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Optimization of process parameters for carbon nanotubes synthesis using Green precursors

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Abstract: It is necessary to optimize the process parameters for multi-walled carbon nanotubes (MWCNTs) synthesis to get better yield. This needs to be done for each precursor type used for the synthesis of MWCNTs. To achieve the twin objective of physical optimization of the process parameters for better yield for each precursor type poses almost an impossible task because of time and cost involved in the process. However, statistical technique such as Taguchi robust method is expected to be an efficient and effective tool to do this. The process needs to be optimized for each of the precursors selected for MWCNT synthesis for higher yield and acceptable relative quality conforming to requirement of applications. In the present work, a few parameters such as temperature, catalyst and flow rate that influence the yield and quality of MWCNT synthesized from three green precursors viz. *Azadirachta indica*, *Sesamum indica* and *Mesua ferrea* essential oil have been identified.

Keywords: Carbon nanotube, MWCNT, Essential oil, Green precursors, Taguchi.

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1. Introduction: Carbon nanotubes (CNTs) have evolved into one of the most intensively studied materials due to their unique combination of structure, topology, and dimensions. CNTs are therefore exploited through a wide range of potential application areas, such as nanoprobes, molecular reinforcements in composites, displays, sensors, energy-storage media, and molecular electronic devices **[1,2]**. CNT-related commercial activity has grown most substantially during the past decade and worldwide CNT production capacity has increased many folds **[2]**. It is also reported that chemical vapour deposition (CVD) technique is the dominant mode of high-volume CNT production and typically uses fluidized bed reactors that enable uniform gas diffusion and heat transfer to metal catalyst nanoparticles **[2]**. However, the yield and quality of CNTs depend on various process parameters like temperature of synthesis, flow rate of carrier gas and catalyst type **[3]**. Thus, it becomes very important to explore the optimum conditions for better yield and acceptable quality for synthesis of CNTs from various precursors.

Taguchi robust method was, hitherto, used by researchers to optimize the process parameters for wastewater treatment, CVD method for film deposition, carbon nanotube growth and optimization of catalyst formation conditions for synthesis of carbon nanotubes **[4-8]**. Taguchi method is a fractional factorial design which uses an orthogonal array that can significantly reduce the number of experiments and with analysis of variance (ANOVA) can estimate the effect of a factor on the characteristic properties. The variability is decisive for choosing the optimal condition [9]. Therefore, Taguchi robust method may be employed to optimize the process parameters and also to evaluate the effect of these parameters on the synthesis of MWCNTs from renewable plant precursors [10]. The present work is an endeavour to optimize the process parameters and to study the level of influence of each parameter on the yield and quality of MWCNT from plant based green precursors using taguchi robust technique.

2. Materials and method:

2.1 Materials:

The essential oil obtained from *Azadirachta indica*, *Sesamum indica* and *Mesua ferrea* were considered as green precursor for the synthesis of MWCNT. The essential oils are used as obtained from the seeds without further distillation.

2.2 Synthesis of catalysts:

Three metal oxides (viz. iron, cobalt and nickel) were synthesized using solution combustion method [11] with some modification. For synthesis, the combustion of redox mixture, iron nitrate was used as oxidizing reactant and urea as reducing fuel. Iron nitrates were mixed with urea in the ratio of 1:3 w/w. The appropriate ratio of iron nitrate and urea was dissolved in water (50% w/v) in a quartz crucible. The crucible containing the solution was kept for aging of 60 min at 80 ^{0} C inside an oven with limited supply of air. The samples after aging were directly put into a muffle furnace at 650 °C for calcination.

2.3 Synthesis of CNT using CVD technique:

CVD technique was used to synthesize MWCNTs using 25 ml of plant based precursor [12]. The process parameters were set as per the Taguchi orthogonal table, as discussed in the later section. Nitrogen (N2) gas as carrier gas flow was controlled by using a gas flow meter whereas the temperature was regulated using a PID controller attached to the CVD unit. After synthesis of CNT they were heated to 400 °C for an hour to remove amorphous carbon and weighed. The weight of catalyst was deducted to get the exact weight of CNT synthesized.

2.4. Taguchi robust method:

Taguchi method is a robust optimization method based on “Orthogonal Array” (OA) experiments, which is very useful in identifying and optimizing dominant process parameters with a minimum number of experiments [13, 14]. This method gives much reduced “variance” in the results. The OA provides a set of well balanced (minimum) experiments and has a set of combination of parameters’ levels [15]. For each experiment (which is a particular combination of the parameters) the signal-to-noise ratio (S/N), which is the logarithmic function of desired output; serves as objective function for optimization [16]. Taguchi technique can not only be used to optimize the parameters but also provides the effect of each parameter [17]. There are 3 types of signals-to-noise ratios (S/N ratio) for optimization as used by researchers for optimizing the process parameters - smaller-the-better, larger the better and nominal-the-best [14, 17, 18].

i) Smaller-the-better

$$\eta = -10 \log [\text{mean of sum of squares of measured data}] \qquad (1)$$

This is usually the chosen S/N ratio for all undesirable characteristics like "defects" etc. for which the ideal value is zero. Also, when an ideal value is finite and its maximum or minimum value is defined, then the difference between measured data and ideal value is expected to be as small as possible. The generic form of S/N ratio then becomes,

$$\eta = -10 \log [\text{mean of sum of squares of (measured – ideal)}] \quad (2)$$

$$\eta = -10\log \frac{1}{n} \sum_i^n (y_i^2) \quad (3)$$

where, y_i is the signal (reaction rate) and n is the number of repetitions in each experiment. If "defect" in the CNT is taken as the parameter then this S/N ratio may be used. But it is not the case in the present work.

ii) Larger-the-better

$$\eta = -10 \log [\text{mean of sum squares of reciprocal of measured data}] \quad (4)$$

$$\eta = -\log \frac{1}{n} \sum_i^n (1/y_i^2) \quad (5)$$

This case may to obtained considering *smaller-the better* and taking reciprocals of measured data and followed by calculation of S/N ratio as in the *smaller-the-better* case. As the quality of MWCNT has to be higher under optimum condition, this S/N ratio is used in the present chapter.

iii) Nominal-the-best

$$\eta = 10\log \left[\frac{\text{Square of mean}}{\text{Variance}}\right] \quad (6)$$

This case arises when a specified value is desired, meaning that neither a smaller nor a larger value is desirable. Taguchi method can be used to obtain effect of parameter level (deviation it causes from overall mean of the signal). To determine the effect of each parameter level (m_i), average value of S/N ratios are calculated using analysis of mean (ANOM). For this calculation, the S/N ratios of experiments with corresponding parameter levels are employed **[19]**. The parameters effects (or factor effect), i.e. the contribution of each experimental parameter to the reaction rate are calculated by the analysis of variance (ANOVA). This is done by summing the squares (SoS) of variance of all levels of a given parameters which then is normalized with respect to the degrees of freedom (DoF) of the corresponding parameters (DoF = number of parameter levels - 1).

$$m_i = \frac{1}{N_i} \sum \eta \quad (7)$$

where, N_i is the number of experiments conducted with the same parameter levels. Sum of squares (SoS) of variances for all levels for a given parameter are obtained using equation 8. This term is divided by degree of freedom (DoF) of corresponding parameter to obtain factor effects of various experimental parameters given by equation 9.

$$Sum\ of\ Squares\ (SoS) = \sum_{i=1}^{i=j} (N_i (m_i - \langle m_i \rangle)^2 \quad (8)$$

where, $\langle m_i \rangle$ is the average of m_i's for a given parameter and the coefficient N_i represents the number of times the experiment is conducted with the same factor level.

$$\text{Factor effect} = \frac{\text{SoS}}{\text{DoF X } \sum \frac{\text{SoS}}{\text{DoF}}} \quad (9)$$

Finally, it is used in data analysis and prediction of optimum results **[13, 14, 20]**. Again, the primary aim of the Taguchi experiments - to minimize variations in output even though noise is present in the process- is achieved by getting improved linearity in the input/output relationship.

2.5. Processes parameters to be optimized:

As discussed by many researchers the quality and quantity of MWCNT synthesized mostly depends on the synthesis conditions for the conventional non-renewable precursors. The physical parameter during MWCNT synthesis for a particular precursor depends mostly on temperature of synthesis, catalyst type and flow rate of carrier gas. Thus, these physical parameters are to be optimized for higher yield. It was envisaged to investigate the influence of temperature, catalyst type, flow rate and different precursors for the synthesis of MWCNT using an L9 orthogonal array, where the inputs could be tested at three levels. It was further assumed that no interaction exists between the factors considered in the experiments. The parameters for the synthesis of MWCNTs are shown in Table 1.

Table (1): Parameters to be optimized for better yield of MWCNT

Parameter	Level 1	Level 2	Level 3
Temperature (^oC)	750	875	1000
Catalyst	Iron oxide	Cobalt oxide	Nickel oxide
Flow rate (cc/min)	150	175	200

2.6. Design of L9 experiments:

The L9 table (experiment L1-L9) was designed for optimization of the process parameters shown in Table 1. The parameter levels for the L9 experiments were designed as per Taguchi robust technique.

Larger-the-better type of objective function for getting maximum yield of MWCNTs from the plant precursors is used hence the equation 7 was used for calculating S/N ratio.

3. Results and discussion:

3.1. L9 experiments:

The nine experiments were performed and controlled on the basis of Taguchi L9 table as shown in Table 2. S/N ratio, which determines the success of an experiment for each experimental yield, was obtained using equation 7. Table 2 also displays the experimental parameter matrix and corresponding S/N ratios of MWCNT synthesis.

The Figure (1) shows the TEM micrographs of MWCNTs obtained in L9 experiments, L1-L3 shows the TEM micrograph of MWCNTs synthesized using *Azadirachta indica* oil. The MWCNTs are found to have a diameter distribution of 50-60 nm, 100-120 nm and 90-100 nm at the synthesis conditions L1, L2 and L3 respectively. The MWCNTs synthesized using *Sesamum indicum* oil is shown in L4-L6, and has a diameter distribution of 100-120 nm, 90-100 nm and 80-90 nm for L4, L5 and L6, respectively. The L7-L9 shows the TEM micrographs of MWCNT obtained from *Mesua ferrea* oil. The diameter distribution for the MWCNTs synthesized at different conditions are 80-110 nm, 80-90 nm and 70-90 nm for L7, L8 and L9, respectively.

Table 2: Taguchi L9 experiment showing the calculated S/N ratio obtained for each L9 experiment

Exp. No	Parameter Levels				Yield of CNT (g/25ml)	S/N (η)
	Precursor oil (Level 1)	Temperature (˚C) (Level 2)	Catalyst type (Level 3)	Flow rate of gas (cc/min) (Level 4)		
L1	*Azadirachta indica*	750	Iron oxide	150	3.2	1.01
L2	*Azadirachta indica*	875	Cobalt oxide	175	3.0	0.95
L3	*Azadirachta indica*	1000	Nickel oxide	200	1.8	0.51
L4	*Sesamum indicum*	750	Cobalt oxide	200	2.2	0.68
L5	*Sesamum indicum*	875	Nickel oxide	150	4.2	1.24
L6	*Sesamum indicum*	1000	Iron oxide	175	2.6	0.82
L7	*Mesua ferrea*	750	Nickel oxide	175	2.2	0.68
L8	*Mesua ferrea*	875	Iron oxide	200	3.4	1.06
L9	*Mesua ferrea*	1000	Cobalt oxide	150	3.2	1.01

The selected area diffraction (SAD) pattern obtained by TEM is shown in figure 2 for the Taguchi experiments, respectively. The diffuse halos in the SAD micrograph may be due to the amorphous carbon film on the grid. The prominent sharp rings are due to the concentric graphitic planes of MWCNTs. The variation of crystallinity due to the variation of the process parameters could be seen. The results show that the best quality MWCNT samples were obtained under the condition L5 for the Taguchi experiment. Thus, it is evident that *Sesamum indicum* oil produces acceptable quality MWCNTs as can be seen in the TEM micrographs.

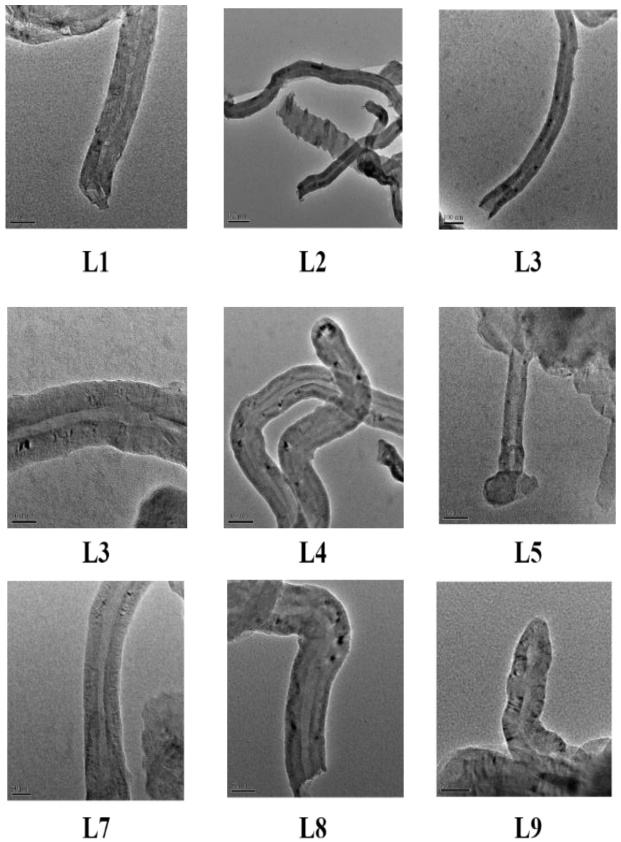

Figure (1): TEM micrographs for Taguchi L9 experiments.

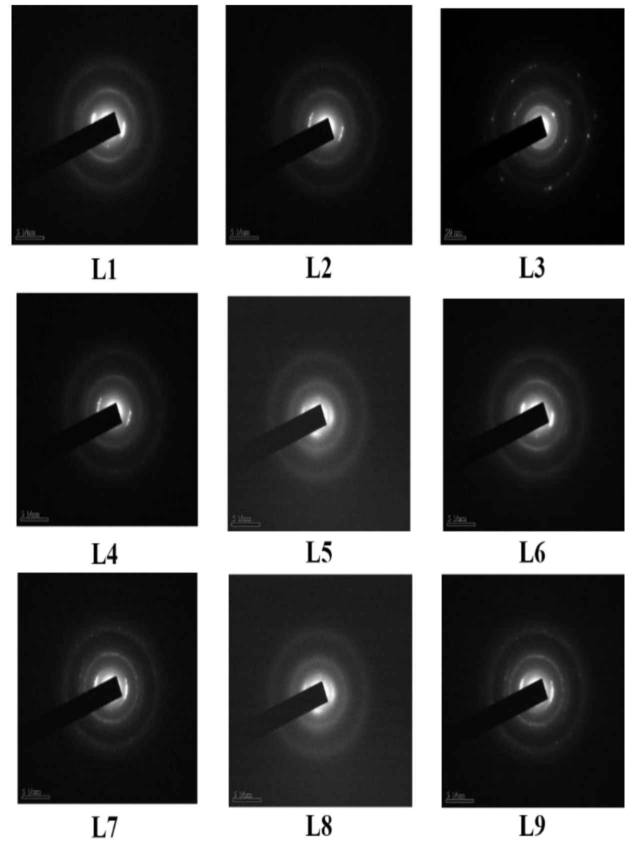

Figure (2): SAD pattern of synthesized MWCNTs corresponding to Taguchi.

3.2. Effect of each parameters:

According to the Taguchi method, the parameter levels leading to the maximum yield can be found by using the results given in Table 2 as calculated elsewhere **[19]**. SoS, DoF and Factor effects were obtained employing corresponding equations 2, 3 and 4. The influence of each parameter for optimum yield was obtained by ANOVA using equation 5. The contribution of each parameter level towards the S/N ratio (η) as obtained from ANOM is displayed along with it and shown in Table (3).

Table (2): Effect of parameters of synthesis of CNT for first and second Taguchi L9 experiment

Parameter	Taguchi L9 experiment		
	Level 1	Level 2	Level 3
Oil	0.825	0.920	0.919
Temperature (°C)	0.841	1.087	0.784
Catalyst	0.968	0.883	0.814
Flow rate	1.089	0.823	0.753

The effect of each parameter on yield was obtained using equation 7. The effect of the parameters for both the Taguhi L9 experiments is summarized in the Table (3). The results of Taguchi experiment with GREEN precursors reveals that the best temperature of synthesis to be 875 °C.

Iron oxide was found to be the most effective catalyst out of the catalysts chosen, whereas, a flow rate of 150 cc/min showed best result. Out of the precursors in the group *Sesamum indicum* oil gave the best yield.

From the Taguchi analysis, it was found that the temperature of synthesis, catalyst type and flow rate affects the yield of MWCNTs. Out of these four parameters optimized, temperature of synthesis and flow rate were found to have greater impact on the yield. The descending order of the effect of parameters for yield is found out to be Temperature>Flow rate>Catalyst>Precursor. MWCNTs synthesized were found to have acceptable quality as is evident from SAD analysis.

4. Conclusions:

This work presents the Taguchi optimization for the synthesis parameters of MWCNTs using plant based green precursors for better yield. Relative effects of four experimental parameters in determining the output of the experiments and their optimum factor levels are quantitatively obtained. All parameters are found to be contributing to the yield of MWCNTs, while temperature of synthesis and flow rate of carrier gas are found to be dominant parameters influencing the yield. The results also proved that the precursor type and catalyst have low impact on the yield as compared to synthesis temperature and flow rate of carrier gas. The CNT tubular structure is found to have minor defects when synthesized GREEN precursors. Thus, these precursors may be suitable for thin film fabrication devices like organic solar cells.

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