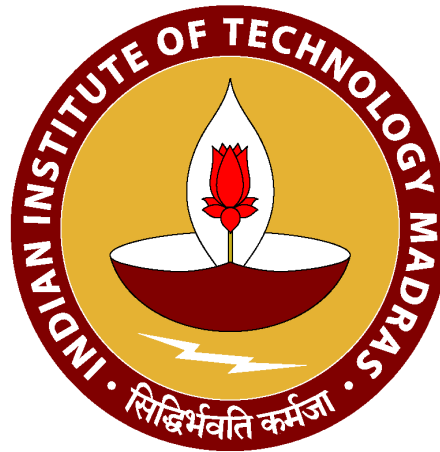


# Development and Exploitation of Carbon Materials from Plant Sources



**P. Indra Neel**  
**CY02D013**

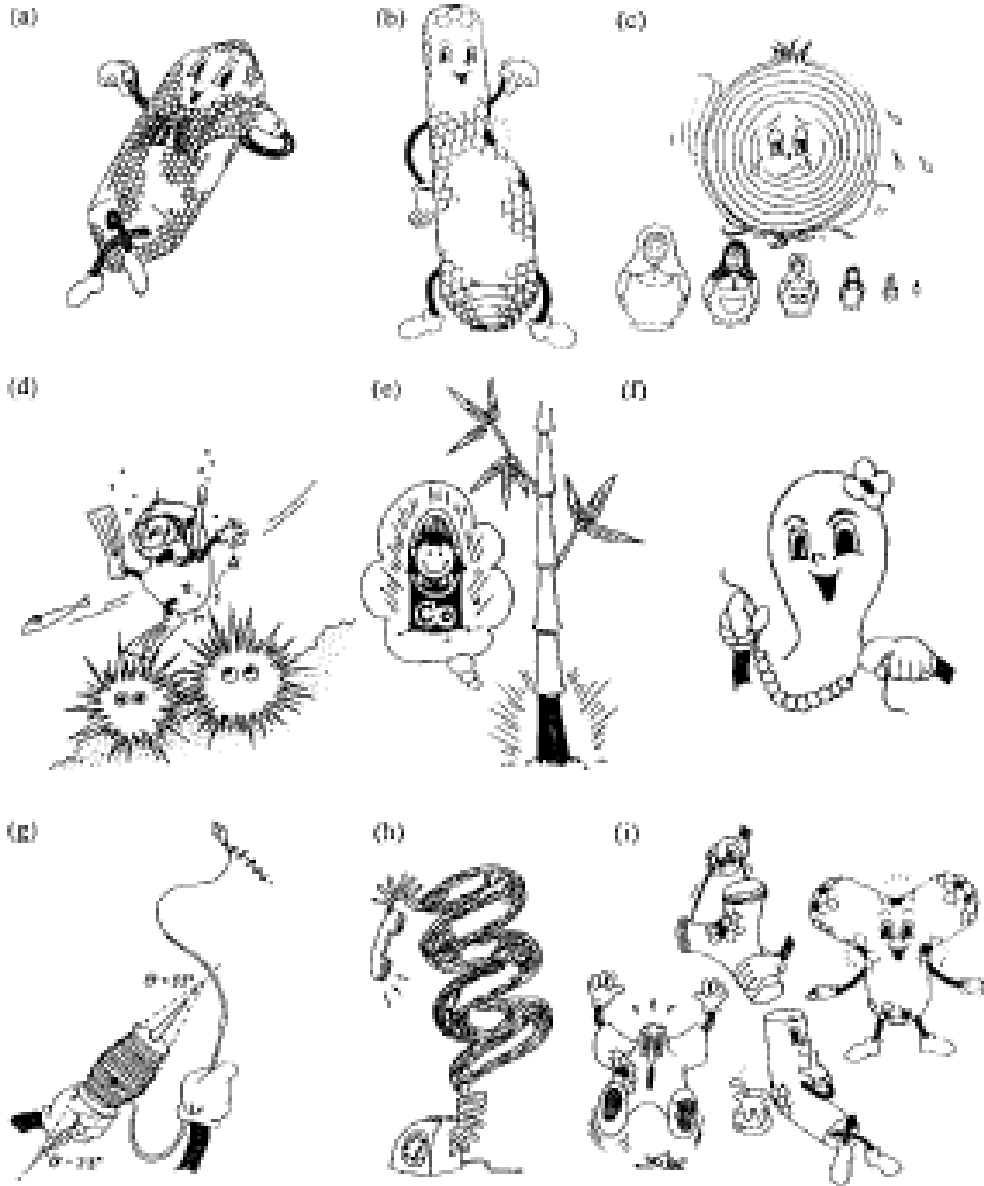
**Ph D Viva-voce exam dated 11<sup>th</sup> May 2010**

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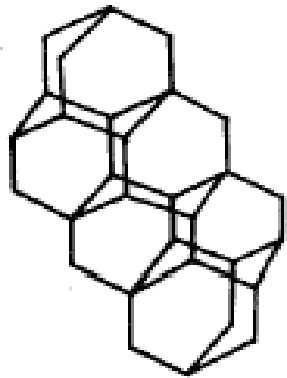
# 1. Introduction

Carbon materials exhibit many different *morphologies*

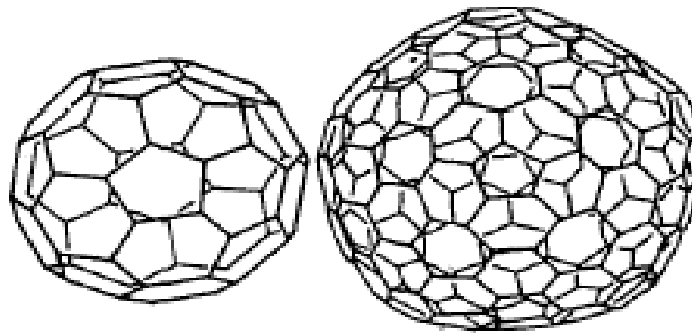


A simple representation of carbon materials with PECULIAR morphologies

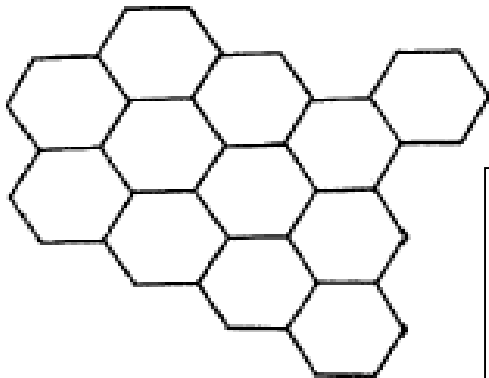
# Different allotropic forms of Carbon materials



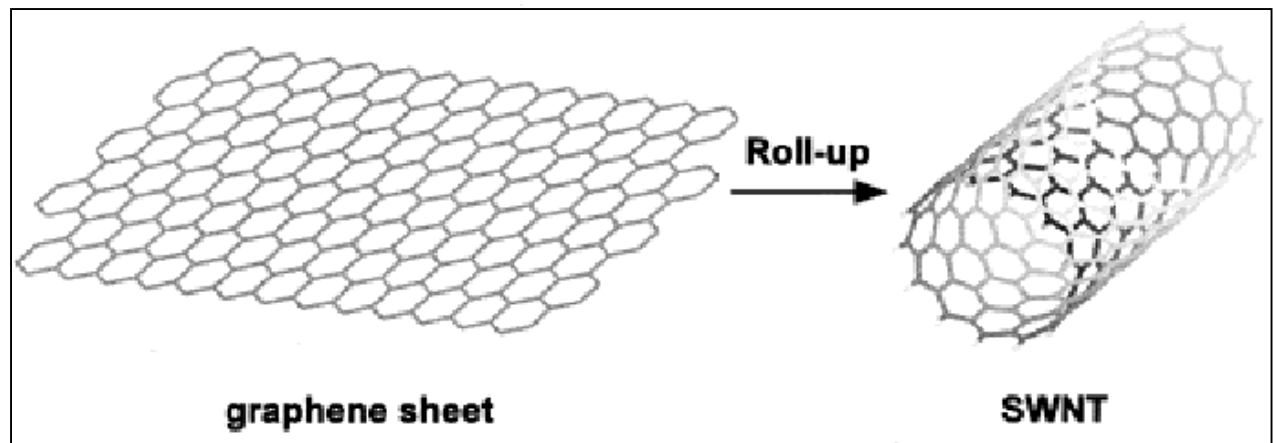
**Diamond**



**Fullerenes**



**Graphite**



# Activated Carbon Materials

- ❑ Highly porous structure
- ❑ High specific surface area and tunable porosity
- ❑ Hydrophobic and Hydrophilic surface co-exist

## Applications

- i. Catalysts
- ii. Catalyst supports
- iii. Energy storing media  
(Methane, Hydrogen, Batteries, Electrodes for super capacitors)
- iv. Energy conversion (Fuel cells, Solar cells)
- v. Effective in removing pollutants  
(regulate  $\text{SO}_x$  and  $\text{NO}_x$  emissions from fuel combustion in automobiles)
- vi. Production of fine and bulk chemicals and catalysis



Structure of Activated Carbon

# Activated Carbon Materials – Challenges

## ❖ Production of activated carbon – Designing economic way

### ➤ Major Sources

- i. Coal
- ii. Petroleum pitch
- iii. Lignocellulosic materials

### ❑ Lignocellulosic materials for Activated Carbon

- i. Renewable
- ii. Inexhaustible supply
- iii. Evenly distribution around the globe
- iv. Viable option compared to fossil fuels
- v. Retention of the structural features of the original plant tissue (biotemplating feature)
- vi. High carbon content (because of easy removal of H and O)

### ❑ Exploration of new sources of carbon materials - Necessary

#### Desired physico-chemical properties

- i. High specific surface area
- ii. Porosity
- iii. Surface functionality
- iv. Thermal stability
- v. Carbon content
- vi. Carbon purity
- vii. Adsorptive capacity

Michal Kruk, Bruno Dufour, Ewa B. Celer, Tomasz Kowalewski, Mietek Jaroniec and Krzysztof Matyjaszewski, *J. Phys. Chem. B*, 109 (2005) 9216

An-Hui Ru and Jing-Tang Zheng, *Journal of Colloid and Interface Science*, 236 (2001) 369

Junichi Hayashi, Atsuo Kazehaya, Katsuhiko Muroyama, A. Paul Watkinson, *Carbon* 28 (2000) 1873

# Activated Carbon Materials – Methods of Activation

- ❑ Surface area values can be modulated from few  $\text{m}^2/\text{g}$  to few 1000  $\text{m}^2/\text{g}$  due to the micro architecture of the pores.
- ❑ Variety of activating agents can be used.
- ❑ Functional groups can be easily introduced and altered

## Process of Activation

- Creates porosity
- Generates desired surface functional groups

### Activation Methods

#### Chemical Activation

##### Activating agents

Alkali Metal Hydroxides (KOH, NaOH)  
Alkali Metal Carbonates ( $\text{K}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ )  
Mineral acids ( $\text{H}_3\text{PO}_4$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ )

Lower reaction temperature  
Better porous structure  
Higher carbon yield

Environmentally  
unfriendly

#### Physical Activation

##### Activating agents

Steam ( $\text{H}_2\text{O}$ )  
 $\text{CO}_2$   
Air

Higher reaction temperature  
Lower Carbon yield

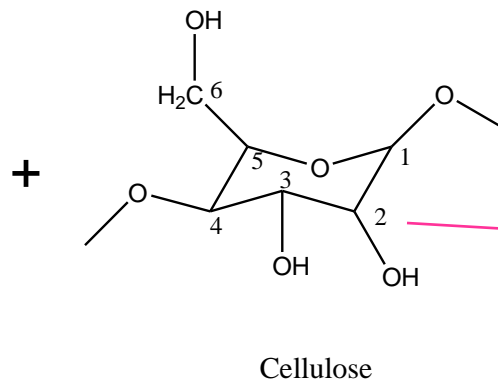
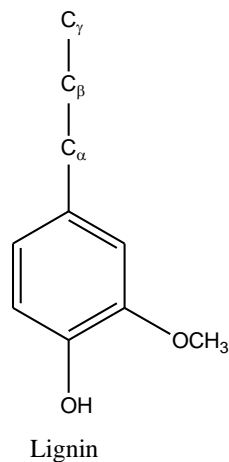
Environmentally  
friendly

## Objectives

- 1. To develop a viable process for the production of high surface area activated carbon materials from a widely available, inexpensive carbon precursor and also to exploit the same for energy and environmental applications.**
- 2. Choosing an appropriate carbon support for HPAs, for typical acid catalyzed reactions like tert amyl methyl ether (TAME) and methyl tert butyl ether (MTBE) syntheses is a challenge which has been one of the objectives of the study.**
- 3. To design a cost effective and highly active electro catalyst by developing new porous carbon material as support for Pt and as an alternative to Vulcan XC 72 R.**
- 4. Developing low cost and effective activated carbon based sorbents (modified with S) for the removal of Hg from water bodies has been one of the objectives of the study owing to the environmental significance of the issue.**
- 5. To develop adsorbents with a high sorption capacity and also appreciable selectivity for sulfur-containing species relative to aromatic and olefinic compounds from diesel fuel (Adsorptive desulphurization process).**



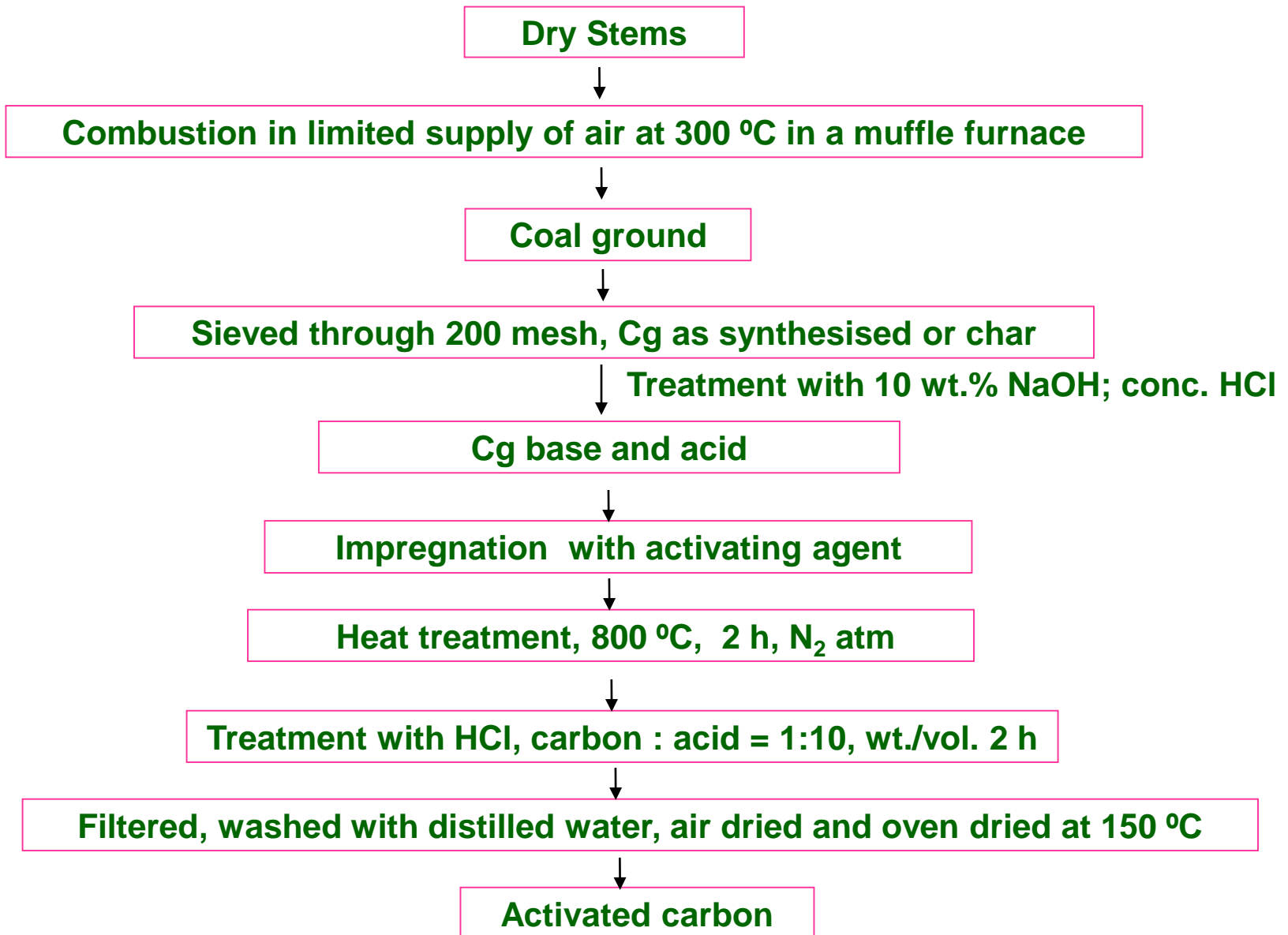
## 2. Activated Carbon from *Calotropis gigantea*



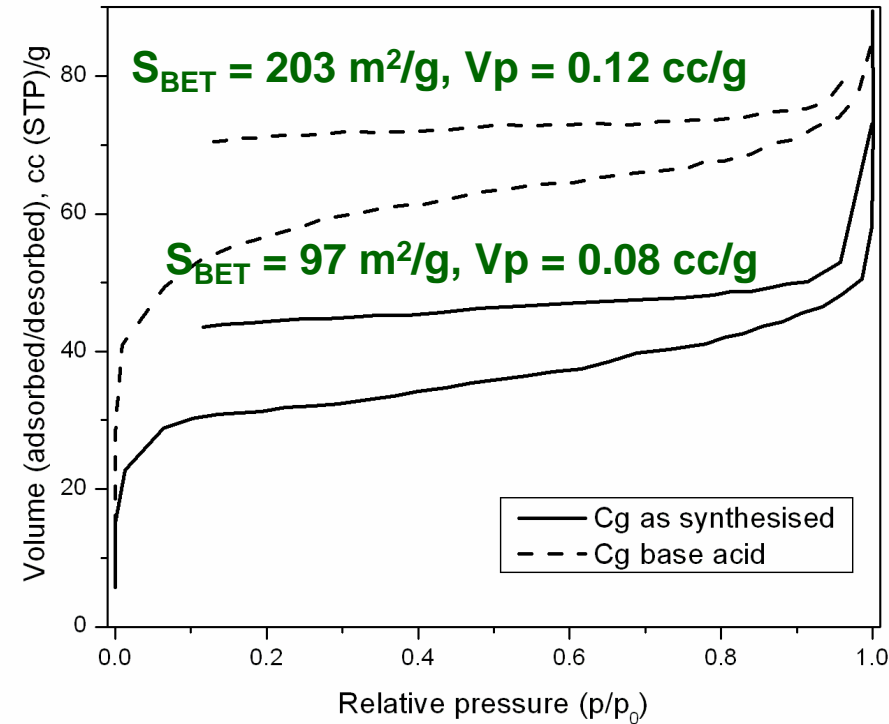
- **Synthesis**
- **Effect of Activating Agents**
- **Characterization**
- **Application as catalyst (HPW) support**

***Calotropis gigantea* -  
A waste land weed native of India**

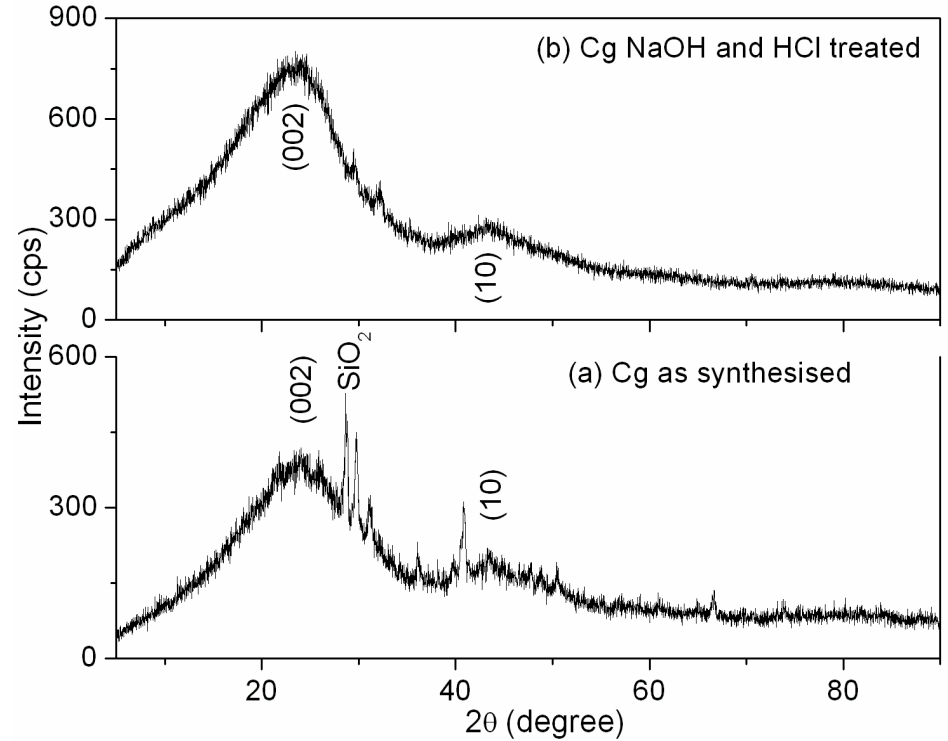
# General Method of Preparation of Activated Carbon



# Effect of NaOH and HCl treatment on the textural property of the char



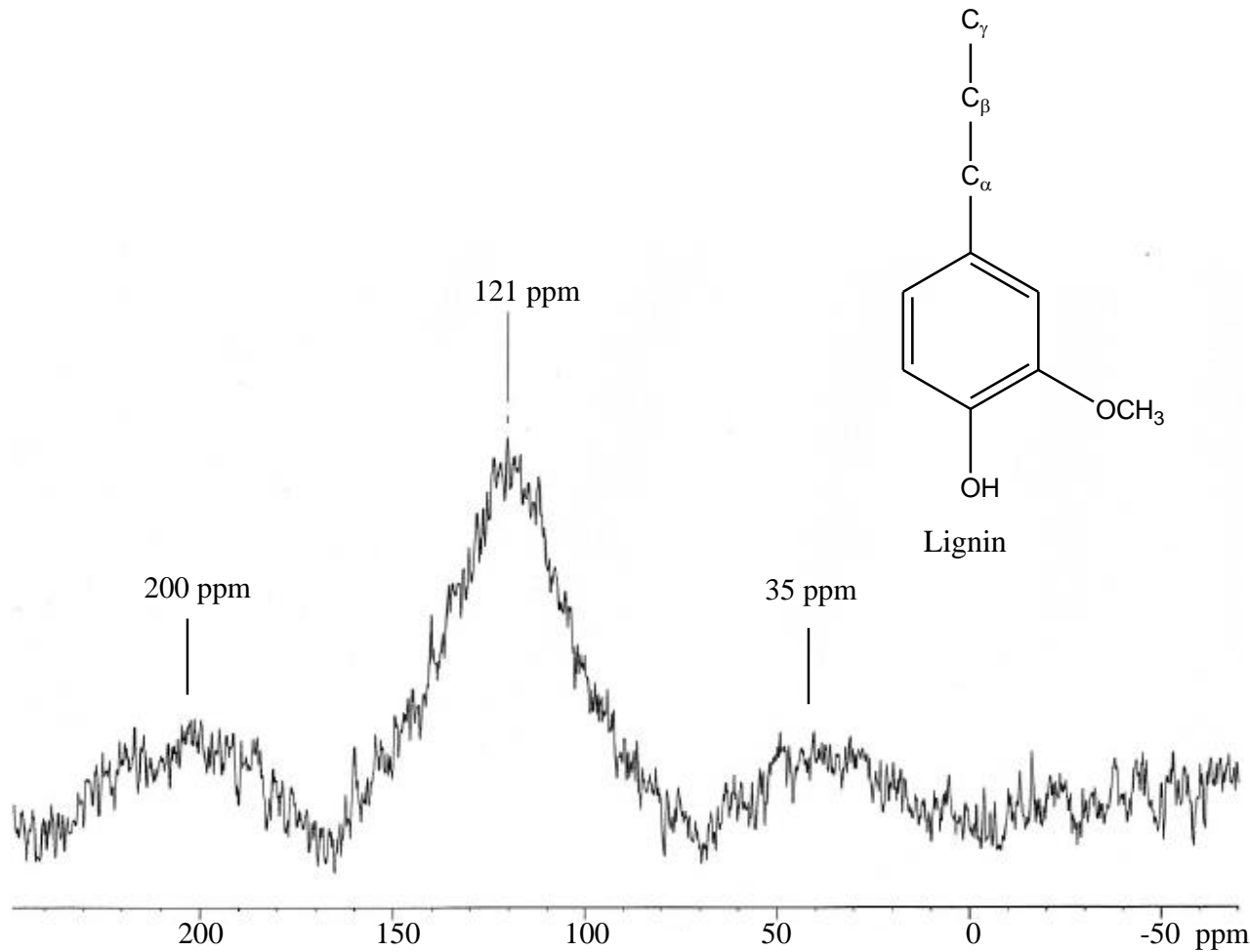
**N<sub>2</sub> adsorption-desorption isotherms**



**XRD - patterns**

Carbon materials prepared from *Calotropis gigantea*, (a) Cg as synthesized (char), and (b) Cg base acid,

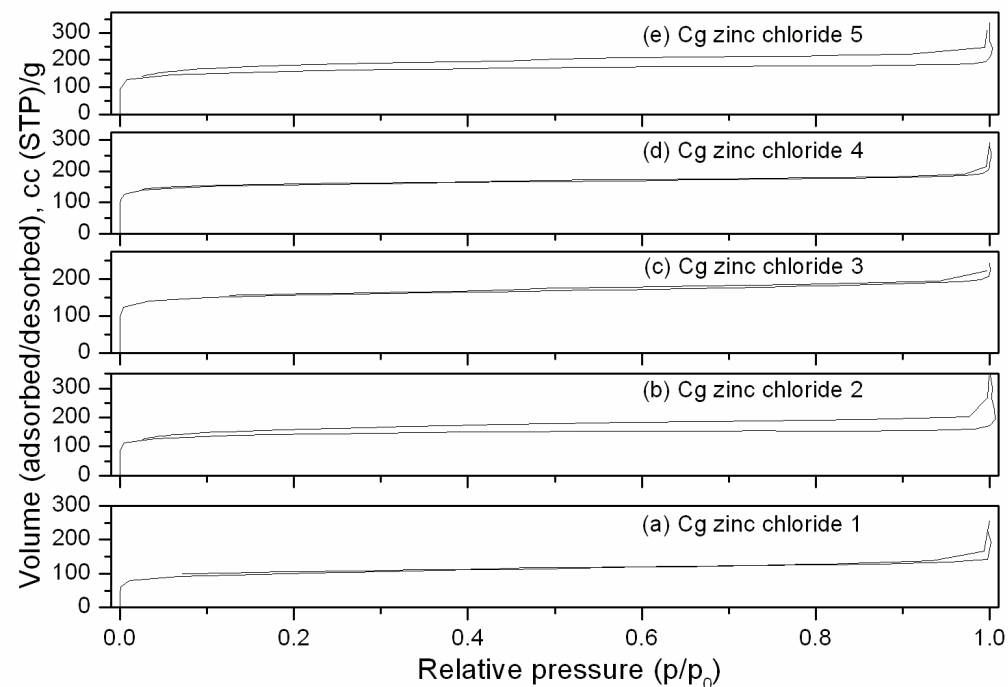
# Chemical Structure of Carbon Material (Char)



**$^{13}\text{C}$  MAS NMR spectrum of the char (C<sub>g</sub> as synthesized)**

- 121 ppm - carbon nuclei in aromatic plane**
- 35 ppm - aliphatic chains of polymethylene**
- 200 ppm - ketonic carbon groups**

# Activation with Transition Metal Salt ( $ZnCl_2$ ) – Effect on Textural Properties



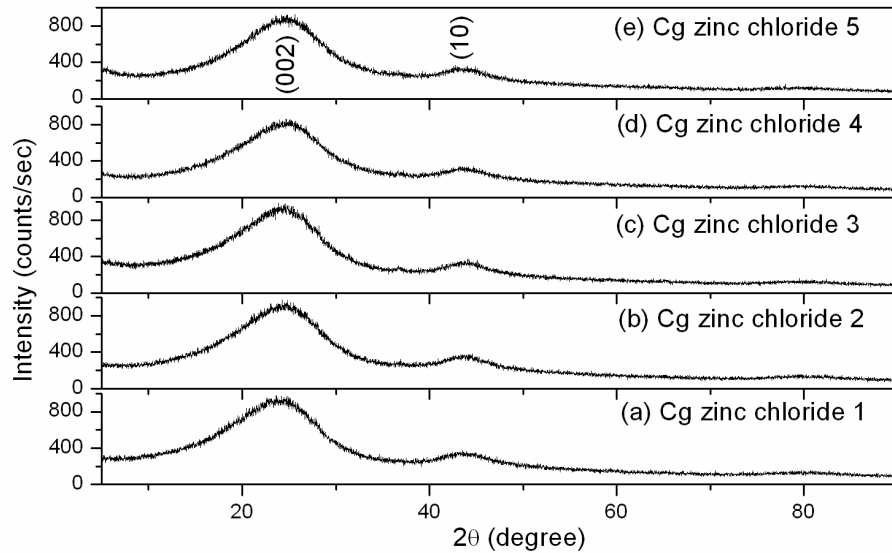
## Textural properties

S. No.	Carbon Material	$S_{BET}$ ( $m^2/g$ )	$V_P$ ( $cm^3/g$ )	Mean Pore Diameter (nm)
1	Cg zinc chloride 1	356	0.21	2.36
2	Cg zinc chloride 2	493	0.25	2.03
3	Cg zinc chloride 3	564	0.30	2.13
4	Cg zinc chloride 4	573	0.29	2.02
5	Cg zinc chloride 5	553	0.29	2.1

## $N_2$ adsorption-desorption isotherms

Activated carbon materials with a Cg base acid to  $ZnCl_2$  ratio (wt./wt.%) of (a) 1:1, (b) 1:2, (c) 1:3, (d) 1:4 and (e) 1:5

# Activation with Transition Metal Salt ( $\text{ZnCl}_2$ ) – Effect on Structural Properties



**XRD pattern**

## Structural properties

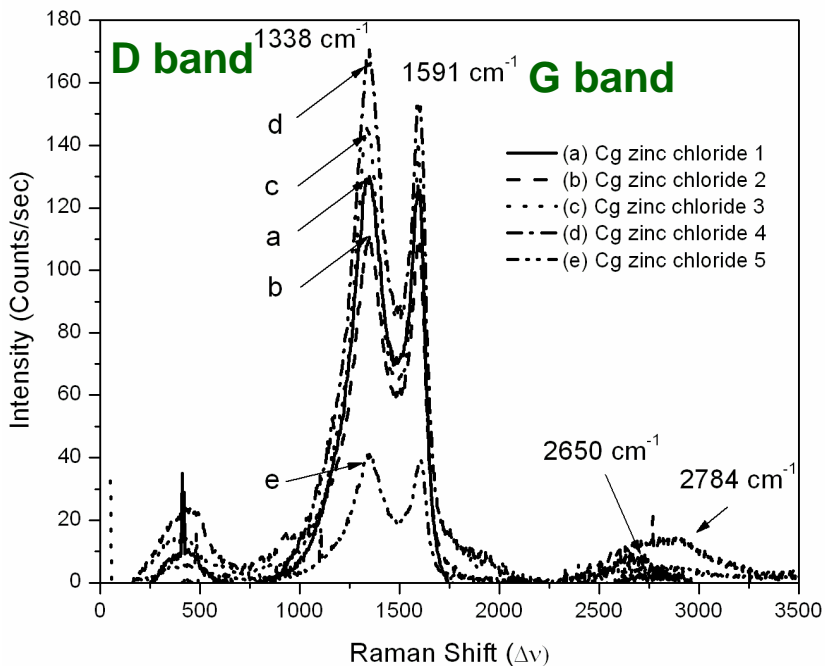
S. No.	Carbon material	$d_{002}$ (nm)	$L_c$ (nm)	$L_a$ (nm)
1	Cg zinc chloride 1	0.356	1.04	3.94
2	Cg zinc chloride 2	0.356	1.02	3.50
3	Cg zinc chloride 3	0.353	1.03	3.96
4	Cg zinc chloride 4	0.356	0.91	3.72
5	Cg zinc chloride 5	0.350	0.94	3.80

**Activated carbon materials prepared from *Calotropis gigantea*, with a Cg base acid to  $\text{ZnCl}_2$  ratio (wt./wt.%) of (a) 1:1, (b) 1:2, (c) 1:3, (d) 1:4 and (e) 1:5**

- ✓ For typical graphitic carbon,  $L_c$  and  $L_a$  values are 0.06708 and 0.2461 nm
- ✓  $L_c$  values of activated carbon materials are of the order of 1 nm
- ✓  $L_a$  values of activated carbon materials varied in the range of 3.5 to 3.96 nm
- ✓ Thus the carbon material is made up of crystallites with dimensions of about 15 cell lengths<sup>14</sup> along the c-direction and about 14-16 cell lengths along the a-direction

# Activation with Transition Metal Salt ( $ZnCl_2$ ) – Study of order and disorder in the structure

## Structural parameters from Raman spectra



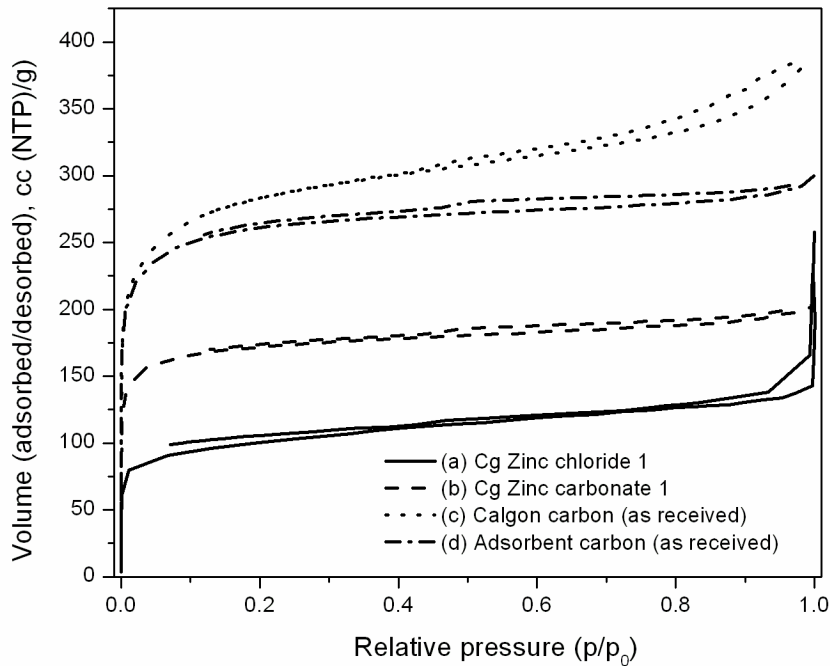
## Raman spectra

S. No.	Carbon material	R = $I_D/I_G$	$L_a$ (nm) = $4.4/R$ (From Raman)	$L_a$ (nm) (from XRD)
1	Cg z c1	1.40	3.14	3.94
2	Cg z c 2	1.42	3.09	3.50
3	Cg z c 3	1.33	3.30	3.96
4	Cg z c 4	1.48	2.97	3.72
5	Cg z c 5	1.53	2.87	3.80

- ✓ Extent of crystallographic disorder (concentration of lattice defects) was analyzed using Raman spectroscopic studies
- ✓  $1200 - 1600 \text{ cm}^{-1}$  – first order Raman lines – structural order or disorder with in the carbon layer (along a-axis)
- ✓  $2400 - 3300 \text{ cm}^{-1}$  – second order Raman lines – structural disorder along c-axis
- ✓  $1590 \text{ cm}^{-1}$  – graphitic carbon structure – G band
- ✓  $1348 \text{ cm}^{-1}$  – disordered carbon structure – D band
- ✓ R – Raman intensity ratio – A measure of disorder

# Activation with ZnCO<sub>3</sub> and ZnCl<sub>2</sub> – A comparison

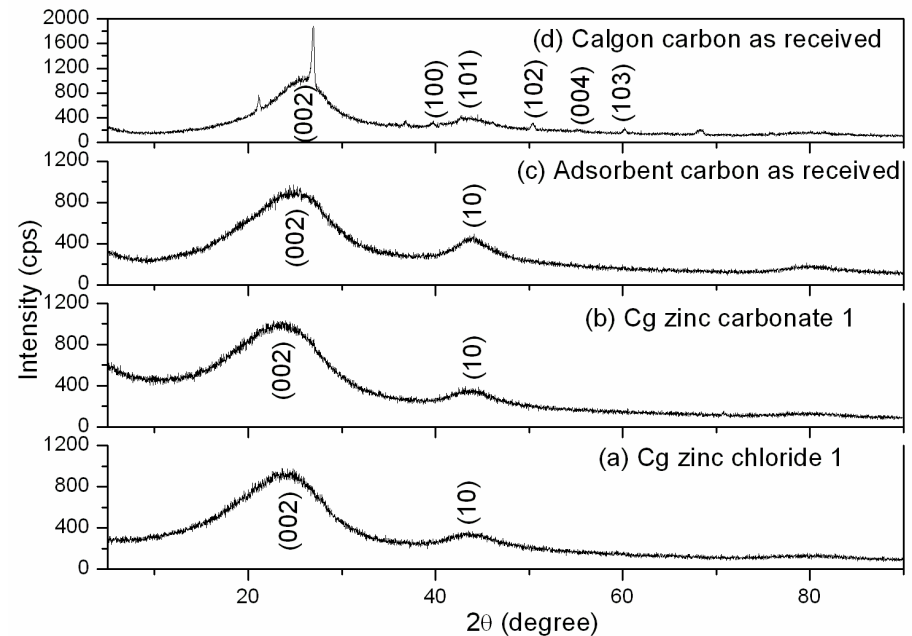
## Textural properties



S. No.	Carbon Material	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>P</sub> (cm <sup>3</sup> /g)	Mean Pore Diameter ((nm))
1	Cg zinc chloride 1	356	0.213	2.39
2	Cg zinc carbonate 1	623	0.306	1.96
3	Calgon carbon	950	0.451	1.90
4	Adsorbent carbon	1014	0.587	2.31

## N<sub>2</sub> adsorption-desorption isotherms

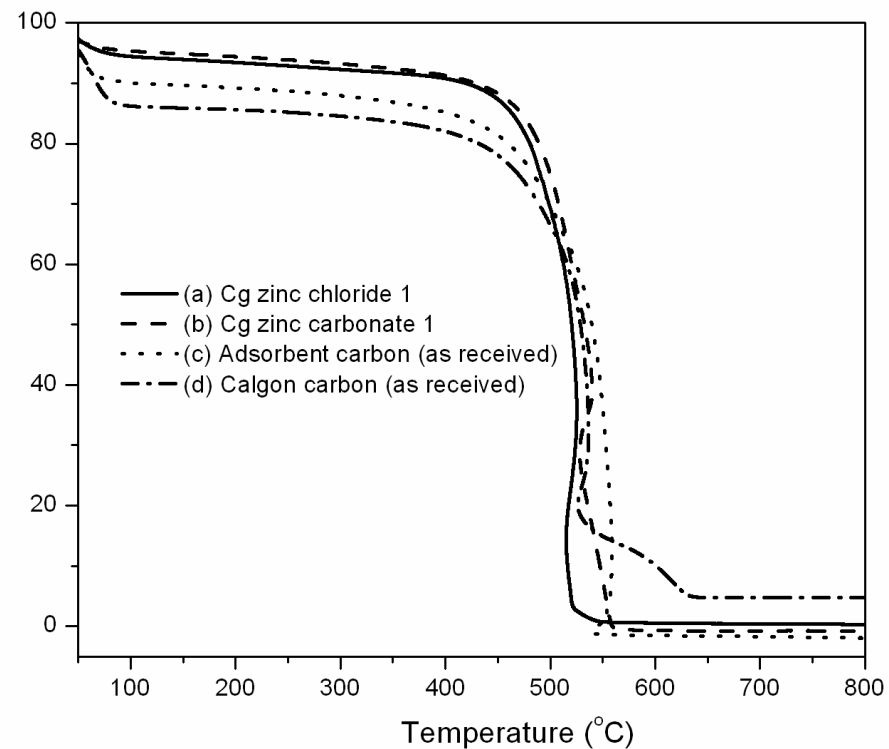
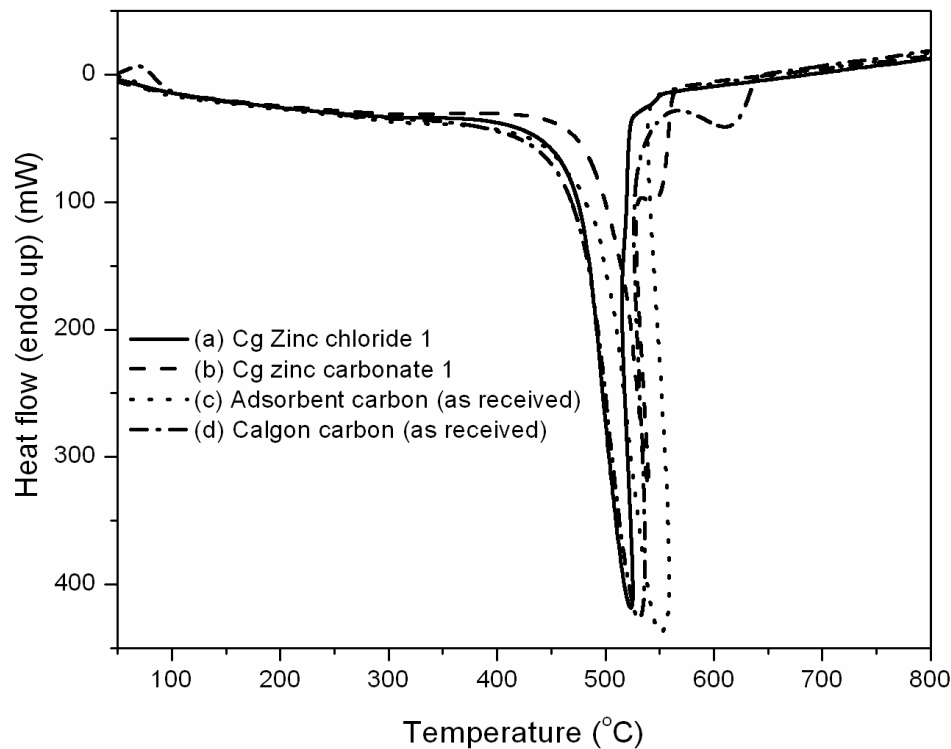
S. No.	Carbon Material	FWHM (d <sub>002</sub> )
1	Cg zinc chloride 1	8.80
2	Cg zinc carbonate 1	9.88
3	Adsorbent	8.89
4	carbonCalgon carbon	6.39



## XRD pattern

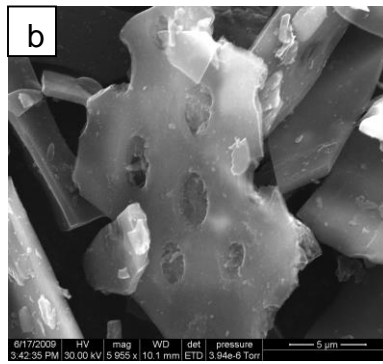
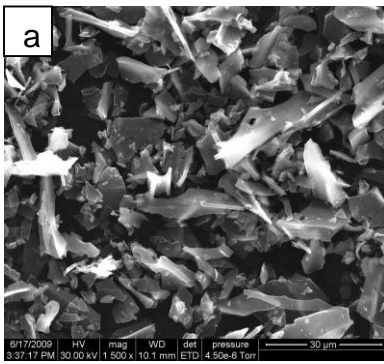


## Activation with $\text{ZnCO}_3$ and $\text{ZnCl}_2$ – A comparison

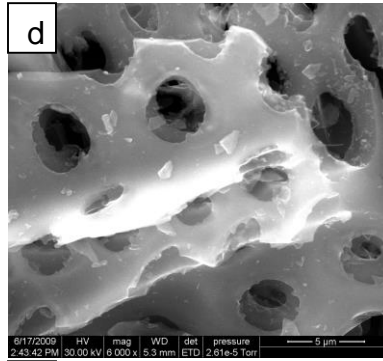
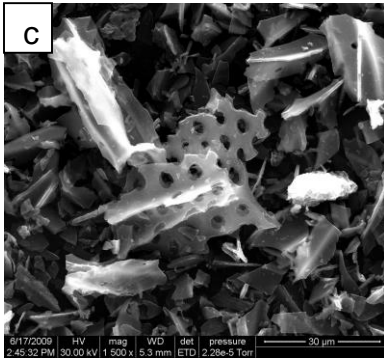


**TG – DTA curves of (a) Cg zinc chloride 1, (b) Cg zinc carbonate 1, (c) Adsorbent carbon (as received) and (d) Calgon carbon (as received)**

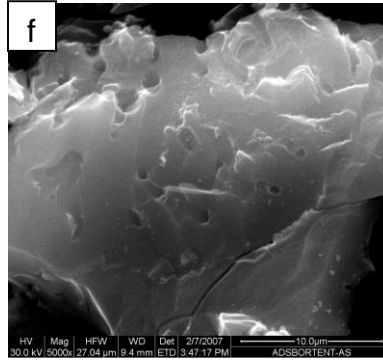
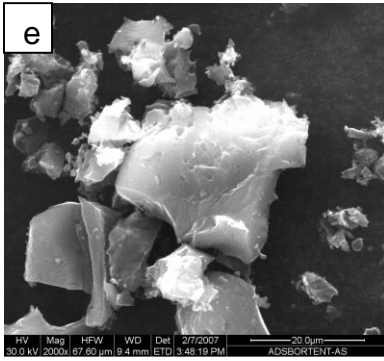
# Scanning Electron Microscopic (SEM) Analysis



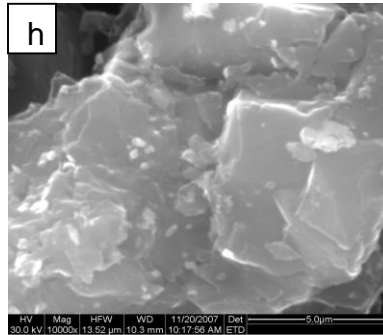
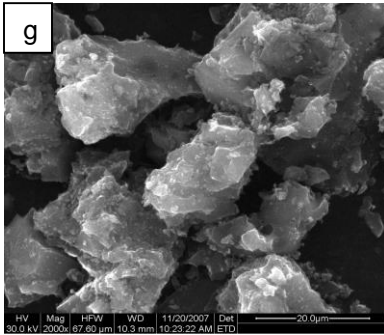
Cg zinc chloride 1  
(a) 1500 X  
(b) 5,955 X



Cg zinc carbonate 1  
(c) 1500 X  
(d) 6000 X



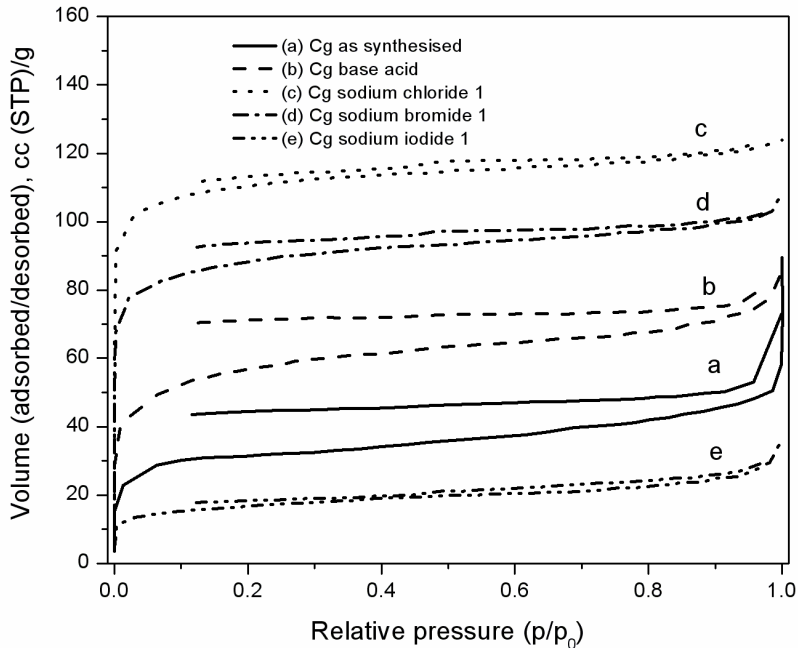
Adsorbent carbon  
(as received)  
(e) 2000 X  
(f) 5000 X



Calgon carbon  
(as received)  
(g) 2000 X  
(h) 10,000 X

# Activation with Alkali Metal Halides – Effect on Textural Properties

## Textural properties

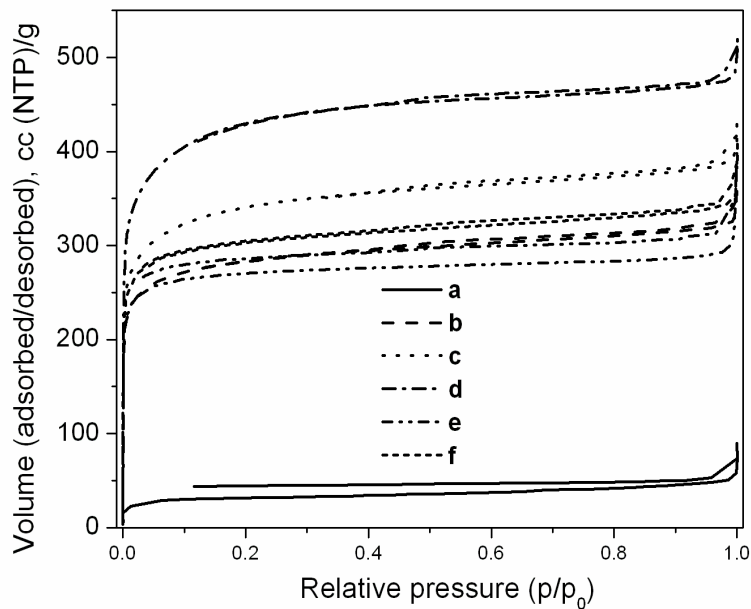
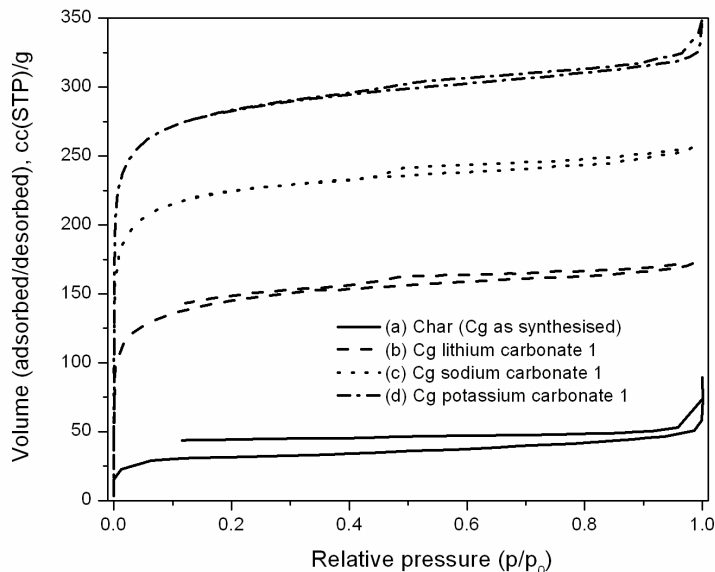


S. No.	Carbon Material	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\text{P}}$ (cm <sup>3</sup> /g)
1	Cg as synthesised	97	0.08
2	Cg base acid	203	0.12
3	Cg sodium chloride 1	400	0.2
4	Cg sodium bromide 1	319	0.16
5	Cg sodium iodide 1	58	0.04

## N<sub>2</sub> adsorption – desorption isotherms

✓ The observed trend in the decrease in the textural parameters with the use of NaCl, NaBr and NaI as activating agents is in line with the decrease in ionicity and an increase in covalency from NaCl to NaI.

# Activation with Alkali Metal Carbonates – Effect on Textural Properties



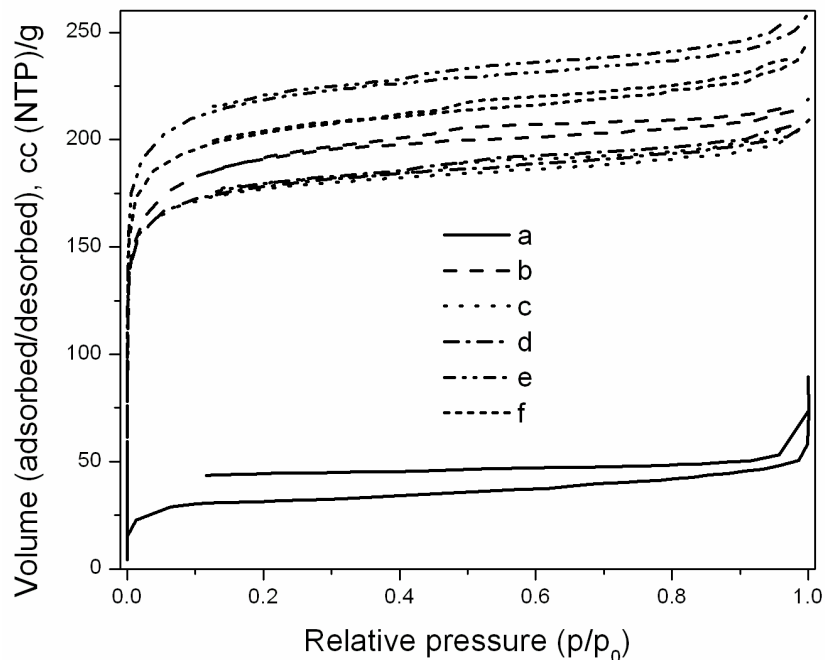
## Textural Properties

S. No.	Activating agent	Ionic radii of the cation (Å)	Textural parameters	
			$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_p$ (cc/g)
1	Li <sub>2</sub> CO <sub>3</sub>	0.60	480	0.263
2	Na <sub>2</sub> CO <sub>3</sub>	0.96	811	0.395
3	K <sub>2</sub> CO <sub>3</sub>	1.33	892	0.497

Code	Carbon Material	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_p$ (cm <sup>3</sup> /g)
a	Cg as synthesised	97	0.08
b	Cg potassium carbonate 1	892	0.5
c	Cg potassium carbonate 2	1083	0.59
d	Cg potassium carbonate 3	1296	0.73
e	Cg potassium carbonate 4	765	0.45
f	Cg potassium carbonate 5	922	0.50

## N<sub>2</sub> adsorption-desorption isotherms

# Activation with Alkali Metal Salts of Carboxylic Acids – Effect on Textural Properties

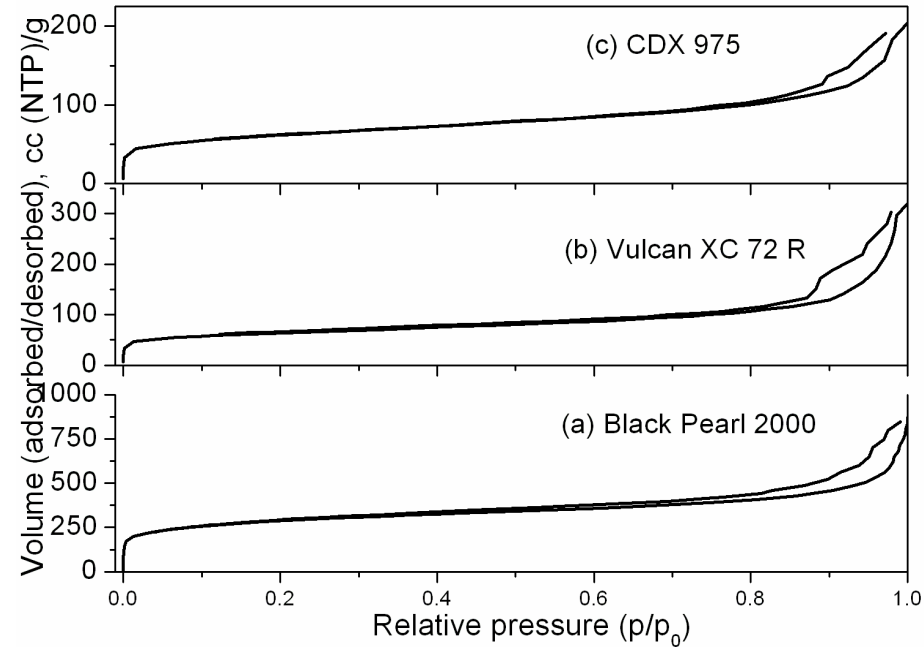


**N<sub>2</sub> adsorption-desorption isotherms**

<b>Code</b>	<b>Carbon Material</b>	<b>S<sub>BET</sub> (m<sup>2</sup>/g)</b>	<b>V<sub>P</sub> (cm<sup>3</sup>/g)</b>
a	Cg as synthesised	97	0.08
b	Cg sodium oxalate 1	707	0.33
c	Cg sodium oxalate 2	647	0.31
d	Cg sodium oxalate 3	655	0.32
e	Cg sodium oxalate 4	785	0.39
f	Cg sodium oxalate 5	734	0.37

<b>S. No.</b>	<b>Carbon Material</b>	<b>S<sub>BET</sub> (m<sup>2</sup>/g)</b>	<b>V<sub>p</sub> (cm<sup>3</sup>/g)</b>
1	Cg oxalic acid 1	317	0.14
2	Cg sodium oxalate 1	707	0.33
3	Cg citric acid 1	127	0.07
4	Cg sodium citrate 1	419	0.21
5	Cg tartaric acid 1	42	0.04
6	Cg di sodium tartarate 1	394	0.20
7	Cg sodium potassium tartarate 1	394	0.18

# Carbon materials from *Calotropis gigantea* Vs commercial carbon blacks – A comparison of textural properties

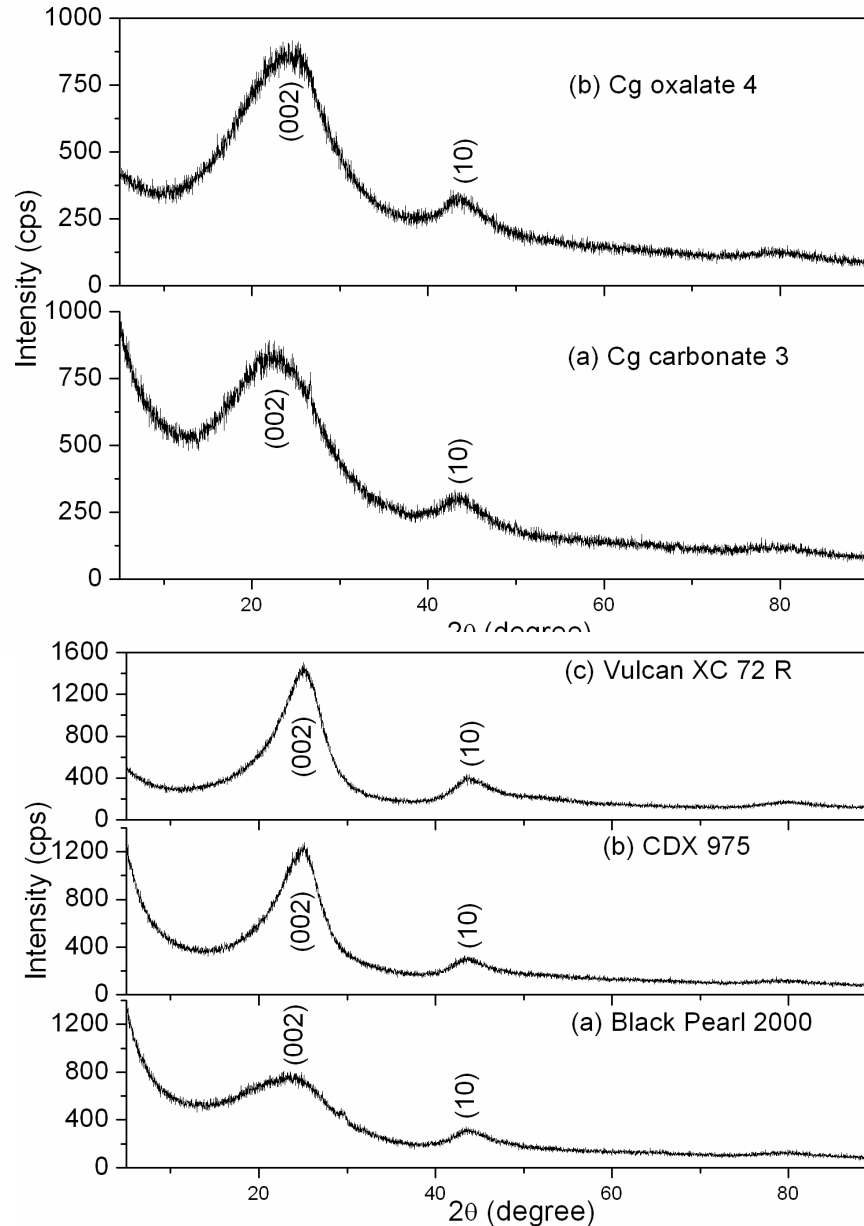


**N<sub>2</sub> adsorption - desorption isotherms**

## Textural properties

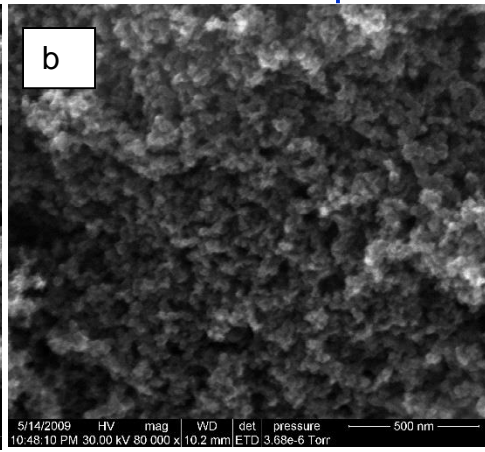
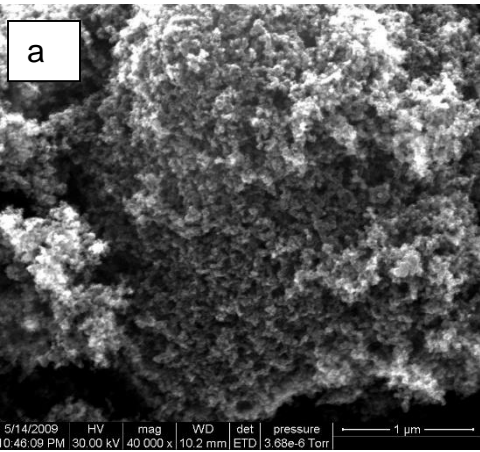
S. No.	Carbon Material	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>p</sub> (cm <sup>3</sup> /g)
1	Black Pearl 2000	1012	1.14
2	Vulcan XC 72 R	224	0.46
3	CDX 975	215	0.28
4	Cg carbonate 3	1296	0.73
5	Cg oxalate 4	745	0.39

# Carbon materials from *Calotropis gigantea* Vs commercial carbon blacks – A comparison of structural properties



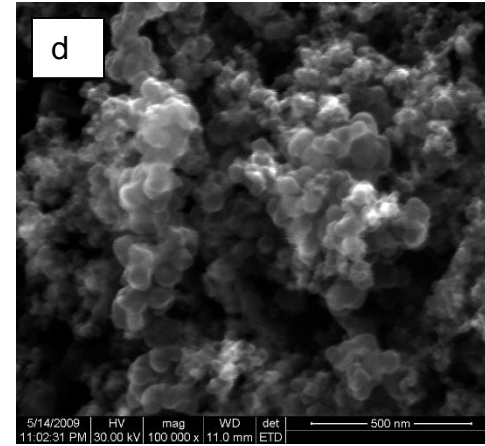
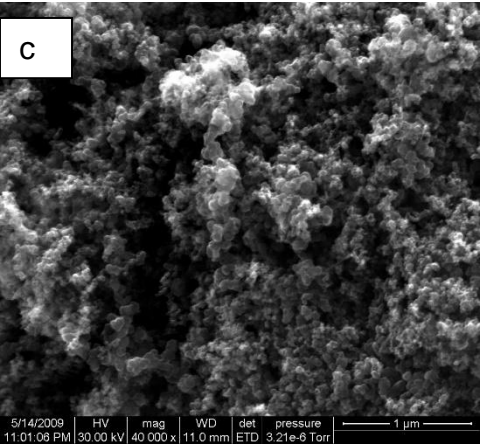
S. No.	Sample	$d_{002}$ (nm)	FWHM (002) reflection
1	Cg carbonate 3	0.411	12.5
2	Cg oxalate 4	0.385	9.8
3	Black Pearl 2000	0.407	13.8
4	Vulcan XC 72 R	0.364	5.2
5	CDX 975	0.370	5.5

# Carbon materials from *Calotropis gigantea* Vs commercial carbon blacks – A comparison of morphology

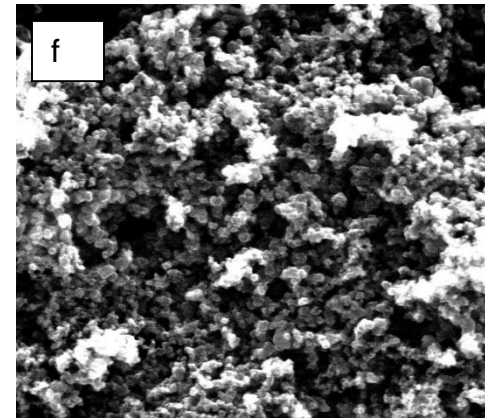
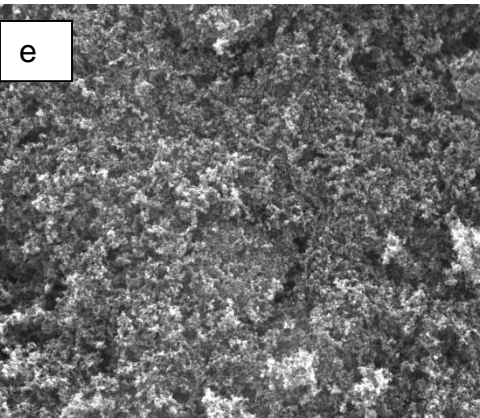


**FEG SEM images of commercial carbon material (at different magnifications)**

**(a & b) Black Pearl 2000 (40, 000 X, 80, 000 X),**



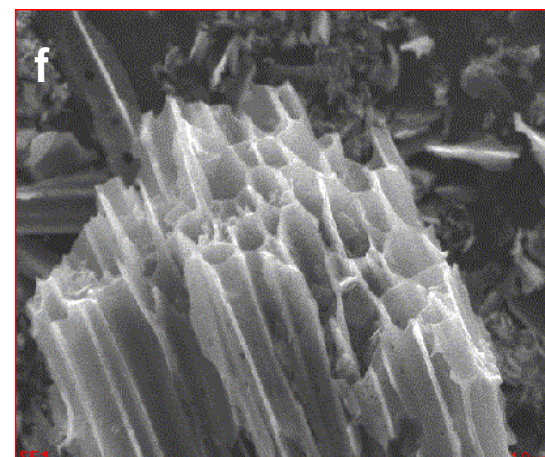
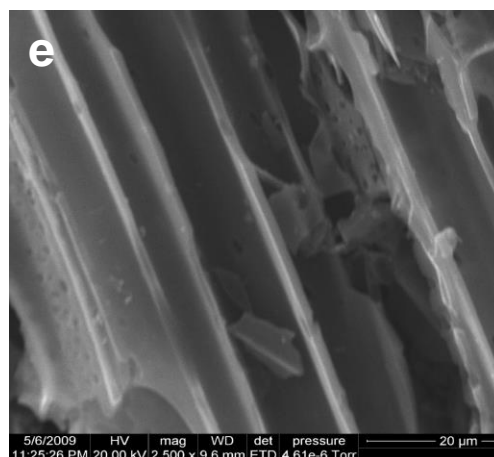
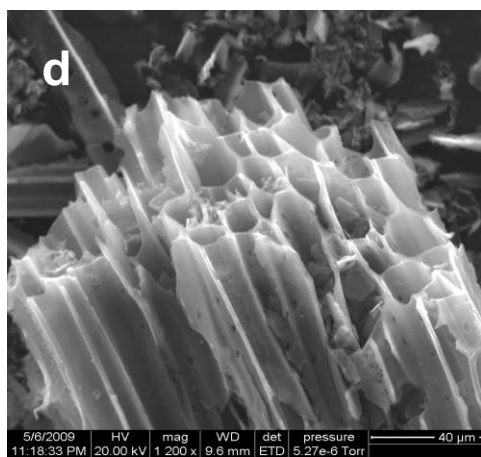
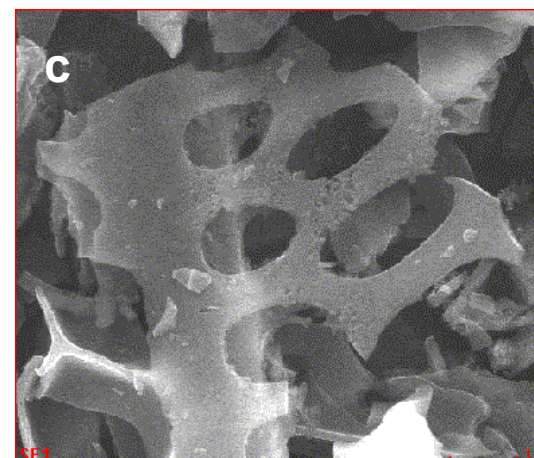
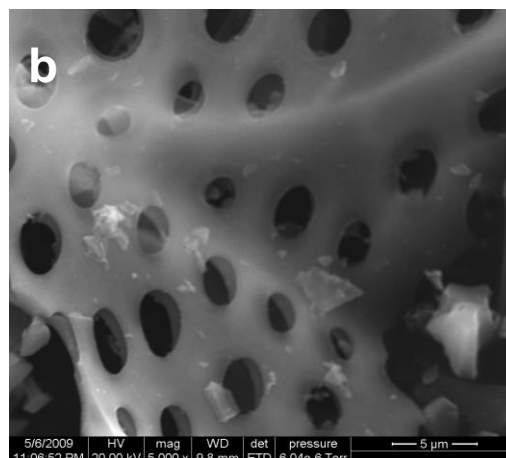
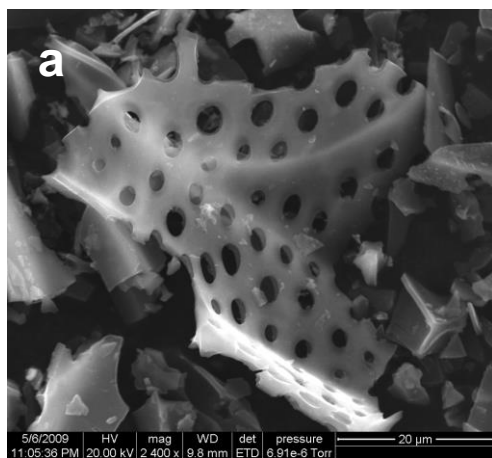
**(c & d) Vulcan XC 72 R (40, 000 X, 1,00, 000 X) and**



**(e & f) CDX 975 (6000 X, 40, 000 X)**



# Carbon materials from *Calotropis gigantea* Vs commercial carbon blacks – A comparison of morphology



**FEG SEM images of carbon material from *Calotropis gigantea* (at different magnifications)  
(a, b & C) Cg potassium carbonate 3 and (d, e & f) Cg sodium oxalate 4**

# Heteropoly acids – Unique features

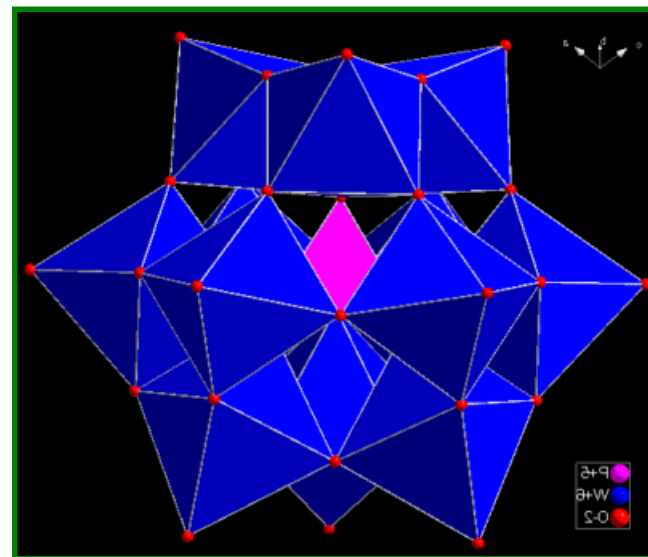
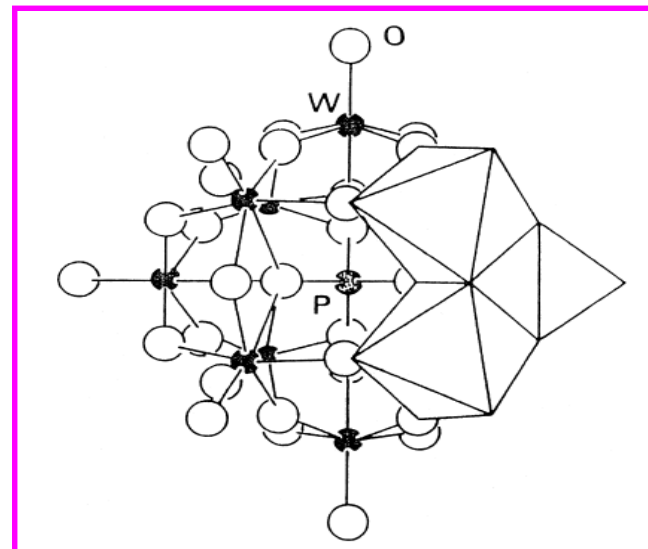
- Multifunctional
- Strong Bronsted acidity
- Homogeneous as well as heterogeneous
- Efficient oxidants
- Easy alteration of chemical composition
- Structure preserved upon substitution
- High solubility in polar solvents
- Environmentally friendly

## Draw backs :

- ❖ Low specific surface area (1-10 m<sup>2</sup>/g)
- ❖ Thermally stable only up to 773 K

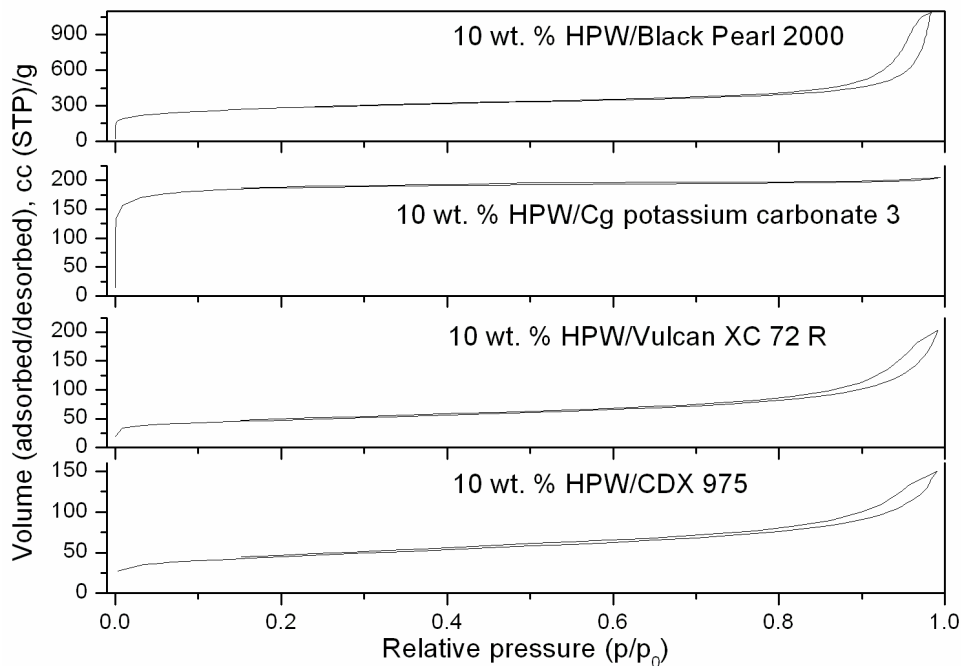
## Solution :

- ◆ Search for a suitable carrier

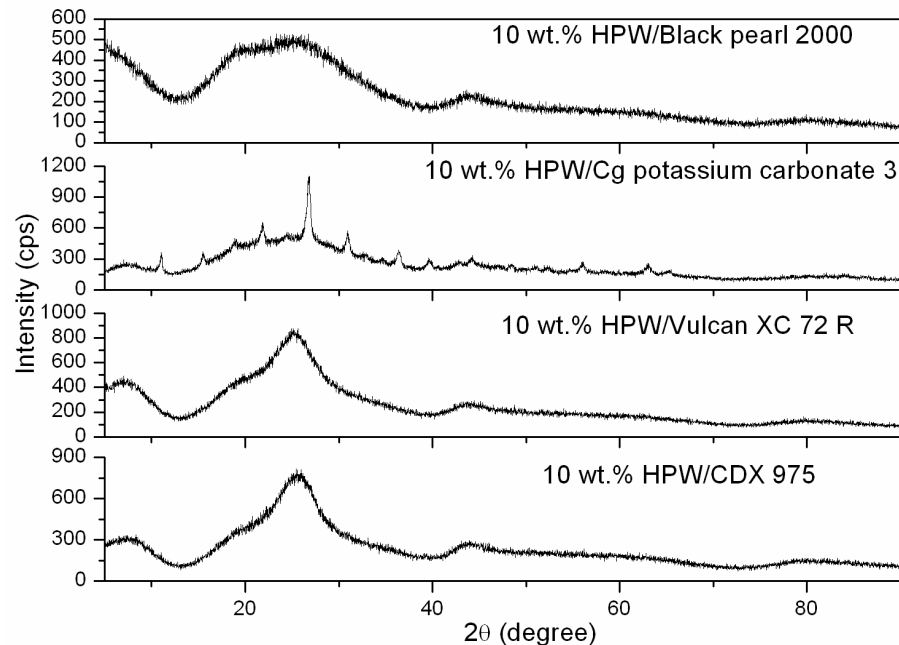


**Keggin ion structure**

# Supported heteropoly acid catalysts (HPW/C) – Textural properties



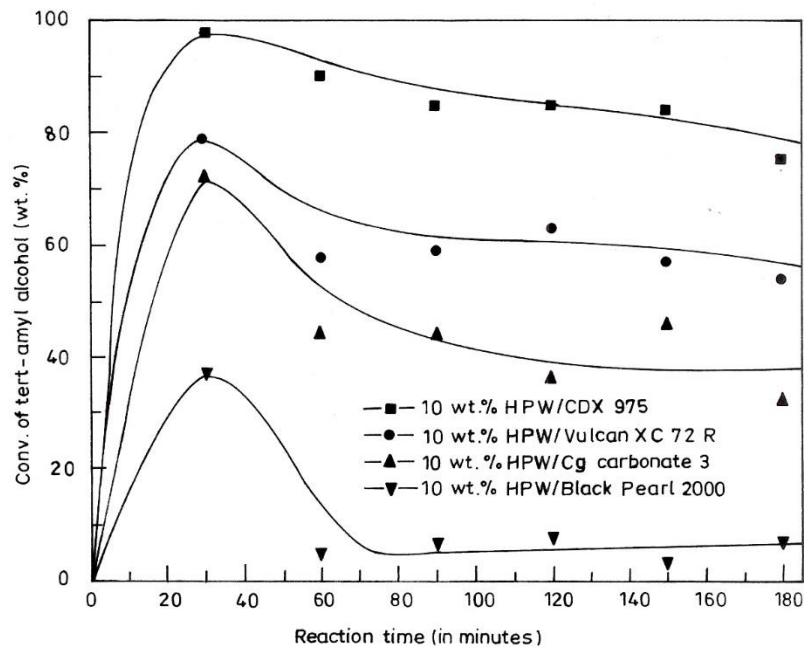
**N<sub>2</sub> adsorption - desorption isotherms**



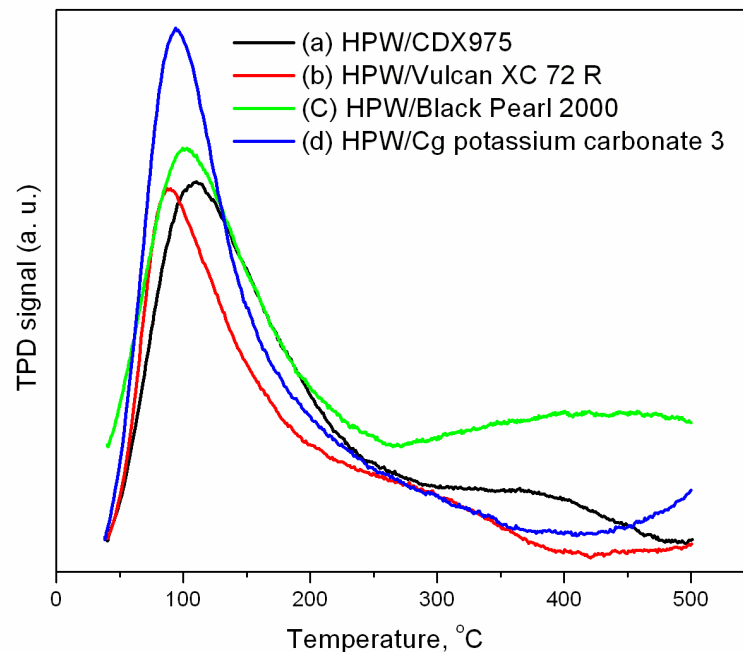
**XRD pattern**

S. No.	Catalyst	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>p</sub> (cc/g)
1	10 wt. % HPW/ CDX 975	156	0.23
2	10 wt.% HPW/ Vulcan XC 72 R	169	0.30
3	10 wt.% HPW/ Black Pearl 2000	980	1.65
4	10 wt.% HPW/ Cg potassium carbonate 3	711	0.32

# Synthesis of tert - amyl methyl ether using HPW/C catalysts



Plot of Conversion of IAA (wt. %) Vs Reaction time (in minutes)



NH<sub>3</sub> – TPD profiles of HPW/C catalysts

Catalyst	Conversion (wt. %)	Selectivity (%)	
		Olefins <sup>a</sup>	TAME
10 wt. % HPW/ CDX 975	75	35	65
10 wt.% HPW/ Vulcan XC 72 R	54	13	87
10 wt.% HPW/Black Pearl 2000	7	47	53
10 wt.% HPW/Cg potassium carbonate 3	32	37	73

**Reaction Conditions:** Time on stream = 3 h; tert-amyl alcohol/methanol (mole) = 1:5; flow rate of the feed = 10 mL/h; flow rate of the carrier gas = 30 mL/min; amount of catalyst = 0.5 g;  
a. iso-amylenes (2-methyl-1-butene, 2MB1, and 2-methyl-2-butene, 2MB2)

# Summary

1. Microporous activated carbon materials with high specific surface area values have been prepared from the dried stems of *Calotropis gigantea*.
2. Uniformity in properties (physical and chemical) through out the samples and low ash content were the unique advantages of activated carbon produced from *Calotropis gigantea* stems compared to the carbon materials produced from either coal or lignocellulosic materials.
3. Ecological imbalance caused by *Calotropis gigantea* stem waste generation and disposal is solved in a productive way by transforming the waste *Calotropis gigantea* stems into technologically useful high specific surface area microporous carbon.
4. Methods for tuning the textural and structural parameters of activated carbon materials have been proposed.
5. Many activating agents, transition metal compounds, alkali and alkaline earth metal compounds, alkali metal salts of carboxylic acids have been used for activation purposes.
6. Among several classes of activating agents,  $K_2CO_3$  has been found to be the best yielding with textural properties superior to those of commercial activated carbon materials (Adsorbent carbon, Black Pearl 2000, Calgon, CDX 975 and Vulcan XC 72 R).
7. In addition to alkali metal carbonates, alkali metals salts of carboxylic acids, like,  $Na_2C_2O_4$ , have been found to be potential activating agents.
8. The carbon material obtained from plant source, Cg potassium carbonate 3, has been successfully exploited as support for HPW and employed as a catalyst for the synthesis of TAME, a preferred gasoline additive.

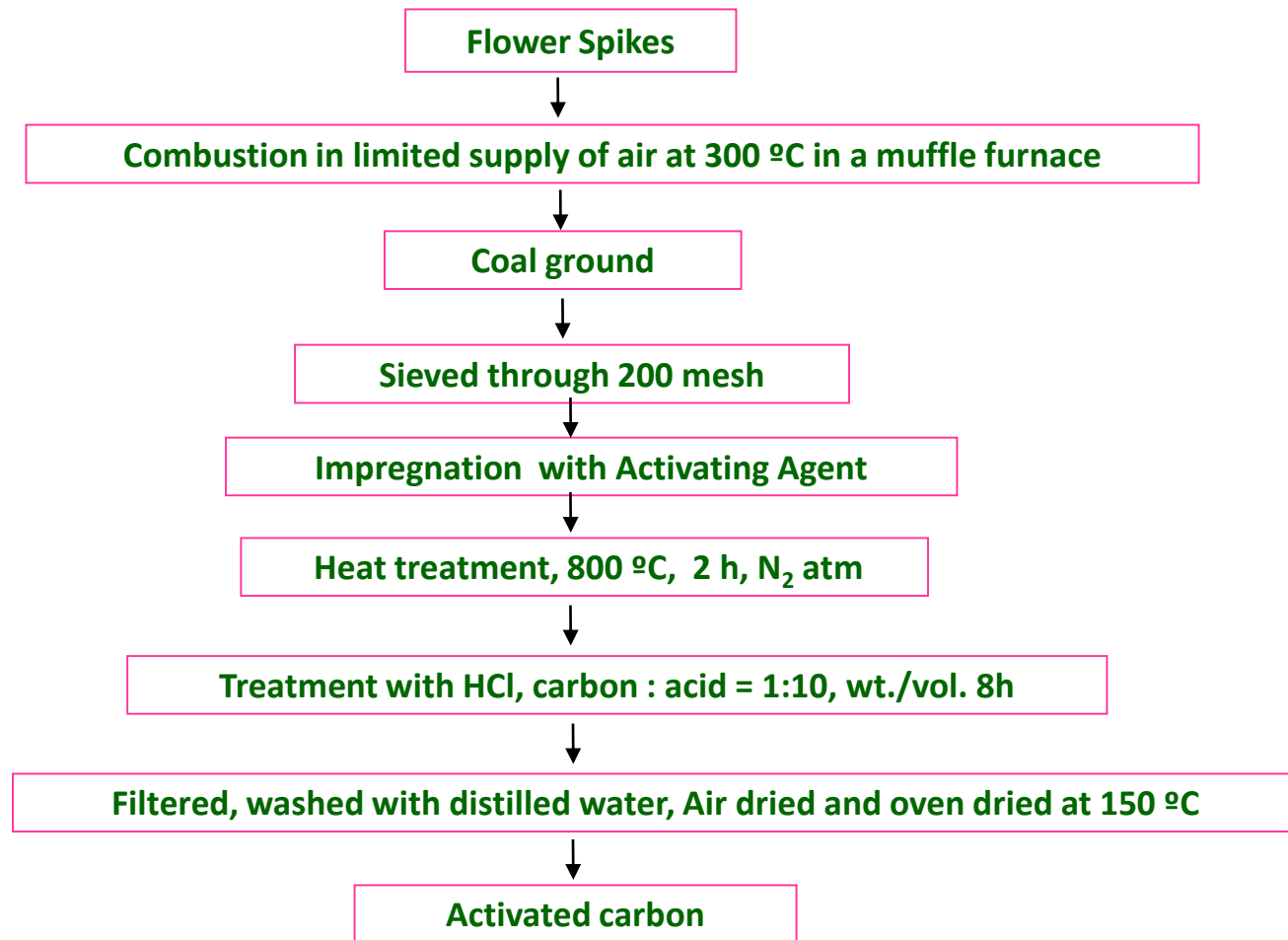


### 3. Activated Carbon from *Borassus Flabellifera*

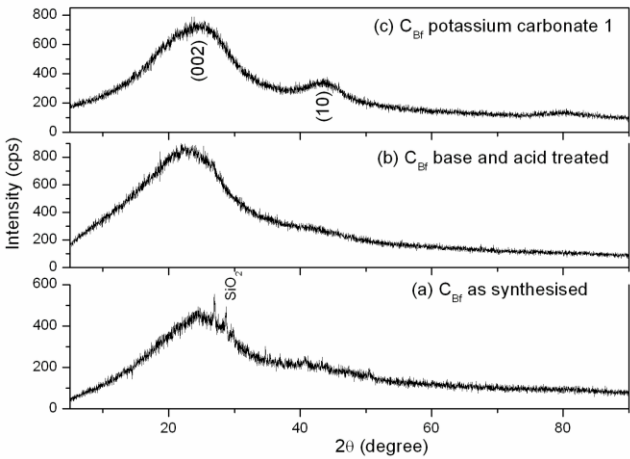
Synthesis  
Characterization  
Application as Catalyst  
(HPW) support

**Common Names** : Palmyra palm, Toddy palm,  
wine palm, Talauriksha palm

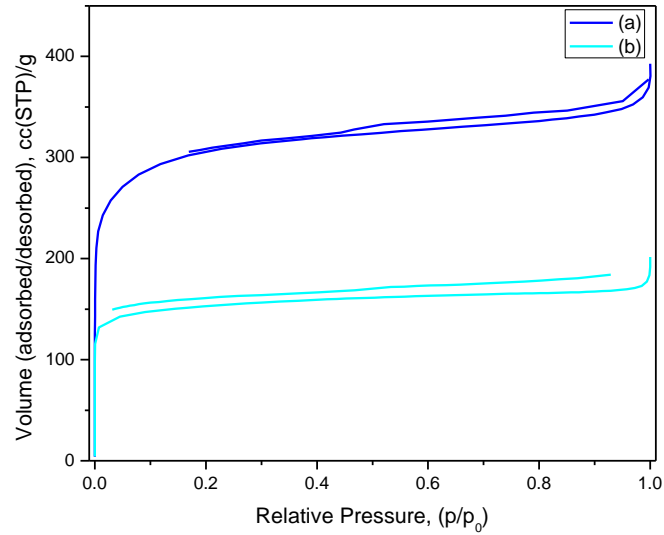
**Distribution** : India, Srilanka



# Activated Carbon from *Borassus Flabellifera* Structural, Textural and Morphological Properties

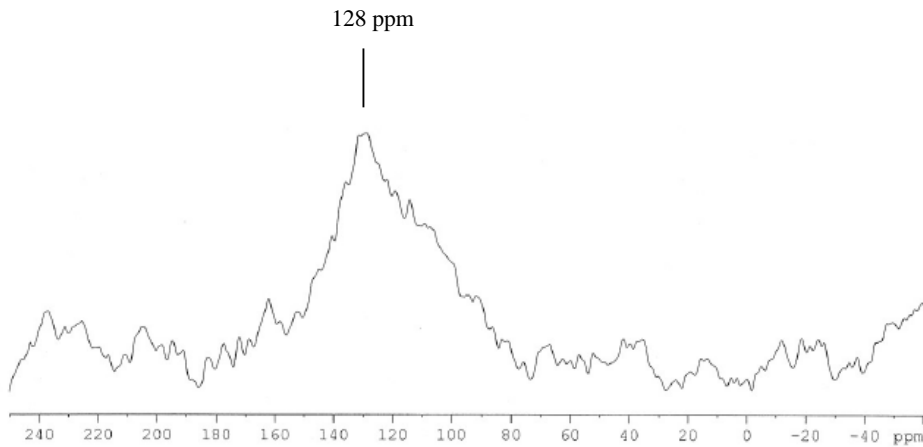
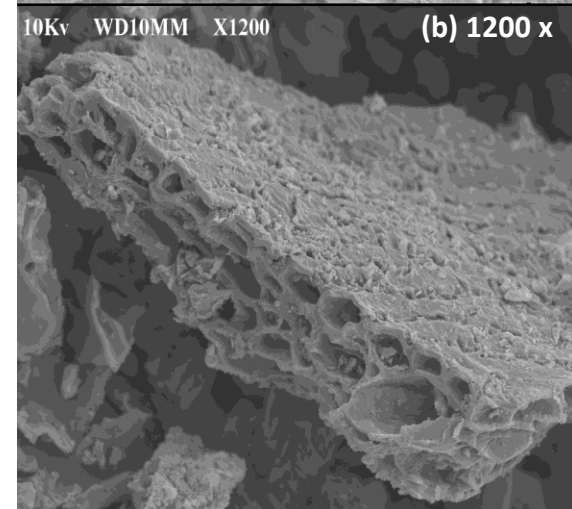
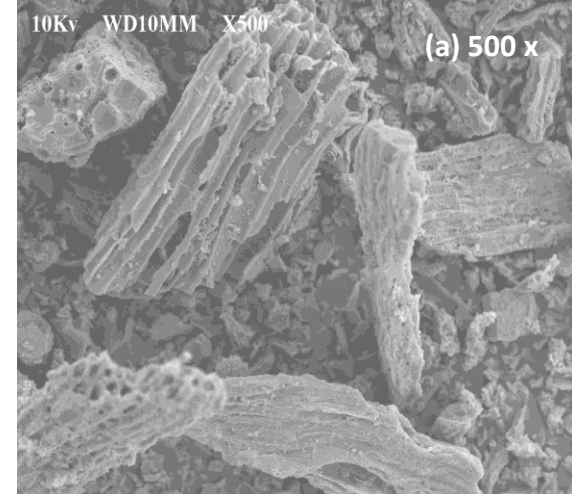


**XRD pattern**



**$N_2$  adsorption-desorption isotherms**

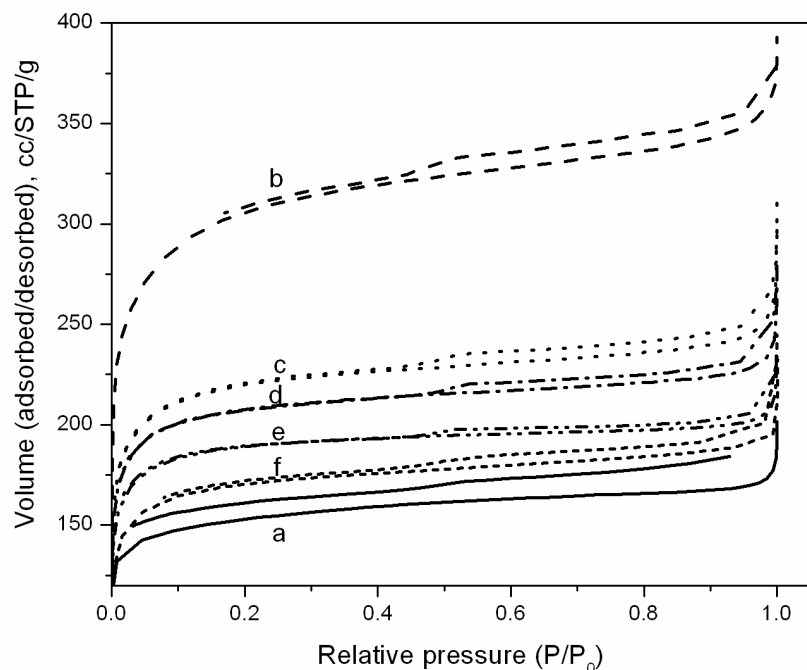
- (a)  $C_{Bf}$  potassium carbonate 1  
(b)  $C_{Bf}$  thermal activated



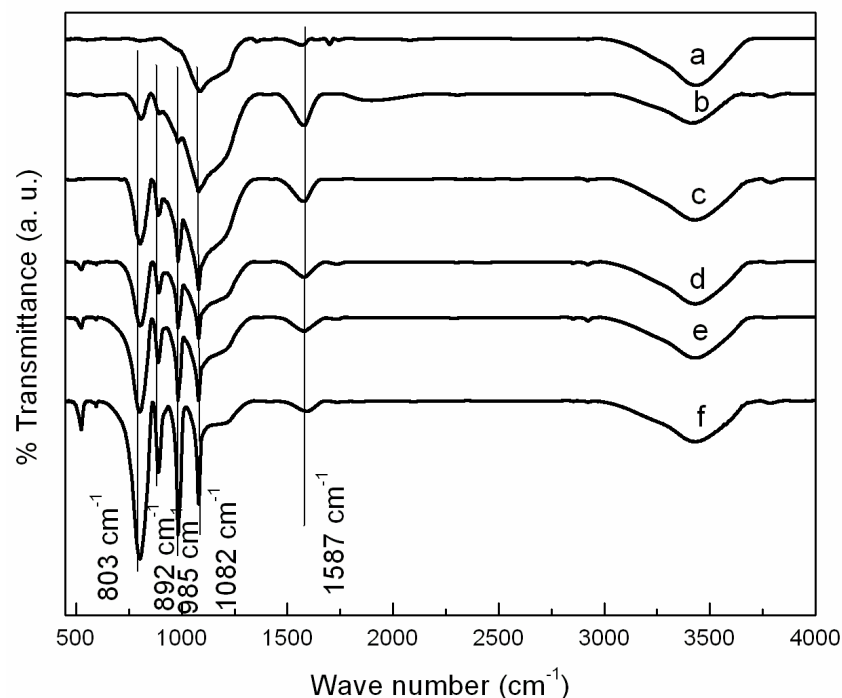
**$^{13}C$  MAS NMR spectrum**

S. No.	Carbon Material	$S_{BET}$ ( $m^2/g$ )	$V_P$ ( $cm^3/g$ )
1	$C_{Bf}$ as synthesised	17	0.07
2	$C_{Bf}$ thermal activated	550	0.55
3	$C_{BF}$ potassium cabronate 1	1070	0.28

# Activated Carbon from *Borassus Flabellifera* – Support for HPW



**N<sub>2</sub> adsorption-desorption isotherm**



FT – IR spectra of (a) C<sub>Bf</sub> potassium carbonate 1, (b) 10 wt% HPW/C<sub>Bf</sub> potassium carbonate 1, (c) 20 wt% HPW/C<sub>Bf</sub> potassium carbonate 1, (d) 30 wt% HPW/C<sub>Bf</sub> potassium carbonate 1, (e) 40 wt% HPW/C<sub>Bf</sub> potassium carbonate 1, (f) 50 wt% HPW/C<sub>Bf</sub> potassium carbonate 1

Code	HPW/C <sub>Bf</sub>	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>P</sub> (cm <sup>3</sup> /g)
a	C <sub>Bf</sub> thermal activated	550	0.55
b	C <sub>BF</sub> potassium carbonate 1	1070	0.28
c	10 wt. % HPW/C <sub>BF</sub> potassium carbonate 1	786	0.39
d	20 wt. % HPW/C <sub>BF</sub> potassium carbonate 1	756	0.36
e	30 wt. % HPW/C <sub>BF</sub> potassium carbonate 1	678	0.31
f	40 wt. % HPW/C <sub>BF</sub> potassium carbonate 1	583	0.29

Band Position, ν, cm <sup>-1</sup>		Assignment
Bulk HPW	HPW/C <sub>BF</sub>	
1080	1072 - 1091	P-O
983	964 - 988	W=O <sub>t</sub>
889	895 - 910	W-O-W <sub>c</sub>
839	795 - 819	W-O-W <sub>e</sub>



# Carbon Vs Silica – A comparison of support performance

## Synthesis of SBA-1 Mesoporous silica

CTAB ( 3.494 g ) + H<sub>2</sub>O ( 600 ml )

82 ml HCl, Temp. 273 K, Slow stirring

TEOS ( 10.7 ml )

Solution Stirred for 8 h, Temp. 273 K

Gel

Aged for 2 days; Filtered,  
Vacuum dried, Oven dried at 423 K

Washed with a solution of EtOH : HCl : H<sub>2</sub>O mixture

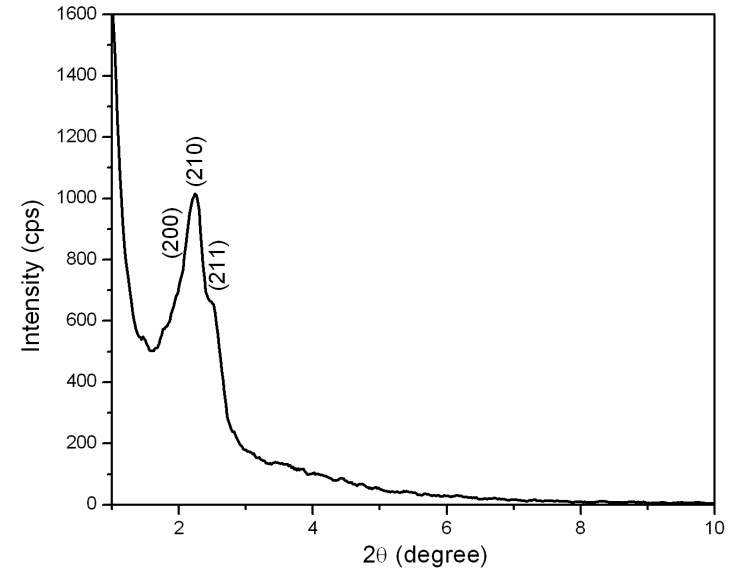
Air dried at 373 K for 3 h

SBA-1 as-synthesised

Calcined in Ar atm at 873 K for 1 h and in air for 6 h

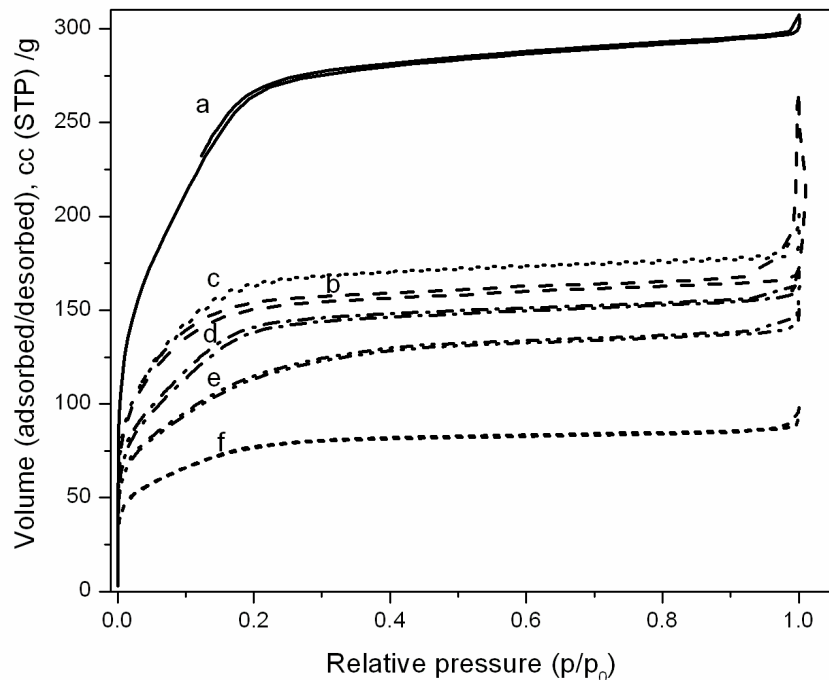
SBA- 1 calcined

Molar composition :  
1 TEOS : 0.2 Surfactant : 56 HCl : 700 H<sub>2</sub>O

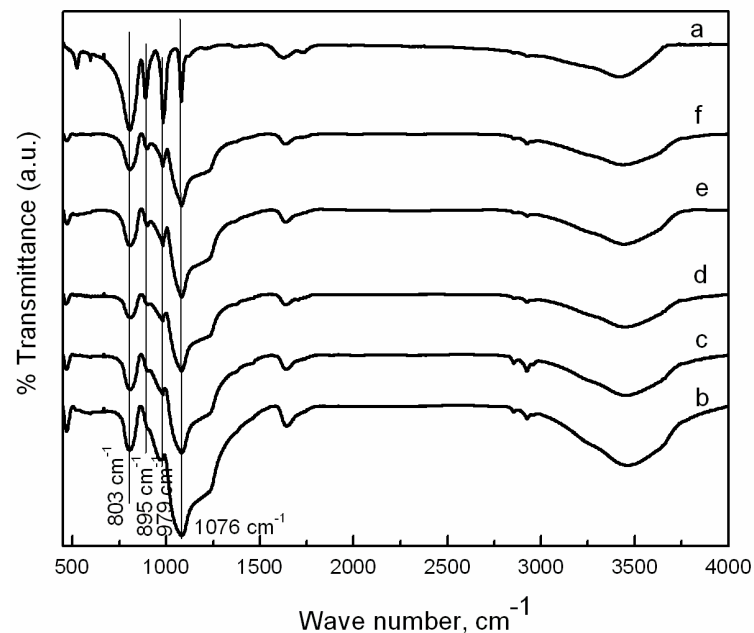


XRD pattern of SBA-1

# Mesoporous SBA – 1 as Support for HPW



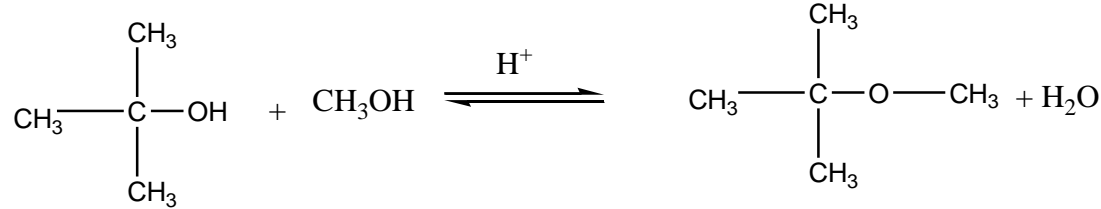
**N<sub>2</sub> adsorption-desorption isotherm**



**FT-IR spectra of (a) HPW (bulk), (b) 10 wt.% HPW/SBA-1, (c) 20 wt.% HPW/SBA-1, (d) 30 wt.% HPW/SBA-1, (e) 40 wt.% HPW/SBA-1 and (f) 50 wt.% HPW/SBA-1**

Code	HPW/SBA-1	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>P</sub> (cm <sup>3</sup> /g)
a	SBA-1	918	0.462
b	10 wt.% HPW/SBA-1	535	0.28
c	20 wt.% HPW/SBA-1	567	0.26
d	30 wt.% HPW/SBA-1	480	0.24
e	40 wt.% HPW/SBA-1	393	0.22
f	50 wt.% HPW/SBA-1	265	0.15

# Synthesis of methyl tert - butyl ether – HPW/SBA – 1 Vs HPW/C catalysts



## MTBE - Special Features

### Favourable performance qualities

- High octane number
- Low sulfur content
- High miscibility in gasoline
- Stability in storage
- Cost comparable to other high-octane component
- Economical choice in the refinery market place
- Preferred over several gasoline oxygenates including DIPE, TAME and ETBE

### Reaction conditions

**Amount of catalyst : 0.5 g**

**Reaction temperatures employed :**

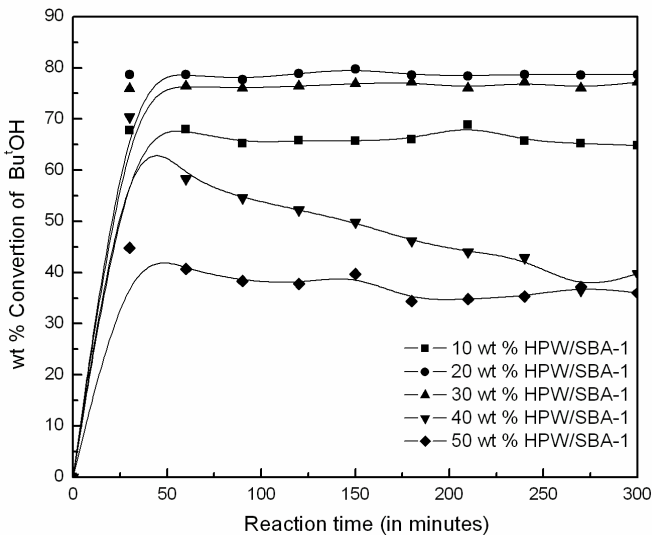
80, 90, 100, 110, 120 °C

**Flow rate of the feed : 10 mL/h**

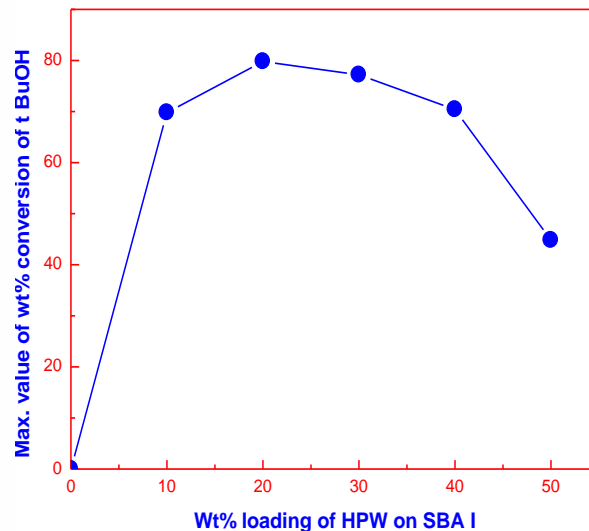
**Flow rate of carrier gas : 30 mL/h**

**MeOH : Bu<sup>t</sup>OH = 10 : 1, 10:2, 10:4, 10:6, 1:1  
(mole ratio)**

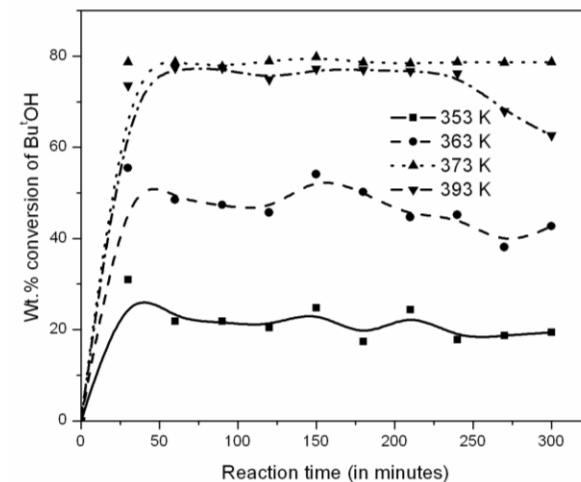
# HPW/SBA-1 Catalysts – MTBE Synthesis



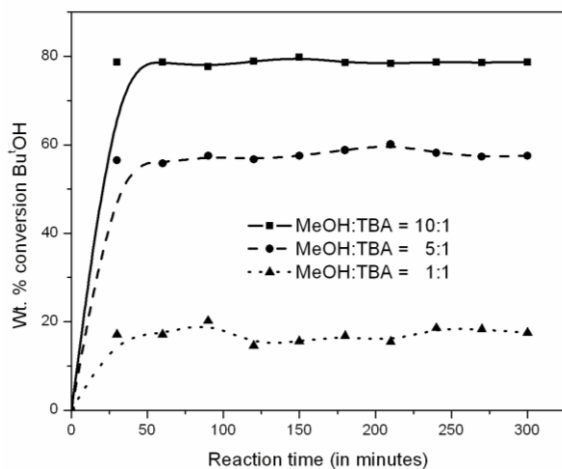
Effect of Wt. % loading of HPW on SBA - 1



Plot of wt % Conv. of t-BuOH Vs wt % loading of HPW on SBA-1



Effect of reaction temperature on the conv. Of TBA

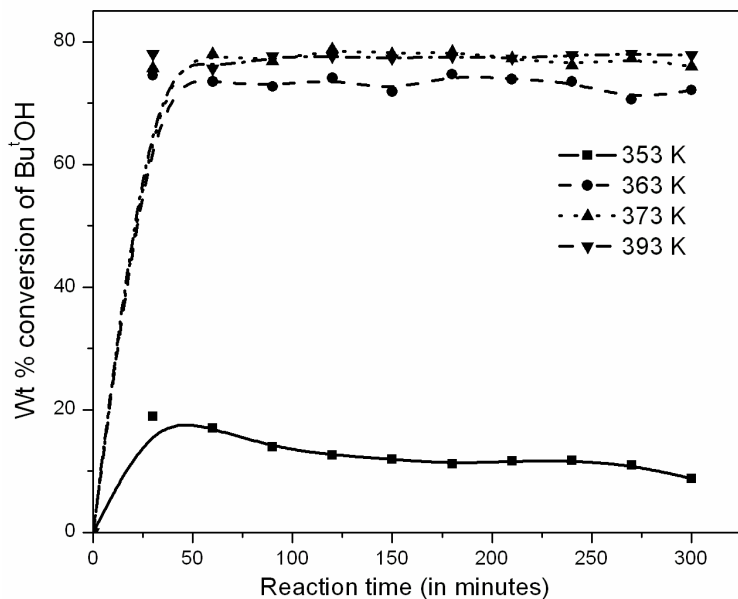


Effect of mole ratio of the feed

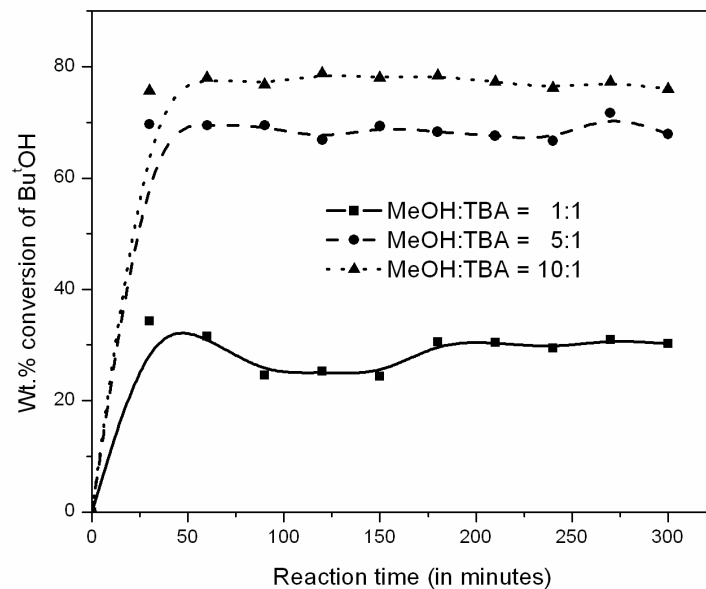
- ❑ Optimum loading of HPW – 20 wt.%
  - ❑ Optimum temperature is 100 °C with a maximum t-BuOH conv. of 80 wt %
  - ❑ Optimum mole ratio of MeOH : t-BuOH should be 10 : 1
  - ❑ Optimum flow rate of the feed – 10 ml/h
- Flow rates of the feed used: 4, 6, 8, 10, 12 and 14 ml/h

# HPW/Cbf potassium carbonate 1 – MTBE Synthesis

## Effect of Reaction Temperature



## Effect of Mole Ratio of Feed

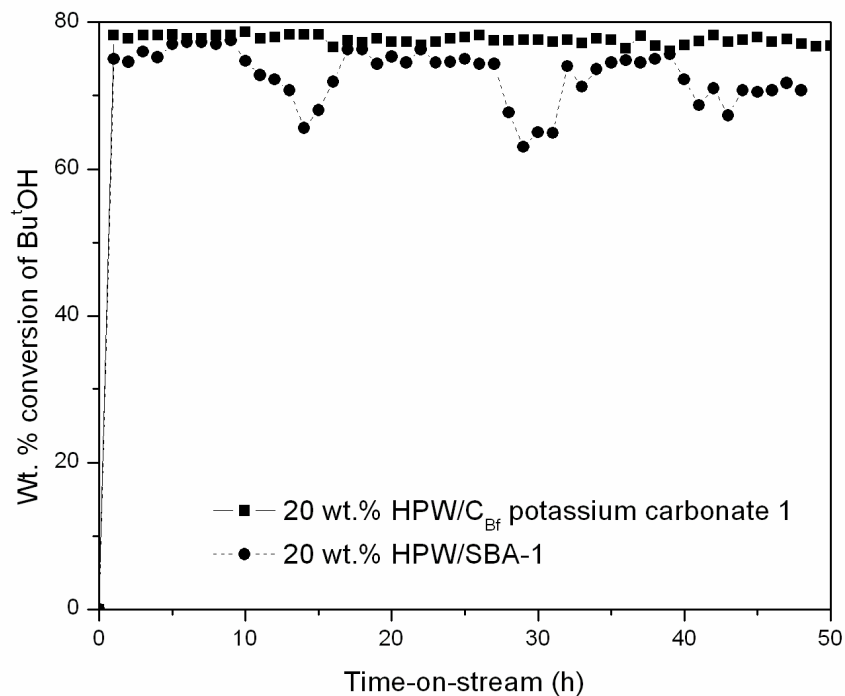


## % conv. of Bu<sup>t</sup>OH Vs reaction time (in minutes)

- ❖ Optimum reaction temperature - 100 °C
- ❖ Optimum mole ratio of feed (MeOH:Bu<sup>t</sup>OH) - 10:1
- ❖ HPW/C<sub>BF</sub> is a potential catalyst for MTBE synthesis

# Evaluation of on stream stability - HPW/SBA – 1 Vs HPW/C<sub>BF</sub> potassium carbonate 1

Reaction temperature = 100 °C  
MeOH : t-BuOH (Mole ratio) = 10 : 1  
Flow rate of the feed = 10 mL/h  
Carrier gas = N<sub>2</sub>  
Flow Rate of carrier gas = 30 mL/h  
Catalyst = 20 wt % HPW/SBA-1 ; 20 wt. % HPW/C<sub>BF</sub> potassium carbon 1  
Amount of catalyst = 0.5 g



**Comparison of on-stream stability**

The catalysts are stable  
(active and selective) upto  
50 h on stream

# Summary

1. Flower spikes of *Borassus flabellifera* are a potential precursor for high specific surface area (1070 m<sup>2</sup>/g) activated carbon material with a peculiar porous (bunch of carbon tubes) morphology.
2. The activated carbon material prepared was found to be a suitable support for heteropoly acid (HPW).
3. The carbon supported heteropoly acid catalysts exhibited appreciable conversion of tertiary butyl alcohol (TBA) to MTBE and also a unique selectivity towards MTBE
4. The optimal reaction conditions for the vapour phase MTBE synthesis over HPW/C<sub>Bf</sub> potassium carbonate 1 and HPW/SBA-1 catalysts have been established.
5. The activity, selectivity and stability of carbon supported HPW catalyst were found to be on par with the well acclaimed mesoporous silica (SBA-1) supported HPW solid acid catalysts.
6. Thus, an environmentally benign, economically viable and industrially adoptable carbon supported heteropoly acid (HPW) catalyst has been developed.

## 4. Activated Carbon from *Limonea Acidissima*

- Source of carbon** : Shell of wood apple
- Tree** : wood apple tree, Bilva patra, Bel, Elephant wood
- Binomial nomenclature**: *Feronia Limonia*, *Limonia Acidissima*, *Limonia elaphantum*
- Habitat** : Found all over the deciduous forests in India

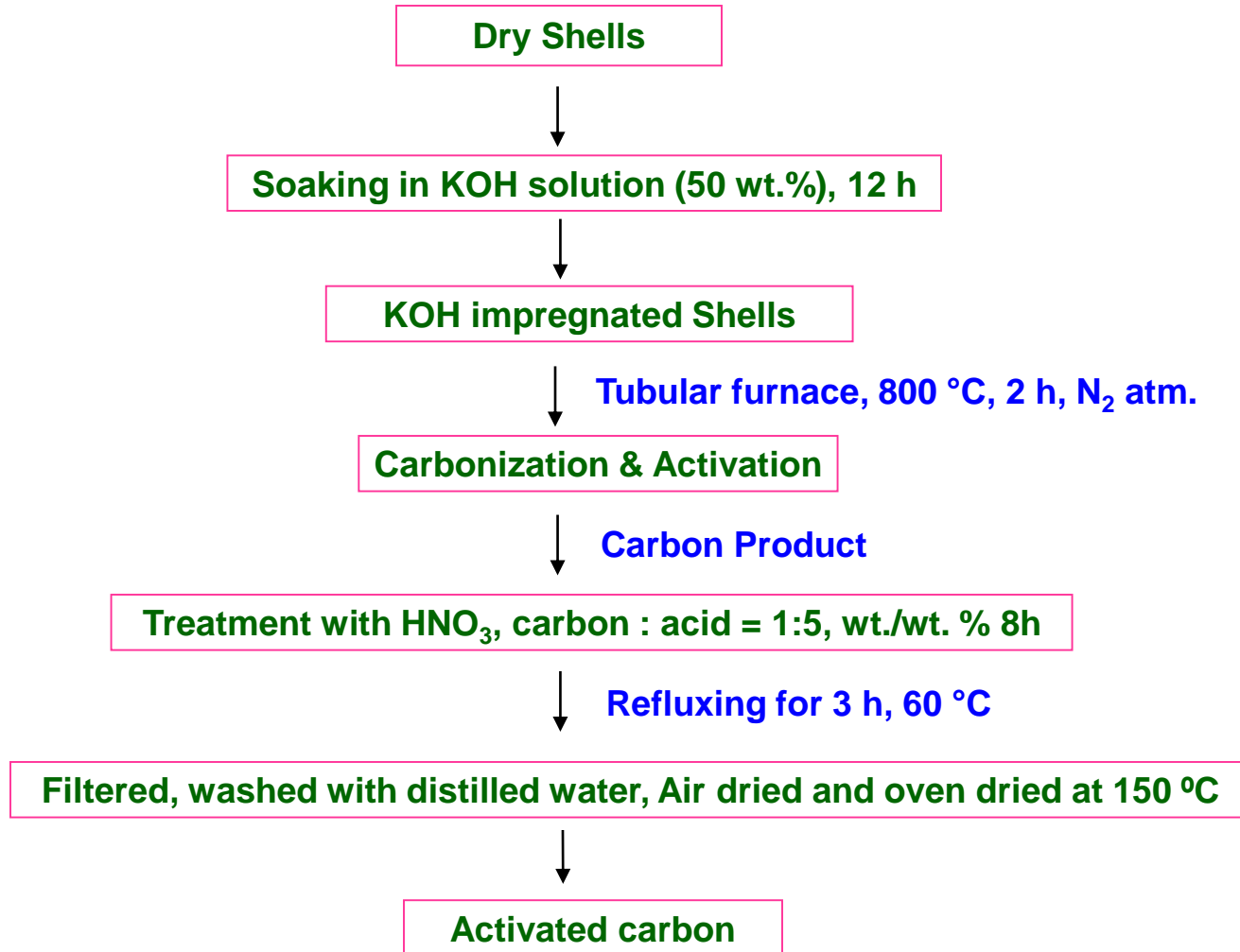


**Synthesis**  
**Characterization**  
**Application as Catalyst (Pt) Support**

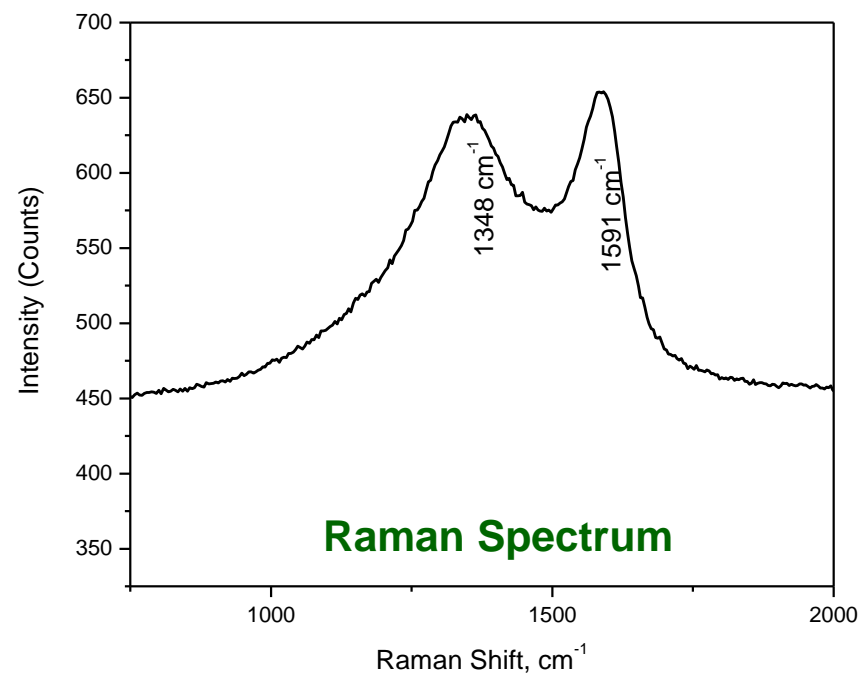
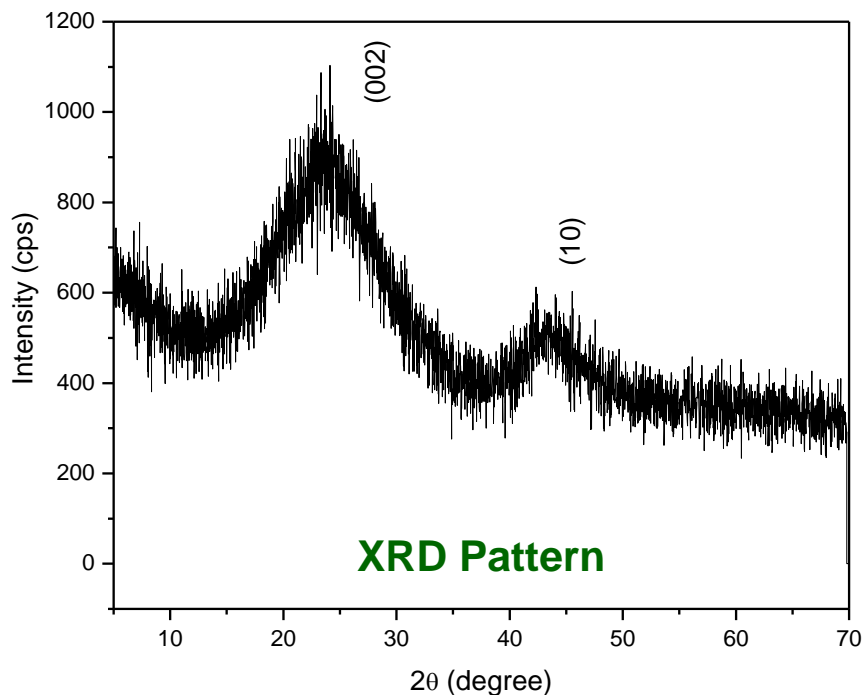




# Activated Carbon from Limonea Acidissima – Method of Preparation



# Activated Carbon from Limonea Acidissima - Structural Properties



## Crystallographic structural details deduced from XRD studies

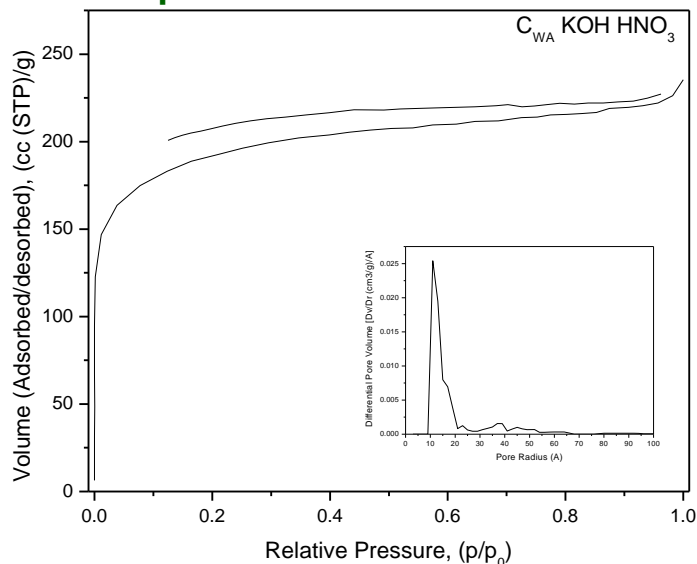
S. No.	Sample	$d_{002}$ (nm)	* $L_c$ (nm)	* $L_a$ (nm)
1	Activated Carbon, $C_{WA}$	0.377	1.1	3.656

## Structural parameters deduced from the confocal Raman spectroscopic studies

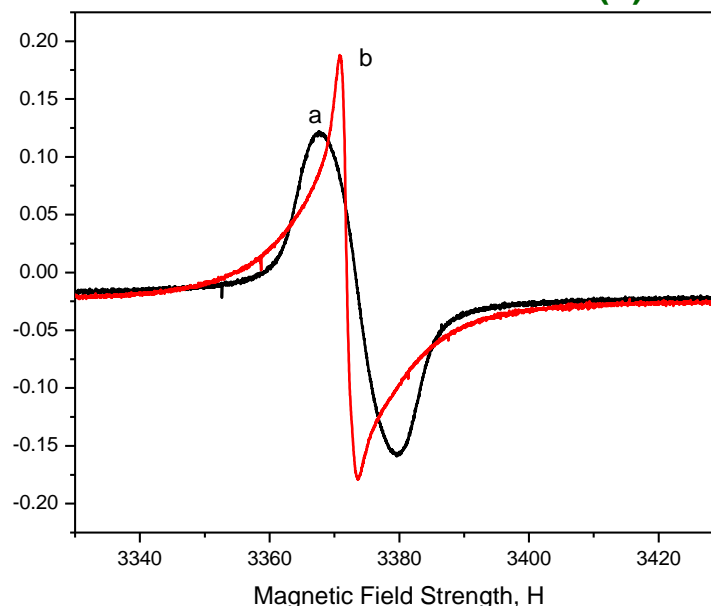
S. No.	Sample	Peak Intensity Frequency, $\nu_x$ , $cm^{-1}$		$R = I_D/I_G$	$L_a$ (nm) = $4.4/R$ (From Raman)	$L_a$ (nm) (from XRD)
		G band	D band			
1	$C_{WA}$	1591	1348	1.408	3.125	3.656

# Activated Carbon from Limonea Acidissima Textural Properties and Electron Spin Density

## N<sub>2</sub> adsorption-desorption isotherm and pore size distribution curve



## EPR spectrum of (a) Activated Carbon from Limonea Acidissima and (b) DPPH



### Textural Properties deduced from Isotherm

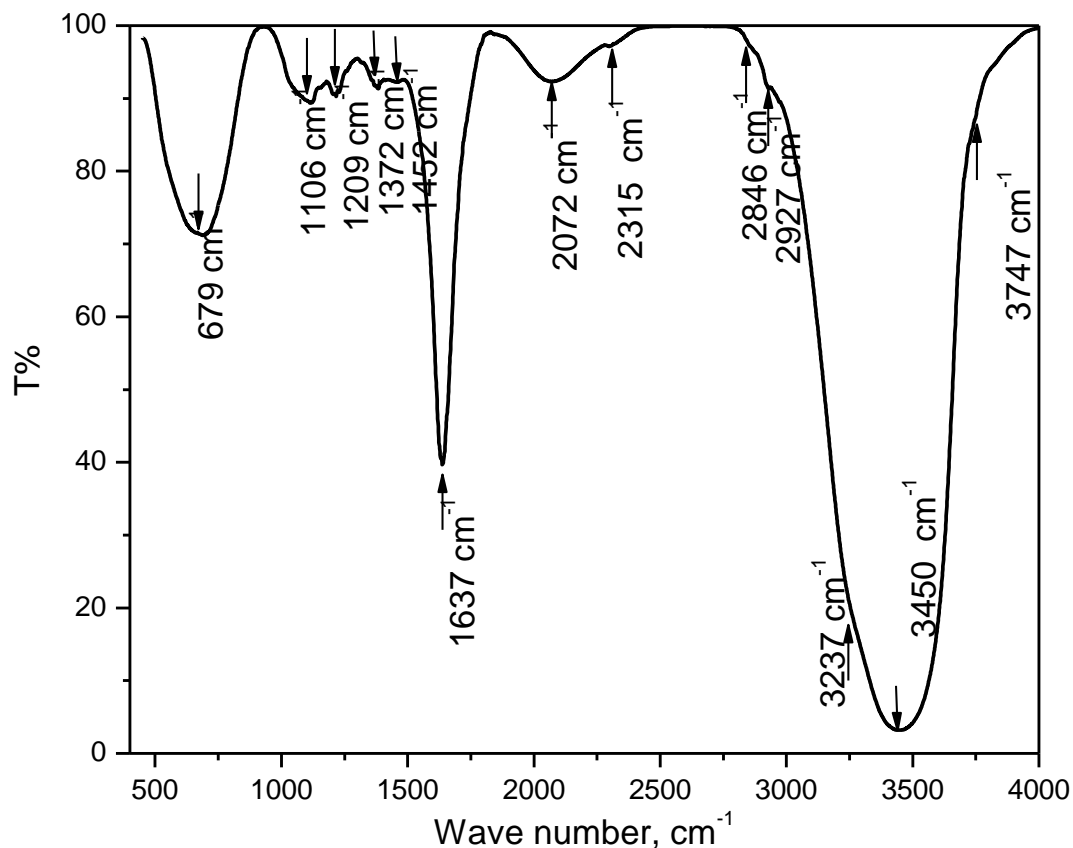
S. No.	Sample	$S_{BET}$ (m <sup>2</sup> /g)	$V_p$ (cm <sup>3</sup> /g)	Mean Pore Diameter <sup>i</sup> (nm)
1	Activated carbon, $C_{WA}$	698	0.35	2.0

### Electron Spin Concentration deduced from Isotherm

S. No.	Carbon Material	g-factor value	$\Delta H$ (in Gauss) Peak to peak separation	Spin Concentration per gram of carbon material
1	$C_{WA}$	2.03095	12	$0.13 \times 10^{19}$

The spin concentration values are comparable with those of commercial acetylene black ( $3.8 \times 10^{19}$ ) and graphon ( $1.1 \times 10^{19}$ )

# Activated Carbon from Limonea Acidissima – Surface Functionality

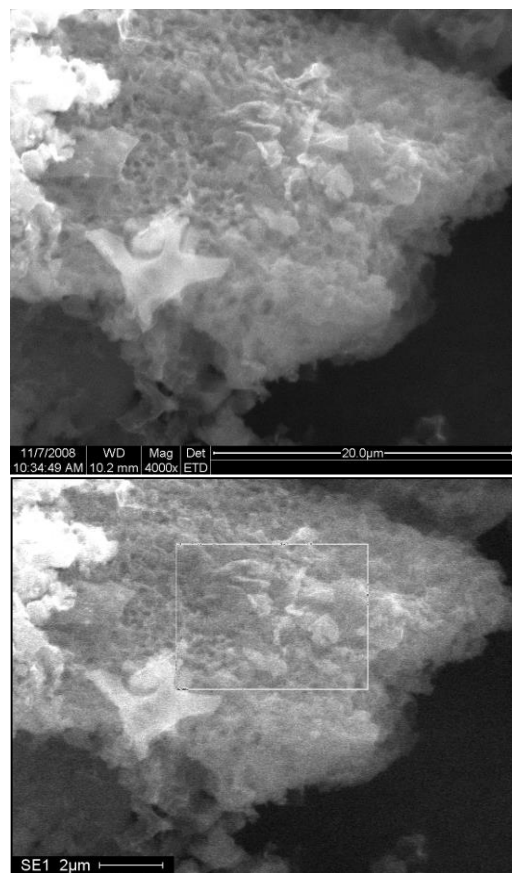


**FT – IR spectrum of Activated Carbon (KOH activation)**

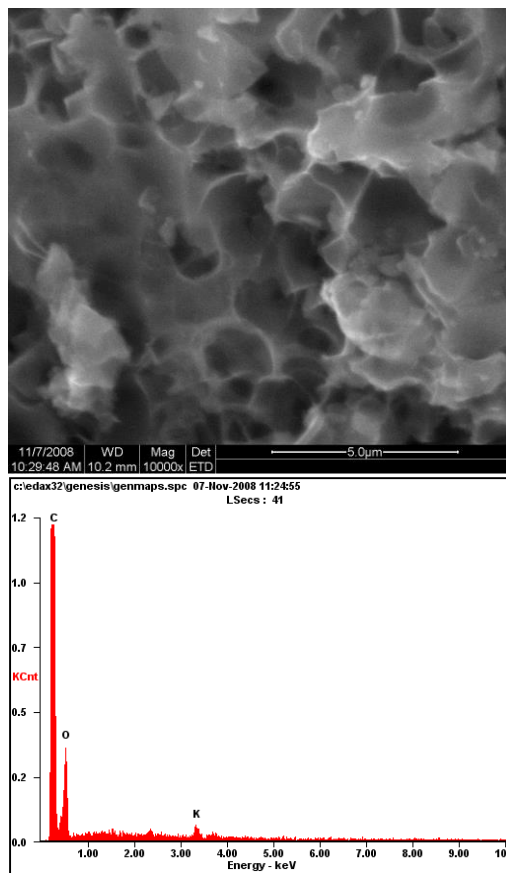
<b>Band position <math>\nu</math>, cm<sup>-1</sup></b>	<b>Assignment</b>
<b>3747</b>	Isolated –OH groups
<b>3450</b>	O-H stretching vibration of surface hydroxyl groups and adsorbed water. Asymmetry (shoulder like feature at 3237 cm <sup>-1</sup> ) indicated presence of hydrogen bonding interaction
<b>2927</b>	Aliphatic, asymmetric C-H stretching vibration of methylene group
<b>2846</b>	Aliphatic, symmetric C-H stretching vibration of methylene group
<b>2315</b>	Ketone group
<b>1637</b>	C=O (carbonyl) stretching vibration in quinone
<b>1452</b>	In plane bending vibration of C-H of methylene group
<b>1372</b>	In plane bending vibration of C-H in methyl group
<b>1000 - 1300</b>	C-O stretching in phenols, alcohols, acids, ethers and esters
<b>679</b>	Out of plane deformation vibration of C-H groups located at the edges of aromatic planes

# Activated Carbon from Limonea Acidissima – Morphology and Composition

4000 x



10,000 x



SEM images and EDAX spectrum

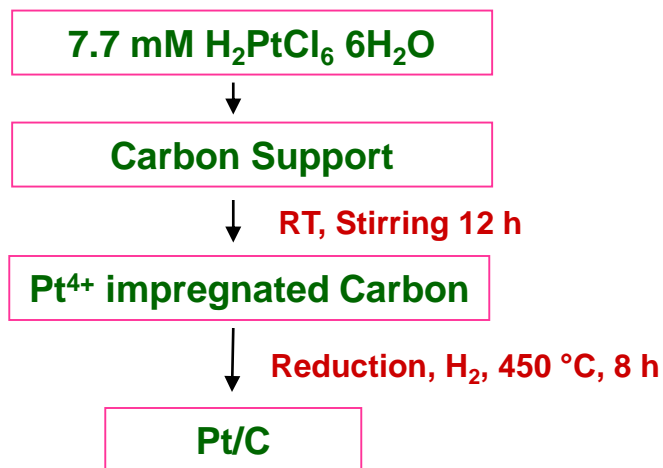
S. No.	Element	Wt. %	At. %
1	Carbon	74.84	80.02
2	Oxygen	24.70	19.83
3	Potassium	0.45	0.15

The elemental composition from EDAX

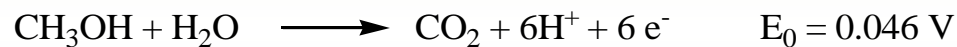
❖ Ash content – 1.04%

# Activated Carbon from Limonea Acidissima – Catalyst (Pt) Support

## Catalyst Preparation: Dry impregnation



### Evaluation of Electrocatalytic Activity of Pt/C catalysts:

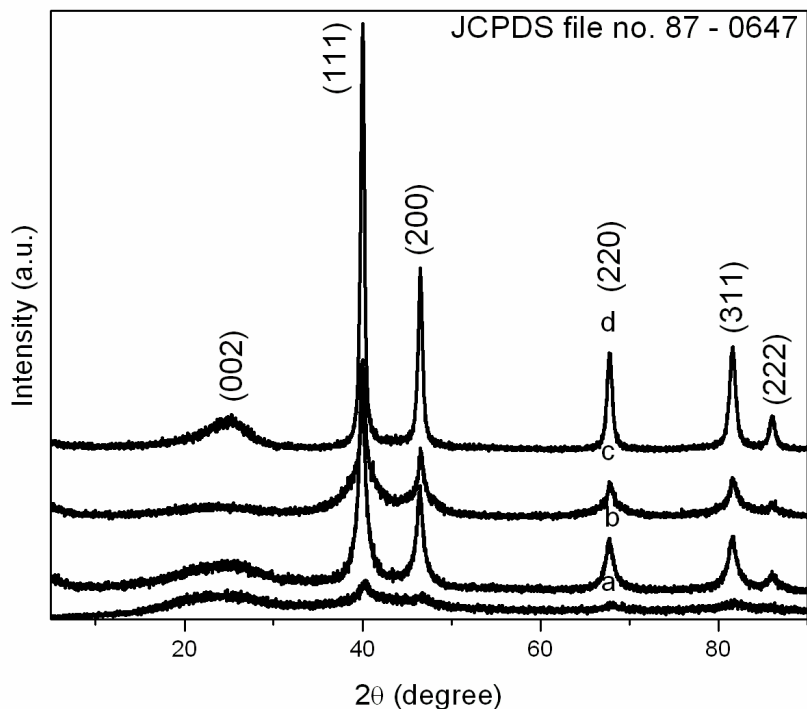


Reaction studied: MeOH electrooxidation

### Objective

- i. Increase Pt utilization
- ii. Produce active, stable and CO tolerant electrocatalyst

# Dispersion of Pt crystallites on Carbon Support



- ❖ The crystallite size of Pt is found to be dependent on the Pt loading and also on the nature of the carbon support

X-ray diffraction patterns of (a) 5 wt. % Pt/C<sub>WA</sub> (crystallite size ~5.0 nm) (b) 10 wt. % Pt/C<sub>WA</sub> (crystallite size ~10.2 nm) (c) 20 wt. % Pt/C<sub>WA</sub> (crystallite size ~10.4 nm) and (d) 20 wt. % Pt/Vulcan XC 72 R (crystallite size ~13.1 nm)

S. No.	Electro catalyst	S <sub>BET</sub> (m <sup>2</sup> /g)	iS <sub>Micropore</sub> (m <sup>2</sup> /g)	iiV <sub>P</sub> (cm <sup>3</sup> /g)	Mean Pore Diameter <sup>iii</sup> (nm)
1	5 wt. % Pt/C <sub>WA</sub>	505	267	0.289	2.28
2	10 wt. % Pt/C <sub>WA</sub>	526	318	0.288	2.19
3	20 wt. % Pt/C <sub>WA</sub>	195	102	0.119	2.447
4	20 wt. % Pt/Vulcan XC 72 R	123	-	0.29	9.43

# Electrochemical Measurements

## Electrode Fabrication

Catalyst (Pt/C) dispersed in distilled water 20 mg/ml

Ultrasonicated for 10 min

10  $\mu$ lit ink pipetted onto the GC disk

Dried in air oven at 60 °C

5  $\mu$ lit nafion pipetted onto the catalyst deposited on the GC disk

Dried at room temperature

GC/Carbon- Pt - Nafion electrode

## Experimental Conditions

Electrolyte : 0.5 M H<sub>2</sub>SO<sub>4</sub>

Working Electrode : Pt/C catalyst deposited on GC disk

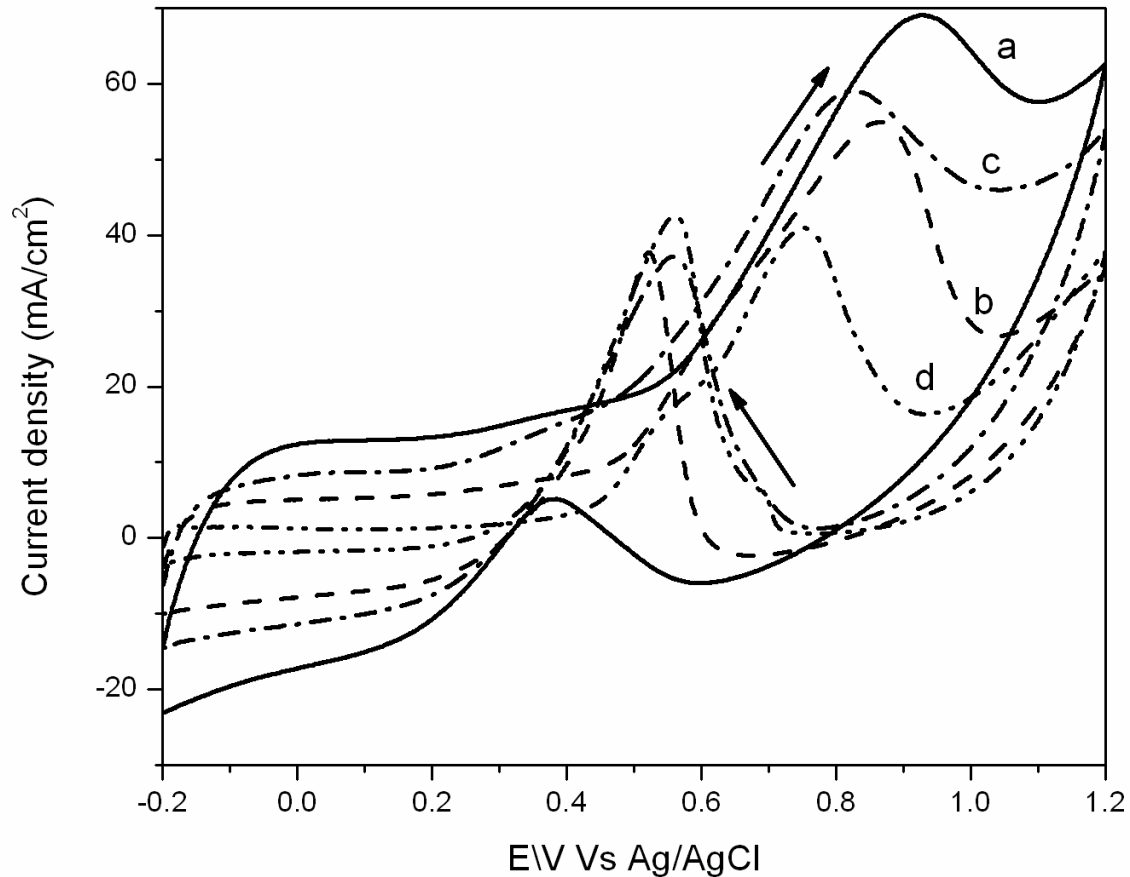
Reference Electrode : Ag/AgCl, 3.5 M KCl (+ 0.205 V Vs NHE)

Counter Electrode : Pt foil (1.5 cm<sup>2</sup>)

Scan rate : 5, 10, 15, 20 and 25 mV/sec



# MeOH Electro-oxidation Activity of Pt/C catalysts



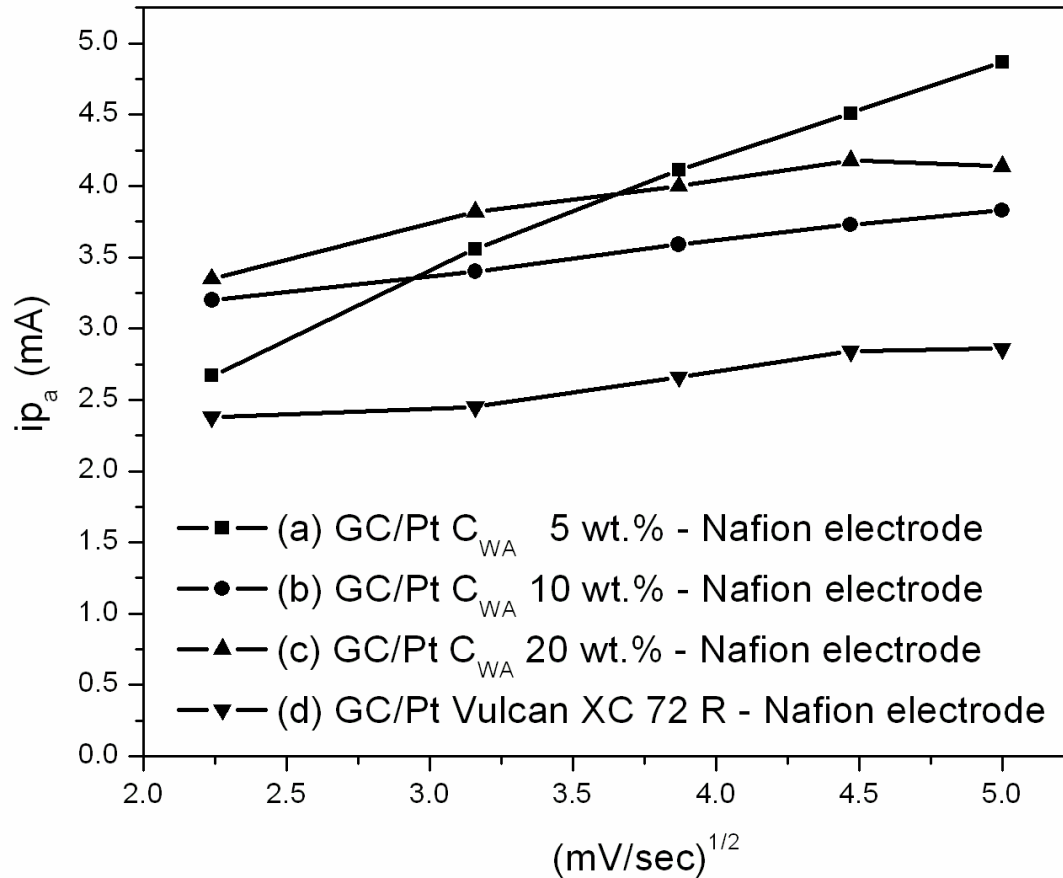
**Cyclic Voltammetric response of (a) GC/C<sub>WA</sub> - 5 wt.% Pt - Nafion electrode  
(b) GC/C<sub>WA</sub> - 10 wt.% Pt - Nafion electrode  
(c) GC/C<sub>WA</sub> - 20 wt.% Pt - Nafion electrode and  
(d) GC/Vulcan XC 72 R - 20 wt.% Pt - Nafion electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1 M CH<sub>3</sub>OH, at a scan rate of 25 mV/sec between -0.2 to 1.2 V Vs Ag/AgCl**

## MeOH Electro-oxidation Activity of Pt/C catalysts

S. No.	Electrode	Onset Potential, V	$i_r/i_b$	Activity*			
				Forward sweep		Reverse sweep	
				I (mA/cm <sup>2</sup> )	E (V)	I (mA/cm <sup>2</sup> )	E (V)
1	GC/C <sub>WA</sub> -5 % Pt-Nafion	0.21	14.4	69.0	0.92	4.97	0.37
2	GC/C <sub>WA</sub> -10 % Pt-Nafion	0.18	1.45	55.0	0.86	37.6	0.52
3	GC/C <sub>WA</sub> -20 % Pt-Nafion	0.18	1.60	58.9	0.82	37.28	0.51
4	GC/Vulcan XC 72 R-20 % Pt-Nafion	0.25	0.96	40.9	0.75	42.6	0.56

\*Activity evaluated in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1 M CH<sub>3</sub>OH, at a scan rate of 25 mV/sec between -0.2 to 1.2 V Vs Ag/AgCl

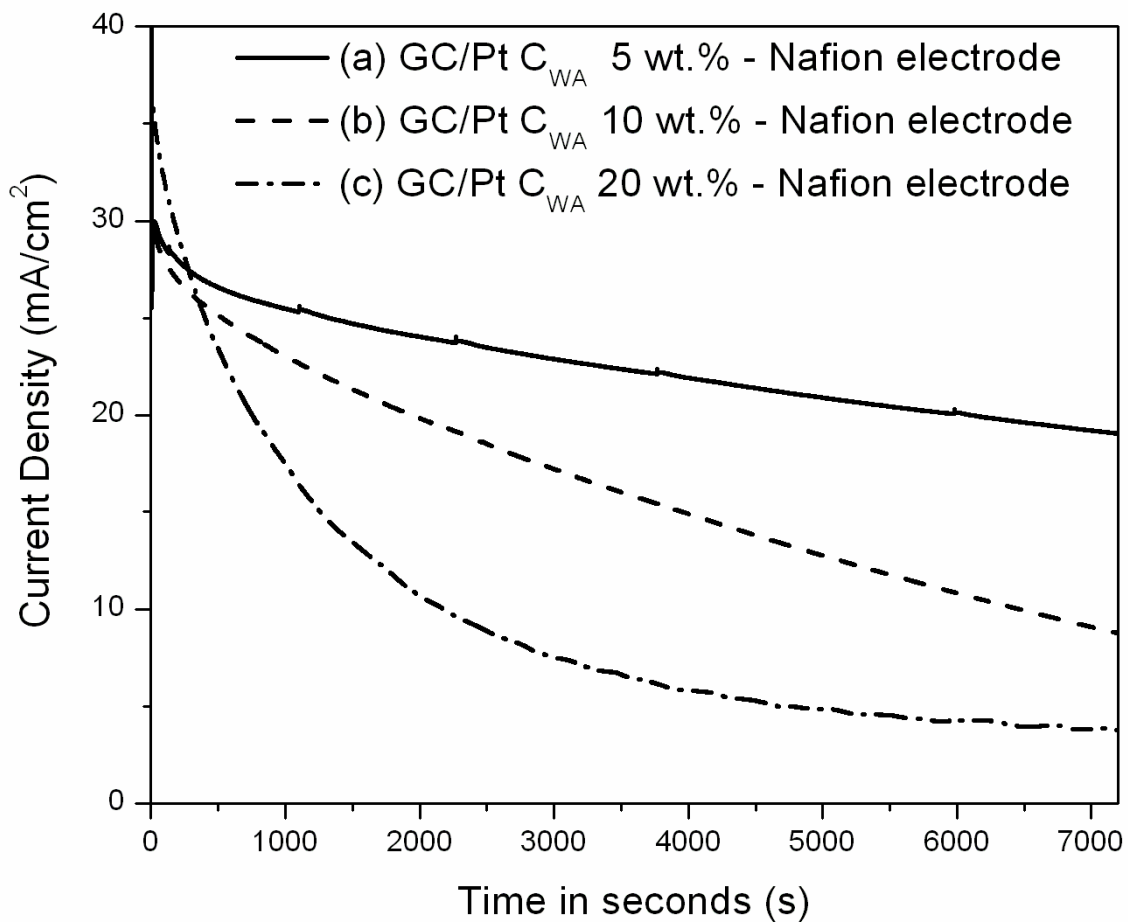
## Effect of Scan Rate on Current response of GC/Carbon- Pt – Nafion electrode



Dependence of peak currents on the square roots of scan rates for Pt/C electrocatalysts in 0.5 M  $\text{H}_2\text{SO}_4$  and 1 M  $\text{CH}_3\text{OH}$ , at different scan rates (5, 10, 15, 20 and 25 mV/sec) between -0.2 to 1.2 V Vs Ag/AgCl

- Current varied linearly as a function of sq. root of scan rate
- MeOH electrooxidation on Pt/C catalysts is diffusion controlled

# Electrochemical Stability of Pt/C catalysts - Chronoamperometry



Chrono amperometric response of (a) GC/C<sub>WA</sub> - 5 wt.% Pt - Nafion electrode  
(b) GC/C<sub>WA</sub> - 10 wt.% Pt - Nafion electrode and (c) GC/C<sub>WA</sub> - 20 wt.% Pt - Nafion electrode  
polarized at + 0.6 V Vs Ag/AgCl in 0.5 M H<sub>2</sub>SO<sub>4</sub>/ 1 M CH<sub>3</sub>OH for 3 hours

## Evaluation of the stability of $C_{WA}$ based electrodes for the electro oxidation of Methanol in half cell mode

S. No.	Electrode	Activity*		% Decrease in activity after 3 h at + 0.6 V
		Initial (I), $\text{mAcm}^{-2}$	Final (I), $\text{mAcm}^{-2}$	
1	GC/ $C_{WA}$ -5 % Pt-Nafion	25.2	19.1	24
2	GC/ $C_{WA}$ -10 % Pt-Nafion	29.7	19.0	36
3	GC/ $C_{WA}$ -20 % Pt-Nafion	36.1	3.7	89

\*Activity evaluated in 0.5 M  $\text{H}_2\text{SO}_4$  and 1 M  $\text{CH}_3\text{OH}$  for 3 h with the electrode being polarized at + 0.6 V Vs Ag/AgCl

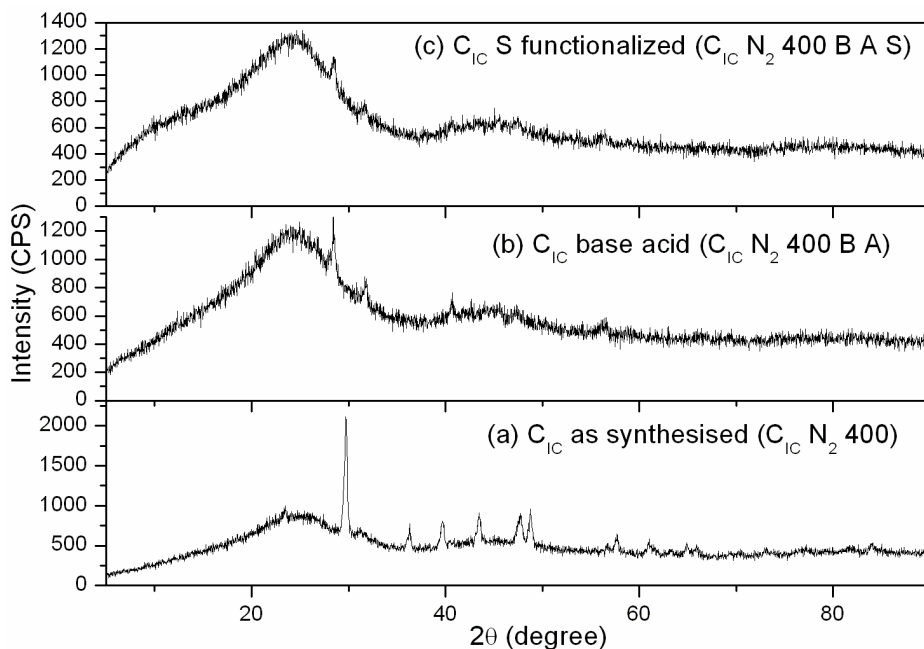
## Summary

1. The activated carbon material produced from *Limonea acidissima* by KOH activation is a promising support for Pt for the electro oxidation of methanol.
2. The excellent performance of 5 wt. % Pt/C<sub>WA</sub> is attributed to the increase in the extent of utilization of Pt metal.
3. Thus the use of carbon material from *Limonea acidissima* as support for Pt offers the promise of effective utilization of Pt, high electro oxidation (methanol) activity, high CO tolerance and long term stability.
4. A strong correlation was found between the Pt crystallite size and the electro oxidation activity and stability of the carbon supported Pt catalysts.

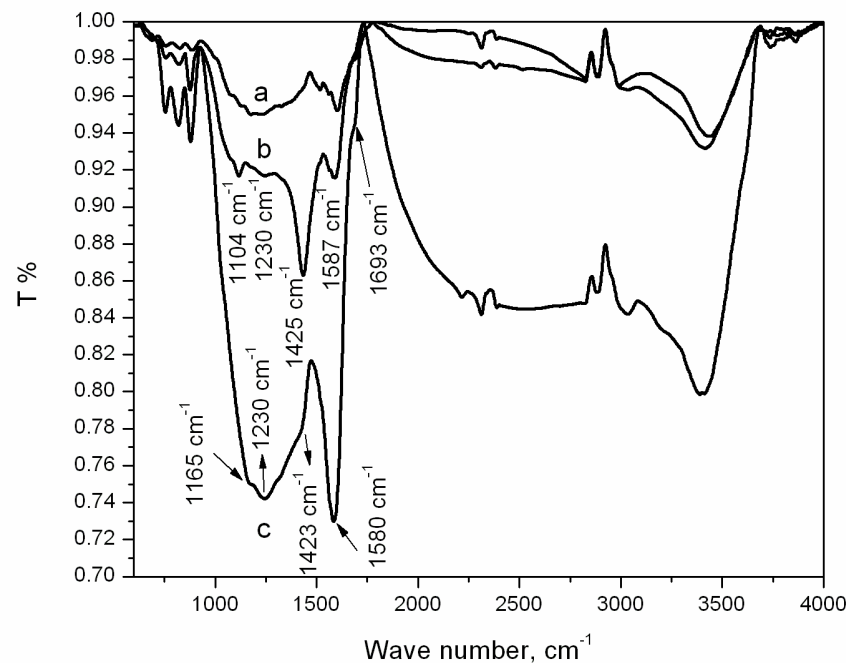
## 5. Carbon materials from Ipomoea carnea for Mercury Sorption Application

### Salient features:

- ✓ A new botanical source, Ipomoea Carnea, is exploited for the production of activated carbon and is subsequently used as sorbent for Hg (II)
- ✓ S/Hydrazine solution is used as a S precursor for functionalizing carbon material with S
- ✓ S functionalization has improved the Hg (II) sorption by the carbon material

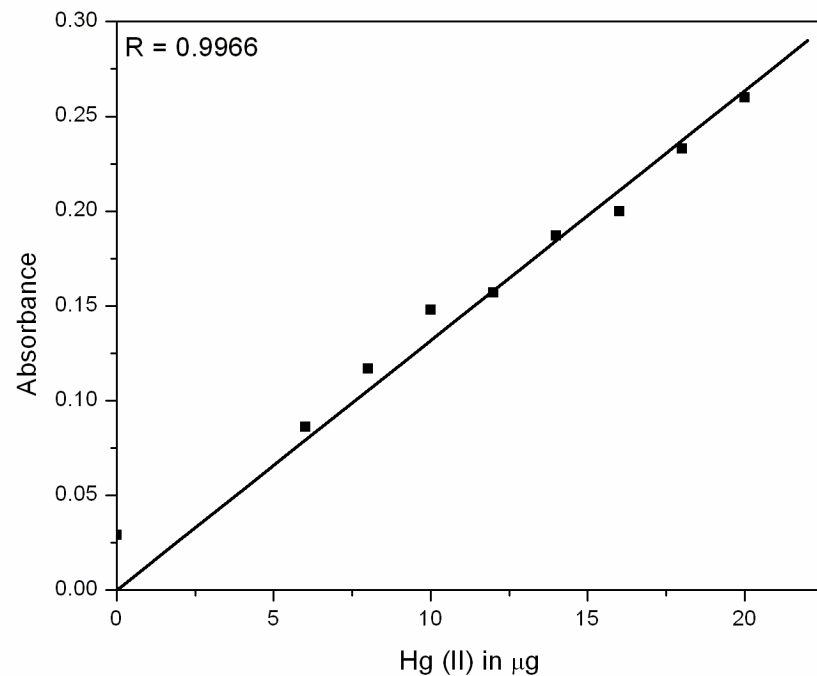
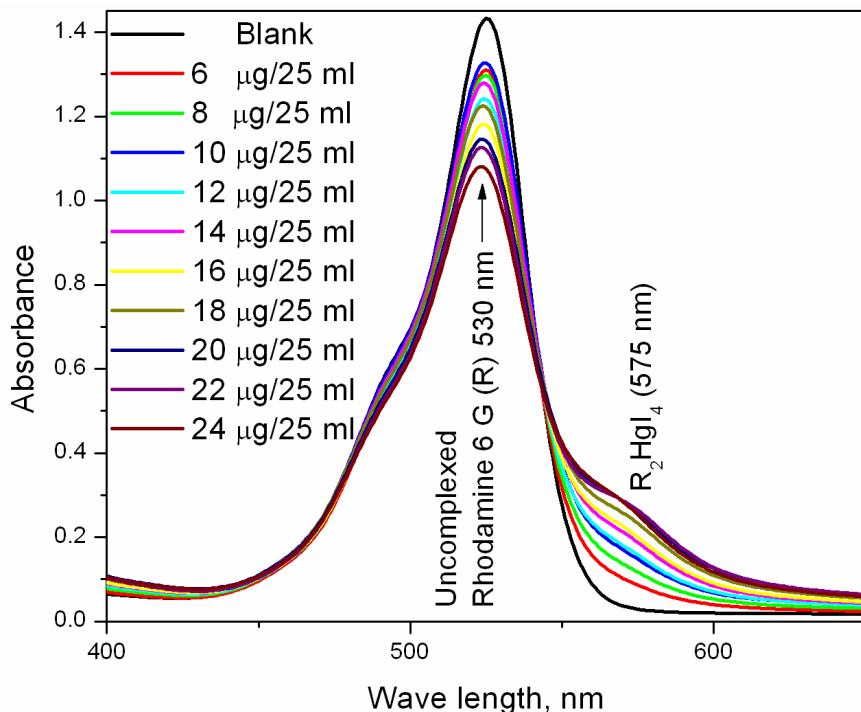


XRD pattern



FT IR spectra

## Method for estimating the Hg (II) concentration in the filtrate

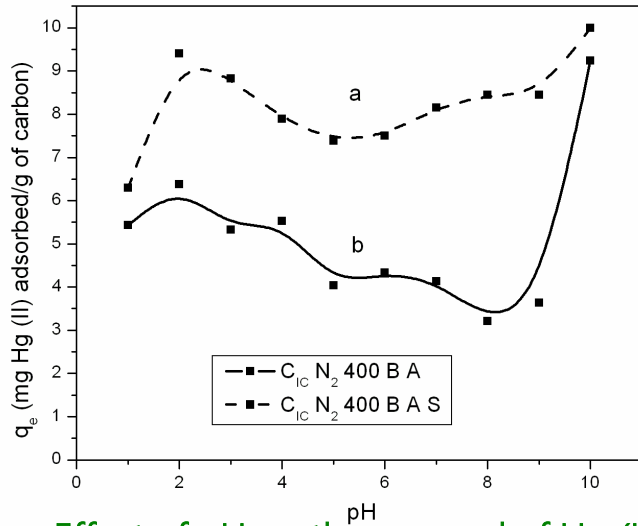


**Absorption spectra (total volume 25 ml): 5 mL of 0.005 wt.% Rhodamine 6 G and 5 mL of buffered KI solution with 1 ml (1 wt/vol %) gelatin (Blank). (6 – 24  $\mu\text{g}$  Hg (II) : As in the blank with the addition of 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2 ml of  $1 \times 10^{-4}$  M mercury solution**

**Calibration plot of Hg (II) conc. in  $\mu\text{g}$  Vs absorbance of  $R_2HgI_4$  at 575 nm**

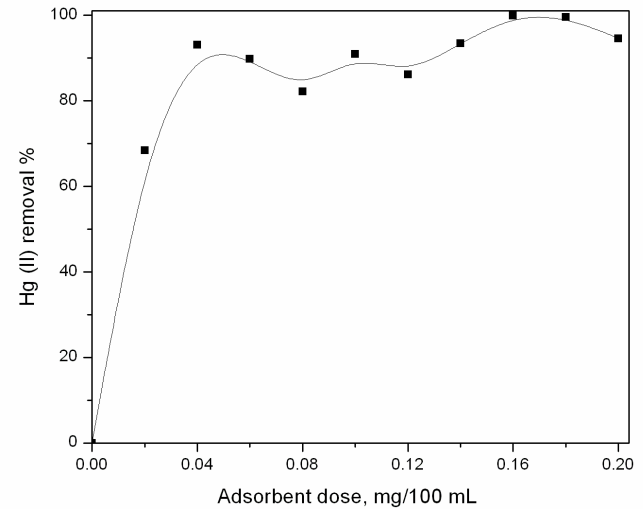


## Effect of pH on the sorption of Hg (II)

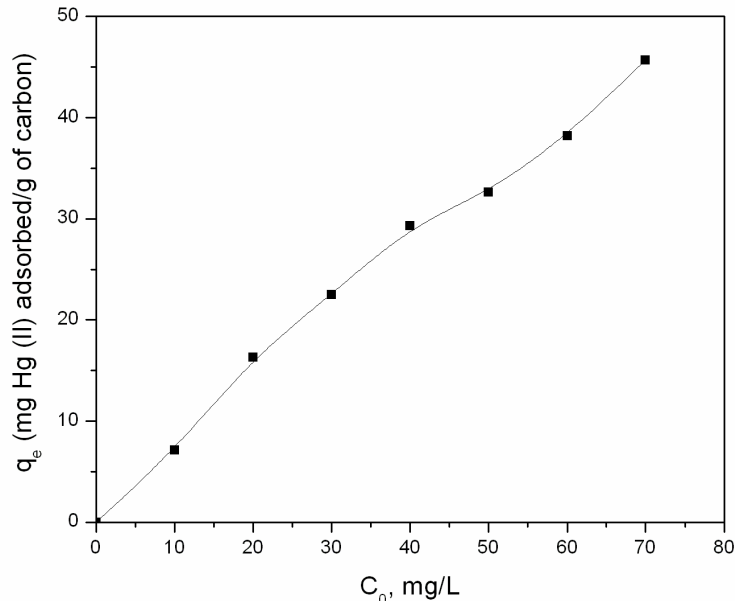


Effect of pH on the removal of Hg (II) using carbon materials as sorbents

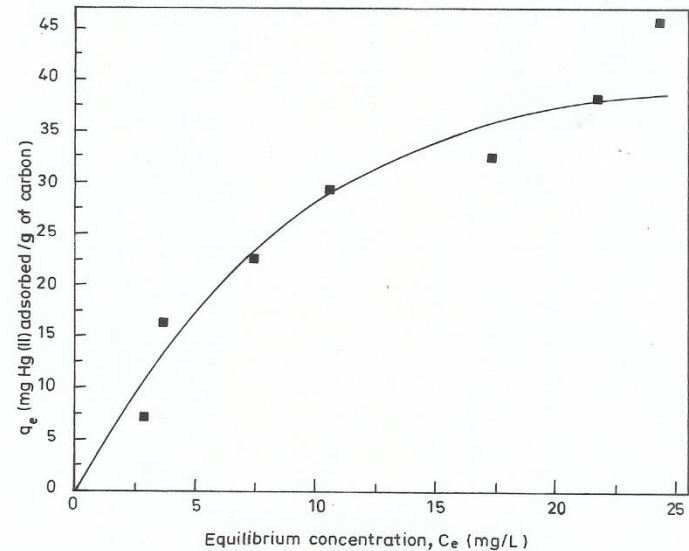
## Effect of adsorbent dosage



Effect of adsorbent dose for the removal sorption of Hg (II) onto S functionalized carbon

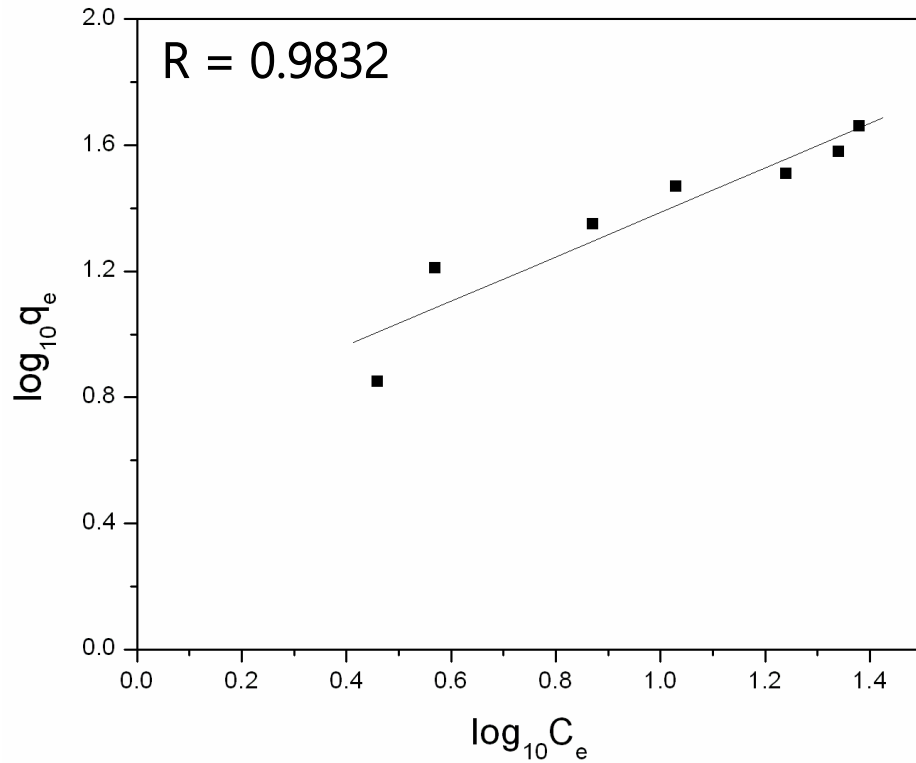


Effect of initial concentration of metal ion on the removal of Hg (II)

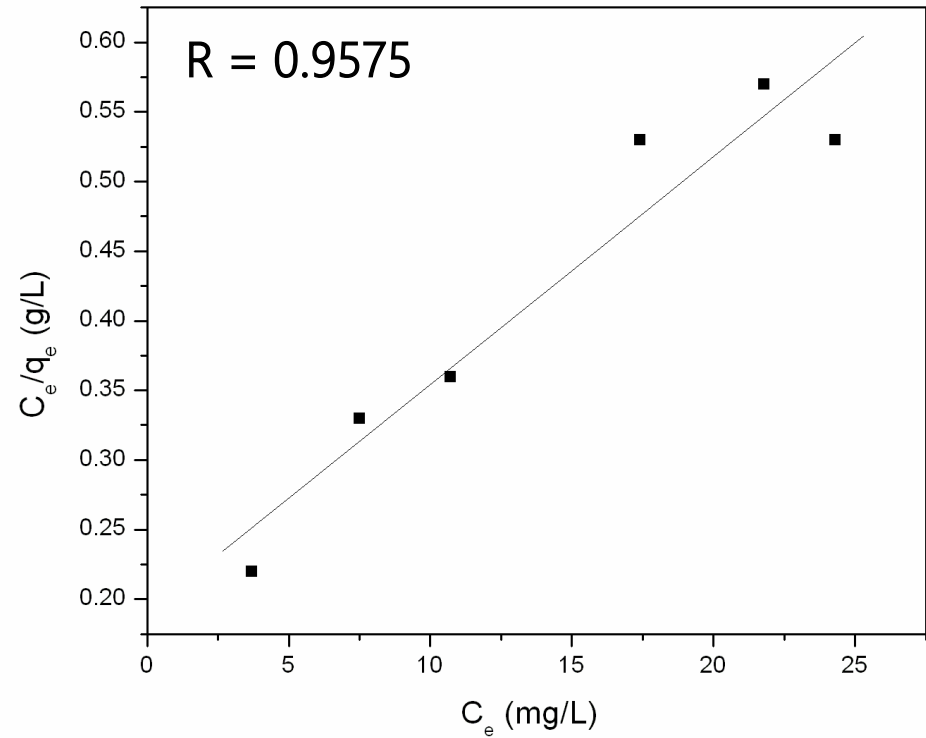


Adsorption isotherm of Hg (II) sorption (Sorbent :  $C_{IC} N_2 400 B A S$ ; sorbent dose: 0.1 g/100 ml Hg (II) solution; pH = 6; equilibration time – 1 h)

# Evaluation of equilibrium adsorption data with Freundlich and Langmuir models



Freundlich plot of mercury (II) adsorption



Langmuir plot of mercury (II) adsorption

## Comparison of Freundlich and Langmuir constants

Adsorbent	Freundlich constants	Langmuir constants	Reference
S functionalized activated carbon	$K_F = 8.3$ $1/n = 0.51$ $R = 0.9832$	$q_m = 55.6; b = 0.095$ $R_L = 0.51$ $R = 0.9575$	Present study
Activated carbon from Cieba pentandra hulls	$K_F = 11.24$ $1/n = 0.24$ $R = 0.9686$	$q_m = 25.88; b = 0.45$ $R_L = 0.06$ $R = 0.8167$	Madhava Rao <i>et al.</i> , 2009
Activated carbon from phaseolus aureus hulls	$K_F = 9.51$ $1/n = 0.27$ $R = 0.9661$	$q_m = 23.66; b = 0.51$ $R_L = 0.04$ $R = 0.9016$	Madhava Rao <i>et al.</i> , 2009
Activated carbon from Cicer arietinum	$K_F = 8.36$ $1/n = 0.275$ $R = 0.966$	$q_m = 22.88; b = 0.36$ $R_L = 0.05$ $R = 9273$	Madhava Rao <i>et al.</i> , 2009
Fullers earth (clay)	$K_F = 0.375$ $1/n = 0.334$ $R = 0.996$	$q_m = 1.145; b = 0.359$ $R_L = 0.053$ $R = 0.991$	Oubagaranadin <i>et al.</i> , 2007
Activated carbon from Sago waste	$K_F = 3.58$ $1/n = 0.53$	$q_m = 55.6; b = 0.375$ $R = 0.9871$	Kadirvelu <i>et al.</i> , 2004
Carbon cloth	$K_F = 5.25$ $1/n = 0.21$	$q_m = 37 ; b = 0.0068$	Meenakshi and Amutha, 2008
Char coal from camel bone	$K_F = 14.457$ $1/n = 0.283$ $R = 0.9637$	$q_m = 28.24; b = 1.09$ $R = 0.9901$	Hassan <i>et al.</i> , 2008
Activated carbon from Terminalia catappa shell	$K_F = 38.25$ $1/n = 0.25$ $R = 0.9128$	$q_m = 94.43; b = 0.49$ $R = 0.9956$	Inbaraj and Sulochana, 2006

# Summary

1. A botanical source, *Ipomoea carnea*, is exploited for the production of activated carbon which is used as sorbent for Hg (II). For the first time S/Hydrazine solution is exploited as a S precursor for functionalizing carbon material with S.
2. S functionalization has enhanced Hg (II) sorption by carbon material from *Ipomoea carnea* stems.
3. The equilibrium adsorption data fitted well with both the Freundlich and Langmuir adsorption models.
4. Observation and comparison of the Freundlich and Langmuir constants corresponding to various adsorbents reveal the fact that the S functionalized carbon material produced from *Ipomoea carnea* out performed various sorbents like activated carbon materials produced from *Cieba pentandra* hulls, *Phaseolus aureus* hulls, *Cicer arietinum*, sago waste, *Bolluca* coal and also adsorbents other than activated carbon like the fuller's earth (clay), char coal produced from camel bone, guava bark, used tyre waste and vulcanized rubber. Improvement in the sorption capacity of C<sub>1C</sub> N<sub>2</sub> 400 B A S is anticipated with an increase in the density of C=O and C=S surface functional groups.

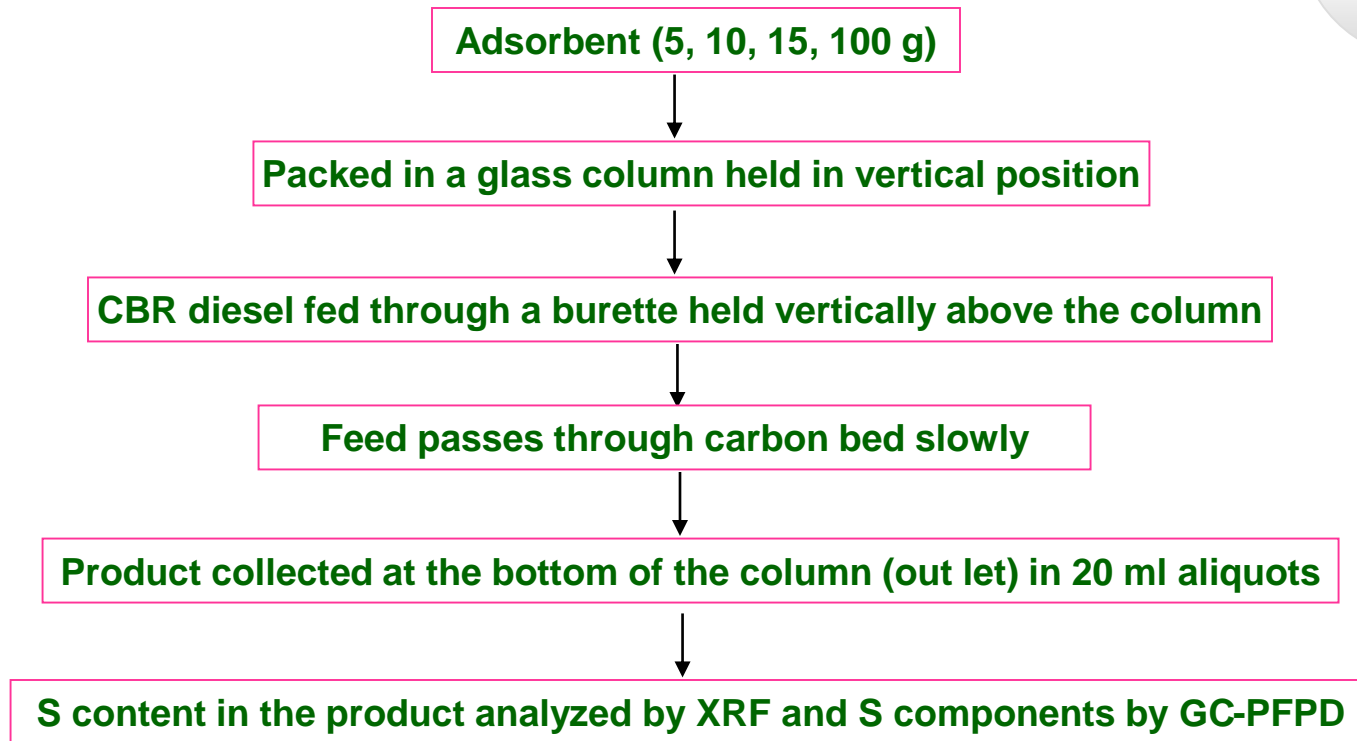
## 6. Carbon Materials for Adsorptive Desulphurization

### Objectives

- ❑ Develop suitable adsorbents for desulfurisation
- ❑ Adsorbent - Reduction of S from 700 ppm to > 300 ppm
- ❑ Regenerable to sustain continuous operation
- ❑ Work under mild operating conditions

Sulphur  
Adsorption  
Process

A simple, inexpensive and efficient process for desulphurization is designed



“Adsorptive desulphurization carried out in a simple experimental set up at RT and atmospheric pressure”

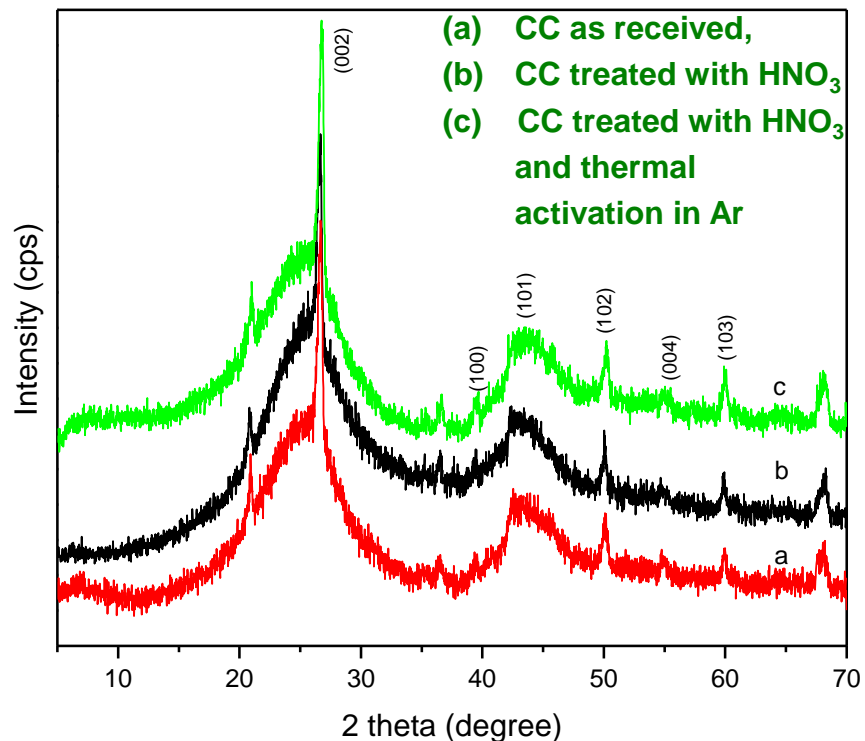
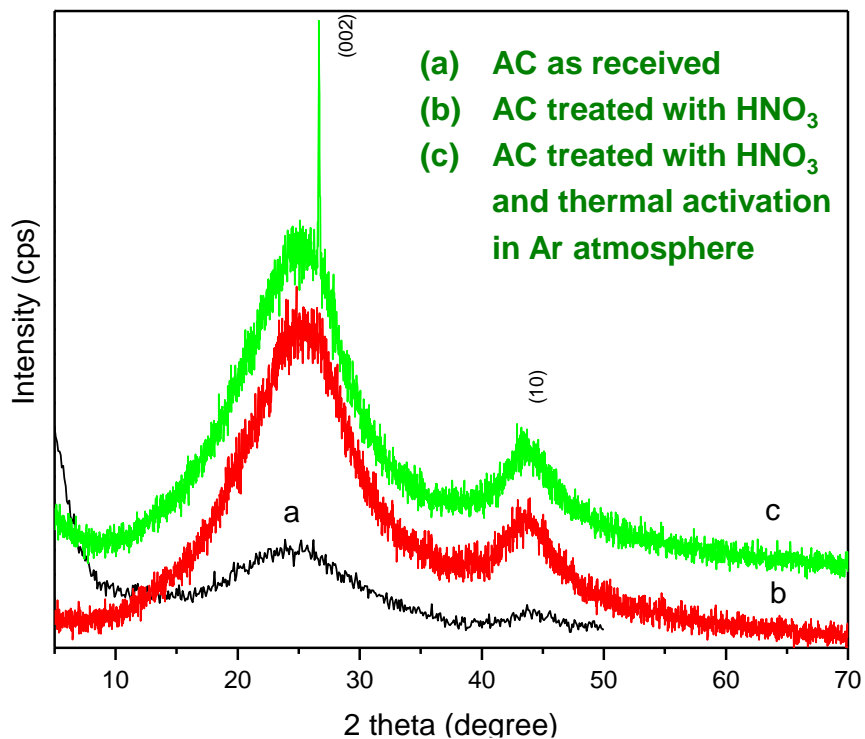
## S sorbing ability of different commercial activated carbon materials

<b>S. No.</b>	<b>Activated Carbon as Sorbent</b>	<b>*ml-diesel treated/ g of adsorbent</b>	<b>S removed (ppm)</b>
<b>1</b>	<b>IG 18 x 40</b>	<b>4</b>	<b>134</b>
<b>2</b>	<b>IG 12 x 10</b>	<b>4</b>	<b>81</b>
<b>3</b>	<b>IG 8 x30</b>	<b>4</b>	<b>76</b>
<b>4</b>	<b>AC 4 x 8</b>	<b>4</b>	<b>12</b>
<b>5</b>	<b>AC 6 x 12</b>	<b>4</b>	<b>73</b>
<b>6</b>	<b>AC 12 x 30</b>	<b>4</b>	<b>92</b>
<b>7</b>	<b>Calgon carbon as received</b>	<b>4</b>	<b>181</b>
<b>8</b>	<b>Adsorbent carbon</b>	<b>4</b>	<b>229</b>

\*20 ml initial product collected from the column packed with 5.0 g activated carbon and analyzed for S

- ❑ **Adsorbent carbon as received and Calgon carbon as received showed outstanding performance by adsorbing 229 and 181 ppm of S per g of adsorbent from 4 ml of treated diesel**
- ❑ **So intensive studies of adsorptive desulphurization were carried out on Adsorbent carbon and calgon carbon**

# Modified Adsorbent (AC) and Calgon Carbon (CC) – Structural and Textural Properties



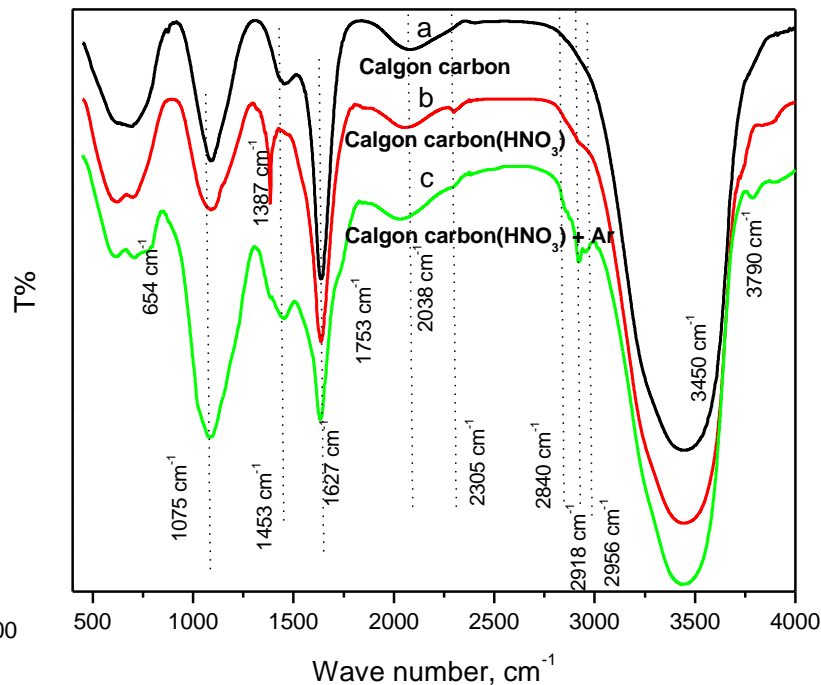
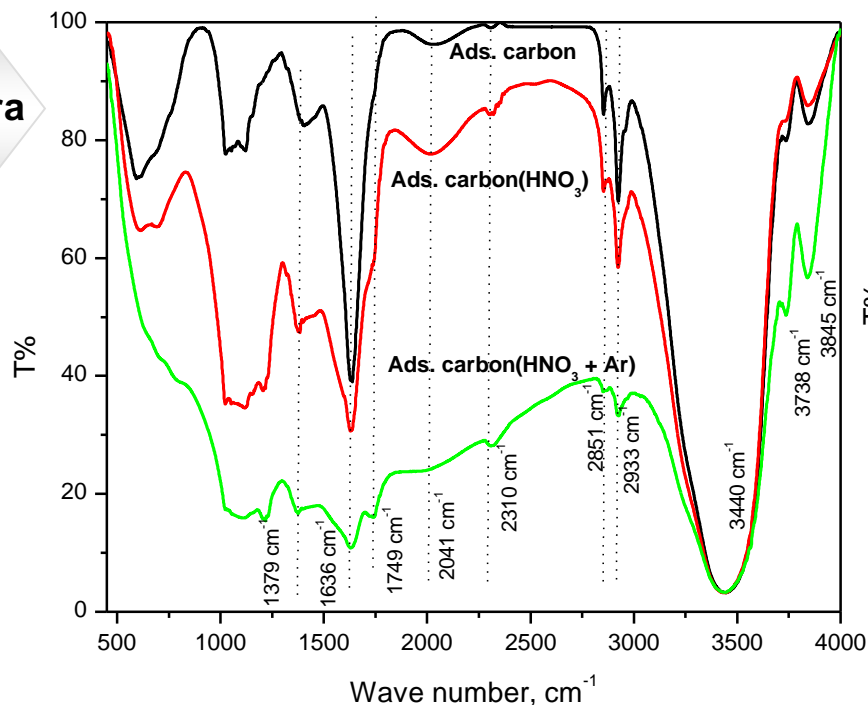
Crystallinity increased upon thermal activation in Ar activation at 800 ° C

Diffraction peaks are typical of graphitic carbon structure

Sample	Carbon Sorbent	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>p</sub> (cm <sup>3</sup> /g)
a	Adsorbent Carbon as received	950	0.451
b	Adsorbent Carbon treated with conc. HNO <sub>3</sub>	882	0.398
c	Adsorbent Carbon treated with conc. HNO <sub>3</sub> followed by Ar activation	1048	0.523
d	Calgon carbon as received	1014	0.587
e	Calgon carbon treated with conc. HNO <sub>3</sub>	649	0.387
f	Calgon carbon treated with conc. HNO <sub>3</sub> followed by ar activation	996	0.598

## Modified Adsorbent (AC) and Calgon Carbon (CC) – Surface Functionality

FT-IR Spectra



### S sorption capacity – Adsorbent Carbon Vs Calgon Carbon

Sorbent Amount	5.0 g	10.0 g	15.0 g
Sorbent Type	S removed*, (in ppm)		
<b>Adsorbent carbon as received</b>	<b>229</b>	<b>380</b>	<b>410</b>
<b>Adsorbent carbon treated with HNO<sub>3</sub></b>	<b>105</b>	<b>186</b>	<b>577</b>
<b>Adsorbent carbon treated with HNO<sub>3</sub> followed by Ar activation</b>	<b>346</b>	<b>518</b>	<b>586</b>
<b>Calgon carbon as received</b>	<b>181</b>	<b>371</b>	<b>451</b>
<b>Calgon carbon treated with HNO<sub>3</sub></b>	<b>280</b>	<b>378</b>	<b>488</b>
<b>Calgon carbon treated with HNO<sub>3</sub> followed by Ar activation</b>	<b>340</b>	<b>399</b>	<b>619</b>



## Adsorptive Desulphurization – Removal of refractory S compounds

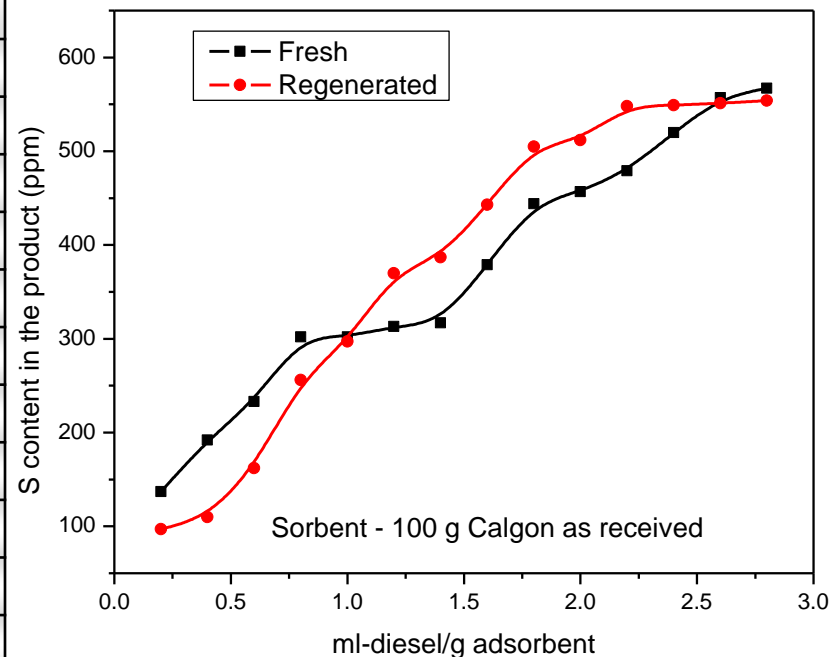
Sulphur Species	S content (in ppm)		
	CBR diesel (Feed)	Adsorbent carbon HNO <sub>3</sub> followed by Ar treatment, 15.0 g	Calgon carbon, HNO <sub>3</sub> followed by Ar treatment, 15.0 g
C <sub>1</sub> BT	4.6	Nil	Nil
C <sub>2</sub> BT	119.6	Nil	Nil
C <sub>3</sub> BT	137.5	75.2	67.2
C <sub>3</sub> <sup>+</sup> BT	79.6	68.9	47.4
DBT	91.5	2.6	1.3
C <sub>1</sub> DBT	157.7	Nil	Nil
C <sub>2</sub> DBT	116.7	Nil	Nil
C <sub>3</sub> DBT	29.5	4.3	2.1
Total S	737	151	118

Analyzed by GC – PFPD

- ❑ Adsorptive desulphurization process removed refractory S compounds more easily compared to conventional hydrodesulphurization process

# Process Scaling up & Adsorbent Regeneration Methods

S. No.	ml-diesel/g adsorbent	S content in the product (S content removed) (in ppm)	
		Adsorbent carbon activated with HNO <sub>3</sub> followed by Ar activation	Calgon carbon as received
1	0.2	13 (724)	137 (600)
2	0.4	68 (669)	192 (545)
3	0.6	110 (627)	233 (504)
4	0.8	169 (568)	302 (435)
5	1.0	194 (543)	302 (435)
6	1.2	233 (504)	313 (424)
7	1.4	263 (474)	317 (420)
8	1.6	290 (447)	379 (358)
9	1.8	325 (412)	444 (293)
10	2.0	375 (362)	457 (280)
11	2.2	415 (322)	479 (258)
12	2.4	443 (294)	520 (217)
13	2.6	463 (274)	557 (180)
14	2.8	486 (251)	567 (170)
15	3.0	496 (241)	519 (218)
16	3.2	505 (232)	532 (205)
17	3.4	510 (227)	548 (189)



**S removal capacity of fresh vs toluene (500 ml) regenerated sorbent**

➤ The desulphurization process was scaled upto 100 g and a proportionate increment in S sorption capacity is noticed relative to 5, 10 and 15 g batches

## Summary

- 1. An efficient desulphurization process based on adsorption, operated under modest conditions of temperature (room temperature) and pressure (atmospheric) is developed.**
- 2. New method of activation, which is a unique combination of nitric acid treatment and Ar activation, of carbon based adsorbents to induce desired surface functionality, polarity, phase structure and pore texture is adopted for the first time.**
- 3. It is found that subsequent Ar activation of nitric acid treated carbon adsorbents is inevitable to derive the best out of oxidative modification of carbon surface chemistry.**
- 4. The utility of adsorbent carbon as well as calgon carbon and their tailored forms as adsorbents for organo sulphur compounds is clearly elucidated.**
- 5. The highly refractive compounds such as substituted di benzothiophenes which are difficult to be removed by conventional HDS process, have been effectively eliminated from the diesel feed.**
- 6. The process of adsorptive desulphurization is scaled upto 100 g (adsorbent) batch.**
- 7. In addition to the successful removal of appreciable amounts of S from diesel feed stocks using tailored carbon based adsorbents, simple, inexpensive, efficient, environmentally benign and reliable solvent (toluene) based regeneration has also been developed.**
- 8. From the studies, it can be anticipated that newer and promising desulphurization<sup>67</sup> technologies are not too far to the refinery industry.**

# Conclusion

- ✦ Activated carbon materials with desired properties were synthesized from novel lignocellulosic materials, such as, *Calotropis gigantea* stems, *Borassus flabellifera* male flower spikes, *Limonea acidissima* shells, *Ipomoea carnea* stems
- ✦ The properties and performance of the carbon materials produced were evaluated relative to commercially available carbon materials like Black Pearl 2000, Vulcan XC 72 R, CDX 975, Nuchar, Calgon and Adsorbent
- ✦ The carbon materials developed were successfully exploited as sorbent (for mercury from aqueous solution and organo sulphur compounds from diesel) and as catalyst support (for Pt and HPW) in designing catalysts for the methanol electro oxidation (Pt/C) and also for the synthesis gasoline additives such as MTBE and TAME (HPW/C)

Thus the common carbon materials from natural sources have been exploited for strategically important catalytic processes

# List of Publications

## Refereed Journals

1. B. Viswanathan, P. Indra Neel and T. K. Varadarajan (2009) Development of carbon materials for energy and environmental applications, *Catalysis Surveys from Asia*, 13, 164-183.
2. B. Viswanathan, P. Indra Neel and T. K. Varadarajan (2009) The role of activating agents in the preparation of carbon materials, *Indian Journal of Chemistry Section A* (communicated).

## Patent

1. B. Viswanathan, T. K. Varadarajan and P. Indra Neel (2008) A process for the preparation of activated carbon from botanical sources, Indian Patent IN 2007CH00376 A 20081128, 2008.

## National/International conference

1. P. Indra Neel, B. Viswanathan and T. K. Varadarajan (2005) Preparation, characterization and evaluation of catalytic activity of dodeca tungsto phosphoric acid (HPW) and dodeca tungsto silicic acid (HSiW) supported on SBA-1 mesoporous silica, 17<sup>th</sup> National Symposium on Catalysis, 18-20<sup>th</sup> January, 2005, CSMCRI, Bhavnagar, Gujarat, India.
2. P. Indra Neel, B. Viswanathan and T. K. Varadarajan (2005) Spectroscopic analysis of supported heteropoly acid catalysts, International Conference on Spectrophysics, INCONS-2005, 9-12<sup>th</sup> February, 2005, Pachaiyappa's college, Chennai, Tamil Nadu, India.
3. P. Indra Neel, B. Viswanathan and T. K. Varadarajan (2005) Nanoclusters of polyoxometalates dispersed on SBA-1 mesoporous silica for the production of gasoline additives, National Symposium and Conference on Solid State Chemistry, ISCAS-2005, 1-3<sup>rd</sup> December, 2005, University of Goa, Goa, India.
4. P. Indra Neel, B. Viswanathan and T. K. Varadarajan (2007) Hydrogenation behaviour of W/C systems, 18<sup>th</sup> National Symposium on Catalysis, 16-18<sup>th</sup> April, 2007, IIP Dehradun, India.
5. P. Indra Neel, B. Viswanathan and T. K. Varadarajan (2010) Methanol electro oxidation on activated carbon supported Pt catalysts in alkaline medium, Indo-Hungarian workshop on "Future frontiers in Catalysis", 16-18<sup>th</sup> February, 2010, IIT Madras, Chennai.

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Mr Mohan

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