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Optimization of Chemical Treatment Conditions for Adenia Lobata Fiber Using CCD

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Abstract:- In natural fiber composites, natural fibers are used as reinforcement and binder materials are polymeric. In reinforcement of natural fiber in composites, several problems occur along the interface due to the presence of hydrophilic hydroxyl groups on the fiber surface. This hydrophilic nature hinders effective reaction with matrix. To optimize effective interfacial bonding between the fiber and matrix, the fiber surface needs to be modified with different chemical treatments. The present study focused on optimizing the process parameters for the chemical treatments of Adenia lobata fiber. The optimization was done using central composite design (CCD) involving numeric and categoric factors. The numeric factors involved were chemical concentration and pretreatment time, while the categoric factor was the type of chemicals used for the pretreatments. The levels of the categoric factors were Sodium hydroxide, acetic anhydride, nitric acid and zinc chloride. Two factors interaction (2FI) model was developed to predict the tensile strength of the treated fiber. The optimum conditions obtained based on the categoric factor were; 6% NaoH for 50minutes, 14%acetic anhydride for 70minutes and 6% zinc chloride for 20minutes. Sodium hydroxide had highest effect on the chemical treatments. These optimum conditions were validated with little errors of less than 2.0%.

Keywords **–Adenia lobata, ANOVA, CCD, optimization tensile strength,**

I. INTRODUCTION

During the past decades, natural fibers have attracted the interest of material scientists, researchers, and industries because of their specific advantages as compared to conventional or synthetic fibers. Because of their biodegradable nature, natural fibers have been increasingly adopted to replace synthetic fibers in the industrial applications [1][2]. Currently, the most viable way toward eco-friendly composites is the use of natural fibers as reinforcement [3]. Composite is a heterogeneous substance consisting of two or more materials which do not lose the characteristics of each component. However, natural fiber composites face some difficulties that prevent their widespread use [4]. Fiber-polymer incompatibility has been the subject of previous studies [5-8]. This incompatibility is caused by the hydrophilic nature of the fibers and the hydrophobic nature of many polymers used in this field [4]. Hence, various chemical treatments have been done to improve the adhesion or compatibility between natural fibers and polymers [9]. Various factors can influence the effectiveness of the chemical treatment of the fibers. The factors can be the type of chemical used in the treatment, the strength of the chemical and the treatment time. All these factors, when combined at the optimum conditions can increase the tensile strength of the fiber but deviation from the optimum can result to excess delignification which leads to low tensile strength of the resultant fibers. The aim of this research is to develop a mathematical model for the chemical treatment of Adenia lobata fiber and to optimize it using Response Surface Methodology. Response Surface Methods (RSM) is a statistical technique for modeling responses via designed experiments and polynomial equations. RSM leads to peak process performance. It can put responses together via sophisticated optimization approaches, which ultimately leads to the discovery of sweet spots where you meet all specifications at minimal cost [10].

II. EXPERIMENTAL DESCRIPTIONS.

A. Raw Materials Preparation

Adenia lobata fibre was obtained from well defined locations in Ebonyi State of Nigeria. This plant fibre was extracted from the plant stem using water retting extraction process, giving fibre of different lengths and diameters. Before usage, the fibre was visually selected in order to verify the absence of defects along the length of the fibre.

B. Alkali treatment

The Adenia lobata fiber was treated with 6% NaoH in accordance with work done by nural and Ishak with slight modifications [11]. The fiber was immersed in the alkali solution for 50 minutes, then neutralized with acetic acid and washed with distilled water repeatedly until all sodium hydroxide was eliminated. Finally, the fiber was washed with distilled water and dried at room temperature for 48h.

C. Acetic anhydride treatment

The acetylation process was in accordance with work done by A.K bledzki, with slight modifications [12]. The Adenia lobata fiber was soaked in distilled water for an hour, filtered and placed in a round bottom flask containing 10% acetic acid solution for 30 minutes. After which it was placed on flask containing 14% acetic anhydride solution. The process temperature of acetylation was 30^0C and duration was 70 minutes. After modification, the fiber was washed periodically with

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distilled water until acid free. Finally, modified fiber was air dried for certain time before analysis.

D. Nitric acid treatment

The nitric acid treatment was in accordance with F. Vautard etal 2013 [13] and W. Z. etal 2010 [14] with slight modifications. The size reduced adenia lobata fiber was oxidized with 6% nitric acid. The prepared oxidizing solution was boiled to a temperature of 60^0C and the fiber immersed in the solution at maintained said temperature for 50 minutes. It was then neutralized with NaoH solution and washed with distilled water repeatedly until all the nitric acid was eliminated. Finally, the fiber was washed again with distilled water and dried to a constant weight temperature.

E. Zinc chloride treatment

Zinc chloride treatment was done in accordance with the work done by V. Nadanthangam etal 2013 with modification [15]. The fiber was soaked in 3% zinc chloride solution for 70 minutes after which it was washed with distilled water until the washing solution became chloride free. The fiber was washed with distilled water and dried at room temperature for 48 hours.

F. Tensile Strength

Tensile strength is a measurement of the ability of material to withstand forces that tend to pull it apart. It determines to what extents the material stretches before breaking. The fiber tensile strength tests were performed by a computer controlled Hounsfield tensometer testing machine (model 5566) with a gauge length of 40mm and crosshead speed of 5mm/min. The round bars were covered with surgical glove fingers, and the flax was clamped at the top and bottom. The fiber bundle was wrapped one revolution around each of the two bars and was spread out over the entire gauge length in a parallel. The machine was wet up to display a force deformation curve at loading and to read the load at maximum or the break point

G. Determination of lignin content by gravimetric method

This was done according to work done by G.N Onyeagoro 2012 [13]. 2.0g of the sample were weighed and placed inside a beaker. 72% H_2SO_4 was added and allowed to stand for 2 hours. 8% H_2SO_4 was later added and the solution refluxed for 3 hours. The residue was filtered with purpling cloth and washed severally with hot water. A crucible was weighed and the sample was scraped into it. The sample was oven dried at 110^0C for 1 hour and then cooled inside desiccators after which the weight was taken. The sample was ashed in a furnace at 500^0C for 3 hours. It was then cooled inside desiccators and finally weighed. The % lignin was calculated using equation

$$\% \text{ Lignin} = \frac{W_2 - W_1}{W_S} X\ 100 \qquad (1)$$

Where,

W_1 = weight of ash sample + crucible

W_2 = weight of oven dried sample + crucible

W_S = initial weight of dried sample

H. Determination of cellulose content

This was done according to work done by G.N Onyeagoro 2012 [15]. 1.5g of fiber sample was weighed into a beaker followed by addition of 20ml of 80% acetic acid, 1ml of concentrated nitric acid and 3 glass beads. The content was refluxed for 30 minutes. The sample was cooled and washed into 50ml centrifuge tube containing hot 95% ethanol, and then centrifuged at 15,000rpm for 5 minutes. Thereafter, the liquid was decanted and 95% ethanol was added, stirred and filtered by suction. The sample was washed three times with hot benzene, two times with 95% ethanol and once with ether. The sample was placed inside a weighed crucible and placed in the oven maintained at 110^0C for 1 hour. The crucible was then cooled in desiccators and weighed. For ash content determination, the crucible and its content was placed inside a furnace maintained at 500^0C for 3 hours after which it was cooled in desiccators and weighed. The % cellulose was calculated from equation 2.

$$\% \text{ cellulose} = \frac{w_2 - w_1 x100}{ws} \qquad (2)$$

Where,

W_1 = weight of crucible + sample after ashing

W_2 = weight of crucible + sample after drying

Ws = weight of sample

I. Holocellulose content

This was according to the work done by A.K Bledzki et al 2008 [12]. Three grams of air dried fibre was weighed and placed in an Erlenmeyer flask and then, 160 ml of distilled water, 0.5 ml of glacial acetic acid and 1.5 g of sodium chloride were added successively. The flask was placed in water bath and heated up to 75°C for an hour and then additional 0.5 ml of glacial acetic acid and 1.5 g of sodium chloride were added. The additions of acetic acid and sodium chloride were repeated two times hourly. The flask was placed in an ice bath and cooled down below 10°C. The holocellulose was filtered and washed with acetone, ethanol and water respectively and at the end; sample was dried in oven at 105°C before weighed.

J. α-cellulose content

This was according to the work done by A.K Bledzki et al 2008 [12]. Two grams of holocellulose were placed in a beaker and 10 ml of sodium hydroxide solution

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(17.5%) was added. The fibre was stirred up by glass rod so that they could be soaked with sodium hydroxide solution vigorously. Then sodium hydroxide solution was added to the mixture periodically (once every five minutes) for half an hour and the mixture temperature was kept at 20°C. About 33 ml of distilled water was added in the beaker and kept it for an hour. The holocellulose residue was filtered and transferred to the crucible and washed with 100 ml of sodium hydroxide (8.3%), 200 ml of distilled water, 15 ml of acetic acid (10%) and again water successively. The crucible with α-celluloses was dried and weighed.

K. Hemicellulose content

The content of hemicelluloses of flax fibre was calculated from Equation below

Hemicelluloses = Holocellulose – α-celluloses [12]. (3)

L. Response Surface Methodology (RSM)

RSM is a collection of statistical and mathematical techniques that uses quantitative data from appropriate experiments to determine regression model equations and operating conditions which are useful for developing, improving and optimizing processes [16], [17]. Central composite design (CCD) [18], Box Behnken and Doehlert design (BBD) [19] are among the principal response surface methodologies used in experimental design. The CCD consists of a 2^k factorial runs with the 2^k axial runs and a n_o center runs. In CCD each variable is investigated at two levels and as the number of factors, k, increases, and the number of runs for a complete replicate of the design increases rapidly. The center points are used to determine the experimental error and the reproducibility of the data. In this work, CCD was used to study the effect of chemical treatments on adenia lobata fiber. The variables consist of both numerical and categoric factors. Numeric factors are the common ones used and they can be easily adjusted to any level over a continuous operating range. The introduction of categoric factors to RSM increases the complexity of the design exponentially [10]. This will cause the number of runs generated to be multiplied by the number of combinations of the categorical factor levels. The numeric factors are chemical strength (%) and treatment time (minutes) while the categoric factor is the type of chemical used for the treatment. The categoric factor was studied at four levels namely: NaOH, acetic anhydride, Nitric acid and zinc chloride. The two numeric factors gave 13 experiment multiplied by four levels of the categoric factors giving a total of fifty two (52) experiments. The factors with their levels and the design matrix used in coded form are shown in table 1.0 and table 5.0 respectively.

Factors	Levels				
	-α	-1	0	+1	+α
1. Chemical strength (%)	2	6	10	14	18
2. Treatment time (mins)	30	50	70	90	110
3. Type of chemical					
Level 1.	Sodium hydroxide				
Level 2.	Acetic anhydride				
Level 3.	Nitric acid				
Level 4.	Zinc chloride				

Table I. Factors and levels for CCD

III. RESULTS AND DISCUSSIONS

The chemical and mechanical properties of the natural fibre used in thus study are shown in table 2. Cellulose is the primary component of natural fibres. Cellulose is a semi-crystalline polymer containing many hydroxyl functional groups along its long chain macromolecular structure. The hydroxyl groups hydrogen bind with water vapor in the air making the cellulose naturally hydrophilic in nature. The mechanical properties of the natural fibres are dependent on the cellulose content in the fibre, and the degree of polymerization of the cellulose [20].

Table 2. Chemical and mechanical properties of the fiber

Parameters	Units	Values
Cellulose	(%)	55.20
Hemi cellulose	(%)	9.321
Lignin	(%)	28.22
Ash	(%)	2.572
Wax	(%)	0.08
Moisture	(%)	3.21
Density	g/cm3	1.41
Tensile Strength	Mpa	588.94
Elastic modulus	Mpa	2,030.82
Elongation at break	(%)	6.75

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A. Selection of a good model

The sequential model sum of square was used to compare different models. It shows the statistical significance of adding new model terms step by step in increasing order. It provided accounts of variation and associated P-values (Prob>F) so that one can see how far it is worth going in degree of polynomial. The objective was to add a higher level source of term only if it explains a significant amount of variation beyond what was already accounted for. The model was selected based on the highest order model that was significant (P-value small) and not aliased, on lack of fit (P-value > 0.10) and reasonable agreement between Adjusted R-squared and predicted R-squared (within 0.2 of each other). The summary table of the sequential model sum of square for fiber is shown on table 3. The lack of fit tests were included because extra design points beyond what was needed for the model were involved and some points were replicated (center points) to provide estimate of pure error. It compares the residual's error mean square to the pure error's mean square. Since it is a measure of risk, it is not desirable, so a small F value and probability greater than 0.1 were desired. A model that showed significant lack of fit will not be used to predict the response. From table 4.4 all in the fibers displayed non significant lack of fit for the suggested models. For the fibre, the predicted R-squared was in close range to the adjusted R-squared for all the sources of the model, but the models were suggested based on the model p-value and lack of fit p-values. The suggested model for the fiber was two factor interaction models (2FI), addition of quadratic terms to the model did not improve the model. Although the linear model had low p-value for the fibre, it was discarded due to significant lack of fit. The linear model been insignificant in the sequential model sum of square means that the error term at that stage still contains variation that can be explained by higher order terms, in this case the 2FI. Therefore, it will be a mistake to say that the class of terms was not significant. As will be seen later on ANOVA, all the three linear terms A, B, and C may be significant at the 0.05 probability level. Even if all linear terms were insignificant according to ANOVA, one or more of them would be included in the final model to maintain model hierarchy. Notice from table 3 that adding cubic terms would not significantly improve the model because it have P-value above 0.05. Even if it did, the central composite design lacks the design points needed to fit all terms required for the cubic, thus labeled as being aliased.

B. Inspection of selected model

ANOVA was used to interpret the relative contribution of each factors to the total variations "equally, R-square, predicted R-squared and adjusted R-squared values were used to ascertain if the model selected will produce good production for average outcome. Attention was focused on predicted R-square and adjusted R-square because the regular R-square can be artificially inflated by simple continuing to add terms to the model, even if the terms are not statistically significant. The adjusted R-square plateaus when insignificant terms are added to the model, and the predicted R-square will decrease when there are too many insignificant terms. The model was deemed appropriate in this study based on the significance of the model p-value, insignificant lack of fit test, good agreement between adjusted and predicted $R^{\Lambda}2$, adequate precision over 4 and well behaved residuals. Insignificant lack of fit was desired because significant lack of fit means that the variation of the replicates about their mean values is less than the variation of the design points about their predicted values. Either the runs replicated well or their variance is small, or the model does not predict well, or some combination of the two. Adequate precision measures the signal-to- noise ratio. It compares the range of the predicated values at the design points to the average prediction error. Ratio greater than 4 indicated adequate model discrimination [21]. The ANOVA for the fibre is shown in table 4.

Table 3. Summary table for sequential sum of square

Source	Sequential P-Value	Lack of fit P-Value	Adjusted R-Square	Predicated R-Square
Linear	<0.0001	0.0394	0.6469	0.591
2FI	0.018	0.1195	0.9233	0.8247 suggested
Quadratic	0.1039	0.1597	0.7419	0.6339
Cubic	0.133	0.2913	0.7856	0.3357 aliased

SEQUENTIAL MODEL SUM OF SQUARES

Source	Sum of Squares	df	Mean Square	F Value	P-Value Prob<F
Mean	1.78E+07	1	1.78E+07	19.69	
Linear	2.26E+05	5	45241.02	2.81	<0.0001
2FI	35461.78	7	5065.97	2.41	0.0180 suggested
Quadratic	8091.11	2	4045.55	1.69	0.1039
Cubic	25672.27	11	2352.02		0.1330 aliased
Residual	36276.39	26	1395.25		
Total	1.82E+07	52	3.50E+05		

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Table 4. ANOVA Table

Source	Sum of Square	df	Mean Square	F Value	P-Value Prob>F
Model	2.59E+05	8	32333.51	18.98	<0.0001 significant
A-Chemical Concentration	15731.07	1	15731.07	9.24	0.004
B-Time	8123.44	1	8123.44	4.77	0.0345
C-Chemical Type	2.02E+05	3	67450.19	39.6	<0.0001
AC	32462.97	3	10820.99	6.35	0.0012
Residual	73238.58	43	1703.22		
Lack of fit	53481.73	27	1980.8	1.6	0.167 not significant
Pure error	19756.84	16	1234.8		
Cor Total	3.32E+05	51			

F – Value of 18.98 implied that the selected model was significant and can explain the process well. There was only 0.01% chance that this large value of F-value can occur due to error. Values of prob>F less than 0.0500 indicated significant model terms. Values greater than 0.100 indicated insignificant model terms. Analysis of Adenia lobata showed that the linear effects of chemical concentration, Time, chemical and the interaction effect of the chemical concentration and chemical type were significant, with prob>F values less than 0.05. The lack of fit test came out insignificant with F-value of 1.6. There is 16.7% chance that this large value of lack of fit will occur due to error. The insignificancy of lack of fit is desirable because we want our model to fit. The predicted R-squared of 0.824 is in close range with the adjusted R-square of 0.9233. R-square of 0.97793 is high which showed that 97.8% of the total variation of the outcome will be explained by the model. Adequate precision of 18.650 was adequate and indicated a good signal.

C. Predictive models in coded versus actual units

Predictive models are mathematical representation of the chemical treatment process using the selected model. The model equations were presented in both coded and actual values. The coded values works only if the factors are converted to the standard coding scale – 1 to + 1 for the low versus high values, respectively of the factorial ranges. Due to dependency of the actual values on units, their coefficients did not tell anything, coding factors removes their units of measure. The intercept in coded value represents the center of the design of experiments, and the regression coefficients tell us how the response changes relative to this point of reference. Thus, the coded model facilitates knowledge of the process. Regardless of the form of the model, it is only an approximation, not the real truth. It is good enough to help you move in the proper direction, but not to make exact prediction particularly outside the actual experimental region. Typically, a categoric factor's level are represented by indicator "dummy" variables in regression. The value of the dummy variables are "0" if that types is not present in that treatment/run, and "I" if it is present, therefore, the four chemical types were represented by 100, 010, 001, and -1-1-1 respectively. The "100" meant that the first chemical type was present while the other ones were absent. "010" meant the second type of chemical was present while others were absent. "001" meant the third chemical was present, while other ones were absent and "-1-1-1" meant that none of chemicals were present. These codes were assigned randomly to different chemicals. The coded equation involving categoric factor can be seen as being four equation one comprising C[I] with its interactions, two comprising C[2] with its interaction, three comprising C[3] with all its interactions, and C[4] is seen as the reference level of the categorized factors. The Equation for C [4] is one with all the C terms and interaction terms were eliminated. Each chemical type adjusts the intercept by the amount of its coefficient, while its effect on interaction with other factors affects the slope due to the factor. Equation involving C[1] was used with the chemical type "100" for response prediction, C[2] equation used for chemical type "010" for respond predication, C[3] equation was used for chemical type "001" while C[4] being the reference level was used for chemical type "1-1-1- " for response prediction.

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Final equation in terms of coded factors:

Tensile strength (Mpa) = +585.76 – 18.10A – 13.01B + 67.10 C[1] – 4.1 C[2] +35.82C[3] – 1.23AC[1] + 8.45AC[2] + 32.49AC[3] (4)

Final equation in terms of Actual factors:

NaOH: Tensile strength (Mpa) = +746.72705 - 4.83396 chemical concentration - 0.65048 Time (5)

Nitric acid: Tensile strength (MPa) = +651.30731 – 2.41229 chemical concentration – 0.650 Time (6)

Acetic Anhydride: Tensile strength (Mpa) = +631.5551 + 3.59604 chemical concentration – 0.65046 Time (7)

Zinc chloride: Tensile strength (Mpa) = + 677.01333 – 14.45313 chemical concentration – 0.65046 time (8)

The four components of the coded equation;

Tensile strength (Mpa) = + 585.76 – 18.10A – 13.01B +67.10 C [1] – 1.23AC [1] (9)

Tensile strength (Mpa) = + 585.76 – 18.10A – 13.01B +4.11 C [2] +8.45 AC [2] (10)

Tensile strength (Mpa) = + 585.76 – 18.10A – 13.01B +35.82 C [3]+32.49A C[3] (11)

Tensile strength (Mpa) = + 585.76 – 18.10A – 13.01B (12)

For Adenia lobata fiber, the effect of chemical type affected the tensile strength of the fiber and the sensitivity of the fiber due to chemical concentration. Effect of sodium hydroxide increased the overall average tensile strength by 67.10 and decreased the sensitivity due to chemical concentration by 1.23. Effect due to nitric acid decreased the intercept by 4.11 and increased the sensitivity due to chemical concentration by 8.45. Effect due to acetic anhydride increased the overall means by 35.82 and increased the slope due to chemical concentration by 32.49.

D. Diagnosing residuals to validate statistical assumptions

A good way to check your model is to enter factor levels from the design and generate the predicated response. When the predicated values are with the actual (observed) value, one will always see a discrepancy. This is called the residuals (noise). Residuals are differences between the predicated values and the actual values and estimate the error terms (*ei*) in the model. The *ei* are assumed to be random and normally distributed with mean equal to zero and constant standard deviation. If the error terms follow a normal distribution, they will fall on a straight line on the normal probability plot. Because they are estimate of the error terms, the residuals should exhibit similar properties. If the assumptions are valid, plots of the residuals versus run order, predicted values, and other independent variables should be random and structure less. If structure remains in the residuals, residual plots may suggest modifications to the model that will remove the structure. Investigation of residuals has been used to evaluate the model adequacy. The residuals calculated with the actual values and predicted values are shown on table 6 below.

These residuals generated according to Ejikeme P.C.N et al 2014 [22] were examined for patterns that indicate that some something other than noise was present. If the residuals were pure noise (i.e., they contain no signal), then, the analysis is complete. Table 6 show s the actual value, predicated value and the residuals for the fiber. A quick but effect tool for diagnosing residuals is the normal plot of residuals, residuals versus predicated level and predicated values versus actual values [21].

Table 5. Design matrix for CCD with the experimental values

Std Order	Run Order	Chemical concentration (%)	Time (Mins.)	Chemical type	Tensile Strength (Mpa)
11	1	10	70	NaOH	750
27	2	6	50	Acetic Anhydride	609.39
8	3	10	110	NaOH	590
38	4	10	70	Acetic Anhydride	639
7	5	10	30	NaOH	690.39
32	6	18	70	Acetic Anhydride	647.27
5	7	2	70	NaOH	630
35	8	10	70	Acetic Anhydride	647.33
46	9	10	30	Zncl	509
4	10	14	90	NaOH	580.85
40	11	6	50	Zncl	612.72
9	12	10	70	NaOH	751
3	13	6	90	NaOH	652.56
37	14	10	70	Acetic Anhydride	600.22
28	15	14	50	Acetic Anhydride	632.44
48	16	10	70	Zncl	461.33
36	17	10	70	Acetic Anhydride	640.44
47	18	10	110	Zncl	400.72
52	19	10	70	Zncl	498.22
16	20	6	90	Nitric Acid	600
33	21	10	30	Acetic Anhydride	620.3

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41	22	14	50	Zncl	450.87
34	23	10	110	Acetic Anhydride	540
17	24	14	90	Nitric Acid	568.33
6	25	18	70	NaOH	570
49	26	10	70	Zncl	465.22
29	27	6	90	Acetic Anhydride	614.98
45	28	18	70	Zncl	422.78
19	29	18	70	Nitric Acid	560.39
30	30	14	90	Acetic Anhydride	650
13	31	10	70	NaOH	700
24	32	10	70	Nitric Acid	584.01
1	33	6	50	NaOH	640.32
12	34	10	70	NaOH	732
39	35	10	70	Acetic Anhydride	649.22
10	36	10	70	NaOH	600
15	37	14	50	Nitric Acid	570.36
43	38	14	90	Zncl	411.32
2	39	14	50	NaOH	600
20	40	10	30	Nitric Acid	580.32
14	41	6	50	Nitric Acid	595.12
31	42	2	70	Acetic Anhydride	590
23	43	10	70	Nitric Acid	582.66
25	44	10	70	Nitric Acid	592.31
44	45	2	70	Zncl	590.72
42	46	6	90	Zncl	607.34
18	47	2	70	Nitric Acid	590.07
50	48	10	70	Zncl	467.33
22	49	10	70	Nitric Acid	580.92
26	50	10	70	Nitric Acid	587
51	51	10	70	Zncl	432.78
21	52	10	110	Nitric Acid	569.99

Table 6. Actual values, Predicted values and residuals according to standard order

Standard order	Actual Values	Predicated Values	Residuals
1	640.32	685.20	-44.88
2	600.00	646.53	-46.53
3	652.56	659.18	-6.62
4	580.85	620.51	-39.66
5	630.00	691.53	-61.53
6	570.00	614.18	-44.18
7	690.39	678.87	11.52
8	590.00	626.84	-36.84
9	751.00	652.86	98.14
10	600.0	652.86	-52.86
11	750.00	652.86	97.14
12	732.00	652.86	79.14
13	700.00	652.86	47.14
14	595.12	604.31	-9.19
15	570.36	585.01	-14.65
16	600.00	578.29	21.71
17	568.33	558.99	9.34
18	590.07	600.95	-10.88
19	560.39	562.35	-1.96
20	580.32	607.67	-27.35
21	569.99	555.63	14.36
22	580.92	581.65	-0.23
23	582.66	581.65	1.01
24	584.01	581.65	2.36
25	592.31	581.65	10.66
26	587.00	581.65	5.35
27	609.39	620.21	-10.82
28	632.44	648.98	-16.54
29	614.98	594.19	20.79
30	650.00	622.96	27.04
31	590.00	592.82	-2.82
32	647.27	650.35	-3.08
33	620.30	647.60	-27.30
34	540.00	595.57	-55.57
35	647.33	621.58	25.75
36	640.44	621.58	18.86
37	600.22	621.58	-21.36
38	639.00	621.58	17.42
39	649.22	621.58	27.64
40	612.72	557.77	54.95
41	450.87	442.15	8.72
42	607.34	531.75	75.59
43	411.32	416.13	-4.81
44	590.72	602.58	-11.86
45	422.78	371.33	51.45
46	509.00	512.97	-3.97
47	400.72	460.93	-60.21
48	461.33	486.95	-25.62
49	465.22	486.95	-21.73
50	467.33	486.95	-19.62
51	432.78	486.95	-54.17
52	498.22	486.95	11.27

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E. Normal plot of residuals

Normal plot of residuals indicates whether the residuals followed a normal distribution; in which case the points will follow a straight line one should expect some moderate scatters which are normal even with normal data. The normal plot of residuals for the fiber is shown in fig.1.

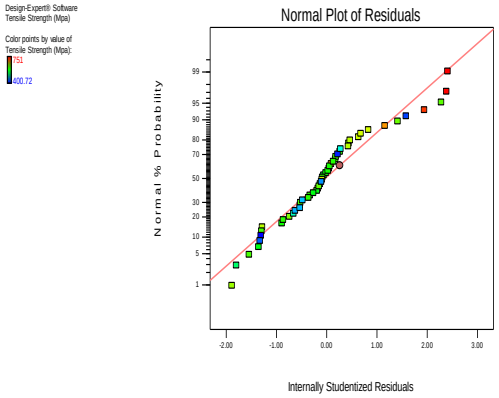

Fig. 1. Normal plot of residuals

F. Residual versus predicated levels.

This plot of residuals versus predicated response values was used to test the assumption of constant variance. The plot should be a random scatter (constant range of residuals across the graph). The plots of residuals versus predicated levels for the fiber is shown in fig.2 below;

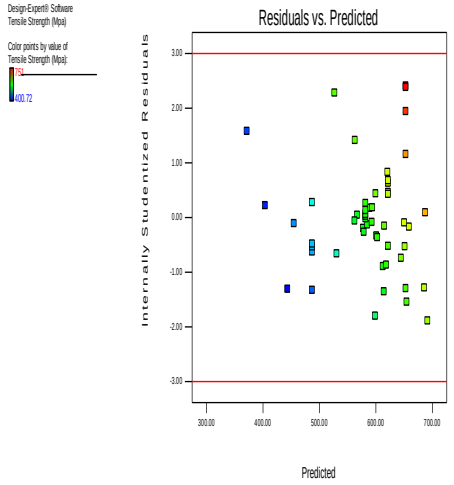

Fig. 2. Plot of residual vs. Predicted

G. Predicated versus Actual value

A graph of the actual response value versus the predicated response values was used to detect a value, or group of values that were not easily predicated by the model. The condition is that the data point should be split evenly by the 45 degree line. Fig.3 shows the plot of predicated versus actual values for the fibre.

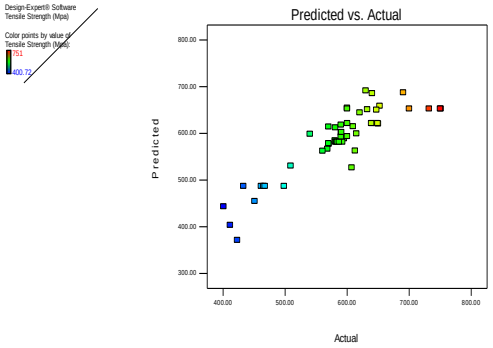

Fig. 3. Plot of residual vs. Actual

From the plot, it showed that the data points were split evenly by the 45 degree line. This means that all the values where well predicated by the model. The results of the diagnosis revealed no problem, which showed that the model met the assumptions of ANOVA and can be used to navigate the design space.

H. Effect of chemical type on the tensile strength of the fiber

Chemical types been a categoric factor was used to compare the magnitude of the effects of different chemical on the tensile strength of the fiber. The graph of the effect of chemical types on the tensile strength of Adenia lobata fiber is shown in fig. 4. From the graph, it can be seen that NaoH had highest effect on the tensile strength of the fiber, followed by acetic anhydride, zinc chloride and lastly nitric acid. The effects were ascertained at time of 70mins and 10% chemical concentration.

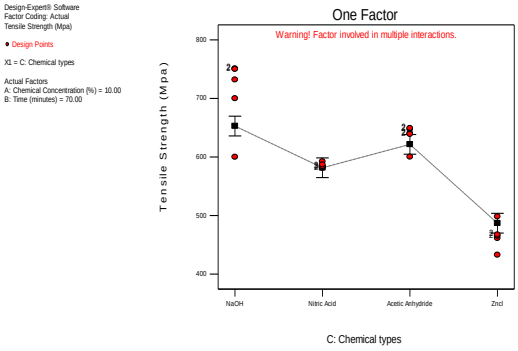

Fig. 4. Effect of chemical types on the tensile strength

I. Process optimization

Numerical optimization was used to search the design space using the model created during analysis to find factor settings that met the defined goal. Maximization of tensile strength was set as goal to be met for the optimization. The software automatically generated a list of potential factor settings that met the specific criteria based on the desirability. The factor setting used for the optimization was selected base on the highest desirability.

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Optimum Conditions Based on the Categoric Factor for Adenia Lobta Fiber is;

(a) 6% Na0H for 50minutes with predicated tensile strength of 685.2 Mpa

(b) 14% acetic anhydride for 70minutes with predicated tensile strength of 684.75 Mpa

(c) 6% nitric acid for 70munites with predicated tensile strength of 604.311 Mpa

(d) 6% zinc chloride for 20minutes with predicated tensile strength of 600.772 Mpa

The optimum conditions obtained based on the predicated models were validated to confirm the predicated response and obtain the percentage deviation (error) from the predicated ultimate conditions. Table 7 shows the model desirability, the optimum conditions, and the predicated and experimental ultimate strength with the percentage errors for the fiber. The results shown on table 7 confirmed the optimum conditions obtained with different chemicals with little errors of less than 2.0%.

J. Validation of optimum conditions

Table 7. Validation of Optimum conditions

				Tensile strength		
Model desirability	**Chemical strength**	**Chemical**	**Time**	**(Mpa)**		**Error**
	(%)	**type**	**(minutes)**	**Predicated**	**Experimental**	**(%)**
				Values	**Values**	
1	6	NaOH	50	685.2	676.292	1.3
0.958	14	Acetic anhydride	70	684.565	674.16	1.52
0.911	6	Nitric acid	70	604.311	595.851	1.4
0.852	6	Zinc chloride	20	600772	600.1	1.11

IV. CONCLUSION

This study focused on solving the problems of natural fibers as reinforcements on composites. Natural fibers are amendable to modifications as they bear hydroxyl groups from cellulose and lignin. Chemical modification may activate these groups or expose more reactive groups on the fiber surface and thus facilitate efficient coupling with the matrix. Optimization of the chemical treatments process of adenia lobata fiber was done using central composite design (CCD). The numeric variables involved were pretreatment time and chemical concentrations. The categoric factor involved was the chemical type involved which has four levels; NaoH, acetic anhydride, nitric acid and zinc chloride. Two factors interaction (2FI) model was suggested based on sequential sum of square method. The model was validated using residual plots. The analysis of residuals showed that they had normal distribution with constant variance. The conditions were optimized based on the categoric factors as follows;

- 6% NaoH for 50 minutes,
- 14% acetic anhydride for70minutes,
- 6% nitric acid for70minutes,
- 6% zinc chloride for 20minutes

These optimum conditions were verified by repeating the experiments using the optimum conditions obtained. The deviation of the experimented values from the predicted values were less than 2.0%

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