



## Carbon Nano Spheres and Nano Tubes Synthesized from Castor Oil as Precursor: For Removal of Arsenic Dissolved in Water

Suman Tripathi<sup>1</sup>, Maheshwar Sharon<sup>2</sup>, N.N. Maldar<sup>3</sup>, Jayashri Shukla<sup>1</sup>  
and Madhuri Sharon<sup>2\*</sup>

<sup>1</sup> Department of Chemistry, K. M. Agrawal College, Kalyan-421301, Maharashtra, India

<sup>2</sup> Nanotechnology Research Centre, S.I.C.E. College, Ambernath, Maharashtra, India

<sup>3</sup> Solapur University, Kegoan, Solapur-413255, Maharashtra, India

### ABSTRACT

Carbon Nano Spheres were synthesized using three different transition metals (Ni, Zn & Co) as catalyst in a thermal catalytic vapor reactor using natural non-edible Castor oil as the carbon source. After purification of yielded carbon it was characterized by high resolution scanning electronic microscope (HRSEM) to know its morphology and by X-ray diffraction (XRD) and Raman spectroscopy to know the structural details. The results reveal that castor oil when pyrolyzed in presence of Co as catalyst at 900<sup>o</sup> C it synthesized carbon nanotubes along with some carbon nano spheres. Use of Zn resulted in formation of smooth walled spherical nano to micro sized carbon. Ni Use of Ni resulted in formation of carbon nano beads, some of them had Ni encapsulated into the beads. The graphitic nature both CNT and Beads were confirmed by XRD. The possible use of carbon nano-sphere in adsorbing Arsenic present in water was assessed. It was found that carbon nano-spheres prepared using Co as catalyst could adsorb as much as 49% Arsenic in 12 hr of exposure; though they had same surface area as the carbon nano-spheres prepared using Zn (30.88 m<sup>2</sup>/gm).

**Keywords:** Carbon Nanomaterial, Taguchi-optimization, Castor oil, Catalyst, CVD, Arsenic, Pyrolysis, Carbon nano-sphere, carbon nano tubes.

### INTRODUCTION

Nanotechnology is the creation of functional materials, devices and systems through control of matter on the nanometer scale and the exploitation of novel phenomena & properties of matter (physical, chemical, biological, electrical etc.) at that length. Carbon nano tubes (CNT) have attracted growing interest owing to their unique physico-chemical and mechanical properties and many potential applications. Majority of the synthetic methods such as arc-discharge, laser ablation, chemical vapor deposition (CVD) and spray pyrolysis are directly or indirectly based on the petroleum products [1-2]. Considering the environmental effects and decreasing petroleum product sources, efforts are now directed to away from them and switch over to reproducible natural carbon sources such as camphor [3] and turpentine oil [4] etc. as they are good source of hydrocarbons.

In search of identifying non-edible oil rich in hydrocarbon, to produce carbon nano materials after screening many oils we found castor oil to be a suitable precursor. It is an essential oil obtained from seeds of the castor (*Ricinus communis*). It is colorless to pale yellow liquid with boiling point 313<sup>o</sup> C. Chemically it consists of various fatty acids such as Ricinoleic acid, Oleic acid, Linoleic acid, Stearic acid etc. with different percentage composition [5]. For synthesizing the carbon nano material (CNM), CVD method was selected which has attracted attention due to simplicity and the possibility of producing different types of carbon nanomaterials on commercial scale.

Transition metals are generally used as catalyst owing to their catalytic decomposition of carbon source, ability to form carbides and possibility for carbon to diffuse through & over the metals extremely rapidly [6]. Since it is catalyst that initiates the nucleation of carbon nano tube (CNT); it is imperative that the size of metal to be used as catalyst should be in nano scale. In the present paper we report our attempt to synthesize carbon nano material (CNM) by catalytic decomposition of castor oil (an eco - friendly natural carbon precursor) using three different transition elements; nickel (Ni) and cobalt (Co). They are selected because of the two main reasons one is the high solubility of carbon in these metals at high temperatures and the other is high carbon diffusion rate in these metals.

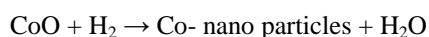
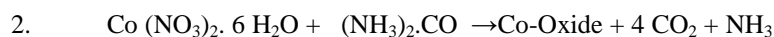
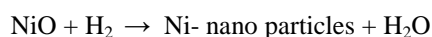
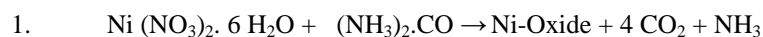
Arsenic is a naturally occurring dissolved element in ground and surface waters throughout the world [7]. It exists in a different oxidation state in organic and inorganic forms in many environmental matrices such as natural water and soil. The predominant oxidation states of arsenic are As (III) i.e. arsenite and As (V) i.e. arsenate ions [8] and they can bind to give organic materials commonly present in the environment. The toxicity, availability and environmental mobility of arsenic are very much dependent on the chemical forms in which they exist [9, 10]. The problem with Arsenic is that it is frequently found at higher than accepted concentration due to anthropogenic contributions including pesticides, herbicides, industrial waste and the burning of fossil fuels [11]. Arsenic poisoning has become one of the major environmental worries worldwide, as millions of people, which have been exposed to high arsenic concentrations through contaminated drinking water, developed severe health problems.

Hence our efforts were directed towards the preliminary studies of removing arsenic from water using carbon nano materials.

### MATERIALS AND METHODS

**Castor oil** – was procured from local market and its major elemental content analysis was done, mainly to know the amount of carbon present in the oil.

**Preparation of transition metal catalyst:** pure metal oxide of Ni and Co was synthesized by standard urea decomposition method. And the metal oxide was then reduced in the atmosphere of hydrogen gas using a horizontal furnace at 500°C for 3 hrs. Following reaction takes place during the oxidation & reduction processes of Ni, Zn and Co respectively:



**Preparation of Carbon Nano Materials from castor oil** - The CVD furnace used is divided into two parts (i) oil vaporizing zone and (ii) pyrolyzing zone of furnace for carbonization. In oil vaporizing zone a quartz boat containing 5 ml castor oil was placed in the centre and in pyrolyzing zone the 300 mg of catalyst was kept in a quartz boat in the centre so that they could get uniform temperature. A cylindrical quartz tube was inserted through both the furnaces (Figure – 1) and both of them were connected to the temperature controller. One end of the quartz tube was connected to gas cylinder through a flow meter and the other end was connected with water bubbler through which the excess gas could be allowed to escape. After flushing the quartz tube with a carrier gas i.e. argon, the temperature of vaporizing furnace was adjusted to little higher than the boiling point of the castor oil (i.e. 350°C) whereas the pyrolyzing furnace was heated to 900°C temperature and kept at that temperature for 3 hrs. After completion of process, the furnace was allowed to cool down to the room temperature. The carbon soot accumulated on the quartz boat was collected and purified by acid treatment. Yield of carbon was recorded prior to as well as after purification.

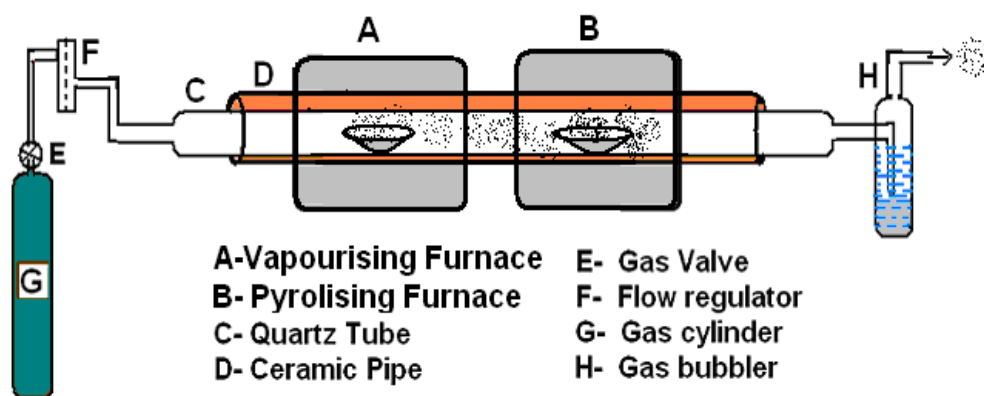


Figure – 1: Schematic diagram of chemical vapor deposition set-up

**Purification of Carbon Nano Materials:** The collected soot contains impurities like amorphous carbon, metal catalyst etc. To remove these impurities soot was first soaked in 100 ml of 1M HCl in and heated at 80°C for 20 mins. Then they were cooled and kept at room temperature for 24 hrs then filtered and thoroughly washed with distilled water five times. Finally it was rinsed with acetone to remove the traces of water and then dried in oven at 120°C for 24 hrs.

**Characterization:** The morphological observations of as-synthesized and purified CNM were carried out by High resolution scanning electron microscopy (SEM and HRSEM), using a Hitachi (S-4700) SEM; by placing the as-prepared samples on conductive carbon tape. SEM of catalyst was also taken to know their size and shape.

X-ray diffraction (XRD) was performed with a powder X-ray diffractometer with CuK $\alpha$  source to calculate the crystallographic parameters.

Raman spectra of samples were measured in a backscattering geometry at room temperature using Ar ion laser (488nm).

**Measurement of Surface Area of CNM samples:** was done by standard methylene Blue Absorption method [12].

**Methods of Assessing Arsenic in Water:** Analysis was done using.....method [13]. All reagents and chemicals used were of analytical reagent grade or chemically pure grade and distilled water was used throughout the study.

Arsenic (III) stock solution (1000  $\mu\text{gml}^{-1}$ ) was prepared by dissolving 0.1734 g of NaAsO<sub>2</sub> in 100 ml of water. Working standard was prepared by appropriate dilution of stock. Toluidine blue (0.01 %), hydrochloric acid (1 M), potassium iodate (2 %) and sodium acetate (1 M) were used.

5.0 ml of sample solution containing 1.0 - 10.0  $\mu\text{gml}^{-1}$  of arsenic (III) was transferred in to a series of 50 ml calibrated flasks. First 5ml of 2% Potassium iodate and then 5 ml 1 M hydrochloric acid was added and mixture was gently shaken until the appearance of yellow color indicating the liberation of iodine. This was followed by addition of 2.5 ml, 0.01% Toluidine blue and 10.0 ml of sodium acetate solution. The solution was kept for 2 min and made up to the mark with distilled water. The absorbance was measured at 628 nm against the corresponding reagent blank using UV-Vis spectrophotometer (Perkin Elmer). Reagent blank was prepared by replacing the analyte (arsenic) solution with distilled water. The absorbance corresponding to the bleached color, which in turn corresponds to the analyte (arsenic) concentration, was obtained by subtracting the absorbance of the blank solution from that of the test solution.

This method involves the liberation of iodine by the reaction of arsenic (III) with potassium iodate in an acidic medium. The liberated iodine bleaches the blue color of toluidine blue and measured at 628 nm. This decrease in absorbance is directly proportional to the As (III) concentration.

The calibration curve passing through origin was plotted by considering the different concentration of arsenic i.e. in between 1.0-10.0  $\mu\text{gml}^{-1}$  on X-axis and the absorbance corresponds to the arsenic concentration on the Y- axis.

**Method used for Assessing Adsorption of Arsenic by CNM:** 0.005 gm of CNMs synthesized from castor oil was added into 5.0 ml of  $1.0 \times 10^{-5}$  M As (III) solution and different dilutions were prepared into a series of 50 ml calibrated flask. The mixture was kept overnight at room temperature. Then, in the same solution 5.0 ml of 1M HCl

and 5.0 ml of 2% Potassium iodate was added; followed by addition of 2.5 ml of 0.01% toluidine blue and 10.0 ml of sodium acetate solution, after 2 min all the mixtures were made up to the mark with distilled water. The resulted solution was then filtered through Whatmann filter paper No.41.

Then absorbance of resulting solution was measured at 628 nm. From the observed absorbance of each solution, the concentration of arsenic adsorbed by the CNMs as well as % sorption and adsorbate to adsorbent ratio i.e.  $X/m$  was calculated.

## RESULTS AND DISCUSSION

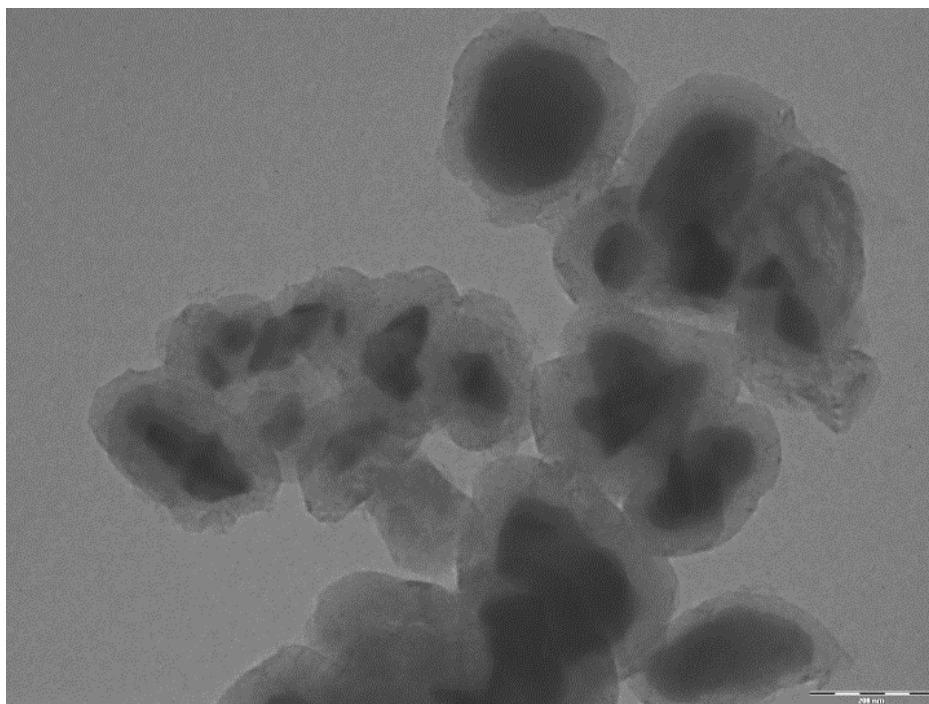
**Impact of transition metal as catalyst on the yield of CNM:** The growth of carbon nanomaterials is catalyzed by transition metals i.e. d- block elements, Ni and Co. Due to the existence of covalent bonding, they have high heats of sublimation i. e. they require large amount of energy to change them from solid to vapor state. The metal ions because of their comparatively large size and low charge density do not get hydrated easily. Thus, on account of their high heat of sublimation, high ionization energies and low heats of hydration of their ions, the transition elements have a small tendency to react. They have rather a tendency to remain unreactive or noble. Hence these metals can be used as a catalyst in type of chemical reactions.

There was a differential response to both the tried catalysts by the precursor Castor oil.. The yield as recorded using Ni or Co as catalyst is shown in Table-1; use of Ni yielded 35% and Co yielded 42% CNM. The elemental analysis of Castor oil shows presence of 77.271% carbon in it; rest of the carbon might have evaporated as gas or remained as complex carbon residue.

Table.-1 showing impact of catalyst on yield of CNM from Castor oil

Catalysts	% yield of Carbon	Morphology of Carbon	Size of Carbon
Ni	35 %	Spherical	100 – 500 nm
		Ni encapsulated in graphite layers	200 – 1000 nm
Co	42%	Coiled CNT	34 – 37 nm Diameter
		Spheres	50 – 100 nm

**HRSEM observation of CNM:** A typical HRSEM micrograph of CNMs synthesized at 900<sup>0</sup>C, using Ni as nano catalyst, in presence of Ar gas using castor oil as precursor showed two types of carbon structures (i) Ni nanoparticles entrapped in graphitic layers having almost spherical conformation, having 200 – 1000 nm size and (ii) carbon nano spheres having 100 to 500 nm diameter (Figure – 2)





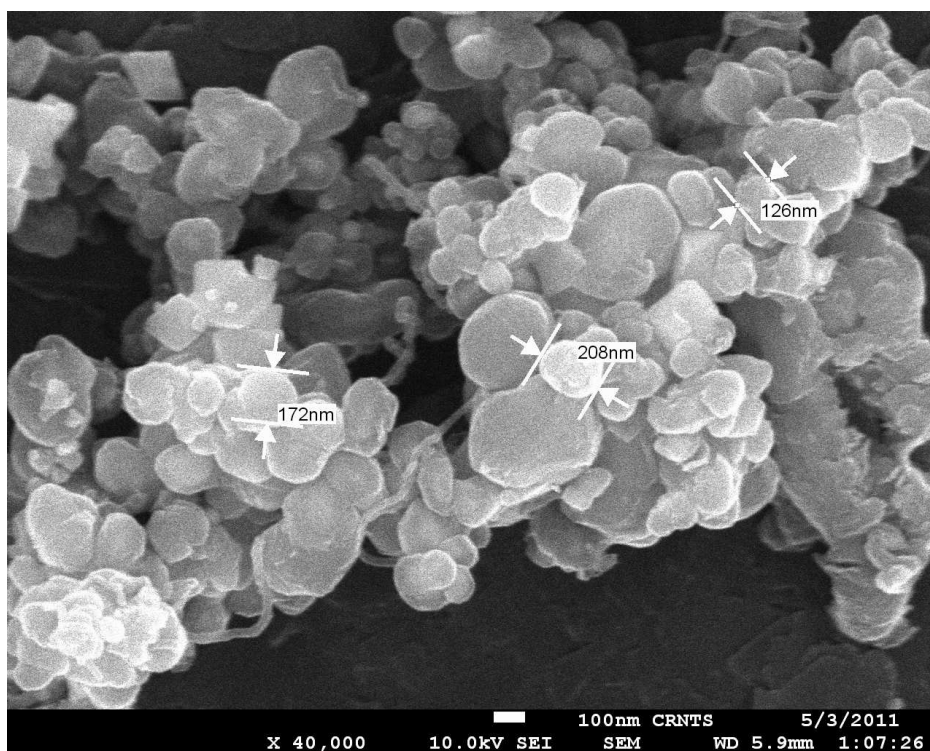
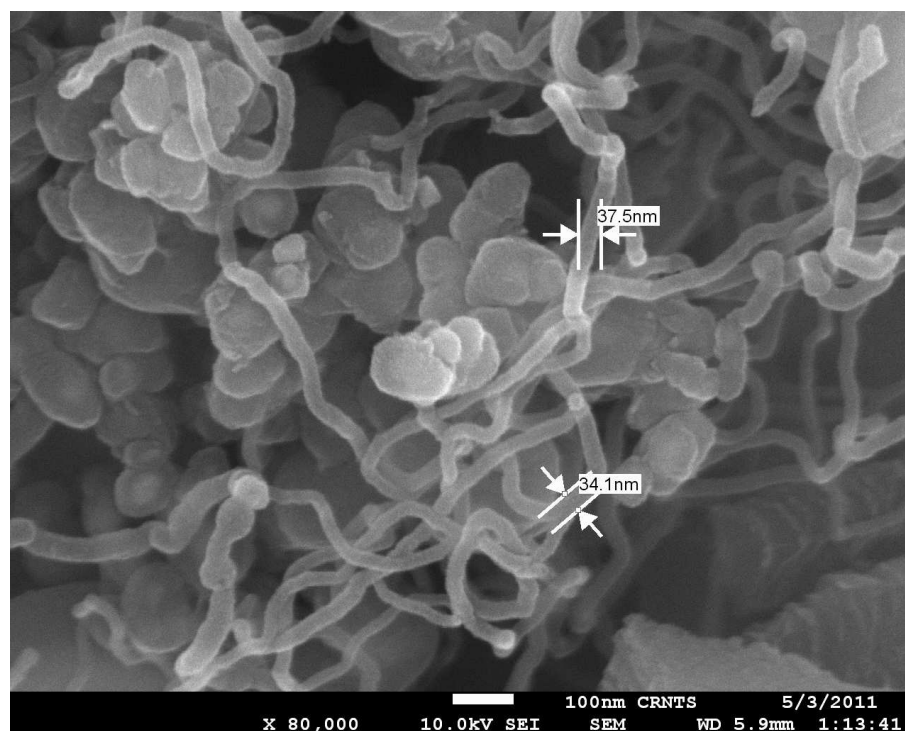


Figure – 2: HRSEM micrograph of CNMs synthesized at 900°C, in presence of Ar gas using castor oil as precursor and Ni as catalyst showing (A) Ni nanoparticles entrapped in graphitic layers having almost spherical conformation, the size of the particle vary from 200 – 1000 nm.(The graphitic nature of outer carbon layer was confirmed by XRD & Raman spectra) and (B) carbon nano spheres having 100 to 500 nm diameter



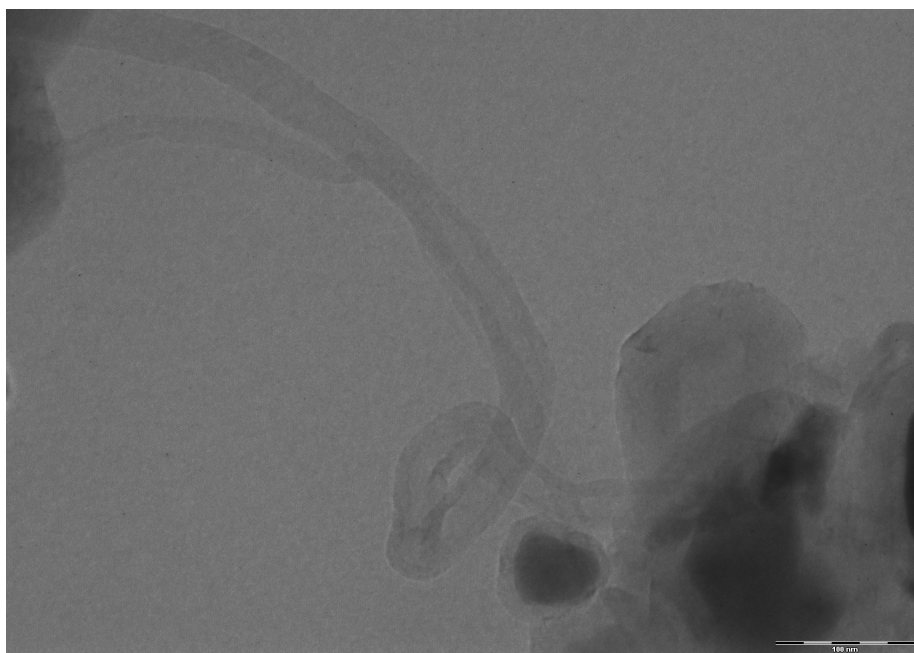


Figure – 3: HRSEM micrograph of CNMs synthesized at 900°C, in presence of Ar gas using castor oil as precursor and Co as catalyst showing (A) some coiled tubular having 34 – 37 nm outer diameter and some spherical structures of 100 to 500 nm diameter and (B) TEM of CNT confirming it to be MWCNT

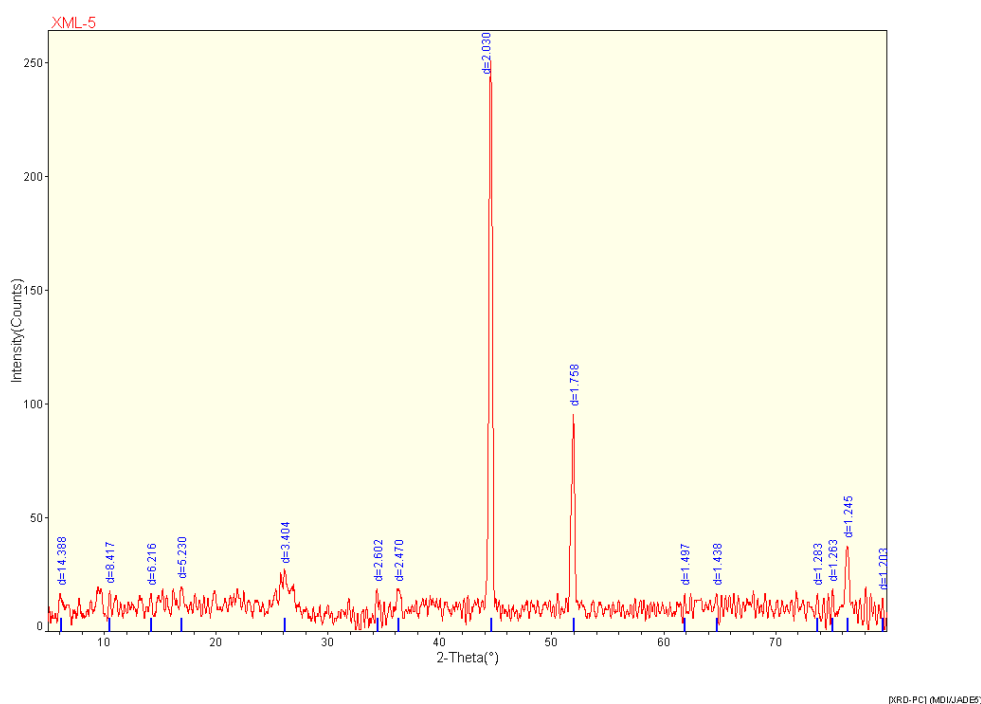


Figure 4: XRD pattern of MWCNT obtained at 900°C from Castor oil using Co as catalyst

Use of Co as catalyst at the same temperature as used for Ni i.e. 900°C, in presence of Ar produced a mixture of coiled CNT and CNB, as can be seen in HRSEM micrograph (Figure – 3A). The CNTs were confirmed to have multi walled morphology by TEM (Figure – 3B). The carbon nano spheres are having a diameter of 100 to 500 nm whereas MWCNTs have outer diameter of 34 – 37%. (Figure – 3A).

**XRD Analysis** – of both CNB and CNT was done. One representative typical XRD of CNT and CNB is presented in figure - 4. All of them show a diffraction peak at 26° {002}, which is designated to graphitic carbon. Moreover, peak at 44° is also seen in all three graphs that is known to be associated with carbon {111}. A small peak present at 78°

of XRD of castor oil depicts the presence of the Silica, which could be due to the boat in which the catalyst was placed.

**Raman Spectrum Analysis-** Raman spectra of purified CNB and CNTs was taken. Both show D band as well as G band thus confirming its graphitic nature (Fig 5).

Raman spectroscopy is used to differentiate between graphite, MWCNT, SWCNT and layers. The Raman spectrum of each sample shows two typical peaks of MWCNT one at around  $1562\text{ cm}^{-1}$  and the other around  $1318\text{ cm}^{-1}$ ; which corresponds to the typical Raman peaks of graphitic carbon and defects in graphitic carbon respectively. The peak at  $1562\text{ cm}^{-1}$  is attributed to the Raman active  $E_{2g}$  in plane vibrational mode and is related to the vibration of  $sp^2$  bonded carbon atoms in a two dimensional hexagonal lattice. The peak at  $1318\text{ cm}^{-1}$  is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite. The CNT synthesized from Castor oil shows stronger D band and comparatively very weak G band and it has an intense peak at 500 corresponding to silicon. XRD pattern of CNT from castor oil has also shown a small peak at  $78^\circ$  and a suggested above it could be due to the boat in which the catalyst was placed.

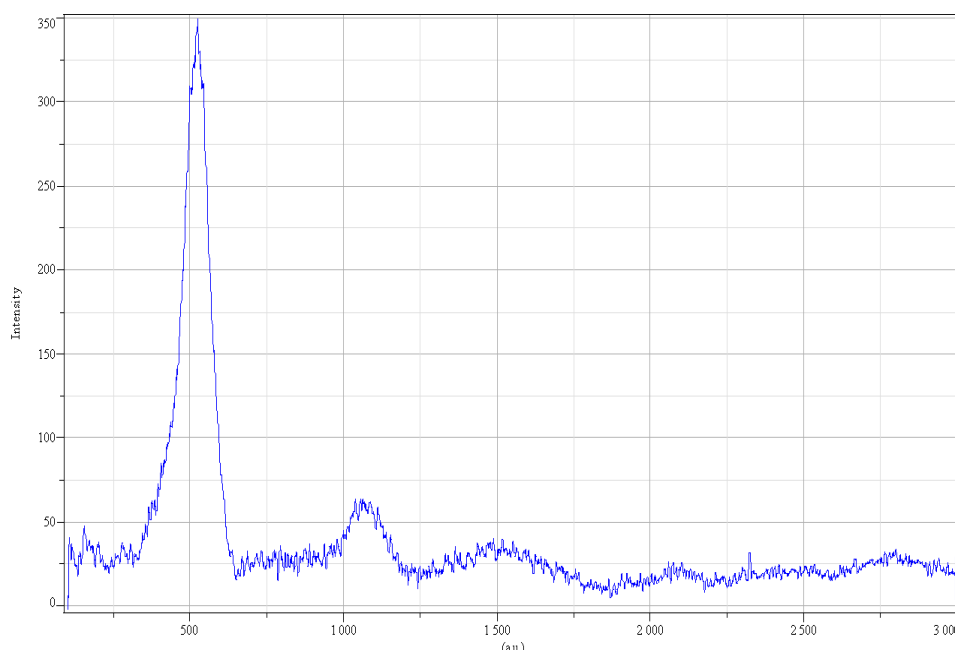


Figure 5: Raman spectroscopic analysis of MWCNT obtained at  $900^\circ\text{C}$  from Castor oil using Co as catalyst

**Surface Area of CNB & CNT & Arsenic Uptake-** whether CNMs were synthesized using Ni or Co, the surface area was calculated to be the same for both of them i.e.  $30.88\text{ m}^2/\text{gm}$ . But the % arsenic adsorbed by them varied. CNM synthesized using Ni were mostly spherical and could adsorb only 43% arsenic. Whereas, under same conditions CNTs (and some CNBs) synthesized using Co adsorbed as much as 49% arsenic. This variation in uptake capacity can be attributed to different morphology of CNM. It could be that CNTs having dangling bonds on the surface can uptake more arsenic.

Percentage of sorption was calculated using the relationship:

$$\% \text{ Sorption} = \frac{A_i - A_f}{A_f} \times 100$$

Where  $A_i$  and  $A_f$  are initial (inlet) and final (outlet or effluent) concentrations of arsenic and then the amount of sorption per unit mass of sorbent ( $x/m$ ) was calculated using the relationship:

$$\frac{X}{m} = \frac{A_i - A_f}{A_f} \times \frac{V}{m}$$

Where  $V$  is the volume of adsorbate ( $\text{cm}^3$ ) and  $m$  is the amount of adsorbent(g). .

The adsorption of heavy metals by CNT has been studied by Li's group [13, 14]. They found that CNTs show exceptional adsorption capability and high adsorption efficiency for lead removal from water. The adsorption is significantly influenced by the pH value of the solution and the CNT's surface status

#### Acknowledgements

Authors wish to acknowledge the support by authorities of N.Shankaran Nair research Centre for Nanotechnology & Bionanotechnology

#### REFERENCES

- [1] Jaybhaye, S.; Maheshwar Sharon, Singh, L. N.; *Madhuri Sharon SRIMNC*, **2006**, 36(1)37
- [2] Maheshwar Sharon; Mukul .; Kichambre,P.D.; Ando, Y.; Xinluo Z. hao, *Diamond Films and Technology*, **1998**, 8, 143
- [3] Maheshwar Sharon, Mukhopadhyay, K.; Krishna, K.M. *Phys. Rev. Lett.* **1994**,72(20), 3182
- [4] Afre, R.A.; Soga, T.; Jimbo, T.; Mukul K.; Ando, Y.; Maheshwar Sharon, *Chem. Phys. Letts.* **2005**, 414(1-3),6
- [5] Ogunniyi D. S.; **2006**, *Bioresource Technology*, 97, pp 1087-1091
- [6] Fonesseca A.; Harnadi K.; Nagy J. B.; Bernaetrs D.; Lucas A.A.; **1996**, *J. Mol. Cat. A. Chem.*; 07, pp 159-68.
- [7] Kohnhorst A, Allan L, Pokethitiyoke P, Anyapo S (**2002**) Sustainable environmental sanitation and water services. 28th WEDC Conference, Kolkata, India
- [8] Smedley PL, Kinniburgh DG (**2002**) *Appl Geochem* 17:517–568
- [9] Tatken RL, Lewis RJ (**1983**) Registry of toxic effects of chemicals substances. US Department of Health and Human Services, Cincinnati, OH
- [10] Deveral SJ, Millard SP (**1988**) *Environ SciTechnol* 22:697-702.doi:10.1021/es00171a013
- [11] Sandbery GR, Alken IK, Woolson EA (**1975**) Arsenical pesticides.Americal Chemical Society, Washington, DC
- [12] S. Bhardwaj, A. Gupta, S. Pandey, G. Oza, S. Kawale, N. Mishra, Madhuri Sharon, A. Durve, M. Thandu,. Maheshwar Sharon & C. Cepek; *Methylene Blue Adsorption Isotherm For Carbon Nano Material Synthesized from Menthol*” in V. Rajendran, K. Hillbr&. K. Saminathan & K.E. Geskeler Ed. Synthesis & Characterization of Nano structured Materials; 399 -404, Macmillan Publisher India Ltd. **2010**
- [13] Li, Y.H., S.G. Wang, J.Q. Wei, X.F. Zhang, C.L. Xu, Z.K. Luan, D.H. Wu, and B.Q.Wei, *Chemical Physics Letters*, (**2002**) 357(3-4): p.263-266.
- [14] Li, Q.L., D.X. Yuan, and Q.M. Lin, *Journal of Chromatography A*, **2004**. 1026(1-2): p. 283-288.