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A Comparative Study of Carbon Nano Materials Synthesized from Karanja-Oil, Using Metal and Mixed Metal Catalysts

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ABSTRACT

Karanja oil, on pyrolysis using different catalysts at different temperatures in inert atmosphere produces different types of Carbon Nano Materials (CNM). The Chemical Vapor Deposition (CVD) technique was used for synthesis of carbon nano materials through pyrolysis. In the present work two nano metal catalysts i.e. Nickel (Ni) and Zinc (Zn) (Copper) were used. The morphology of CNMs was examined by scanning electron-microscopy, Raman spectra and XRD analysis. The CNM morphology was affected by the catalysts and other parameters of CVD process. In presence of Ni as catalyst, formation of clusters of carbon nano beads (CNB) occurred whereas carbon nano tubes (CNTs) were produced when Zn was used as a catalyst. Most of the CNTs grew according to base growth mechanism. XRD pattern of CNB synthesized using Ni and Zn as catalyst suggested that the CNMs formed were mostly graphitic and almost negligible amorphous carbon was also present. Raman spectrum of both CNT & CNBs synthesized using Ni and Zn as catalyst also confirms its graphitic nature. However when mixed metal alloy were used the Ni + Zn alloy showed tubular carbon in which alloy was entrapped, where as Ni + Cu alloy showed coiled tubular carbon. XRD of these carbons showed. Maximum yield of CNM was obtained when Ni was used as catalyst.

Key-words: Chemical Vapor Deposition, CVD, Carbon Nano Materials, CNM, CNB, CNT, Catalyst, Karanja oil

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INTRODUCTION

The discovery of carbon nano tubes (CNT) by Iijima in 1991 started the onset of activity in this novel class of materials [1, 2]. Carbon based nano structured materials continues to attract a disproportionate share of research effort, because of their unique physical properties which span a wide range from structural to electronic. Several carbon species such as methane, acetylene, benzene, xylene etc. have been used as a carbon feedstock to synthesize carbon nano materials. The carbon precursors are related to fossil fuels which may not be sufficiently available in near future. So in order to develop a more competitive carbon nano material (CNMs), it is necessary to consider developing carbonaceous materials from the natural resource. Sharon's group[3-6] are the first research group who explored the possibility of using plants (bagass, cotton, tea leaves etc) and plant derived materials (camphor, terpene, various plant oils etc) as precursors for the synthesis of carbon nano materials by chemical vapor deposition (CVD) method. The idea being that these precursors are renewable & cheap and have the potential to be the green alternative for industrial scale production of carbon nano materials.

Considering these aspects, for the present study we selected Karanja oil (*Pongamia glabra*) a non-edible oil, as precursor to synthesize CMN using CVD technique. CVD is a simple and economic technique for synthesizing CNM at relatively low temperature and ambient pressure. It is a versatile technique that can harness a variety of precursors in any state (solid, liquid or gas), enables the use of various substrates and allows CNM growth in variety of forms such as powder, thin or thick film, aligned, straight or coiled nano tubes or nano fibres as well as nano beads. It also offers better control over growth parameters. This technique has a great ability to promote growth of a layer of CNMs over the catalysts. To catalyze the growth of CNMs; nano-meter sized transition metals such as Ni and Zn were used because they have:

1. High solubility of carbon in these metals at high temperature.
2. High carbon diffusion rate in these metals.
3. High melting point and low equilibrium- vapor pressure of these metals offer wide temperature window of CVD for a wide range of carbon precursors.
4. Also they have stronger adhesion with the growing CNMs and hence are more efficient in forming high-curvature CNTs.

MATERIALS AND METHODS

Karanja Oil- Karanja is a well known novel Indian medicinal plant [7]. Karanja is a drought tolerant plant that grows in arid and semi- arid regions in the tropical and sub-tropical areas (Fig. – 1). The seeds of this plant are rich in oil that is composed mostly of Oleic acids (Table – 1). The oil, which is brownish in color has boiling point of >100^{0}C. Oil was procured from the local market.

Elemental Analysis Karanja Oil –was done to know the percentage carbon, hydrogen and nitrogen content of the oil.

Figure 1: Parts of Karanja tree and seeds

Table – 1: Fatty acid composition of Karanja oil

Name of Fatty acid	**% Content**
Dosocasnoic acid	4.45 %
Eicosenoic acid	1.35 %
Linolenic acid	16.64 %
Oleic acid	**51.59 %**
Palmitic acid	11.65 %
Stearic acid	7.5 %
Tatracosanoic acid	1.09 %
Other fatty acids	5.68%

Preparation of transition metal catalyst:

Nickel - Crystal metal powder of Nickel was synthesized by urea decomposition method where known amount of Ni $(NO_3)_2$ was mixed with urea in proportion of 1:4 by weight, grinded and then dissolved in distilled water. The solution was then stirred at room temperature for 10-15 min in order to ensure that all the particles of metal salts are completely dissolved. The mixture was then dried and heated in muffle furnace for about 3 hrs, followed by calcinations in air at 600^{0}C for 3 hrs.

The resulting product was pure metal oxide i.e. Nickel oxide. The metal oxide was then reduced in the atmosphere of hydrogen gas using a horizontal furnace at 500^0C for 3 hrs.

Following reaction took place during the oxidation & reduction processes:

$Ni(NO_3)_2 6H_2O + (NH_3)_2.CO \rightarrow$ Ni-Oxide $+ 4 CO_2 + NH_3$

$NiO + H_2 \rightarrow$ Ni- nano particles $+ H_2O$

Zinc – Known amount of $Zn(NO_3)_2$ was mixed with urea in proportion of 1:4 by weight, grinded and then dissolved in distilled water. The solution was then stirred at room temperature for 10-15 min in order to ensure that all the particles of metal salts are completely dissolved. The mixture was then dried and heated in muffle furnace for about 3 hrs, followed by calcinations in air at 600^0C for 3 hrs.

The resulting product was pure metal oxides i. e. Zinc oxide and Nickel oxide. The metal oxides were then reduced in the atmosphere of hydrogen gas using a horizontal furnace at 500^0C for 3 hrs.

Following reaction took place during the oxidation & reduction processes:

$Zn(NO_3)_2. 6H_2O + (NH_3)_2.CO \rightarrow$ Zn-Oxide $+ 4 CO_2 + NH_3$

$ZnO + H_2 \rightarrow$ Zn- nano particles $+ H_2O$

Alloy (Mixed Metal) **-** The mixed metals or alloys used in the present study are the mixture of two metals of transition elements i.e. of copper, zinc and nickel. The prepared alloys are nickel-zinc (Ni+Zn) and nickel- copper (Ni+ Cu).

The mixture of **Ni+ Zn** was also prepared by co- precipitation method, where the halides of both the metals were mixed together in 1:1 proportion and then NH4OH added to convert the halides into hydroxides of metals. The precipitate formed were filtered and dried at about 100^0 C and then heated at 500^0C in muffle furnace for about 3 hrs followed by calcination in air at 600^0C for 3 hrs. The resulting product was oxides of mixed metals which were then reduced in hydrogen atmosphere using horizontal furnace at 800^0C for 3 hrs.

$NiCl_2 + ZnCl_2 + NH_4OH \rightarrow$ Ni-Zn hydroxides $+ NH_4Cl$

Ni-Zn hydroxides → dried → Ni-Zn-Oxides

Ni-Zn-Oxides + H2 → Ni-Zn nanoparticles

Similarly, **Ni + Cu** was also prepared by co- precipitation method.

Preparation of Carbon Nano Materials: Karanja oil was selected as a precursor for the preparation of CNMs by CVD method. The CVD furnace was composed of two parts i.e. (i) oil vaporizing zone and (ii) pyrolyzing zone (Fig.- 1). A cylindrical quartz tube was inserted through both the furnaces 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 gas bubbler, through which the excess gas was allowed to escape. The positioning of the precursor containing boat and catalyst containing boat was placed in the center of vaporizing furnace and pyrolyzing furnace respectively, so that they could get uniform temperature. After flushing the quartz tube with a carrier gas i.e. argon, hydrogen or nitrogen, the temperature of vaporizing furnace was adjusted according to the boiling point of the oil whereas the pyrolyzing furnace was heated at different test temperatures (500, 700 and 900^0C) for 3 hrs. After completion of process, the carbon nano materials was collected and purified to remove traces of catalyst and amorphous carbon; by acid treatment. Yield of CNM was recorded prior to as well as after purification.

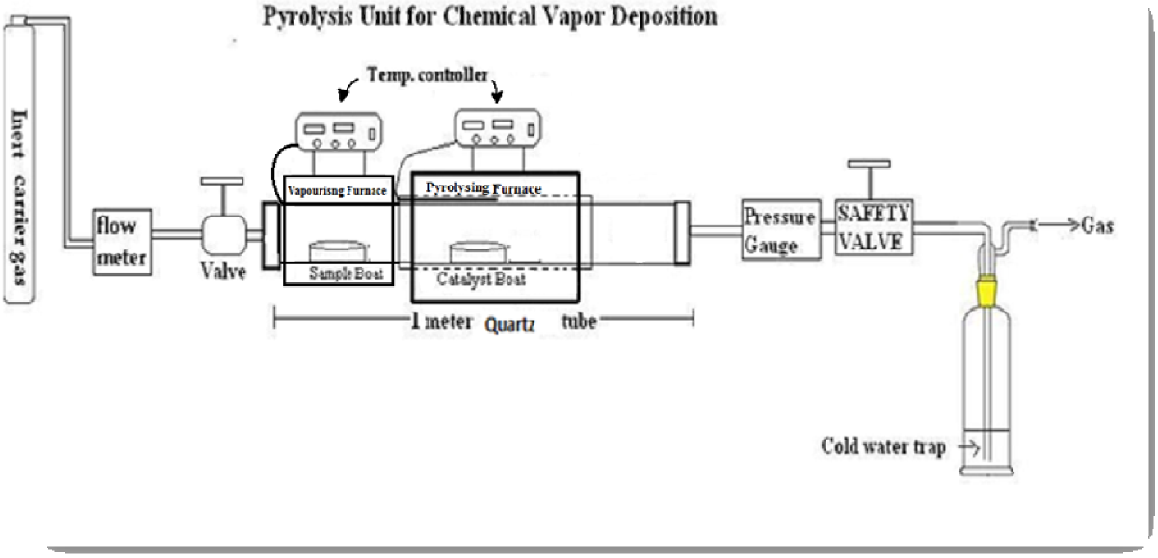


Fig. 2: Schematic diagram of chemical vapor deposition set up.

***Purification of Carbon Nano Materials*:**
The recovered soot material contains a lot of impurities like graphite sheets, amorphous carbon, metal catalyst etc. These impurities are needed to be removed by acid treatment which involves an initial exposure of metal surface to oxidation. As-synthesized soot materials were first soaked in 100ml of 10M HCl in 250ml beaker and heated at 80^{0}C for 20 min. Then they were kept at room temperature for 24 hrs and filtered. It was washing with distilled water for at least five times and finally rinsed with acetone to remove the traces of water and then dried in oven at 120^{0}C for 24 hrs.

Characterization of Carbon Nano Material:
The morphology of as-synthesized and purified carbon nanomaterials as well as catalysts (Ni, Zn and Co) were carried out by Scanning Electronic Microscope (SEM) and HRSEM using a Hitachi (S-4700) SEM by placing the as-prepared samples on conductive carbon tape.

The XRD of CNM synthesized from karanja oil was taken by the Phillips Panalytical Xpert. For this purpose Kα of Cu (0.154056 Å) was used. XRD of carbon nanomaterials was performed with a powder X-ray diffractometer with CuKα source to calculate the crystallographic parameters.

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

RESULTS AND DISCUSSION

***Catalyst* –** Since the transition elements form carbide when they interact with carbon and nano size of these catalysts provide a large surface area for the reactants to be adsorbed and thus come closer to one another for the reaction to occur readily. Hence, these elements act as a catalyst for the production of CNMs. In the present study nickel and zinc were used as catalysts. Moreover, 2 alloys of Ni (Ni+ Zn and Ni+ Cu) were also used. It is their size that helps in orchestrating the shape and size of the CNMs. The SEM micrograph of synthesized nano-metals shows the size and morphology of synthesized nanometals (Fig – 3).

Size of nano Ni ranged from 50 to 100 nm with different shapes viz. circular, rod like and irregular; all having various stages of development (Fig 2a). Zinc shows various stages of formation of spherical structure (Fig 2b) from tubular or elongated structures with the bead size in the range of 500 to 1000 nm.
Both the alloys used as catalyst, show (2c & 2d) mixture of various shapes and sizes.

Impact of catalyst on the yield of CNM: The elemental analysis of Karanja oil (Table – 1) shows presence of 76.66% carbon. Karanja oil in presence of argon gas at 700^{0}C with the help of various nano catalyst like Zn, Ni, Ni + Zn and Ni + Cu gives different amount of carbon nano materials.

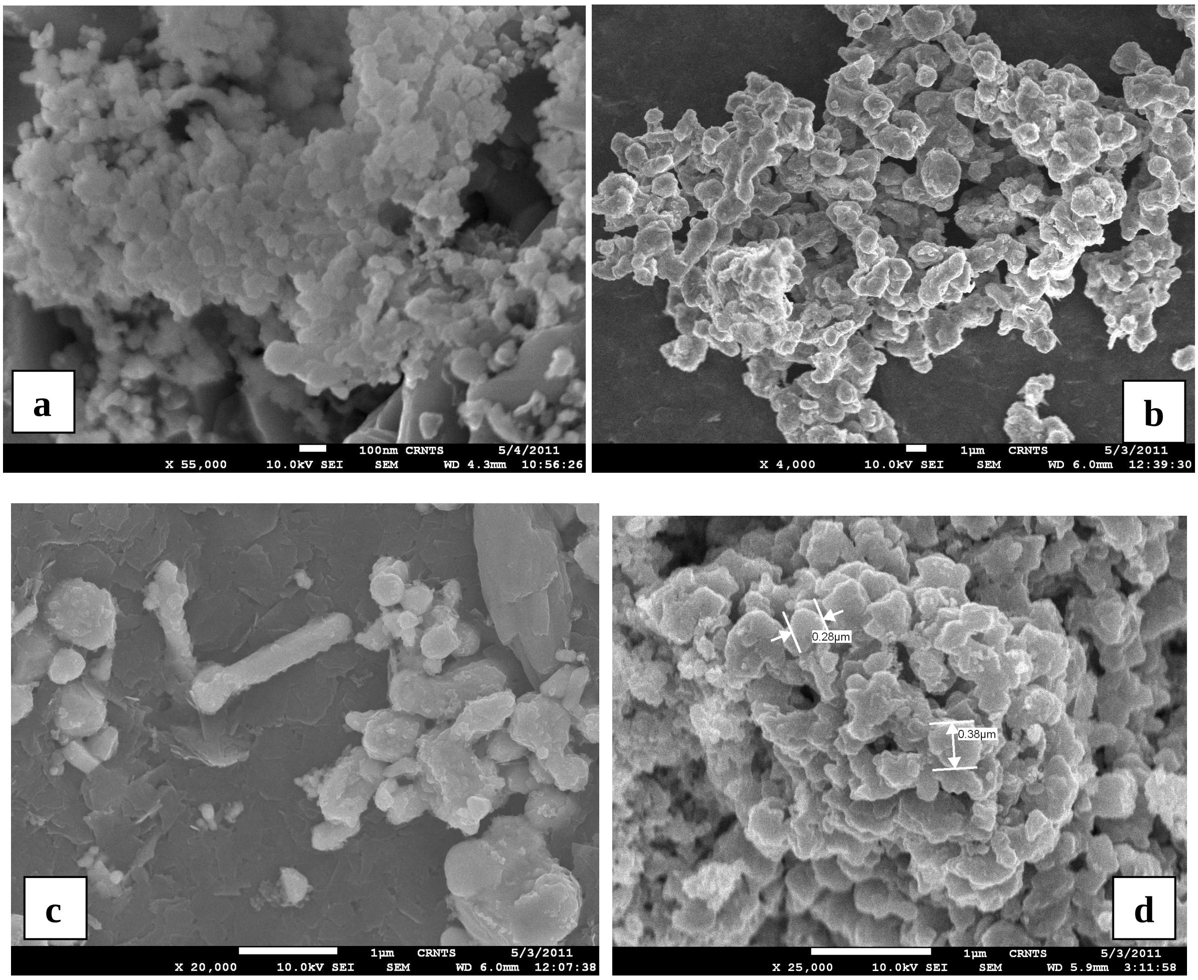


Fig.-3: SEM of nano-metal catalysts (Ni), (b) Zn, (c) Ni + Zn alloy and (d) Ni + Cu alloy; synthesized by urea decomposition method (used for synthesis of CNM from Karanja oil)

Table - 2: Elemental composition of Karanja oils

OIL	% of C	% of H	% of N	% of O
Karanja oil	**76.686**	9.995	1.005	12.313

The yield of carbon was recorded under different experimental conditions. As shown in Table-2 maximum yield (45.60%) was obtained when Ni was used as catalyst. Rest of the carbon might have evaporated as gas or remained as complex carbon residue. It must be mentioned here that Ni nanoparticles were the smallest of the three synthesized nano metal catalysts used, which might have resulted in higher yield. Ni has been successfully used for synthesis of carbon nano materials [8, 9,10]

Use of Zn as catalyst yielded minimum amount of carbon nano tubes (13.7%). However, addition of Ni to Zn slightly increased the carbon produced to 15.49 %. Ni along with Cu as could produce little higher amount. Therefore, it can be concluded that Ni is better catalyst for the production of CNM from karanja oil by CVD process. Formation of CNM is due to the catalytic decomposition of karanja oil at 700^{0}C in an inert atmosphere of Argon gas.

Table.-3: Impact of catalyst on yield of CNM from karanja oil

S. N.	Catalysts used	% yield of nano carbon	Morphology of nano carbon
1	Ni	45.69 %	Carbon Nano Beads
2	Zn	13.70 %	Coiled Carbon Nano Tubes
3	NI + Zn	15.49 %	Tubular Carbon entrapping Alloy
4	Ni + Cu	27.04 %	Coiled Carbon Nano Tubes

It must be mentioned here that the exact role of the catalyst in the mechanism of growth of CNT is still controversial. Catalyst has been shown to be necessary for the growth of SWCNT, though growth of SWCNT without catalyst is also reported [11.12.13.14,15]. One of the proposed explanations for the growth of SWCNT during CVD method suggests the adsorption and decomposition of the hydrocarbon source into carbon and hydrogen on the surface of the catalyst. The carbon atoms dissolve in the metal catalyst forming metal-carbon solution. When the solution becomes supersaturated with carbon, precipitation of crystalline tubular carbon solids in sp^2 structure take place [16, 17, 18,19,20]. Precipitation of carbon does not take place at the apex of the catalyst sphere, accounting for the hollowness of the tube. Due to absence of dangling bonds and low energy, formation of tubular structure occurs.

SEM observation of Carbon Nano Material: SEM micrographs obtained using Ni and Zn nano catalyst, showed differential response i.e. use of Ni caused formation of beads like structures beads like structures (Figure 3a) whereas Zn and Ni + Cu alloy induced synthesis of coiled nano tubes (Figure 3b and 3d). Moreover, the SEM images show that the synthesized carbon nano materials have a smooth surface without amorphous carbon deposits.

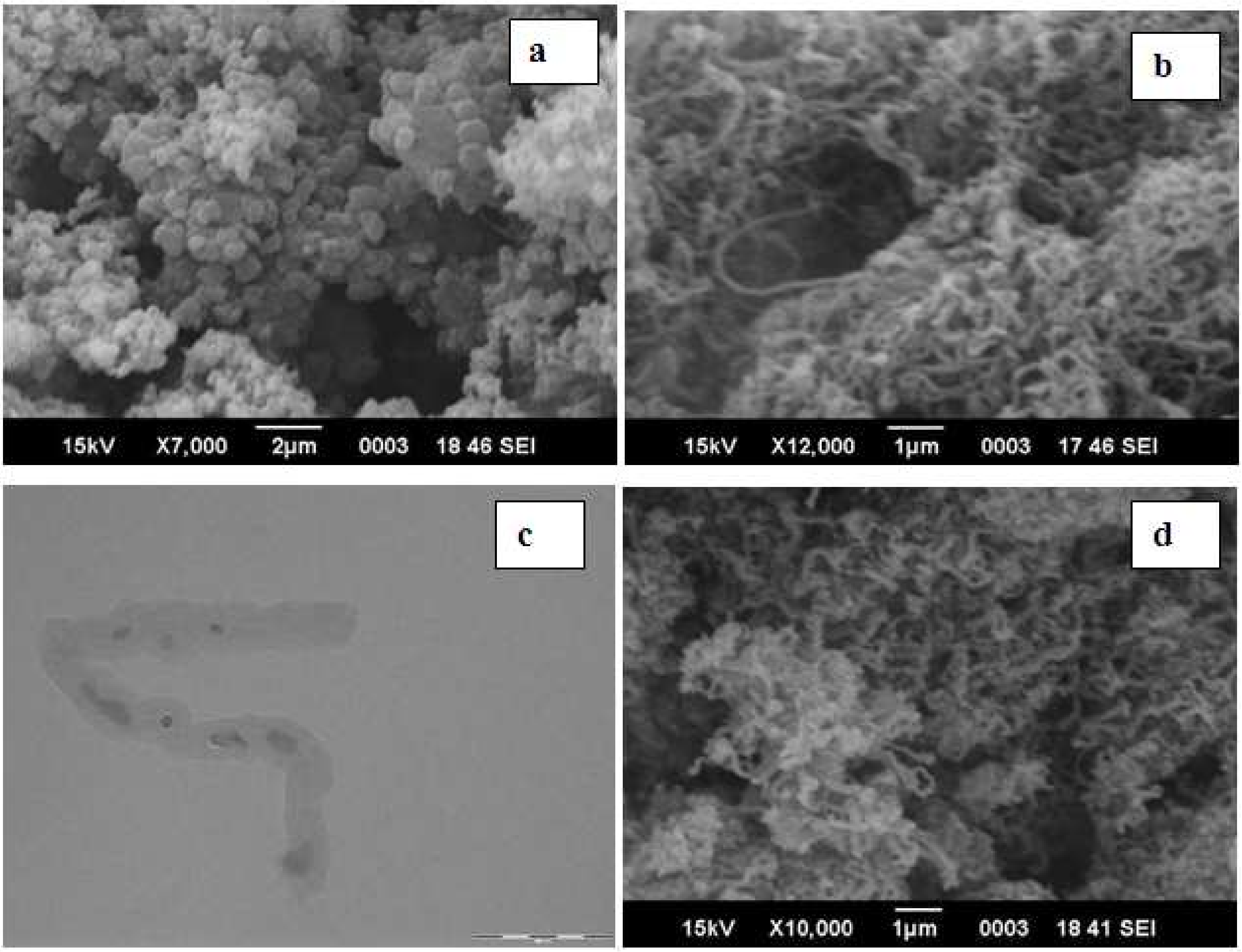
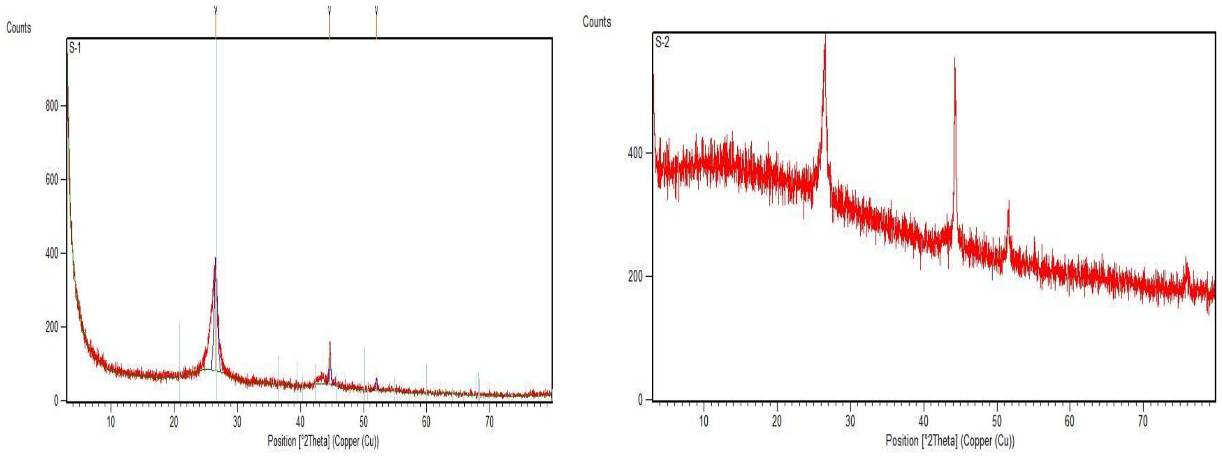


Figure - 4: SEM micrograph of Carbon synthesized using (a) Ni as catalyst showing carbon nano beads (b) Zn as catalyst showing coiled carbon nano tubes (c) Ni + Zn alloy as catalyst showing tubular structure in which alloy particles are entrapped and (d) Ni + Cu alloy as catalyst showing carbon nano tubes

XRD Analysis of CNM: The XRD of CNT and CNB synthesized using Zn and Ni catalyst respectively are shown in figure 4A & B. The characteristic planes for each carbon nano materials are shown in the spectra.

XRD pattern of CNB synthesized using Ni as catalyst (Fig 4A) shows peaks at 26.4^0, 44^0, 52^0 and 78^0 for (002), (111), (200) and (311) planes respectively. The most intense peaks appears close to (002), (111) and (200) for graphitic carbon and almost negligible amorphous carbon. Whereas The XRD pattern of CNTs synthesized using Zn as catalyst (Fig. 4B) shows peaks at 26.4^0, 44^0 and 520 for (002), (111) and (200) planes respectively



A **B**

Figure–5: XRD pattern of (A) CNBs synthesized from Karanja oil using Ni as catalyst and (B) CNTs synthesized from Karanja oil using Zn as catalyst

CONCLUSION

From the present study, it can be concluded that the single metal catalyst used during chemical vapor deposition process gives better yield of carbon nano materials as compared to mixed metal catalysts. Ni was found to be better catalyst than Zn so far as the yield of CNM is concerned. However, use of Zn as catalyst induced synthesis of synthesis of CNTs whereas when Ni was used as catalyst formation of carbon nano beads took place.. XRD report confirms it to be of graphitic nature.

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