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Carbon Nano Tubes obtained from Plant Based Oil (*Nigella sativa)* and it's Hydrogen Storage Capacity

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Abstract: ***The spray pyrolysis technique of plant based oil i.e. Kalonji seed oil (Nigella sativa) at 800°C temperature under inert gas atmosphere and in presence of Nickel catalyst, carbon nanotubes (CNTs) were obtained. In this paper we discussed the synthesis of CNT from Kalonji oil. The synthesis is carried out over Nickel catalyst by spray pyrolysis at 800°C in an inert atmosphere of Hydrogen gas. The obtained CNT's were purified using diluted solution of 1:1 HCL: HNO_3 so as to remove the nickel catalyst and amorphous carbon. Then the obtained CNT's were characterized by using, SEM (Scanning Electron Microscope) X-ray Diffractometry. The specific surface area measurement of CNT was carried out by using adsorption of methylene blue (MB) dye and BET method. Both the results obtained from BET method and MB method was correlated. The amount of hydrogen stored by as grown CNT was measured by pressure method. We also studied the effect of pressure on the storage of hydrogen. The optimal hydrogen storage capacity was 0.8 wt. % at 11 kg/cm^3 and 2.5 wt. % at 100kg/cm^3.***

Keywords: Kalonji oil, CNT, Specific Surface area, Spray pyrolysis.

1. Introduction

Recently carbon nanotubes have been receiving interest because of its unique structure and arrangements of atoms. Apart from nanotubes, carbon shows some other morphology too e.g. beads, fibers and many more. Most of the researchers are using petroleum products for the preparation of carbon nano materials, Sharon and his group [1] at nanotechnology Research lab is able to produce these materials from plant derived precursors.

There are various physical and chemical properties of CM and CNM has been carried out for different applications like hydrogen adsorption [2] super capacitor [3] solar cell applications [4] micro wave absorption for lithium ion battery [5] study has been studied.

Specific surface area is one of the important properties of carbon nanomaterial that can be related to their physical or chemical behavior. The most commonly used methods to evaluate the specific surface area of carbon nanomaterials are based on adsorption of nitrogen [6], water vapor [7], ethylene glycol mono ethyl ether [8] or color dye [9].

A very simple adsorption of methylene blue hereafter will be called as MB is used in lab to determine the specific surface area of the carbon nanomaterial synthesized in laboratory. In this method MB is used to adsorb on CNM and is then evaluated by using a UV-Vis spectrophotometer.

Methylene blue powder behaves like a cationic dye when mixed with water and is identified with the chemical formula: C16H18N3SCI and molecular weight of methylene blue is 373.9g. Which corresponds to methylene blue hydrochloride with three groups of water structurally as shown in figure below, Methylene blue adsorption is a reliable and simple method to obtain information on the specific surface area. The obtained values by this method are correlated with BET surface area measurement values and those are found to be comparable.

2. Materials and Methodology

CNT synthesized from kalonji oil by direct spray pyrolysis at 800°C in an inert atmosphere of hydrogen gas in furnace and are used for further study.

The small quantity of kalonji oil was directly spread in the horizontal furnace. Initially the furnace was heated up to 800°C temperature in presence of inert gas i.e. hydrogen and as such oil is sprayed using a spray tube. The vapour of oil is formed and those are allowed to pass from a quartz boat containing fine powder of nickel catalyst. During this process the care is taken that the flow rate of hydrogen gas is decreased so that the oil vapour is retained on the catalyst for long time. The pyrolysed sample is annealed for one hour at the same temperature i.e. the temperature of horizontal furnace is maintained at 800°c for an hour. It is then allowed to cool and carbon material is removed from furnace and characterized by using SEM and powder XRD.

The CNT is purified with the help of soaking with diluted solution of HCL and HNO_3 and CNT formation is confirmed by different characterization tools.

3. Characterization

3.1 SEM study

Scanning Electron Microscopy study of this sample is carried out at SAIF (Sophisticated Analytical Instrument Facility available at IIT- Mumbai and the obtained SEM photograph is given in figure below,

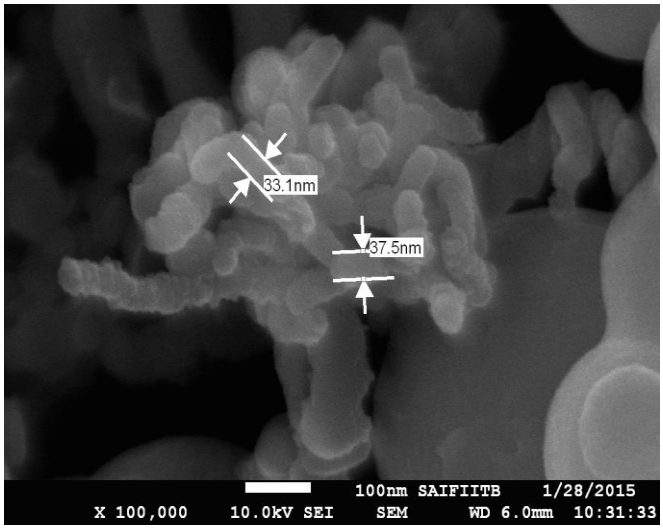


Figure 1: SEM Image of CNT obtained from Kalonji oil

3.2 X-Ray Diffraction study

The diffractogram of CNT is taken on PANalytical X-ray diffractometer with Cu Kα.

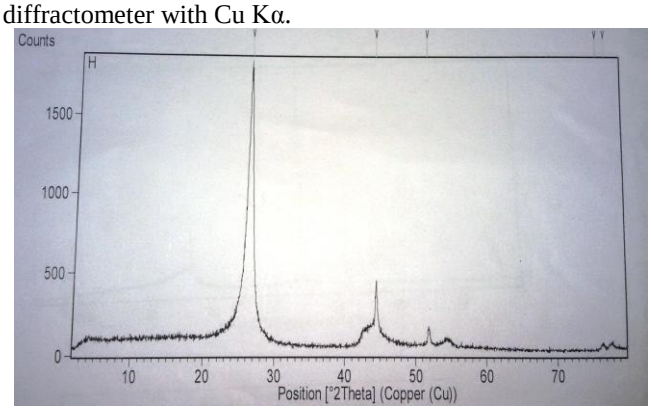


Figure 2: X-Ray Diffractogram of CNT obtained from kalonji oil

Table 1: XRD values from X-ray diffractometer

Pos. [°2 Th.]	d-Spacing [°A]	Rel.Int .[%]	FWHM Left [°2Th.]	Area [cts*°2Th.]	Planes
26.61	3.35	100	0.33	527.35	002
44.52	2.04	32.53	0.23	120.07	111
51.94	1.76	9.46	0.23	34.91	200

4. Measurement of Surface Area

Surface area of CNT is measured by two techniques i.e. by using MB adsorption technique and by using conventional BET method.

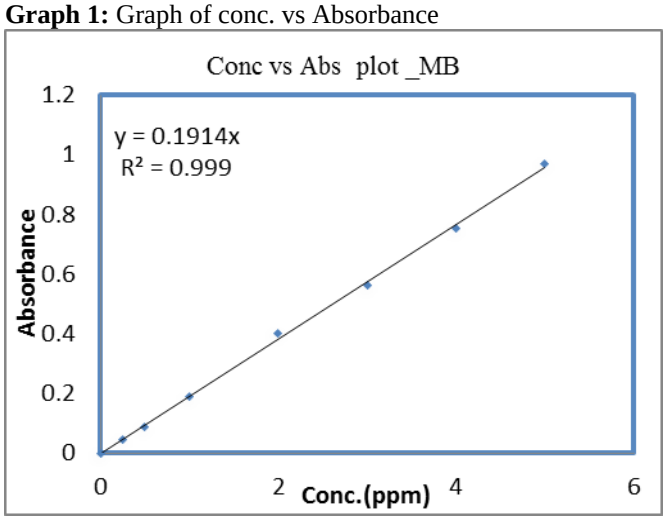
4.1 Using MB Adsorption technique

For MB adsorption measurement the dye used was 'Methylene blue, from Qualigens fine Chemicals'. Aqueous Solutions of different concentrations of MB are prepared ranging from 0.25 to 5.0 ppm and the absorbance of these solutions are measured using a UV-visible spectrophotometer at a fixed wavelength of 662 nm. This wavelength is selected for absorption measurement as MB solution shows highest absorbance at 662nm. Linearity curve of concentration v/s absorbance is plotted, the absorbance is found to be linear with regression factor (R^2) 0.999 weighed exactly 100 mg of test sample (CNT) in 500 ml round bottom flask and added 100 ml of 5 ppm MB solution, shaken to mix properly then this solution is refluxed at 260 ºC temperature for 1 hr. Allowed to cool the solution in same flask and kept for 24 Hrs. to adsorb the MB on test sample. The absorbance of this solution is measured by UV-Vis spectrophotometer at 662nm wavelength and found the amount of MB dye adsorbed on the test sample from linearity curve.

Table 2: Conc.of MB and its Absorbance values at 662 nm

Sr.No.	conc.(ppm)	Absorbance
1	0.00	0.00
2	0.25	0.044
3	0.50	0.089
4	1.00	0.188
5	2.00	0.401
6	3.00	0.563
7	4.00	0.751
8	5.00	0.97

Graph 1: Graph of conc. vs Absorbance



The linearity curve of concentration of MB solution in ppm v/s absorbance values as mentioned in above table are plotted and regression factor (R^2) is calculated which is found to be 0.999 which shows that the absorbance and concentration has a linear relation.

Following equation is used to calculate the specific surface area of this sample,

$$\text{Surface Area (a)} = \frac{1187.736 \text{ X C X V}}{\text{Wt.}}$$

C= Concentration difference in moles/ltr.
V=Volume of MB solution in ml.
Wt. = Wt. of CNT in g.

4.2 Measurement of surface area by BET method

The surface area of carbon nano tube is measured using BET technique. The different set parameters during BET analysis are as shown in below figure. The CNT sample is dried in dry air oven at 100°C for almost one hour and then this sample is used for the specific surface area measurement using BET Experiment. The sample is again regenerated at

250°C for 30 minutes before actual analysis and then the specific surface area is measured as per the standard operating procedure of BET instrument setup with liquid and gaseous stage nitrogen.

Smart Instruments Co P Ltd

Surface Area Analyser	**Model: Smart Sorb 92/93**
From Smart Instruments Co.Pvt.Ltd	**WebSite: www.smartinstrument.com**
Run Time:09:13 pm	Date:April 1 2014
% of N2 :30.5	Room temp.in Deg.C:25
Sample Name : CNM_Kalonji_800°C_Ni_H2	
Wt of Tube (gms) :22.483	Wt of Tube+Sample (gms) :22.729
Sample Wt (gms) :.2460	Sample Wt after Reg. (gms) : .2420
Sample Loss : 1.6 %	
Regeneration Temp.(deg.C) : 250	
Time for regeneration (min.) :30	
Desorption count : 122803.8	
Injection count : 69087	
Injected volume (cc) : 5	

Surface Area in (Sq.m/gm) : 102.42

Remarks: vinod | | |

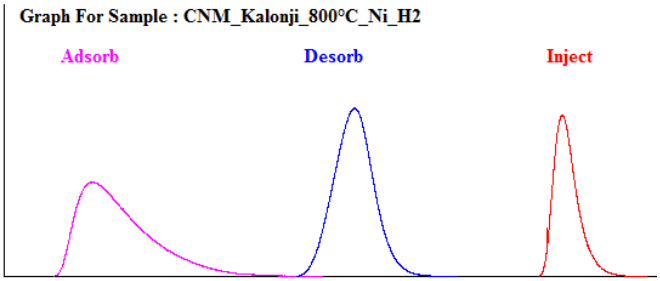


Figure 3: BET-Adsorption-desorption graph of CNT obtained from kalonji oil

5. Hydrogen Gas Adsorption Measurement

Adsorption of hydrogen gas on CNT is carried out using low pressure Sharon's apparatus (LPSA) at 11 Kg/cm^3 and that of Sieverts apparatus at 100 Kg/cm^3. SLPA apparatus enables us to measure the hydrogen adsorption of CNT by measuring decrease in hydrogen pressure. A detailed about both the apparatus, leak test and hydrogen adsorption measurement is discussed elsewhere [10]. The optimal hydrogen storage capacity was 0.8 wt. % at 11 Kg/cm^3 and 2.5wt% at 100 Kg/cm^3.

6. Results and Discussion

Table 3. Surface area and hydrogen storage comparison

	Surface Area m^2/gm		Hydrogen Gas Storage	
Sample Details	BY MB Adsorption	By BET	At 11 Kg/cm^3	At 100 Kg/cm^3
CNT	98.87	102.42	0.8	2.5

From surface area measurement and hydrogen gas storage it is observed that the surface area measured using MB technique is 98.87 m^2/g and that of BET technique is 102.42 m^2/g.

7. Conclusion

From Scanning Electron Microscopy image of Carbon nano Tubes obtained from natural precursor i.e. Kalonji oil it is observed that there is formation of CNT but structurally these are broken CNT's and the average diameter is found in the range of 30 to 40 nm.

X-ray diffraction study has been carried out to see the crystallinity of carbon. From X-ray diffractogram of CNT it is observed that CNT shows one prominent graphitic peak at 26.61° and other peaks are may be due to the metal contents in it i.e. it may be due to nickel catalyst. The diffraction planes i.e 200 , 111 and 002 are of carbon nickel and nickel respectively.

MB adsorption technique allows the determination of specific surface area of carbon nano tubes and this method is found to be cost effective, simple and comparable to that of BET method.

Hydrogen storage capacity measurement is done using different apparatus and the optimal hydrogen storage capacity was 0.8 wt. % at 11 Kg/cm^3 and 2.5wt% at 100 Kg/cm^3.

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