Summary

More than 1000 specific organic and inorganic chemical compounds have been found to be present in drinking waters. These compounds are derived from the industrial and municipal discharge, urban and rural runoff, natural decomposition of animal and vegetable matter and from water and waste water chlorination practices. Many of these chemicals are carcinogenic and cause many other ailments of varying intensity and character. Several methods such as coagulation, aeration and oxidation have been used for purification of water. But the ever increase of the variety and the amount of these chemicals makes these methods inadequate and sometimes ineffective. Many studies including laboratory tests and field operations have indicated that the activated carbon adsorption is perhaps the best broad spectrum technology available at the present moment.

A perusal of the literature shows that the adsorptive removal of organic and inorganic chemical compounds by activated carbons involve different factors and parameters. Consequently a large of research effort has been directed towards delineating these parameters and to develop newer modified activated carbons for the removal of these organic and inorganic compounds from water. The present thesis discusses the role of surface area and the surface chemistry of carbons in the adsorption of some organic and inorganic compounds from water.

The adsorptive removal of some very harmful metal cations such as Hg(II), Pb(II) and Cd(II) and of organic compounds such as nitrobenzene and dissolved natural organic compounds like gallic acid and tannic acid has been examined using several samples of granular activated carbons obtained form Norit N.V. The Netherlands, Active carbon India Limited and Industrial Carbons Private Limited., India. A sample of activated carbon fibre obtained form Ashland Petroleum company, U.S.A. and a sample of activated carbon cloth obtained form Environ Care Products, New Delhi have also been used in these investigations. The surface chemistry of these activated carbons was modified by oxidation with nitric acid, ammonium persulphate and hydrogen peroxide in the solution phase and by oxidation with oxygen gas at 350°C. The oxidized carbons were degassed in vacuum at gradually increasing temperatures of 400°, 650° and 950°C to eliminate varying amounts of different types of carbon-oxygen surface chemical groups. The adsorption isotherms have generally been determined in the concentration range 20-1000 mg/L.
The adsorption of Hg(II) ions from aqueous solutions of mercuric nitrate (Chapter III) is significantly large at lower concentrations but tends to attain a constant value at higher concentrations. The adsorption data follows both the Langmuir and Freundlich isotherm equations. The Freundlich equation parameter $n$ which characterizes quasi-Gaussian energetic heterogeneity of the adsorbent surface is always less than unity. The value of $n$ decreases on oxidation of the carbon surface and increases on degassing. It is minimum for the carbon samples oxidized with nitric acid which have the highest amount of associated surface oxygen and maximum (close to unity) for the 950°-degassed carbon samples which are almost completely free of any associated oxygen. This indicates that the presence of associated oxygen on the activated carbon surface renders the carbon surface heterogenous in character.

The adsorption of Hg(II) ions increases on oxidation of the activated carbons, the increase in adsorption depending upon the nature of the oxidative treatment. The increase in adsorption is considerably larger when the oxidation is carried out with nitric acid compared to other oxidative treatments. The adsorption increases from 4% to 20% on oxidation of the activated carbon cloth with nitric acid and from 4% to 9% on oxidation with oxygen gas. This large increase in adsorption has been attributed to the fact that the oxidation with nitric acid is a much stronger oxidative treatment and results in the chemisorption of a larger amount of oxygen on the carbon surface. Furthermore, the increase in the amount of surface acidic groups which are evolved as CO$_2$ on degassing and which have been postulated as carboxylic and lactones is considerably larger on oxidation with nitric acid than by oxidation with oxygen gas. When the oxidized carbon samples were degassed at gradually increasing temperatures, the adsorption of Hg(II) ions was found to decrease gradually with increasing temperature of degassing.

It is interesting to note that the decrease in adsorption on degassing at 400°C is only small varying between 1-3% for both GAC-1240 and the carbon cloth. However, when the temperature of degassing is increased to 650°C, the decrease in adsorption is appreciably larger. This has been attributed to smaller elimination (~15%) of the acidic surface groups in the case of 400°-degassed carbon samples and to larger (~85%) elimination of the acidic surface groups in case of the 650°-degassed carbon samples. It may be significant to mention here that the 400°-degassed carbon samples retain the non-acidic surface groups almost completely while the 650-degassed carbon samples...
retain a larger portion of their non-acidic surface oxygen groups. The carbon samples degassed at 950°C show still smaller adsorption of Hg(II) ions because these samples are almost completely free of any carbon-oxygen surface groups.

The surface area covered by hydrated Hg(II) ions was calculated using Langmuir monolayer capacity \((x_m)\) and 0.56 nm as the radius of hydrated Hg(II) ions. It has been found that only a very smaller fraction varying between 5-15% of the BET carbon surface is covered by the hydrated Hg(II) ions. This indicates that BET surface area of a carbon surface is only of little consequence in determining the adsorption of Hg(II) ions from aqueous solutions. Furthermore, the adsorption capacity or the area covered increases on oxidation of the carbon surface although the BET surface area slightly decreases on oxidation. This indicates that the adsorption of Hg(II) ions takes place on certain specific sites. These sites appear to be acidic surface oxygen groups. This is supported by a linear relationship between the surface acidity of a carbon surface and the amount of Hg(II) ions adsorbed.

The uptake of Hg(II) ions is very small at solution pH values below 3, increases sharply at pH values between 3 and 5 and remains more or less unchanged at higher pH values. This has been attributed to a change in the carbon surface charge with a change in solution pH. A sudden change in the adsorption of Hg(II) ions in the pH range 2-3 indicates that the zero point charge (ZPC) of the carbon surface lies between these values. At pH values lower than ZPC the carbon surface has a positive charge due to excessive protonation of the surface. This results in repulsive electrostatic interactions between the positively charged carbon surface and the mercury cations resulting in a small adsorption. When the pH of the solution is above ZPC, the carbon surface attains a negative charge resulting in attractive electrostatic interactions causing an increase in adsorption of Hg(II) ions.

The mechanism of adsorption of Hg(II) ions on the activated carbon surface involves the ionization of acidic carbon-oxygen surface groups (identified as carboxyls and lactones) into \(H^+\) ions which are directed towards the liquid phase leaving the carbon surface with negatively charged surface sites on which the adsorption of mercury cations present in the solution can take place. On oxidation of the carbon surface, the number of these negatively charged sites increases thereby the adsorption increases. When the acidic carbon-oxygen surface groups which impart negative charge to the carbon surface are eliminated on degassing, the concentrations of the negative
sites becomes smaller and smaller. This results in a decrease in adsorption of mercury cations. This also explains the maximum adsorption of Hg(II) ions on the nitric acid oxidized samples as this oxidation treatment creates maximum amount of surface acidic groups. When the oxygen groups are removed almost completely by degassing at 950°C, the carbon surface becomes more or less positively charged resulting in a decrease in the adsorption. Thus the adsorption of Hg(II) ions in the case of 950°-degassed carbons can be attributed to the micropores made available by the removal of carbon-oxygen surface groups.

The adsorption isotherms of Pb(II) ions from aqueous solutions of lead nitrate in the concentration range 50-500 mg/L at a controlled solution pH=5 are Langmuir in shape. The amount adsorbed increases with increases in surface area of the carbon but there is no linear relationship between the amount adsorbed and the BET surface area. The surface area occupied by hydrated Pb(II) ions in the case of each carbon was calculated using 0.802 nm as the average molecular diameter of hydrated lead ions. The surface area covered by Pb(II) ions is only a fraction amounting to about 8% of the BET surface area. This indicates that as in the case of Hg(II) ions, the BET surface area of activated carbons does not play a significant role in the adsorption of Pb(II) ions from aqueous solutions. The adsorption increases on oxidation and decreases on degassing. The increase in adsorption on oxidation depends on the nature of the oxidative treatment and is at a maximum in case of the carbon samples oxidized with nitric acid which is the strongest oxidative treatment. The decrease in adsorption on degassing depends on the temperature of degassing. It is interesting to note that the increase in adsorption on oxidation and the decrease in adsorption on degassing follow the same order as the increase in the amount of acidic carbon-oxygen surface groups on oxidation and the decrease in the amount of acidic groups on degassing.

The adsorptive removal of Cd(II) ions from aqueous solutions in the concentration range 20-500 mg/L at a controlled solution pH = 5 has been studied. The pH of the solution was controlled by the addition of small amounts of nitric acid or sodium hydroxide. The adsorption data obeys both the Langmuir and the Freundlich isotherm equations. The Langmuir monolayer capacity, x_m, although increases with BET surface area of the carbon, it does not show a linear relationship with the surface area. This indicates that, as in the case of adsorption of Hg(II) and Pb(II) ions, the adsorption of Cd(II) takes place at some specific sites available on the carbon surface.

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and that whole of the surface area is not involved in the adsorption of Cd(II) ions. The adsorption of Cd(II) ions increases significantly on oxidation of each carbon, the amount of increase being maximum in case of the oxidation with nitric acid and minimum for oxidation with oxygen gas. The adsorption decreases on degassing of the oxidized carbons, the decrease in adsorption depending upon the amount of acidic surface groups eliminated from the carbon surface on degassing. Thus the adsorption of Cd(II) ions like that of Hg(II) ions and Pb(II) ions takes place on specific sites provided by acidic carbon-oxygen surface groups. These results are supported by a linear relationship between the maximum amount of Cd(II) ions adsorbed and the surface acidity of GAC-E activated carbon before and after oxidation and degassing.

The adsorption of nitrobenzene which essentially exists in the molecular state in aqueous solutions are Langmuir is character. All the carbon samples adsorb appreciable amounts of nitrobenzene, the maximum amount adsorbed varying between 18-28% for the different carbons. Although the amount adsorbed increases with increase in surface area of the carbon only a fraction (less than 50%) of the BET surface area is available for the adsorption of nitrobenzene indicating that the rest of the surface in these carbons is present in the form of very fine micropores which are inaccessible to nitrobenzene molecules. The oxidation of the carbons is seen to result in considerable decrease in the adsorption, the extent of decrease being about 50% of its value on the as-received carbon samples. The adsorption increases on degassing of the oxidized carbons, the increase in adsorption being maximum in the case of 650°-degassed carbon samples.

As the nitrobenzene molecules are essentially unionized in aqueous solution the electrostatic interactions between the negatively charged carbon surface and the nitrobenzene molecules are expected to be at a minimum. Therefore, the adsorption of nitrobenzene mainly involves dispersive interactions between the aromatic ring of nitrobenzene and the carbon surface. The oxidation of the carbon surface results in a decrease in the \( \pi \) electron density on the grapheme layers due to withdrawal or localization of \( \pi \) electrons and as the nitro group in nitrobenzene is also an electron withdrawing group, the dispersive interactions between the carbon surface and the nitrobenzene molecule will be much smaller. These two factors will result in a reduced adsorption of nitrobenzene when the carbons are oxidized. The decrease in adsorption on oxidation can also be due to the size and nature of the acidic groups. As these groups which have been identified as carboxyls and lactones are bulky molecules, they may
block some of the narrow micropores and make them inaccessible to nitrobenzene molecules. In addition the polar water molecules will cluster around the polar acidic surface groups in the micropore system resulting in a decrease in the adsorption. When the carbon oxygen surface groups are eliminated on degassing, these micropores become available for the adsorption of nitrobenzene. The π electron density on the graphene layers is also increased due to the removal of carbon-oxygen surface groups enhancing the dispersive interactions between the carbon surface and the nitrobenzene molecules.

The maximum adsorption in the case of 650°-degassed carbon samples has been attributed partly to the elimination of acidic surface groups which inhibit the adsorption and partly to the dominance of quinonic surface groups. These quinonic surface groups can adsorb additional amounts of nitrobenzene through an interaction between the partial positive charge on the carbonyl carbon atom in quinonic and π electron clouds of the benzene ring in nitrobenzene. These quinonic groups are eliminated almost completely in the case of 950°-degassed carbons. These samples, therefore, show a smaller adsorption.

The adsorption of nitrobenzene at solution pH values of 2.95, 6.18 and 10.85 on a sample each of oxidized and degassed carbons was found to be independent of the pH. All the points for a given carbon could be collected on a single isotherm. This once again indicates that the adsorption of nitrobenzene from aqueous solution by activated carbons involves only dispersive interactions, the electrostatic interactions being more or less absent.

The adsorption isotherms of two naturally occurring organic materials, gallic acid and tannic acid which are always present in surface waters are also Type I of the BET classification and the adsorption data confirms to Freundlich isotherm equation. The adsorption of both gallic acid and tannic acid is the largest in case of the activated carbon cloth which has the smallest surface area. This indicates that the chemical structure of the carbon surface plays a dominant role in the adsorption of these compounds. In contrast to the adsorption of metal cations Hg(II), Pb(II) and Cd(II) the adsorption of both the acids decreases on oxidation of the carbons. The decrease in adsorption is maximum in case of the carbon samples oxidized with nitric acid and minimum for the samples oxidized with oxygen gas. Since the nitric acid oxidized samples have the largest amounts of acidic carbon – oxygen surface groups, it appears
that the presence of acidic surface groups inhibits the adsorption of these acids. When
the oxidized carbon samples are degassed at gradually increasing temperatures, the
adsorption gradually increases as the temperature of degassing is enhanced. In other
words, the adsorption of both these acids increases when the acidic surface groups are
eliminated from the carbon surface on degassing. It is thus apparent that while the
presence of acidic surface oxygen groups on the carbon surface inhibits the adsorption
of both gallic and tannic acid, their removal from the carbon surface enhances the
adsorption. This can be attributed to the fact that the presence of acidic surface groups
renders the carbon surface hydrophilic and negatively charged. The increase in the
hydrophilicity of the carbon surface results in the formation of water clusters around
the pore entrance while the negative charge of the carbon surface produces repulsive
electrostatic interactions between the carbon surface and the gallic or the tannic acid
anions which are present in aqueous solutions of these acids. Both these factors tend to
reduce the adsorption of gallic acid or tannic acid. As the surface acidic groups are
removed gradually on degassing the carbon surface at increasing temperatures, the
carbon surface tends to become hydrophobic and lesser and lesser negatively charged.
This increases the adsorption of gallic and tannic acids. Furthermore, the removal of
bulky acid surface groups from the carbon surface also makes some of the micropores
available for the adsorption of these acids.