SUMMARY

Increasing awareness and stricter environmental regulations have made it essential that waste water from industrial and municipal discharge be given some treatment before dumping it into waterways. This waste water contains large amounts of varied chemical compounds which include organic and inorganic compounds. As the amounts and the variety of chemicals is always increasing, the conventional water treatment procedures have become inefficient and sometimes ineffective. Consequently attempts have been underway to develop new methods for treatment of waste water.

Activated carbons, because of their large surface area, highly porous character and high degree of their surface reactivity are excellent adsorbents both for organic and inorganic compounds. A survey of the literature shows that the adsorption of organic and inorganic compounds involve different factors. Consequently there is an upsurge in research activity in developing newer activated carbons so as to provide a choice for the removal of organic and inorganic compounds. The present thesis delineates some of the surface properties of activated carbons which influence the adsorption of organic and inorganic compounds.

The adsorption isotherms of metal ions such as Cr(III), Cr(VI), Co(II) and organic compounds such as phenol, oxalic acid and two dyes metanil yellow and rhodamine-B have been studied using two samples of activated carbon fibres ACF-307 and ACF-310 obtained as gift from Ashland Petroleum Company of USA and two samples of granulated activated carbons GAC-E and GAC-S obtained as gift from Norit Company Netherlands. The surface of these activated carbons has been modified by oxidation with
nitric acid, ammonium persulphate and hydrogen peroxide in the liquid phase and with oxygen at 350°C in the gaseous phase. The surface of the carbons has also been modified by evacuating (degassing) the oxidised carbon samples at 400°, 650° and 950°C, in order to eliminate varying amounts of the carbon-oxygen surface chemical structures. The adsorption isotherms have generally been carried out in the concentration range 20-1000 mg per litre.

The adsorption isotherms of Cr(III) ions from aqueous solutions (Chapter II) of chromium chloride are Langmuirian in character. All the four activated carbons adsorb appreciable amounts of Cr(III) ions although the amounts adsorbed are different for different carbons. In general the adsorption is several times larger on the granulated carbons compared with the fibrous activated carbons. This cannot be attributed to surface area because GAC-S which has a surface area of 1156 m²/g adsorbs larger amounts of Cr(III) than ACF-310 which has a surface area of 1284 m²/g. It appears that fibrous activated carbons may have a larger proportion of extremely fine micropores which are inaccessible to larger molecules of Cr(III) ions (molecular diameter 0.922 nm) which are present in the solution as hydrated ions.

The adsorption of Cr(III) ions increases on oxidation of the carbons although the increase in adsorption depends upon the nature of the oxidative treatment. The increase in adsorption is maximum in case of the samples oxidised with nitric acid and minimum in case of the oxidation with hydrogen peroxide. This has been attributed to the fact that the oxidation with nitric acid enhances the amount of chemisorbed oxygen by considerably large amounts compared to oxidation with other oxidative treatments. When the oxidised carbon samples were degassed at gradually increasing temperatures, it is found that adsorption of Cr(III) ions decreases gradually as the temperature of degassing is enhanced. Furthermore, it is interesting to note that the decrease in adsorption is only
slight on degassing at 400°C. However, when the temperature of degassing was increased to 650°C the adsorption in the case of GAC-S decreased from 1.24 % in the case of the as-received samples to less than 0.65 % in the case of the 650°-degassed sample. In the case of the oxidised samples also, the adsorption of Cr(III) decreased considerably on degassing at 650°C. When the carbon samples were degassed at 950°C, there is little or no adsorption of Cr (III) ions. This increase in adsorption on oxidation and the decrease in adsorption on degassing has been attributed to the formation of acidic oxygen surface groups on oxidation and removal of these acidic surface groups on degassing.

The surface area covered by Cr(III) ions has been calculated using 0.922 nm as the molecular diameter of Cr(III) ions. It has been found that only a small fraction of the BET surface area, in all the carbons, is occupied by Cr(III) ions. Furthermore, the area covered increases on oxidation and decreases on degassing. This indicates that the adsorption of Cr(III) ions takes place on certain specific sites. These sites appear to be acidic surface oxygen groups. These acidic groups ionise in aqueous solutions producing H⁺ ions which are directed towards the aqueous phase. The carbon surface in turn becomes negatively charged which adsorbs the positively charged Cr(III) ions which exist as [Cr(H₂O)₆]³⁺ in aqueous phase. When the oxygen surface groups which impart negative character to the carbon surface are removed on degassing, the carbon surface becomes lesser and lesser negatively charged, thereby resulting in a decrease in the adsorption of Cr(III) ions. This also explains the maximum adsorption of Cr(III) ions on the nitric acid-oxidised samples as this oxidative treatment creates maximum amount of surface acidic groups. When all the surface oxygen groups are removed almost completely on degassing at 950°C, the carbon surface loses its capacity to adsorb Cr(III) ions almost completely as the carbon surface tends to acquire a positive charge.
The adsorption isotherms of Cr(VI) have been determined from potassium dichromate solutions of different concentrations. The amount of Cr(VI) ions adsorbed is comparatively much larger than the amount of Cr(III) ions. This larger adsorption in the case of Cr(VI) ions has been attributed partly to the smaller size of Cr(VI) ion in aqueous phase so that it can enter a larger proportion of the pores and partly to the fact that Cr(VI) ion is adsorbed as an anion. As the pH of the as-received activated carbons is in the range 7.2-10.0, there is preponderance of positively charged sites where negatively charged Cr(VI) ions can be adsorbed. In contrast to the adsorption of Cr(III) ions, the adsorption of Cr(VI) ions decreases on oxidation of the carbons. Furthermore, the decrease in adsorption is maximum in case of the samples oxidised with nitric acid. This decrease in adsorption has been attributed to the formation of carbon-oxygen surface groups which impart negative character to the carbon surface (acidic carbon-oxygen surface groups). It may, however, be mentioned that oxidised carbons are also associated with appreciable amounts of non-acidic carbon-oxygen surface groups which have been postulated as quinones. These quinonic groups can cause reduction of Cr(VI) into Cr(III) ions. However, the reduction of Cr(VI) into Cr(III) under the conditions used in these investigations is very small so that there is an overall decrease in the adsorption of Cr(VI) ions in all cases. The adsorption of Cr(VI) ions increases on degassing, being maximum in case of the 650° C-degassed carbon samples. This is due to the fact that the 650° degassed sample has lost a larger proportion (80-85%) of the acidic groups but retains most of the non-acidic quinonic groups. This sample has a pH of around 5.5 which is very favourable for the reduction of Cr(VI) into Cr(III) ions, since the standard reduction potential of the system Cr(VI) - Cr(III) in acid medium is +1.195 V. In the case of 950°-degassed carbon samples, the adsorption decreases considerably because there are no interactive surface oxygen groups on the carbon surface.
The adsorption of Co(II) ions (Chapter III), like the Cr(III) ions is larger in case of the granulated carbons. The adsorption isotherms have been explained by Freundlich adsorption isotherm equation. The linear Freundlich adsorption isotherms have been used to calculate the value of Freundlich constant n. The adsorption of Co(II) ions increases on oxidation and decrease on degassing. The increase in adsorption is maximum in case of the oxidation with nitric acid which produces maximum amounts of acidic surface oxygen groups. The oxidation of carbons and the formation of acidic carbon oxygen surface groups also causes a change in the pH of the carbon surface. The pH of as-received ACF-307 is about 7 while that of GAC-E is almost 10. When these carbons are oxidised with nitric acid, the pH of the carbon surface is reduced to between 4 and 5. The oxidation with oxygen gas reduces the pH to between 5 and 6. As the adsorption of metal ions is very sensitive to pH of the solution and as it increases with decrease in pH in this range, the increase in adsorption of Co(II) ions can be visualised. This receives further support from the adsorption isotherms of Co(II) ions on the degassed samples. The adsorption of Co(II) ions decreases gradually as the carbon surface oxygen groups are being eliminated from the carbon surface. As in the case of Cr(III) ions (Chapter II), the decrease in adsorption of Co(II) ions is very small in case of the 400°C-degassed carbon samples because only a very small part of the acidic carbon oxygen surface groups have been eliminated on degassing at this temperature. When the carbon samples are degassed at 650°C, a large part of the acidic surface oxygen groups is eliminated resulting in a considerable decrease in the adsorption of Co(II) ions.

The adsorption of phenol (Chapter IV) is considerably larger on the fibrous activated carbons ACF-307 and ACF-310 than the adsorption on the granulated activated carbons GAC-E and GAC-S. The maximum amount adsorbed in case of fibrous activated carbons is between 17 - 20% while in the case of granulated activated carbons it varies...
between 9-12%. This has been attributed to the existence of chemical groups on the two types of activated carbons. A comparison of the oxygen present on the four samples of activated carbons indicates that while the GACs are associated with larger amounts of oxygen groups evolved as CO$_2$, the fibrous activated carbons contain a larger amount of oxygen evolved as CO. The former are postulated as carboxylic or lactonic groups which are acidic in nature and render the carbon surface hydrophilic and polar in character. These surface groups tend to increase the adsorption of water molecules rather than that of phenol. The carbon-oxygen groups which are evolved as CO have been postulated as quinonic groups which are known to enhance the uptake of phenol by activated carbons.

This receives support from the adsorption isotherms on the oxidised carbon samples. The oxidation of carbon decreases the adsorption of phenol and this decrease is maximum in case of the carbon samples oxidised with nitric acid and minimum when the carbon is oxidised with hydrogen peroxide. The maximum uptake of phenol decreases from 20% to 10% on oxidation with nitric acid and from 20% to 15% on oxidation with hydrogen peroxide. Similarly the adsorption of phenol increases when the oxidised carbon samples are degassed at 400°, 650° and 950°C. The increase in adsorption, however, is maximum in case of the sample degassed at 650°C. This has been attributed to the fact that the 650°C-degassed sample has lost a greater part of its acidic surface groups which suppress the adsorption of phenol but still retains a greater portion of its non-acidic surface groups (quinonic groups) which enhance the adsorption of phenol.

The adsorption of oxalic acid (Chapter V) like that of the adsorption of phenol is also considerably larger in the case of the fibrous activated carbons than the granulated activated carbons. The adsorption decreases on oxidation. The decrease in adsorption is maximum in case of the oxidation with nitric acid which produces the maximum amount of acidic surface groups. For ACF-307 the decrease in adsorption is from 14% to 3% in
the case of oxidation with nitric acid and from 14% to 9% in case of the oxidation with gaseous oxygen. Similarly, in the case of GAC-E, the adsorption of oxalic acid decreases from 8% to 1.5% when oxidised with nitric acid and from 8% to 6% when oxidised with oxygen gas. When these oxidised carbons are degassed at gradually increasing temperatures, the adsorption of oxalic acid gradually increases. These results indicate that the adsorption of oxalic acid by carbons is suppressed by the presence of acidic surface groups and is not influenced by the presence or absence of non-acidic surface groups. When the maximum amount of oxalic acid adsorbed per unit area was plotted against the base adsorption capacity for ACF-307 and GAC-E before and after oxidation with different oxidising agents and subsequently degassing, two separate linear plots are obtained for the two carbons indicating that the adsorption of oxalic acid is related inversely to the amount of surface acidic groups present on the carbon surface. The two separate lines indicate a difference in the microporous structure of the two carbons.

The adsorption of metanil yellow (Chapter VI) is maximum in case of ACF-310 which has the largest surface area and minimum in case of ACF-307 which has the smallest surface area. However, there is no linear relationship between the amount adsorbed and the surface area. This indicates that in addition to surface area, the chemical nature of the carbon surface also influences the adsorption of metanil yellow. The adsorption decreases on oxidation, the decrease being maximum in case of the oxidation with nitric acid which produces the maximum amounts of acidic surface groups. When these acidic surface groups are removed on degassing, the adsorption of metanil yellow shows an increase. The increase in adsorption is maximum in case of the 650°C-degassed samples which have lost a larger portion of their acidic surface groups.
The adsorption isotherms of Rhodamine-B (Chapter VI), however show an exactly opposite trend. The adsorption of Rhodamine B increases on oxidation, being maximum in case of the oxidation with nitric acid and decreases on degassing.

These results have been explained on the basis of the chemical nature of the two dyes. While the metanil yellow is an anionic dye, Rhodamine B is a cationic dye. When the carbon surface is negatively charged due to the presence of acidic carbon-oxygen surface groups, it prefers adsorption of Rhodamine-B because of the attractive interactions between the negatively charged carbon surface and the positively charged cation of the dye. The same negatively charged surface inhibits the adsorption of metanil yellow due to repulsive interactions between the negatively charged carbon surface and the negatively charged anion of metanil yellow. When these acidic oxygen groups are eliminated on degassing, the preference of the carbon surface is more for the metanil yellow than Rhodamine-B.

The results presented in this thesis clearly show that while the presence of acidic surface oxygen groups on the carbon surface enhance the adsorption of cations, it suppresses the adsorption of non-polar organic compounds.