EXPLOITATION OF ACTIVATED CARBON MATERIALS FOR THE SORPTION OF MERCURY

DISSERTATION

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

Master of Science

in

CHEMISTRY

By
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Under the guidance of

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Dedicated

to my

Parents

CERTIFICATE

This is to certify that the project entitled, **"EXPLOITATION OF ACTIVATED CARBON MATERIALS FOR THE SORPTION OF MERCURY",** being submitted by **Mr. Amitava Srimany** to the Indian Institute of Technology Madras, for the award of the degree Master of Science in Chemistry, is the bonafide record of the project work carried out by him under my supervision.

Place :   Prof. T. K. Varadarajan

Date :   Project Guide

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Finally I bow down before the **HOLY MOTHER** for **HER** all sufficient blessings.

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CHAPTER - 1

INTRODUCTION

Mercury is an element well known to mankind from times immemorial (1500 BC). It was used by the people of ancient civilizations like China, Egypt, Roman, Greek as well as India. It was believed by Alchemists to be the first matter from which all other metals have been formed.

Though in the modern world, mercury has several applications ranging from domestic (mercury vapour lamps, fluorescent lamp, silvering mirrors, batteries), medicinal (thermometer, dental amalgam), industrial (chlor alkali process, gold and silver mining), research (calomel electrode), the use of mercury is being reduced day by day because of its bad impact on human health and eco-system. Mercury released into the environment gets accumulated in various organisms and enter into the ecosystem causing various health problems to human beings and also effects the flora and fauna [1, 2].

The abundance of mercury in the earth's crust is as low as 0.08 parts per million (ppm). But when we consider the release of mercury into the environment, the toxic effect is highly prominent even in very low concentrations both in the aquatic and air environments. Mercury is released into the environment both by natural and anthropogenic sources. Volcanic eruption is one of the major sources of release of

mercury into the environment. Other sources include various industries like coal-fired power plants, gold and silver mining, cement and caustic soda production industries [3] Disposal of domestic wastes such as batteries and thermometers also contribute to merecury pollution. The mercury thus released into the environment gets bio-accumulated and comes into the food chain.

Mercury Poisoning – The first incidence of ill effects

The Minamata disaster that took place in Japan is one of the examples of the ill effects of mercury poisoning. In the year 1932, the Chisso corporation, Japan's leading chemical industry started producing acetaldehyde in Minamata city. Mercury sulphate was used as catalyst in the production process. Methyl mercury, the most toxic form of mercury was produced as a result of one of the side reactions. The industrial waste water containing this methyl mercury was dumped by the Chisso corporation into the Minamata bay. The production of acetaldehyde was increased from 210 tons in 1932 to 6000 tons per year by 1951 which has resulted in an increase in the concentration of methyl mercury in waste water. This compound being bio-accumulated into the fish entered into the food chain and caused the out broke of the Minamata disease or Chisso-Minamata disease in 1956. The nervous system gets affected because of the Minamata disease causing muscle weakness, numbness in hands and feet, hearing damage, narrowing of vision and finally leading to paralysis, coma and death. The disease claimed more than thousand lives and 10, 000 people were left affected.

Mercury Poisoning – Mode of action and treatment

Though elemental mercury is less toxic than other Hg (II) compounds, but it has the potential to get converted into the most toxic forms of mercury like methyl mercury compounds in biological systems. Hg (II) being soft acid prefers to bind with sulfhydryl groups of proteins which contain soft basic sulfur centre, thus preventing the proteins to act normally. As Hg (II) has the tendency to bind with soft bases, the treatment of this type of heavy metal poisoning involves chelation therapy where a good chelating agent is used. This includes compounds like British Anti-Lewisite (BAL), 2, 3-dimarcapto-1-propanesulfonic acid (DMPS), dimercaptosuccinic acid (DMSA) and few others. All of them contain adjacent – SH groups which binds effectively with Hg (II) and remove it from the body.

Mercury Poisoning – Measures to control

After the fatal effect of mercury poisoning as noticed in Minamata, various rules and regulations have been formulated to control mercury pollution and poisoning. According to the USA's Environmental Protection Agency (EPA), the permissible limit of mercury in waste water is nil. According to the Bereau of Indian Standards (BIS), the permissible limit of mercury is 0.01 mgL^{-1} and the same is 0.001 mgL^{-1} as per the regulations of the Indian Standard Institution (ISI) [4, 5].

Owing to the harmful nature of mercury poisoning, it is important to treat the industrial waste water to remove mercury from it before discharging the same into the environment. Till date, several methods have been developed which includes chemical

(sulphide) precipitation, solvent extraction, ion exchange, membrane separation (electrodialysis and reverse osmosis), alum and iron coagulation, lime softening, activated carbon adsorption, electro deposition, photo reduction and some biological processes. Among all these physical and chemical methods adsorption by activated carbons is economically most effective, and indeed most widely used to remove mercury from aqueous phase. Methods other than adsorption are either energy intensive or require large quantities of chemicals. Thus there is a need for both developing new and effective carbon materials (adsorbents) at lower cost and also optimize the experimental parameters for the process of adsorption, such as equilibration time, sorbent dose, pH and the effect of initial metal ion concentrations for the adsorption of mercury (II) on carbon adsorbents [6-9].

Objectives of the research work

1.   To search for a potential adsorbent based on activated carbon for the removal of mercury from aqueous solutions
2.   To explore the optimum conditions for the process of the adsorptive removal of Hg (II) species from water streams
3.   To evaluate the adsorption capacity of the activated carbon material (adsorbent) for Hg (II) species
4.   To analyze and interpret the equilibrium adsorption data using Freundlich and Langmuir adsorption models and to evaluate which model best fits the experimental data.

CHAPTER – 2

EXPERIMENTAL

2.1 CHEMICALS AND MATERIALS USED

Carbon materials, such as, IG 8 x 30 mesh, IG 12 x 40 mesh and IG 18 x 40 mesh were purchased from German Carbon Limited, India; AC 550 and AC 950 were purchased from Chemicals (India) Co., Madras, India; AC 4 x 8 from Sushrut Chemicals, India. Mercuric chloride ($HgCl_2$), Potassium iodide (KI), Rhodamine 6G and Gelatin were purchased from Sisco Research Laboratory, India. All the chemicals and solvents used for the investigation were of analytical (AR) grade. The chemicals were used as such without further purification.

2.2 CHARACTERIZATION TECHNIQUES

2.2.1 Powder X-ray diffraction (XRD) analysis

XRD patterns of various materials were recorded using Rigaku miniflex II desktop X-ray diffractometer operated at 30 kV and 15 mA using CuKα radiation (λ = 1.5418 Å) at a scan rate of 3 °/min. The diffraction profiles were obtained in the scan range (2θ) of 5 - 90°.

2.2.2 FT-IR spectroscopic studies

The FT-IR spectra of various samples were recorded on Shimadzu spectrophotometer. The spectral range of analysis is 600 - 4000 cm^{-1} with a resolution of 4 cm^{-1}. The spectra

were obtained in transmission mode at 16 scans. Pressed KBr pellets were prepared by grinding 200 mg of carbon samples with 0.5 g of KBr.

2.2.3. UV Vis spectrophotometric measurements

UV-Vis spectra of the coloured (R_2HgI_4) solutions were recorded on a Jasco V – 530 UV/Vis spectrophotometer. The residual Hg (II) concentration in the filtrate was analyzed by monitoring the adsorbances at 575 nm (characteristic of R_2HgI_4 complex) using rhodamine 6G (R) and buffered potassium iodide as reagents.

2.3 Batch mode Hg (II) sorption studies

Removal of Hg (II) using various activated carbons was carried out by batch method. The influence of various experimental parameters such as the effect of pH, contact time, activated carbon dose and initial sorbate concentration were studied. For each experiment, 100 mL of the metal ion solution of desired concentration was taken in a 250 mL stoppered reagent bottle. The pH was adjusted to the desired values using dilute solutions of HCl and NaOH. A known amount of activated carbon (sorbent) was introduced into the reagent bottles. The solutions in the bottles were agitated at room temperature using a mechanical shaker for a desired time to attain equilibrium. At the end of the required time intervals, the samples were taken out and the solutions were separated from the activated carbon by filtering through a sintered funnel. Blank solutions were also treated similarly (without adsorbent) and the concentration was taken as initial concentration. The effect of pH was studied in the range of 2 – 9 by adjusting the pH with the addition of dilute aqueous solution of HCl or NaOH. The effect of

adsorbent dose was studied in the range of 50 – 600 mg. The effect of contact time on the process of adsorption was determined at different time intervals of 10 minutes - 6 h. Adsorption isotherms and the effect of initial concentration were studied by varying the initial metal ion concentration from 10 to 90 mg/L, keeping the carbon dosage at a constant level. The % removal of mercury (R) was calculated according to the following equation:

$R = [(C_0 – C_e)/C_0] \times 100$, where C_0 and C_e are the initial and residual concentrations (mg/L) of mercury (II) respectively.

Adsorption capacity of the carbon sorbent was evaluated using the following equation:

q_e (mg/g) $= V/m (C_0 - C_e)$, where V is the total volume of mercury (II) solution in L, m is the mass of the adsorbent in g,

C_0 is the initial concentration of mercury (II) solution (mg/L) and

C_e is the residual concentration of Hg (II) in solution (mg/L).

2.3.1 Reagents used

2.3.1.1. Mercury (II) solution

1.354 g of mercury (II) chloride and 10 g of NaCl were dissolved in water and diluted to 1000 ml. This stock solution (1 mg mL^{-1}) was diluted with water to prepare required solutions of concentrations 10, 20, 30, 40, 50, 60, 70, 80 and 90 mg/L which were used for further studies. Presence of NaCl provides sufficient chloride ion concentration to hold the mercury (II) in the solution as anionic complex $HgCl_4^{2-}$. The reduction of Hg (II) to Hg (I) by activated carbon sorbent is avoided by bringing all the Hg (II) ions into the anionic form (tetrachloro mercurate (II)).

2.3.1.2. Buffered potassium iodide solution

5 g of potassium iodide and 5 g of potassium hydrogen phthalate were dissolved in water and a few crystals of sodium thiosulphate was added to it and diluted to 250 ml with water.

2.3.1.3. Rhodamine 6G solution (0.005 wt.%)

0.05 g of rhodium 6G was dissolved in water and diluted to 1 liter.

2.3.1.4. Gelatin solution (1 % (wt./vol.)

1 g of gelatin powder was dissolved in water for 15 minutes on a magnetic stirrer at 60 °C and diluted to 100 mL.

2.3.1.5. Method of estimation of residual Hg (II) in the filtrate [10]

A suitable aliquot (up to 10 ml) of the sample solution containing not greater than 25 μg of mercury was transferred to a 25 ml volumetric flask. 5 mL of the buffered potassium iodide and 5 mL of the Rhodamine 6 G solution were added followed by addition of 1 mL of 1 % (wt./vol.) gelatin solution. The solution was diluted to the mark with distilled water and the absorbance was measured at 575 nm against a blank using spectrophotometry.

2.4. Preparation of calibration plot

1. The calibration plot for the estimation of Hg (II) concentration (in the filtrate after treating the Hg (II) solutions with carbon adsorbents) is obtained from measuring

the absorbances of the Hg (II) solutions containing 6, 8, 10, 12, 14, 16, 18, 20, 22 and 24 μg Hg (II) in 25 mL solutions.

2. The Hg (II) solutions with 6, 8, 10, 12, 14, 16, 18, 20, 22 and 24 μg of Hg (II) per 25 ml were prepared by diluting 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1 and1.2 ml of 1×10^{-4} M mercury solution.
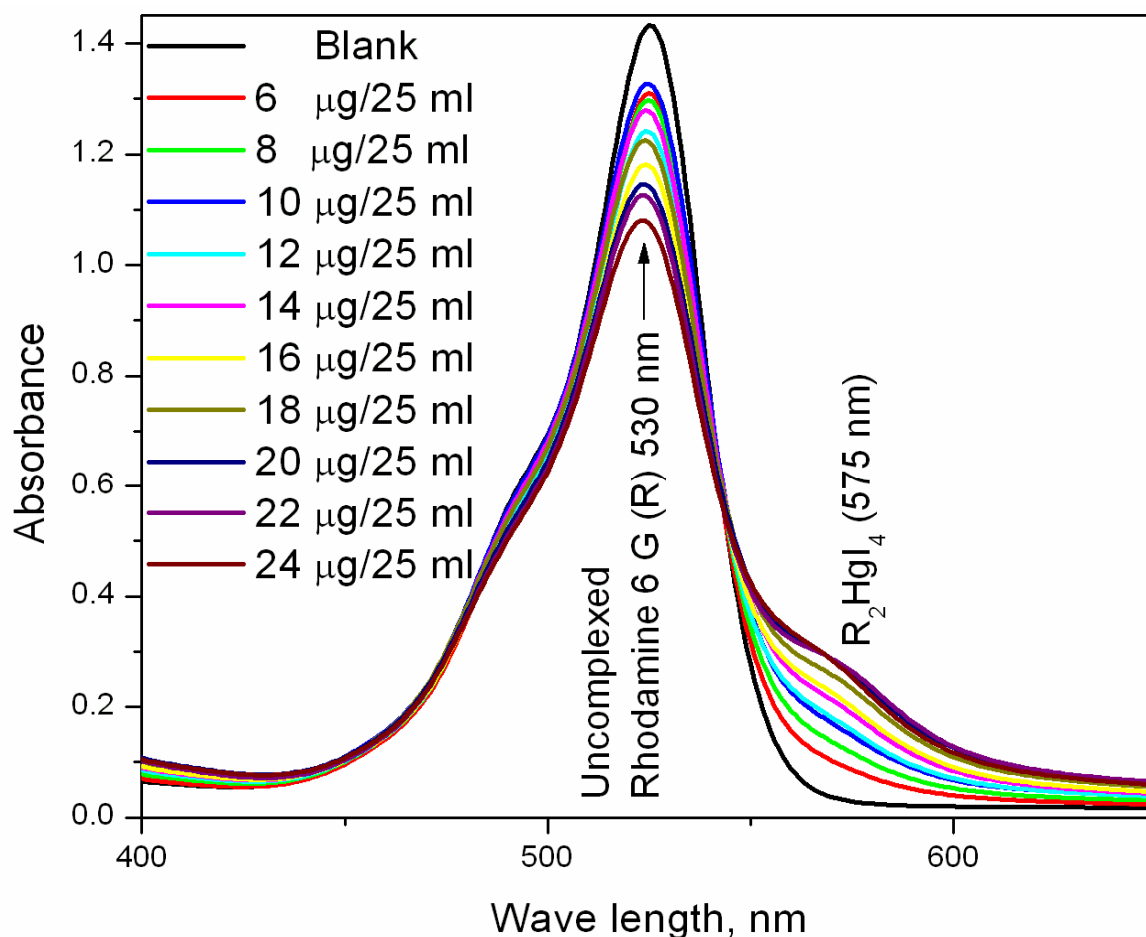

Fig. 2.1. Absorption spectra (total volume 25 mL): 5 mL of 0.005 wt.% Rhodamine 6G and 5 mL of buffered KI solution with 1 ml (1 wt/vol %) gelatin (Blank). (6 – 24 μg Hg (II) : As in the blank with the addition of 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2 ml of 1×10^{-4} M mercury solution

3. To each of the 25 ml volumetric flask containing 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1 and 1.2 ml of 1×10^{-4} M mercury solution, 5 ml of buffered KI, 5 mL of

Rhodamine 6 G reagent and 1 mL of 1 % (wt./vol.) were added and then the solutions are made up to the mark using distilled water which yielded 6, 8, 10, 12, 14, 16, 18, 20, 22 and 24 µg of Hg (II) in 25 mL.

4. The solutions are shaken thoroughly. Dark pink colouration is developed by the formation of R_2HgI_4 complex which absorbs at 575 nm. The UV-Visible spectra are recorded for the 10 sample solutions prepared (Fig.) and a calibration plot is drawn (**Fig. 2.2**).
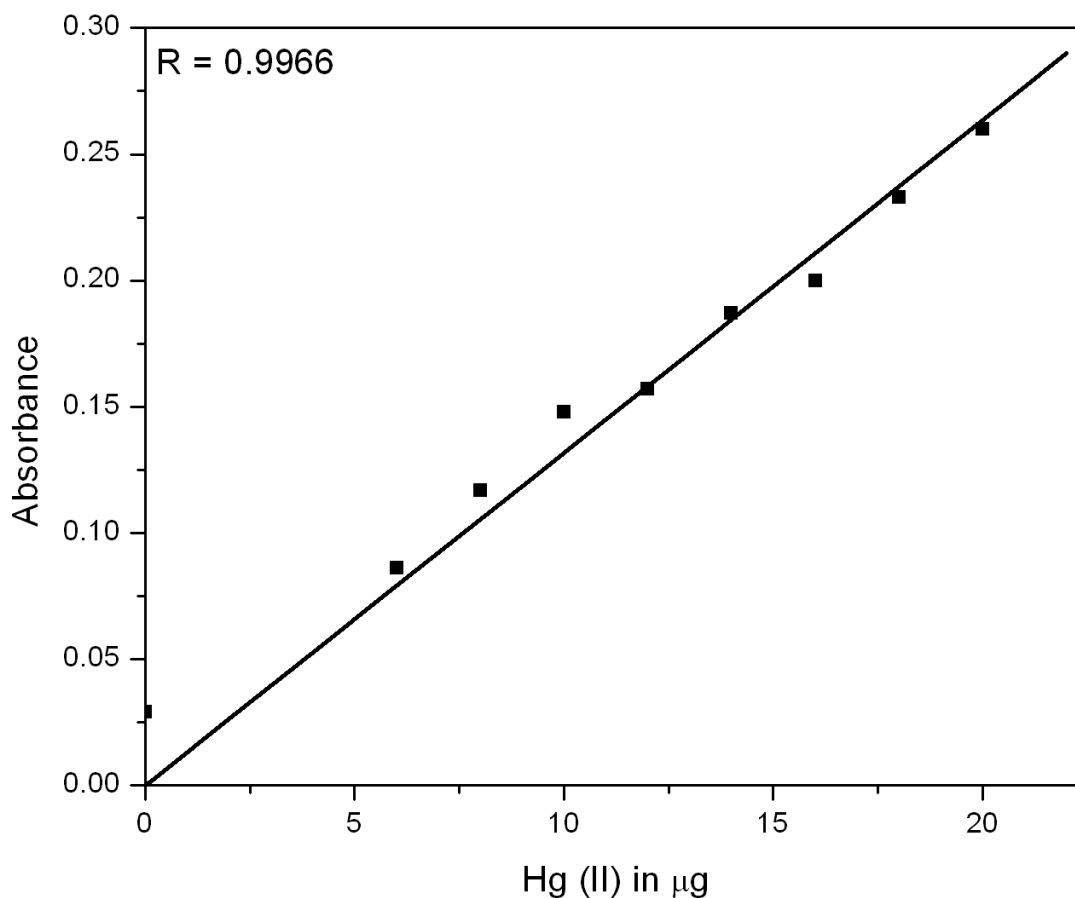

Fig. 2.2. Calibration plot of Hg (II) conc. in µg Vs absorbance of R_2HgI_4 at 575 nm

The complex species formed, R_2HgI_4 (λ_{max} = 575 nm), is pink in colour in contrast to the red colour of the reagent, Rhodamine 6G (λ_{max} = 530 nm). The absorbance of the

complex remains unchanged at 575 nm for at least 24 h when we add gelatin (anticoagulation agent) which retarded the precipitation of the complex.

Linearity (correlation coefficient, R = 0.9966) in the relation between Hg (II) concentration and absorbance of R_2HgI_4 complex is observed up to 25 μg Hg (II)/25 mL concentration beyond which the Beer Lambert's law is not valid (Fig. 2.2). Blank, 6, 8, 10, 12, 14, 16, 18, 20, 22 and 25 μg Hg (II) in 25 mL volumetric flasks were used as standard solutions to obtain the calibration plot. The standard solutions were prepared from the stock solution of 1 x 10^{-4} M Hg (II).

CHAPTER – 3

RESULTS AND DISCUSSION

Commercially available activated carbon materials, namely, AC 550, AC 950, IG 8 x 30, IG 12 x 40, IG 18 x 40, AC 4 x 8 (Sushrut) have been systematically characterized by X-ray diffraction to know their crystallographic structure and also by FT-IR spectroscopy to know the nature and type of the surface functional groups present on the surface of the activated carbon materials. After thorough physicochemical evaluation, the activated carbon materials have been exploited for the sorption of Hg (II) species from aqueous solutions.

3.1. XRD analysis

X-ray diffraction study provides the most fundamental and vital information regarding the structure and crystallinity of the activated carbon materials. The X-ray diffractograms of activated carbon materials, namely, AC 550, AC 950, IG 8 x 30, IG 12 x 40, IG 18 x 40, AC 4 x 8 (Sushrut) were shown in **Figs. 3.1, 3.2., 3.3., 3.4., 3.5.** and **3.6.** respectively. Simple observation of X-ray diffractograms indicate that the XRD pattern offered by AC 550 (**Fig. 3.1**.) is drastically and strikingly different compared to all other carbon materials under the study. Several sharp diffraction peaks are seen in the X-ray diffractogram of activated carbon material AC 550. This imply that this particular carbon material is more crystalline compared to other carbon materials. The diffraction peaks from AC 550 have been indexed and are typical of graphitic carbon structure [11]. The diffraction patterns resulting from carbon materials other than AC 550 were all similar. Typically, two broad peaks centered around the 2θ values of 25 and 44° were observed in the carbon materials, namely, AC 950, IG 8 x 30, IG 12 x 40, IG 18 x 40, AC

4 x 8 (Sushrut). The two diffraction peaks were indexed to (002) and (10) diffraction peaks of turbostratic carbon structure [12]. The (00l) line is because of interlayer scattering where as the (hk) line is because of intra layer scattering. Thus the extent of graphitization is revealed by the appearance of general (hkl) reflections [13, 14, 15]. The occurrence of broad diffraction bands centered around 2θ values of 25 and 44° indicate better layer alignment as well as an increased regularity in the crystal structure [16].
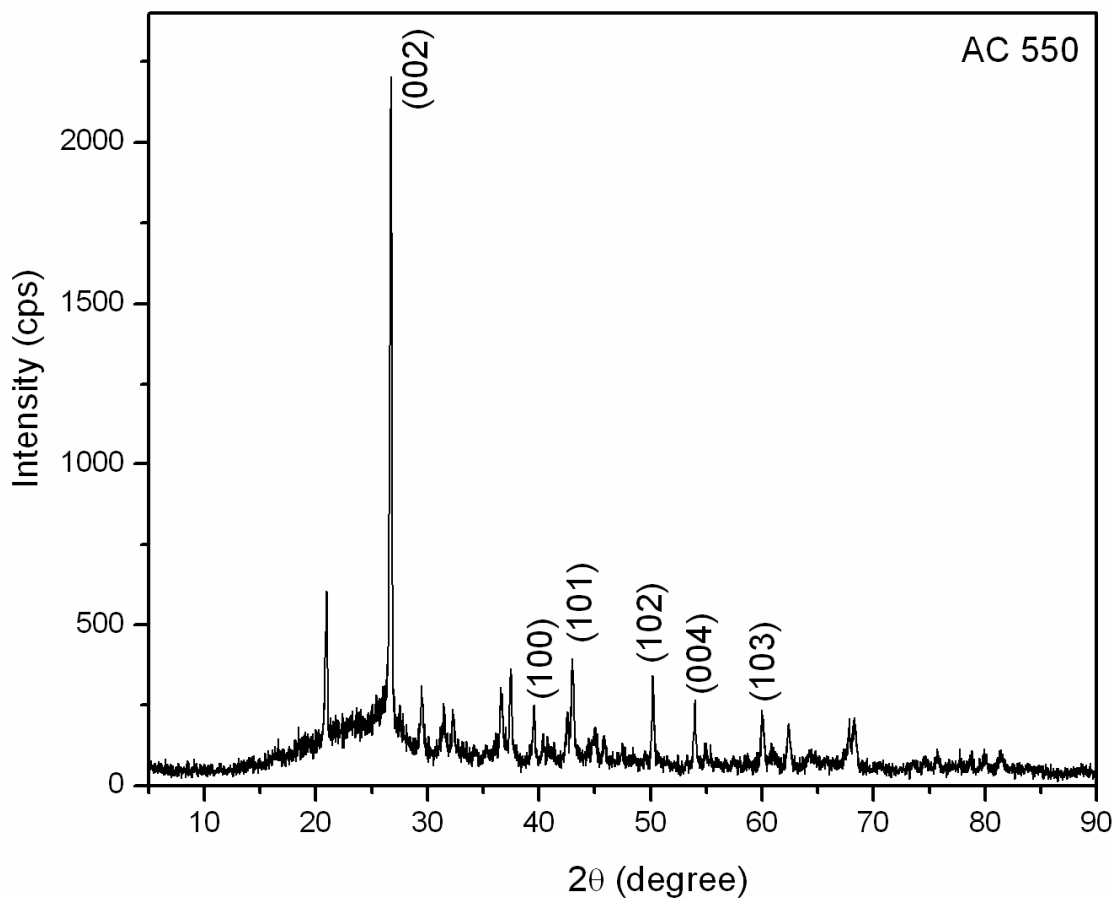
Fig. 3.1. XRD pattern of activated carbon, AC 550
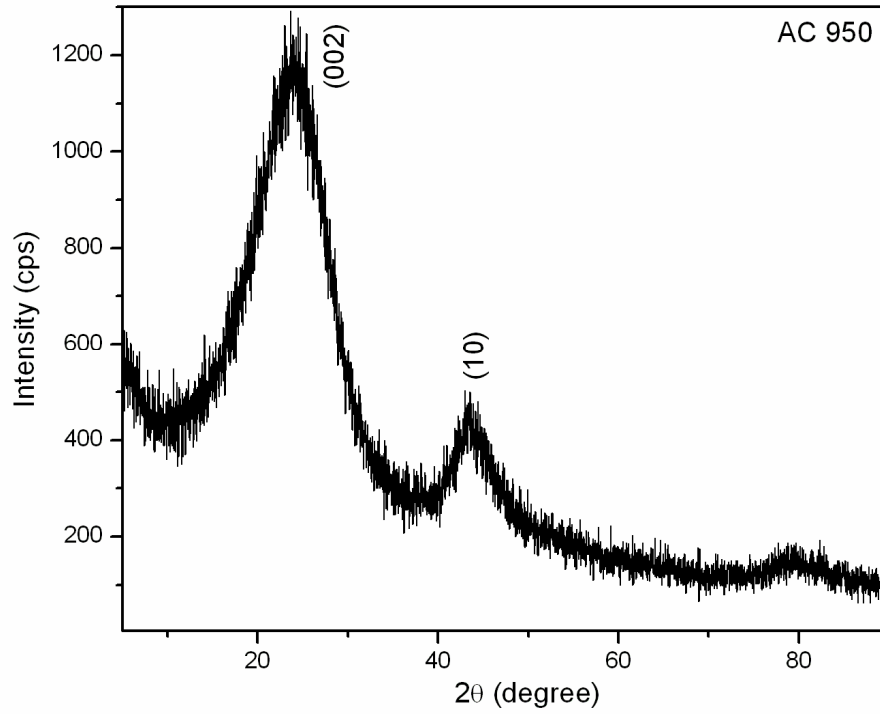
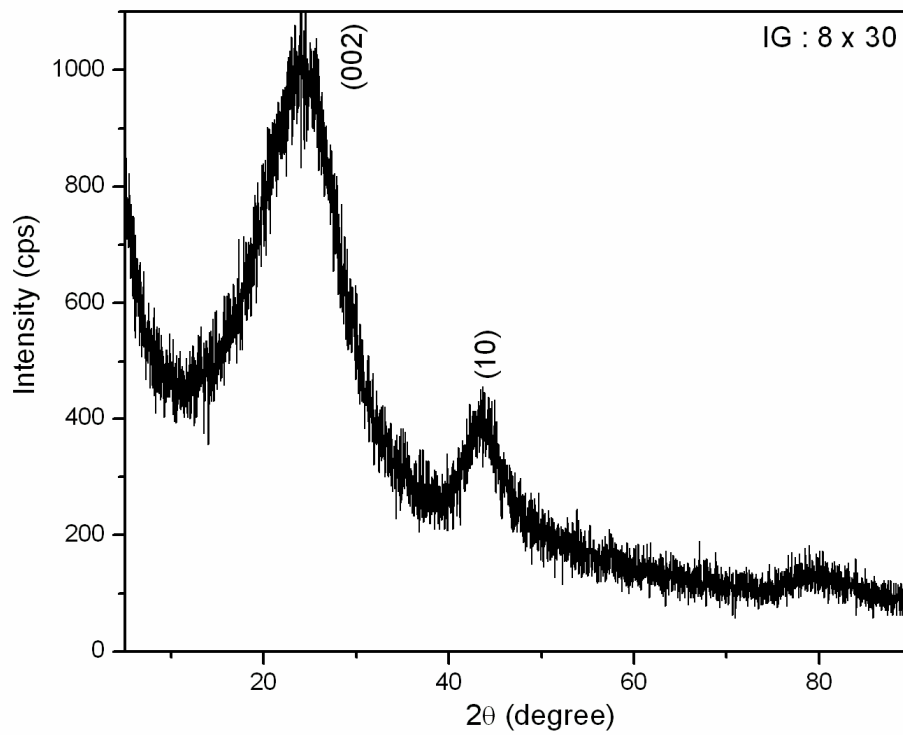**Fig. 3.2.** XRD pattern of activated carbon, AC 950

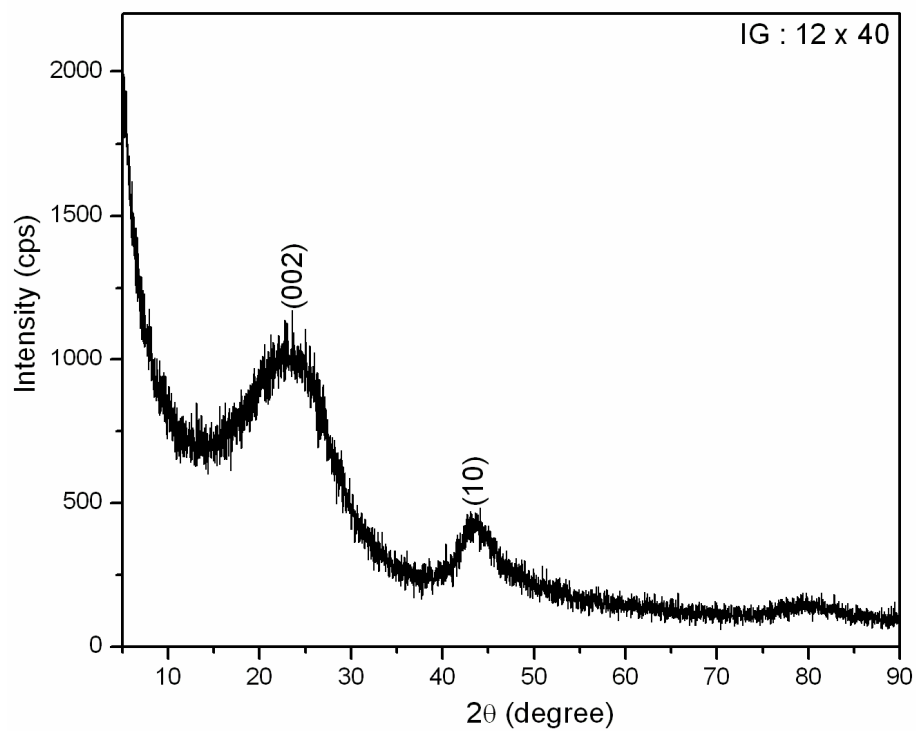**Fig. 3.3.** XRD pattern of activated carbon, IG 8 x 30

22

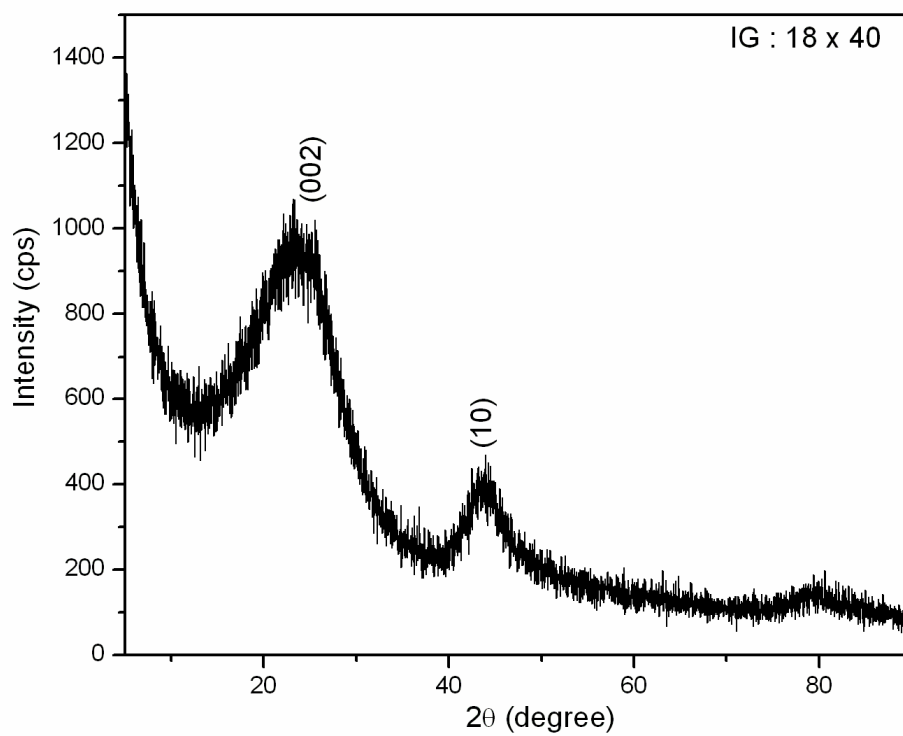**Fig. 3.4.** XRD pattern of activated carbon, IG 12 x 40

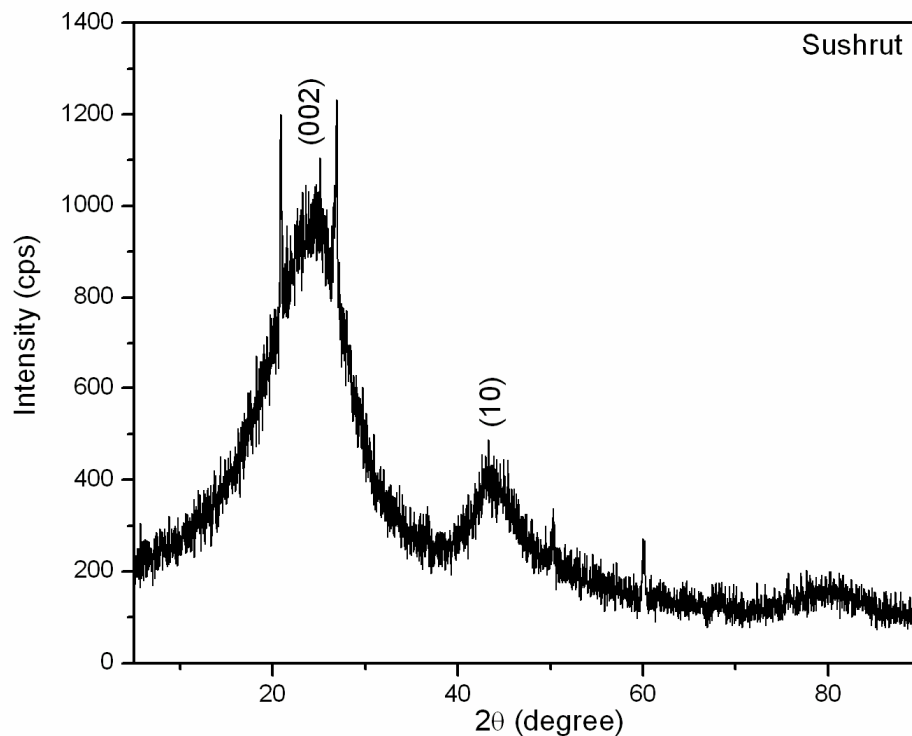**Fig. 3.5.** XRD pattern of activated carbon, IG 18 x 40

Fig. 3.6. XRD pattern of activated carbon, AC 4 x 8 (Sushrut)

3.2. FT-IR analysis

Apart from structural diversity, another unique feature of carbon materials is the richness in surface functional groups. Activated carbon materials do possess a variety of oxygen containing surface functional groups, such as, phenolic, carbonyl, carboxyl and several others which do govern the chemical nature of the carbon surface and do effect the sorption properties of the carbon material. A wealth of information is available in literature related to the carbon surface functionality and a brief account of the assignment of various FT IR bands to specific surface functional groups is given in **Table 3.1.**

Table 3.1. Assignment of FT IR bands to specific surface functional groups

Band position (cm^{-1})	Assignment	Reference
600 – 800	out of plane deformation mode of C-H in various substituted benzene rings	2, 19
1300 – 1000	C-O stretching in acids, alcohols, phenols, ethers and esters	2, 19
1387	in-plane bending vibration of C-H in methyl group	16
1640	carbonyl groups in quinone	2, 19
1749	stretching vibration of C=O bond (aldehydes, ketones, lactones or carboxyl groups)	17, 18
2305	ketone surface groups	22
2855	symmetric C-H stretching vibrations of the methylene group	19, 20, 21
2922	asymmetric C-H stretching vibrations of the methylene group	19, 20, 21
3200-3600	O-H stretching mode of hydroxyl groups and adsorbed water	2
3738	isolated OH groups	2

The FT IR spectra of activated carbon materials, namely, AC 550, AC 950, IG 8 x 30, IG 12 x 40, IG 18 x 40, AC 4 x 8 (Sushrut), were shown in **Figs. 3.7. 3.8. 3.9, 3.10, 3.11** and **3.12.,** respectively. A variety of C-O (carbon oxygen) surface functional groups were observed in all the carbon materials mentioned.
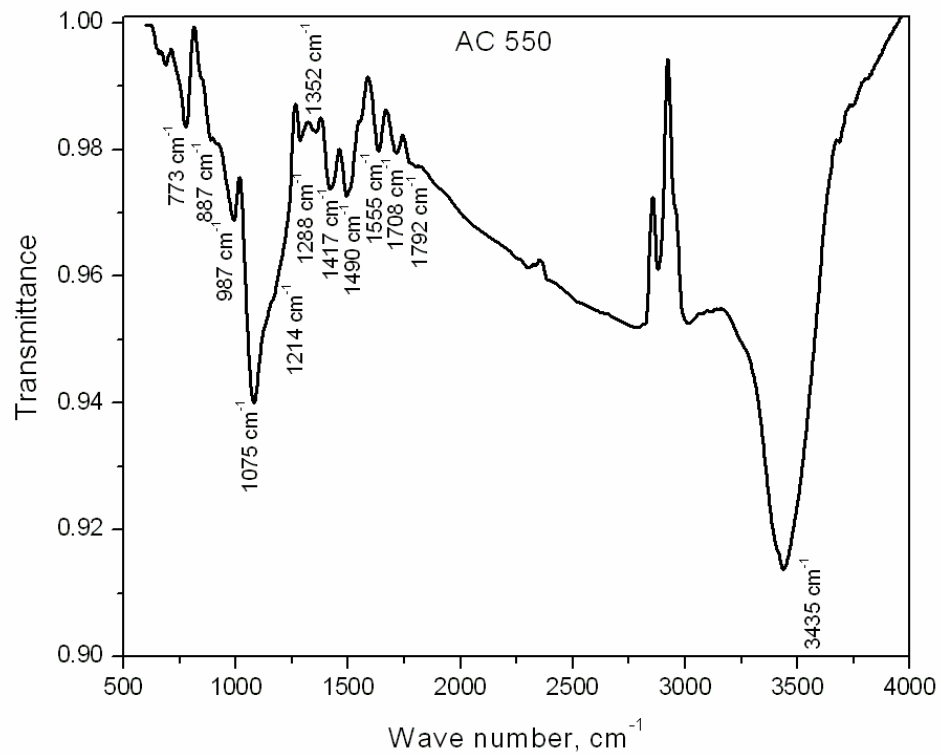
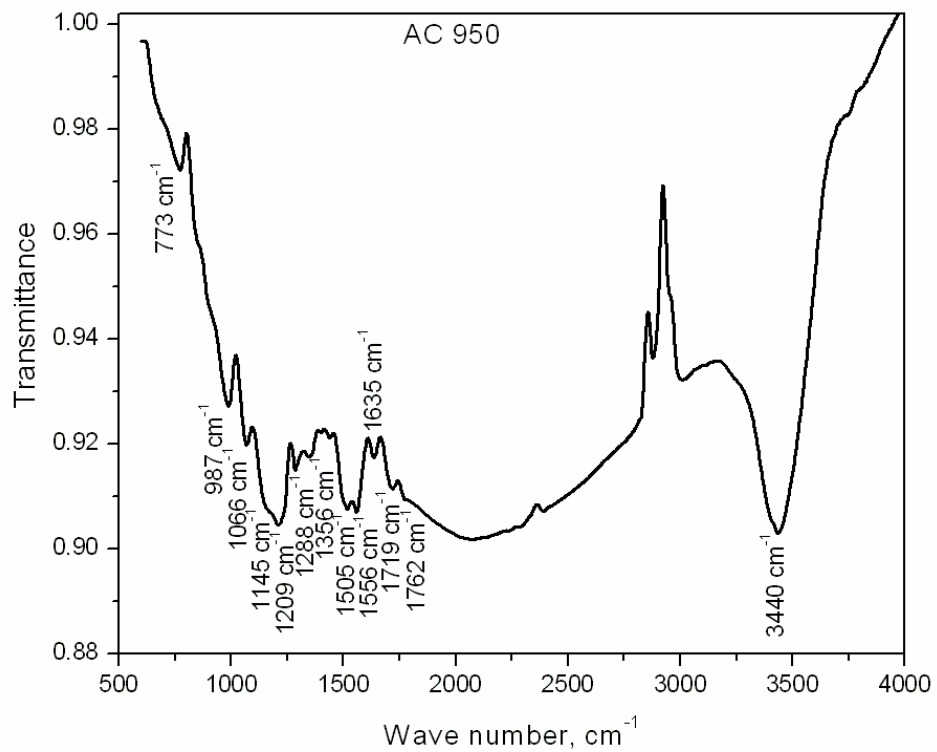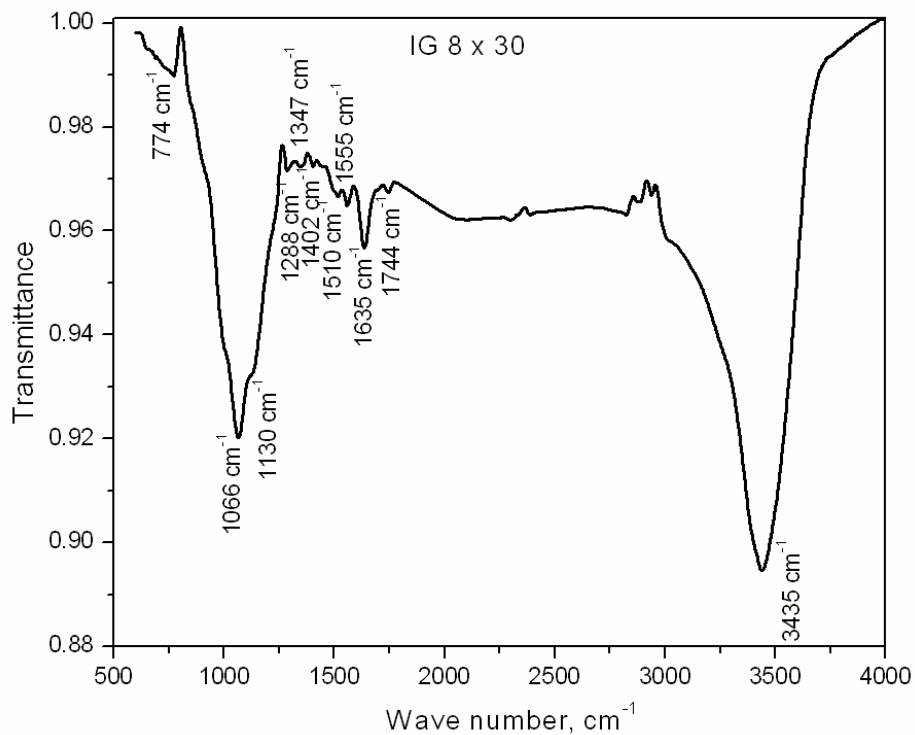**Fig. 3.7.** FT IR spectrum of AC 550

Fig. 3.8. FT IR spectrum of AC 950

Fig. 3.9. FT IR spectrum of IG 8 X 30

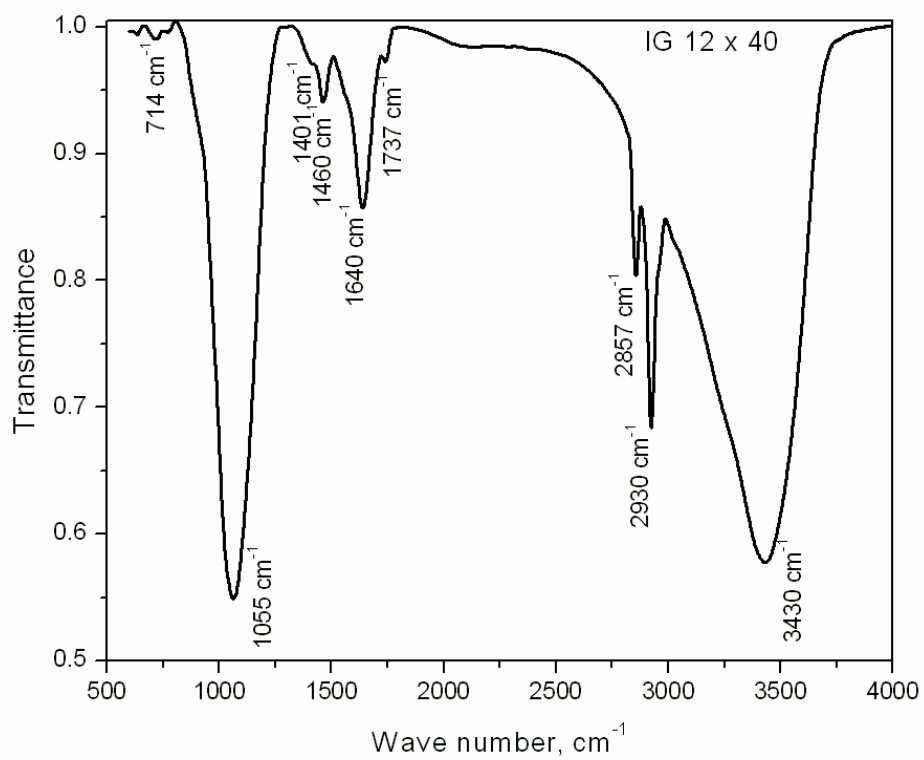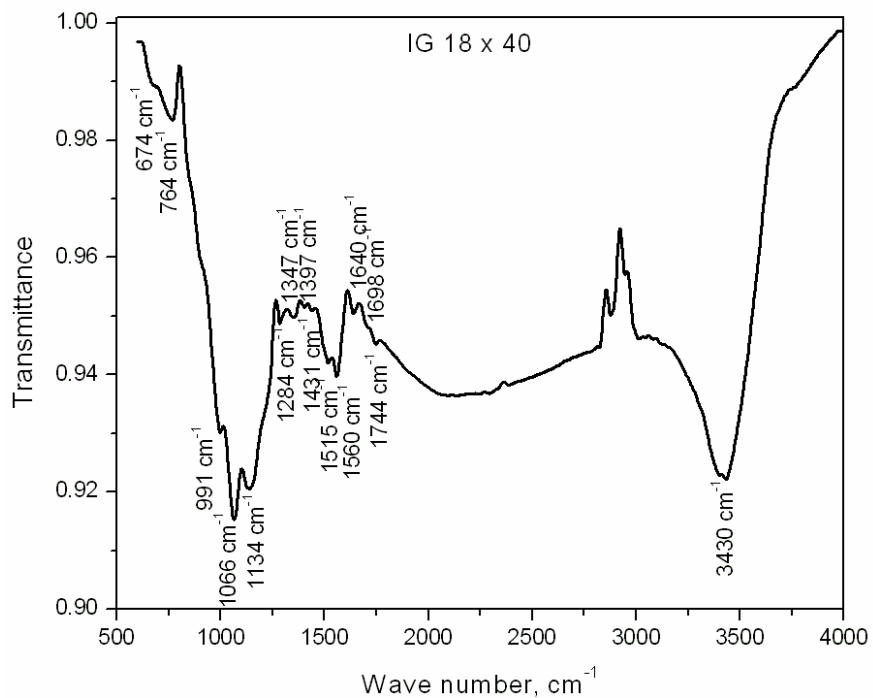**Fig. 3.10.** FT IR spectrum of IG 12 X 40

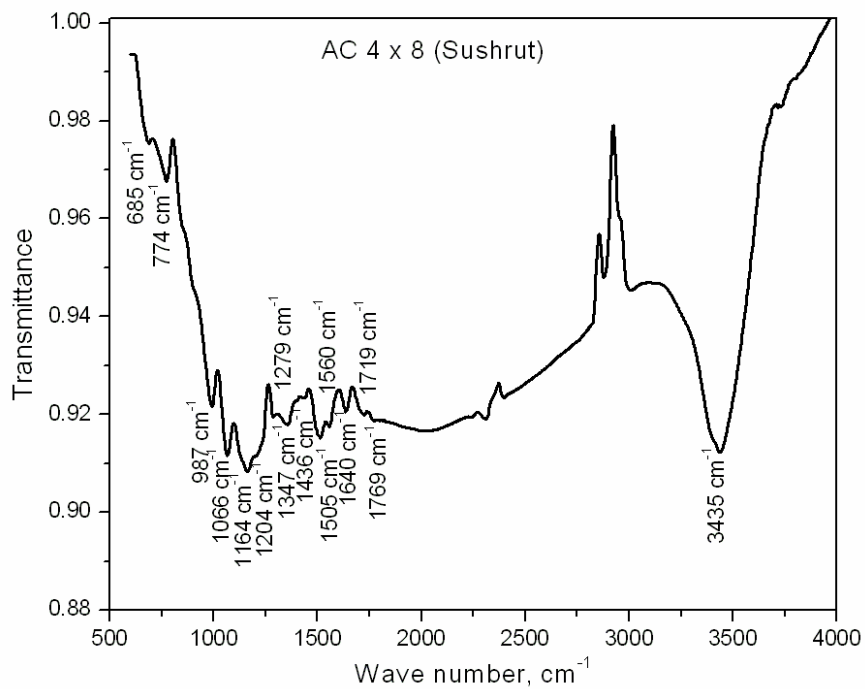**Fig. 3.11.** FT IR spectrum of IG 18 X 40

Fig. 3.12. FT IR spectrum of AC 4 x 8 (Sushrut)

Interestingly the FT-IR spectrum of the activated carbon material, IG 12 x 40 showed significant contrast compared to the FT-IR spectra resulting from other carbon materials. Not only the C-O of phenolic, carbonyl and carboxylic groups were present in the FT IR spectrum of IG 12 x 40, but also the asymmetric and symmetric stretching of C-H stretching vibrations of methylene group were observed. The presence of such methylene groups induces hydrophobicity into the carbon material.

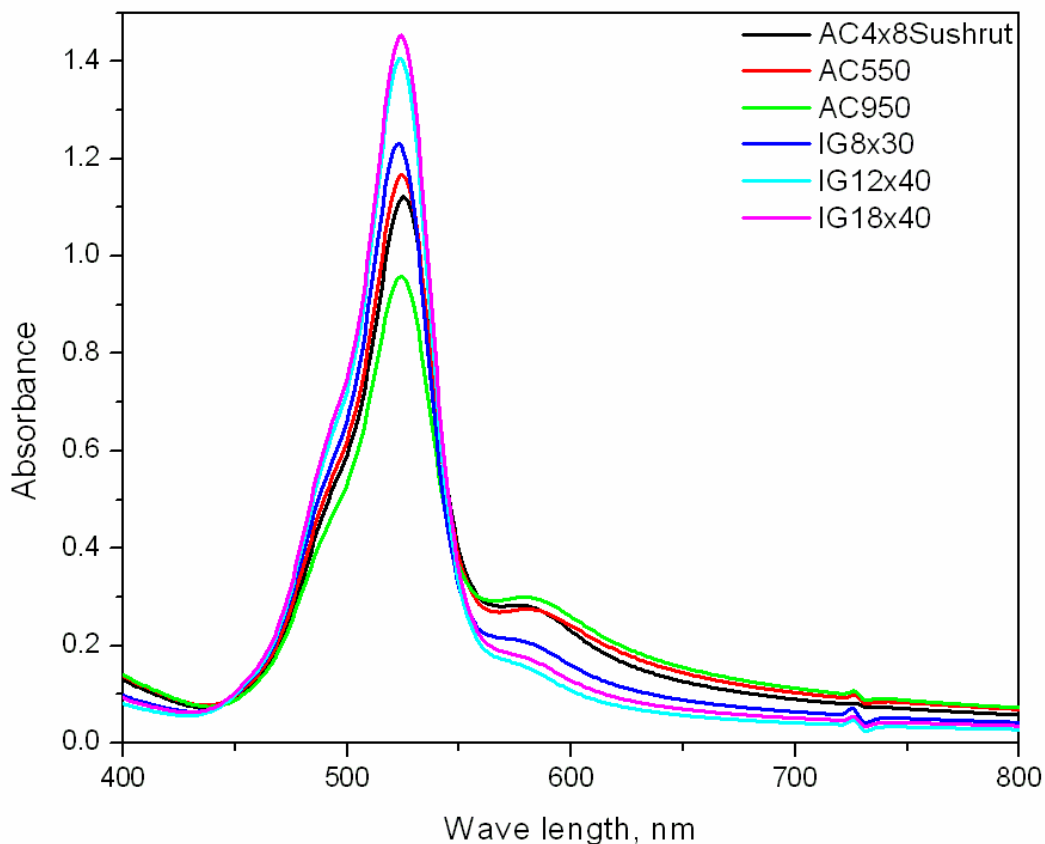## 3.3. Search for Appropriate Sorbent for Hg (II) sorption

Fig. 3.13. Absorption spectra resulting from use of different activated carbon materials as sorbents

The potential of the activated carbon materials, namely, AC 550, AC 950, IG 8 x 30, IG 12 x 40, IG 18 x 40, AC 4 x 8 (Sushrut), has been evaluated for the sorption of mercury. The intensity of the absorption band at 575 nm in Fig. 3.13. is a measure of the amount of Hg (II) remaining in the filtrate with out being adsorbed on the carbon material. The intensity of the absorption band is the lowest for the activated carbon material IG 12 x 40 and highest for the activated carbon material AC 950 indicating that the IG 12 x 40 is the best adsorbent among the carbon materials under evaluation. Thus, after screening several activated carbon materials, IG 12 x 40 was chosen as the adsorbent for mercury for further studies.

The process of adsorption has been optimized by studying thoroughly, the effect of equilibration time, sorbent dose, pH and initial concentration of mercury. The equilibrium adsorption data has been analyzed by both the Freundlich and Langmuir equilibrium adsoption models. The Freundlich and Langmuir constants have been calculated from the respective plots.

3.3.1. Effect of Equilibration Time

The effect of contact time on the removal of Hg (II) from an aqueous solution with an initial concentration of 50 mg/L is evaluated for a period of 6 h and the result is shown in Fig. 3.14. An increase in the removal of Hg (II) with time is noticed and equilibrium has been attained in 1 h of agitation (mechanical shaking).
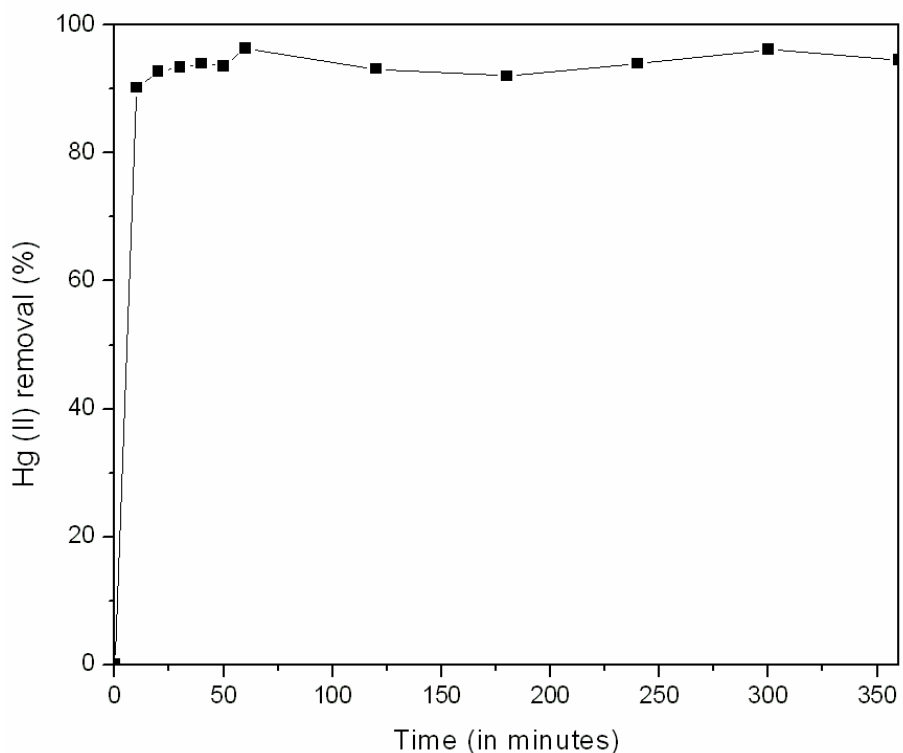
30

Fig. 3.14. Effect of equilibration time on the removal of Hg (II) species from solution

3.3.2. Effect of Sorbent Dose

Adsorbent dosage is a necessary parameter in sorption studies as it determines the sorption capacity of the adsorbent for a given initial concentration of metal ion solution. With an increase in the adsorbent dosage from 50 to 500 mg the percent removal of Hg (II) increased up to ~ 95 % (**Fig. 3.15**). The increase in the percent removal of Hg (II) with an increase in the adsorbent dosage is expected as the number of active sites (surface functional groups) increase with the dosage.
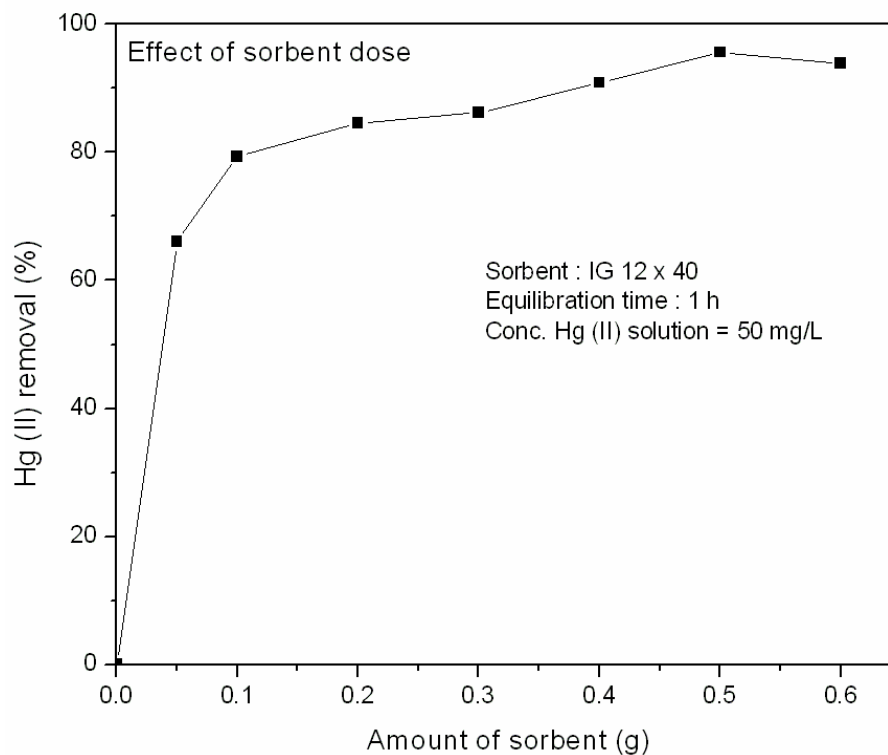
Fig. 3.15. Effect of adsorbent dose for the sorption of Hg (II) onto the activated carbon material, IG 12 x 40, (Initial Hg (II) concentration = 50 mg/L with 10 g/L NaCl; contact time = 1 h)

3.3.3. Effect of pH

To evaluate the most suitable pH for the removal of Hg (II) the sorption studies were carried out at varying pH values in the range from 2 – 9. 100 mL of 50 mg/L Hg(II) with 10 g/L NaCl solutions were taken in polyethylene reagent bottles (250 mL capacity). Dilute solutions of HCl and NaOH were used for adjusting the pH. 0.5 g of the sorbent (IG 12 x 40) was added to each of the 8 reagent bottles. The solutions were equilibrated for 1 h. The contents were filtered after 1 h. The filtrate was tested for the presence of

Hg (II) and the amount of Hg (II) adsorbed was estimated. The optimum pH was found

to be 3.5 where ≈ 97 % Hg (II) is removed.
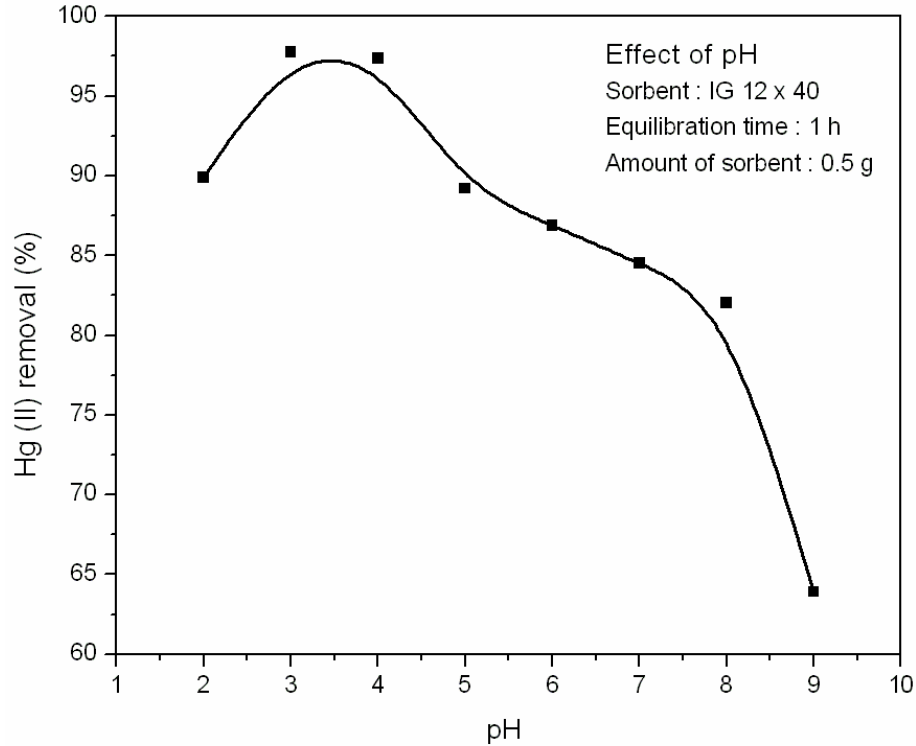
Fig. 3.16. Effect of pH on the removal of Hg (II) using activatead carbon material, IG 12
        x 40, as sorbent (Initial Hg (II) concentration = 50 mg/L with 10 g/L NaCl;
        contact time = 1 h)

3.3.4. Effect of initial metal ion concentration on the sorption of Hg (II)

The effect of initial mercury concentration (10 – 90 mg Hg (II)/L) in the aqueous solution

on the removal of Hg (II) by the activated carbon material, IG 12 x 40, is shown in **Fig.**

3.17. An increase in the removal capacity with an increase in the initial concentration of

Hg (II) is observed.
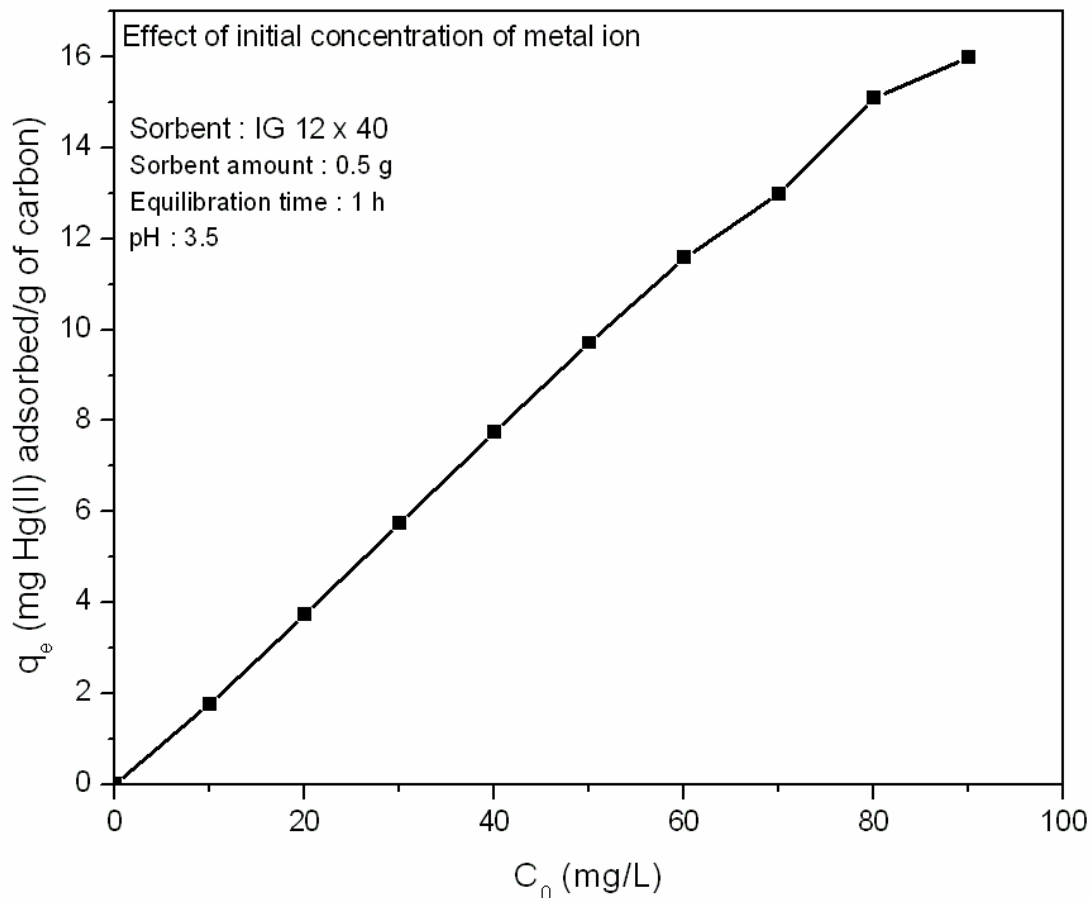
Fig. 3.17. Effect of initial concentration of metal ion on the removal of Hg (II)
(Sorbent : IG 12 x 40; Dose: 0.5 g/100 mL Hg (II) solution; pH = 3.5;
equilibration time – 1 h)

3.3.5. Adsorption isotherm

Adsorption isotherm for the removal of Hg (II) by activated carbon material, IG 12 x 40, was depicted in **Fig. 3.18.** The two most commonly used equilibrium models, namely, Freundlich and Langmuir adsorption models were applied for analyzing and interpreting the equilibrium adsorption data and also to evaluate which model best fits the experimental data.
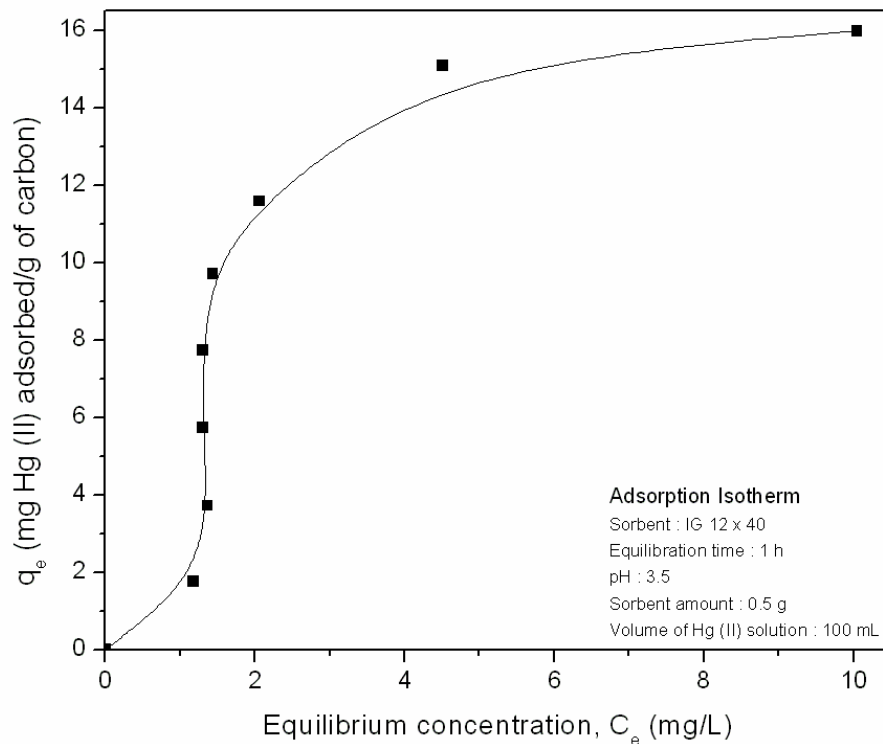
Fig. 3.18. Adsorption isotherm of Hg (II) sorption (Sorbent : IG 12 x 40; sorbent dose: 0.5 g/100 mL Hg (II) solution; pH = 3.5; equilibration time :1 h)

Freundlich isotherm is the most widely used non-linear sorption model and is given by the general equation:

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

where K_F and n are the Freundlich constants related to the sorption capacity $(mg^{1-1/n}L^{1/n}\,g^{-1})$ and n to the sorption intensity respectively.   Thus higher values of K_F indicate higher adsorption capacity. q_e is the amount of the adsorbate adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration of the adsorbate is solution (mg/L).

The logarithmic form of the above equation is generally used to fit the data from batch equilibrium studies.

The logarithmic form of Freundich equation is shown below:

$\log q_e = \log K_F + 1/n \; \log C_e$

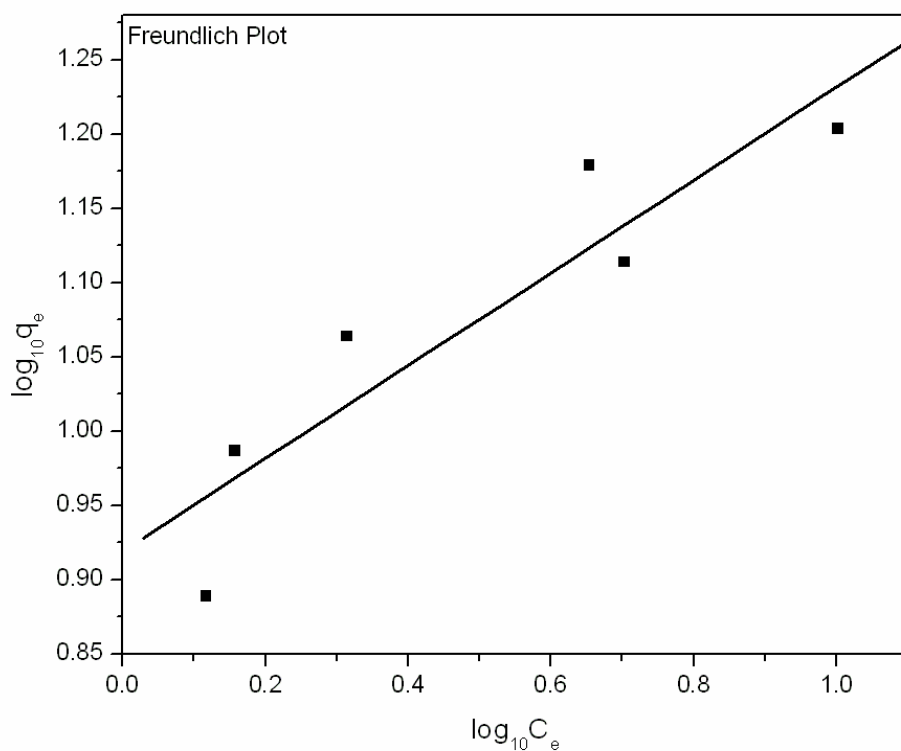A plot of $\log q_e$ Vs $\log C_e$ is shown in **Fig. 3.19**.

Fig. 3.19. Freundlich plot of mercury (II) adsorption

A straight line indicates that the adsorption follows Freundlich isotherm model and the equilibrium data were fitted well by the Freundlich isotherm model. The Freundlich constants, K_F and $1/n$, were calculated from the intercept and slope of the plot of $\log q_e$ Vs

logC$_e$.   High value of correlation factor close to 1 (R = 0.9161) indicate that the adsorption follows Freundlich isotherm model perfectly.   The K$_F$ and 1/n values were 8.3 and 0.31 respectively.

The Langmuir isotherm is given by the following equation:

$q_e = q_m b C_e /(1 + bC_e)$

where q$_m$ and b are the Langmuir constants related to the adsorption capacity and the energy of adsorption respectively.   q$_m$ is the maximum adsorption capacity of the adsorbent corresponding to the complete monolayer coverage (mg/g).   'b' is the adsorption coefficient and is a measure of the energy of adsorption (L/mg).   C$_e$ is the equilibrium metal ion concentration in solution (mg/L) and q$_e$ is the amount of Hg (II) adsorbed at equilibrium on the sorbent surface (mg/g).

The linear form of Langmuir equation is shown below:

$C_e/q_e = C_e/q_m + 1/bq_m$

The above equation is used to analyze the batch equilibrium adsorption data.   The values of q$_m$ and b were determined from the slope and the intercept of the plot of C$_e$/q$_e$ Vs C$_e$ as shown in **Fig. 3.20.**   A good representation of the Langmuir's dependence is observed. The high value of the correlation coefficient close to 1 (R = 0.9929) suggests that the experimental data can be represented by the Langmuir sorption model.   From the correlation coefficient values and the Freundlich and Langmuir plots, it can be concluded that the fit is better with Langmuir model (R = 0.9929) rather than with Langmuir model (R = 0.9196).   The values q$_m$ and b deduced from Langmuir plots are 18.87 mg/g and 0.67.
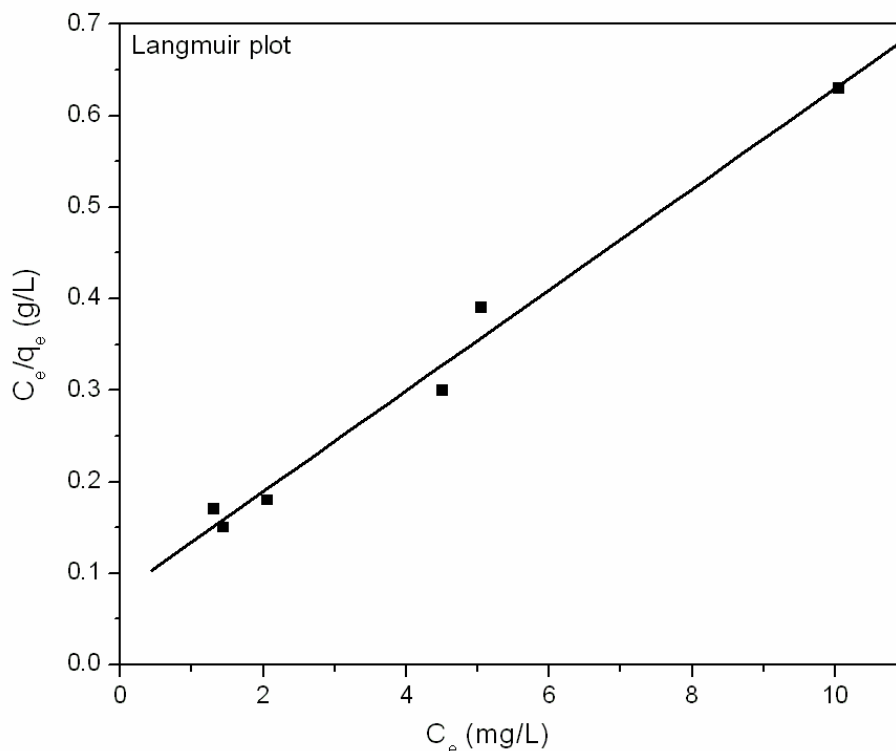
Fig. 3.20. Langmuir plot of mercury (II) adsorption

For Langmuir type adsorption process, a dimensionless separation factor is defined to determine if the adsorption is favourable or not. The essential features of the Langmuir isotherm can be expressed in terms of R_L. R_L is an equilibrium parameter defined as follows: $R_L = 1/(1+bC_0)$, where C_0 is the initial metal ion concentration (mg/L) and b is the Langmuir constant (L/mg). This type of isotherm is said to be unfavourable, linear, favourable and irreversible if the values of R_L are respectively as follows: $R_L > 1$, $R_L = 1$, $0 < R_L < 1$ and $R_L = 0$. In the case of the activated carbon material, IG 12 x 40, the value of R_L is 0.13 (for $C_0 = 10$ mg/L) ($0 < R_L < 1$) indicating that the isotherm (adsorption process) is favourable on the adsorbent developed for Hg (II) sorption. Thus, the equilibrium adsorption data fitted well with both Freundlich and Langmuir adsorption models.

CHAPTER – 4

SUMMARY AND CONCLUSION

1. Activated carbon materials, namely, AC 550, AC 950, IG 8 x 30, IG 12 x 40, IG 18 x 40, AC 4 x 8 (Sushrut), have been characterized by XRD and FT IR spectroscopy to know their physcochemical characteristics.

2. AC 550 possesses graphitic carbon structure where as the other activated carbon materials exhibited turbostratic carbon structure.

3. A variety of C-O (carbon-oxygen) surface functional groups have been observed on the surface of the activated carbon materials. The features offered by the activated carbon material, IG 12 x 40, were distinctly different from those exhibited by all other carbon materials under the study. In addition to carbon-oxygen functional groups like, phenolic, carbonyl and carboxylic, hydrophobic groups like methylene groups were present on the surface of IG 12 x 40 carbon material.

4. The carbon materials, namely, AC 550, AC 950, IG 8 x 30, IG 12 x 40, IG 18 x 40, AC 4 x 8 (Sushrut), have been evaluated for their ability to adsorb Hg (II) species from water and the carbon material IG 12 x 40 was found to be the best.

5. The adsorption process parameters, like, the pH, equilibration time, sorbent dose and initial concentration of the metal ion have been evaluated.

6. The optimum values of equilibration time, sorbent dose and pH were found to be 1 hour, 0.5 g/100 mL and 3.5 respectively.

7. The equilibrium adsorption data has been analyzed by using Freundlich and Langmuir isotherm models and the experimental data fitted well with both the models.

8. The values of Freundlich and Langmuir constants were found to be K_F = 8.3 ; 1/n = 0.31; q_m = 18.87 mg/g and b = 0.67. The adsorption capacity of the activated carbon material, IG 12 x 40 (18.87 mg/g) is found to be greater than that of either fullers earth clay (q_m = 1.145 mg/g; b = 0.359) [23] or used tyre rubber (q_m = 14.6 mg/g; b = 4.71) [24].

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