OPTIMIZATION OF PROCESS PARAMETERS FOR HIGHER SPECIFIC CAPACITANCE USING TAGUCHI METHOD

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Abstract: In the present research work to find out the best experimental condition to get high specific capacitance, the Taguchi method was used which involves reducing the variation in a process through robust design of experiments. The overall objective of the method is to produce high product result in minimum steps. From capacitance studies done by cyclic voltammetry technique for carbon materials obtained from plant precursors like bamboo fiber, rice straw and sugarcane bagasse; shows that highest specific capacitance is obtained with carbon obtained from rice straw. Taguchi optimization methodology predicted that pyrolysis of rice straw at 800^{o}C temperature for 2 hrs. duration and treatment of carbon with 50 % KOH solution gives the carbon of best quality for maximum capacitance and thereby for developing supercapacitor. It is also observed that, first major impactful parameter on the specific capacitance is the nature of the precursor and second is treatment with KOH; pyrolyzing time and temperature had very little impact.

Keywords: ***Taguchi, Parameter, Carbon, Capacitance, Supercapacitor***

I. INTRODUCTION

Dr. Taguchi of Nippan Telephones and Telegraph Company, Japan has developed a method based on "orthogonal array" experiments, which gives much reduced "variance" for the experiment with “optimum setting" of control parameter. Thus the marriage of design of experiments with optimization of control parameters to obtain the best result is achieved in the Taguchi method." Orthogonal arrays" (OA) provide a set of well balance (minimum) experiments and Signal to Noise ratios (S/N), which are log function of desired output, serve as objective function for optimization, helping data analysis and prediction of optimum results [1-3].

Taguchi method is a scientifically disciplined mechanism for evaluating and implementing improvements in products, processes, materials, equipment and facilities. These improvements are aim at improving the desired characteristics and simultaneously reducing the number of defects by studying the key variables controlling the process and optimizing the procedures or design to get the best results.

Optimization of quality characteristics using parameter design of the Taguchi method are summarized in various steps by Nian et al., 1999 [4]. Literature survey indicates that there are many attempts to synthesis of CNM from plant derived and plant based precursors such as camphor [5], turpentine oil [6] , tea leaves[7], cotton [8] etc.

In the present work, we have attempted to optimize the parameters and synthesis of porous carbon using fibrous plant materials. Different set of experiments were designed using four different parameters like Precursor, Temperature (^{0}C), Time (hour) and Chemical Treatment to synthesized carbon material. The purpose behind this was to get the carbon material which can give the best result of higher specific capacitance.

Thus number of variables required to get carbon material which could give the highest capacitance were more than 5-6. In order to carry out minimum number of experiments to get the optimum condition to get carbon material which could give the highest capacitance, Taguchi optimization methodology has been found to be most suitable. Under this statistical technique minimum number of experiments were carried out and got the advantage as if we have carried out all possible combinations.

II. EXPERIMENTAL

According to the carbonization experimental condition the variable parameters are precursors, temperature of pyrolysis, duration of pyrolysis and treatment. To optimize these conditions; Taguchi optimization technique was applied which is based on analysis of Variance (ANOVA) & Analysis of Mean (ANOM) [9-11].

Selection of three fibrous plant materials (Bamboo, Rice straw and Sugarcane bagasse) were decided to use as precursors for the synthesis of carbon material. L9 orthogonal matrix for these selected plant precursors was prepared [12]. Different parameters and different levels were selected as shown in Tables 1.

Table 1. Different parameters and its levels for L9 orthogonal matrix of fibrous plant precursors

Parameter	Level 1	Level 2	Level 3
A. Precursor	Bamboo	Rice straw	Sugarcane bagasse
B. Temperature (^{0}C)	700	800	900
C. Time (hour)	2	3	4
D. Treatment	None	50 % HCl	50 % KOH

For L9 orthogonal array matrix experiments the arrangement of different parameters and levels 1, 2 and 3 are as shown in following Tables 2.

Table 2. L9 orthogonal matrix table for fibrous plant precursors

Exp. No.	Precursor	Temp(°C)	Time (hrs.)	Treatment
L1	Bamboo	700	2	None
L2	Bamboo	800	3	50 % HCl
L3	Bamboo	900	4	50 % KOH
L4	Rice straw	700	3	50 % KOH
L5	Rice straw	800	4	None
L6	Rice straw	900	2	50 % HCl
L7	Sugarcane bagasse	700	4	50 % HCl
L8	Sugarcane bagasse	800	2	50 % KOH
L9	Sugarcane bagasse	900	3	None

The carbon materials from various fibrous materials as mentioned in Table 2 were synthesized using carbonization technique in a single zone furnace [13]. In furnace, unit weighed of precursor was taken in quartz boat and kept at centre of furnace. Carrier gas H_2 was allowed to flow into the quartz tube with a fixed flow rate (6ml/min) to make oxygen free atmosphere. After 15 min of flow, furnace was switched on to reach the desired temperature condition. At the end of the desired time the furnace was switched off and allowed to cool at room temperature. Carbon material formed inside the quartz boat was collected. Same way carbon materials from all selected precursors were prepared as per above orthogonal array of L9 experiments.

Treatment to synthesized carbon materials were given as per above orthogonal array of L9 experiments. To remove the metal impurities and amorphous nature of carbon from synthesized carbon, it was treated with 50 % HCl. The carbon material was soaked overnight in 50 % HCl solution and washed with distilled water to neural pH condition [14]. For KOH treatment carbon material was mixed with 50 % KOH solution and this mixture was kept for overnight in oven at 80°C temperature. Then after cooling it was filtered and carbon material containing KOH was kept inside the quartz tube of the pyrolysis unit and then heated to 750°C for a period of 1 hour with constant flow of argon. Then after cooling, this mixture was washed several times with distilled water through decantation to remove excess of free KOH present on surface of carbon. Finally it was dried in oven [15].

Measurement of capacitance of porous carbon materials synthesized from fibrous Plant Precursors (i.e. Bamboo fiber, Rice straw and Sugarcane bagasse) was done by two electrode method [16]. A cell of configuration "Carbon / 30 % KOH // 30 % KOH/ Carbon" was made for this purpose. Two Pt plates were used as current collector and whatman filter paper as separator.

To find out the potential window, CVs with scan rate using 20mV/s were recorded for all porous carbon materials synthesized from plant precursors. The potential windows were selected in which there were no prominent oxidation or reduction peaks. These potential windows were found to be slightly different with some carbon materials. Accordingly under the selected potential windows, CVs were measured at the scan rate of 20mV/s. Specific capacitance based on weight of carbon materials for each set of experiments were calculated.

III. RESULTS AND DISCUSSION

Capacitance measurement by cyclic voltammetry

As mentioned earlier; experiments were repeated three times as a requirement of Taguchi method. Measurement of specific capacitance for all synthesized carbon materials were done by cyclic voltammetry technique and results obtained are given as E, F and G in the table 3.

Table 3. Specific capacitance of carbon materials synthesized as per orthogonal array of L9 experiments

Exp. No.	Precursor	Temp (°C)	Time (Hrs.)	Treatment	Specific Capacitance (F/g)		
	A	B	C	D	E	F	G
L1	Bamboo	700	2	None	36.65	37.45	37.68
L2	Bamboo	800	3	50 % HCl	42	41.48	42.48
L3	Bamboo	900	4	50 % KOH	51.36	52	52.48
L4	Rice straw	700	3	50 % KOH	93.75	92.5	92.25
L5	Rice straw	800	4	None	72.88	73.28	73.25
L6	Rice straw	900	2	50 % HCl	84	84.5	85
L7	Sugarcane bagasse	700	4	50 % HCl	23.9	23.55	23.6
L8	Sugarcane bagasse	800	2	50 % KOH	32.69	33.43	33.55
L9	Sugarcane bagasse	900	3	None	18.35	18.45	19.15

Calculation of Signal to noise ratio

Details of the Taguchi optimization technique is discussed elsewhere [17] however; a brief description is given here. Basic unit of this methodology is the calculation of "signal to noise (S/N)" ratio. There are three major ways to use this methodology: (i) "smaller the better" i.e. when the interest is to find the best parameters to get the minimum amount of the desired product, (ii) "larger the better" i.e. when interest is to get the largest amount of the desired production (iii) "nominal the better" i.e. when interest is to get the exact amount of the desired product. Since there was interest in getting the high specific capacitance of carbon, "larger the better" technique has been used in the present work and the same is discussed here. The S/N ratio is calculated using the formula given for "larger the better" (Eq. 1).

$$S/N\,(dB) = -10\,Log_{10}\left(1/n\right)\sum 1/{y_i}^{2} \qquad (1)$$

Where "yi" is the mean response calculated as y =1/n Σyi and n is the number of experiments carried out under similar conditions. All the results obtained after calculation of S/N ratios by using equation 1 are shown in table 4.

Table 4. S/N ratios in orthogonal array of L9 experiments with measured specific capacitance of carbon material

Exp. No.	Precursor	Temp (ºC)	Time (Hrs.)	Treatment	Specific Capacitance (F/g)			S/N Ratio
	A	B	C	D	E	F	G	
L1	Bamboo	700	2	None	36.65	37.45	37.68	31.423
L2	Bamboo	800	3	50 % HCl	42	41.48	42.48	32.461
L3	Bamboo	900	4	50 % KOH	51.36	52	52.48	34.3101
L4	Rice straw	700	3	50 % KOH	93.75	92.5	92.25	39.3534
L5	Rice straw	800	4	None	72.88	73.28	73.25	37.2826
L6	Rice straw	900	2	50 % HCl	84	84.5	85	38.5368
L7	Sugarcane bagasse	700	4	50 % HCl	23.9	23.55	23.6	27.4883
L8	Sugarcane bagasse	800	2	50 % KOH	32.69	33.43	33.55	30.4271
L9	Sugarcane bagasse	900	3	None	18.35	18.45	19.15	25.4089
					Mean S/N Ratio			32.9657

As discussed in Taguchi optimization technique, arrangement was done for parameters (precursor, temperature, time and treatment) and corresponding S/N ratios for L9 experiment. This arrangement is as shown in table 5.

Table 5. Arrangement of parameters and corresponding S/N ratios.

Exp. No.	Precursor			Temperature (ºC)			Time (Hrs.)			Treatment		
	Bamboo	Rice straw	Sugarcane bagasse	700	800	900	2.00	3.00	4.00	None	50 % HCl	50 % KOH
	S/N	S/N	S/N	S/N	S/N	S/N	S/N	S/N	S/N	S/N	S/N	S/N
L1	31.423			31.423			31.423			31.423		
L2	32.461				32.461			32.461			32.461	
L3	34.3101					34.3101			34.3101			34.3101
L4		39.3534		39.3534				39.3534				39.3534
L5		37.2826			37.2826				37.2826	37.2826		
L6		38.5368				38.5368	38.5368				38.5368	
L7			27.4883	27.4883					27.4883		27.4883	
L8			30.4271		30.4271		30.4271					30.4271
L9			25.4089			25.4089		25.4089		25.4089		
y	98.19	115.17	83.32	98.26	100.17	98.26	100.39	97.22	99.08	94.11	98.49	104.09
y-y mean	-0.70	16.28	-15.57	-0.63	1.27	-0.64	1.49	-1.67	0.18	-4.78	-0.41	5.19

Effect of each parameter

To determine the effect of each parameter level (m_i) equation 2 was used, in which average value of S/N ratios are calculated for each parameters using analysis of mean (ANOM). For this calculation, the S/N ratios of each experiment with corresponding parameter levels are employed.

$$m_i = \left(1/N_i\right)\sum S/N \qquad (2)$$

Where, *Ni* is the number of experiments conducted with the same parameter levels. Two types of values for S/N ratio are calculated. One is the overall mean S/N ratio calculated from the entire experiments *viz.* from 9 experiment of L9 orthogonal array. The second value for S/N ratio is calculated by summation of S/N ratio of each parameter.

When this summed value of S/N ratio of each parameter is lower than the mean S/N ratio, are considered to be least effective parameters as compared to those parameters whose summed value of S/N ratio of each parameter are larger than the mean S/N ratio. In present case this will be the required information.

The parameters effects, i.e. the contribution of each experimental parameter to the quality characteristic are calculated by the analysis of variance (ANOVA) [18]. 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 process parameters (DoF = number of parameter levels – 1). The relations that are used to determine the sum of the squares and the factor effect are given by:

$$\text{Sum of Squares} = \sum_{i=l}^{i=j} Ni(mi - \langle mi \rangle)^2 \qquad (3)$$

Where m_i gives the average of the levels contributions for each parameters levels to S/N ratio, $\langle m_i \rangle$ is the average of m_i for a given parameter and the coefficient and N_i represents the number of times the experiment is conducted with the same factor level. In the L9 for first parameter N_i is 3. The factor level of each parameter, is obtained using equation, $Ni\,(mi-\langle mi \rangle)^2$. Sum of squares (SoS) of variances for all levels for a given parameter are obtained using equation 3. This term is divided by degree of freedom (DoF) of corresponding process parameter to obtain factor of effects (FoE) of various experimental parameters (equation 4).

$$\text{Factor of effect (FoE)} = \frac{SoS}{DoF \times \sum (SoS/DoF)} \qquad (4)$$

Thus, A plot of S/N ratios for each parameter for its each level is plotted verses the each levels of each parameters. That value of S/N which is greater than the mean values of S/N is considered to be the desired level of each parameter.

Taguchi plot for L9

From the results obtained for S/N ratio for each level of each parameter, a plot was made between the S/N ratios versus the various parameters (Figure 1.) for carbon materials synthesized by pyrolysis of fibrous plant precursor. This plot suggests that the best conditions for getting the higher specific capacitance are when rice straw precursor is pyrolysed at 800ºC temperature for 2 hrs and its carbon formed is treated with 50% KOH solution.

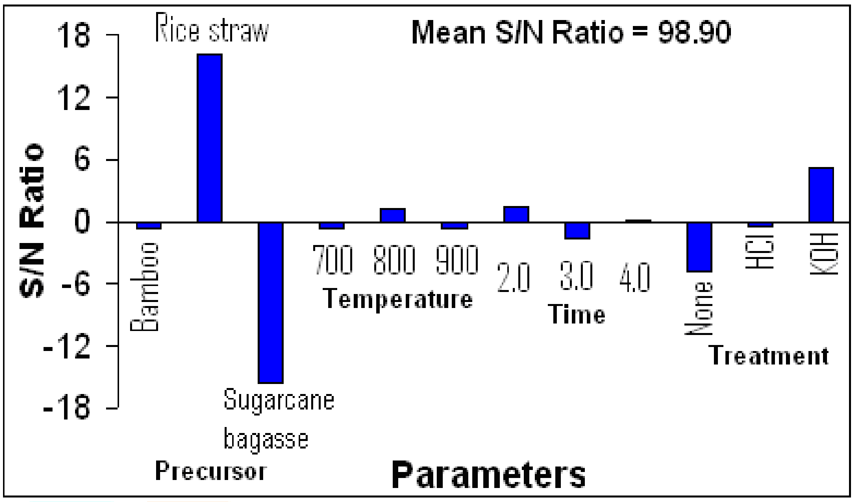

Figure 1. S/N ratio vs. Parameters (considering mean S/N ratio 98.90 = 0; values which are in positive direction are considered as parameters influencing the carbon materials to get the best result)

Amongst the various parameters influencing the results of the capacitance, which of them influences the most can also be calculated from the Taguchi optimization methodology. This is achieved by calculating the values for: m_i, <mi>, mi-<mi>, (mi-<mi>)^2, Ni (mi-<mi>)^2, SoS, SoS/DoF and FoE by using the formulae discussed in Taguchi technique. Values of these calculations are shown in Table 6.

Finally, percentage parameter effect is calculated as following:

$$\text{Parameter effect } \% = 100 \times \text{FoE} \qquad (5)$$

Percentage of impact of each parameter as calculated from equation 5 of Taguchi methodology is plotted in Figure 2.

Table 6. Effect of control parameters on specific capacitance in which specific capacitance of carbon material was measured by cyclic voltammetry

Control parameters	Levels	m_i(dB)	SoS	SoS/DoF	Parameter effect (%)
Precursor	Bamboo	32.7314	169.3019	84.6509	89.83
	Rice straw	38.391			
	Sugarcane bagasse	27.7748			
Substrate temperature	700^{0}C	32.7549	0.8111	0.4055	0.43
	800^{0}C	33.3903			
	900^{0}C	32.752			
Pyrolysis time in hours	2	33.4623	1.6850	0.8425	0.9
	3	32.4078			
	4	33.027			
Treatment to the carbon	None	31.3715	16.6718	8.3359	8.84
	50 % HCl	32.8287			
	50 % KOH	34.6969			

Taguchi optimization calculations suggest that; capacitance values obtained from these carbons are influenced as 89.83 % on the type of precursor used, 0.43 % on the temperature used for pyrolysis, 0.9 % on the pyrolysis time and 8.84 % on the treatment to carbon material synthesized from fibrous plant materials.

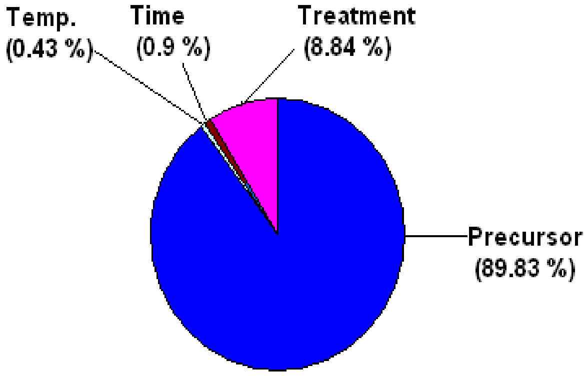

Figure 2. A pie diagram of percentage impact of various parameters on the maximum capacitance value of carbon material

IV. CONCLUSION

From capacitance studies done by cyclic voltammetry technique for carbon materials obtained from plant precursors like bamboo fiber, rice straw and sugarcane bagasse; shows that highest specific capacitance is obtained with carbon obtained from rice straw. Taguchi optimization methodology also predicted that pyrolysis of rice straw at 800°C temperature for 2 hrs. duration and treatment of carbon with 50 % KOH solution gives the carbon of best quality for maximum capacitance and thereby for developing supercapacitor. It is also observed that, first major impactful parameter on the specific capacitance is the nature of the precursor and second is treatment with KOH; pyrolyzing time and temperature had very little impact.

V. ACKNOWLEDGEMENT

Financial support by University of Mumbai, Mumbai, India is gratefully acknowledged.

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