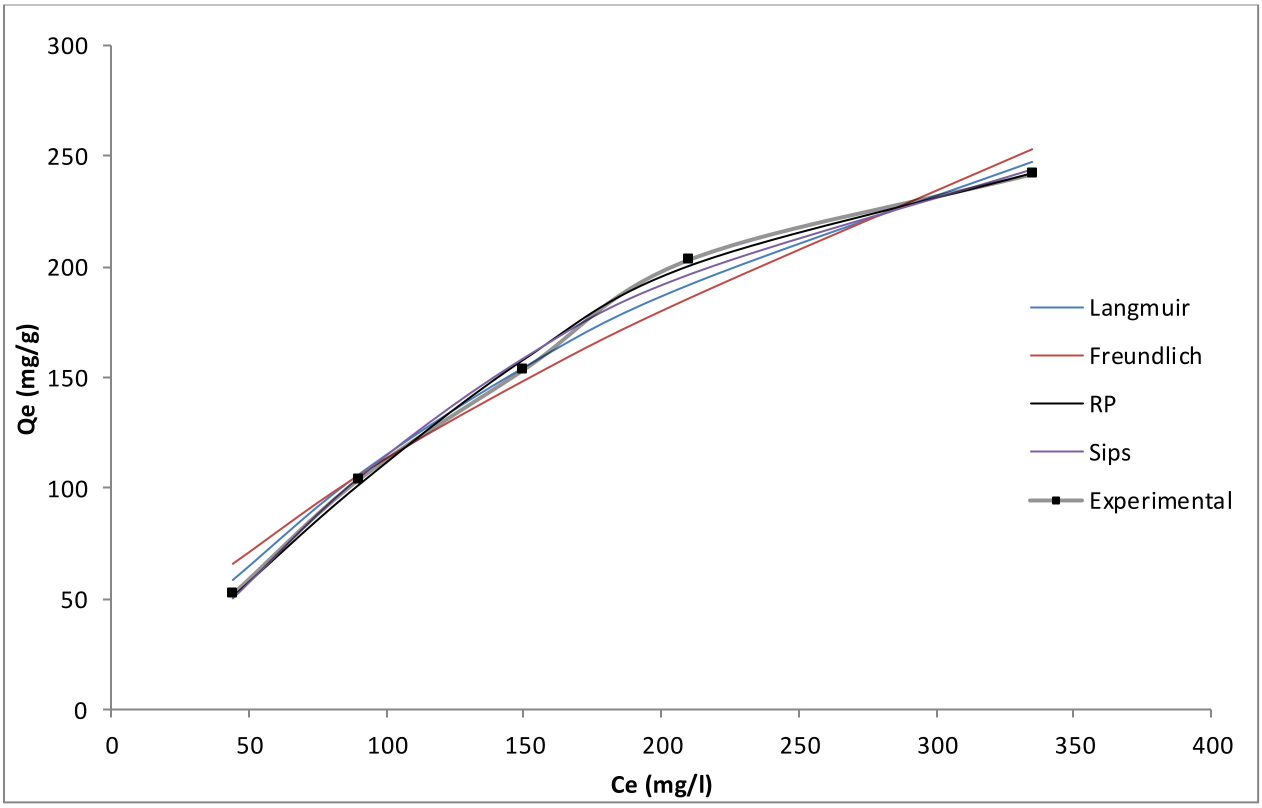

Fig 4.12 Isotherm plots for colour removal at 15°C

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

- The adsorbent prepared from the corn cob did not have surface area as high as the commercially available activated carbon but it was efficient in reducing the levels of COD and colour within the norms set by CPCB. Therefore it can be seen as a cheap alternative for the commercial activated carbon, making the agricultural waste useful
- The removal of colour and COD were studied by varying parameters, the following results were concluded

  - Adsorption of colour and COD increased with the increase of dosage, optimum quantity was found out to be **0.6g/100 ml** of wastewater

  - The equilibrium time was established as **3.5 hours** from the conducted experiments

  - At higher pH there wasn't enough removal of COD and colour, while at lower pH the reduction in pH and colour were relatively high. Best results were obtained at **pH=3**

  -The removal percentage increased at lower temperatures and at 15°C maximum removal was achieved.

- The removal of colour remained more than that of COD, except for at very high pH.
- The removal of COD and colour in two stage batch adsorption was as high as 93.76 % and 96.19 % in comparison to the single stage where the corresponding removal of COD and colour were 76.9 % and 81.3 % respectively.

5.2 RECOMMENDATIONS

- ACC can be prepared with various impregnation ratios and different temperatures for carbonisation to observe its effect in the surface area and other such properties.

- Studies can be carried to see whether it is possible to retain the dyes form activated carbon after adsorption as polymer based adsorbents give this option but their cost is very high.

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