CHAPTER – 1

GENERAL INTRODUCTION

1.1 Activated Carbons

Activated carbons are excellent and versatile adsorbents because of their high interparticulate surface area, a high degree of microporosity and a high degree of surface chemical reactivity. Consequently they are extensively used for purification, detoxification, decolourisation, dechlorination and deodorization of substances. They are also being considered as potential materials for the removal of organic and inorganic compounds from industrial waste water and for purification of drinking water.

Activated carbons can be prepared from a variety of raw materials such as wood, peat and waste vegetable products such as coconut shell, fruit stones, saw dust. More recently, however they are also being prepared using various forms of natural coal. The preparation of activated carbons involves two main steps namely the carbonisation of the carbonaceous material at temperatures between 800-900°C in an inert atmosphere and the activation of the carbonized product. Thus almost all carbonaceous materials can be used to prepare activated carbons. However, the adsorbent properties of the final product are determined by the source raw material, the nature of the activating agent and the history of their preparation.

The carbonisation of the source raw material results in the elimination of non-carbon elements as volatile gaseous products while the residual elementary carbon atoms are grouped into stacks of irregular aromatic sheets cross-linked in a random fashion. This arrangement of irregular aromatic sheets leaves interstices which are called pores. The chars obtained after carbonisations do not have a well developed porous structure because the pores are filled with tarry matter and disorganized carbon. The activation process which involves heating the char in the presence of oxidizing gases such as oxygen, CO$_2$, air or steam results in the oxidation of some of the regions within the char in preference to others so that as combustion proceeds, a preferential burning of the char occurs resulting in the development of a large internal surface area which in some cases may be as large as 2000 m$^2$/g.
The pores in activated carbons have been classified into three groups depending upon their width which represents the distance between the walls of slit shaped pore or the radius of a cylindrical pore. The micropores have a diameter less than 2 nm and contribute to about 95% of the total surface area and pore volume while the mesopores which have diameters between 2-50 nm contribute to only about 5% of the total surface area of an activated carbon. The micropores are filled at low relative vapour pressures while the mesopores are filled at higher relative pressures. The third type of pores which are known as the macropores do not contribute much towards the surface area and are not of considerable importance to the adsorption process in activated carbons. They merely act as conduits for the passage of the adsorbate molecules into the micro and mesopores.

Activated carbon surface has two types of structures. The porous structure which involves the surface area, microporosity and the pore size distribution which determines the adsorption capacity and a chemical structure which strongly influence the adsorption capacity. The random ordering of the aromatic sheets in activated carbon causes a variation in the arrangement of electron clouds in the carbon skeleton and results in the creation of unpaired electrons and unsaturated valencies which undoubtedly influence the adsorption characteristics and adsorption behaviour of these materials.

The chemical structure of an activated carbon surface is due to the presence of associated oxygen and hydrogen which are invariably present on a carbon surface. The oxygen and hydrogen is derived from the source raw material and becomes a part of the chemical structure of the carbon surface as a result of imperfect carbonization or they become chemically bonded to the surface during the activation process. These oxygen and hydrogen atoms are bonded at the edges and dislocations of the aromatic sheets or to carbon atoms at defect positions in the form of carbon-oxygen and carbon-hydrogen surface groups. As these edges of the activated carbon surface constitute the main adsorbing surface, it is little wonder that these surface groups would influence the adsorption properties of activated carbons.

Carbon-oxygen surface groups are by far the most important in influencing the adsorption characteristics of activated carbons. In fact, these surface groups have often been found to be the source of the property by which an activated carbon becomes useful or effective in certain respects. Although the determination of the number and
nature of these surface groups began more than half a century ago, the precise nature of the surface groups is not yet entirely established. The identification and estimation of these carbon-oxygen surface groups has been carried out using several physical, chemical and physico-chemical techniques such as neutralization with alkalis (1-20), high temperature evacuations (21-31) potentiometric titrations, spectroscopic methods such as IR spectroscopy (32-38) X-ray photoelectron spectroscopy (39-48) FTIR spectroscopy (49-53). Although these investigations have postulated the existence of such functional groups as carboxyls (54), lactones (9,55), phenols and quinones (56, 57) but these investigations have not yielded comparable results because the activated carbon surface is very complex and difficult to reproduce.

1.2 Adsorption

When a solid is brought into contact with a gas, a vapour or a solution, there is excess concentration of the gas or the vapour or the solute on the interface of the solid than in the bulk phase. This process of excess concentration on the interface is called adsorption. The solid surface in this case is called the adsorbent while the bulk phase is called the adsorbate. The adsorption arises either from a weak interaction between the adsorbent and the adsorbate as in the case of simple condensation of a gas or from a strong interaction as in the case of a chemical reaction. The phenomenon in the first case is called physical adsorption or van der walls adsorption since the forces involved are the same as the van der walls forces as in the case of the condensation of a gas or a vapour. The second type of adsorption occurs on account of exchange or sharing of electrons between the adsorbent and the adsorbate and the forces involved are valency or chemical forces and therefore, is known as chemisorption. Physical adsorption is non-specific and in general occurs between all adsorbents and all adsorbates while chemisorption is specific in nature and occurs only when the adsorbate can enter into some sort of chemical combination with the adsorbent. Physical adsorption is reversible while the chemisorption is irreversible. In physical adsorption the adsorbate molecules may form a monolayer or a multilayer depending upon the conditions of temperature and pressure. In chemisorption, however, the adsorption layer is only one molecule thick since the adsorbate molecules are linked to the adsorbent surface by valency bonds. The most important distinction between physical adsorption and chemisorption is that while in the former case, the enthalpy change (heat of adsorption) is of the same
order of magnitude as the enthalpy of the condensation, in the latter case, the enthalpy change is much higher and is of the same order as that in a chemical reaction.

1.3 Adsorption Isotherms

Adsorption equilibrium is generally expressed in the form of an adsorption isotherm which is a relationship between the amount adsorbed and the pressure or the concentration of the solute at a given temperature. It gives useful information about the adsorption process and helps in the determination of surface area of the adsorbate and the volume of pores and their size distribution and the magnitude of the heat of adsorption.

Several adsorption isotherms have been derived to express the adsorption equilibrium and have been used by different workers to express their adsorption data. The more important of these adsorption isotherms are the Langmuir isotherm, the Freundlich isotherm, the Brunauer – Emmett – Teller equation (BET equation) and the Polanyi potential theory and the Dubinin equation.

1.3.1 Langmuir Adsorption Isotherm

Langmuir equation is the first adsorption isotherm developed theoretically. Many of the equations proposed later which fit the experimental results much better or over a wide range, are either based on the Langmuir equation or the concepts used in the derivation of Langmuir’s equation are used in their development. The Langmuir equation still retains its key position to explain both physical and chemisorptions processes.

The Langmuir equation in its simple form is written as

$$V = V_m \frac{kP}{1 + kP}$$

where $V$ is the volume of a gas or vapour adsorbed at pressure $P$ of the gaseous adsorbate and $V_m$ is the volume needed for a monomolecular coverage. By rearrangement the above equation can be written as:

$$\frac{P}{V} = \frac{1}{V_m k} + \frac{P}{V_m}$$
which is the expression more often used for verifying the applicability of the equation in a particular case. The linear plot between \( P/V \) and \( P \) also helps calculation of \( V_m \).

Langmuir equation however, many a times does not show linearity in \( P/V \) versus \( P \) plots because the surface of the solid may not be completely uniform. Consequently, the isotherm has limited application to explain experimental results. However, still it remains of basic importance for expressing adsorption equilibria on dynamical principles. Of special significance is the calculation of \( V_m \) which helps to determine the surface area of the solid adsorbent.

1.3.2 Freundlich Adsorption Isotherm

According to this isotherm the volume, \( V \), of an adsorbate adsorbed at a pressure, \( P \), is given by the equation.

\[
V = kP^n \quad \text{or} \quad V = KP^n
\]

where \( k \) is a constant, the value of which depends on the temperature and specific surface area of the adsorbent, and \( n \) is a constant which depends on the temperature and has a value always greater or lesser than unity depending on which equation has been used. The applicability of the isotherm equation is tested in its linear form.

\[
\log V = \log k + \frac{1}{n} \log P
\]

which gives a linear plot between \( \log V \) and \( \log P \). The values of \( k \) and \( n \) can be calculated from the linear plot. However, the equation has a limited application and is of greater significance for chemisorption. It has also been widely applied for adsorption from solutions.

1.3.3 BET equation

The derivation of the equation is based on the extension of the Langmuir concept to multimolecular adsorption (58,59). The equation is derived on the assumption that the forces acting in multimolecular adsorption are the same as involved in the condensation of vapours. Only the first layer of adsorbed molecules, which is in direct contact with the surface, is bound by adsorption forces originating from the
interaction between the adsorbent and adsorbate. As these forces are short range, the second and further adsorbed layers are not influenced by them so that the molecules in this second and successive layer have the same properties as in the liquid state. The heat of adsorption for the second and higher layers is thus constant and equal to the heat of condensation of the adsorbate. Based on these assumptions Brunauer, Emmett and Teller derived the equation for multimolecular adsorption as:

\[
\frac{P}{V(P^\circ - P)} = \frac{1}{V_n C} \left[ \frac{C - 1}{V_n C} \right] \frac{P}{P^\circ}
\]

where \( V \) is the volume of the adsorbate adsorbed at pressure \( p \) and \( V_m \) is the volume of the adsorbate required to form a unimolecular layer, \( P/P^\circ \) is the relative vapour pressure and the constant \( C \) is given by:

\[
C = \text{Exp} \left( \frac{(E_1 - E_L)}{RT} \right)
\]

where \( E_1 \) is the heat of adsorption in the first layer and \( E_L \) is the heat of condensation of the adsorbate.

A plot of \( P/V \) \( (P^\circ-P) \) against \( P/P^\circ \) gives a straight line. The slope and intercept of which can be used to calculate the value of \( V_m \) and \( C \). The isotherms are, however, linear in a limited range of relative vapour pressures from 0.05 to 0.35. At lower pressure the equation is usually not valid because the effect of the energetic heterogeneity of the surface makes itself felt and at higher pressures, it looses its validity because of the combination of physical adsorption and capillary condensation, and because of the limitation of the heat of adsorption in the first and higher layers not being the same. Cases, however, are known where the validity of the BET equation is displaced towards considerably lower pressure.

### 1.3.4 Potential Theory of Adsorption and Dubinin’s Equation

The potential theory of adsorption which is primarily developed for microporous adsorbents is based on the assumption that the molecules of a gas at the surface of the solid are compressed by the forces of attraction acting from the surface to a certain distance into the surrounding space. The quantitative formulation of this theory has been carried out by Polanyi and Dubinin and coworkers (60-64). Polanyi characterized the field of the forces of attraction of the adsorbent surface by the adsorption potential, defined as the work done by the surface adsorption forces in...
transferring the molecules from the gaseous phase to the given point. For an ideal, energetically homogenous and plain surface, all the points at any particular distance from the surface will have the same potential and will, therefore, form an equipotential plane. The magnitude of the adsorption potential of the parallel equipotential planes decreases as their distance from the surface increases until it falls to zero. Each equipotential surface encloses between itself and the surface of the adsorbent a volume $W_i$ called adsorption volume. The maximum volume $W_0$ enclosed by the adsorbent surface and the limiting equipotential plane at which the potential has decreased to zero is called total adsorption space of the given surface. On the surface of the solid $W = 0$ and the adsorption potential is maximum. The adsorption potential $\varepsilon$ is given by the expression.

$$\varepsilon = RT \ln \frac{P^o}{P}$$

where $P^o$ is the saturation vapour pressure and $P$ is the equilibrium vapour pressure.

The dependence of $W$ on $\varepsilon$ has led to the development of an equation of the adsorption isotherm on active carbon which is known as the Dubinin equation (61). In its present formulation the theory of micropore volume filling is expressed by the equation of Dubinin and Astakhov (61,62).

$$W = W_0 \exp \left[ \left( -\frac{A}{\beta E_0} \right)^n \right]$$

where $W$ represents the volume filled at temperature $T$ and relative pressure $P/P^o$, $W_0$ is the total volume of the micropores. The quantity $A = RT \ln P/P^o$ and $n, E_0$ and $\beta$ are specific parameters of the system under investigation.

The DA (Dubinin – Astakhov) equation is applicable to the adsorption of a variety of organic vapours at relative pressure $P/P^o < 0.05 – 0.1$ where the influence of nonmicroporous surface area is negligible. For typical active carbons $n=2$ which corresponds to the original empirical equation postulated by Dubinin and Radushkevich (63,64) known in the literature as DR equation. The DR equation has been used to describe the adsorption of organic compounds (65) and of iodine (66) from aqueous solutions. For such systems pressures are replaced by concentration.
1.4 Removal of Inorganic and Organic pollutants from water

Availability of safe drinking water in most developed countries and in big cities has become a big problem. First of all this concerns large urban agglomerations of highly industrialized countries where the demand for municipal water supply is very large and where there is heavy concentration of industry. Liquid waste from chemical and other industry together with municipal sewerage constitute a huge amount of polluted water. The increasing use of chemicals in agriculture and other day to day life also brings about a continuous increase in the concentration of impurities in the source of water supplying urban water lines. This continuously increasing variety and amount of hazardous pollutants present in our lakes, rivers and sometimes also in underground water reservoirs makes the conventional methods of water purification insufficient and many times, ineffective. Consequently attempts have always been directed to develop adsorbents for the removal of these pollutants. Activated carbon, due to its large surface area, high adsorption capacity and a high degree of surface reactivity appears to have a high potential for the removal of organics and inorganics from water. Furthermore, activated carbons can be obtained in various forms such as powder form, granulated form and now in the fibrous and fabric form. The activated carbon surface can also be modified by certain post preparation treatments to treat a particular industry waste water.

Powdered activated carbons generally have a finer particle size of about 40 μm and, therefore, the adsorption takes place at a faster rate but they are difficult to handle when used in fixed beds. They can choke the bed resulting in a high pressure drop. The powdered activated carbons are also difficult to regenerate in the bed. The granulated activated carbons have larger granule size varying between 0.6 to 4.0 mm and are generally hard, abrasion resistant and relatively dense to withstand operating conditions. Granulated carbons although more expensive than the powdered carbons, they do not cause choking in the bed and can be regenerated and used again. The granulated carbons can be made into a capsule which serves as the fixed bed and can be removed after saturation and regenerated by heat treatment in steam to desorb the pollutants. The fibrous activated carbons are more expensive than the powdered or
granulated carbons but they can be moulded into the shape of the adsorption system and do not produce resistance to flow.

The adsorption capacity of an activated carbon depends on the surface, the pore volume and the pore size distribution in the activated carbon. However, the adsorption capacity is strongly influenced by the surface chemistry of the carbon. Most of the activated carbons are hydrophobic in nature and are associated with only small amounts of non-acidic surface oxygen groups and are non-polar in character. These activated carbons can be used for the removal of non-polar or neutral organic compounds. The activated carbon surface, however, can be modified by suitable surface treatments to make it polar and suitable for the adsorptive removal of polar and cationic pollutants from water.

More than 1000 specific organic and inorganic chemical compounds have been identified in surface and ground waters. These chemical compounds include phenols, dyes, haloforms, polyaromatic hydrocarbons, surfactants, pesticides, nitro compounds, amines, organic sulphur compounds and inorganic metal cations. Many of these chemical compounds are carcinogenic and cause several ailments and interfere with many body processes. Thus a considerable amount of research effort has been directed towards removing these organic and inorganic pollutants from water using activated carbons. A huge amount of literature is available on the organic and inorganic compounds from aqueous solutions and it is difficult to review the whole literature in the thesis. More attention has therefore been paid to the organic and inorganic compounds studied in the thesis and to more recent literature.

1.4.1 Removal of Inorganics from water

Petrov et al (67) studied the adsorptive removal of zinc, copper and lead cations from aqueous solutions using oxidized anthracite. The metal cation uptake increased with increasing pH of the solution. The individual cations, however, competed with each other for the same active sites which resulted in a decrease in the adsorption of a particular cation when others were present.

Naganuma et al (68) investigated the adsorption of Cu and Zn on topical peat soils as a function of pH while Saito (69) used activated carbon and sulphonated coal to remove copper, cadmium and iron from waste water. Rivera-Utrilla and Ferro-Garcia (70) studied the adsorption of Na⁺, Cs⁺, Ag⁺, Sr²⁺ and Co²⁺ on activated carbons.
associated with carbon-oxygen and carbon-nitrogen surface groups. Na+ and Cs+ ions were adsorbed strongly by carbons containing acidic surface groups while Ag+, Sr2+ and Co2+ were adsorbed by carbons associated with acidic as well as basic surface groups. Corapcioglu and Huang (71), however, observed that the solution pH, the surface loading of the carbon and the nature of the carbon surface influenced the adsorption of metal cations. Andreev et al (72) examined the adsorption of Cu, Zn, Pb, Fe, Cd, Ni, Co, Mn, Ag and Cr on several samples of carbon fibres and ion exchangers while Mathur et al (73) investigated the removal of many of these metal ions from sewer water by adsorption on fly ash and blast furnace slag. These adsorbents were found to remove appreciable amounts of the cations. The adsorption of Hg (II), Cd (II) ions was studied by several workers (74-76) using modified granular activated carbons. The carbons obtained by treatment of rice husk with concentrated H2SO4 could remove significant amounts of these metal ions in the pH range 2 – 7.

Shirakashi et al (77), Huang and Blankenship (78) Ma et al (79) and Ranganathan (80) studied the adsorptive removal of Hg(II) ions from aqueous solutions in the presence of several chelating agents such as EDTA and Peptone and found that the adsorption was decreased due to the formation of complexes. Tonini et al (81) and Muthukumaran et al (82) investigated the removal of Hg(II) ions from chloralkali waste waters using sulphur impregnated and chemically modified activated carbons and found that effluent Hg levels of 100 µg/kg could be obtained. Activated carbons prepared from several waste materials such as coir pith (83), wood and Cashew nut shell (84), tamarind nuts (85, 86), Coconut oil cake (87), organic sewerage sludge (88) and furfural (89) have been used for the removal of Hg(II) ions at different pH values, metal ion concentration and adsorbent dose. These activated carbons were found to be quite effective for the removal of Hg(II) from industrial waste water. Starvin and Rao (90), used several functionalized activated carbons for the removal of Hg(II) ions from effluents of chloralkali plants. Rangel – Mandez and Streat (91) compared the adsorption of Hg(II) ions by activated carbon with ion-exchange resins and a bioadsorbent. The activated carbon was found to be a better adsorbent. The removal of mercury involved the reduction of Hg(II) into Hg(I) as the controlling reaction mechanism on the carbon surface.

Jayson et al (92) used an activated carbon cloth for the removal of Hg(II) ions in the pH range 2.6 – 5.5. The adsorption capacity of the carbon cloth increased as the pH
of the solution was enhanced from 3 - 5.5. The calculation of surface area covered by Hg(II) ions showed that the adsorption occurred as hydrated Hg(II) ions. Gomez-Serrano et al (93) compared the adsorption of Hg(II) ions by a sulphurised activated carbon with the activated carbon degassed in nitrogen at 900°C in the pH range 2 - 5 and observed that the adsorption was increased by both the treatments. The adsorption was attributed to involve adsorbate – adsorbent interaction.

Rangel-Mendez and Streat (94) has reported the adsorption of Hg(II) ions from aqueous solutions of HgCl₂ on commercial activated carbon after electrochemical oxidation. These workers suggested that the adsorption involved the cations such as Hg²⁺, HgCl⁻ and Hg(OH)⁺ and partly reduction of HgCl₂ to Hg₂Cl₂ by the phenolic and quinonic groups present on the carbon surface. Namasivayam and coworkers (95, 96) studied the adsorption of Hg(II) ions on several activated carbons and observed that the adsorption increased with solution pH from 2 - 5 and remained almost constant at higher pH values. Ammons et al (97), while studying the adsorption of methyl mercuric chloride on Filtrasorb 200 activated carbon from aqueous solutions found that the adsorption did not fit either the Freundlich or the Langmuir isotherm equations. Carrott et al (98) carried out adsorptive removal of Hg(II) ions on several activated carbons associated with acidic and basic surface groups and found that significant amounts of HgCl₃ and HgCl₄²⁻ were adsorbed while there was little adsorption of neutral HgCl₂ or Hg²⁺ ions.

Leyva-Ramos et al (99) and Rangel-Mendez and Streat (100) studied the influence of surface properties, solution pH and temperature on the adsorption of Cd(II) on a sample of activated carbon cloth. The adsorption capacity of the carbon cloth was larger when it was oxidized compared to the original carbon cloth. The maximum adsorption was observed at pH = 8. Qadeer and Khalid (101) and Ramos et al (102) while studying the adsorption of Cd(II) ions on an activated charcoal and on activated carbon fiber observed that the oxidation of the carbon fiber enhanced the uptake of Cd(II) ions. Reed and Matsumoto (103) investigated Cd(II) ions adsorption on two types of powdered activated carbons in single and binary adsorbent systems and observed that both the activated carbons effectively removed Cd(II) from the solution and the adsorption increased with increasing pH of the solution. Oezer and Tuemen (104) studied the adsorption of Cd(II) ions by an activated carbon prepared by carbonization of sugar beet pulp impregnated with 30% phosphoric acid and observed...
that the adsorption capacity of the activated carbon increased by increasing the temperature of carbonization. Chang and Ku (105) studied the adsorption isotherms of Cd(II) ions on activated carbons in the presence of chelating agents such as EDTA, citric acid and nitrilotriacetic acid. They observed that the extent of adsorption was a function of solution pH and cadmium chelate species distribution. Meena et al (106) found that the adsorption of Cd(II) ions by activated carbons involved monolayer coverage. Gupta and Bhatnagar (107) and Levy – Ramos and coworkers (108, 109) studied the adsorption for Cd(II) and Zn(II) ions in single and simultaneous adsorption from aqueous solutions on activated carbons. The amount of the metal cations removed was found to depend on the pH of the solution. The overall rate of adsorption of Cd(II) and Zn(II) ions was mainly controlled by the intra particle diffusion which was solely due to pore volume distribution. The adsorption of each individual ion was reduced by the presence of the other ion which competed for the same adsorption sites.

Ferro-Garcia and coworkers (110,111) studied the influence of pH, nature of the carbon surface and presence of electrolytes in solution on the adsorption of Cd(II) ions by activated carbons obtained from almond shells, olive stones and peach stones and observed little or no adsorption at pH = 3 but the adsorption increased sharply in the pH range 3 - 5 attaining almost a constant value at higher pH values. Babic et al (112) also studied the influence of pH and concentration on the adsorption of zinc, cadmium and mercury on an activated carbon cloth. The adsorption of zinc and cadmium ions increased while that of Hg(II) remained constant with increase in pH value of the solution. Tekker et al (113) has reported the adsorptive removal of Cu(II) and Cd(II) ions from aqueous solutions by adsorption on an activated carbon prepared from rice hull as a function of pH, contact time, initial metal concentration and temperature and found that the adsorption data followed both the Langmuir and Freundlich isotherm equation.

Marcias – Garcia and Coworkers (114,115) studied the adsorption of Cd(II) ions using a variety of chemically activated carbons while Brennsteiner (116) used a sample of vapour grown fabric, a coal derived foam and a carbon nanofabric for the electrochemical removal of heavy metal including cadmium. These workers were of the opinion that the adsorption was due to the surface area as well as the microporous character of the carbons. Jia and Thomas (117) studied the adsorption of Cd(II) ions on a coconut shell charcoal containing carbon-oxygen surface groups and found that the
adsorption was considerably enhanced by the surface groups. Saha et al (118) determined the batch and column adsorption of transition metal ions from aqueous solutions on samples of wood based activated carbons modified by acid and air oxidation. The adsorption capacity was markedly enhanced by these modifications due to the formation of weakly acidic functional groups on the carbon surface.

Bhattarcharya and coworkers (119, 120), Reed and Nonavinakere (121) and Rubin and Mercer (122) studied the influence of chelating agent EDTA on the adsorption of Cd(II) ions from aqueous solutions by activated carbons. While Rubin and Mercer observed little effect of the chelating agent on the adsorption, Bhattarcharya and coworkers did find an increase in adsorption in the presence of EDTA at least in the case of basic carbons. These workers even proposed the formation of an electron donor – acceptor complex of chelate and carboxyl group on the carbon surface. Reed and Nanovinakare, on the other hand suggested that the negatively charged chelate complex adsorbed on the carbon surface and was followed by the reaction of the positively charged Cd(II) ions with carbon-ligand complex. Periasamy and Namasivayam (123) observed that the adsorption capacity of a peanut hull charcoal for Cd(II) ions was higher than a commercial activated carbon although the surface area of the commercial activated carbon was larger. These workers suggested that the electrostatic interaction forces and specific chemical interactions played an important role in the adsorption of Cd(II) ions.

Mu Guannan and Yang (124, 125), investigated the influence of addition of surfactants on the adsorption of Cd(II) ions by oxidized carbons and oxidized charcoal. The adsorption capacity of these carbons increased considerably by the addition of anion surfactant SDS while it was decreased by the addition of cationic and nonionic surfactants. Marcias –Garcia et al (126) and Nath et al (127) studied the adsorptive removal of Cd(II) ions by activated carbons treated with H₂S, SO₂ and nitrogen. The adsorption decreased considerably by these treatments.

Netzer and Hughes (128), Corapcioglu and Huang (129) and Shekinah et al (130) studied the adsorption of Pb (II) ions from aqueous solutions by activated carbons at different pH values of the solution and found that the adsorption involved hydrolysis, complex ion formation, ion exchange and precipitation of the metal as Pb(OH)₂. Cheng et al (131) while studying the adsorption of Pb (II) ions on activated carbon containing varying amounts of carbon-oxygen surface groups suggested that the adsorption was
influenced by these surface groups. Marcias–Garcia et al (132) investigated the adsorption of Pb (II) ions on heat treated and sulphurised activated carbons at different solution pH and temperatures and observed that the adsorption decreased with the decreasing pH and temperature. Park et al (133), while studying the adsorption of heavy metal cations on an activated carbon and activated carbon fiber observed that the activated carbon fibre had higher adsorption capacity and a higher rate of adsorption. The maximum pH for the optimum adsorption was about 8 for the carbon fibre and 11 for the activated carbon. Mohamed and Fahmi (134) and Koby et al (135), however, found a pH between 5 and 6 as the optimum pH for the maximum adsorption of Pb (II) ions.

Malik et al (136) studied the adsorption of ions from aqueous solution in the presence of Cu(II) ions on activated carbons associated with oxygen and phosphorus surface groups and observed that carboxylic acid groups played a larger role in the adsorption. Ferro Garcia et al (137) determined the adsorption of ions on activated carbons prepared from almond shell, olive stones and peach stones and found that the adsorption increased with surface area but only a fraction of the surface area was covered by the ions indicating that only a small fraction of the micro porosity was available for the adsorption. Goel et al (138) observed that the multicomponent adsorption by coconut based activated carbons using single, binary and ternary systems composed of Cu(II), Pb (II) and Hg(II) ions followed both the Langmuir and Freundlich models of adsorption. Bansode et al (139) also observed that the removal of metal ions from a ternary system of Cu(II), Pb (II) and Zn(II) ions using a peacon shell based activated carbons was more effective than the commercial activated carbon. Mostafa (140) prepared steam activated and zinc chloride activated carbons from rice husk and studied the adsorption of Pb (II) ions. It was found that the surface chemistry of the carbon played an important role in determining the removal of ions.

Adsorption of Pb (II) ions onto chemically modified activated carbons prepared from date pits (141) and carbons derived from agricultural wastes (142) has also been studied. The presence of EDTA, acetic acid or citric acid was found to decrease the adsorption significantly. Swiatkowski et al (143) have discussed the role of carbon surface chemistry on the adsorption of ions from aqueous solutions. The role of minerals present in carbonaceous source raw materials on the adsorption of ions by carbons was studied using Oakwood charcoal and an activated carbon prepared from
coal by Machida et al (144). The acidic surface functional groups determined the adsorption of ions but the presence of mineral ash containing oxides of manganese and magnesium influenced the adsorption.

Qadeer and Aktar (145), Giraldo and Moreno (146) Machida et al (147), Zhang et al (148) and Sekar et al (149) also studied the adsorption of Pb (II) ions from aqueous solution on activated carbons. The adsorption involved a mass transfer adsorption process and diffusion through a film was the rate determining step. Mochida et al (150) proposed a two site adsorption model for the adsorption and desorption of the Pb (II) ions. The adsorption was also found to depend on the surface area, mean pore size and hetero atom concentration on the surface of the carbon. Sikorska – Sobiegraj and Zielinski (151, 152) has reported the adsorption of lead and cadmium and copper from multicomponent aqueous solutions. The Pb/Cd sorption capacity ratio was always approximately 3:1 and generally higher under dynamic than under static conditions both in single and two-ion adsorption. The adsorption of the two metals takes place differently depending upon the adsorptive abilities of the two individual metals.

Mustafa et al (153) determined the adsorption of Pd on high surface area carbons and found that the adsorption was not determined by the surface area but the concentration of active sites present on the carbon surface. The concentration of trace metals from water of Sakarya river in Turkey was carried out using activated carbons (154). About 85-90% of the trace metals could be recovered at a concentration of 0.1 µg/L. Youssef (155) carried out the adsorptive removal of heavy metals from aqueous solutions using zinc chloride activated carbons at solution pH ≤ 7.0. The heavy metal ion removal capacity of the carbon was found to depend on the pH of the solution and the degree of activation of the carbon. Aurora (156) studied the adsorption of copper and nickel ions on a granular activated carbon. The metal removal capacity of the carbon increased with solution pH and temperature and decreased on increasing the concentration of the solution at constant carbon dose.

The adsorption of Ag from brine and cyanide aqueous solutions by activated carbons has also been studied (157-159). The adsorption depended on the initial concentration of the solution. The rate of adsorption was slow initially but picked up with time. The carbons could adsorb appreciable amounts of silver from the solution. Tai (160), oxidized, chemviron F-400 activated carbon by treatment with nitric acid and
studied the adsorption of zinc ions from aqueous solutions. The zinc adsorption capacity of the carbon increased by ten times on oxidation although the surface area had slightly decreased.

The adsorption of Cu(II) ions at different solution pH and concentration and in the presence of different electrolytes has been studied using carbons having different surface areas and associated with different amounts of carbon-oxygen surface groups. Petrov et al (67) observed that the metal uptake increased with increasing pH of the solution. The oxidation of the carbon enhanced the uptake of Cu(II) ions whereas the presence of electrolytes decreased the adsorption. Mangalardi et al (161) and Andreeva et al (162), observed that the adsorption of Cu(II) ions was considerable at pH lower than 7. Tarkovskaya et al (163) examined the adsorption of Cu(II) ions on several carbonaceous materials such as oxidized anthracite, semi coke, brown coal and several modified coals and observed that these materials were quite effective for the removal of cations from solution. Khan and Khattak (164, 165) studied the adsorption of copper from copper sulphate solutions on carbon blacks spheron - 9 under varying conditions of time, pH and concentration. Increase in pH increased the extent of adsorption. Goyal et al (166), determined the adsorption isotherms of Cu(II) ions from aqueous solutions on two samples of granulated and two samples of fibrous activated carbons having different surface areas and associated with varying amounts of carbon – oxygen surface groups. The carbon surface was modified by oxidation with nitric acid, ammonium persulphate and oxygen gas and by degassing at different temperatures. The adsorption of Cu(II) ions increased on oxidation and decreased on degassing. The increase in adsorption on oxidation depended on the nature of the oxidative treatment and the decrease in adsorption on degassing depended on the temperature of degassing. This has been attributed to the increase in acidic carbon-oxygen surface groups on oxidation and their decrease on degassing.

Tewari et al (167), studied the removal of Ni(II), Cu(II) and Cr (VI) ions from dilute aqueous solutions by adsorption on activated carbon in the pH range 5.5 - 8. While the adsorption of Cr(VI) ions exhibited a peak at pH=5.5 and Cu(II) ions at 8.0, the adsorption of Ni(II) ions was found to be appreciable in both acidic and basic media. However, the rate of adsorption was faster in the alkaline solution. Singh and Rawat (168) used law grade bituminous coal before and after oxidation for the removal of Ni, Cu, Zn and Cr from aqueous solutions. The rate of adsorption and the adsorption
capacity of the coal enhanced significantly upon oxidation. Vishwakarma (169) Nonavinakere and Reed (170) examined the influence of initial nickel concentration, residence time, temperature and pH on the adsorptive removal of Ni(II) ions on fly ash. Increase in temperature and pH and a decrease in initial nickel concentration favoured the removal of Ni(II) ions on fly ash. Increase in temperature and pH and a decrease in initial nickel concentration favoured the removal of Ni (II) ions. The maximum adsorption was observed at pH around 7. The equilibrium data fitted the Langmuir isotherm equation. Goyal et al (171) determined the adsorptive removal of Ni (II) ions from aqueous solution of nickel nitrate on several activated carbons. The data obeyed Langmuir isotherm equation. The adsorption increased on oxidation and decreased on degassing of the carbon surface. The adsorption has been related linearly to the surface acidity of the carbon surface.

The role of pH in the adsorption of Cr (IV) and Cr VI) ions by activated carbons was studied by Leyva-Ramos and Jueraz-Martinez (172). Cr(VI) adsorption increased significantly when the pH of in solution decreased from 10 to 6 but that of Cr(III) increased with increase of pH from 2 to 5 and decreased drastically at pH =6. Park and coworkers (173, 174) studied the rates of adsorption of Cr(VI) on activated carbons and carbon fibers and found that the adsorption rate increased with increase in the amount of acidic surface oxides. Aggarwal et al (175) carried at adsorption of Cr(III) and Cr(VI) ions from aqueous solutions on granulated and fibrous activated carbons associated with varying amounts of carbon-oxygen surface groups. The uptake of Cr(III) ions increased on oxidation and decreased on degassing while the adsorption of Cr(VI) decreased on oxidation and increased on degassing. This has been attributed to the fact that the oxidation of the carbon surface enhances the amount of acidic carbon oxygen surface groups while degassing eliminates these surface groups.

Lorenzen et al (176) studied the adsorptive removal of arsenic using three impregnated activated carbons prepared from different source raw materials and observed that the adsorption was not determined by the surface area of the carbons but was enhanced by the presence of ash in the carbon. Sen and De (177) determined the influence of several parameters such as the time of equilibrium, pH and adsorbent dose on the removal of As(III) ions from aqueous solutions using coal fly ash and an activated carbon. The adsorption of As (III) increased with increase in solution pH up to pH= 4 and decreased at higher pH values. The adsorption of As (III) ions was larger on the fly ash than the
activated carbon due to the polar nature of the minerals in fly ash. Raji and Anirudhan (178) used copper impregnated sawdust carbon for the adsorptive removal of As(III) ions from aqueous solutions and studied the influence of solution pH and concentration, reaction time and temperature on the extent of removal. The removal of As(III) increased from 3.2% to 84.0% by increasing the pH from 1 to 12.

1.4.2 Removal of Organics from Water

Small amounts of a large number of synthetic organic compounds such as surfactants, phenols, dyes, pesticides, aliphatic and aromatic hydrocarbon nitro compounds, amines and a host of other are present in surface and drinking waters. In addition several halogenated compounds are produced during chlorination practice for disinfection of drinking water. Many of these are carcinogenic and harmful for human and animals. Thus the literature contains a huge amount of research papers dealing with their removal using activated carbons. It is not within the scope of this thesis to give a complete survey. The thesis thus contains a brief review of the removal of important groups of organic compounds and that too of the latest publications.

Juang et al (179) studied the adsorption of eight phenolic compounds on activated carbon fibres and observed that the adsorption was more in the case of chlorinated phenols compared to methyl substituted phenols. Vidic and coworkers (180-182) observed that the adsorption capacity of granular activated carbon for several phenolic compounds was highly influenced by the presence of molecular oxygen. The adsorption capacity of a carbon was enhanced by about 200% in the presence of oxygen. The adsorption was reversible in the absence of oxygen and could be recovered almost completely by solvent extraction but only 10-30% of the phenolic compound could be recovered when the adsorption was carried out in the presence of oxygen.

Leng and Pinto (183) studied the adsorption of phenol and o-cresol on activated carbons in the presence of dissolved oxygen and observed no relationship between the amount adsorbed and the BET surface area of the carbon. The adsorption was much higher in the presence of oxygen. Teng and Tsieh (184, 185), while studying the adsorption of phenol on partially oxidized bituminous coal observed that although the surface coverage of the carbon with low burn off was about 100% it was only about 40% with a burn off of 60%. This was attributed to the larger concentration of associated oxygen on the carbon surface in the latter case.
Levya – Ramos (186) studied the adsorption of phenol from aqueous and cyclohexane solutions on activated carbon and found that the amount adsorbed was more from aqueous solutions of phenol. This was attributed to a large affinity of phenol to cyclohexane. In aqueous solutions the adsorption of phenol increased with decrease in particle size of the carbon but decreased with increasing temperatures of adsorption. In the cyclohexane solution the amount adsorbed was independent of the particle size. Sam (187) studied the dynamic adsorption of phenol, p-chloro phenol and p-nitro phenol from aqueous solutions and compared the pore diffusion model and the surface diffusion for adsorption. The pore diffusion model was found to be more satisfactory for the adsorption process. Goyal (188) and Bansal et al (189) studied the adsorption of p-nitro phenol and phenol on two samples of granulated and two samples of fibrous activated carbons from aqueous solutions before and after modifying their carbon surface by oxidation with nitric acid and oxygen gas and by degassing under vacuum at gradually increasing temperatures. The adsorption of both phenol and p-nitro phenol did not depend on the surface area of the carbon but was influenced by the surface chemistry of the carbons. The adsorption decreased on oxidation while the degassing of the oxidized carbon increased the adsorption of both the phenols. The decrease in adsorption was found to depend on the nature and the strength of the oxidative treatment while the increase in adsorption depended upon the temperature of degassing. These workers suggested that while the presence of acidic surface groups decreases the adsorption, the presence of non-acidic quinonic groups enhances the adsorption. Srivastava et al (190) studied the adsorption of phenol on carbon rich bagasse fly ash (BFA) and activated carbon commercial grade (ACC) and lab grade (ACL). They evaluated the influence of initial pH, contact time, adsorbent dose and initial concentration on the removal of phenol. They found that the adsorption of phenol followed pseudo – second order kinetics with the initial sorption rate for adsorption of ACL being the highest followed by these of BFA & ACC. They also found that Redlich Peterson isotherm fitted the best to represent the data for phenol adsorption on all the adsorbents.

King et al (191) studied the adsorption technique for the removal of phenolic compounds from a synthetic phenolic effluent solution using activated carbon prepared from coconut shells. The effect of time of contact, adsorbed dosage, initial concentration of phenol, size of the adsorbent and concentration of other pollutants...
were studied on the adsorption of phenolic effluents from aqueous solutions. The adsorption behavior was studied by adsorption isotherms. Mohanty and Biswas (192) studied the adsorption of phenol from aqueous solution using activated carbons prepared from sawdust. ZnCl₂ activation effects of carbonisation level and time were found to be important variables which had effect on the pore structure of carbon. The activated carbon showed capability to adsorb phenol from waste water. The Freundlich and Langmuir isotherms were well fitted. The solution pH markedly affected the sorption process.

Sui and Ma (193) studied the adsorption of nitrobenzene on a sample of ozone oxidized activated carbon and observed that the adsorption rate was six times larger than on the non-oxidized carbon. Aggarwal et al (194) examined the adsorption of nitrobenzene from aqueous solutions on five different commercial grade activated carbon having surface areas varying between 600 – 1300 m²/g. The amount adsorbed increased with increase in surface area but no linear relationship could be found between the two. The oxidation of the carbon considerably decreased the adsorption while degassing of the oxidized carbons enhanced the adsorption. The adsorption was suppressed by temperature, presence of acidic surface groups and was enhanced when these surface groups were eliminated on degassing. Xiaosha and Jingtian (195) studied the adsorption of nitrobenzene from water by irradiation in the presence of activated carbons and observed that the irradiation resulted in a greater adsorption of nitrobenzene. Zhongqi and Lu (196) observed that the equilibrium and dynamic adsorption of nitrobenzene from aqueous solution was influenced by the surface area and the pore size distribution of the activated carbon. Nouri (197) and Nouri and Haghseresht (198) found that the adsorption of nitrobenzene and several ionisable organic compounds under controlled pH was influenced by the solubility of the adsorbate and the electron density of its aromatic ring. Jain and Bryce (199) investigated the adsorption of several explosives such as TNT, RDX and HMX from armament waste water using granulated activated carbon in the absence and presence of ozone as oxidant. These workers observed that the adsorptive removal of the explosives was much larger when the oxidant was present. Aggarwal et al (200) determined the adsorption of styphenic acid which contains both a nitro and a phenolic group and observed that the adsorption was determined by the surface area but the fraction of the surface occupied by styphenic acid at a monolayer coverage increased with surface
area. The adsorption increased on oxidation of the activated carbons. A linear relationship was found between the amount adsorbed and the oxygen associated with the carbon surface. Radovic et al (201) studied the adsorption of aniline and nitrobenzene on activated carbons after modifying their surface by oxidation, devolatalisation and nitrification with ammonia gas. These workers observed that while the adsorption of aniline involved both the dispersive and electrostatic interactions, the adsorption nitrobenzene involved dispersive interactions only. These workers have proposed a theoretical model that can account for the adsorption of organic compounds by activated carbon. Kaneko et al and Brasquet and Le Cloirec (202, 203) measured the adsorption characteristics of low molecular weight organic compounds dissolved in water using hydrogenated activated carbon fiber, activated carbon cloth and granular activated carbons and observed that the adsorption of low molecular weight organics was influenced by the presence of polar functional groups on the carbon surface. Rajagopal and Kapoor (204) studied the adsorption of nitrobenzene, dinitrotoluene and TNT on granular activated carbons and developed a model which could predict the dynamics of the adsorption process.

Bornehoff (205) studied the adsorption of several nitrosamines from water using activated carbons and observed that when one litre of dosed water was passed though 23g. of an activated carbon, the removal was more than 99% in the case of dimethyl, diethyl and diphenyl nitrosamines. Fochtman and Dobbs (206) used Darco and Filtrasorb activated carbons for the removal of several carcinogenic nitrosamines and hydrocarbons such as naphthalene and benzidine from water and observed that appreciable amounts of these compounds were removed. The extent of adsorption was dependent on the nature, molecular weight and the molecular dimensions of the compound. The adsorption data obeyed the Freundlich isotherm equation.

Terzyk et al (207) described the influence of temperature on the adsorption of paracetamol from pH 7 aqueous solution on to de-ashed commercial activated carbon. Three carbon samples D 43%, WD-extra and AHD were investigated. They were de-ashed and characterized using nitrogen adsorption, proximity and Bachmann’s method as well as by different theoretical approaches. Carbon surface properties were characterized by the method of Boehm and enthalpy of immersion in water. The adsorption / desorption isotherms of paracetamol in the temperature range 300-320 K were measured together with the enthalpy of immersion in paracetamol solution. The
carbon adsorption properties towards paracetamol were discussed. Relationships describing the dependence of absorbability on the temperature are proposed as well as the dependence on the relative enthalpy of adsorption on the concentration of basic carbon surface groups.

Sobezak (208) measured the sorption of 6β - adrenolytic drugs in basic and acidic media on domestic medicinal charcoal. For all the substances under study, n-octanol-water partition coefficient was determined. Moreover, desorption of all these substances from charcoal into hydrochloric acid and phosphate buffer was examined. A good correlation between the Langmuir constants of sorption isotherm and the partition coefficient P of β-adrenolytics was obtained, which indicated the possibility of applying the sorption data to assess the bioavailability of these drugs.

Kovelenko et al (209) studied regularities of the adsorption of proteins, enzymes and non proliferating bacterial cells on new porous carbanaceous materials differing in the structure of the porous matrix and the microstructures of the immobilized cells of microorganisms on the surface of carbonaceous adsorbents. These studies were carried out using SEM.

Bao et al (210) studied the effect of activated carbon on adsorption of norfloxacin, ofloxacin (OFX) and Ciprofloxacin (CFX). The factors including absorbent concentration, temperature, pH and isotonic regulating agent on the adsorption were analyzed and saturating adsorption capacity was computed. The F test showed that adsorption of three fluoroquinolones by activated carbon was influenced markedly by above factors. The saturating adsorption capacity of activated carbon was 374, 290 and 320 mg/g for NFX, OFX and FX respectively. Adsorption equilibrium coefficient increased with the pH and temperature value ascent.

Zhang (211) studied spectrophotometrically the adsorption of tinidazole in tinidazole –glucose injection by activated carbon. The adsorption was affected by high temperature and was steady at pH 3.5 – 5.5. Thus activated carbon was not suitable for adsorbent or filter aid and 0.8 mm micro porous membrane was preferably used to filter.

Anisimov (212) studied prevention of spontaneous and chemically induced carcinogenesis using activated carbon fiber adsorbent ‘aqualen’ on 1,2 –dimethyl hydrazine – induced intestinal carcinogenesis in rats. Two months old outbread female
L10 rats were exposed weekly to 15 (ex. 1, groups 1,2 and 3) or to 5 (exp. 11, gps. 4,5 and 6) S.C. injections of 1,2-dimethyl hydrazine (DMH) at a single dose of 21 mg/kg. From the day of the 1st injection of the corecinogens the rats from gps. 2,3,5 and 6 were given Aqualen in their diet. In both experiments rats were fed 5 times per week together with lab chow at daily dose of 0.1/Kg (gps. 2nd 5) or 1.0 g/Kg (gps. 3 and 6) or body weight additional. Other rates were not exposed to the carcinogen and served as an intact control (group 7) or were given aqualen with the diet as the daily dose of 0.1g/Kg (group 8) or 1.0g/kg (group 9). These experiments were finalized 6 months after the first injection of DMH. In experiments 1 and 11 the majority of tumors were localized in the descending colon. Tumors of smal intestines developed only in rats from experiment 1. The total incidence of colon tumors as well as tumors in different parts of the colon and the mean number of tumors per rat were much higher in rats from all groups.

Dutta et al (213) studied the adsorption of semi synthetic cephalosporin such as 7-amino cephalosporanic acid (7-ACA), cephalexin and Cef- from aqueous solutions using activated carbon as the adsorbent. The pH dependence of the adsorption intensity was interpreted from a model from neutral –species adsorption. 7 – ACA exhibited relatively low adsorption intensity compared to cephalexin and cephadroxil, which showed nearly equal adsorption intensities. The adsorption isotherm for all the three could be interpreted from the Langmuir model with a reasonable degree of accuracy. The adsorption rate curves for the cephalosporin exhibited identical profiles generated for cephalexin in an agitated slurry system indicated that external film diffusion controls the adsorption rate initially while the particle diffusion controls solute uptake in the later stages.

Newcombe (214) studied the adsorption of natural organic matter (NOM) ultrafiltration fractions on ten activated carbons. The aim of research was to understand the influence of surface charge and pore volume distribution and NOM charge and molecular weight on adsorption. The effect of pH and ionic strength on adsorption mechanisms was also examined. At neutral pH the NOM has a significant negative charge which can effect the adsorption in several ways. At low surface concentrations of carbon surface groups there was direct surface NOM-electrostatic attraction which reduced adsorption. At higher surface concentrations the adsorption becomes predominantly a physical surface –NOM attraction possibly due to the hydrophobic or
aromatic ring interactions. The electrostatic effects are mainly caused by the lateral repulsion of the NOM that prevents the close – packed arrangements apparent at pH =3. For one activated carbon it was shown that the degree of ionization of the adsorbed NOM is strongly dependent on the surface concentration.

Karanfil (215) investigated the role of GAC surface chemistry on the adsorption of four model dissolved organic material (DOM) isolates and four surface water natural organic material (NOM) samples by using ten carbons prepared by modifying the surfaces of a coal-based and a wood based carbon and seven different as-received granulated activated carbons. Because changes in the pore structure resulting from surface treatment were small, while changes in the surface chemistry were significant, the impact on the DOM and NOM uptake by surface treated carbons was systematically linked to the changes in the surface chemistry alone. For the surface-treated coal-based carbons there was no significant capacity difference between acid-washed and heat treated carbon samples. The oxidation of the carbon surface significantly decreased the uptake, and the capacity was partially restored by subsequent heat treatment of the oxidized surfaces. A decreasing uptake with increasing surface acidity was evident. The experiments with as-received coal-based carbons exhibited the same behavior. However, the reactivity of modified and as-received carbons for DOM and NOM uptake was significantly different. For the wood based carbon, the impact of surface treatment on adsorption of DOMs and NOM was surprisingly minimal or absent. This finding was in contrast to the effect of surface acidity on uptake of the two SOCs, studied. Overall, the reactivity of carbon surfaces to DOM and NOM uptake depended on the raw material type activation conditions and surface treatment.

Youssef and Faust (216) studied that adsorption of chloroform, bromoform, bromodichloro methane, dibromochloro methane and carbon tetrachloride on activated carbons from aqueous solutions at a controlled pH = 7. The adsorption data followed both the Langmuir and the Freundlich isotherm equations. The dynamic adsorption studies showed that the breakthrough time followed the order CHCl3 > CHCl2Br > CHCl Br2 > CHBr3. The breakthrough point was attained quite easily indicating the high potential of using activated carbons for the control of THM (trihalomethane) in drinking water. Kim et al (217) studied the adsorption isotherms of chloromated volatile organic compounds on an activated carbon and found that the adsorption affinity on activated carbons was greater for dichloromethane than for 1,1,2 trichloro
and 1,2,2, trifluoro ethane. Chiang et al (218) studied the effect of surface characteristics of activated carbons on the adsorption of volatile organic compounds and found that boiling point, critical temperature, cross sectional area, pore volume and surface area were the most important factors determining VOC adsorption. Ishizaki et al (219) investigated the adsorption of chloroform from aqueous solutions on activated carbons before and after degassing and observed that the degassed carbon samples adsorbed larger amounts of chloroform compared to the as-received activated carbons. The adsorption data obeyed the Langmuir adsorption equation. Rey and Oles (220) removed chlorinated aromatic hydrocarbons from aqueous solutions by stripping with air and then adsorbing on activated carbons. Yu et al (221) used activated carbon fibers for the adsorptive removal of dichloromethane and trichloromethane from ground water. Both the halogenated hydrocarbons were adsorbed rapidly on the carbon surface. The adsorption of two synthetic organic pollutants trichloroethylene and trichlorobenzene on coal based and wood based granulated activated carbons has been reported by Karanfil and Kilduff (222). Wood based carbons showed significantly lower adsorption than the coal based carbons indicating that the adsorption did not depend on the surface area alone. The oxidation of the carbons decreased the adsorption of both the compounds while degassing of the oxidation carbons at 650°C enhanced the adsorption. The adsorption was found to be influenced by the surface acidity of the carbon. Xio et al (223) studied the adsorption of chlorobenzene and 1,3 dichlorobenzene on a wood based charcoal activated with CO$_2$. The adsorption isotherms were Langmuir in shape. The amount adsorbed increased with increasing temperature. The amount adsorbed depended on the total pore volume of the carbon. The adsorption was physical in nature and involved micropores. The adsorption of atrazine and atrazine diethyl was studied by Cougnaud et al (224) and by krysova et al (225) on activated carbon fibres (ACF) and granulated activated carbon. The data followed Langmuir and Freundlich isotherm equations. But the adsorption was larger on ACF than on GAC.

The adsorptive removal of two pesticides diquat and paraquat from aqueous solutions on three activated carbons obtained from different source raw materials and activated with steam was studied by Parkash (226). The activated carbons had different surface area and were activated to different degrees. The adsorption for both the pesticides fitted the Langmuir isotherm equation. The values of thermodynamic
quantities such as activation energy and differential enthalpy of adsorption indicated that the rate of removal of these pesticides was an endothermic process which agreed with the interparticle transport rate control mechanism. However, the equilibrium adsorption was an exothermic process. Ralph et al (227), treated aqueous solutions of atrazine with powdered activated carbon (PAC) and a granulated activated carbon and found that the removal was better with PAC, Klaus (228) used PAC in an adsorber and passed atrazine containing water through it. The effluent water from the adsorber was found to contain atrazine well below the safety limits i.e. below 0.1 mg/L. The influence of the addition of anionic, cationic and non-ionic surfactants on the adsorption of atrazine from aqueous solutions was examined by Ayele et al (229). The adsorption decreased in the presence of all the three types of surfactants but the decrease was larger in the case of cationic surfactants. The ionization of water with a low doze enhanced the removal of atrazine while the addition of acetate did not make any change. The removal of a fungicide dodine and an insecticide lindane in the presence of several coagulants by activated carbon was studied by Kauras and coworkers (230, 231). The removal of dodine at pH between 5-8 at a dodine concentration of 250 mg/L was more than 98%. However, when 10 mg/L of the coagulant was added, the removal of dodine increased even with 50% of the carbon doze. The adsorption of lindane, however, was not influenced by the solution pH and the adsorption decreased with the addition of coagulants. Becker and Wilson (232) studied the adsorptive removal of a large number of pesticides from water by activated carbons and by several other methods and found that activated carbon method was the best. Activated carbon beds could remove more than 95% of the pesticides. Matsui et al (233) on the other hand found that pesticides with higher water solubility were weaker adsorbates and showed lower adsorption efficiency. Ashley et al (234) carried out the adsorptive removal of triazines using granular and powdered activated carbons and found that the data obeyed Freundlich isotherm equation. The adsorption was a function of the solution pH.

The adsorptive removal of three highly reactive dyes from textile industry was studied by Al-Degs and coworkers (235, 236). All the dyes showed appreciable adsorption but the adsorption was not related to surface area of the carbons. The different amounts adsorbed on different activated carbons was attributed to difference in carbon surface charge. Chen et al (237) and Chen and Wu (238) used sisal based
activated carbon fibers for the adsorption of dyes and observed different rates of adsorption on different activated carbons fibers. The variation in adsorption rates and adsorption capacity were found to depend on the surface properties of the carbon fiber and on molecular dimensions of the dye. Houas et al (239) and Khalil and Girgis (240) studied the adsorption of methylene blue on several activated carbons and observed that the adsorption was larger in the alkaline solutions than in the acidic solutions. The adsorption data followed Langmuir isotherm equation. The adsorption decreased with increase in the degree of activation of the carbon surface because activation produced finer pores which could not accommodate larger methylene blue molecules. Viraraghavan and Mihial (241) found the removal of an acidic and a basic dye on peat obeyed both Langmuir and Freundlich isotherm equation. The adsorption was larger in the case of the basic dye. Lin (242, 243), however, observed that the adsorption involved multilayer formation and the data fitted BET isotherm better than the Langmuir or the Freundlich isotherm equation.

Mittal and Venkobachar (244) studied the removal of Rhodamine B and acid red 1 dye on sulphonated coal from aqueous solutions and found only a moderate adsorption of the two dyes on the coal. The Freundlich isotherm equation constants showed that the removal of the basic dye was larger than the acidic dye. The desorption studies showed that the adsorption of both the dyes was chemical in nature but rhodamine involved ion-exchange mechanism. Dai and coworkers (245, 246) determined the influence of pH on the adsorption of anionic dyes and found that the adsorption was determined by the zeta potential of the carbon surface. Gao et al (247) observed that the adsorption of anionic and non-ionic dyes by activated carbons from aqueous solutions depended on the nature of the carbon surface. Mckay (248) studied the adsorption of two basic dyes on activated carbons from industrial waste water and found that the adsorption data involved intra-particle diffusion mechanism. Dusart et al (249) carried out dynamic adsorption studies for the removal of dyes on peat from aqueous solution and found that the breakthrough curves indicated that peat could remove larger quantities of the dyes than the charcoal.

Miau and Dai (250, 251) investigated the influence of solution pH on the adsorption of an anionic dye by an activated carbon. The adsorption varied considerably with the pH of the solution. Juang and Swei (252) in their studies on the adsorption of cationic and anionic dyes observed that the adsorption involved
electrostatic interactions between the electrons acceptor groups on the carbon surface and the positive charge ion the basic dye molecule. Sasaki et al (253), while studying the adsorption of an acid and a direct dye on pitch based activated carbon fibers (ACF) which had different isoelectric points observed that the adsorption of the acid dye was lower on the metal doped carbon fibers than the metal free carbon fibers. However, the adsorption of the direct dye decreased with increasing pH. The adsorption was found to depend on the pore size distribution in the ACF and on the electrostatic interactions between the dye molecule and the carbon surface. Guzel (254) observed that the adsorption of methylene blue and metanil yellow on the carbon surface involved attractive interactions between the carbon surface and the dye molecules while Tamai et al (255) found the adsorption on the surface of activated carbon fibers depend on the size of the micropores and mesopores in the activated carbon fiber samples.

Goyal et al (256) studied the equilibrium and dynamic adsorption of methylene blue, rhodamine B and metanil yellow from aqueous solutions by activated carbons having different surface areas and associated with varying amounts of carbon-oxygen surface groups. The adsorption of methylene blue and rhodamine B which are cationic dyes increased on oxidation of the activated carbons and decreased on degassing. The increase in adsorption was attributed to the formation of acidic carbon-oxygen surface groups and the decrease in adsorption on degassing to their elimination. In the case of anionic dye metanil yellow, the adsorption was found to be decreased on oxidation and increased on degassing. These results have been explained on the basis of electrostatic attractive interactions between the negatively charged carbon surface and the positively charged cations of methylene blue and rhodamine B and repulsive interactions in the case of metanil yellow. The dynamic adsorption studies in the case of methylene blue were carried out at different feed concentration and hydraulic loading rates and breakthrough points were determined. Several workers (257-264) have studied the adsorptive removal of a number of acidic and basic dyes using activated carbons from olive stones and wood. These workers observed that the adsorption is not directly related to surface area but depends on the solution which determines the carbon surface charge.

Gao et al (265) studied the adsorption of a surfactant on several chars after modifying their surface by oxidation and observed that the adsorption decreased considerably on oxidation. The adsorption increased with increase in surface area but a
linear relationship was obtained between the amount adsorbed and the surface area contained in pores larger than 2nm. Nawack et al (266) studied the adsorption 2-methyl isoborneol (MTB), which causes abnoxious odour in surface waters using lignite based activated carbon. The adsorption of MIB increased on heat treatment of the carbon which was attributed to changes in the microstructure and the carbon-oxygen surface groups on heating the carbon. Ishizaki and cookson (267) investigated the removal of n-butyl mercaptan, butyl disulphide, decane and p-hydroxy benzaldelyde on granulated carbons. The adsorption isotherms of all the four compounds fitted the Langmuir isotherm equation. Garcia-Garcia et al (268) used a wood charcoal activated with varying amounts of potassium hydroxide for the adsorption of benzene from aqueous solutions in the concentration range 0.5 – 500 ppm. The kinetic studies showed that the adsorption rate and the adsorption capacity increased progressively as the KOH to char ratio was enhanced. This was attributed to the formation of mesopores along with the micropores in the carbon. Kamegawa et al (269) used water soluble nanographite (WSNG) prepared from a carbon black for the adsorption of several organic compounds. The adsorption of 2-naphthol was larger on WSNG than on the graphitized carbon black. The amount adsorbed indicated that each molecule of WSNG, on average absorbed 1.5 molecules of 2-naphthol. The adsorption of lower aliphatic and some organic unsaturated fatty acids on activated carbons from aqueous solution was studied by Usmani and Wahab (270). The adsorption was found to depend on the microporosity and the chemical structure of the carbon surface. The adsorption data followed both the Langmuir and Freundlich isotherm equations.

1.5 Scope of The present Work

The rapid development of chemical, pharmaceutical, polymer and other process industries, the use of pesticides, insecticides and chemical fertilizers in agriculture and of a variety of chemical compounds in every day life has caused an increase in the amount and variety of chemical pollutants in surface and ground water. This, in turn, has rendered the conventional methods of waste water treatment inefficient and many times ineffective. Environmental pollution regulations for safe drinking water supply are becoming more stringent everyday because many of these compounds are carcinogenic. Thus there is need to develop newer technologies and alternative techniques for waste water treatment. Several laboratory experiments and field operations have shown that the activated carbon...
adsorption is perhaps the best broad spectrum technology which has great potential for the removal of organics and in inorganics from waste water.

Activated carbons are excellent adsorbents because they have a large surface area, a highly developed microporous structure and a high degree of surface reactivity. The adsorption capacity of an activated carbon depends on the surface area but is highly influenced by the surface chemistry of the carbon surface. The surface of most of the as-received activated carbons is hydrophobic and can only adsorb appreciable amounts of non-polar organic compounds and show little affinity for polar and ionic chemical compounds. It is, therefore, essential that the activated carbon surface be modified by certain treatments to make them suitable for the adsorption of a large variety of polar and non-polar organic and inorganic compounds from water. The present thesis is an attempt in this direction. The thesis describes the adsorptive removal of some heavy metal cations and polar and non-polar organic compounds from water using activated carbons of different origin and form before and after modifying their surface by oxidation and degassing.

The thesis has been divided into seven chapters which include a chapter on General Introduction (Chapter I) and a chapter containing the details of the materials, methodology and experimental procedures (Chapter II). The chapter on General Introduction includes a comprehensive survey of the more important and latest literature on the adsorption of important organic and inorganic compounds.

The adsorptive removal of heavy metal cations Hg(II) ions, Pb(II) ions and Cd(II) ions has been discussed in Chapters III - V. The influence of surface area, the chemical structure of the carbon surface, the effect of the solution pH and carbon surface charge on the adsorption of these cations has been studied and suitable mechanisms commensurate with the data have been proposed. The data has also been analyzed using Langmuir and Freundlich adsorption isotherm equation.

Chapter VI has been devoted to the adsorptive removal of essentially non-polar nitrobenzene from aqueous solution. The influence of dispersive and electrostatic interactions in determining the adsorption of nitrobenzene has been examined.

The removal of two naturally occurring materials namely gallic acid and tannic acid which are invariably present as dissolved materials in water, by adsorption on activated carbons is the subject matter of the seventh chapter (Chapter VII).
interaction between the carbon – oxygen surface groups and the acid anions has been discussed and a suitable mechanism for the adsorption process has been proposed.


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contents were shaken at room temperature for 24 hrs. in a shaker after which the carbon sample was filtered and washed with distilled water until free of sulphate ions. This carbon sample was dried in an electric oven at 120°C, out gassed at 120°C and stored in stoppered borosil glass bottles.

2.2.3 Oxidation with Gaseous Oxygen

About 5g of the carbon sample was spread in a platinum boat. The boat was covered with a platinum lid having holes through which oxygen gas could make contact with the carbon. The boat along with carbon sample was placed in a resistance tube furnace. The temperature of the furnace was maintained at 350°C. Pure and dry oxygen gas was passed over the carbon sample for four hours at the rate of two litres per hour. The sample was then cooled in oxygen gas and transferred to reagent bottles flushed with nitrogen gas.

2.3 Degassing of Carbons

As-received and oxidized carbons were degassed at temperatures of 400°C, 650°C, and 950°C to eliminate gradually varying amounts of the carbon-oxygen surface groups(1,2). The degassing was carried out by placing 5g of the carbon sample in a temperature controlled tube furnace. The carbon sample was spread in a thin layer about 5 inches long in the quartz tube furnace. It was kept in position by means of porous copper guaze plugs. The tube furnace was then connected to a Hyvac. Cenco Vacuum pump capable of giving vacuum to an order of 3 X 10^-3 mm of Hg and its temperature was set to the appropriate level by applying the appropriate voltage. The temperature was allowed to rise gradually and before it was raised by another 50°C, complete elimination of the gases at the preceding temperature was ensured. After degassing at each temperature, the sample was allowed to cool in vacuo to avoid reformation of the complexes. Cooled sample was then transferred to a stoppered bottle flushed with nitrogen. These samples are referred to as ‘degassed sample’ in the text and are prefixed by the temperature at which they are degassed.

2.4 Characterization of Activated Carbons

As-received, oxidized and degassed activated carbon samples have been characterized for their surface area, surface chemical groups and surface acidity using standard procedures. BET surface area has been determined using micromeritics surface
area analyzer using nitrogen gas as the adsorbate. The carbon-oxygen surface groups have been determined using high temperature evacuations, base neutralization, and pH determination.

2.4.1 High Temperature Evacuations

About 1 g of carbon sample oven dried at 150°C was kept in a platinum boat \(\left(4\times1\right)^{\frac{1}{2}}\). The boat was covered by a platinum cover which had small openings for the evolved gases to escape. The boat was then heated to 1200°C in a resistance tube furnace which was connected to a Hyvac. Cenco vacuum pump (capable of giving vacuum to the order of 3 X 10^-4 mm) through weighed calcium chloride U-tubes and a series of Erlenmeyer flasks (Fig. 2.1) containing a known volume of standard barium hydroxide solution.

The amounts of surface oxygen complexes were determined by analyzing the gases evolved. Water vapours were absorbed in the calcium chloride U-tubes, carbon dioxide was absorbed by barium hydroxide while the rest of the gases were collected over water, an aliquot volume of which was examined for its CO and \(\text{H}_2\) contents in Orsat – Lunge gas analysis apparatus. The amount of total oxygen evolved as water, carbon monoxide, and carbon dioxide was in close agreement with the oxygen obtained by ultimate analysis of the activated carbons(3,4).

2.4.2 Base Neutralization Capacity (Surface Acidity)

50 ml of 0.2N NaOH solution was added to 0.5 g of each carbon sample in a borosil flask of 100 ml capacity. The suspension was shaken mechanically for 72 hrs. An aliquot portion of the clear supernatant liquid was drawn and titrated against standard hydrochloric acid (IN) solution and the amount of unused alkali was determined. A blank was run every time and the necessary corrections were applied.

2.4.3 Determination of pH of the carbons

0.5 g of the carbon sample was placed in contact with 50 ml of carbon dioxide free distilled water in a borosil stoppered glass bottle. The suspension was shaken mechanically for 6 hrs. and the pH of the suspension was determined using a glass electrode pH meter.
Fig. 2.1 APPARATUS FOR HIGH TEMPERATURE EVACUATION STUDIES

I – INSULATION
E – ELECTRIC COIL
S – SILICA TUBE
U – CALCULUM CHLORIDE TUBE
F – FLASKS
S₁, S₂ – TWO-WAY STOP COCKS
V.P. – VACUUM PUMP
2.5 Adsorbates

Adsorption of inorganics and organics like lead, cadmium, mercury ions, nitrobenzene, gallic acid and tannic acid on activated carbons was examined following standard analytical procedures. All chemicals used in these investigations were of analar grade and demineralised water was employed in all EDTA titrations.

2.6 Analysis of Adsorbates

2.6.1 Adsorption of Lead

Stock solution of Pb(II) ions of 1000 mg/L was prepared by dissolving 1.598 grams of lead nitrate of analar grade in 1 liter of demineralised water. It was used to prepare standard solutions of different concentrations by dilution with demineralised water. 20 ml of standard lead (II) nitrate solutions of different concentrations were titrated against 0.005M EDTA solution at pH=6 using hexamine as buffer and xlenol orange as indicator. The volume of EDTA solution used till end point was noted and a calibration curve (cf Fig 2.2) was obtained.

Activated carbon sample was dried in an electric oven at 120°C for four hours and then cooled in a desiccator. A known weight of each carbon sample (0.5 g) was placed in contact with a known volume (50 ml) of lead nitrate solutions of different concentrations. The suspensions were placed in a thermostat for 24 hrs with occasional shaking and a blank was also placed for each solution. 10 ml of lead solution was titrated against standard EDTA (0.005 M) solution using xlenol orange as indicator at pH=6 (1) and the volume of EDTA used was noted. The blank was run every time and necessary corrections were applied. The amount of Pb(II) ion concentration in solution was determined using the calibration curve.

Disodium dihydrogen ethylene dianiminetetraacetate of analytical quality was dried at 80°C for four hours to get composition with the formula Na₂H₂C₁₀H₁₂O₄N₂·2H₂O with relative mass 372.24. About 20 g of the salt was dissolved in 200 ml of water to get saturated solution at room temperature. To this was added ethanol slowly until a permanent precipitate appeared. The solution with the precipitate was diluted with equal volume of ethanol and filtered through a sintered glass funnel, washed with acetone and then with diethyl ether. The precipitate was air-dried at room temperature overnight and
Fig 2.2 Calibration of Lead

Volume of EDTA used (mL) vs Concentration (mg/L)
then dried in an oven at 80°C for 30 hours to get pure salt. Approximately 3.8 g of the dihydrate was dissolved per litre of the solution to get approximate strength of 0.01 M EDTA solution. It was standardized by titration with a solution made from specially dried lead nitrate.

1 mole of EDTA = 1 mole of Pb²⁺

0.01 molar solution was further diluted to get 0.005M solution and employed in all EDTA titrations. All EDTA solutions were prepared by employing de-ionised water and stored in polythene bottles. pH of the Pb(II) ion solution was maintained at 6 by adding solid hexamine as buffer before titration with EDTA. To achieve narrow limits of control a glass electrode pH meter was used. Xylenol orange used as indicator is 3, 3′-bis [N, N-di(carboxymethyl) aminomethyl]–o–cresol sulphophthalin. It was prepared by mixing one part of indicator (AR) with 100-200 parts of potassium nitrate (AR) and the mixture well ground in a glass mortar. The resultant mixture is usually stable indefinitely if kept dry and in tightly stoppered bottle.

In the titration of lead (II) ions using xylenol orange as indicator at pH=6, the initial reddish-purple colour becomes orange-red and then with the addition of one or two further drops of reagent, the solution acquires the final lemon yellow colour. This end point anticipation, which is of great practical value, may be virtually lost if too much of the indicator is added so that the colour is too intense. In general, a satisfactory colour was achieved by the use of 30-50 mg of a 1 per cent solid mixture of the indicator in potassium nitrate.

2.6.2 Adsorption of Cadmium

Stock solution of cadmium (II) ions of 1000 mg/L was prepared by dissolving 2.744 g of cadmium (II) nitrate (Cd(NO₃)₂·4H₂O of analar grade in 1 lit. of demineralised water. It was used to prepare standard solutions of different concentrations by dilution with demineralised water. 10 ml of standard cadmium (II) nitrate solutions of different concentrations were titrated against 0.005 M EDTA solution at pH = 5 using hexamine as buffer and xylenol orange as indicator. The volume of EDTA solution used till end point was noted and a calibration curve was obtained by plotting values of concentration of cadmium (II) solution against the volume of EDTA solution used.(cf Fig 2.3).
Fig 2.3 Calibration of Cadmium
Activated carbon samples were dried in an electric oven at 120°C for four hours and then cooled in a desiccator. A known weight of each carbon sample (0.05g) was placed in contact with a known volume (50 ml) of cadmium (II) nitrate solutions of different concentrations. The suspensions were then placed in a thermostat for 24 hours with occasional shaking and a blank was also placed for each solution. Suitable aliquot portion of the sample containing not more than 0.05 millimole of the metal ion in a volume of 20 ml of solution was transferred into a volumetric flask. If the metal ion concentration is too high, the test solution is diluted with demineralised water to required volume and the solution was titrated against standard EDTA solution (0.005 M) using xylenol orange as indicator at pH = 5 and the volume of EDTA used till end point was noted. The blank was run every time and necessary corrections were made. The amount of Cd(II) ions in solution was determined using the calibration curve. Methods of preparation of standard EDTA solution, maintaining pH of the solution, use of indicator and end point were the same as explained in the adsorption of lead in this chapter.

2.6.3 Adsorption of Mercury

Stock solution of Mercury (II) ions of 1000 mg/L was prepared by dissolving 1.708 grams of mercury (II) nitrate of analar grade in 1 lit. of demineralised water. It was used to prepare standard solutions of different concentrations by dilution with demineralised water. 20 ml of standard mercury (II) nitrate solutions of different concentrations were titrated against 0.005 M EDTA solution at pH = 6 using hexamine as buffer and xylenol orange as indicator. The volume of EDTA solution used till end point was noted and a calibration curve was obtained by plotting values of concentration of Hg (II) ions in solution against and the volume of EDTA solution used (cf Fig 2.4)

A known weight of each carbon sample (0.5g) dried and cooled was placed in contact with a known volume (50 ml) of mercury (II) nitrate solutions of different concentrations. The suspensions were then placed in a thermostat for four hours and a blank was also placed for each solution. Suitable aliquot portion of the sample containing not more than 0.05 millimole of the metal ion in a volume of 20 ml of solution was transferred into a volumetric flask. If the metal ion concentration is too high, the test solution is diluted with demineralised water to required volume and the solution was titrated against standard EDTA solution (0.005 M) using xylenol orange as indicator at
Fig 2.4 Calibration of mercury

Volume of EDTA used (mL) vs. Concentration (mg/L)
pH = 5 and the volume of EDTA used till end point was noted. The blank was run every
time and necessary corrections were applied. The amount of cadmium in solution was
determined using the calibration curve. Methods of preparation of standard EDTA
solution, maintaining pH of the solution, use of indicator and end point were same as
explained in the determination of lead in this chapter.

2.6.4 Adsorption of Nitrobenzene

Stock solution of nitrobenzene of 1000 mg/L was prepared by dissolving 1 gm. Of
nitrobenzene in 1 lit. of demineralised water. It was used to prepare standard solutions of
different concentrations by dilution with demineralised water. Absorbance at 266 nm was
noted for nitrobenzene solutions of different concentrations using a UV-Visible
spectrophotometer. A calibration graph was obtained by plotting values of concentration
of solutions against the corresponding absorbance at 266 nm. A known weight of each
carbon sample (0.2g) dried and cooled was placed in contact with a known volume (20 ml)
of Nitrobenzene solutions of different concentrations. The suspensions were then placed in
a thermostat for 24 hours and shaken frequently. The concentration of the nitrobenzene
solution was determined spectrophotometrically at a wavelength of 266nm using the
calibration curve shown in Fig 2.5.

2.6.5 Adsorption of Gallic Acid

Absorbance at a wavelength of 258.8 nm was noted for gallic acid solutions of
different concentrations using UV-Visible spectrophotometer. A calibration graph was
obtained by plotting values of concentration of solutions against their corresponding
absorbance (cf Fig 2.6).

Activated carbon samples were dried in an electric oven at 120° C for four hours
and then cooled in a desiccator. A known weight of (0.2g) each carbon sample was placed
in contact with known volume (20ml) of gallic acid solution of different concentrations.
The suspensions were then placed in a thermostat for 24 hours and shaken frequently were
diluted to a required volume and their absorbance at a wavelength of 258.8 nm was noted.
The concentration of gallic acid before and after adsorption was determined
spectrophotometrically.
Fig 2.5 Calibration of Nitrobenzene
Fig 2.6 Calibration of Gallic acid
2.6.6 Adsorption of Tannic Acid

Absorbance at a wavelength of 276 nm was noted for tannic acid solutions of different concentrations using UV-Visible spectrophotometer. A calibration curve was obtained by plotting values of concentration of solutions and their corresponding absorbance and is shown in Fig 2.7.

Activated carbon samples were dried in an electric oven at 120° C for four hours and then cooled in a descicator. A known weight of (0.2g) of dried and cooled carbon sample was placed in contact with a known volume (20ml) of tannic acid solution of different concentrations. The suspensions were then placed in a thermostat for 24 hours and shaken frequently. An aliquot of clear supernatant solution was pipetted out and the concentration of tannic acid determined spectrophotometrically.
Fig 2.7 Calibration of Tannic acid

Absorbance vs. Concentration (mg/L)
2.7 References


