Summary

Wood based activated carbons and modified wood fibre were well characterized by different surface properties and used as adsorbents. The extent of activation, yield and development of porosity of the carbon during carbonisation are directly related to the activation temperature and the concentration of Zn\(^{2+}\) ions incorporated in the precursor matrix. In all cases of ZnCl\(_2\) activation, the yield was progressively increased from X\(_{Zn}\) 0.20 to 0.30. Wood samples with identical heating (723 K, 2.5h and 5 K/min) profiles recorded a burn off value in the range of 57-70% and were predominantly microporous. Wood fibres grafted with polyacrylamide (GWD) shows the presence of carboxylic acid (–COOH) and amide (–NH–CO–) bands in the FTIR spectra which are characterized by weak acid centres. Similarly formaldehyde polymerised or immobilised wood (FWD) contains more exchangeable sites than the original wood.

The chemical surface modifications of carbon brings large differences in properties. The resulting chemically activated carbon had much less conjugated ring structures. Carbons obtained by Zn\(^{2+}\) activation viz., CZ1 and CZ2, are susceptible to oxidation, while carbon CS, based on H\(_2\)SO\(_4\) activation of wood acted as a char, dissolving in oxidation medium. The modification procedures described in the study can be used to prepare an adsorbent with tailor-made properties.

X-ray diffraction profiles of carbon CS, CZ1 and CZ2 revealed that the carbon skeleton of these samples are disorganised and are structurally non graphitisable. Carbons oxidised with HNO\(_3\) such as CZ1-26, CZ1-13 and CZ1-4 showed changes with regard to surface modifications. The FTIR spectra clearly indicate a small increase in intensity of absorbance upon nitric acid oxidation when the absorbances are at 1700 and 1585 cm\(^{-1}\).

In all oxidation procedures, the oxygen containing surface groups are produced within three hours unless the reagent is refreshed. The increase in absorbance with concentration of HNO\(_3\) used indicates that the extent of surface groups generated is directly proportional to the concentration of oxidising agent. In the diffractograms of wood compared with grafted wood, to determine the changes in crystallinity, diffraction maxima occurred at 22.34° on wood and 21.41° on grafted wood. This corresponds to the 020 plane (higher ordered fractions). The broad peak centred around 16.5° in wood is a combination of lower ordered fractions. The width changed from 0.80 to 1.44Å during grafting.
The types of sites present on the surface of carbon and wood are identified as strong, weak and very weak acid centres from the potentiometric $n$-butylamine consumption data. Wood in native form contains only weak acid sites while formaldehyde and polyacrylamide grafted wood behaves as solids with strong and weak sites. These results were used for the qualitative categorisation of the new adsorbents with respect to their relative acidity and acid sites. The quantitative estimation of surface groups were done using Boehm's acid/base titration. The thermal behaviour of the sorbents were studied by TG/DTG profiles where the evolution of gases occurs by decomposition of surface groups. The results confirm the presence of more surface acid groups on the oxidised carbon surface.

Carbon CZ1 showed three distinct temperature ranges. A sharp shoulder forms at 388 K, for adsorbed interstitial water (28%), a broad TG step constituting a loss of 21.92% between 398–1138 K. A third stage between 1143 and 1473 K with weight loss of 28.16% is mainly due to the evolution of CO gas. The results obtained from FTIR spectra provide valuable information about the various surface structures present on the adsorbents. The increase in intensity of the peak at 1600 cm$^{-1}$ on the oxidised carbons with respect to parent carbon is due to a quinone structure. Five major peaks were observed at various wavelengths for the oxidised carbons. They are at 1722, 1595, 1537, 1384 and 1349 cm$^{-1}$. The peak at 1722 cm$^{-1}$ can be assigned to a carboxyl group and one at 1595 cm$^{-1}$ is attributed to carboxyl group conjugated with an aromatic system. In carbon CZ1-26 a broad absorption band existing between 1000 and 1349 cm$^{-1}$ is mainly due to the $> C = O$ stretching frequencies of the $-COOH$ groups to which contribution of their groups were summed up. Hence, the major surface groups identified include phenols, lactones, carbonyls, quinones, carboxyls and pyrones.

The morphological features revealed by SEM shows a total reduction of cellulose fibre thickness by 24.24% for carbon CS and 62.12% for CZ2. Uniform and parallel macropores were visible over the whole length. These were well interconnected by former precursor cell walls at regular intervals through meso and micropores.

By selecting the right carbon material and right modification technique, it is possible to adjust the amount of oxygen surface groups, surface acidity and zero point charge seperately. The yield, porosity and surface area of chemically activated carbons directly depends upon the quantity of impregnating agent used. Oxidation creates carbon surfaces with relatively large ion exchange capacities. Combining the results obtained from amine and acid/base consumption, chemical composition, FTIR, XRD, TGA/DTG, SEM, the adsorption reaction occurring at the carbon or wood fibre surface can be understood reasonably well. The porosity and pore size distribution of an adsorbent is very important to describe its relative sorption capacity and mechanism of adsorption.

The adsorption affinity of N$_2$ at 77 K and CO$_2$ at 298 K for seven newly developed adsorbents (five carbons CS, CZ1, CZ2, CZ1-26 and CZ2-26 and wood FWD and GWD) has been compared using a multiple process equilibrium analysis.
Attempts have been made to separate the process of ultramicropore-supermicropore adsorption and adsorption by the remaining surfaces. Highly activated carbons (CZ1 and CZ2) were characterised by a wide micropore size distribution. The results obtained by BET and $\alpha_5$ analysis were similar to each other. The new activated carbons and wood based adsorbents were found to be predominantly microporous. They retain the porosity even after surface modifications. The adsorption affinity towards N$_2$ and CO$_2$ decreased by oxidation with 26% nitric acid. The adsorption capacity of FWD was found to be higher than GWD.

The BET plots of N$_2$ adsorption isotherms were found to be linear up to P/P$_0$ of 0.35. The D-R plots were also linear up to P/P$_0$ equal to 0.30 for all samples with a C type positive deviation. Most of the micropore volume was contributed by the pores with width <1.8-2.0 nm. The adsorption capacities of oxidised carbons were lesser than that of the parent irrespective of the nature of gas molecules. The D-R equation generally estimated a higher value for micropore volume for N$_2$ at 77K. The carbon CS showed a narrow-porosity exhibiting molecular sieving properties towards large adsorbate molecules. Carbons CZ1 and CZ2 showed slight C type positive deviations at the origin of the D-R plots where log$^2$($P_0/P$) values were small which indicate larger proportions of mesopores. The D-R plots of wood are slightly linear with ranges of pressures, which shows the existence of a heterogeneous porous structure. The pore width values calculated by various methods show close agreement with each other. The results indicate the presence of super micropores (1.4 to 3.2 nm) for CS, CZ1 and CZ2. The first two parent carbons possess high surface acidity.

The adsorption of CO$_2$ gas at 298 K in narrow micropores occurs by a primary filling process. The estimated micropore volume was always higher. Diffusion of adsorbate molecules may cause the adsorption at the constrictions of the pore structure. The results obtained from $\alpha_5$ plots are useful to calculate the total micropore volume which is the contribution of micro and super or wide micropores filled by a secondary filling process. The results obtained from D-R/N$_2$ analysis show that during oxidation, widening of pores occurs for CZ1-26 and that the pore dimension has decreased for CZ2-26. Contrary to this, CO$_2$ isotherm results showed a lower pore width for CZ1-26 compared to CZ2-26 and the calculated micropore surface area was very high. The high pore volume and surface area are contributed by the CO$_2$ isotherm which can be interpreted in terms of activated diffusion effect. The porosity and chemical composition of the carbons and wood are the predominant factors determining adsorption. The results from BET, D-R and $\alpha_5$ plots indicate porosity due to ultra and super micropores as a contributing factor. John’s isotherm has been tried to evaluate the dispersion of pores, range and degree of microporosity and categorisation of new carbons and wood based adsorbents.

John isotherm plots based on N$_2$ adsorption data have been constructed for all carbon and wood samples. The graph was extrapolated at the low pressure region where isotherm is more or less linear. The categorisation was made from slope
and shape of the isotherms. Accordingly, carbon CS was found to be the one with bidisperse pores similar to carbons produced from coals. The small proportion of mesopores, evidenced by the deviation of the data from the extrapolated straight line in the J plot of CZ1, indicates the presence of monodisperse micropores along with mesopores. The J isotherm plots obtained for CZ2 behaved identically to that of CZ1. The limiting micropore pore volume ($V_0$) was found to be 0.354 and 0.473 ml/g for CZ1 and CZ2 respectively. The pore volume ($V_0$) and surface area ($S_1$) for the carbons were in good agreement with that obtained from D-R plots.

The J plots of modified carbons CZ1-26 and CZ-26 showed three distinct phases. The preferential widening of micropores can be assumed as a contributing factor during oxidation. On oxidation, mesoporosity of the carbon material increased considerably. The carbon CS and modified wood FWD and GWD were characterized by two types of micropores; finer and coarser. The carbon CS has a higher degree of micro or finer porosity which contribute a surface area of 75.650 m$^2$/g with gradient $n$ 1.313 while the coarser pores contribute 21.540 m$^2$/g having a small $n$ of 0.599.

The samples FWD and GWD showed the presence of bidisperse pores having a wide range of pore size or wider dispersion of pores. Hence, these samples indicate small fine pored porosity and large coarse pored porosity.

The surface acidity or polarity of the new materials have a direct relationship with their surface area. The micropore surface area, $S_{mi}$, increased with a decrease in O/C ratio or oxygen based surface polarity for all solids. The bulk of the microporosity was contained in pores < 1.8-2.0 nm in size. The overall correlation between, the micropore width (L) and the surface characterisation energy ($E_0$), shows that for 1.55 < $L$ < 3.69 nm, $E_0$ varies from 14.33 to 18.36 kJ/mol for which $n$ varies from 0.5 to 5.53. The resulting plot obtained for the new adsorbents revealed an interesting concave pattern common for typical activated carbon materials. The surface area of the oxidised carbons was determined using N$_2$ and CO$_2$ and was found to be low compared to the parent carbons. The results of these investigations illustrate that the degree of information obtained depends on the different isotherm techniques used. The analysis of isotherm data using the above methods provides the safest way to characterize the new porous carbons and wood materials. The evaluated low porosity in the case of oxidised carbons are more due to the contribution of heterogeneous micropored mesoporosity. Study of adsorption parameters from aqueous solutions on new samples is of great importance and have many applications in evaluating adsorption capacity.

Batch experiments have been conducted to investigate the kinetics of adsorption of organic molecules described by the solute uptake rate. It determines the residence time required for the completion of adsorption process. The sorption of phenols on carbon CZ2 which has less acid sites compared to CZ1, revealed a high initial rate of uptake with a slower subsequent phase that gradually approached equilibrium. In the initial stages of the contact time of 35 minutes almost 65.44% of the total amount of 40.78 mg/g was adsorbed by CZ2 from the initial concentration.
of 100 mg/l. Meanwhile, the same carbon adsorbed a higher amount of nitrophenol constituting 77.69% of the adsorbed quantity at equilibrium (76.74 mg/g) from the same initial amount. The adsorption of phenols on modified wood occurs through a two stage process. The sorption capacity of FWD with carbon CZ2 is in the ratio of 0.412 for phenol and 0.460 for nitrophenol for an initial concentration of 100 mg/l. However for 250 mg/l, it was observed as 0.440 for phenol and 0.513 for nitrophenol.

The adsorption rate data for different phenol concentrations (50, 100, 150 and 250 mg/l) varies almost linearly with half power of time $t^{0.5}$, which indicated the intraparticle diffusion mechanism. The results of study on kinetics of phenol adsorption on CS, CZ2, CZ2-26 and FWD confirm that the adsorption phenomena is a diffusion controlled first-order reversible process.

The effective internal diffusion coefficient, $D_e$, increases with the amount adsorbed for both phenol and p-nitrophenol. The coefficient has a magnitude of $10^{-8}$ cm$^2$/s and is higher for p-nitrophenol. This shows that the surface diffusion coefficient increases with concentration of adsorbed layer or phase as a result of a lower adsorption energy. Straight line graphs were obtained corresponding to potential functions in the form of $D_e = a(n)^b$ where a good fit was obtained for CZ2-phenol, CZ2-p.nitrophenol, FWD-phenol and FWD-p-nitrophenol. The values of coefficients $a$ and $b$ were higher for p-nitrophenol (except $b$ for FWD) which are in good agreement with earlier observations. It was possible to predict all the experimental concentration decay curves with reasonable accuracy using a single constant external mass transfer coefficient $K_L$ and a single constant pore diffusion coefficient $K_p$.

BET, D-R, Freundlich, Langmuir and John isotherm models have been used to test the validity of equilibrium isotherm data to determine the useful parameters such as sorption capacities, adsorbabilities and energetics. Langmuir monolayer coverage $b$ and sorption affinity $a_L$ are the important parameters mostly used to evaluate theoretical and experimental results. The BET analysis of phenol sorption data on CZ2 showed an unusually low value for monolayer $x_m$, equal to 16.42 mg/g and it gives a surface area of 54.25 m$^2$/g only. The surface area, $S_{BET}$ was found to be 806.5 m$^2$/g and the $C_{BET}$ value was 2.24. The values of $a_L$ and $b$ were 1.321 and 416.66 mg/g respectively. Similarly, maximum adsorption capacity, $q_m$ obtained by D-R method was 180.0 mg/g. The value of $K'$, the D-R constant, related to adsorption energy was equal to 57.74 kJ/mol. Among the solids the carbon recorded a higher gradient $n$ for phenol. The gradient $n$ from standard 1N$_2$ plot was also high (2.25).

Analysis of equilibrium isotherm data using the above models provided higher values of the adsorption parameters for p-nitrophenol indicating a favourable adsorption phenomena. John isotherm plots were linear over the entire range of concentration for CZ2 with $n$ equal to 0.468. The constants for Langmuir plots of $a_L$ and $b$ for CZ2 were 1.557 l/g and 666.7 mg/g respectively at 293 K. The D-R analysis of the data showed less linearity for the lower ranges of concentrations. The value of
was found to be 246.83 mg/g. The K' obtained was very small (0.767 kJ/mol).

The sorption of phenols on new adsorbents were exothermic and occurs by a mechanism which involves a decrease in the number of molecules acquiring sufficient energy to undergo physical interactions with surface groups. The wood surface is negatively charged in aqueous phase. At pH above pH$_{zpc}$ the hydrostatic driving force attracts the un-ionised phenols (solution pH is 7.0 in all experiments) to anionic wood surface. The energetics of phenol adsorption on new carbons and wood were investigated using standard thermodynamic relationships.

Kinetic, equilibrium, isotherm and thermodynamic parameters revealed the formation of a donor-acceptor type charge transfer complex between phenols and carbonyl functional groups on the carbon edges. Molar heat of adsorption of phenols on modified wood falls within the ranges of energetics of partition or van der Waals forces. Adsorptive capacities of carbons and wood cannot be solely described by their pore volume and surface area. Adsorbents with very different surface area measured by BET, D-R/N$_2$, D-R/CO$_2$, Stoeckli, Langmuir and John's relationships established that capacity under equilibrium is not proportional to the surface areas. Kinetic experiments in combination with mathematical modelling provide significant information about the diffusion of molecules inside the pore structure of new activated carbons and modified wood.

The adsorption behaviour of metal ions such as Hg$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Cr$^{6+}$ and Cr$^{3+}$ towards the new sorbents was studied in relation with surface properties and porosity. The adsorption capacity has been varied in accordance with the surface acidity of the adsorbent. Hence, the carbon and wood surface were modelled as a number of weak monoprotic acids based on characterization results. High temperature favours the adsorption of metal ions from aqueous solution and equilibrium is attained mostly after 80 minutes. The ion adsorption occurs in two distinct stages; a relatively fast initial stage is followed by a slow one. The activation energies are in the range of 12.167 to 18.408 kJ/mol for the first stage and 20.202 to 24.41 kJ/mol for second stage. The diffusion of metal ions into the pores of the adsorbents controls the kinetics of the adsorption process. The pH of the medium and speciation of metal ions have a direct influence upon metal uptake. The adsorption obeys the Langmuir and Freundlich isotherm equations in the concentration range studied. The evaluated thermodynamic parameters $\Delta G$, $\Delta H$ and $\Delta S$ indicate that the adsorption process is endothermic and spontaneous. Results of the studies indicate that the adsorption phenomenon is favourable in the concentration range studied and is useful in the designing of equilibrium batch reactors. The data are important for the recovery of metal ions from aqueous solutions using the new adsorbents.

The preparation, characterization and evaluation of adsorption properties of activated carbons and related adsorbents based on similar precursor materials, by activation and pyrolysis or other heating techniques form further extension of this work. Comparison of adsorption properties of the resulting carbon products with commercial carbon materials using sophisticated instruments like STEM, XPS,
Laser Raman spectroscopy and porosimetric studies by state-of-the-art techniques is another aspect for further research in this area.

The study of the physicochemical changes caused by the heat treatment of activated carbons impregnated with heavy metals will be a fruitful area of further research. The new carbons have a more homogeneous pore structure. The efficiency of the removal process is greatly enhanced due to newly developed porosity caused by the reduction of the metals and the oxidation of the carbons. These carbons are technologically important materials and have a wide variety of applications.