Different Modification Techniques and Characterization of Modified Activated Carbons

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Abstract

Activated Carbon (AC) is widely used as an adsorbent in several applications. The varied uses include treatment of water and wastewater, separation and hazardous waste treatment. Despite its large market of applications in industries, adsorption of organic compounds can occur via different mechanism and still remains a subject of study. This is due to the complex and heterogeneous nature of the surface. Hence, it is important to understand the nature of the surface to determine adsorption isotherm for the organic compounds adsorbed on activated carbon.

1. Introduction

The heterogeneity of the surface of the activated carbons can be generally categorized into three main zones: carbon basal planes, heterogeneous surface groups and inorganic ash. The basal planes in AC which cover mostly 90% of the surface form the majority of adsorption sites for organic compounds (liquid form). Hence, the isotherm for adsorption largely depends on the surface chemistry.

In this study, wet incipient impregnation of GAC (Granular Activated Carbon) has been done using several reagents and the comparison of the modified surfaces is studied after its suitable analysis.

2. Characterization of Modified Adsorbent

The reagents used for modification of the surface of adsorbents have great influence on pore development and surface characteristics of the modified adsorbent so produced. Activating agents such as Phosphoric acid (H_3PO_4), Sulphuric acid (H_2SO_4), Potassium hydroxide (KOH), Sodium hydroxide (NaOH), Calcium chloride ($CaCl_2$), Zinc chloride ($ZnCl_2$) etc. have been reported for the chemical modification process (Sahira et al., 2013).

For the present study, modification of Activated Carbon with several reagents has been studied and its characteristics are analyzed in the subsequent paragraphs.

Ferric chloride ($FeCl_3$), Calcium chloride ($CaCl_2$), Sodium hydroxide (NaOH), Potassium permanganate ($KMnO_4$) and Potassium chloride (KCl) have been used to modify the surface of the commercially available GAC. The incipient wet impregnation of carbon with $FeCl_3$, $CaCl_2$ and KCl was done to enhance the surface area of the adsorbents by Chloride process (Karthikeyan et al., 2008). The adsorption capacity of adsorbate is dependent on the charge of metal ions and its chemistry in solution phase (Mondal et al., 2013). $KMnO_4$

was used to oxidize the surface of GAC to form more pores and functional groups on its surface and enhance the adsorption capacity of adsorbate (Zhang, 2013).

2.1. Scanning Electron Microscope (SEM) micrographs

Figure 2.1 to Figure 2.40 show SEM images of unmodified and modified GAC samples taken by Field Emission Gun SEM, Nova Nano FE-SEM 450 (FEI) make which is coupled with an EDAX (Energy Dispersive Spectroscopy) detector.

SEM technique has been used extensively to characterize the microstructure of the modified activated carbon for all the shortlisted reagents. The morphological study by SEM micrographs is summarized in Table 2.1.

These SEM images show cavities, pores and rough surfaces on each prepared carbon samples. The influence of each activating agent on the topographical characteristics is also mentioned in the table. The different pore structures of the activated carbon using various activating agents point to the occurrence of possibility of different reaction mechanism (Sahira et al, 2013). The unmodified GAC was mostly microporous, and less mesopores (Moore et al., 2001).

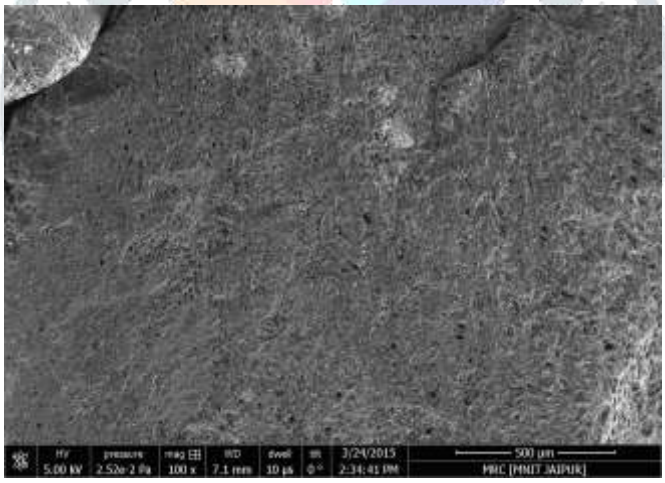

Figure 2.1 SEM micrograph of virgin GAC at 100 X

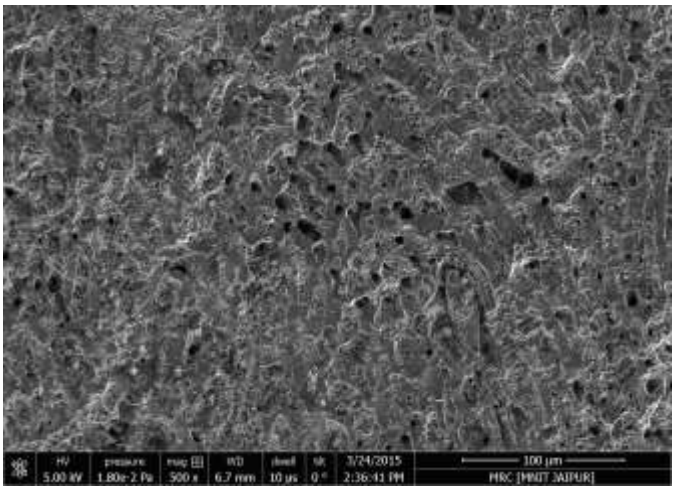

Figure 2.2 SEM micrograph of virgin GAC at 500 X

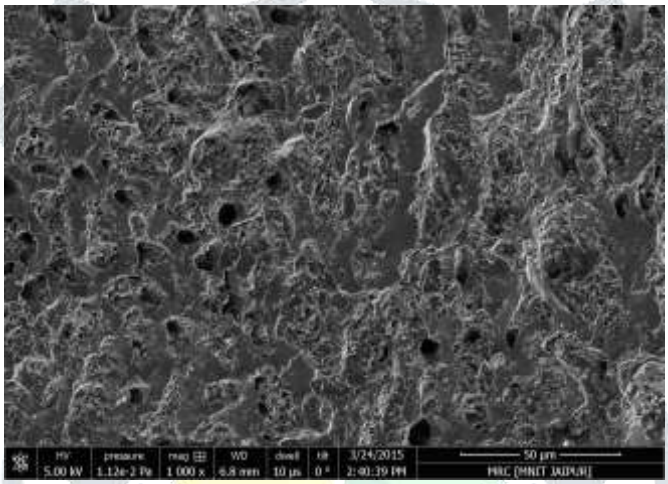

Figure 2.3 SEM micrograph of virgin GAC at 1000 X

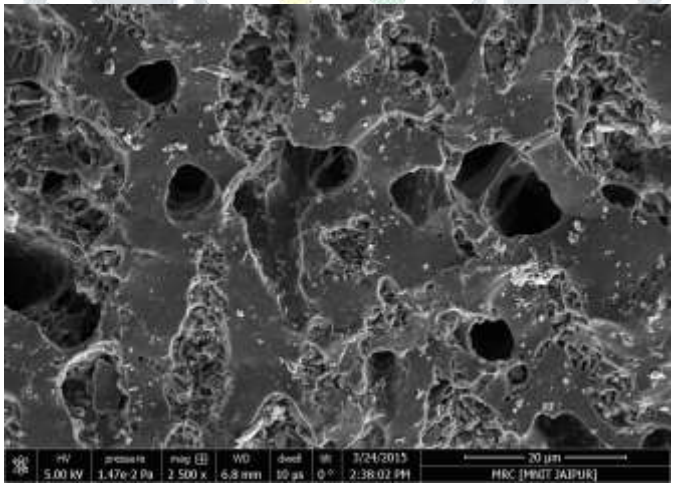

Figure 2.4 SEM micrograph of virgin GAC at 2500 X

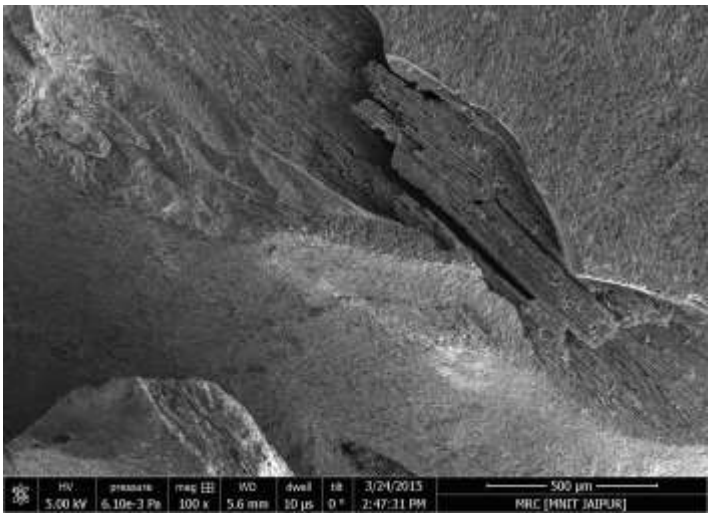

Figure 2.5 SEM micrograph of GAC modified with 0.015 M $FeCl_3$ at 100 X

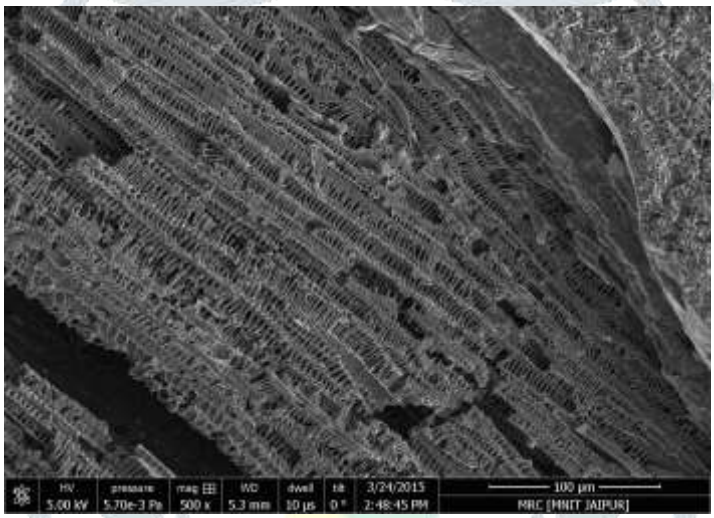

Figure 2.6 SEM micrograph of GAC modified with 0.015 M $FeCl_3$ at 500 X

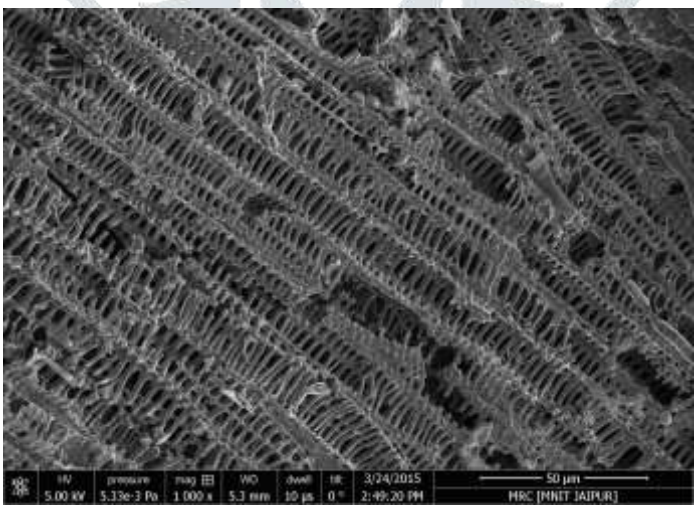

Figure 2.7 SEM micrograph of GAC modified with 0.015 M $FeCl_3$ at 1000 X

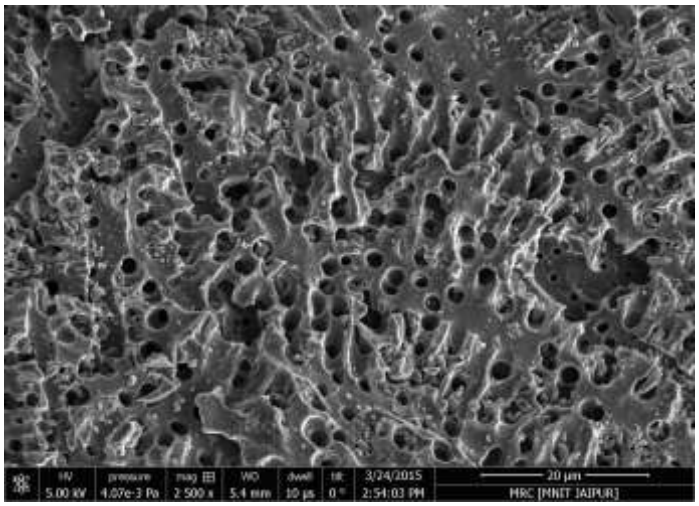

Figure 2.8 SEM micrograph of GAC modified with 0.015 M $FeCl_3$ at 2500 X

Due to impregnation of 9.39% of iron (as estimated using EDAX), the pores of unmodified GAC have appeared to open up and new surface areas seems to have generated (Chen et al., 2012). The structure appears skeleton like and represents a crystalline morphology of iron which might have replaced quartz and silica phase. This co-relates well with the XRD investigation reported. Visually, the sample was pale yellowish confirming the presence of iron element. The formation of Oxides and metal complexes formed by impregnation of metal ions produce both positive and negative sites on surface of the adsorbent depending on the pH of the solution thereby changing the behavior of the surface charge on the adsorbent.

Therefore, any phenolic derivative is expected to be adsorbed through a different mechanism on the surface of Fe-GAC in comparison to Ca-GAC (Mondal, et al, 2013). The number of metals impregnated additionally in GAC-Ca is less than those of GAC-Fe and the positive charge created on its surface is more than that of GAC-Ca (Mondal et al, 2013). This can be well explained by comparing SEM images of all the other samples of GAC. The openings of pores are characterized by shallow hollow tube formed on the surface. From the SEM images, it is seen that Fe-GAC samples show presence of perfect pore structure which is homogeneous in size and distributed randomly on the surface. These clear openings provide accessibility to internal pores with no possibility of clogging (Din et al., 2009).

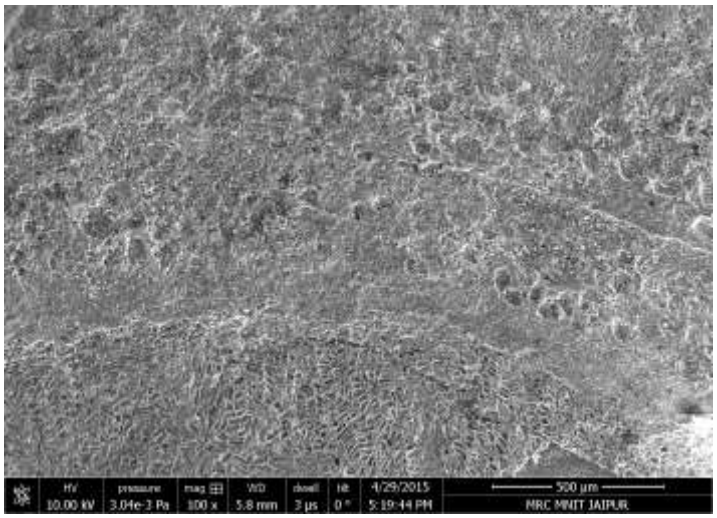

Figure 2.9 SEM micrograph of GAC modified with 0.20 M $FeCl_3$ at 100 X

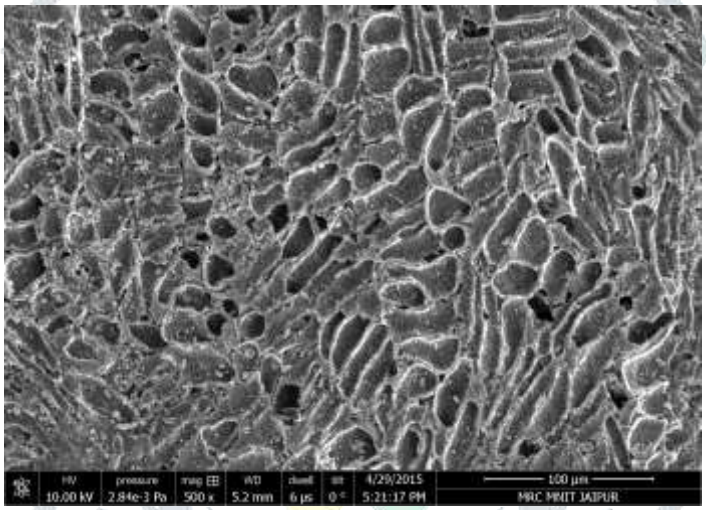

Figure 2.10 SEM micrograph of GAC modified with 0.20 M $FeCl_3$ at 500 X

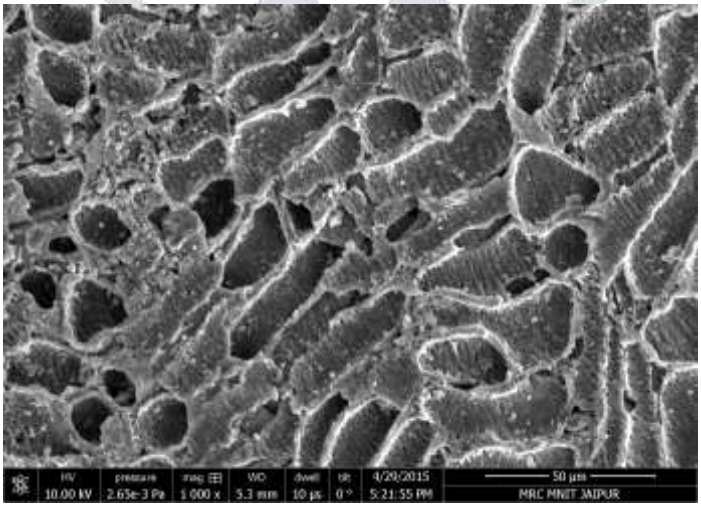

Figure 2.11 SEM micrograph of GAC modified with 0.20 M $FeCl_3$ at 1000 X

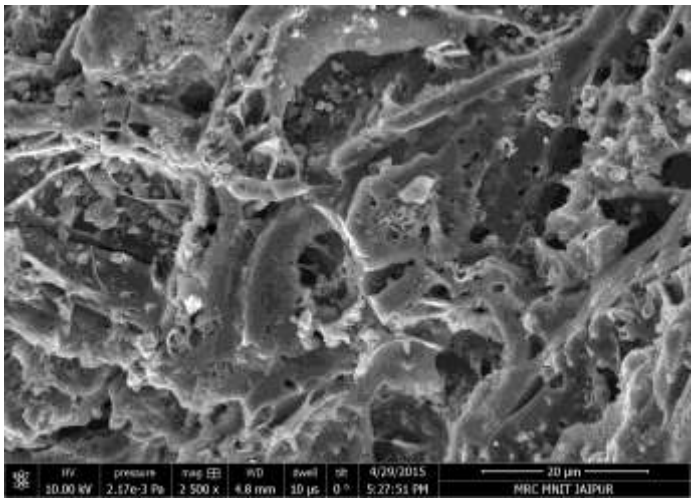

Figure 2.12 SEM micrograph of GAC modified with 0.20 M $FeCl_3$ at 2500 X

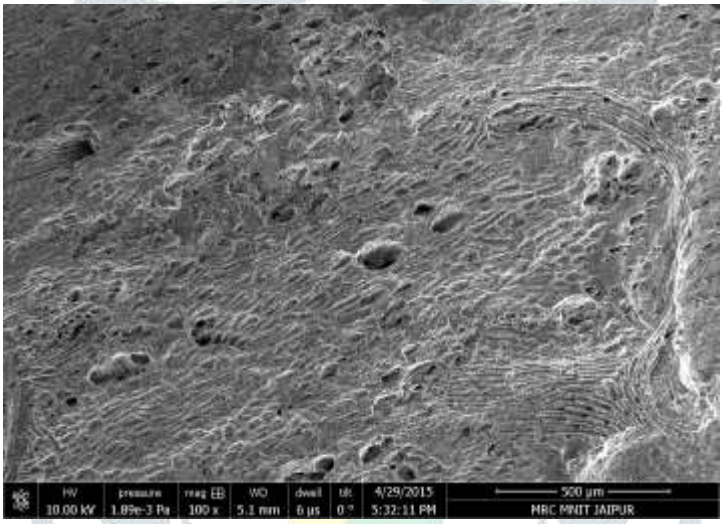

Figure 2.13 SEM micrograph of GAC modified with 0.25 M $FeCl_3$ at 100 X

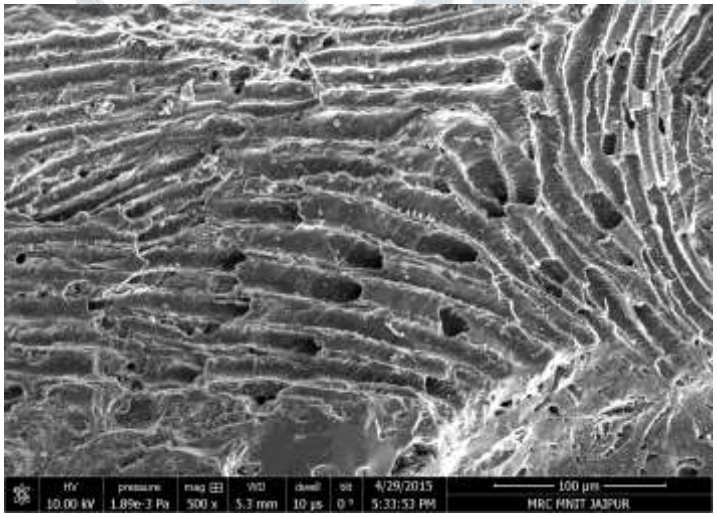

Figure 2.14 SEM micrograph of GAC modified with 0.25 M $FeCl_3$ at 500 X

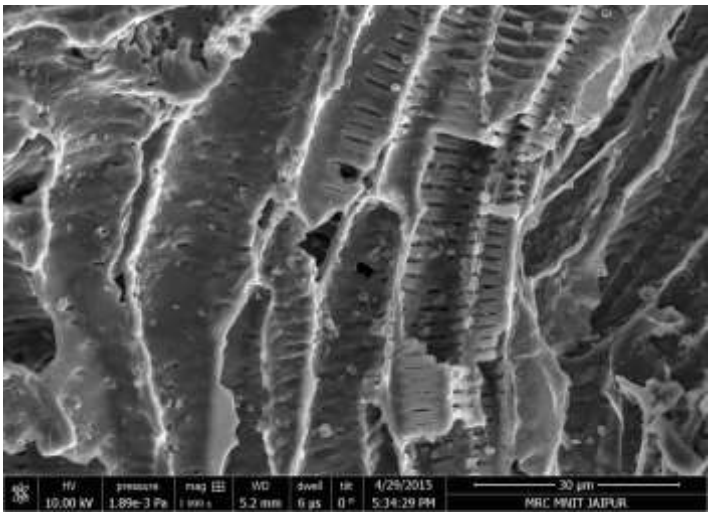

Figure 2.15 SEM micrograph of GAC modified with 0.25 M $FeCl_3$ at 1000 X

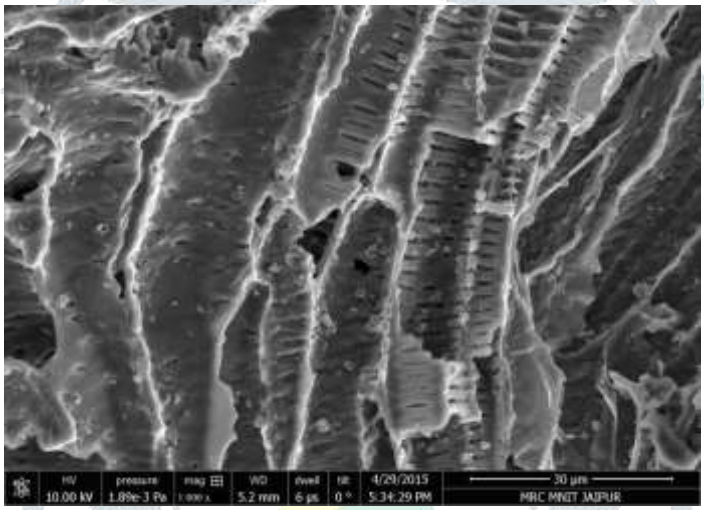

Figure 2.16 SEM micrograph of GAC modified with 0.25 M $FeCl_3$ at 2500 X

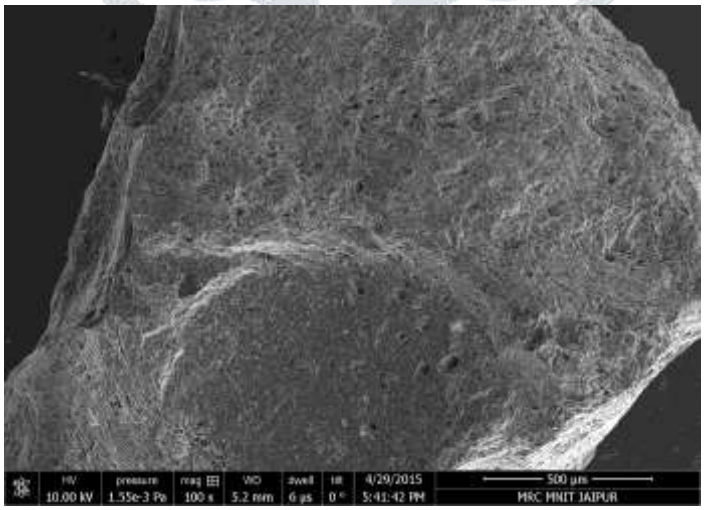

Figure 2.17 SEM micrograph of GAC modified with 0.30 M $FeCl_3$ at 100 X

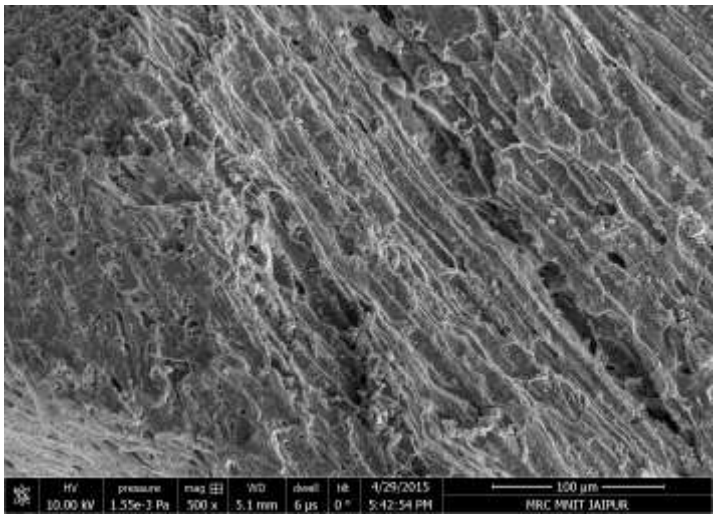

Figure 2.18 SEM micrograph of GAC modified with 0.30 M $FeCl_3$ at 500 X

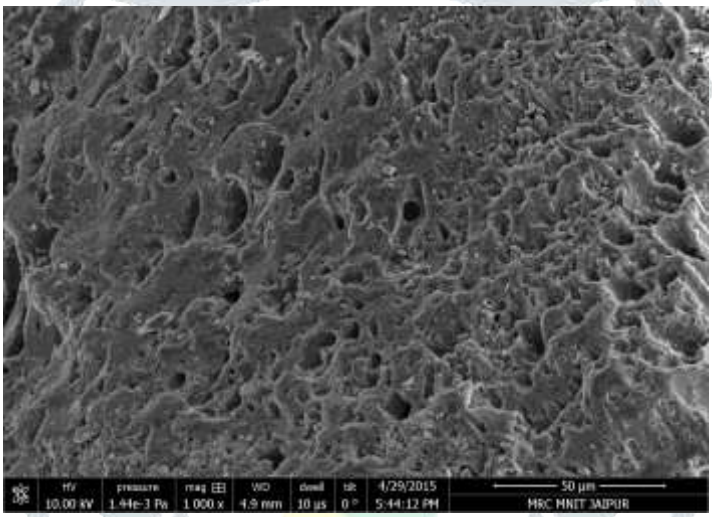

Figure 2.19 SEM micrograph of GAC modified with 0.30 M $FeCl_3$ at 1000 X

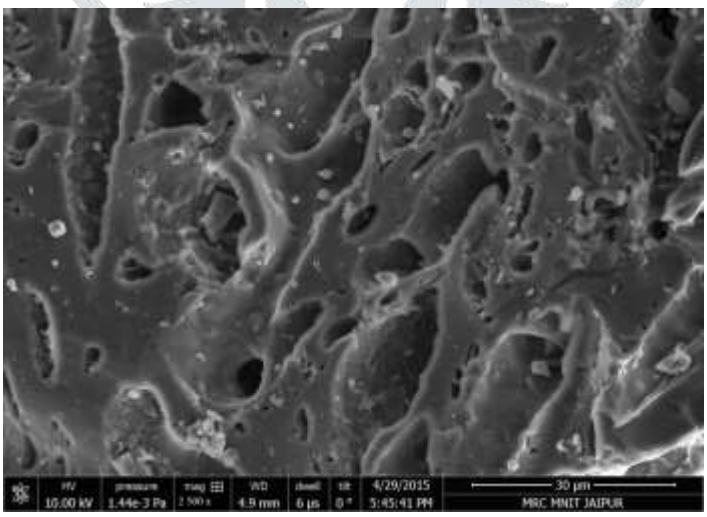

Figure 2.20 SEM micrograph of GAC modified with 0.30 M $FeCl_3$ at 2500 X

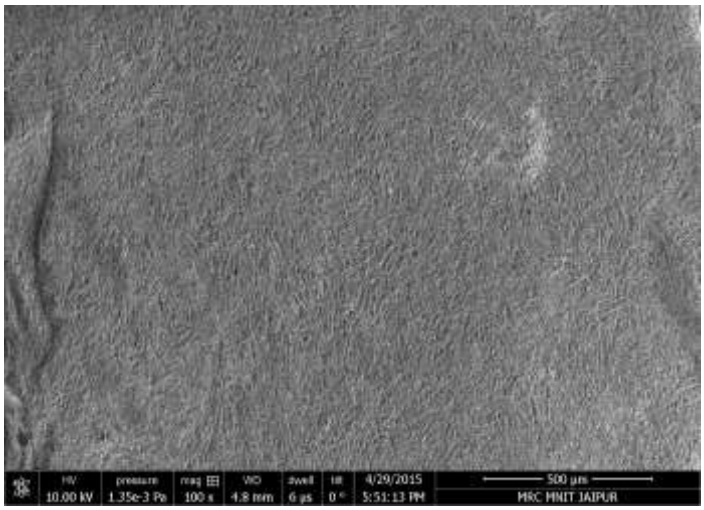

Figure 2.21 SEM micrograph of GAC modified with 0.35 M $FeCl_3$ at 100 X

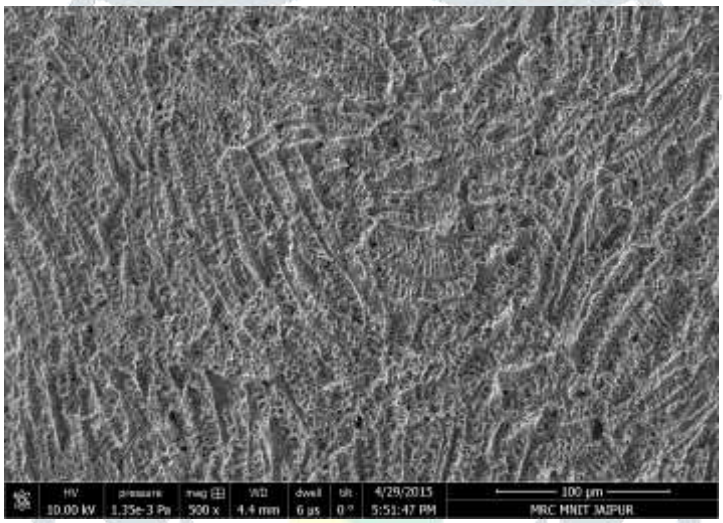

Figure 2.22 SEM micrograph of GAC modified with 0.35 M $FeCl_3$ at 500 X

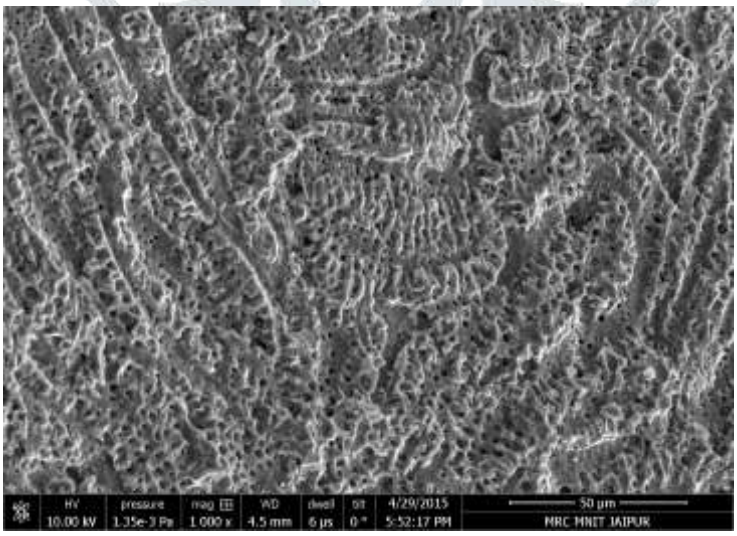

Figure 2.23 SEM micrograph of GAC modified with 0.35 M $FeCl_3$ at 1000 X

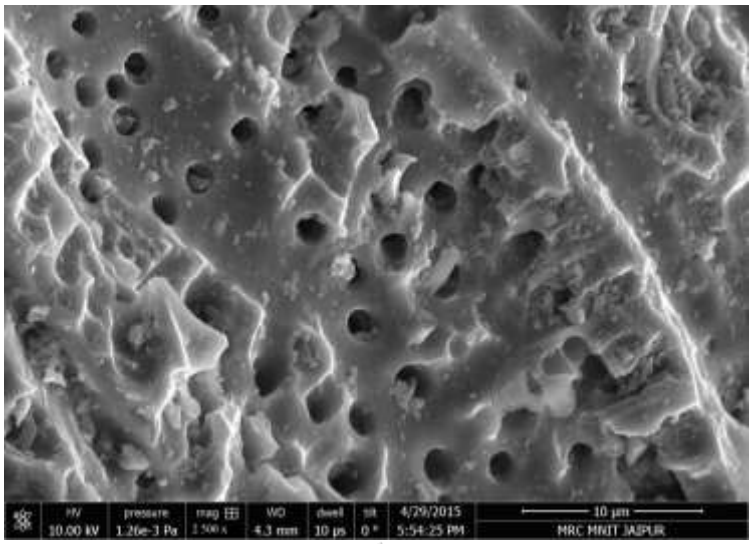

Figure 2.24 SEM micrograph of GAC modified with 0.35 M $FeCl_3$ at 2500 X

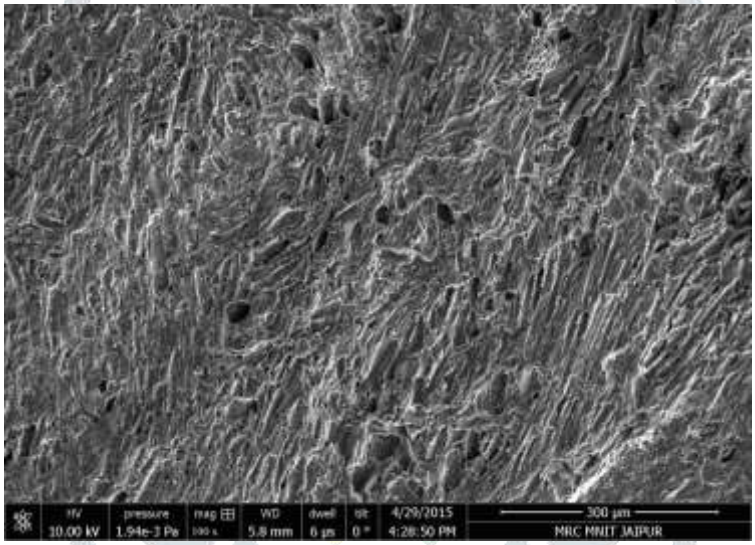

Figure 2.25 SEM micrograph of GAC modified with 0.015 M KCl at 100 X

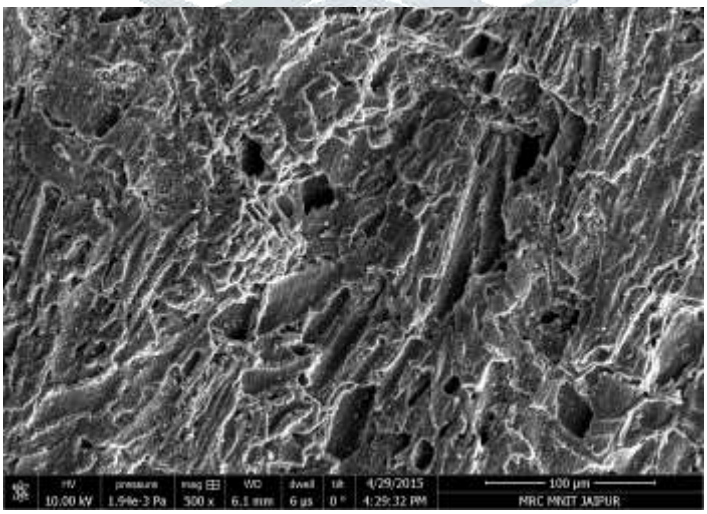

Figure 2.26 SEM micrograph of GAC modified with 0.015 M KCl at 500 X

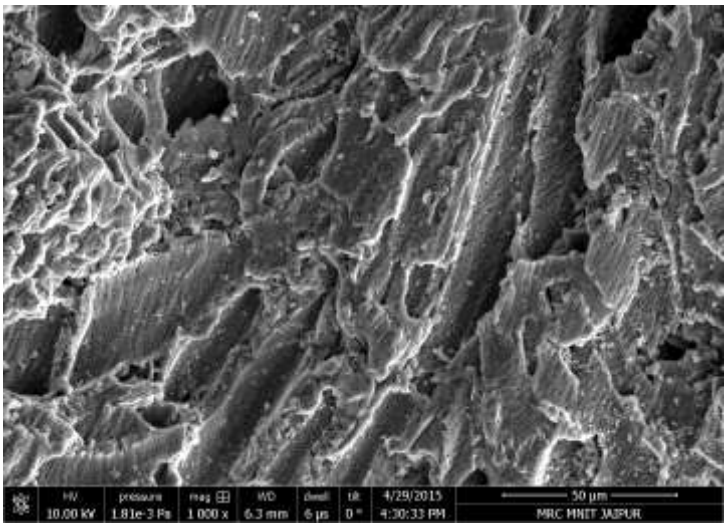

Figure 2.27 SEM micrograph of GAC modified with 0.015 M KCl at 1000 X

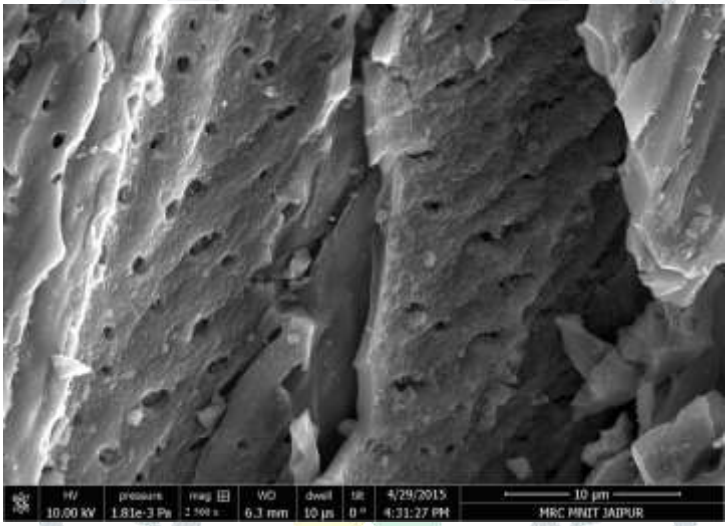

Figure 2.28 SEM micrograph of GAC modified with 0.015 M KCl at 2500 X

The higher surface area of carbon achieved by Chloride process ($FeCl_3$, $CaCl_2$ and KCl) is due to the effective removal of organic matter by this method, therefore these modified carbons are preferred for adsorption of adsorbates in aqueous solutions (Karthikeyan et al., 2008).

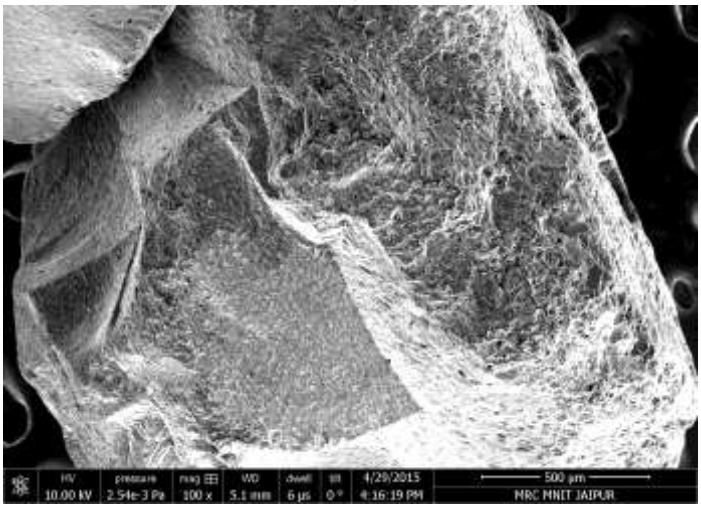

Figure 2.29 SEM micrograph of GAC modified with 0.015 M $KMnO_4$ at 100 X

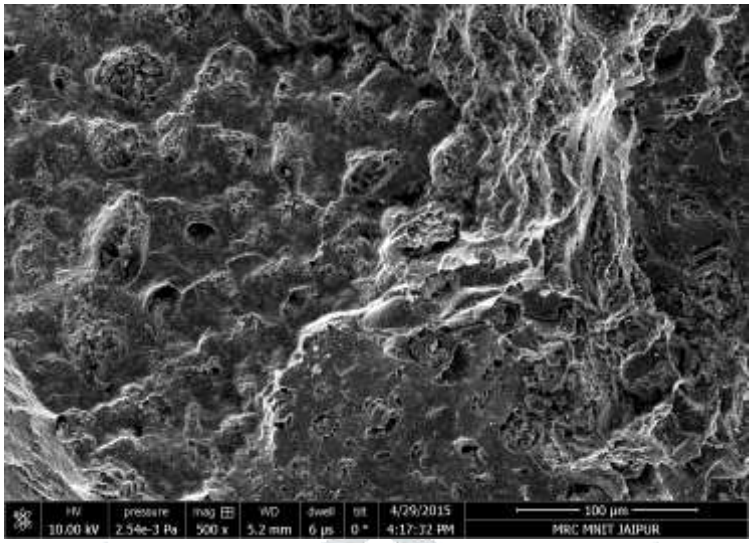

Figure 2.30 SEM micrograph of GAC modified with 0.015 M $KMnO_4$ at 500 X

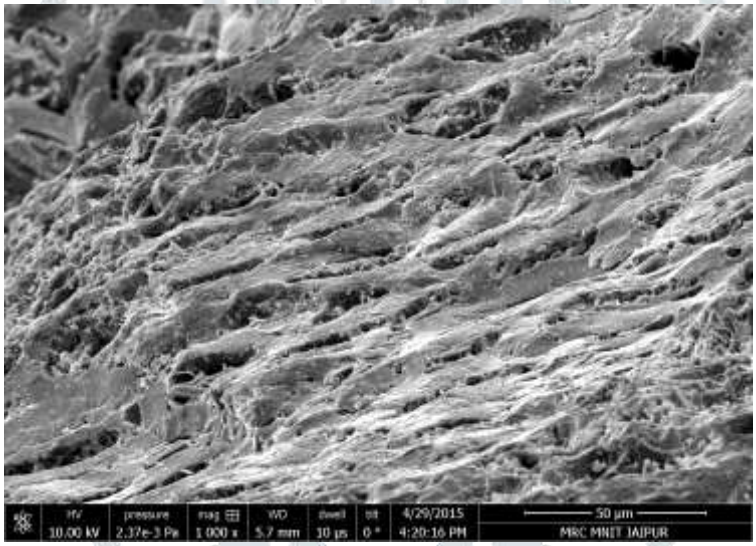

Figure 2.31 SEM micrograph of GAC modified with 0.015 M $KMnO_4$ at 1000 X

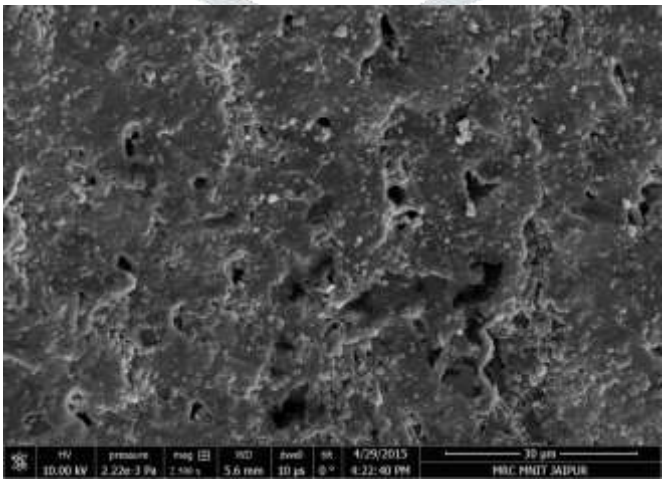

Figure 2.32 SEM micrograph of GAC modified with 0.015 M $KMnO_4$ at 2500 X

$KMnO_4$-GAC exhibits a porous structure which is responsible for highly developed surface area (Baccar et al., 2009). NaOH modified GAC SEM image indicates that the chemical modification is based on the reaction carbon and alkali taking place mostly in the pores of the surface (Li et al., 2011).

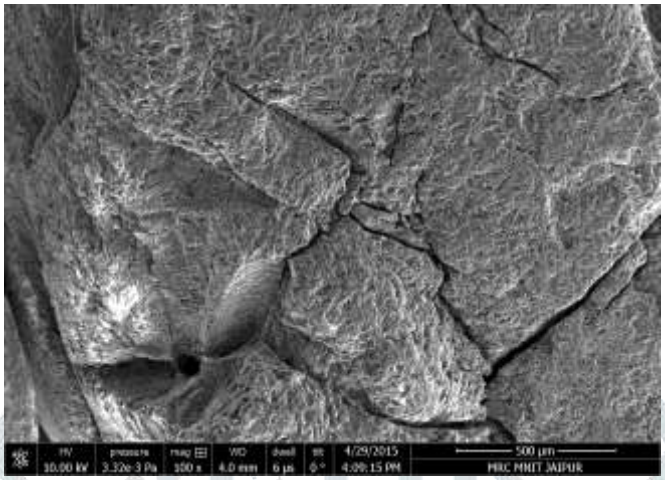

Figure 2.33 SEM micrograph of GAC modified with 0.015 M NaOH at 100 X

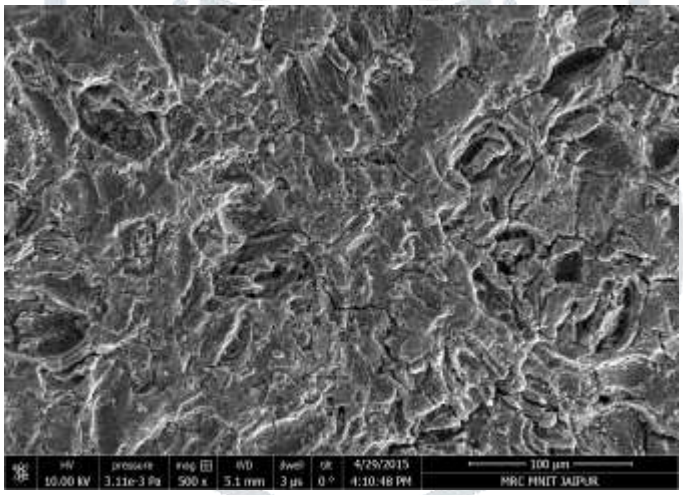

Figure 2.34 SEM micrograph of GAC modified with 0.015 M NaOH at 500 X

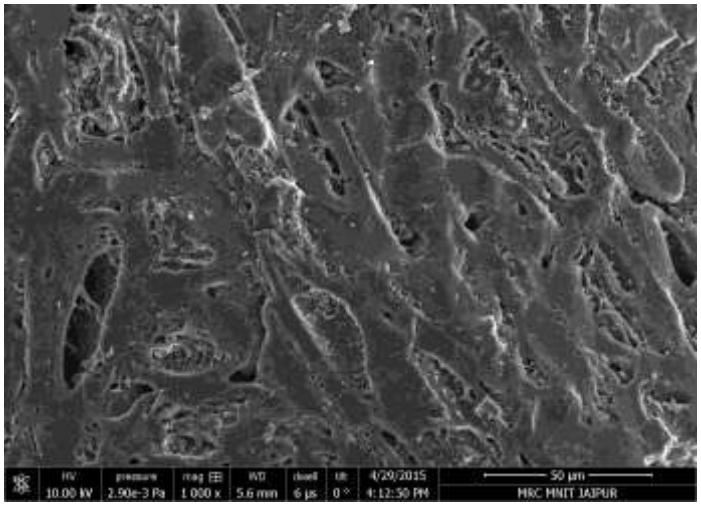

Figure 2.35 SEM micrograph of GAC modified with 0.015 M NaOH at 1000 X

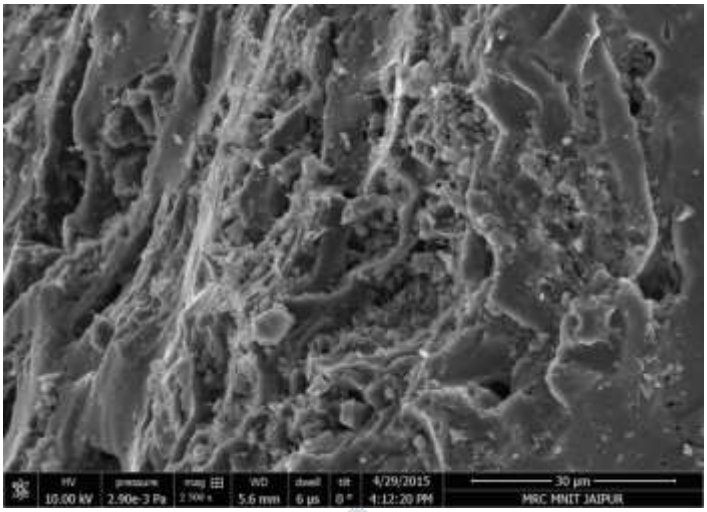

Figure 2.36 SEM micrograph of GAC modified with 0.015 M NaOH at 2500 X

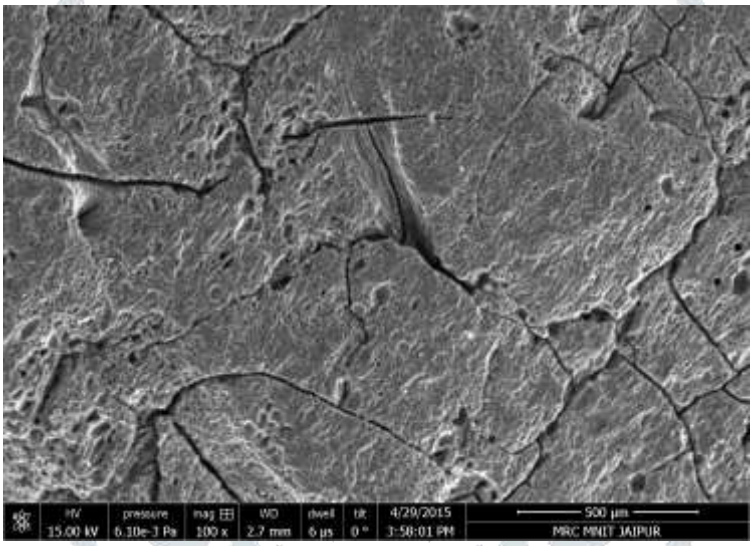

Figure 2.37 SEM micrograph of GAC modified with 0.015 M $CaCl_2$ at 100 X

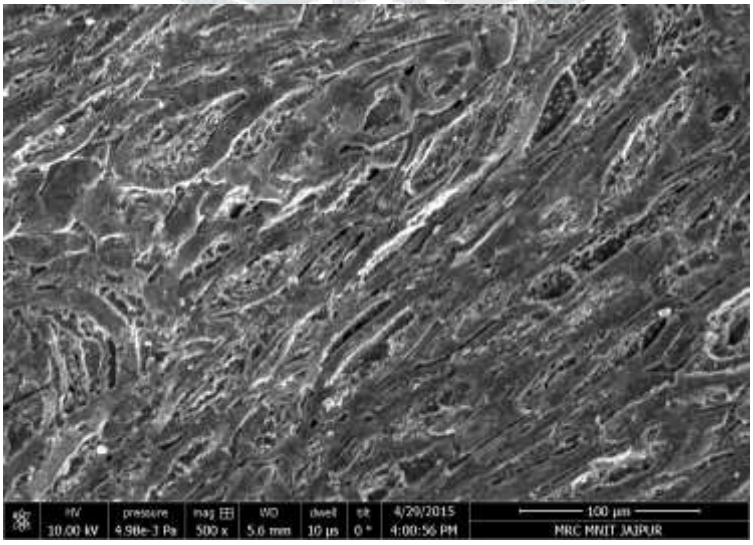

Figure 2.38 SEM micrograph of GAC modified with 0.015 M $CaCl_2$ at 500 X

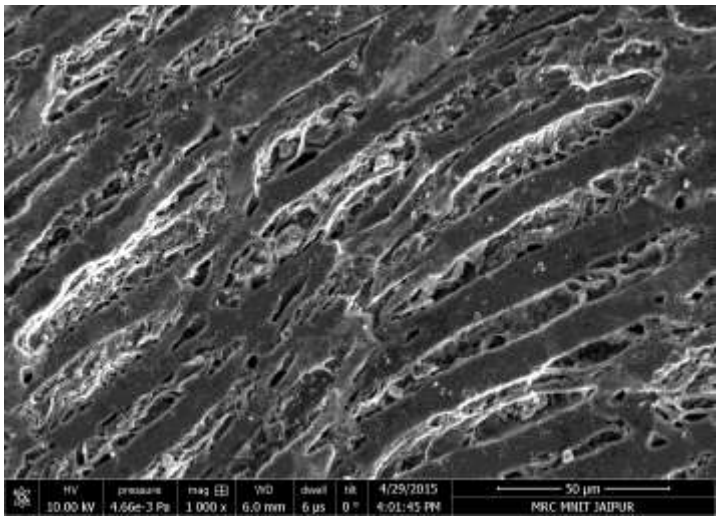

Figure 2.39 SEM micrograph of GAC modified with 0.015 M $CaCl_2$ at 1000 X

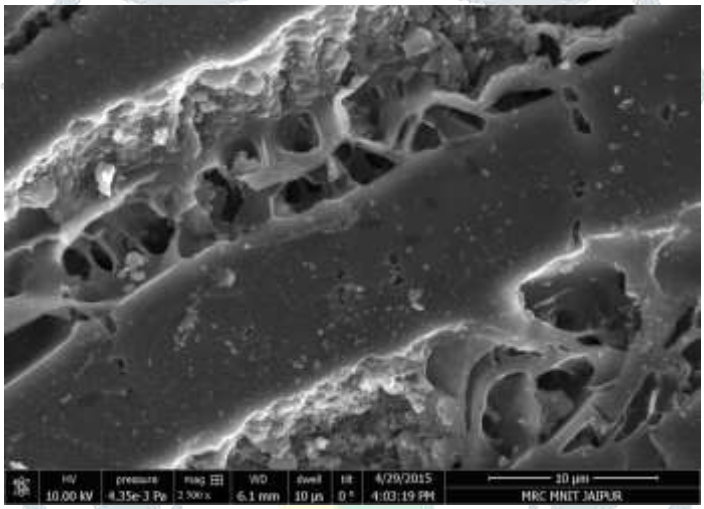

Figure 2.40 SEM micrograph of GAC modified with 0.015 M $CaCl_2$ at 2500 X

Among all the micrographs, it can be seen GAC modified with $FeCl_3$ and $CaCl_2$ show fully developed pores and cavities while GAC modified with NaOH show partially developed honey combed structure having well defined pores and cavities though non-uniform in nature as compared to plain GAC. The surface of $CaCl_2$ – GAC is filled with numerous small pores that are in the shape of the valleys (Sahira et al, 2013). Plain GAC appears to have random pores and cracks and crevices all over the surface (Suresh et al., 2011).

Table 2.1 Consolidated description of virgin and modified GAC samples presented in Figure 2.1 – Figure 2.40

Type of the Granular Activated Carbon	Size of pores (Å)	Characteristics of the surface	Figure
Plain-GAC	8205 - 22460	Less porous, coarse and rough surface, non-uniform	2.1 – 2.4
0.015 M $FeCl_3$-GAC	1008 – 1889	Well defined pores on surface, skeleton like appearance uniform surface	2.5 – 2.8
0.20 M $FeCl_3$–GAC	4032 – 8168	Uniformly defined structure not found all over the surface, high surface areas, large number of pores	2.9 – 2.12
0.25 M $FeCl_3$–GAC	5133 – 9477	Less pores as compared to previous ones though provides a skeleton like long path for adsorption	2.13 – 2.16
0.30 M $FeCl_3$–GAC	772.6 – 1333	Fewer pores on surface appear non – uniform and rough. Pores are not formed distinctly	2.17 – 2.20
0.35 M $FeCl_3$–GAC	1204 – 1911	Pores formed are less dense but are present in large number	2.21 – 2.24
KCl-GAC	1079 – 3106	Large number of pores observed on the surface	2.25 – 2.28

$KMnO_4$–GAC	2297 – 3787	Closed – open pores on the surface	2.29 – 2.32
NaOH–GAC	4618 – 1054	Closed – open pores on the surface	2.33 – 2.36
$CaCl_2$–GAC	-	Fish like elongated pores spread all over surface. Pores present inside these layers	2.37 – 2.40

It can be concluded that the surface of $FeCl_3$ impregnated activated carbon contains most well developed pores, uniformly distributed on the surface and there is a better possibility of adsorption.

Table 2.2 Consolidated description of elemental constituents of virgin and modified GAC samples

Type of the Granular Activated Carbon	Elemental constituents
Plain-GAC	C : 89.38%Ca: 0.17% O: 10.08%
0.015 M $FeCl_3$-GAC	C: 64.43% O: 16.56% Fe: 9.39% Cl: 0.72%
0.20 M $FeCl_3$–GAC	C: 86.07% O: 10.94% Fe: 2.08% Cl: 0.91%
0.25 M $FeCl_3$–GAC	C: 85.92% O: 11.54% Fe: 1.64% Cl: 0.99%
0.30 M $FeCl_3$–GAC	C: 77.44% O: 17.31% Fe: 3.54% Cl: 0.81%
0.35 M $FeCl_3$–GAC	C: 86.01% O: 12.40% Cl: 0.99%
KCl-GAC	C: 89.75% O: 9.81% Cl: 0.30% K: 0.14%
$KMnO_4$–GAC	C: 80.53% O: 14.89% Mn: 8.78% K: 2.31%
NaOH–GAC	C: 89.72% O: 8.75% Na: 0.91%
$CaCl_2$–GAC	C: 89.38% O: 10.08% Ca: 0.17%

On review of EDAX data, it is observed that the modified GAC with 0.015 M $FeCl_3$ is the most suitable candidate for Reactive Adsorption due to presence of maximum iron content amongst other candidates. It is further expected that the increased iron content would help to interact chemically to form intermediate products en route to degradation to less harmful products. From Table 2.2, it is evident that as the concentration of $FeCl_3$ has increased, the percentage of iron content decreases while chloride percentage increases. Since $FeCl_3$ is an ionic salt therefore, it can be assumed that it goes to complete ionization into Fe^{3+} and Cl^- ions according to the following reaction.

$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

From the stoichiometry of the reaction, the iron formed will always be one-third of the chloride ions so formed.

2.2. Surface functional groups using FTIR Spectra

The samples analyzed using FTIR were prepared with powdered activated carbon as a pre-cursor to characterize the functional groups on the adsorbent. The FTIR spectrum of GAC and PAC are similar in nature and hence can be used for comparison (Suresh et al., 2011).

Although the samples were prepared via different activating agents, there is a similarity observed in the absorption pattern. The spectrum shows the surface functional groups of activated carbon that do not exhibit significant differences, independently of activating agents used. The slight difference in intensity of bands is observed (Sahira et al., 2013).

Surface functional group plays an important role in influencing the surface properties and adsorption behavior of the activated carbon. From the basic principles of Chemistry, it is presumed that OH functional group would be of interest for the present investigation. The hydroxyl (OH) function is probably one of the most dominant of all the infrared group frequencies. The impact of hydrogen bonding is to produce significant band broadening. The lowering of frequency tends to be a function of the degree and strength of hydrogen bonding (Coates, 2000).

The expected weakening of O-H bonds is correlated with the actual lowering of frequency observed in the major absorption bands as tabulated below (Coates, 2000).

The FTIR spectrum is obtained from FT-IR Spectrum 2 machine (Perkin Elmer make) capable for measurement in the range of 400 – 4100 cm-1 for solids in KBr (pellets) samples. Figure 2.41 depicts FTIR spectra for various modified activated carbon.

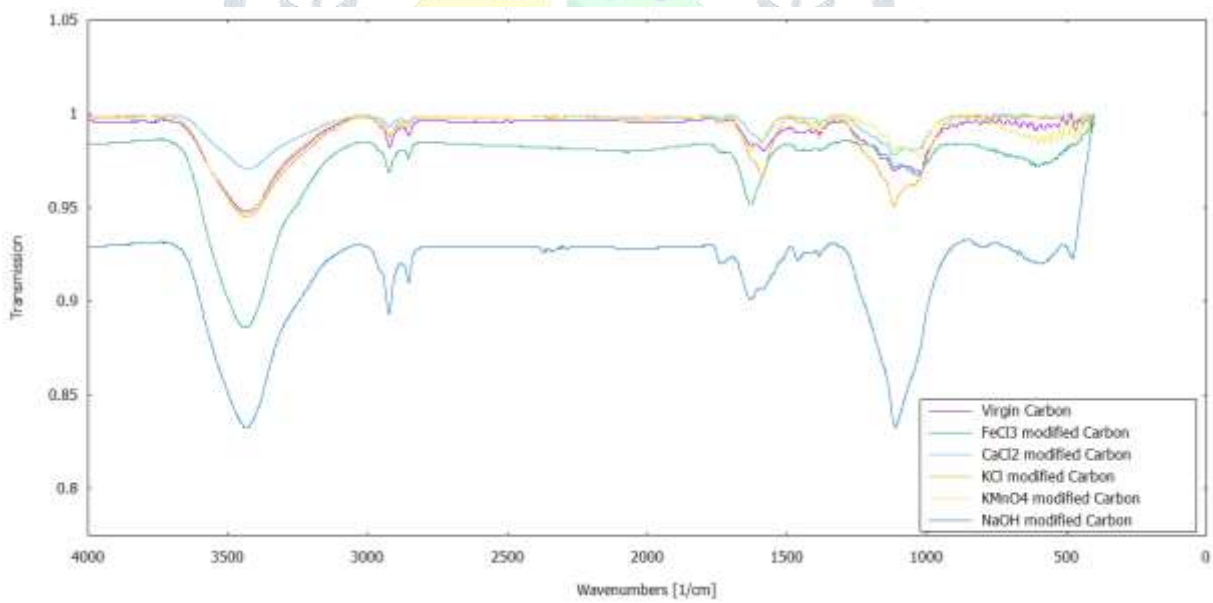

Figure 2.41 FTIR Spectra of various modified activated carbons

The $FeCl_3$ modified carbon exhibits O-H stretching vibration band of hydroxyl group at wavelength 3437 cm^{-1}.It appears to be a very broad and intense peak. The peak at 2922.99 cm^{-1} indicates the presence methyl groups (CH_3) where carbon is sp^3 hybridized. The (CO)-H stretch occurs as a pair of weak bands at 2860 – 2800 cm^{-1}. The particular peak at 2854 cm^{-1} shoes C-H stretch. The occurrence of

alkenes is seen in the band ranging from 1670 – 1640 cm^{-1}. The alkyl halide group of C-Cl is found to occur in the range from 850 – 550 cm^{-1}. In case of plain carbon surface, the broad band with center at 3434. 75 cm^{-1} indicates the presence of free and hydrogen bonded O-H groups on the surface. The FTIR spectra also shows peak at 1115.5 cm^{-1} which is attributed to the C-C group vibration and (CO)-H stretching and deformation of O-H. The spectra of NaOH treated GAC show peak at 3433.27 cm^{-1}owing to the presence of hydroxyl group both free and hydrogen bonded on the surface. Simple alkanes (C-H bond) is present at the peak 2933.44 cm^{-1}while at 2853.36 cm^{-1} there is (CO)-H stretching existing as a pair of weak bands. The peak at 1631.53 cm^{-1} shows presence of alkenes.

2.3. X-Ray Diffraction (XRD) pattern analysis

XRD patterns were obtained using X-Ray Diffractometer (Panalytical X Pert Pro) machine which was equipped with CuKα radiation (40 kV, 40 mA with a 0.003° step size and 1.0 second time over the range of 5°<2θ<60°).

The samples analyzed were prepared using powdered activated carbon. The XRD spectrum of GAC and PAC were found to be similar in nature and hence can be used to compare further with modified carbons (Suresh et al., 2011). Figures 2.42 to Figure 2.47 depict XRD pattern of virgin carbon followed by modified carbon corresponding to each of the selected activating agent using X'Pert High Score software. The list of possible compounds with nearest matching to reference codes is also appended to each of the figures.

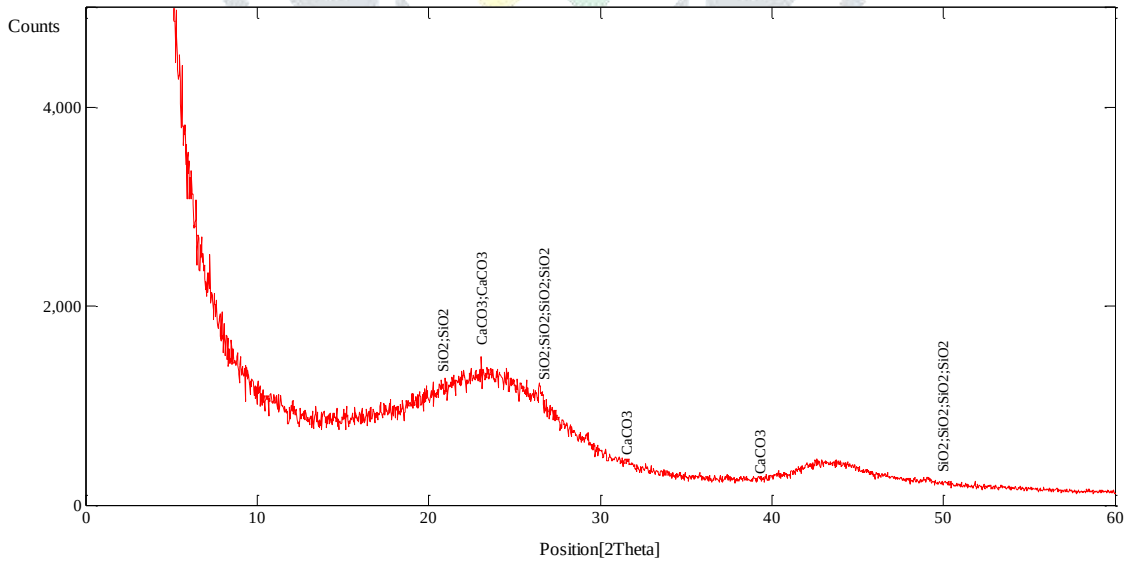

Figure 2.42 XRD spectra of virgin carbon

For the commercial activated carbon, no crystallized compound could be detected by XRD. However, quartz and silica were present in the sample (Girods et al, 2009). The broad peak observed in the

spectrum indicated amorphous nature of the carbon (Suresh et al., 2011). There was no major difference observed in the spectra of untreated and modified form of activated carbon.

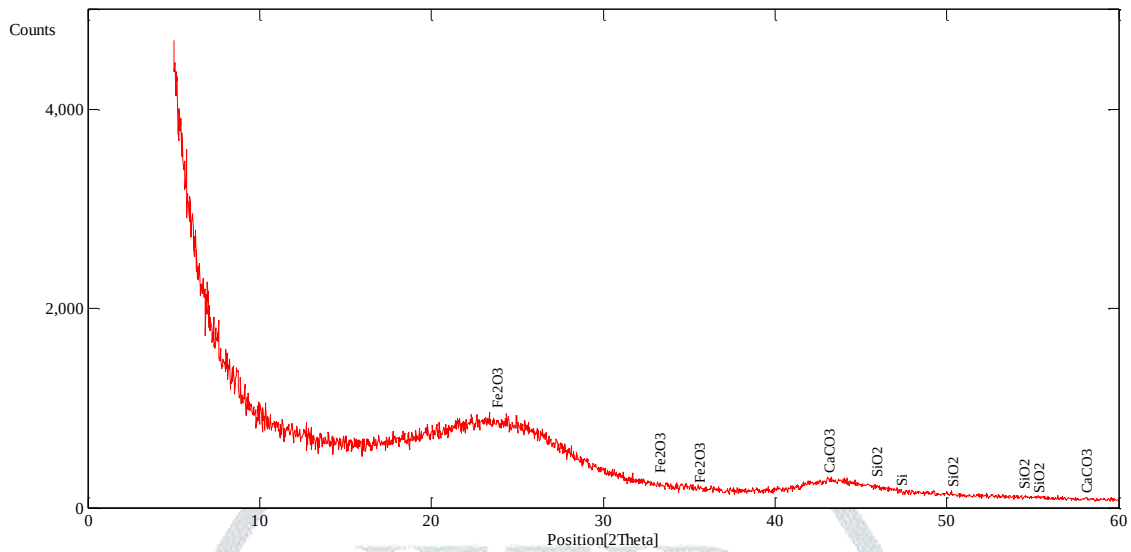

Figure 2.43 XRD spectra of 0.015 M $FeCl_3$ modified carbon

Generally four iron oxides are expected to form under moderate reaction conditions i.e. Fe_3O_4 (magnetite), γ – Fe_2O_3 (maghemite), α – Fe_2O_3 (hematite) and α – FeO(OH) (goethite) (Oliveira et al., 2002). However in the present study the modification of the carbon surface under the reaction conditions could yield Fe_2O_3 as seen in the above XRD spectra.

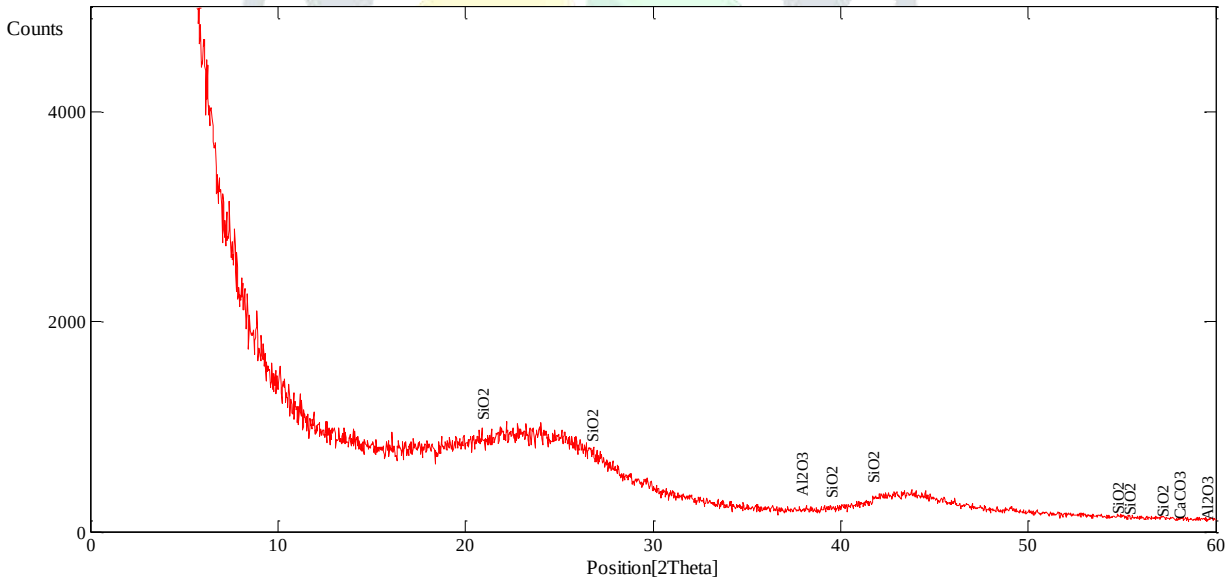

Figure 2.44 XRD spectra of 0.015 M $CaCl_2$ modified carbon

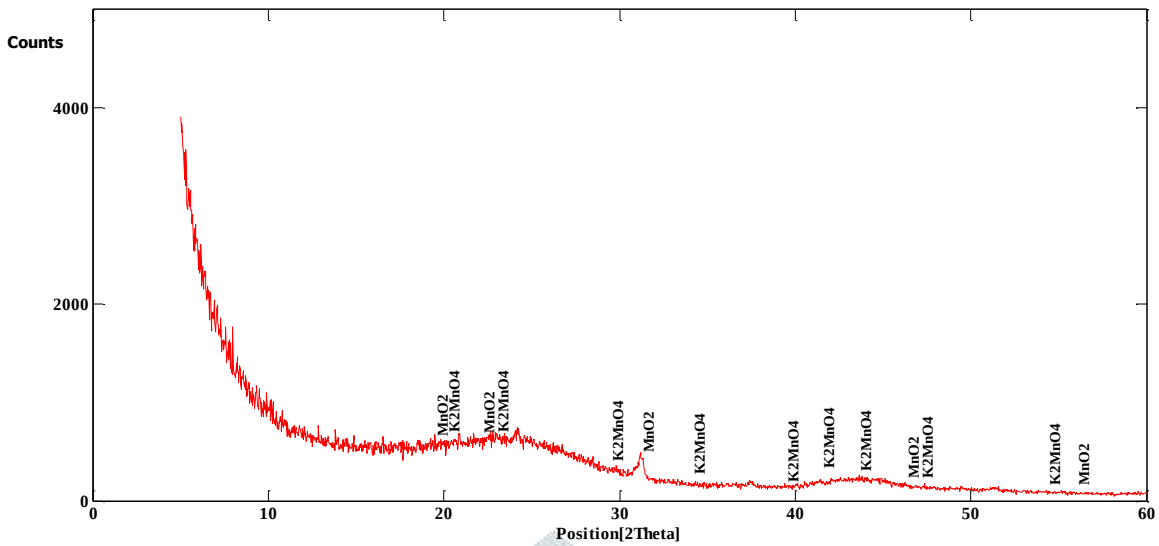

Figure 2.45 XRD spectra of 0.015 M $KMnO_4$ modified carbon

The XRD measurements for the qualitative analytical tool for characterizing the $KMnO_4$ modified carbon. Broad peaks are identified to be carbon itself (Yang et al., 2011). MnO_2 was identified and confirmed manually with standard identification card (JCPD#00-012-0141). Few peaks were identified to be complex compounds of K_2MnO_4 as confirmed using the standard identification card (JCPD#00-012-0264).

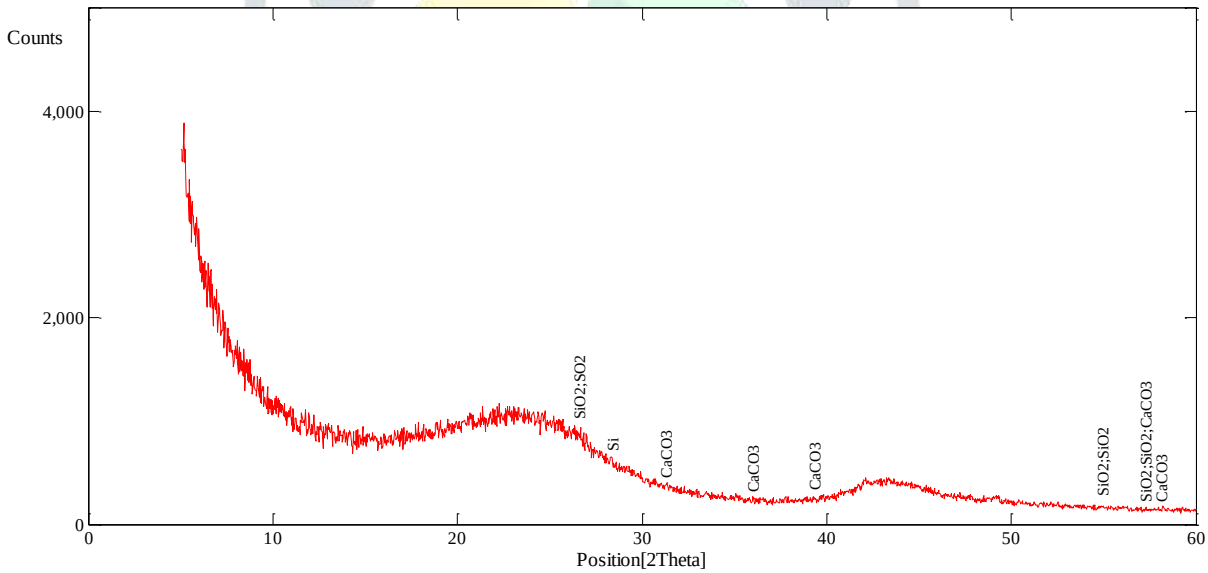

Figure 2.46 XRD spectra of 0.015 M NaOH modified carbon

The XRD pattern for NaOH modified carbon surface exhibits a broad and a weak peak at around 20° that can be identified as the amorphous nature of the carbon surface (Song et al., 2011).

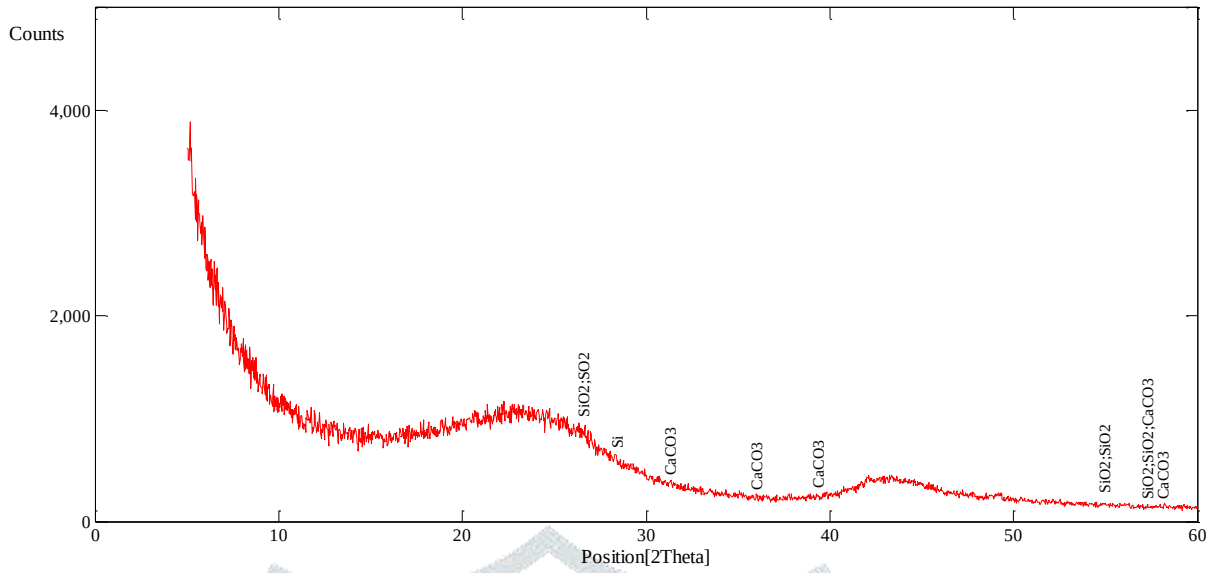

Figure 2.47 XRD spectra of 0.015 M KCl modified carbon

The XRD spectrum peaks of KCl and NaOH modified carbon surface appear to have same spectral peaks as those of virgin activated carbon surface.

3. Conclusion

The modification of the surface of the Activated Carbon via wet incipient impregnation method finds its application in adsorption of phenols and phenolic compounds and/ or other compounds from water (waste water treatment). There are a variety of techniques available for characterization of such modified surfaces. This helps in developing a clear understanding of the changes in the surface morphology. There will be a difference in sorption pattern using both virgin and modified adsorbate.

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