CHAPTER – IV

RESULTS AND DISCUSSION

The latest developments in textiles and their industrial uses have led to the birth and development of technical textiles. Technical textile goods are primarily manufactured for non-aesthetic purposes where the function is its criteria. This is a very vast and rapidly developing sector as it supports many industries. The present study focuses on the utilisation of waste bagasse in technical textile fibre applications. Exploration of this waste bagasse will be an addition to the technical textiles. Bagasse is considered a type of unconventional fibre because of its limited applicability in the textile industry. These fibres needed to be modified for specific end-use. Certain recipes were standardised during the research work, which will make the results sustainable with increased acceptability. The results of the study are discussed under the following sub-heads:

4.1 Extraction of fibres
    4.1.1 Exploring the method
    4.1.2 Optimisation of fibre extraction conditions
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    4.2.1 Physical properties of extracted fibre
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4.3 Fabrication of an apparatus (Sugarcane Fibre Extractor)
4.4 Modification of fibre through Chemical and Enzymatic treatments
4.5 Optimisation of modification treatments
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4.6 Characterisation of untreated and optimised fibre
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4.7 Manufacturing of Non-woven
4.8 Testing of Non-woven for oil sorption

4.1 Extraction of fibres

The fibres were extracted from waste Sugarcane bagasse through mechanical and chemical treatment (Plate 4.3).

4.1.1 Exploring the method

To obtain the fibres from waste Sugarcane bagasse, the following steps were followed:

i) Preparation of raw material

Bagasse is mainly composed of an outer rind and an inner pith. The softcore pith was manually removed from the bagasse. The outer rind was then cut across its length, and nodes were removed to separate all the pithy material from the rind.

ii) Removal of colouring matters and sugar traces

Under this step, the cut outer rind was subjected to hot water (material: liquor ratio1:50) treatment for 60 minutes at 90℃temperature. This process helps to remove the colouring matter, sugar traces and other dust particles.

iii) Chemical treatment

The separated outer rind was subjected to sodium hydroxide (NaOH) solution in concentration of 0.1(N), 0.2(N), 0.3(N) and 0.4(N) in material: liquor ratio 1:100. Treatment time was kept at 60, 120, 180 and 240 minutes and the temperature was kept 90℃.

iv) Neutralisation of fibres

After chemical treatment, fibres were taken out and washed with hot water. Then, the fibres were kept for 15 minutes (room temperature) in diluted hydrochloric acid (HCl) solution, obtaining 4-5 pH for neutralisation, followed by hot water rinse and cold water rinse, respectively. After the neutralisation process, the fibres were kept for drying at room temperature.

Plate 4.1: Waste Sugarcane bagasse (Cleaning)

Plate 4.2: Extracted fibres

Plate 4.3: Fibre extraction process (a) Outer rind without nodes (b) Boiling (c) Sun-drying (d) Chemical treatment (e) Washing and neutralisation of fibre (f) Extracted fibre

4.1.2 Optimisation of fibre extraction conditions

This part of the study aimed to evaluate and optimise conditions for fibre extraction. To enhance extraction efficiency, it is essential to work under optimised conditions. The raw material (outer rind stalks) was subjected to sodium hydroxide (NaOH) solution in three different concentrations of 0.1(N), 0.2(N), 0.3(N) for 60, 120, 180 and 240 minutes for each concentration at 90°C. The extraction at 0.3(N) concentrations for 180 and 240 minutes resulted in the dissolution of fibres. Hence, that could not be considered for the optimisation process.

Therefore, to select optimal extraction parameters, the effect of two independent variables, chemical concentration and time, were observed based on the four response variables, fibre quantity, tenacity, and chemical composition, viz., the cellulose and lignin content of the fibre. The calculated values are presented in Table 4.1.

Table 4.1: Effect of varying treatment conditions on physical and chemical properties of the extracted fibres

Concentration (N)	**Time (min)**	**Tenacity (g/den)**	**Fibre quantity (%)**	**Cellulose (%)**	**Lignin (%)**
0.1	60	2.16	20	66.5	17.5
0.1	120	2.08	30	67.5	15.5
0.1	180	2.05	55	69.5	14.5
0.1	240	1.95	61	70.0	12.5
0.2	60	2.25	55	66.5	15.5
0.2	120	2.16	51	67.0	13.5
0.2	180	2.15	50	67.5	12.0
0.2	240	1.84	47.5	70.0	12.5
0.3	60	1.50	41.5	67.5	13.5
0.3	120	1.23	37	70.0	12.5

4.1.1.1 Statistical analysis

The full factorial experimental design and statistical analysis were performed. The full factorial design of experiment is an efficient experimental procedure for optimising this complex process. Intrinsically, the optimization process involves three substantial steps, which are performing the statistically designed experiments, estimating the coefficients in a mathematical model and predicting the response, and checking the adequacy of the model. The quality of fit of the model was expressed by the coefficient of determination (R^2). Significance of process variables was checked by P value and F value. Analysis of variance (ANOVA) was performed to determine the significance of the models (Ghorbani, 2017).

Table 4.2: Variance analysis of Tenacity, Fibre quantity, Cellulose and Lignin versus different fibre treatment conditions

Tenacity (g/den)						
Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**P-value**	
Model	0.9410	5	0.1882	35.11	0.0021	Significant
A-Concentration (N)	0.5532	1	0.5532	103.18	0.0005	
B-Time (min)	0.1256	1	0.1256	23.43	0.0084	
AB	0.0220	1	0.0220	4.10	0.1129	
A^2	0.4140	1	0.4140	77.22	0.0009	
B^2	0.0016	1	0.0016	0.2942	0.6163	
Residual	0.0214	4	0.0054			
Cor Total	0.9625	9				
Fibre quantity (%)						
Model	1327.47	5	0.1882	8.73	0.0283	Significant
A-Concentration (N)	212.57	1	0.5532	6.99	0.0573	
B-Time (min)	3.24	1	0.1256	0.1066	0.7604	
AB	725.81	1	0.0220	23.87	0.0081	
A^2	537.45	1	0.4140	17.67	0.0137	
B^2	16.74	1	0.0016	0.5505	0.4993	
Residual	121.63	4	0.0054			
Cor Total	1449.10	9				
Cellulose (%)						
Model	13.19	2	6.60	6.68	0.0238	Significant
A-Concentration (N)	1.49	1	1.49	1.51	0.2594	
B-Time (min)	13.16	1	13.16	13.33	0.0082	
Residual	6.91	7	0.9871			
Cor Total	20.10	9				
Lignin (%)						
Model	25.54	2	12.77	33.31	0.0003	Significant
A-Concentration (N)	13.94	1	13.94	36.35	0.0005	
B-Time (min)	18.90	1	18.90	49.29	0.0002	

Residual	2.68	7	0.3834			
Cor Total	28.23	9				

Factors such as chemical concentration and time were identified to be significantly affecting the response variables of the fibre. The summary of the analysis of variance (ANOVA) for the selected quadratic polynomial model for tenacity and fibre quantity has been listed in Table 4.2. The model F-value (tenacity**)** of 35.11 implies the model was significant**.** P-values less than 0.0500 indicate that model terms are significant. In this case, A, B, and A^2 are significant model terms. The model F-value for fibre quantity was 8.73, which implies the model is significant. In this case, B and AB are significant model terms. The ANOVA of the quadratic regression model demonstrated that both models were highly significant, evident from Fisher's F-test with a high F value and low P value.

Table 4.2 denoted that the linear model F-value for cellulose, 6.68, implies the model is significant. In this case, B (time) is a significant model term. The model F-value for lignin, 33.31, implies the model is significant. In this case, A (Concentration) and B (time) are significant model terms. The results show that the developed model is satisfactory and suitable for the extraction process of Sugarcane fibre. The analysis of variance shows a high goodness of model fit.

Table 4.3: Results of the statistical analysis for the optimisation of extraction parameters

Response Variable	**Model**	**R^2**	**Adjusted R^2**
Tenacity(g/den)	0.85+17.72 × Concentration +0.001 × Time -0.01 × Concentration ×Time - 50.50× (Concentration)^2- 3.61×(Time)^2	0.97	0.94
Fibre quantity (%)	-82.62+1006.78 × Concentration +0.58 × Time -2.44 × Concentration ×Time- 1819.64× (Concentration)^2- 0.0003×(Time)^2	0.91	0.81
Cellulose (%)	64.72+5.38×Concentration+0.018 × Time	0.65	0.55
Lignin (%)	19.92-16.49 × Concentration-0.02× Time	0.90	0.87

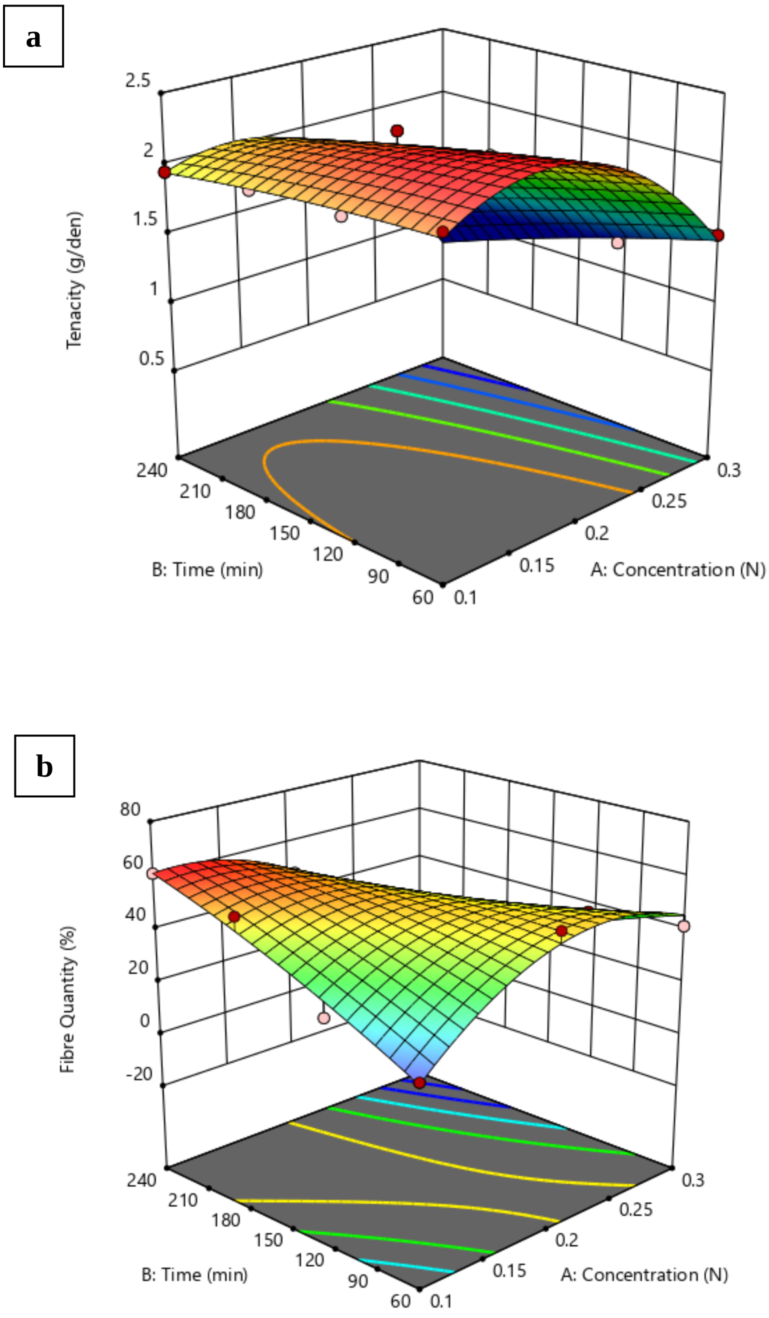
The coefficient of determination (R^2) is defined as the ratio of the sum of squares due to regression to the total sum of squares. It is interpreted as the proportion of the variability in the data explained by the ANOVA. The values of R^2 were 0.97 and 0.91 for tenacity and fibre quantity, respectively (Table 4.3), which are relatively high values which imply that more than 95% of experimental data can be explained by the model. The adjusted R^2 value corrects the R^2 value for the sample size and for the number of terms in the model. The adjusted R^2 for tenacity and fibre quantity were 0.94 and 0.81, respectively, which are also high and indicate a high correlation between the observed and the predicted values.

The coefficient of determination values for cellulose and lignin were 0.65 and 0.90, respectively, and the adjusted coefficient of determination value was 0.55 for cellulose and 0.87 for lignin, which indicated that the model was significant. The results of predicted response optimisation showed that maximum tenacity and fibre quantity with optimum cellulose and lignin content could be attained with a time of 180 minutes and concentration of 0.1(N).

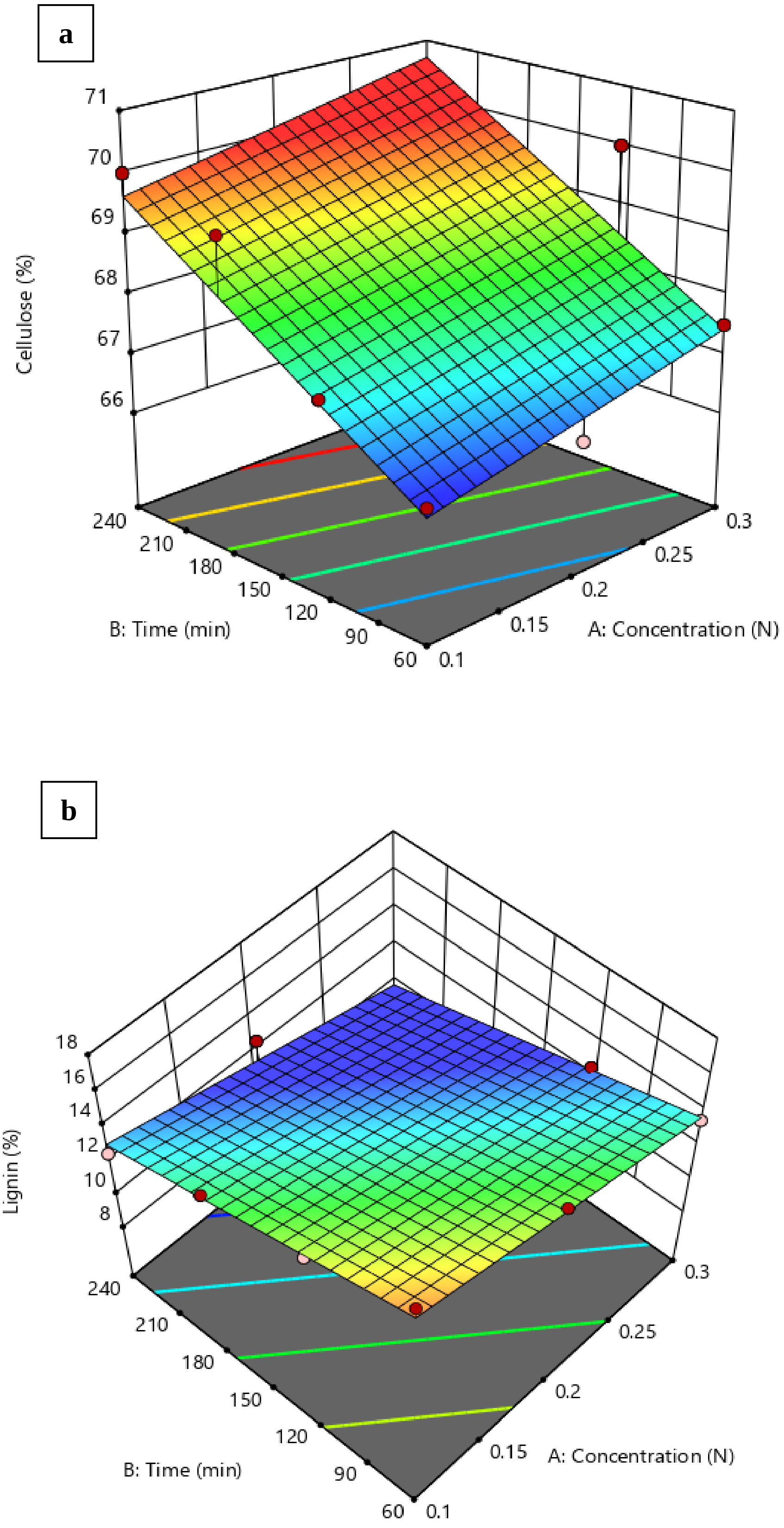
The results of the experimental setup, response surface plots (RSP) for the tenacity, fibre quantity, cellulose and lignin, have been shown in Graph 4.1 and Graph 4.2, respectively. It was observed that there was a reduction in tenacity, with an increase in time and concentration of the NaOH, and the optimised tenacity value, 2.05 g/den, was achieved at 0.1(N) concentration with 180 minutes (Graph 4.1 a). The fibre quantity showed the time and concentration increase till 0.2(N) concentration with 180 minutes, whereas the fibre quantity decreased with a further increase in concentration and time. Therefore, the fibre quantity was 55%, observed at 0.1(N) concentration with 180 minutes (Graph 4.1 b). Cellulose and lignin surface plots (Graph 4.2 a and b) signify the linearity for both the factors, viz. concentration and time as well. In the case of cellulose, it was observed that cellulose content increased with time, and there was a slight decrease with the higher concentration. In the case of lignin content, the amount of lignin kept on decreasing with an increase in cellulose. This may be because the higher concentration of chemicals damaged the fibre structure more as compared to the low concentration level.

Treatment with sodium hydroxide removes the non-fibrous part from the raw sugarcane bagasse. On treatment with alkali the hemicellulose component of multicellular type of fibres like jute / flax /ramie / sugarcane bagasse gets partly dissolves, depending on the concentration of sodium hydroxide, along with other minor components. Hemicellulose acts as a cementing material between the cells and its partial removal causes weakening of the fibre structure which was manifested in the loss of tenacity (Chattopadhyay et al., 1999).

Increase in concentration and treatment duration time further enhances the effect. Gradual removal of non-fibrous part from the raw sugarcane bagasse led to apparent increase in the fibre quantity. Increase in the concentration of sodium hydroxide and treatment time caused gradual removal of hemicellulose and a part of lignin attached to the hemicellulose component which resulted in the relative rise in cellulose content. The drop in lignin content on the rise of time and concentration was due to the loss of a part of the lignin attached to the hemicellulose.



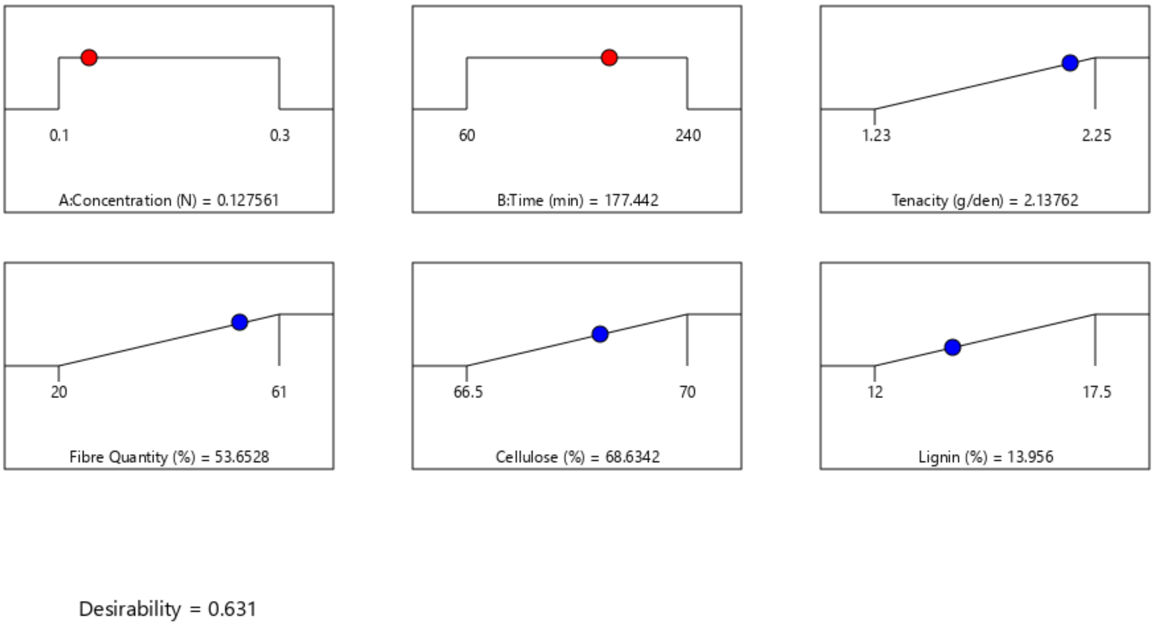
Graph 4.1: Response surface plot showing the effect of concentration and time on different response variables (a) Tenacity, (b) Fibre Quantity



Graph 4.2: Response surface plot showing the effect of concentration and time on different response variables (a) Cellulose content (b) Lignin content

Verification of optimised condition and predictive model

Optimisation of fibre extraction conditions from Sugarcane bagasse was performed by using numerical optimisation. Optimisation requires that goals (i.e., none, maximum, minimum, target, or range) are set for the variables and response, where all goals are combined into one desirability function (Anuar et al, 2013). To find a good set of conditions that will meet all the goals, the two parameters, (i) extraction concentration and (ii) extraction time, are set within range while all four response variables (i) tenacity, (ii) fibre quantity (iii) cellulose (iv) lignin, set at maximum. The optimum level of various parameters was obtained, and desirability ramps developed from optimum points through numerical optimisation are shown in Graph 4.3.



Graph 4.3: Desirability ramp of optimisation for extraction (a) Concentration (b) Time

From Graph 4.3, the results for the optimised extraction condition showed that the predicted values for concentration were 0.12(N), and the time was 177.35 minutes. The predicted value for the response variables for tenacity was 2.13 g/den, fibre quantity was 53.65%, cellulose was 68.63%, and lignin was 13.95%.

Table 4.4: Optimised condition for Sugarcane bagasse fibre extraction

Concentration	0.1(N)
Time	180 minutes
Temperature	90℃

Further, based on model predicted values, the optimized condition for the extraction was 0.1(N) concentration with 180 minutes of time at 90℃(Table 4.4)

4.2 Preliminary testing

4.2.1 Physical properties of extracted fibre

4.2.1.1 Burning test

The fibre catched fire quickly, when approached to flame and propagated faster. The residue was in the form of ash, and after burning, the odour was like burning paper, so the cellulosic nature of fibre was confirmed.

4.2.1.2 Fibre morphology

The longitudinal view of fibre showed the appearance of a fibre-like sugarcane structure. Fibres in bundles were visible with striations; at some places, a single strand of fibre was also observed. The longitudinal view revealed very few shorter, fatter cells, and the bundles appeared to be composed mainly of the longer ultimate cells. Thick walls of the irregular lumen were visible in 45 X under a polarized light microscope (Plate 4.4).

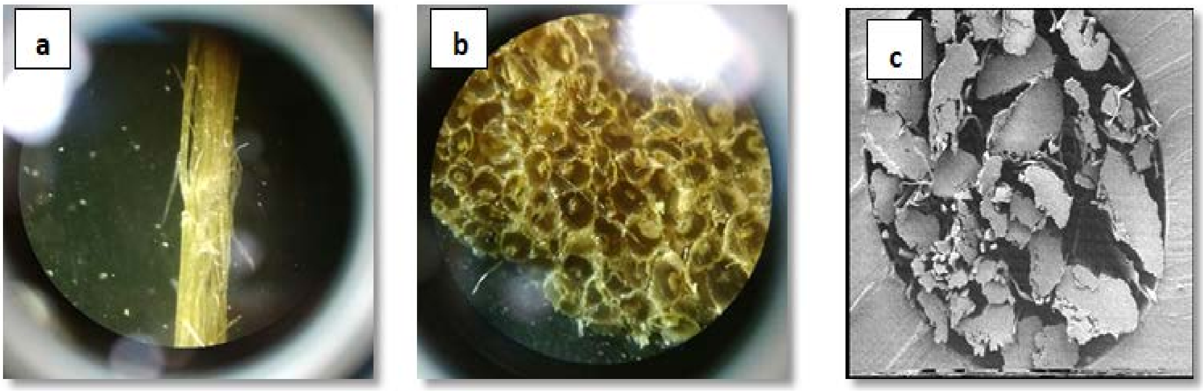


Plate 4.4: Morphology of extracted fibre (a) Longitudinal view 45X (b) Cross-sectional view 45X (c) Cross-sectional view 100X

The SEM photographs revealed that the cross-section of fibre was similar to most of the lingo-cellulosic fibre. Fibre showed irregular shape and variations in diameter. More encrusting material between the ultimate cells was observed in the cross-sectional view of the fibre. Presence of numerous voids around lumen indicated its multi-fibrillar structure showed at different magnification views ranges from 50 X-2000X (Plate 4.5).

4.2.1.3. Fibre length

Sugarcane fibre is a staple length. The length depended on the length between the nodes of the sugarcane. The length was observed between 4.5 cm and 12.5 cm, and the average length was 9.5 cm.

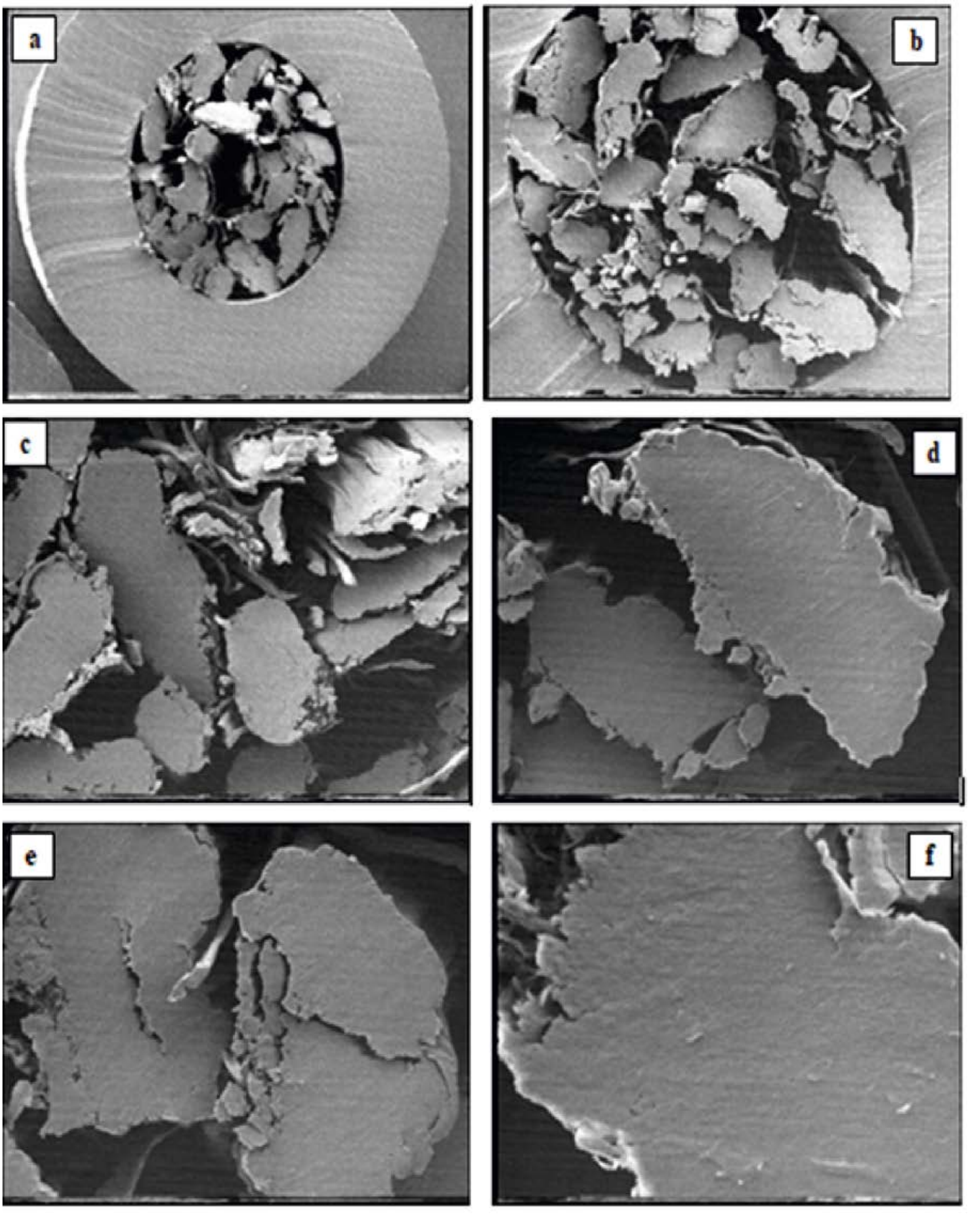


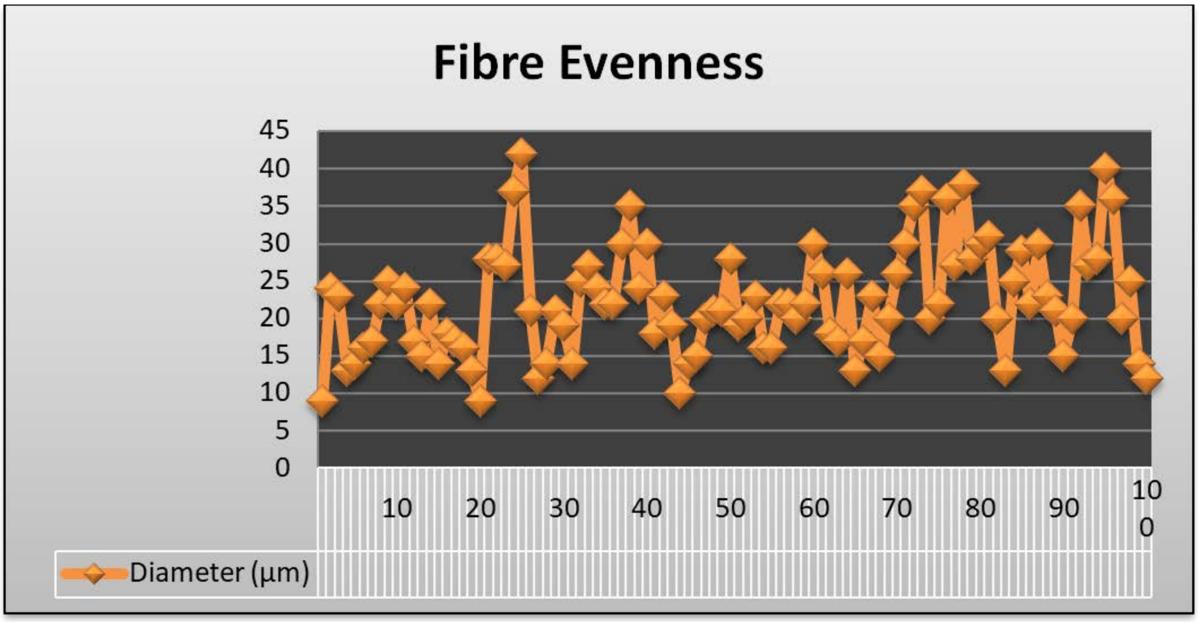
Plate 4.5: Cross-sectional view of fibre by SEM at different magnifications (a) 50X (b) 100X (c) 200X (d) 500X (e) 1000X (f) 2000

4.2.1.4. Fibre diameter

It was observed that fibre had a large variation in diameter. Fibre diameter ranged from 10-35 µm, and the average diameter was 25 µm. It was observed that the fibre length-to-breadth ratio was 3800:1. As the fact associated with the aspect ratio, “the higher the ratio, the finer the fibre", suggests that Sugarcane fibres are not under the class of finer fibres.

4.2.1.5. Fibre fineness and evenness

In the direct system, the fibre fineness value obtained was 228 denier. Fibre evenness was obtained by plotting a graph (Graph 4.4), taking 100 readings of fibre diameter through microscopic observation.



Graph 4.4: Fibre fineness and evenness

The above graph (Graph 4.4) shows a large variation in diameter between the fibres. The graph shows that most of the readings were between 10 and 35 µm. The mean and standard deviation for fibre diameter were obtained as 22.41 µm and 7.23, respectively. Therefore, it was concluded that Sugarcane fibre does not fall in the category of fine fibres and is thus uneven.

4.2.1.6 Fibre moisture content and regain

From the specified method (section 3.4.1.6), fibre moisture content and regain were calculated. The values obtained for moisture content and regain were 7.76% and 8.4%, respectively, which was almost similar to coir fibre' where content and regain were 8-12.5%.

4.2.1.7 Fibre tensile strength

Table 4.5: Tensile strength of extracted fibre

Fibre sample	Denier	Maximum Load (gf)	Extension At Max (mm)	Stress in gf/den	% Strain
Tensile Strength	345.60	738.84	1.06	2.05	1.06
Standard Deviation	184.06	366.77	0.23	0.23	4.66
Coefficient of Variation (%)	53.25	49.64	21.90	10.81	21.90

From the above Table 4.5, the result indicated that the tenacity of extracted fibre was 2.05 gm/den in terms of stress, followed by 1.06% strain, which was found to be good for natural fibres. Tensile strength describes the response of a textile material when an external force is exerted on it until it breaks.

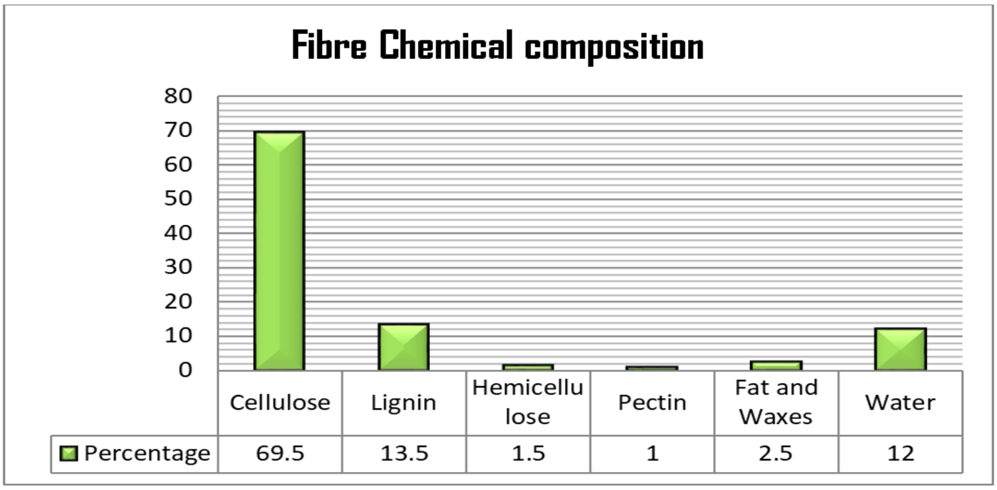
4.2.2 Chemical properties of extracted fibre

4.2.2.1 Chemical solubility test

The solubility test of extracted fibre was done. The fibres were subjected to different alkalines and acids in both cold and hot conditions. The results revealed that the fibre dissolved in 99% of concentrated sulphuric acid (H_2SO_4) when subjected to heat for five minutes, confirming its cellulosic nature.

4.2.2.2. Fibre Chemical composition

Sugarcane bagasse is rich in lignocellulosic biomass and is mainly composed of cellulose, hemicellulose, and lignin. The results of the chemical composition of fibre are presented in Graph 4.5.



Graph 4.5 Chemical composition of extracted fibre

From the above Graph 4.5, it was observed that fibre extracted at optimised conditions had cellulose content of 69.5% and lignin content of 13.5%, followed by water soluble content, fat and waxes content, hemicelluloses and pectin content viz. 12%, 2.5%, 1.5% and 1%.

4.3 Fabrication of an apparatus (Sugarcane Fibre Extractor)

An apparatus for the extraction of fibre was fabricated successfully, and further, the experiment for bulk extraction of fibre was conducted by the researcher using this extractor in the department laboratory. The apparatus was based on the principle of liquor agitation in the presence of heat. The extractor device consists of a stainless steel vessel with a stirrer rod, impellers, and baffles attached for proper agitation, and the motor has a gearbox attached to it. As a heating element, a detachable heating plate is attached to the circular surface of the vessel with the help of screws. A sensor was attached to the upper plate of the vessel that controls the temperature of the heater during the experiment. The apparatus has been granted for patent under the category of utility patent (Indian Patent No: 422455 on 20/02/2023).

4.4 Modification of fibre through Chemical and Enzymatic treatments

Extracted fibres were modified using three different treatments, viz. Acetylation, Cyanoethylation, and Enzymatic treatment as per the recipes mentioned in section 3.6 (Chapter-3).

4.5 Optimisation of modification treatments

After modification treatment, oil sorption capacity, oil retention ability, recovery of sorbed oil and reusability of the fibre samples were tested for each treatment and the average of readings were calculated for further optimisation of treatment parameters. The results of the testing have been discussed under the following sub-heads:

4.5.1 Acetylation treatment

4.5.1.1 Testing of oil sorption capacity

After acetylation treatment, the fibre samples were tested for their oil sorption capacity, oil retention ability, reusability of sorbed oil and recovery of the sample. All the above tests were carried out by following the specified method mentioned in section 3.7(Chapter 3). The results of testing modified fibres for oil sorption capacity are presented in Table 4.6(a).

Table 4.6 (a): Oil sorption capacity of fibres after treatment at 1% concentration

S.No.	**Temperature (℃)**	**Time (min)**	**Sorption (g/g)**
1	30	30	19.19
2	30	60	18.60
3	30	90	15.25
4	50	30	14.64
5	50	60	13.23
6	50	90	14.56
7	70	30	10.80
8	70	60	11.05
9	70	90	8.05

From Table 4.6 (a), it was observed that the maximum oil sorption capacity (19.19 g/g) of fibres was found at room temperature (30℃) for 30 minutes of treatment time. The results showed that as the treatment time increased at room temperature, the sorption was low (15.25 g/g), whereas at 50℃, the highest sorption (14.64 g/g) was found at 30 minutes of treatment time and the lowest (13.23 g/g) was at 60 minutes. It was noticed that for the treatment temperature of 70℃, the maximum sorption (11.08 g/g) was obtained at 60 minutes of treatment time. Overall, the data reported that the sorption capacity decreased as the treatment temperature and time increased.

Table 4.6 (b) Oil sorption capacity of fibres after treatment at 3% concentration

S.No.	**Temperature (℃)**	**Time (min)**	**Sorption (g/g)**
1	30	30	17.71
2	30	60	13.06
3	30	90	13.02
4	50	30	14.01
5	50	60	10.42
6	50	90	8.20
7	70	30	10.24
8	70	60	10.08
9	70	90	8.0

The data presented in Table 4.6 (b) indicates that at 3% concentration of treatment resulted the maximum oil sorption capacity (17.71 g/g) of fibres at room temperature (30℃) for 30 minutes treatment time. The data revealed that at 50℃, the highest sorption (14.01 g/g) was found at 30 minutes of treatment time, and the lowest (8.20 g/g) was at 90 minutes. It was observed that at 70℃, the maximum sorption (10.24 g/g) was obtained at 30 minutes of treatment time. Hence, the data interprets that the highest sorption capacity was found in all three temperatures with 30 minutes of time at a 3% concentration.

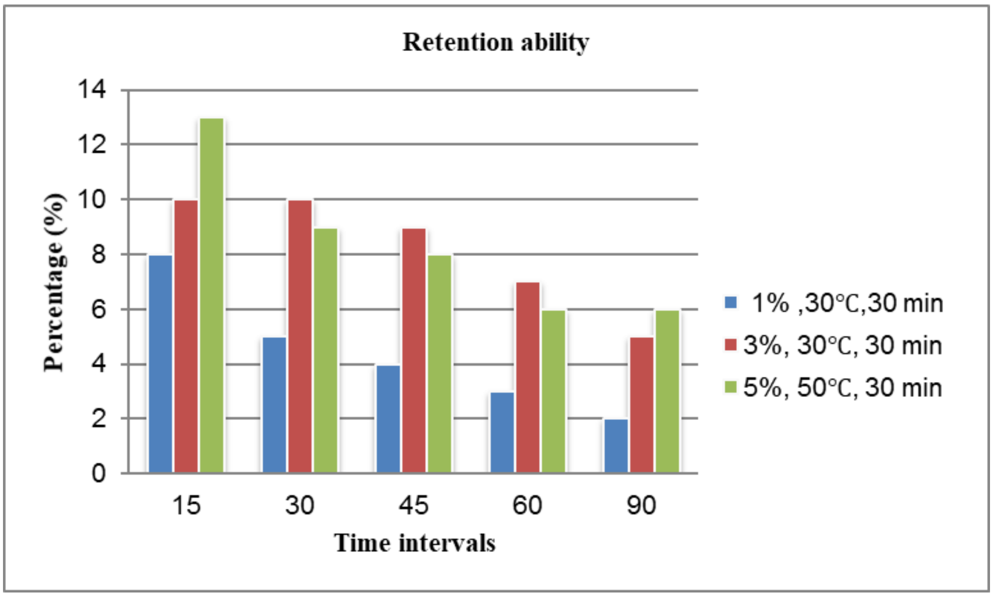
Table 4.6 (c) Oil sorption capacity of fibres after treatment at 5% concentration

S.No.	Temperature (℃)	Time (min)	Sorption (g/g)
1	30	30	12.22
2	30	60	12.75
3	30	90	10.74
4	50	30	13.64
5	50	60	12.23
6	50	90	9.58
7	70	30	10.05
8	70	60	10.34
9	70	90	7.58

The data presented in Table 4.6 (c) depicts that a treatment concentration of 5% showed the maximum oil sorption capacity (13.64 g/g) of fibres at 50℃ for 30 minutes of treatment time, whereas at 30℃, the highest sorption (12.75g/g) was found at 60 minutes. It was observed that at 70℃, the maximum sorption (10.34 g/g) was obtained at 60 minutes of treatment time. The lowest sorption was obtained (7.58 g/g) at 70℃ for 90 minutes.

4.5.1.2 Testing of oil retention ability

The oil retention ability of fibres was tested for the higher and lower sorption capacity of fibres at different concentrations for acetylation treatment. The results of the testing are discussed through the following Graph representations:



Graph 4.6: Oil retention ability of fibres at 1%, 3% and 5% concentration

Graph 4.6 shows the retention ability of fibre treated at different concentrations viz 1%, 3% and 5%. The data was taken between five time intervals, viz. 15, 30, 45, 60 and 90 minutes. It was observed that at 1% concentration, there was a slight reduction in retention ability as the time increased after 30 minutes compared to the time interval between 15-30 minutes. The retention ability at 3% of concentration resulted in less difference in retention between all the time intervals. At 5% concentration, the retention value is higher after 15 minutes, whereas from 30 to 90 minutes, there were fewer differences obtained between the values.

4.5.1.3 Testing of recovery of sorbed oil

The results of the testing of recovery of sorbed oil were calculated and presented in Table 4.7 at different concentration, time and temperature.

Table 4.7 (a) Recovery of sorbed oil after treatment at 1% concentration

S.No.	Temperature (℃)	Time (min)	Recovery (%)
1	30	30	70.76
2	30	60	68.12
3	30	90	65.72
4	50	30	63.87
5	50	60	62.41
6	50	90	63.27
7	70	30	64.50
8	70	60	64.22
9	70	90	62.65

From Table 4.7 (a), it was observed that the maximum recovery of sorbed oil (70.76%) was found at room temperature (30℃) for 30 minutes of treatment time. The results showed that as the treatment time increases at room temperature, the recovery was low (65.72%) due to less sorption of fibre sample as the fact associated that as much higher the sorption, the recovery is more. Hence, at 50℃, 30 minutes, the lowest percentage of oil recovered from the sorbed sample (62.41%). It was noticed that for the treatment temperature of 70℃ with different time durations, the data shows significantly less difference in recovery percent viz. 64.50%, followed by 64.22% and 62.65 % respectively.

Table 4.7 (b) Recovery of sorbed oil after treatment at 3% concentration

S.No.	Temperature (℃)	Time (min)	Recovery (%)
1	30	30	69.16
2	30	60	65.80
3	30	90	67.29
4	50	30	65.57
5	50	60	69.04
6	50	90	66.13
7	70	30	71.29
8	70	60	68.55
9	70	90	64.96

The data presented in Table 4.7 (b) indicates that at 3% concentration of treatment resulted the maximum recovery of sorbed oil (71.29%) at temperature (70℃) for 30 minutes treatment time followed by 69.16% recovery at room temperature 30℃ for 30 minutes of time. The data revealed that at 70℃, the lowest recovery (64.96%) was found at 90 minutes of treatment time.

Table 4.7 (c) Recovery of sorbed oil after treatment at 5% concentration

S.No.	Temperature (℃)	Time (min)	Recovery (%)
1	30	30	63.66
2	30	60	66.87
3	30	90	62.11
4	50	30	64.16
5	50	60	66.24
6	50	90	63.33
7	70	30	70.58
8	70	60	68.10
9	70	90	64.32

The data presented in Table 4.7 (c) depicts that a treatment concentration of 5% showed the maximum recovery of oil (70.58%) at 70℃ for 30 minutes of treatment time, whereas, at 30℃, the highest recovery (66.87%) was found at 60 minutes. At 50℃, the highest recovery (66.24%) was observed at 60 minutes of treatment time. The lowest recovery was obtained (62.11%) at room temperature (30℃) for 90 minutes.

4.5.1.4 Testing of reusability of sample

The results of the testing for reusability of samples are calculated and presented in Table 4.8.

Table 4.8 (a) Reusability of samples after treatment at 1% concentration

S.No.	Temperature (℃)	Time (min)	Reusability(g/g)
1	30	30	15.55
2	30	60	14.78
3	30	90	10.53
4	50	30	10.25
5	50	60	9.83
6	50	90	10.16
7	70	30	9.03
8	70	60	10.74
9	70	90	7.12

From Table 4.8 (a), it was observed that the maximum reusability (15.55 g/g) of the sample was found at room temperature (30℃) for 30 minutes of treatment time. The results showed that as the treatment time increased (90 minutes) at room temperature, the reusability was minimum (10.53 g/g) due to less oil sorption in second time. Therefore, at 50℃, 60 minutes, the lowest reusability of the sample (9.83 g/g) was observed. It was noticed that for the treatment temperature of 70℃, the highest reusability (10.74 g/g) of the sample was obtained at 60 minutes, and the lowest value (9.03 g/g) was at 30 minutes.

Table 4.8(b) Reusability of fibres after treatment at 3% concentration

S.No.	Temperature (℃)	Time (min)	Reusability(g/g)
1	30	30	13.47
2	30	60	11.03
3	30	90	10.9
4	50	30	10.27
5	50	60	10.21
6	50	90	7.53
7	70	30	10.07
8	70	60	10.02
9	70	90	7.22

The data presented in Table 4.8 (b) indicates that at 3% concentration of treatment resulted the maximum reusability of sample (13.47 g/g) at room temperature (30℃) for 30 minutes treatment time followed by 11.03 g/g at room temperature (30℃) for 60 minutes of time. The data revealed that at 70℃, the minimum reusability of the sample (7.22 g/g) was found at 90 minutes of treatment time.

Table 4.8(c) Reusability of fibres after treatment at 5% concentration

S.No.	Temperature (℃)	Time (min)	Reusability(g/g)
1	30	30	9.26
2	30	60	9.55
3	30	90	8.57
4	50	30	12.93
5	50	60	11.28
6	50	90	9.33
7	70	30	9.45
8	70	60	9.77
9	70	90	7.39

The data presented in Table 4.8 (c) depict that a treatment concentration of 5% showed the maximum reusability of the sample (12.93 g/g) at 50℃ for 30 minutes of treatment time, whereas at 70℃, the minimum reusability (7.39 g/g) was found at 90 minutes. It was observed that at room temperature (30℃), the highest recovery (9.55 g/g) was obtained at 60 minutes of treatment time, followed by 9.26 g/g at 30 minutes.

Statistical analysis

The data obtained from the testing results, oil sorption capacity, recovery of sorbed oil, and reusability of the sample were statistically analysed for further treatment optimisation.

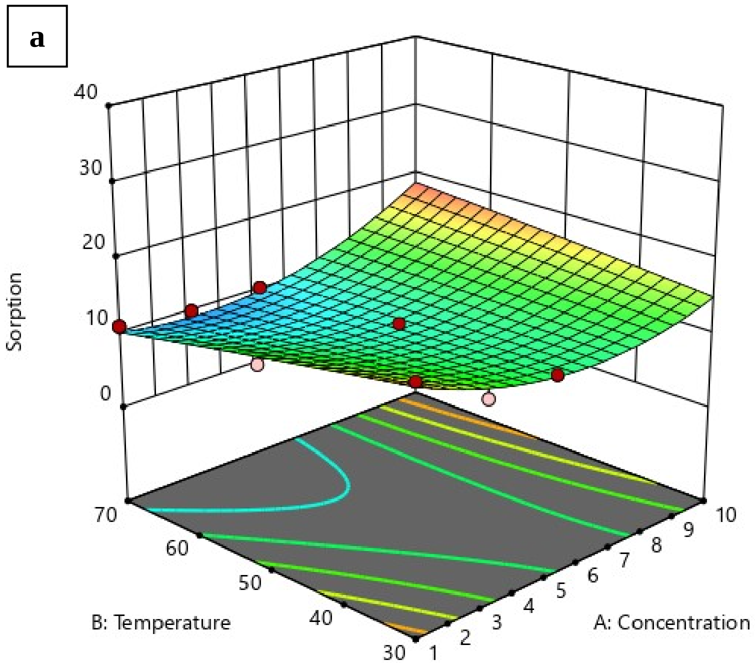
a) Analysis for oil sorption capacity

Analysis of variance (ANOVA) for oil sorption capacity was performed to determine the significance of the models. The results are presented in the following Tables and Graphs.

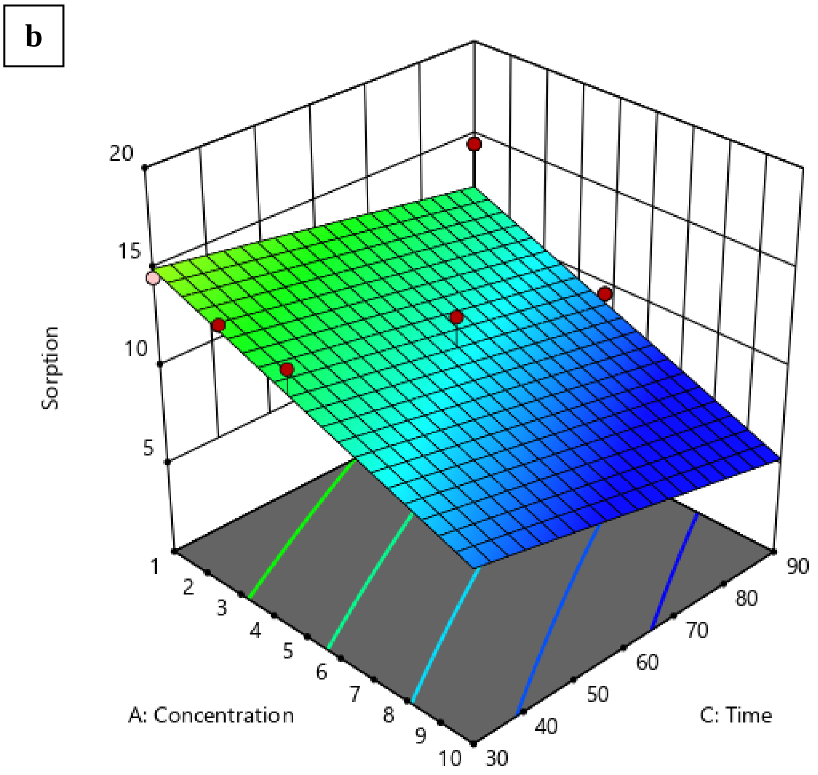
Table 4.9: Variance analysis (ANOVA) of oil sorption capacity of acetylated fibre at different treatment parameters

ANOVA for Reduced Quadratic model : Sorption (g/g)						
Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	224.39	7	32.06	21.14	< 0.0001	Significant
A-Concentration	0.35	1	0.35	0.23	0.0317	
B-Temperature	5.07	1	5.07	3.35	0.0831	
C-Time	42.08	1	42.08	27.75	< 0.0001	
AB	19.76	1	19.76	13.03	0.0019	
A^2	4.18	1	4.18	2.76	0.1134	
B^2	0.09	1	0.09	0.06	0.8029	
C^2	0.67	1	0.67	0.44	0.5125	
Residual	28.81	19	1.52			
Cor Total	253.20	26				

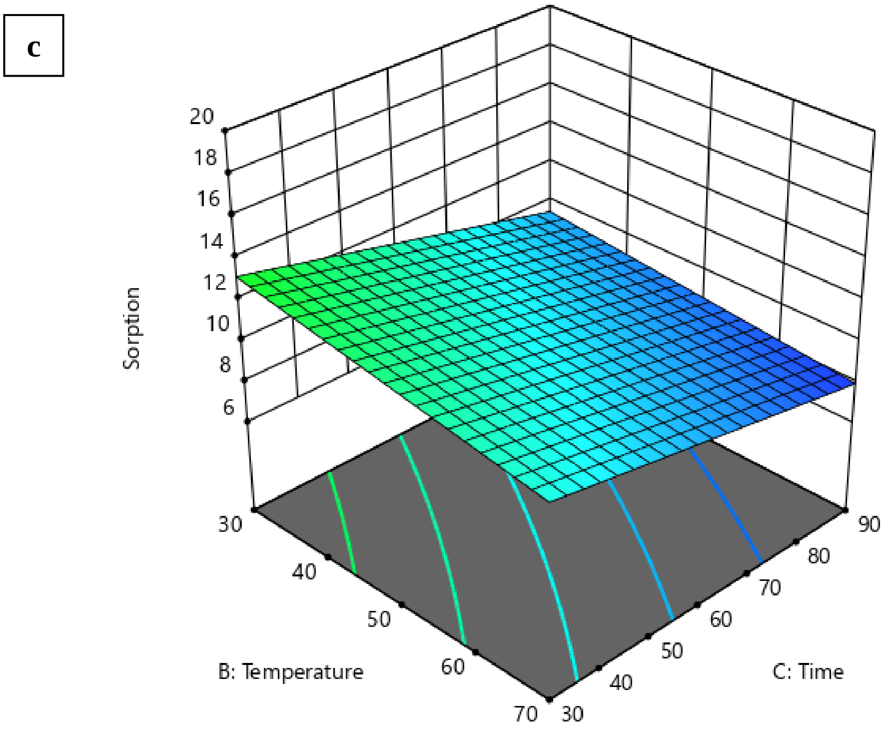
The summary of the analysis of variance (ANOVA) for the oil sorption capacity of the fibre has been listed in Table 4.9. Factors such as treatment concentration, and time were identified as significantly affecting the response variables of fibre sorption. The model F-value (sorption) of 21.14 implies that the model was significant. P-values **(**< 0.0001**)** less than 0.0500 indicate that model terms are significant. The results of ANOVA for model A (Concentration), C (time) and AB (concentration and temperature) were found significant, with p-values of 0.0317, < 0.0001 and 0.0019, respectively. The ANOVA of Reduced Quadratic model demonstrated that the models were highly significant, evident from Fisher's *F*-test with high F value and low *P* value.



Graph 4.7(a) Response surface plot showing the effect of concentration and temperature on sorption



Graph 4.7(b) Response surface plot showing the effect of concentration and time on sorption



Graph 4.7(c) Response surface plot showing the effect of temperature and time on sorption

Graph 4.7 shows the response surface plots (RSP) for the sorption capacity of fibres at different combinations of concentration, time and temperature. The effect of temperature and concentration was observed in Graph 4.7(a), which indicates that both factors significantly affect the sorption capacity as compared to time and temperature (Graph 4.7c). The surface plot of concentration and time (Graph 4.7b) shows the flattened graph, which means that both these factors have less effect on the sorption capacity of the fibre.

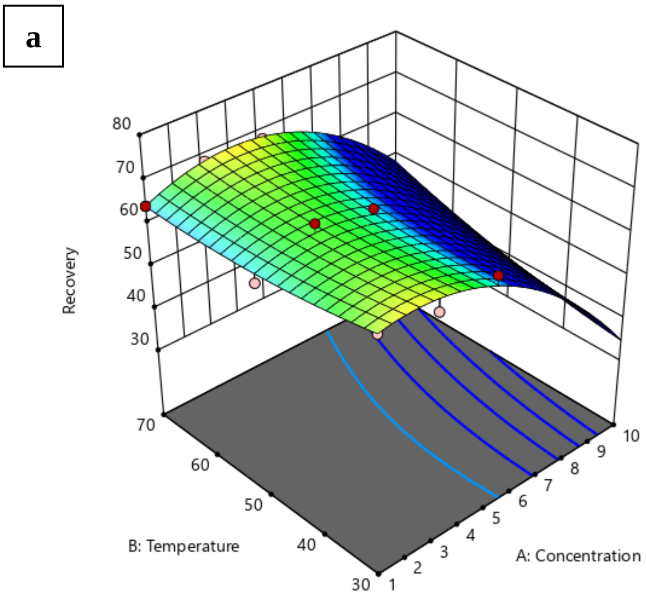
b) Analysis for Recovery of sorbed oil

Analysis of variance (ANOVA) for recovery of sorbed oil was performed to determine the significance of the models. The results are presented in the following Tables and Graphs.

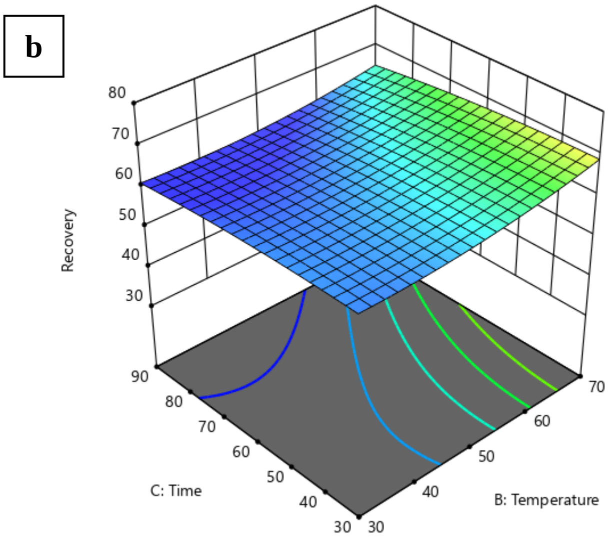
Table 4.10 Variance analysis (ANOVA) of recovery of sorbed oil from Acetylated fibre at different treatment parameters

ANOVA for Reduced Quadratic model: Recovery (%)						
Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	130.99	7	18.71	6.51	0.0005	Significant
A-Concentration	26.95	1	26.95	9.38	0.0064	
B-Temperature	32.04	1	32.04	11.15	0.0034	
C-Time	31.39	1	31.39	10.93	0.0037	
AB	46.37	1	46.37	16.14	0.0007	
A^2	30.66	1	30.66	10.67	0.0041	
B^2	17.36	1	17.36	6.04	0.0237	
C^2	4.37	1	4.37	1.52	0.2323	
Residual	54.59	19	2.87			
Cor Total	185.58	26				

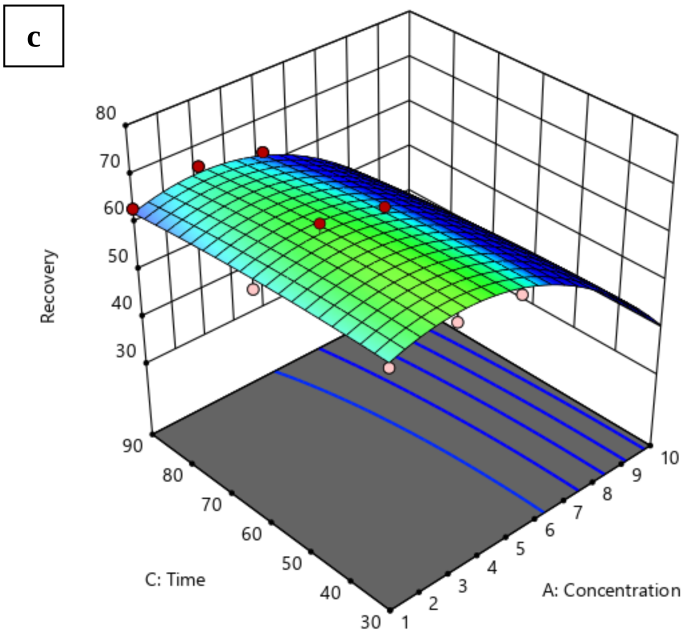
A summary of the analysis of variance (ANOVA) for the selected reduced quadratic polynomial model for the recovery of sorbed oil has been listed in Table 4.10. Factors such as treatment concentration, time, and temperature were identified as significantly affecting the response variables of fibre sorption. The model F-value (sorption) of 6.51 implies that the model was significant. P-values (0.0005) less than 0.0500 indicate that model terms are significant. The results of ANOVA for models A, B, C, AB, A^2, and B^2 were found significant with p- values 0.0064, 0.0034, 0.0037, 0.0007, 0.0041 and 0.0237, respectively. The ANOVA of reduced quadratic regression model demonstrated that the models were highly significant, evident from Fisher's *F*-test with high *F* value and low *P* value.



Graph 4.8(a) Response surface plot showing the effect of temperature and concentration on recovery of sorbed oil



Graph 4.8(b) Response surface plot showing the effect of time and temperature on recovery of sorbed oil



Graph 4.8(c) Response surface plot showing the effect of time and concentration on recovery of sorbed oil

Graph 4.8 shows the response surface plots (RSP) for the recovery of sorbed oil at different combinations of concentration, time and temperature. The effect of temperature and concentration was observed in Graph 4.8(a), which indicates that both factors significantly affect the sorption capacity as compared to time and concentration (Graph 4.8 c). The surface plot of temperature and time (Graph 4.8b) shows the flattened graph, which means that both these factors have less effect on the recovery of sorbed oil.

c) Analysis for Reusability of sample

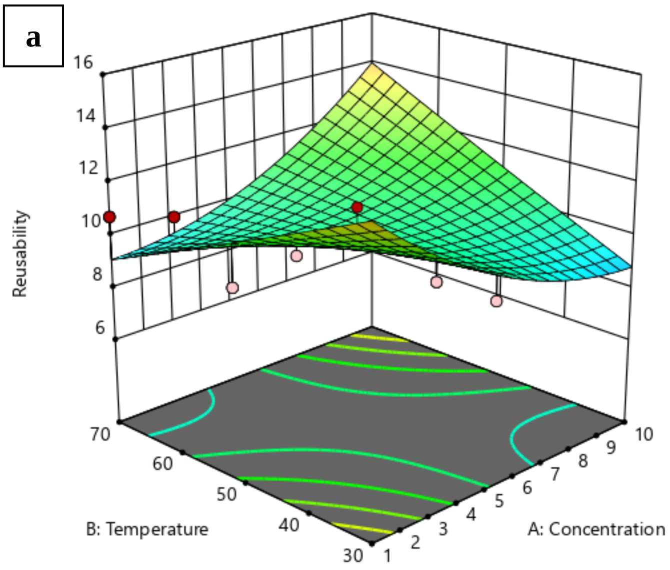
Analysis of variance (ANOVA) for reusability of sample was performed to determine the significance of the models. The results are presented in the following Tables and Graphs.

Table 4.11 Variance analysis (ANOVA) of reusability of Acetylated fibre at different treatment parameters

ANOVA for Reduced Quadratic model: Reusability (g/g)						
Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	80.02	7	11.43	7.03	0.0003	Significant
A-Concentration	0.0002	1	0.0002	0.0001	0.9915	

B-Temperature	0.0612	1	0.0612	0.0377	0.8481	
C-Time	25.75	1	25.75	15.85	0.0008	
AB	14.52	1	14.52	8.94	0.0075	
A^2	0.3083	1	0.3083	0.1897	0.6681	
B^2	0.0140	1	0.0140	0.0086	0.9270	
C^2	4.39	1	4.39	2.70	0.1168	
Residual	30.87	19	1.62			
Cor Total	110.89	26				

Table 4.11 presented the results of analysis of variance (ANOVA) for the selected the reduced quadratic polynomial model for reusability of sample. The model F-value (reusability) of 7.03 implies that the model was significant. P-values (0.0003) less than 0.0500 indicate that model terms are significant. The results of ANOVA for model C (time) and AB(concentration and temperature) were found to be significant, with p-values of 0.0008 and 0.0075, respectively. The ANOVA of the reduced quadratic regression model demonstrated that the models were highly significant.



Graph 4.9(a) Response surface plot showing the effect of temperature and concentration on the reusability of sample

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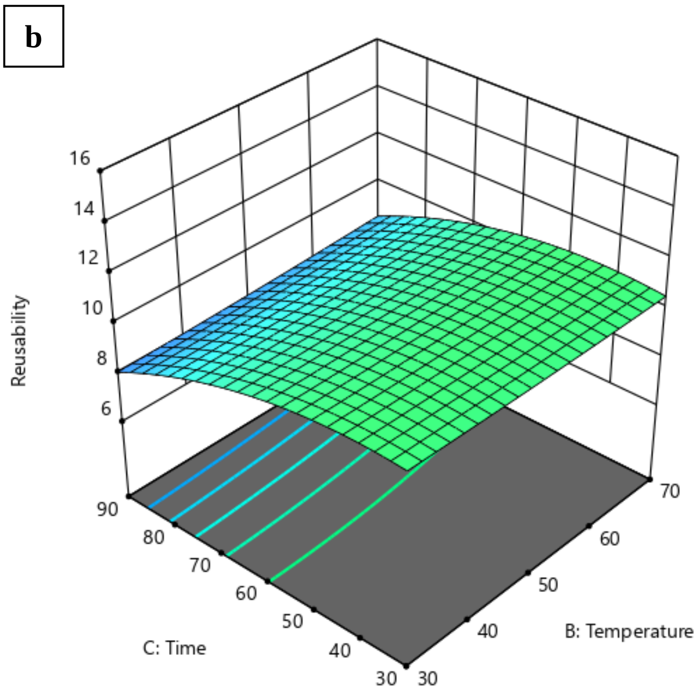
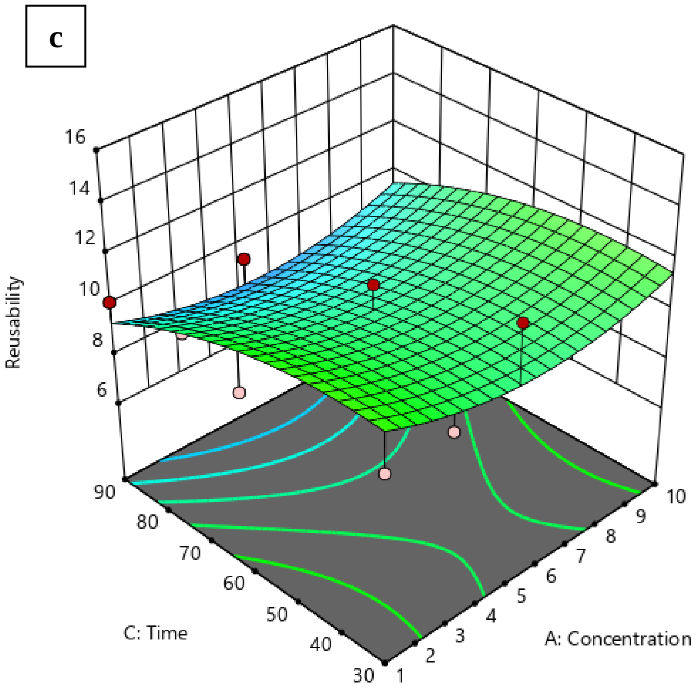


Graph 4.9(b) Response surface plot showing the effect of time and temperature on the reusability of sample



Graph 4.9(c) Response surface plot showing the effect of time and concentration on the reusability of sample

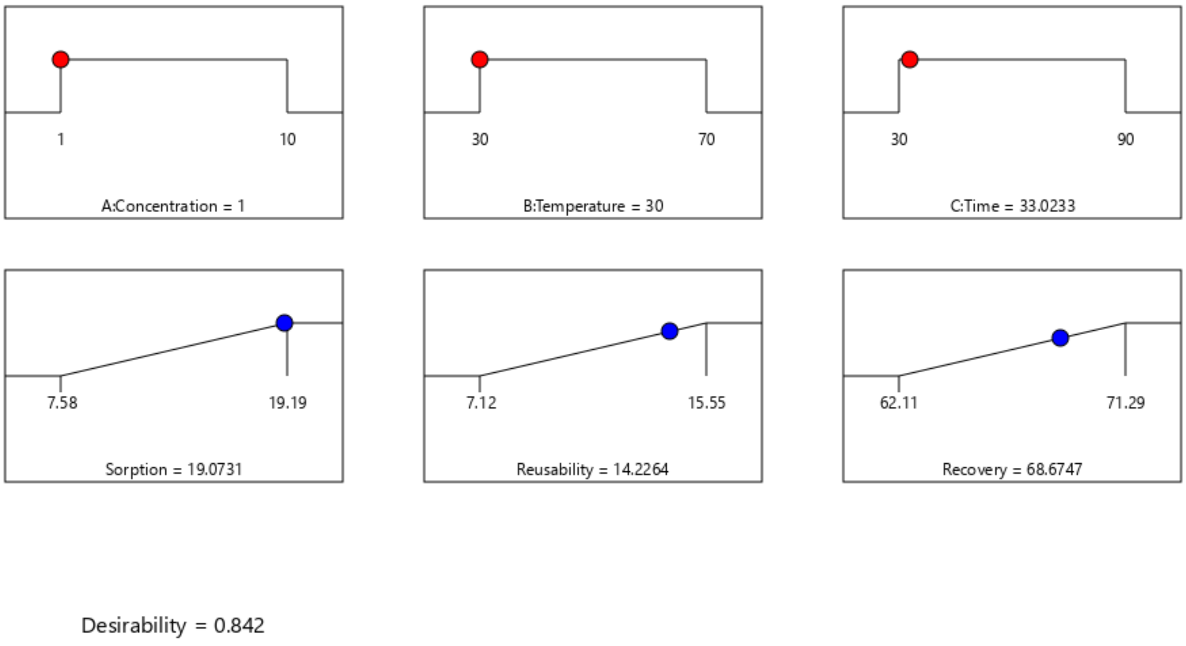
Response surface plots (RSP) for the reusability of the sample interpret that the effect of temperature and concentration was found highly significant in Graph 4.9(a), which indicates that both the treatment parameters affect the reusability more as compared to time and concentration (Graph 4.9c). The surface plot of temperature and time (Graph 4.9b) shows the flattened graph which means that both these factors were less affected for reusability of the sample.

Table 4.12: Results of the statistical analysis for optimisation of Acetylation parameters

Response Variable	**R^2**	**Adjusted R^2**	**Predicted R^2**
Sorption (g/g)	0.88	0.84	0.78
Recovery (%)	0.70	0.59	0.41
Reusability (g/g)	0.72	0.61	0.43

The coefficient of determination (R^2) values for sorption, recovery and reusability were 0.88, 0.70 and 0.72, respectively. The adjusted R^2 values were 0.84 for sorption, 0.59 and 0.61 for recovery and reusability, indicating that the model was significant. The results of predicted R^2 showed 0.78, 0.41 and 0.43 for sorption, recovery and reusability, respectively (Table 4.12).

Verification of optimised treatment parameters and predictive model



Graph 4.10: Desirability ramp for optimisation of acetylation treatment parameters

Graph 4.10 shows the optimised parameters of acetylation treatment based on three response variables, viz. sorption capacity, recovery of sorbed oil and reusability of the fibre sample. The data was obtained by using numerical optimisation. Optimisation requires that goals (i.e., none, maximum, minimum, target, or in range) are set for the variables and response, where all goals then get combined into one desirability function. To find a good set of conditions that will meet all the goals, all three parameters, (i) concentration, (ii) time and (iii) temperature, were set within range while all three response variables (i) sorption, (ii) recovery and (iii) reusability, set at maximum. The optimum level of various parameters was obtained, and desirability ramps were developed from optimum points via numerical optimisation.

From Graph 4.10, the results for optimised parameters for acetylation treatment condition showed the predicted values for concentration was 1%, temperature was 30℃, and time was 33.02 minutes. For the response variables, the predicted value for sorption was 19.07 g/g, recovery was 68.67%, and reusability was 14.22 g/g.

Table 4.13 Optimised parameters for acetylation treatment

Concentration of perchloric acid	1%
Treatment time	30 minutes
Treatment temperature	30℃

Further, on the basis of model predicted values, the optimised parameters for acetylation treatment were 1% concentration, temperature was 30℃and 30 minutes of time (Table 4. 13).

4.5.2 Cyanoethylation treatment

The fibre samples after cyanoethylation treatment were tested for their oil sorption capacity test, oil retention ability, reusability of sorbed oil and recovery of the sample. All the above tests were carried out by following the specified method mentioned in section 3.7 (chapter 3).

4.5.2.1 Testing of oil sorption capacity

The results of testing modified fibres for oil sorption capacity are presented in Table 4.14(a).

Table 4.14 (a) Oil sorption capacity of fibres after treatment at 1% concentration

S.No.	Temperature (℃)	Time (min)	Sorption (g/g)
1	30	30	8.27
2	30	60	8.35
3	30	90	8.42
4	50	30	17.12
5	50	60	20.02
6	50	90	17.99
7	70	30	14.36
8	70	60	19.44
9	70	90	13.22

From Table 4.14 (a), it was observed that the maximum oil sorption capacity (20.02 g/g) of fibres was found at temperature (50℃) for 60 minutes, followed by sorption (19.44 g/g) at temperature 70℃ with 60 minutes of treatment time. The results showed that as the treatment time increased at room temperature, the sorption also increased. It was noticed that for the treatment temperature of 30℃, the minimum sorption (8.27 g/g) was obtained at 30 minutes of treatment time. Overall, the data reported that the maximum sorption capacity was obtained as the treatment temperature increased to 50℃ and 60 minutes of treatment time.

Table 4.14 (b) Oil sorption capacity of fibres after treatment at 5% concentration

S.No.	Temperature (℃)	Time (min)	Sorption (g/g)
1	30	30	12.18
2	30	60	14.22
3	30	90	15.63
4	50	30	16.46

5	50	60	22.99
6	50	90	16.97
7	70	30	20.12
8	70	60	29.35
9	70	90	18.75

The data presented in Table 4.14 (b) indicates that at 5% concentration of treatment resulted the maximum oil sorption capacity (29.35 g/g) of fibres at 70℃ temperature for 60 minutes treatment time. The data revealed that at 50℃; the highest sorption (22.99 g/g) was found at 60 minutes of treatment time, and the lowest (16.46 g/g) was at 30 minutes. It was observed that at room temperature (30℃), the higher sorption (15.63 g/g) was obtained at 90 minutes of treatment time, whereas the lowest sorption was (12.18 g/g) at 30 minutes of time. Hence, the data interprets that the maximum sorption capacity was found at higher temperatures with 60 minutes of time at 5% concentration.

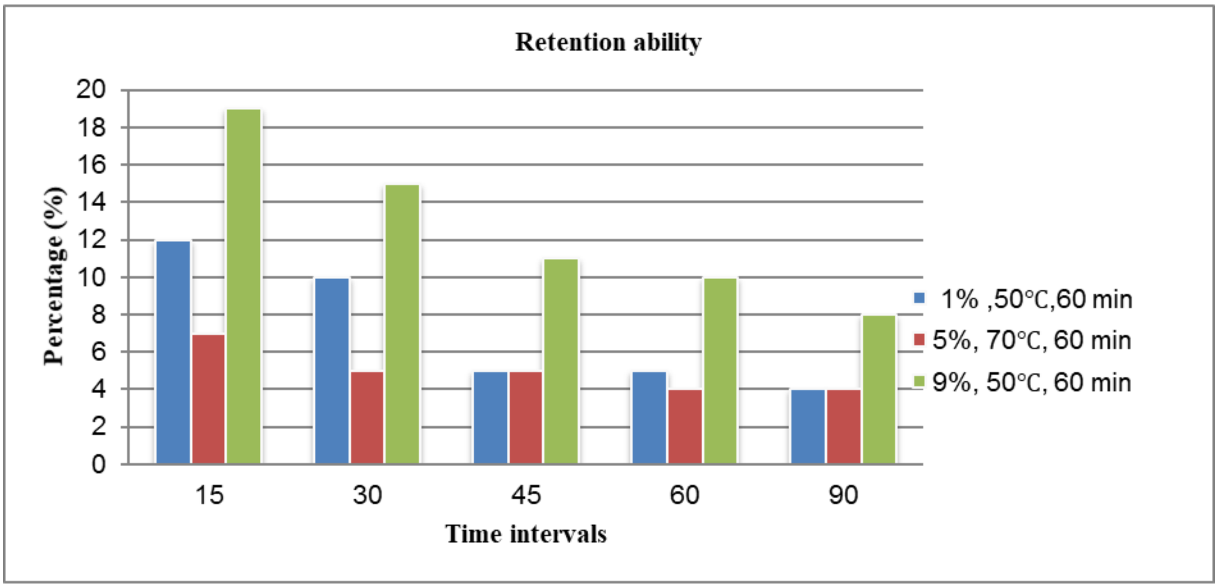
Table 4.14 (c) Oil sorption capacity of fibres after treatment at 9% concentration

S.No.	Temperature (℃)	Time (min)	Sorption (g/g)
1	30	30	12.95
2	30	60	14.92
3	30	90	17.84
4	50	30	16.86
5	50	60	22.33
6	50	90	18.62
7	70	30	14.46
8	70	60	15.75
9	70	90	13.30

The data presented in Table 4.14 (c) depicts that treatment concentration of 9% showed the maximum oil sorption capacity (22.33 g/g) of fibres at 50℃ for 60 minutes treatment time, whereas at 30℃, the minimum sorption (12.95 g/g) was found at 30 minutes. It was observed that at 70℃; the higher sorption (15.75 g/g) was obtained at 60 minutes of treatment time. The lowest sorption (13.30 g/g) was obtained at 70℃ for 90 minutes.

4.5.2.2 Testing of oil retention ability

The oil retention ability of fibres was tested for the higher and lower sorption capacity of fibres at different concentrations for cyanoethylation treatment. The results of the testing were discussed through the following Graph representations:



Graph 4.11 Oil retention ability of fibres at 1%, 5% and 9% concentration

Graph 4.11 shows the retention ability of fibre treated at different concentrations viz 1%, 5% and 9%. The data was taken between five time intervals, viz. 15, 30, 45, 60 and 90 minutes. It was observed that at 1% concentration, there was a slight reduction in retention ability as the time increased after 30 minutes compared to the time interval between 15-30 minutes. The retention ability at 5% of concentration resulted in less difference in retention between all the time intervals. At 9% concentration, the retention value is higher after 15 minutes, whereas from 30 to 90 minutes, there were fewer differences obtained between the values.

4.5.2.3 Testing of recovery of sorbed oil

The results of the testing of recovery of sorbed oil were calculated and presented in Table 4.15 at different concentrations, times and temperatures.

Table 4.15 (a) Recovery of oil from fibres after treatment at 1% concentration

S.No.	Temperature (℃)	Time (min)	Recovery (%)
1	30	30	51.50
2	30	60	54.78
3	30	90	57.24
4	50	30	60.06
5	50	60	65.98
6	50	90	63.55
7	70	30	63.38
8	70	60	67.24
9	70	90	61.35

From Table 4.15 (a), it was observed that the maximum recovery of sorbed oil (67.24%) was found at temperature (70℃), followed by 65.98% at 50℃ for 60 minutes of treatment time. The results showed that as the treatment time decreased at room temperature, the recovery was low (51.50%). Therefore, at 50℃ for 30 minutes, the lowest percentage (60.06%) of oil recovered from the sorbed sample was obtained.

Table 4.15 (b) Recovery of oil from fibres after treatment at 5% concentration

S.No.	Temperature (℃)	Time (min)	Recovery (%)
1	30	30	60.19
2	30	60	65.27
3	30	90	68.96
4	50	30	66.21
5	50	60	73.37
6	50	90	66.98
7	70	30	64.56
8	70	60	71.05
9	70	90	67.51

The data presented in Table 4.15 (b) indicates that at 5% concentration of treatment resulted in the maximum recovery of sorbed oil (73.37%) at temperature (50℃) for 60 minutes of treatment time, followed by 71.05% recovery at temperature 70℃ for 60 minutes of treatment time. The data revealed that at room temperature 30℃, the highest recovery (68.96%) was found at 90 minutes, and the lowest recovery (60.19%) was found at 30 minutes of treatment time.

Table 4.15 (c) Recovery of oil from fibres after treatment at 9% concentration

S.No.	Temperature (℃)	Time (min)	Recovery (%)
1	30	30	58.20
2	30	60	59.51
3	30	90	60.96
4	50	30	63.34
5	50	60	67.70
6	50	90	65.49
7	70	30	64.00
8	70	60	66.12
9	70	90	62.21

The data presented in Table 4.15 (c) depicts that treatment concentration of 9% showed the maximum recovery of oil (67.70%) at 50℃ for 60 minutes of treatment time, whereas, at 30℃, the highest recovery (60.96%) was found at 90 minutes. It was observed that at 70℃, the highest recovery (66.12%) was obtained at 60 minutes of treatment time. The lowest recovery was obtained (58.20%) at room temperature (30℃) for 30 minutes.

4.5.2.4 Testing of reusability of sample

The results of the testing for reusability of samples were calculated and presented in Table 4.16.

Table 4.16 (a) Reusability of fibres after treatment at 1% concentration

S.No.	Temperature (℃)	Time (min)	Reusability(g/g)
1	30	30	8.01
2	30	60	8.21
3	30	90	8.32
4	50	30	16.65
5	50	60	19.06
6	50	90	16.98
7	70	30	16.61
8	70	60	18.81
9	70	90	12.81

From Table 4.16 (a), it was observed that the maximum reusability (19.06 g/g) of the sample was found at room temperature (50℃) for 60 minutes of treatment time, followed by 18.81 g/g at 70℃ temperature with 60 minutes of time. It was noticed that for the treatment temperature of 70℃, the lowest reusability (12.81 g/g) of the sample was obtained at 90 minutes, and the lowest value at 50℃ (16.65 g/g) was found at 30 minutes. The results shows that the minimum recovery of sample was observed at room temperature for 30 minutes of time.

Table 4.16 (b) Reusability of fibres after treatment at 5% concentration

S.No.	Temperature (℃)	Time (min)	Reusability(g/g)
1	30	30	10.51
2	30	60	12.51
3	30	90	14.09
4	50	30	15.21
5	50	60	22.10
6	50	90	16.01
7	70	30	19.29
8	70	60	27.10
9	70	90	17.76

The data presented in Table 4.16 (b) indicates that at 5% concentration of treatment resulted the maximum reusability of sample (27.10 g/g) at temperature (70℃) for 60 minutes treatment time followed by 22.10 g/g at temperature (50℃) for 60 minutes of time. The data revealed that at room temperature (30℃), the minimum reusability of the sample (10.51 g/g) was found at 30 minutes of treatment time.

Table 4.16 (c) Reusability of fibres after treatment at 9% concentration

S.No.	Temperature (℃)	Time (min)	Reusability(g/g)
1	30	30	10.47
2	30	60	13.06
3	30	90	16.67
4	50	30	16.13
5	50	60	21.80
6	50	90	17.41
7	70	30	11.83
8	70	60	13.39
9	70	90	10.22

The data presented in Table 4.16 (c) depicts that a treatment concentration of 9% showed the maximum reusability of the sample (21.80 g/g) at 50℃ for 60 minutes of treatment time, whereas, at 70℃, the minimum reusability (10.22 g/g) was found at 90 minutes. It was observed that at room temperature (30℃), the highest recovery (16.67 g/g) was obtained at 90 minutes of treatment time, and the lowest was 10.47 g/g at 30 minutes.

Statistical analysis

The data obtained from testing results, Including oil sorption capacity, recovery of sorbed oil, and sample reusability, were statistically analysed for further optimisation of Cyanoethylation treatment parameters.

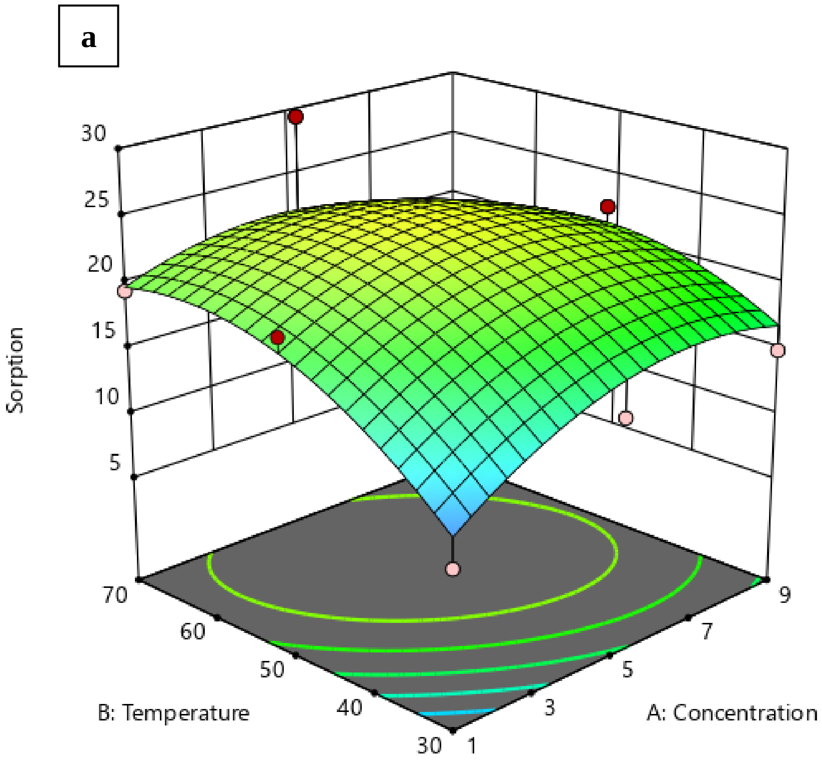
a) Analysis of oil sorption capacity

To determine the significance of the models, oil sorption capacity was analysed using analysis of variance (ANOVA). The results are presented in the following tables and graphs.

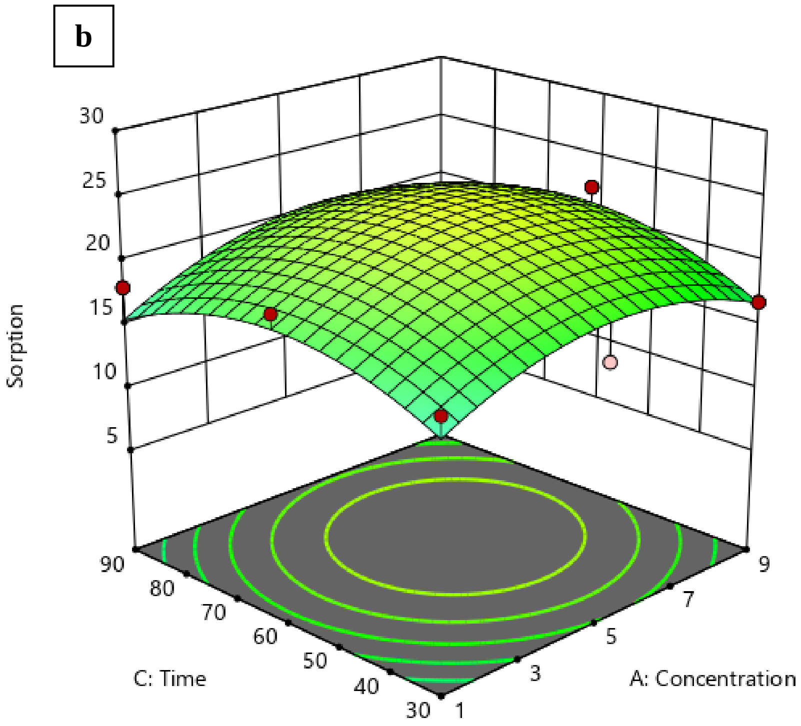
Table 4.17 Variance analysis (ANOVA) of oil sorption capacity of Cyanoethylated fibre at different treatment parameters

ANOVA for Reduced Quadratic model: Sorption (g/g)						
Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	409.25	7	58.46	7.45	0.0002	Significant
A-Concentration	21.87	1	21.87	2.79	0.1115	
B-Temperature	117.40	1	117.40	14.96	0.0010	
C-Time	3.52	1	3.52	0.4485	0.5111	
AB	48.72	1	48.72	6.21	0.0221	
A^2	64.73	1	64.73	8.25	0.0098	
B^2	83.60	1	83.60	10.65	0.0041	
C^2	69.41	1	69.41	8.84	0.0078	
Residual	149.11	19	7.85			
Cor Total	558.35	26				

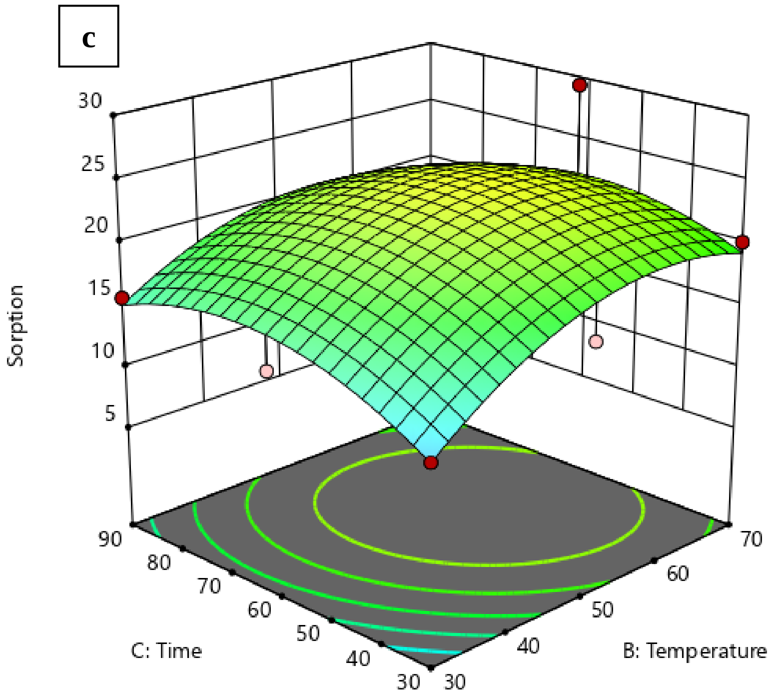
Summary of analysis of variance (ANOVA) for the selected reduced quadratic polynomial model for oil sorption capacity of the fibre has been listed in Table 4.17. Factors such as treatment concentration, time, and temperature were identified as significantly affecting the response variables of fibre sorption. The model F-value (sorption**)** of 7.45 implies that the model was significant**.** P-values (0.0002**)** less than 0.0500 indicate that model terms are significant. The results of ANOVA for model B, A^2, B^2, and C^2 AB (concentration and temperature) were found significant with p- p-values 0.0010, 0.0098, 0.0041, 0.0078 and 0.0221, respectively. The ANOVA of quadratic regression model demonstrated that the models were highly significant, evident from Fisher's *F*-test with high F value and low *P* value.



Graph 4.12(a) Response surface plot showing the effect of temperature and concentration on sorption



Graph 4.12(b) Response surface plot showing the effect of time and concentration on sorption



Graph 4.12(c) Response surface plot showing the effect of time and temperature on sorption

Graph 4.12 shows the response surface plots (RSP) for the sorption capacity of fibres at different combinations of concentration, time and temperature. The effect of temperature and concentration was observed in Graph 4.12(a), which indicates a higher to slightly lower curve, respectively, as compared to time and concentration (Graph 4.12 b), which shows a smooth curve. The surface plot of time and temperature (Graph 4.12 c) shows that the curve reduced in time and increased towards temperature.

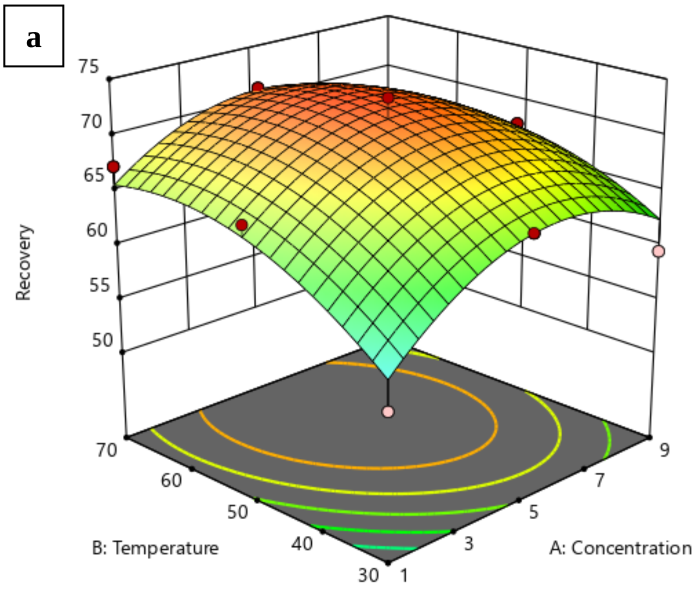
b) Analysis for Recovery of sorbed oil

Analysis of variance (ANOVA) for recovery of sorbed oil was performed to determine the significance of the models. The results are presented in the following tables and graphs.

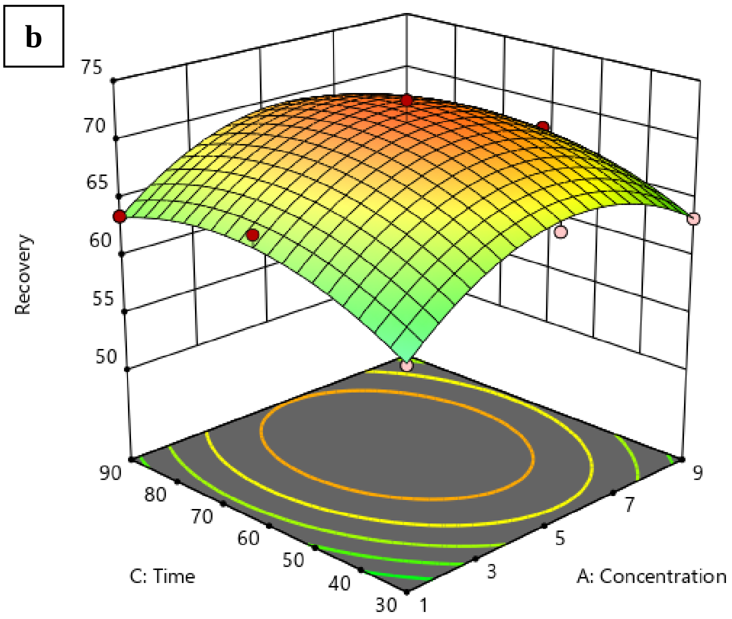
Table 4.18 Variance analysis (ANOVA) of recovery of sorbed oil from Cyanoethylated fibre at different treatment parameters

ANOVA for Quadratic model: Recovery (%)						
Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	545.04	9	60.56	15.49	< 0.0001	Significant
A-Concentration	28.00	1	28.00	7.16	0.0159	
B-Temperature	143.43	1	143.43	36.69	< 0.0001	
C-Time	28.91	1	28.91	7.39	0.0146	
AB	18.23	1	18.23	4.66	0.0454	
AC	1.39	1	1.39	0.3548	0.5592	
BC	27.42	1	27.42	7.01	0.0169	
A^2	169.21	1	169.21	43.28	< 0.0001	
B^2	69.65	1	69.65	17.82	0.0006	
C^2	58.80	1	58.80	15.04	0.0012	
Residual	66.46	17	3.91			
Cor Total	611.50	26				

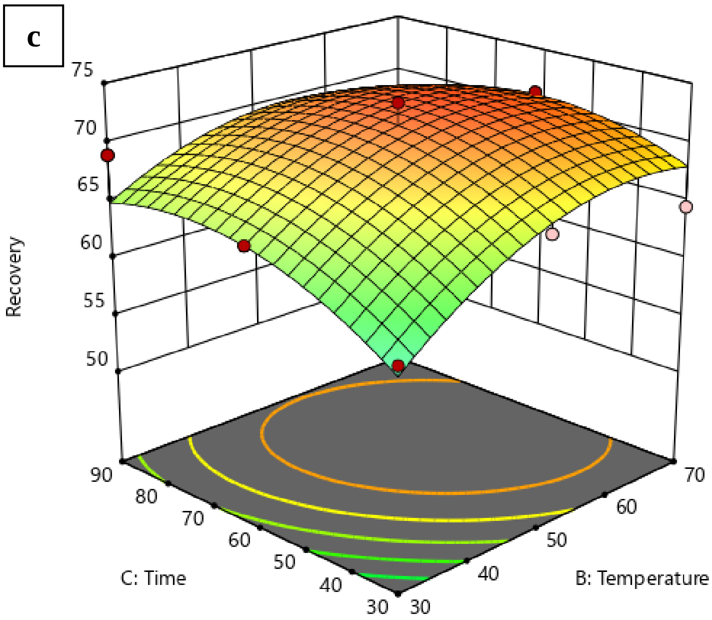
Analysis of variance (ANOVA) for the selected quadratic polynomial model for recovery of sorbed oil has been listed in Table 4.18. The model F-value (recovery) of 15.49 implies that the model was significant**.** P-values **(**< 0.0001**)** less than 0.0500 indicate that model terms are significant. The results of ANOVA for models A, B, C, AB, BC, A^2, B^2, and C^2 were found significant with p- values 0.0159, < 0.0001, 0.0146, 0.0454, 0.0169, < 0.0001, 0.0006, and 0.0012 respectively. The ANOVA of the quadratic regression model demonstrated that the models were highly significant.



Graph 4.13 (a) Response surface plot showing the effect of temperature and concentration on recovery of sorbed oil



Graph 4.13 (b) Response surface plot showing the effect of time and concentration on recovery of sorbed oil



Graph 4.13 (c) Response surface plot showing the effect of time and temperature on recovery of sorbed oil

Graph 4.13 shows the response surface plots (RSP) for the recovery of sorbed oil at different combinations of concentration, time and temperature. The effect of temperature and concentration was observed in Graph 4.13(a), which indicates that the higher the temperature, the better the recovery of oil and the mid-value of concentration. From time and concentration (Graph 4.13 b), it was observed that the recovery was higher with the increase of time. The surface plot of temperature and time (Graph 4.13c) shows a slightly curved graph, which means that both these factors have less effect on the recovery of sorbed oil.

The acetylation and cyanoethylation of cellulose causes substitution of OH groups which increases its oleophilicity. During these treatments a part of the hydroxylic groups are substituted. The improvement in oleophilicity depends on the degree of this substitution. The cyanoethylation treatment must have resulted in a higher degree of substitution (DS) compared to the acetylation which was manifested in higher oil absorption.

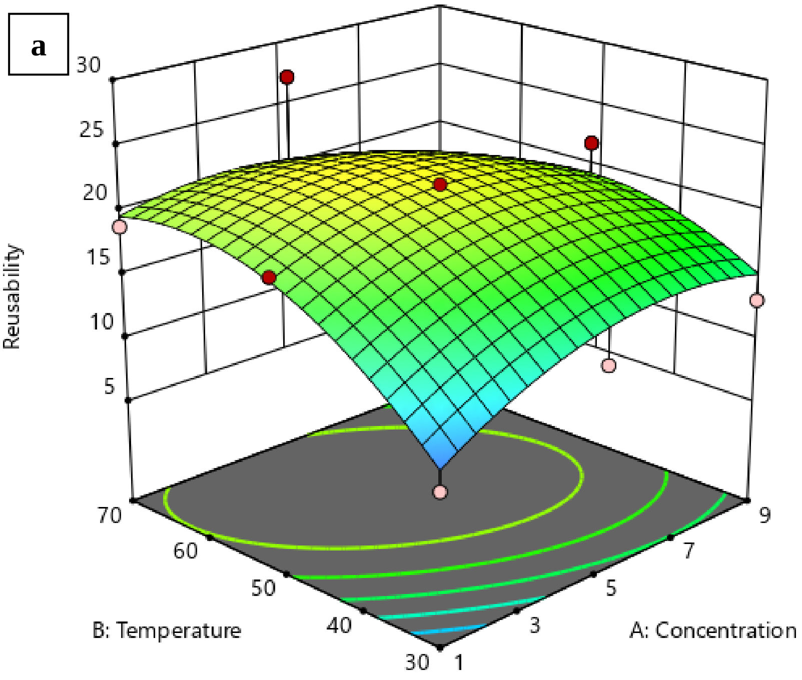
c) Analysis for Reusability of sample

Analysis of variance (ANOVA) for reusability of sample was performed to determine the significance of the models. The results are presented in the following Tables and Graphs.

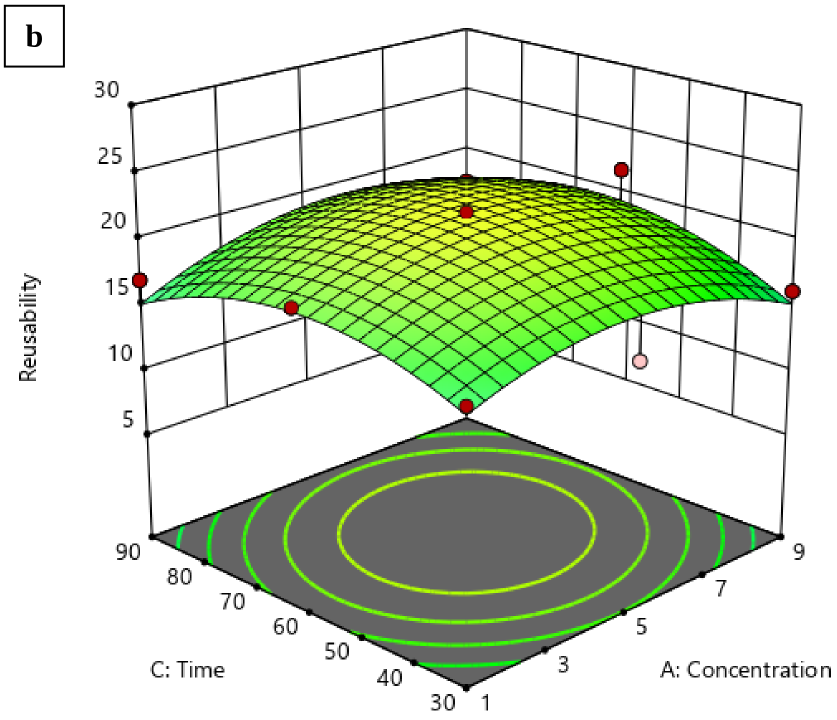
Table 4.19 Variance analysis (ANOVA) of reusability of Cyanoethylated fibre at different treatment parameters

ANOVA for Quadratic model: Reusability (g/g)						
Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	429.84	9	47.76	6.74	0.0004	Significant
A-Concentration	1.69	1	1.69	0.2390	0.6312	
B-Temperature	117.40	1	117.40	16.57	0.0008	
C-Time	1.72	1	1.72	0.2425	0.6287	
AB	67.45	1	67.45	9.52	0.0067	
AC	6.80	1	6.80	0.9593	0.3411	
BC	24.17	1	24.17	3.41	0.0822	
A^2	51.47	1	51.47	7.27	0.0153	
B^2	98.77	1	98.77	13.94	0.0017	
C^2	60.38	1	60.38	8.52	0.0096	
Residual	120.42	17	7.08			
Cor Total	550.26	26				

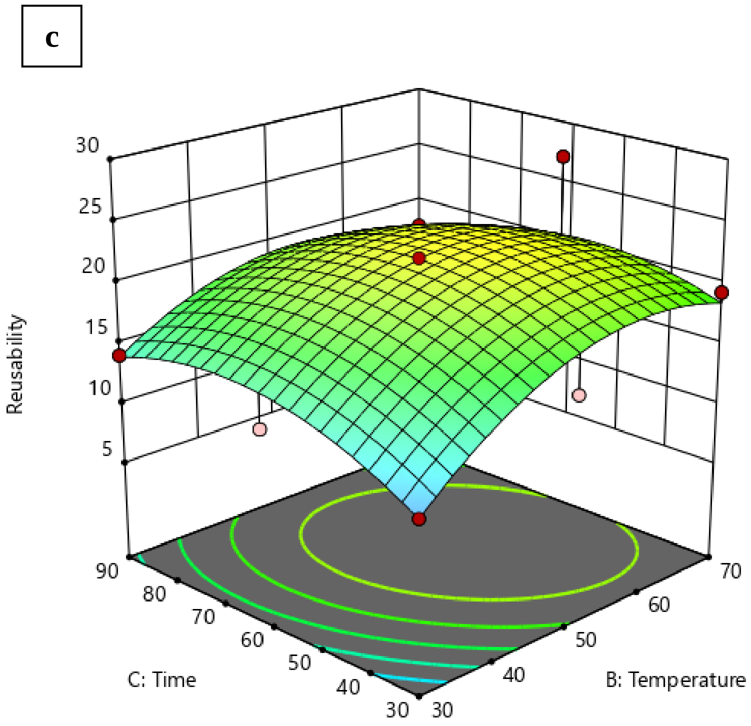
Table 4.19 presented the results of analysis of variance (ANOVA) for the selected the quadratic polynomial model for reusability of sample. The model F-value (reusability**)** of 6.74 implies that the model was significant. P-values **(**0.0004**)** less than 0.0500 indicate that model terms are significant. The results of ANOVA for models B, AB, A^2, B^2, and C^2 were found significant with p- values 0.0008, 0.0067, 0.0153, 0.0017 and 0.0096, respectively. The ANOVA of the quadratic regression model demonstrated that the models were highly significant.



Graph 4.14 (a) Response surface plot showing the effect of temperature and concentration on the reusability of sample



Graph 4.14 (b) Response surface plot showing the effect of time and concentration on the reusability of sample



Graph 4.14 (c) Response surface plot showing the effect of time and temperature on the reusability of sample

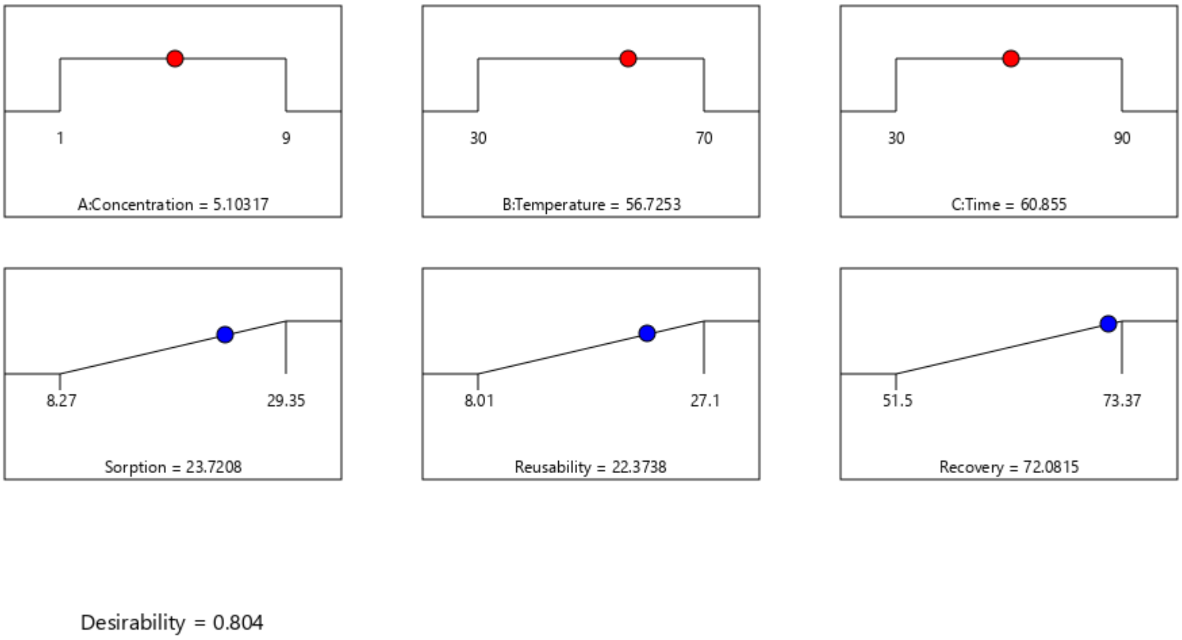
Response surface plots (RSP) for the reusability of the sample interpret that the effect of temperature and concentration was found highly significant in Graph 4.14(a), which indicates that both treatment parameters affect the reusability more than time and concentration (Graph 4.14b). The surface plot of temperature and time (Graph 4.14c) shows a slightly curved graph, and the middle value of both variables shows higher reusability.

Table 4.20: Results of the statistical analysis for optimisation of Cyanoethylation treatment parameters

Response Variable	**R^2**	**Adjusted R^2**	**Predicted R^2**
Sorption (g/g)	0.73	0.63	0.46
Recovery (%)	0.89	0.83	0.74
Reusability (g/g)	0.78	0.66	0.49

The coefficient of determination (R^2) values for sorption, recovery and reusability were 0.73, 0.89 and 0.78, respectively. The adjusted R^2 values were 0.63 for sorption, 0.83 and 0.66 for recovery and reusability, which indicated that the model was significant. The results of predicted R^2 showed 0.46, 0.74 and 0.49 for sorption, recovery and reusability, respectively (Table 4.20).

Verification of optimised treatment parameters and predictive model



Graph 4.15: Desirability ramp for optimisation of Cyanoethylation treatment parameters

Graph 4.15 shows the optimised parameters of cyanoethylation treatment based on three response variables, viz. sorption capacity, recovery of sorbed oil and reusability of the fibre sample. The data was obtained by using numerical optimisation. Optimisation requires that goals (i.e., none, maximum, minimum, target, or in range) are set for the variables and response, where all goals then get combined into one desirability function. To find a good set of conditions that will meet all the goals, all three parameters, (i) concentration, (ii) time and (iii) temperature, were set within range while all three response variables (i) sorption, (ii) recovery and (iii) reusability, set at maximum. The optimum level of various parameters was obtained, and desirability ramps were developed from optimum points via numerical optimisation.

From Graph 4.15, the results for optimised parameters for cyanoethylation treatment condition showed the predicted values for concentration was 5.10%, temperature was 56.72℃, and time was 60.85 min. For the response variables, the predicted value for sorption obtained was 23.72 g/g , recovery was 72.08% and reusability was 22.37 g/g.

Table 4.21 Optimised parameters for Cyanoethylation treatment

Concentration of NaOH (w/v)	5%
Treatment time	60 minutes
Treatment temperature	55℃

Further, on the basis of model predicted values, the optimised parameters for Cyanoethylation treatment were 5% concentration, temperature was 55℃and 60 minutes of time (Table 4.21)

4.5.3 Enzyme treatment

The fibre samples after enzyme treatment were tested for their oil sorption capacity test, oil retention ability, reusability of sorbed oil and recovery of the sample. All the above tests were carried out by following the specified method mentioned in section 3.7(chapter 3).

4.5.3.1 Testing of oil sorption capacity

Table 4.22 (a) presents the results of the testing of modified fibres for oil sorption capacity.

Table 4.22 (a) Oil sorption capacity of fibres after treatment at 1% concentration

S.No.	Temperature (℃)	Time (min)	Sorption (g/g)
1	30	30	13.68
2	30	60	15.24
3	30	90	12.78
4	50	30	14.19
5	50	60	16.16
6	50	90	12.29
7	70	30	15.02
8	70	60	19.89
9	70	90	14.78

From Table 4.22 (a), it was observed that the maximum oil sorption capacity (19.89 g/g) of fibres was found at temperature (70℃), followed by 16.16 g/g at 50℃ for 60 minutes treatment time. The results showed that the minimum sorption capacity (12.29 g/g) was found at temperature (50℃) for 90 minutes. At 30℃, the highest sorption (15.24 g/g) was found at 60 minutes of treatment time, and the lowest (12.78 g/g) was at 90 minutes. It was noticed that for the treatment temperature of 70℃, the lowest sorption (14.78 g/g) was obtained at 90 minutes of treatment time.

Table 4.22 (b) Oil sorption capacity of fibres after treatment at 5% concentration

S.No.	Temperature (℃)	Time (min)	Sorption (g/g)
1	30	30	14.56
2	30	60	16.78
3	30	90	13.25
4	50	30	13.77
5	50	60	15.87
6	50	90	12.51
7	70	30	21.11
8	70	60	23.68
9	70	90	14.93

The data presented in Table 4.22 (b) indicates that at 5% concentration of treatment resulted in the maximum oil sorption capacity (23.68 g/g) of fibres at temperature (70℃) for 60 minutes of treatment time, whereas the minimum sorption capacity (12.51 g/g) was found at 50℃ for 90 minutes. The data revealed that at 30℃, the highest sorption (16.78 g/g) was found at 60 minutes of treatment time, and the lowest (13.25 g/g) was at 90 minutes.

Table 4.22 (c) Oil sorption capacity of fibres after treatment at 9% concentration

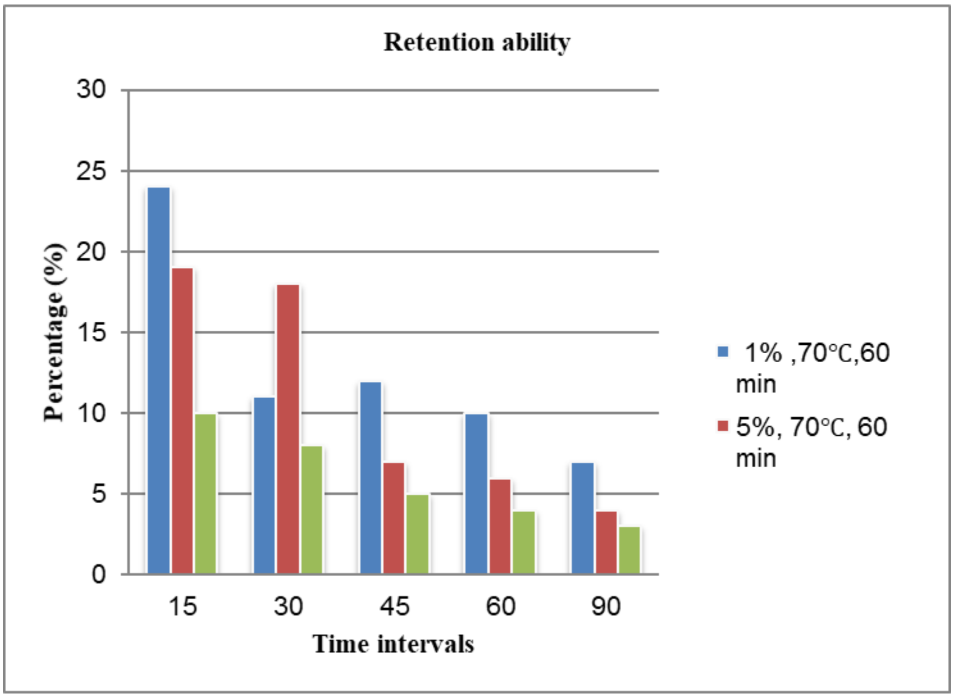
S.No.	Temperature (℃)	Time (min)	Sorption (g/g)
1	30	30	11.74
2	30	60	12.39
3	30	90	10.56
4	50	30	11.19
5	50	60	12.50

6	50	90	10.26
7	70	30	15.87
8	70	60	19.32
9	70	90	14.87

Table 4.22 (c) depicts that treatment concentration of 9% showed the maximum oil sorption capacity (19.32 g/g) of fibres at 70℃ for 60 minutes of treatment time, whereas at 30℃, the highest sorption (12.39 g/g) found at 60 minutes. It was observed that at 50℃, the highest sorption (12.50 g/g) was obtained at 60 minutes of treatment time. The lowest sorption was obtained (10.26 g/g) at 70℃ for 90 minutes. Therefore, the data revealed that with each treatment temperature, the maximum sorption capacity was found at 60 minutes of treatment time.

4.5.3.2 Testing of oil retention ability

The oil retention ability of fibres was tested for the higher and lower sorption capacity of fibres at different concentrations for enzyme treatment. The results of the testing were discussed through the following graph representations:



Graph 4.16 Oil retention ability of fibres at 1%, 5% and 9% concentration

Graph 4.16 shows the retention ability of fibre treated at different concentrations viz 1%, 5% and 9%. The data was taken between five-time intervals, viz. 15, 30, 45, 60 and 90 minutes. It was observed that at 1% concentration, there was a slight reduction in retention ability as the time increased after 30 minutes compared to the time interval between 15-30 minutes. The retention ability at 5% of concentration resulted in 30-45 minutes of time interval shows higher retention than retention between 45-90 minutes of time intervals. At 9% concentration, the retention value is higher between 15-45 minutes, whereas from 45 to 90 minutes, there were fewer differences obtained between the values.

4.5.3.3 Testing of recovery of sorbed oil

The results of the testing of recovery of sorbed oil were calculated and presented in Table 4.23 at different concentrations, times and temperatures.

Table 4.23 (a) Recovery of sorbed oil from fibres after treatment at 1% concentration

S.No.	Temperature (℃)	Time (min)	Recovery (%)
1	30	30	70.66
2	30	60	71.39
3	30	90	69.42
4	50	30	65.73
5	50	60	69.94
6	50	90	65.39
7	70	30	73.19
8	70	60	74.02
9	70	90	72.88

From Table 4.23 (a), it was observed that the maximum recovery of sorbed oil (74.02%) was found at a temperature (70℃) for 60 minutes of treatment time. The results showed at 50 temperature, 90 minutes, the recovery was minimum (65.39%) due to less sorption of fibre sample as the fact associated that as much higher the sorption, the recovery is more. Hence, at 30℃, 90 minutes, the lowest percentage of oil recovered from the sorbed sample (69.42%). It was noticed that for the treatment temperature of 70℃ with different time durations, the data shows very less difference in recovery percent viz. 73.19%, followed by 74.02% and 72.88 % respectively.

Table 4.23 (b) Recovery of sorbed oil from fibres after treatment at 5% concentration

S.No.	Temperature (℃)	Time (min)	Recovery (%)
1	30	30	65.91
2	30	60	69.36
3	30	90	64.66
4	50	30	68.36
5	50	60	70.92
6	50	90	64.15
7	70	30	72.95
8	70	60	73.50
9	70	90	68.67

The data presented in Table 4.23 (b) indicates that at 5% concentration of treatment resulted in the maximum recovery of sorbed oil (73.50%) at temperature (70℃) for 60 minutes of treatment time, followed by 72.95% recovery at 30 minutes of time. The data revealed that at 50℃, the highest recovery (70.93%) was found for 60 minutes, and the lowest recovery (64.15%) was found at 90 minutes of treatment time. The recovery of sorbed oil at room temperature was found to be 65.91 %, 69.36 % and 64.66 % for 30, 60 and 90 minutes of time, respectively.

Table 4.23 (c) Recovery of sorbed oil from fibres after treatment at 9% concentration

S.No.	Temperature (℃)	Time (min)	Recovery (%)
1	30	30	66.44
2	30	60	69.15
3	30	90	65.34
4	50	30	66.05
5	50	60	68.33
6	50	90	64.18
7	70	30	69.26
8	70	60	71.33
9	70	90	68.67

Table 4.23(c) depicts that a treatment concentration of 9% showed the maximum oil recovery (71.33%) at 70℃ for 60 minutes, whereas at 30℃, the highest recovery (69.15%) was found at 60 minutes. It was observed that at 50℃, the highest recovery (68.33%) was obtained at 60 minutes of treatment time. The minimum recovery (64.18%) was obtained at temperature (50℃) for 90 minutes.

4.5.3.4 Testing of reusability of sample

The results of the testing for reusability of samples were calculated and presented in Table 4.24.

Table 4.24(a) Reusability of fibres after treatment at 1% concentration

S.No.	Temperature (℃)	Time (min)	Reusability (g/g)
1	30	30	11.12
2	30	60	12.48
3	30	90	9.42
4	50	30	12.44
5	50	60	13.99
6	50	90	11.41
7	70	30	14.09
8	70	60	17.97
9	70	90	12.23

From Table 4.24(a), it was observed that the maximum reusability (17.97 g/g) of the sample was found at a temperature (of 70℃) for 60 minutes of treatment time. The results showed that as the treatment time increased (90 minutes) at room temperature, the reusability was minimum (9.42 g/g) due to less sorption of oil in second time. The results of 50℃ showed the highest reusability of the sample (9.83 g/g) at 60 minutes and the lowest (11.41 g/g) at 90 minutes.

Table 4.24(b) Reusability of fibres after treatment at 5% concentration

S.No.	Temperature (℃)	Time (min)	Reusability(g/g)
1	30	30	13.05
2	30	60	15.03
3	30	90	11.41
4	50	30	12.92
5	50	60	14.92
6	50	90	10.35
7	70	30	19.70
8	70	60	21.94
9	70	90	13.35

The data presented in Table 4.24 (b) indicates that at 5% concentration of treatment resulted in the maximum reusability of the sample (21.94 g/g) at temperature (70℃) for 60 minutes of treatment time followed by 19.70 g/g at 30 minutes of time. The data revealed that at 50℃, the minimum reusability of the sample (10.35 g/g) was found at 90 minutes of treatment time.

Table 4.24(c) Reusability of fibres after treatment at 9% concentration

S.No.	Temperature (℃)	Time (min)	Reusability(g/g)
1	30	30	10.67
2	30	60	11.9
3	30	90	9.32
4	50	30	10.38
5	50	60	11.43
6	50	90	9.55
7	70	30	13.33
8	70	60	17.18
9	70	90	13.67

The data presented in Table 4.24 (c) depicts that treatment concentration of 9% showed the maximum reusability of the sample (17.18 g/g) at 70℃ for 60 minutes of treatment time whereas at 30℃, the minimum reusability (9.32 g/g) was found at 90 minutes. It was observed that at 50 ℃ temperature, the highest recovery (11.43 g/g) was obtained at 60 minutes of treatment time, followed by 10.38 g/g at 30 minutes.

Statistical analysis

The data obtained from testing results, oil sorption capacity, recovery of sorbed oil and reusability of the sample were statistically analysed for further optimisation of enzymatic treatment parameters.

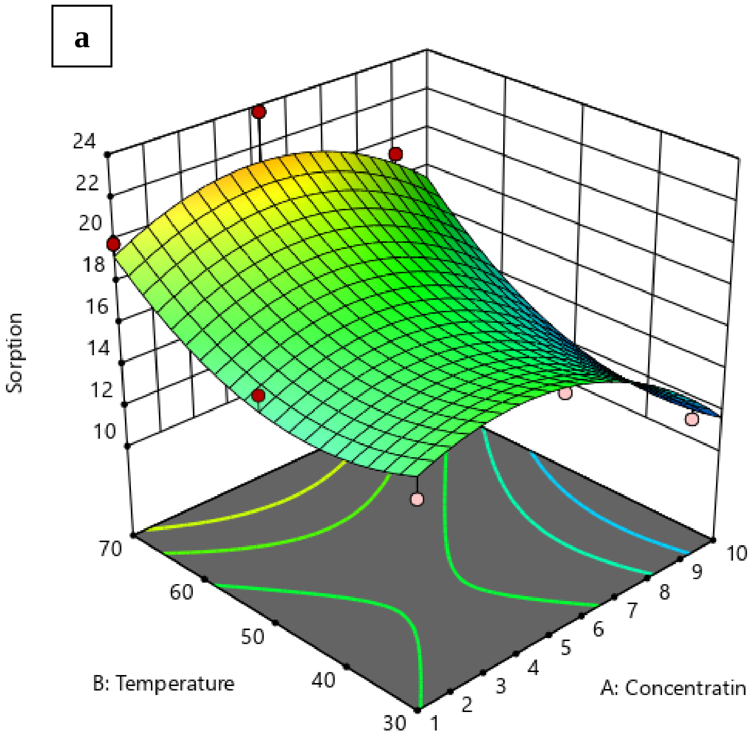
a) Analysis for Oil sorption capacity

Analysis of variance (ANOVA) for oil sorption capacity was performed to determine the significance of the models. The results are presented in the following Tables and Graphs

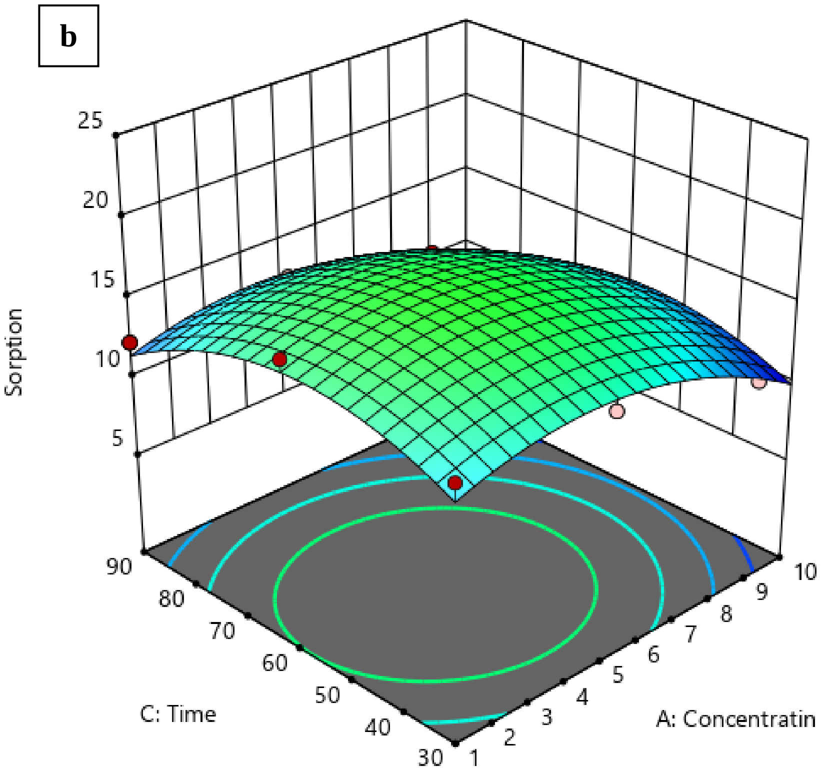
Table 4.25 Variance analysis (ANOVA) of oil sorption capacity of Enzymatic treated fibre at different treatment parameters

ANOVA for Quadratic model: Sorption (g/g)						
Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	236.39	9	26.27	14.99	< 0.0001	Significant
A-Concentration	30.13	1	30.13	17.19	0.0007	
B-Temperature	86.31	1	86.31	49.25	< 0.0001	
C-Time	12.07	1	12.07	6.89	0.0177	
AB	4.54	1	4.54	2.59	0.1260	
AC	0.0004	1	0.0004	0.0002	0.9880	
BC	1.35	1	1.35	0.7723	0.3918	
A^2	29.91	1	29.91	17.07	0.0007	
B^2	34.19	1	34.19	19.51	0.0004	
C^2	58.70	1	58.70	33.49	< 0.0001	
Residual	29.79	17	1.75			
Cor Total	266.18	26				

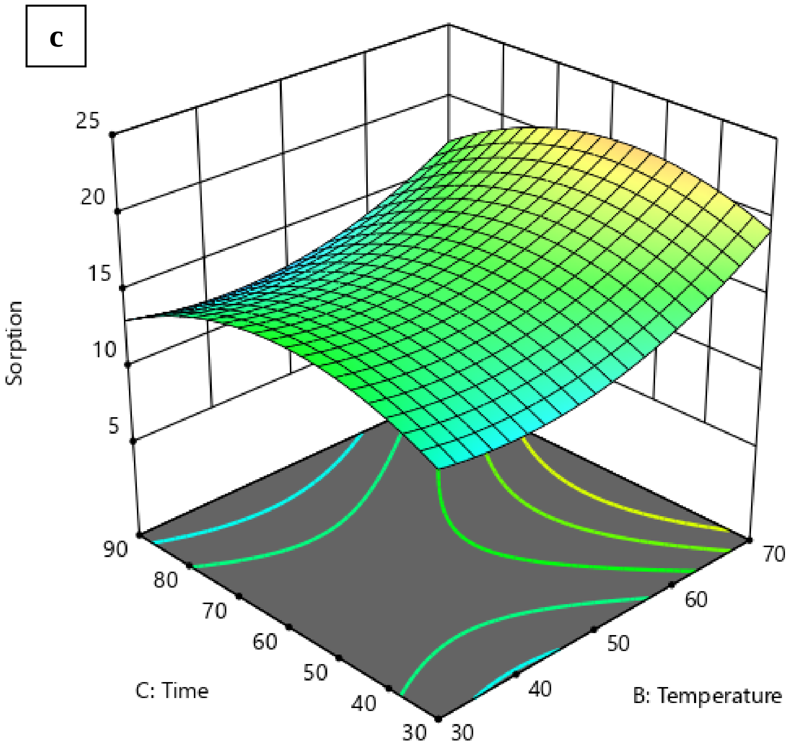
The summary of analysis of variance (ANOVA) for the selected quadratic polynomial model for the oil sorption capacity of the fibre has been listed in Table 4.25. Factors such as treatment concentration, time, and temperature were identified as significantly affecting the response variables of fibre sorption. The model F-value (sorption) of 14.99 implies the model was significant. P-values (< 0.0001**)** less than 0.0500 indicate model terms are significant. The results of ANOVA for models A, B, C, A^2, B^2, and C^2 were found to be significant models with p- values 0.0007, < 0.0001, 0.0177, 0.0007, 0.0004 and < 0.0001, respectively. The ANOVA of the quadratic regression model demonstrated that the models were highly significant, evident from Fisher's *F*-test with a high *F* value and low *P* value.



Graph 4.17 (a) Response surface plot showing the effect of temperature and concentration on sorption



Graph 4.17(b) Response surface plot showing the effect of time and concentration on sorption



Graph 4.17(c) Response surface plot showing the effect of time and temperature on sorption

Graph 4.17 shows the response surface plots (RSP) for the sorption capacity of fibres at different combinations of concentration, time and temperature. The effect of temperature and concentration was observed in Graph 4.17(a), which indicates the highest sorption values lie between 5-6 % of concentration and at 70℃ temperature. The surface plot of temperature and time (Graph 4.17c) shows that the time has less effect compared to temperature. The effect of time and concentration can be seen in Graph 4.17 (b), where the highest sorption was obtained at the middle value of both the variables as the graph showed a smooth curve.

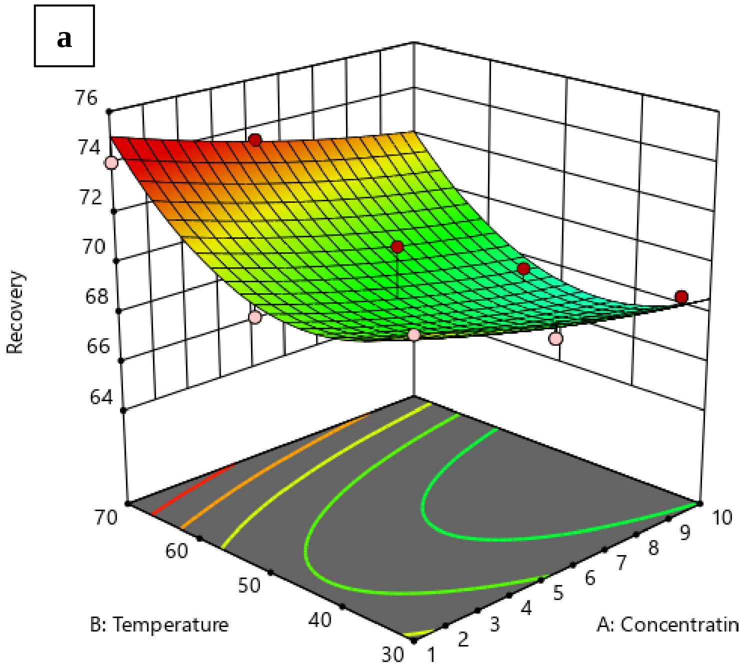
b) Analysis for Recovery of sorbed oil

Analysis of variance (ANOVA) for recovery of sorbed oil was performed to determine the significance of the models. The results are presented in the following Tables and Graphs.

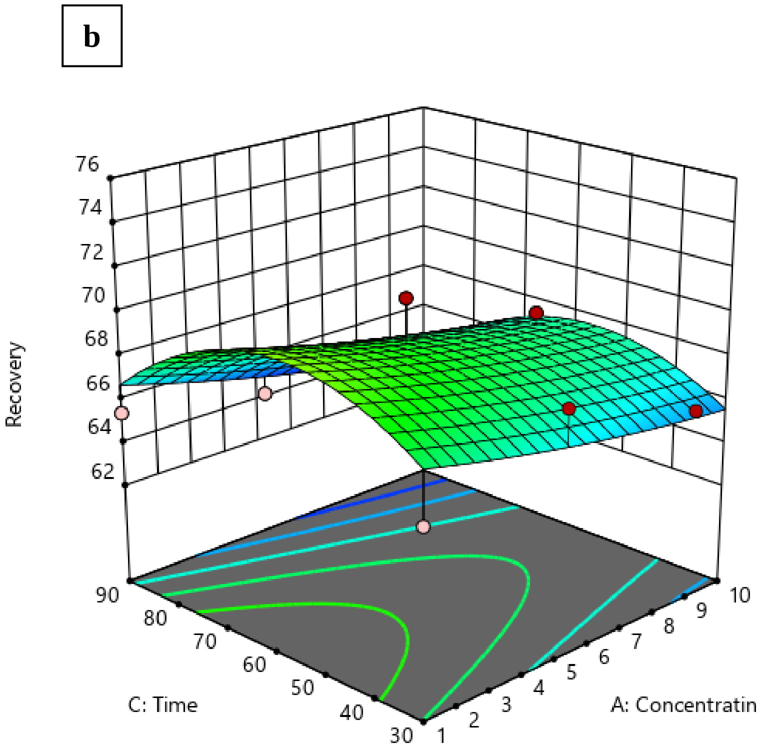
Table 4.26 Variance analysis (ANOVA) of the recovery of sorbed oil from Enzymatic treated fibre at different treatment parameters

ANOVA for Quadratic model: Recovery (%)						
Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	204.21	9	22.69	10.56	< 0.0001	Significant
A-Concentration	24.25	1	24.25	11.28	0.0037	
B-Temperature	55.88	1	55.88	26.00	< 0.0001	
C-Time	13.05	1	13.05	6.07	0.0247	
AB	0.0070	1	0.0070	0.0033	0.9551	
AC	0.2324	1	0.2324	0.1081	0.7463	
BC	0.2107	1	0.2107	0.0980	0.7580	
A^2	0.3601	1	0.3601	0.1676	0.6874	
B^2	47.60	1	47.60	22.15	0.0002	
C^2	53.94	1	53.94	25.10	0.0001	
Residual	36.54	17	2.15			
Cor Total	240.75	26				

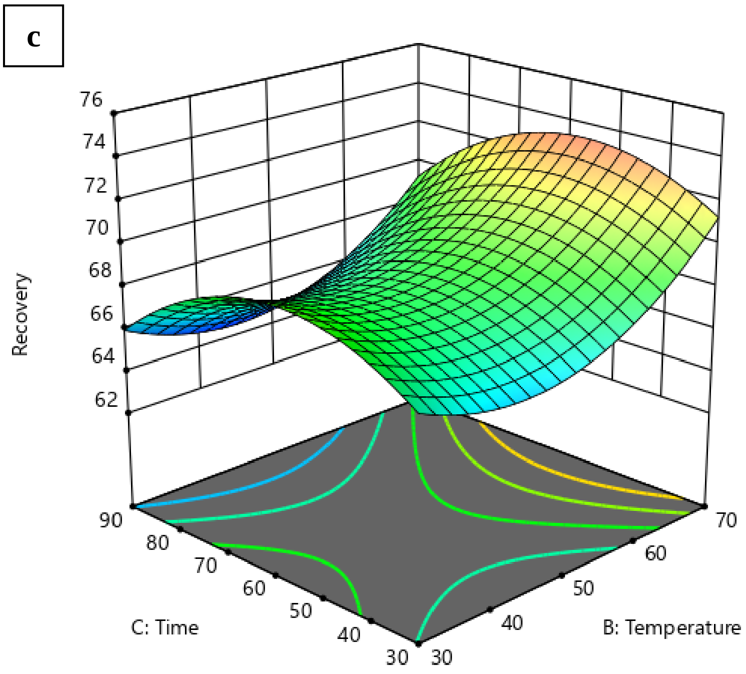
Analysis of variance (ANOVA) for the selected quadratic polynomial model for the recovery of sorbed oil has been listed in Table 4.26. The model F-value (sorption) of 10.56 implies the model was significant. P-values **(**< 0.0001**)** less than 0.0500 indicate model terms are significant. The results of ANOVA for models A, B, C, B^2, and C^2 were found significant with p- values 0.0037, < 0.0001, 0.0247, 0.0002 and 0.0001, respectively. The ANOVA of the reduced quadratic regression model demonstrated that the models were highly significant.



Graph 4.18 (a) Response surface plot showing the effect of temperature and concentration on recovery of sorbed oil



Graph 4.18 (b) Response surface plot showing the effect of time and concentration on recovery of sorbed oil



Graph 4.18 (c) Response surface plot showing the effect of time and temperature on recovery of sorbed oil

Graph 4.18 shows the response surface plots (RSP) for the recovery of sorbed oil at different combinations of concentration, time and temperature. The effect of temperature and concentration was observed in Graph 4.18(a), which indicates that both factors significantly affect the sorption capacity as compared to time and concentration (Graph 4.18 b). The surface plot of temperature and time (Graph 4.18c) shows the highest recovery at 70℃ temperature, and the time was 60 minutes.

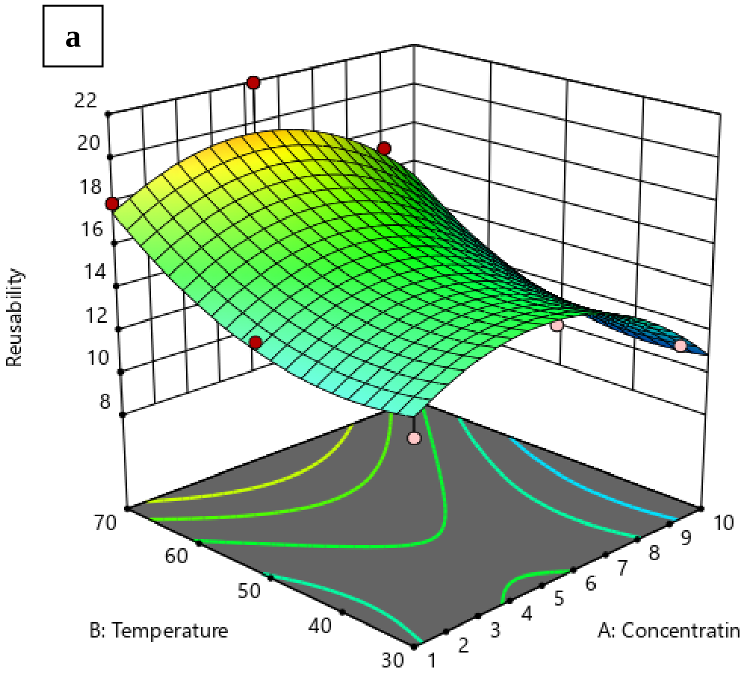
c) Analysis for Reusability of sample

Analysis of variance (ANOVA) for reusability of the sample was performed to determine the significance of the models. The results are presented in the following Tables and Graphs.

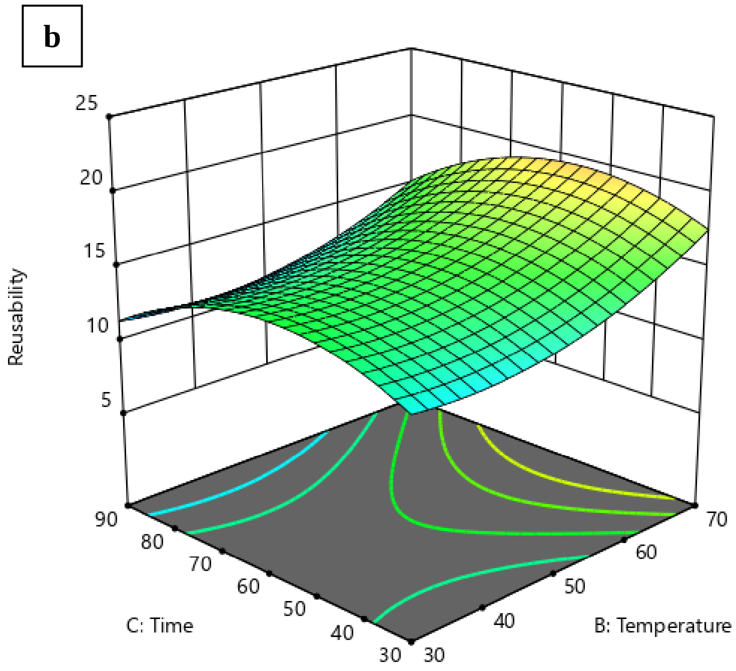
Table 4.27 Variance analysis (ANOVA) of reusability of enzymatic treated fibre at different treatment parameters

ANOVA for Quadratic model: Reusability (g/g)						
Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	216.36	9	24.04	12.92	< 0.0001	Significant
A-Concentration	15.86	1	15.86	8.52	0.0096	
B-Temperature	83.63	1	83.63	44.93	< 0.0001	
C-Time	14.73	1	14.73	7.92	0.0120	
AB	0.0867	1	0.0867	0.0466	0.8317	
AC	0.6302	1	0.6302	0.3386	0.5683	
BC	0.8427	1	0.8427	0.4528	0.5101	
A^2	33.86	1	33.86	18.19	0.0005	
B^2	20.26	1	20.26	10.89	0.0042	
C^2	56.57	1	56.57	30.39	< 0.0001	
Residual	31.64	17	1.86			
Cor Total	248.00	26				

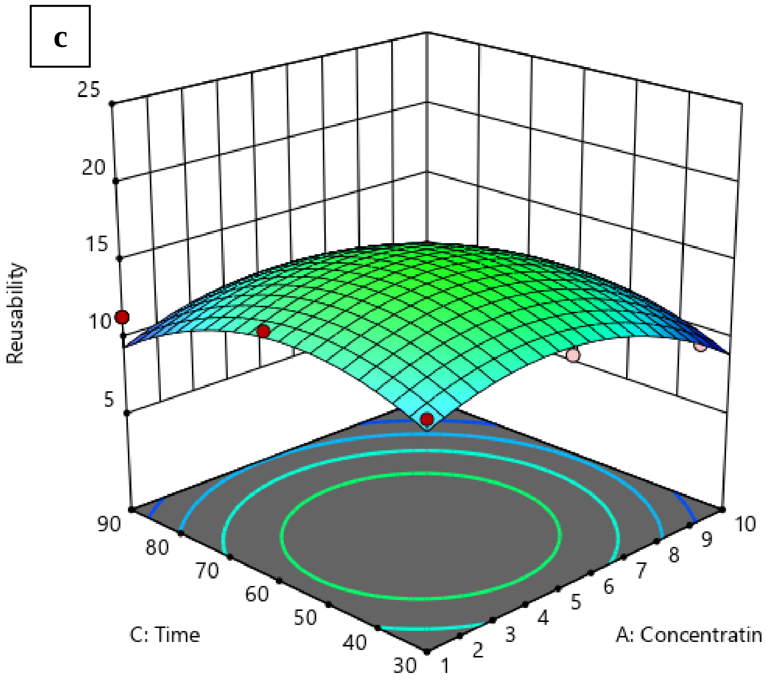
Table 4.27 presents the results of the analysis of variance (ANOVA) for the selected quadratic polynomial model for the reusability of the sample. The model F-value (reusability) of 12.92 implies that the model was significant. P-values (< 0.0001**)** less than 0.0500 indicate that model terms are significant. The results of ANOVA for models A, B, C, A^2, B^2, and C^2 were found significant with p- values 0.0096, < 0.0001, 0.0120, 0.0005, 0.0042 and < 0.0001, respectively. The ANOVA of the reduced quadratic regression model demonstrated that the models were highly significant.



Graph 4.19(a) Response surface plot showing the effect of temperature and concentration on reusability of sample



Graph 4.19(b) Response surface plot showing the effect of time and temperature on the reusability of sample



Graph 4.19(c) Response surface plot showing the effect of time and concentration on the reusability of sample

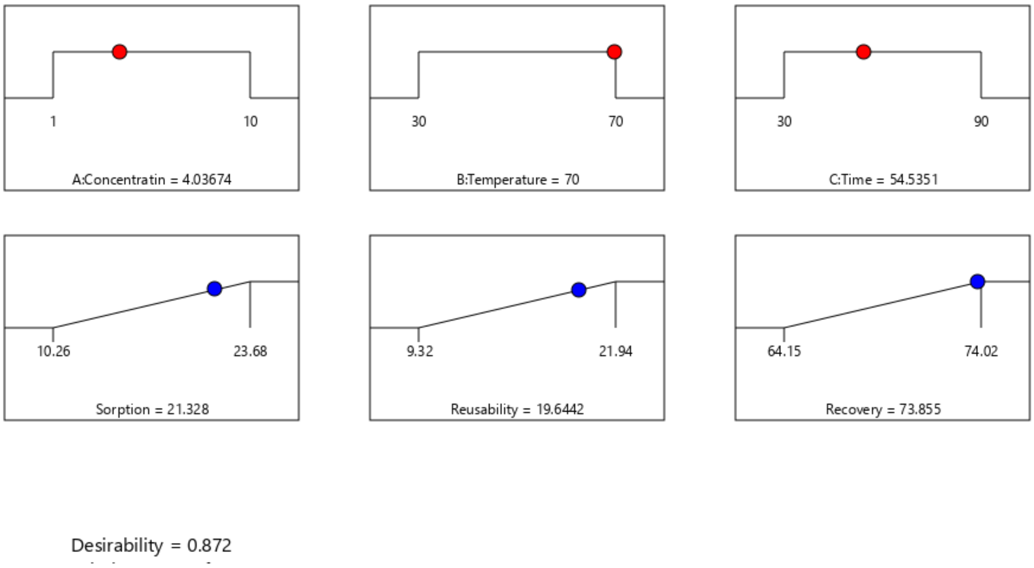
Response surface plots (RSP) for the reusability of the sample interpret that the effect of temperature and concentration was found highly significant in Graph 4.19(a), which indicates that both the treatment parameters affect the reusability more as compared to time and concentration (Graph 4.19c). The surface plot of temperature and time (Graph 4.19b) shows the flattened graph curve which means that both these factors were less affected for the reusability of the sample.

Table 4.28: Results of the statistical analysis for optimisation of enzyme treatment parameters

Response Variable	R^2	Adjusted R^2	Predicted R^2
Sorption (g/g)	0.88	0.82	0.70
Recovery (%)	0.84	0.76	0.59
Reusability (g/g)	0.87	0.80	0.66

The coefficient of determination (R^2) values for sorption, recovery and reusability were 0.88, 0.84 and 0.87, respectively. The adjusted R^2 value was 0.82 for sorption, 0.76 and 0.80 for recovery and reusability, which indicated that the model was significant. The results of predicted R^2 showed 0.70, 0.59 and 0.66 for sorption, recovery and reusability respectively (Table 4.28).

Verification of optimised treatment parameters and predictive model



Graph 4.20 Desirability ramp for optimisation of enzyme treatment parameters

Graph 4.20 shows the optimised parameters of enzyme treatment based on three response variables, viz. sorption capacity, recovery of sorbed oil and reusability of the fibre sample. The data was obtained by using numerical optimisation. Optimisation requires that goals (i.e., none, maximum, minimum, target, or in range) are set for the variables and response, where all goals then get combined into one desirability function. To find a good set of conditions that will meet all the goals, all three parameters, (i) concentration, (ii) time and (iii) temperature, were set within range while all three response variables (i) sorption, (ii) recovery and (iii) reusability, set at maximum. The optimum level of various parameters was obtained, and desirability ramps were developed from optimum points via numerical optimisation.

From Graph 4.20, the results for optimised parameters for enzyme treatment condition showed the predicted values for concentration was 4.03%, temperature was 70℃, and time was 54.53 minutes. For the response variables, the predicted values for sorption obtained were 21.32 g/g, recovery was 73.85% and reusability was 19.64 g/g.

Table 4.29 Optimised parameters for Enzymatic treatment

Enzyme concentration	4%
Treatment time	55 minutes
Treatment temperature	70℃

Further, based on model predicted values, the optimised parameters for enzyme treatment were 4% concentration, temperature was 70℃and 55 minutes of time (Table 4.29).

4.6 Characterisation of untreated and optimised Fibre

The effect of chemical modification treatment on sugarcane bagasse fibres was analysed using physical and chemical characterisation of fibres before and after treatment.

4.6.1 Physical Characterisation through Scanning Electron Microscope (SEM) analysis

The effect of chemical modification treatment on the morphological structure of Sugarcane bagasse fibres was assessed using a Scanning Electron Microscope (SEM). The SEM images of a longitudinal view of untreated and chemically modified fibres are shown in (Plate 4.6).

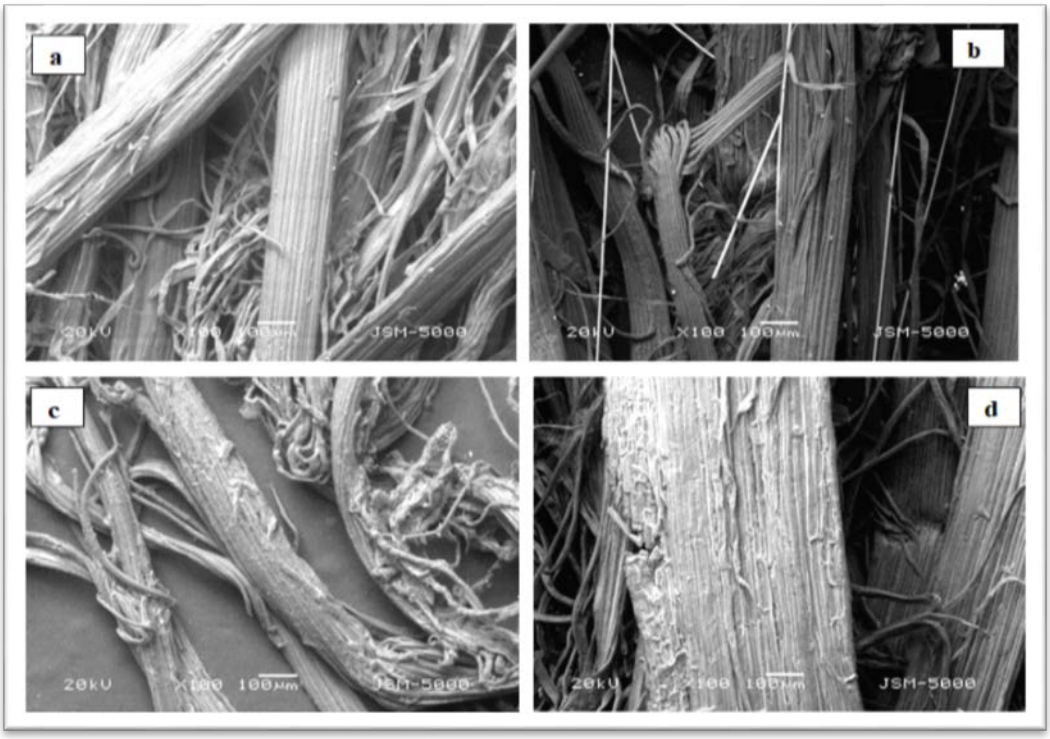


Plate 4.6: Images of untreated and treated Sugarcane bagasse fibre obtained by SEM at 100 X (a) UB (b) AC (c) CY d) EZ

Untreated Sugarcane fibre was examined using SEM characterisation, which reveals that the structure has bundles of fibre together. Plate 4.6(a) showed the smooth surface and compact structure of fibres. The chemical modification through acetylation treatment (Plate 4.6 b) causes changes to the surface structure of the fibre. The modified fibres showed some distinctions, as the presence of pits (bagasse) and the fibres aligned in a loosening structure compared to the untreated fibre.

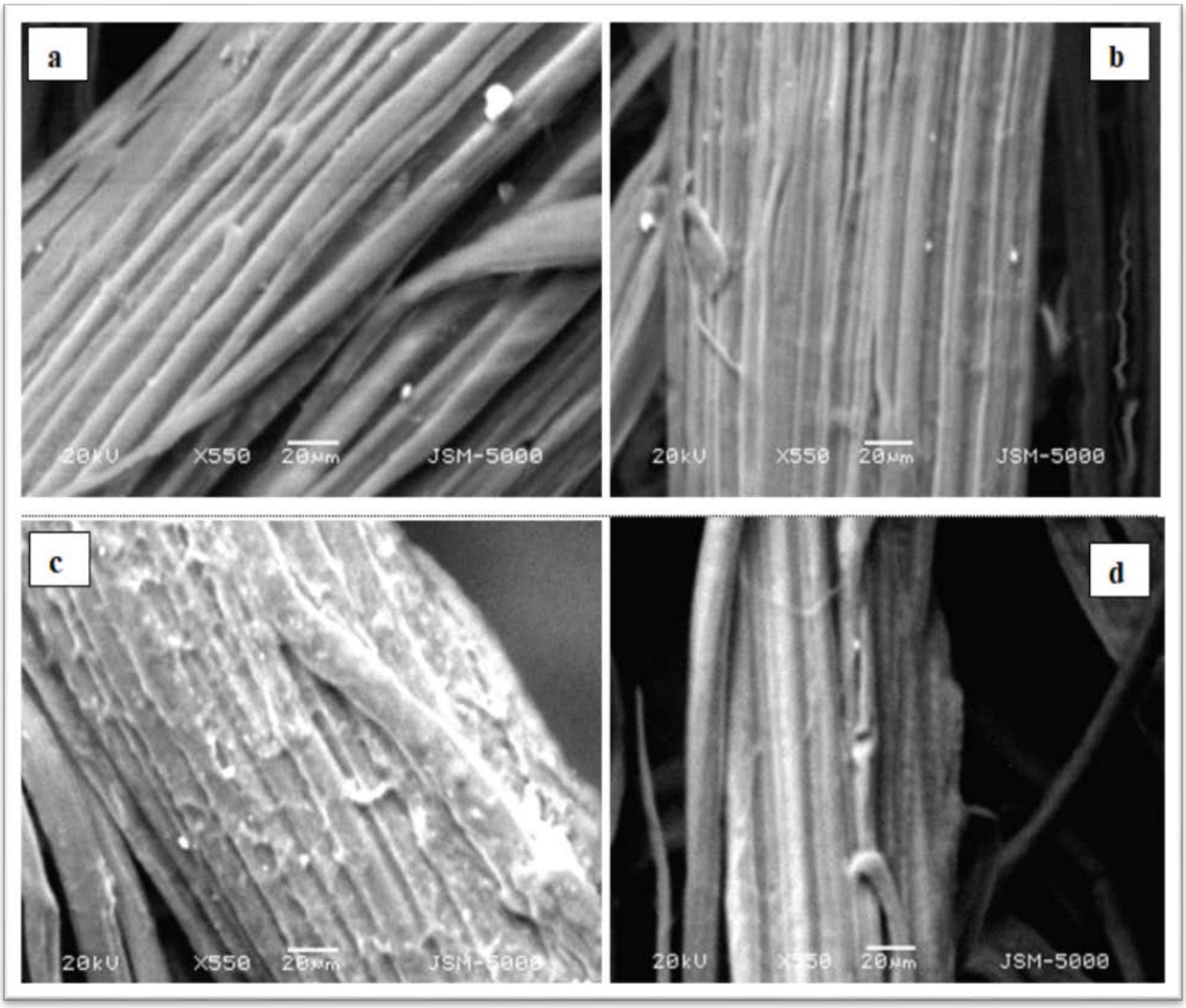
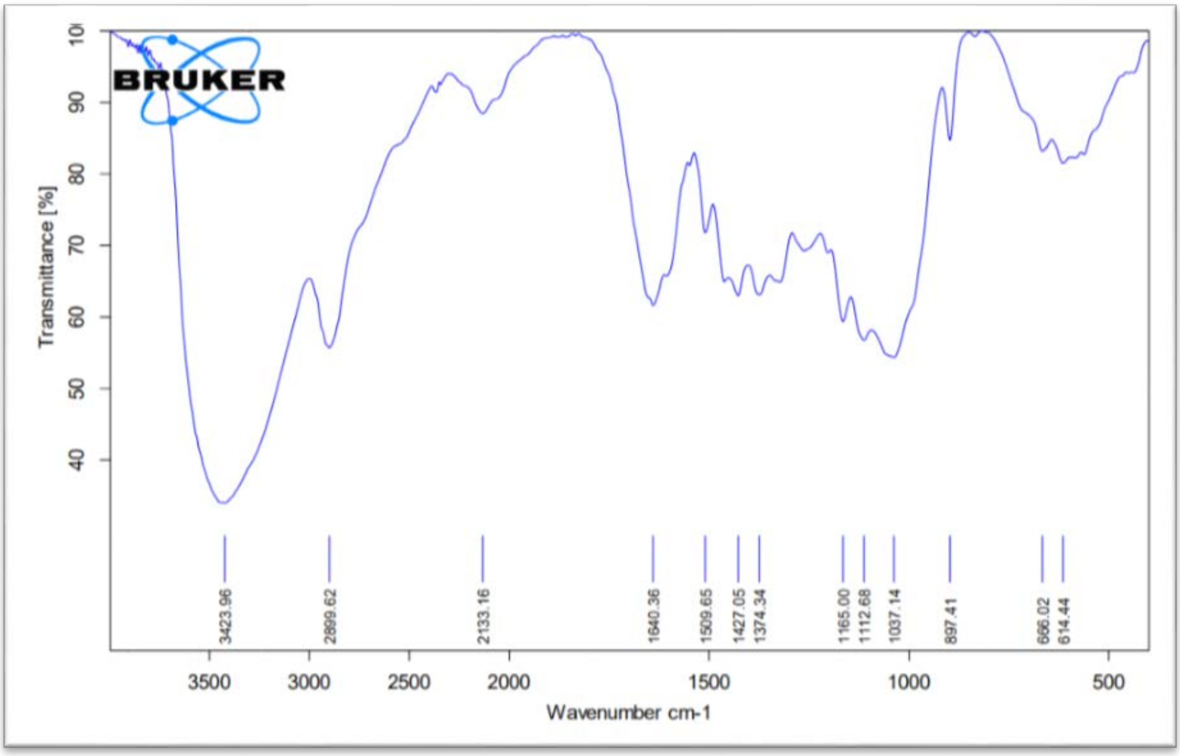


Plate 4.7: Images of untreated and treated sugarcane bagasse fibre obtained by SEM at 550 X (a) UB (b) AC (c) CY(d) EZ

The cyanoethylated modified fibre surface image showed the swelling of the fibre structure, along with the assumption that the diameter would increase due to the NaOH effect. After NaOH pretreatment, fibre bundles were separated and appeared more flexible due to their curved and twisted appearance (Plate 4.6 c). The enzyme-treated fibres look much smoother (Plate 4.6 d) than untreated fibres, which involves bio-polishing the fibres and minor removal of non-cellulosic materials. The SEM images obtained at 550 X magnification (Plate 4.7) showed an in-depth view of surface changes same as observed at 100 X magnification.

4.7.2 Chemical characterisation through Fourier-Transform Infrared Spectroscopy (FTIR) analysis

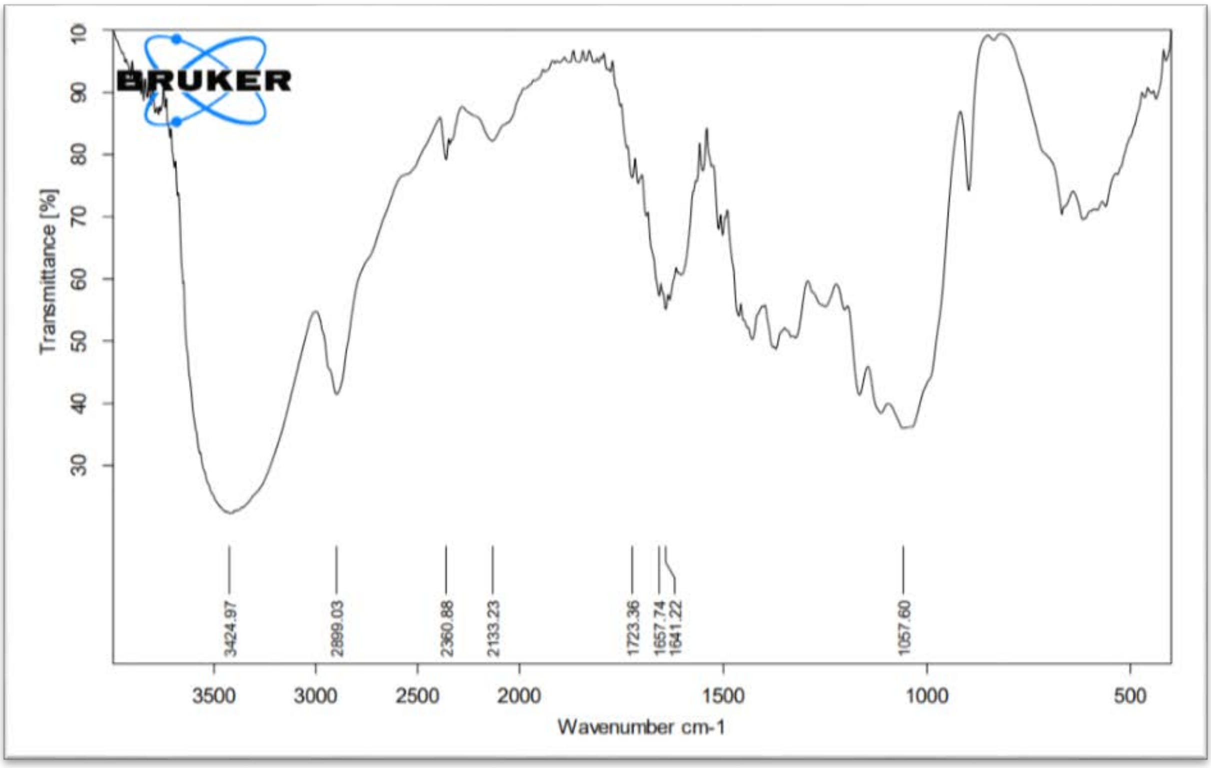
The effect of chemical modification treatment on the functional group of Sugarcane bagasse fibres was assessed using Fourier-Transform Infrared Spectroscopy (FTIR). The FTIR spectra of untreated and chemically modified fibres are shown in the following Graphs:



Graph 4.21 FTIR spectra of untreated fibre

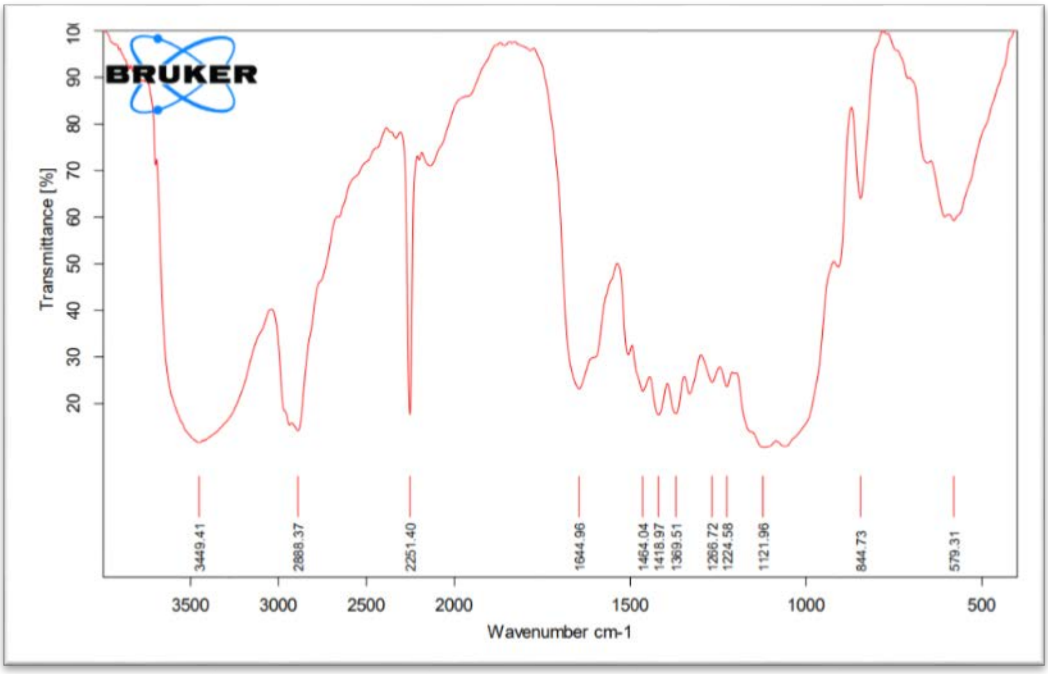
From Graph 4.21, the peak observed at 1374 cm^{-1} is indicative of an ether bond. Ether bonds are found in lignin and hemicelluloses and also as inter-polymer linkage between the two. The negative peak at 1640 cm-1 indicates COO stretching and vibrations. This indicates the presence of lignin. The stretching between 2899 cm-1 indicated C-H stretching and O-H stretching. C-H and O-H bonds are found in cellulose and lignin. These bonds are also found as inter-polymer linkages between cellulose and hemicellulose, hemicelluloses and lignin and cellulose and lignin. Graph 4.21 shows a broad peak around 3423 cm^{-1}, which is attributed to the O-H group of the fibre.

Graph 4.21 represents the FTIR spectra of untreated Sugarcane bagasse fibre. The transmittance bands around 3423 cm^{-1} and 2899 cm^{-1} are indicative of O-H bond and C-H bond stretching respectively. The band at 897 cm^{-1} represents the C-OH band which shows the relationship of β- glycosidic bond between monosaccharide in cellulose and hemicellulose.



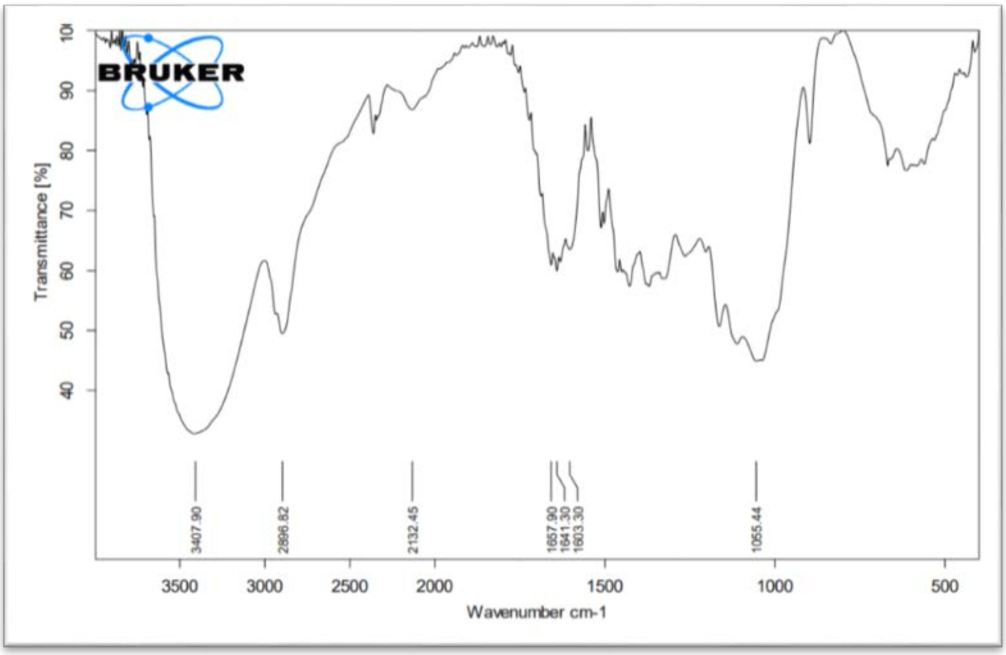
Graph 4.22: FTIR spectra of Acetylated fibre

The peak at 1500 cm^{-1} indicates the introduction of an acetyl group, as shown in Graph 4.22. The absorbance band at 1657-1723 cm^{-1} shows the presence of an amide group. The broadening and reduction in the intensity of the peak for O-H stretching (Graph 4.22) prove that some of the O-H groups utilised by other reactors, which is Acetylation in this case. The ester band appearing between 1723 cm^{-1} - 1641 cm^{-1} (carbonyl C=O stretching of ester) provides evidence of acetylation of the cellulose.



Graph 4.23: FTIR spectra of Cyanoethylated fibre

The change in the chemical structure of fibre as a result of cyanoethylation treatment was followed using FTIR spectroscopy. In the FTIR spectra of cyanoethylated fibre shown in Graph 4.23, a strong transmittance band appeared at 2251 cm^{-1} for the nitrile group (−C≡N), which confirms successful cyanoethylation of the fibre. Also, the increased intensity of the transmittance band at around 2888 cm^{-1} for the CH_2 group is increased, which also provides proof of cyanoethylation.



Graph 4.24: FTIR spectra of Enzyme treated fibre

From Graph 4.24, the FTIR spectra look the same as the enzyme, making the fibre soft, and no major chemical changes take place.

4.7 Manufacturing of Non-woven

After optimisation of extraction conditions, fibre extraction in bulk was carried out through the fabricated apparatus (Sugarcane fibre extractor) under optimised conditions. The extracted fibres were found suitable for manufacturing nonwovens. The Non-woven were created from the following two methods:

a) Hand Lay-up technique

After fibre extraction, the matted fibres were taken out, washed properly and flattened with the hand lay-up technique manually in the department laboratory. After the flattening process, the Non-woven samples were oven-dried at 60°C for 30 minutes. The prepared Non-woven sample GSM was 328 g/m^2.

b) Mechanical bonding: Needle-punching technique

The Non-woven was created using the method specified in section 3.9 (Chapter 3). For web formation, the fibre was fed between the rollers of the miniature carding machine. The fibres were passed in 5 runs in the machine using a feeder speed of 1.53 m/min, cylinder speed of 184.1 m/min and doffer speed of 17.38 m/min for better opening and softening of fibres, which was the requirement of web formation. After the web formation, the web was needle punched through the DILO- Needle punching machine (Plate 4.8) in a randomly laid direction using a needle punch density of 150 cm^{-2} and the depth of penetration was 10 mm. The Non-woven was prepared in two different GSM, i.e. 800 g/m^2 and 1000 g/m^2.

Plate 4.8: Laying of hand-opened carded fibres and web formation

Plate 4.9: Non-woven (Hand lay-up)

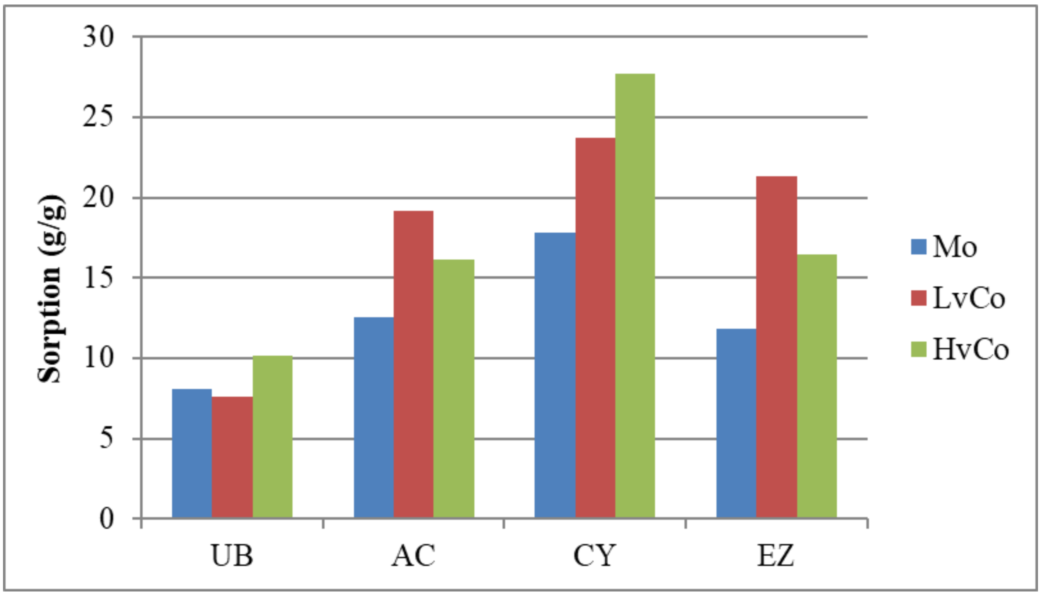
Plate 4.10: Non-woven (Needle- Punched)

4.8 Testing of Non-woven for oil sorption

The prepared Non-wovens were tested in three different viscosities of oil, viz. Motor oil (Mo), Light viscosity crude oil (LvCo), Heavy viscosity crude oil (HvCo). The results of oil testing were discussed through the following sub-heads :

4.8.1 Testing for oil sorption capacity

The prepared Non-wovens were tested for their oil sorption capacity. The results of untreated (UB) and all three treated samples viz. Acetylated (AC), Cyanoethylated (CY) and Enzymatic (EZ) were analysed.

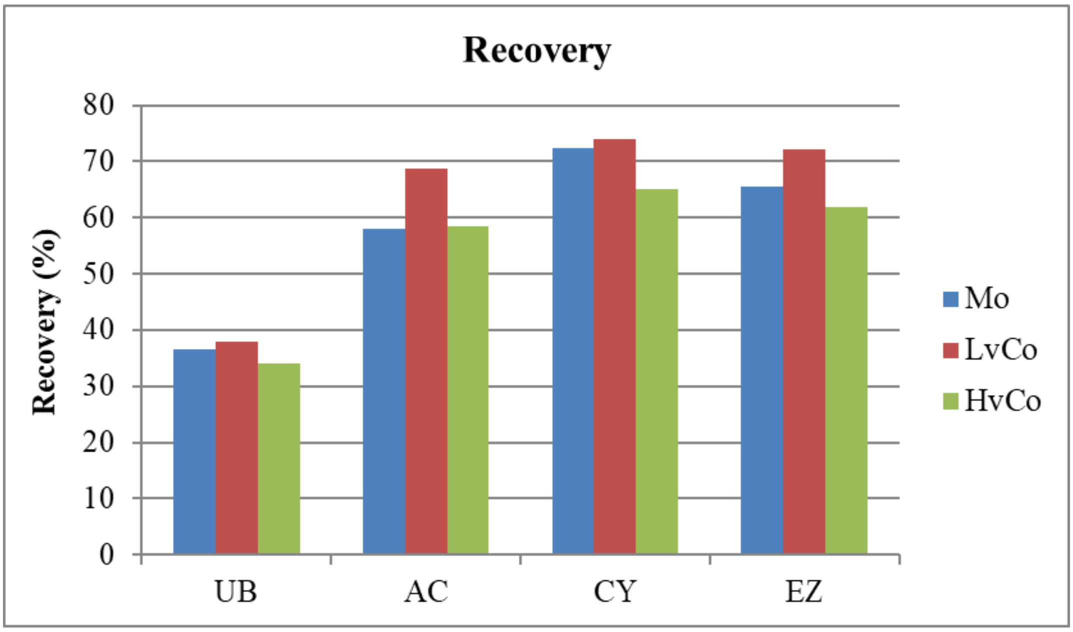


Graph 4.25: Oil sorption capacity of untreated and treated Non-wovens

From Graph 4.25, it was observed that the oil sorption capacity of untreated non-woven in Mo was 7.11 g/g, whereas the acetylated non-woven sorption was 12.52 g/g, which was higher than the untreated sample. The Enzyme treated non-woven sorption capacity was found higher (21.32 g/g) in LvCO than in acetylated non-woven (19.19 g/g). In motor oil, the maximum sorption capacity of 17.84 g/g was observed in the cyanoethylated sample followed by acetylated (12.52 g/g), Enzyme treated 11.84 g/g and untreated sample (7.11 g/g) respectively. In LvCo, the maximum sorption was obtained at 23.72 g/g by cyanoethylated sample followed by enzyme-treated (21.32 g/g), acetylated (19.19 g/g) and untreated (9.87 g/g) respectively. Sorption capacity in HvCo : Cyanoethyalted (27.69 g/g) followed by enzyme treated (16.48 g/g), Acetylated (16.16 g/g) and Untreated 10.16 g/g respectively. The best results showed in Cyanoethylated non-woven sorption capacity, which was found maximum (27.69 g/g) in HvCo followed by LvCo (23.72 g/g) and Mo (17.84 g/g).

4.8.2 Testing for Recovery of sorbed oil

The prepared Non-wovens were tested for recovery of sorbed oil. The results of untreated (UB) and all three treated samples viz. Acetylated (AC), Cyanoethylated (CY) and Enzymatic (EZ) were analysed.

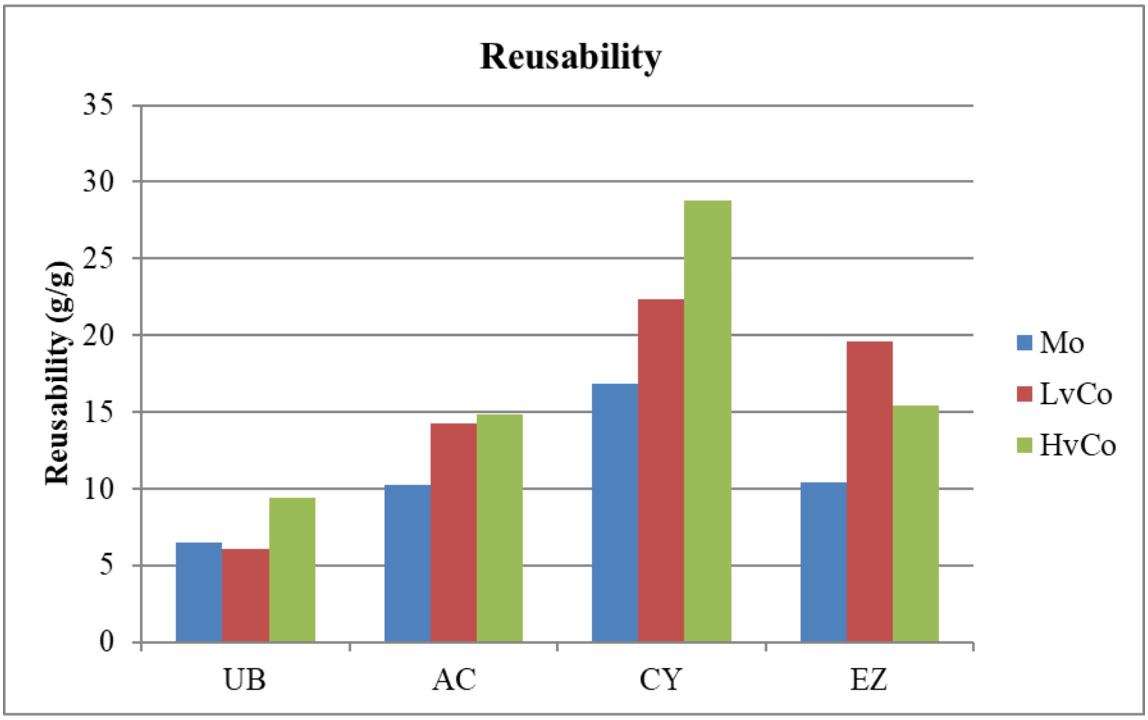


Graph 4.26: Recovery of sorbed oil of untreated and treated Non-wovens

From Graph 4.26, It was observed that the recovery of oil from sorbent in Mo was 36.46% whereas the acetylated Non-woven recovery was 57.99% which was higher than the untreated sample. The enzyme treated Non-wovens recovery was found higher (72.08%) in LvCO than in acetylated non-wovens (68.67%). In motor oil, the maximum sorption capacity of 72.43% was observed in the cyanoethylated sample followed by enzyme treated (65.43%), acetylated (57.99%) and untreated sample (36.46%) respectively. In LvCo, the maximum recovery was obtained at 73.85% by cyanoethylated sample followed by enzyme treated (72.08%), acetylated (68.67%) and untreated (38.00%) respectively. Recovery in HvCo: Cyanoethyalted (64.95%) followed by Enzyme treated (61.96%), Acetylated (58.54%) and Untreated was 34.02% respectively. The best results showed in recovery of LvCo by Cyanoethylated Non-wovens which was found maximum (73.85%) followed by Mo (72.43%) and HvCo (64.95%).

4.8.3 Testing for Reusability of sorbent

The prepared Non-wovens were tested for reusability of sorbent. The results of untreated (UB) and all three treated samples viz. Acetylated (AC), Cyanoethylated (CY) and Enzymatic (EZ) were analysed.

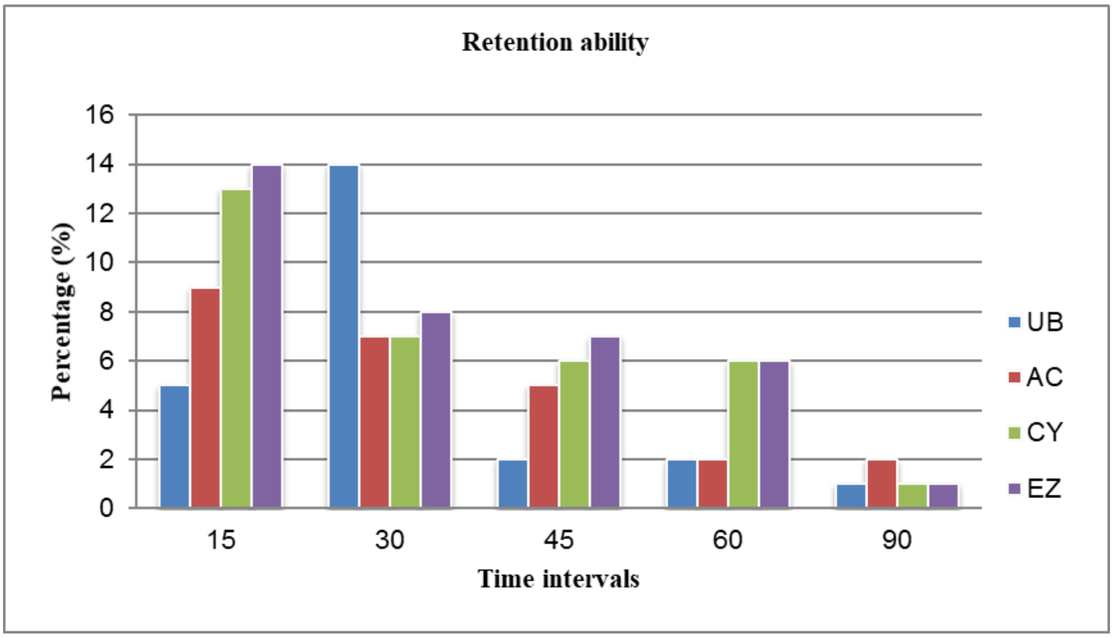


Graph 4.27: Reusability of untreated and treated Non-wovens

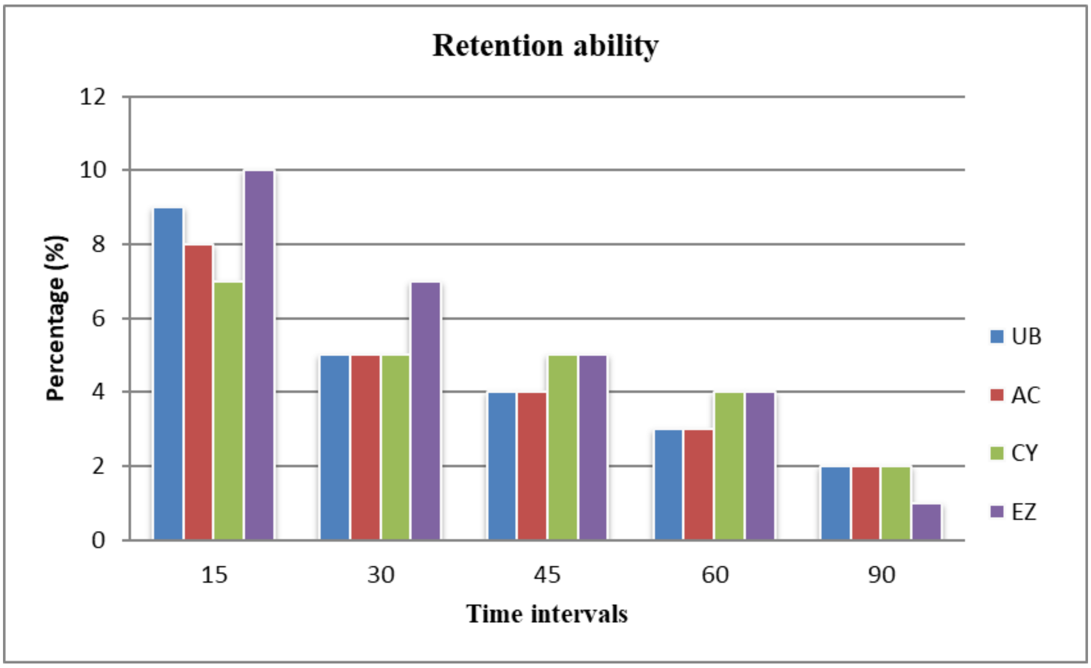
The data presented in Graph 4.27, showed the reusability of untreated Non-woven in Mo was 6.53 g/g whereas the acetylated Non-woven sorption was 10.28 g/g which was higher than the untreated sample. The enzyme treated Non-wovens reusability was found higher (19.64 g/g) in LvCO than in acetylated Non-wovens (14.22 g/g). In motor oil, the maximum reusability of 16.83 g/g was observed in the cyanoethylated sample followed by enzyme-treated 10.41 g/g, acetylated (10.28 g/g), and untreated sample (6.53 g/g) respectively. In LvCo, the maximum reusability was obtained at 22.36 g/g by cyanoethylated sample followed by enzyme-treated (19.64 g/g), acetylated (14.22 g/g) and untreated (6.05 g/g) respectively. Reusability in HvCo: Cyanoethyalted (28.79 g/g) followed by Enzyme treated (15.43 g/g), Acetylated (14.87 g/g) and Untreated 9.38 g/g respectively. The best results showed in Cyanoethylated Non-wovens reusability which was found maximum (28.79 g/g) in HvCo followed by LvCo (22.37 g/g) and Mo (16.83 g/g).

4.8.4 Testing for Oil retention ability

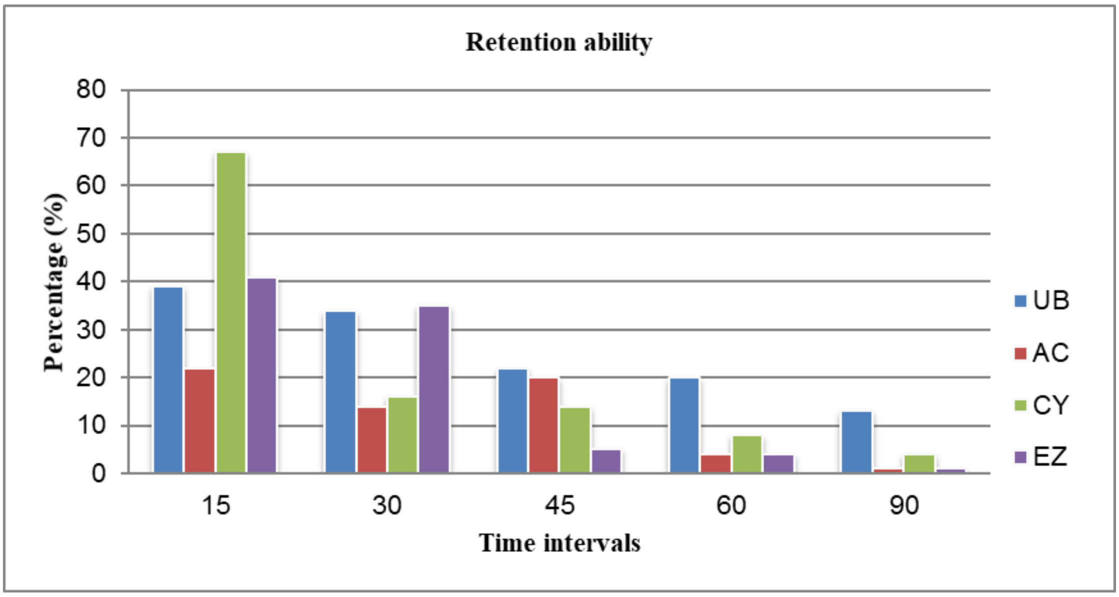
The prepared Non-wovens were tested for oil retention ability. The results of untreated (USB) and all three treated samples viz. Acetylated (AC), Cyanoethylated (CY) and Enzymatic (EZ) were analysed.



Graph 4.28(a): Retention ability of untreated and treated Non-wovens for Mo



Graph 4.28(b): Retention ability of untreated and treated Non-wovens for LvCo



Graph 4.28(c): Retention ability of untreated and treated Non-wovens for HvCo

The oil retention capacity of fibre is a very important parameter in evaluating the ability of sorbents to retain the absorbed oil during transfer and handling operations. The data on the retention ability of sorbent is presented in Graph 4.28. It was found from the result that the dripping of the oil from the untreated sorbent was higher and faster during the first 15 minutes in HvCo followed by LvCo and Mo respectively. This is due to the instantaneous dripping of oil from the external surface of fibres. The results revealed that the retention of the acetylated sample was found fast during initial dripping in HvCo followed by Mo and LvCo respectively. The retention of the cyanoethylated sample was found much faster during initial dripping in HvCo followed by Mo and LvCo respectively. The retention of the enzyme-treated sample was observed fast during initial dripping in HvCo followed by Mo and LvCo respectively. Therefore, the retention ability of Cyanoethylated samples was found good in HvCo, followed by Mo and LvCo respectively.

4.8.5 Non-woven oil sorption capacity testing in oil-layer system

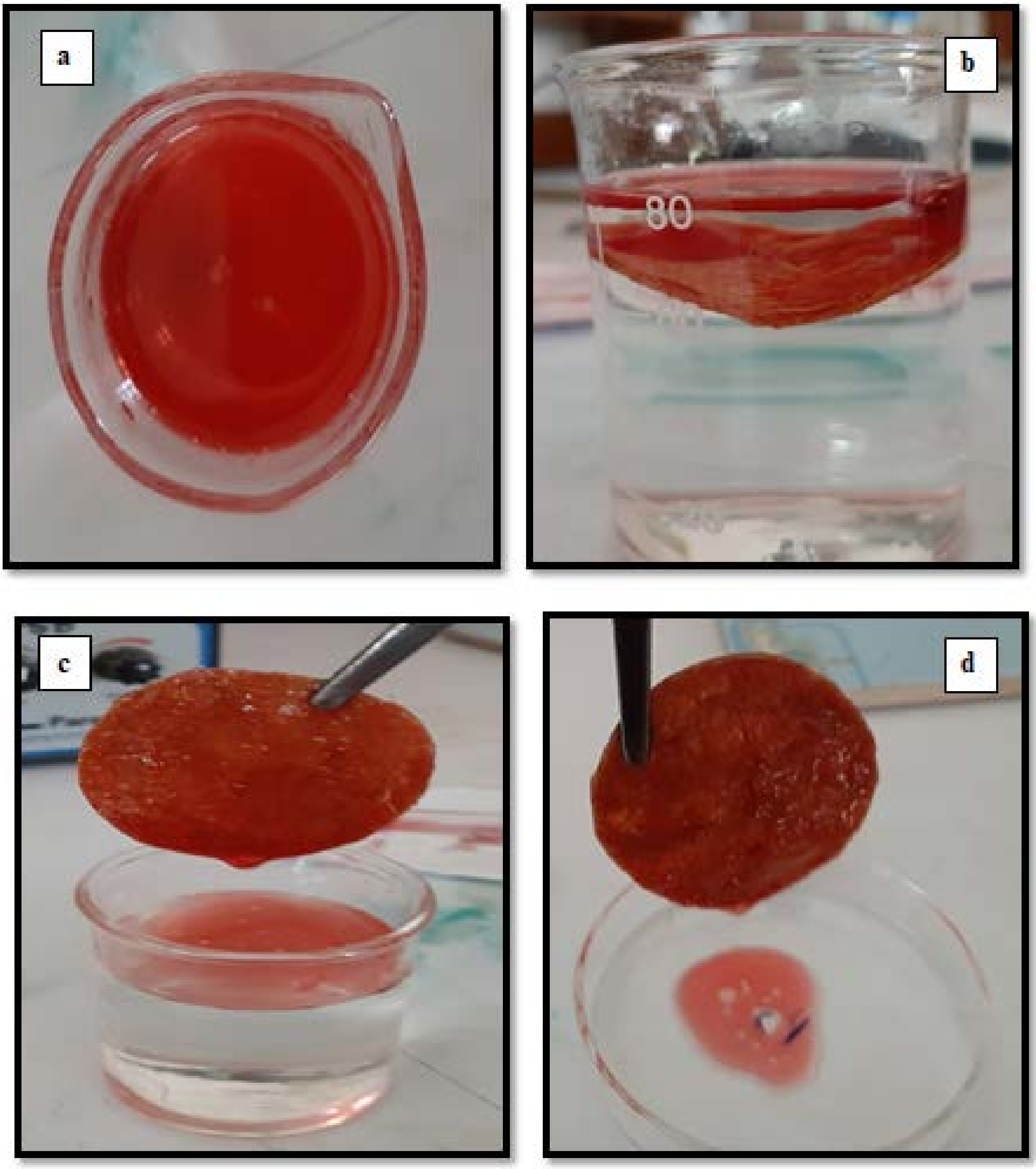


Plate 4.11(a): Oil sorption testing of Non-woven in Mo (a) Water with oil layer (b) Sorption process (c) Sorption by sorbent (d) Recovery of oil

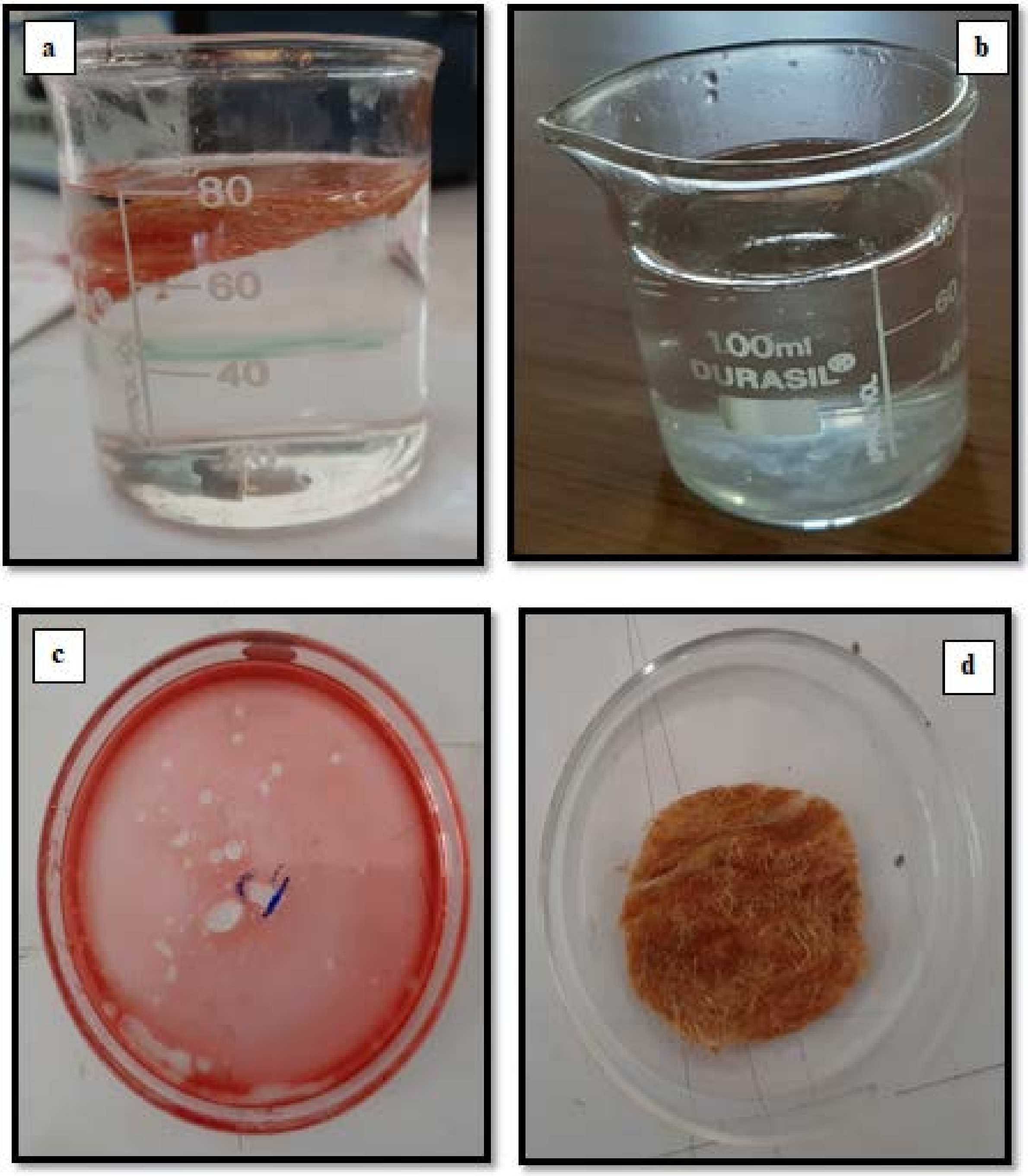


Plate 4.11(b): Oil sorption testing in the oil-layer system of Non-woven in Mo (a) Reusability of sorbent (b) Water after sorption process (c) Recovered oil (d) Sorbent after testing

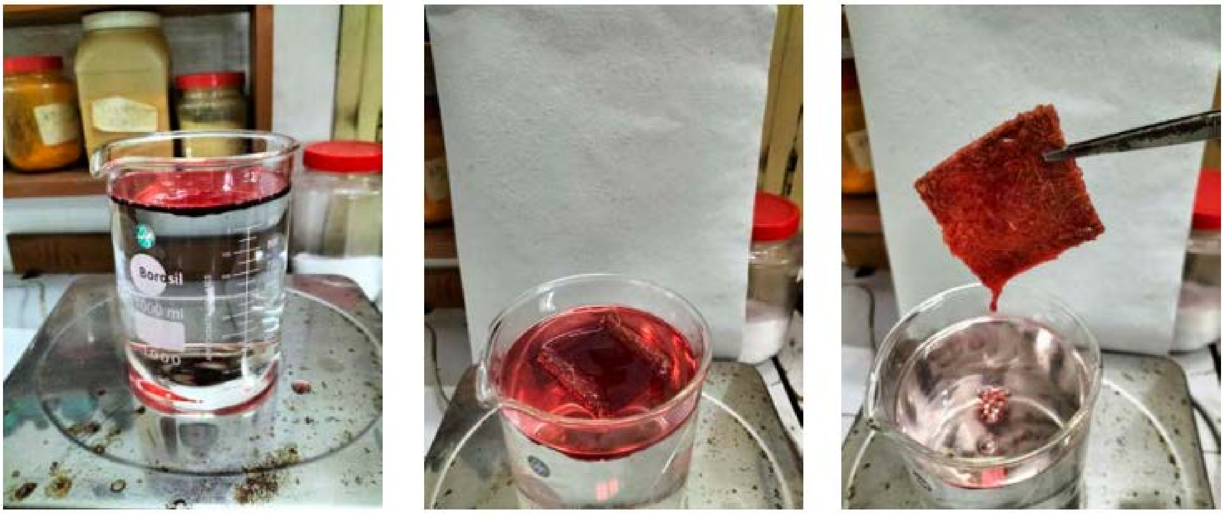


Plate 4.12: Oil sorption testing in oil-layer system of Non-woven in Mo

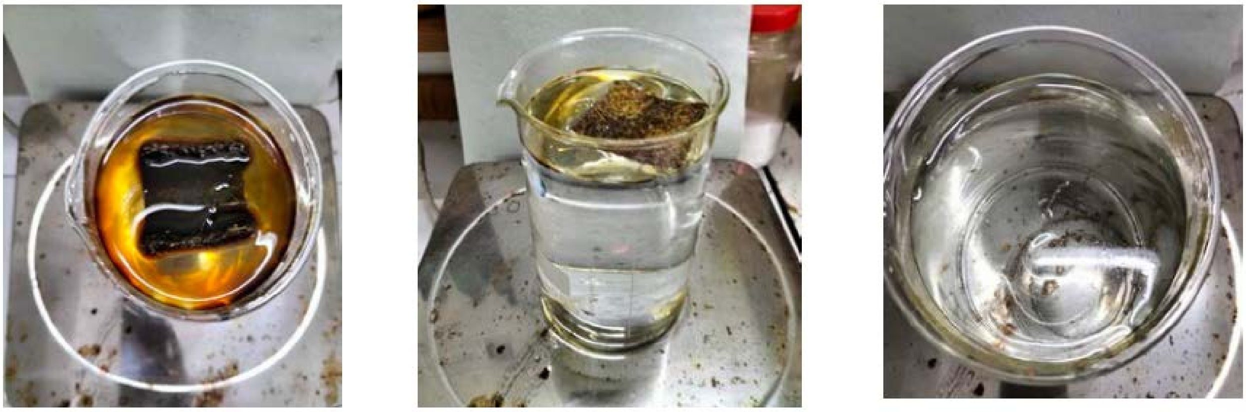


Plate 4.13: Oil sorption testing in oil-layer system of Non-woven in LvCo

Plate 4.14: Oil sorption testing in oil-layer system of Non-woven in HvCo

From the test results of Non-woven oil sorption capacity testing in an oil-layer system, there were two phases of oil and water, in a way that the oil formed a layer on water. It was observed that the Non-woven sample initially quickly picked up the capacity of oil in heavy viscosity crude oil followed by light viscosity crude oil (Plate 4.13). The oil sorption capacity of the sample was slow to pick up in motor oil (Plate 4.12), comparatively crude oil.

The oil sorption capacity of the sample was quickly picked up in HvCo (Plate 4.14), comparatively light viscosity crude oil. The results also indicate that Non-woven sorbent can absorb the oil from the water layer completely (2-3 times) and also recover the oil. The reusability of the sorbent was up to three times. These Non-woven sorbents were biodegradable as the raw material was agro-waste, and good sorption and recovery of oil were observed.

4.8.5 Characterisation of oil-tested fibres through SEM and FTIR analysis

(a) SEM analysis of untreated and treated fibres after oil sorption

To better understanding of the enhanced oil sorption behaviour of Sugarcane bagasse by modification, the morphology of the fibres was examined using SEM (Plate 4.15).

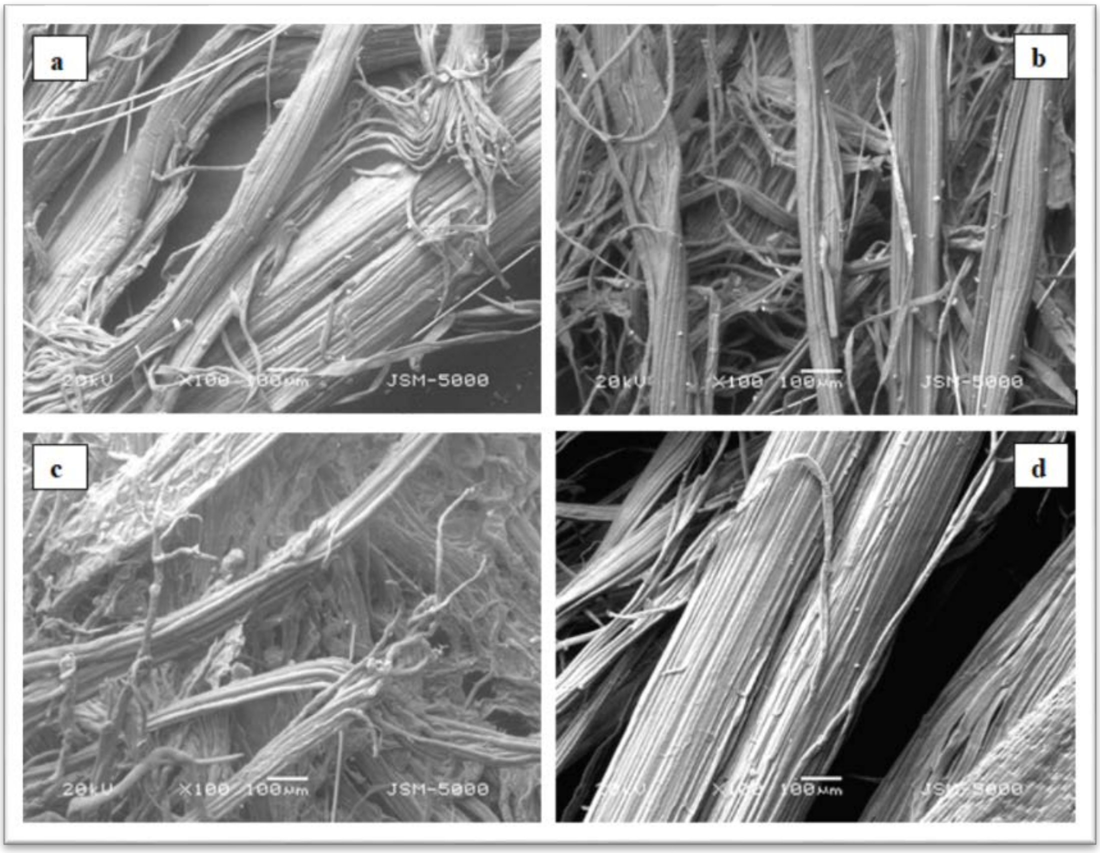


Plate 4.15: SEM images of fibres with Mo sorption (100X): (a) UB (b) AC (c) CY(d) EZ

SEM studies suggested that untreated fibre surface after oil sorption (Plate 4.15 a) showed some smooth surfaces which lead to some amount of oil sorption into the fibre. The surface of Acetylated fibre (Plate 4.15) after oil sorption has more surface smoothness compared to the untreated fibre surface.

It was observed that the Cyanoethylated fibre surface image (Plate 4.15c) showed more sorption of oil into the fibre inside resulting in a very smooth surface. The enzyme-treated fibres after oil sorption showed (Plate 4.15 d) sorption of oil into the surface less as compared to the Cyanoethylation-treated fibre surface.

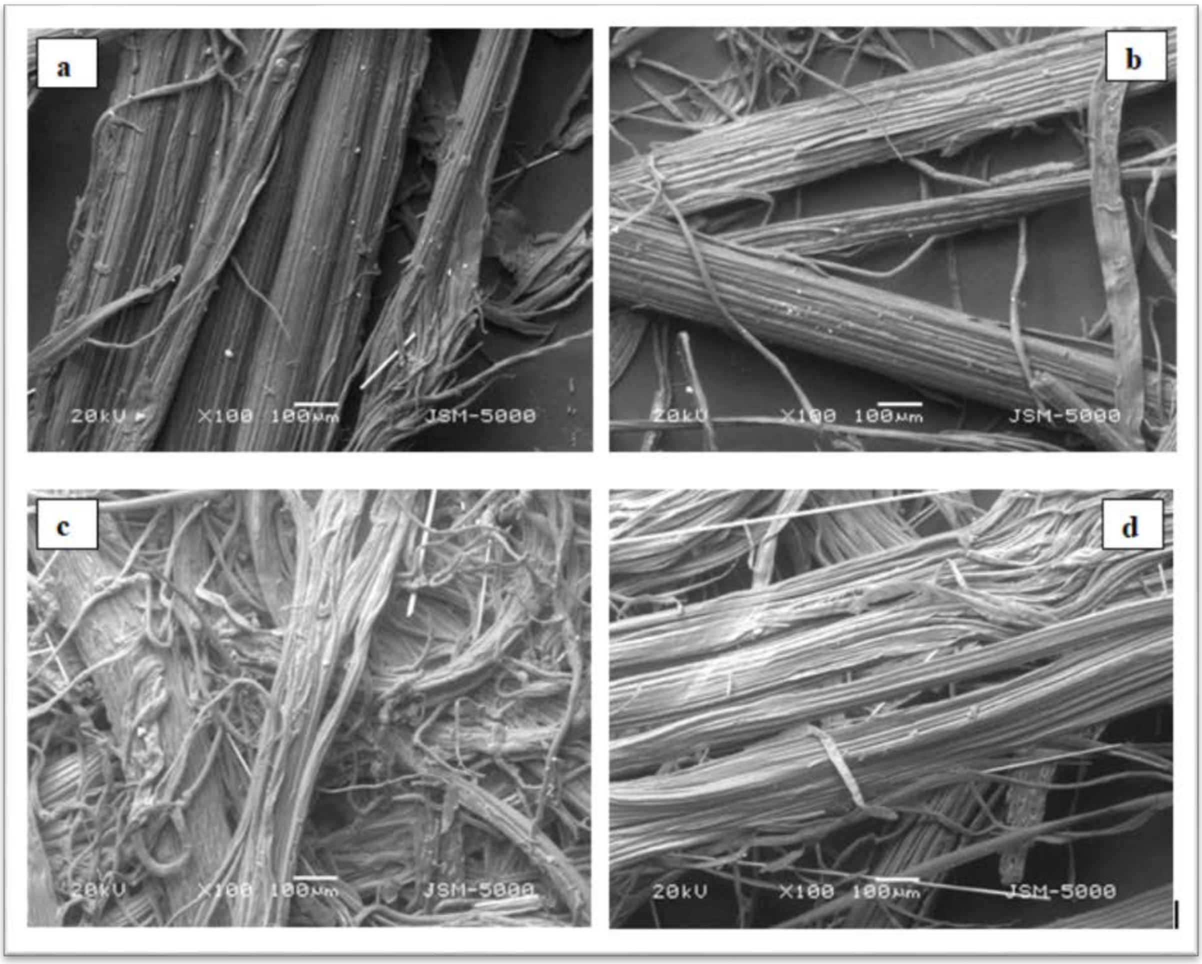


Plate 4.16: SEM Images of fibres with LvCo sorption (100X): (a) UB (b) AC (c) CY(d) EZ

The untreated and treated fibre after sorption in light viscosity crude oil were tested for morphological characterisation under SEM. The images showed that the untreated fibre surface (Plate 4.16 a) was smoother compared to engine oil sorption due to the high sorption of crude oil. Acetylated fibre surfaces, after oil sorption aligned parallel to each other (Plate 4.16 b) as the oil penetrated into the fibre structure.

In Cyanoethylated fibres, the alkaline pretreatment also had a remarkable effect on the fibre morphology (Plate 4.16 c), especially on the fibre bundles. The bundles start to dismantle and the fibres become detached from the others which leads to good sorption of oil. In some regions of the enzyme-treated fibres, the bundle structure is completely lost as shown in (Plate 4.16 d).

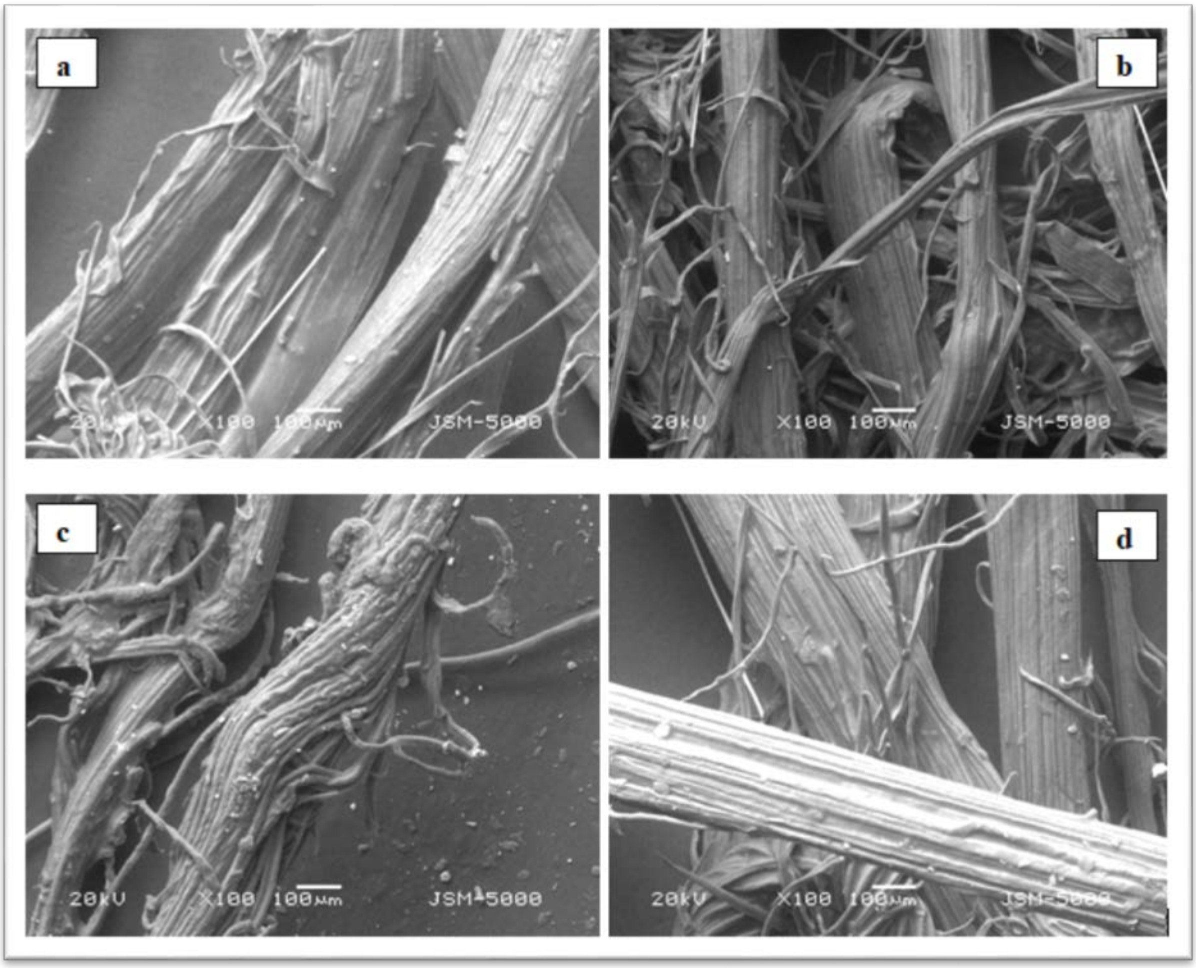
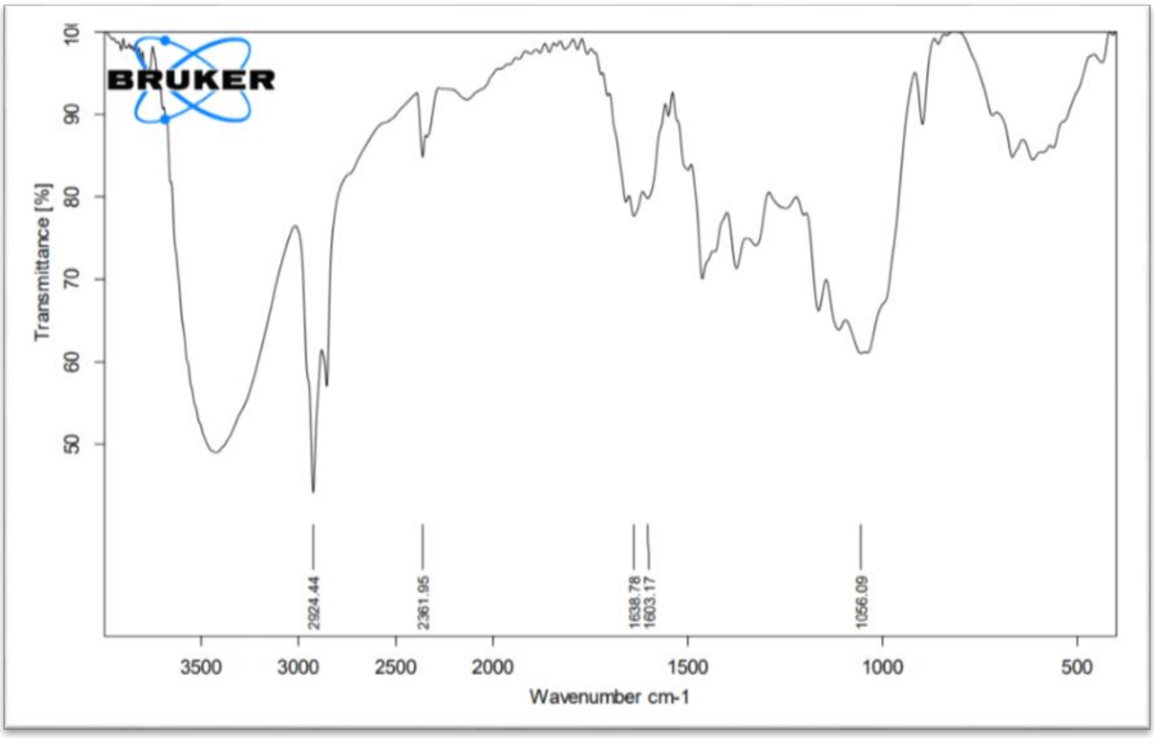


Plate 4.17: SEM Images of fibres with HvCo sorption (100X): (a) UB (b) AC (c) CY(d) EZ

The SEM images (Plate 4.17) showed that the Cyanoethylated fibre surface was maximum sorption of crude oil as compared to enzyme-treated fibre followed by Acetylation-treated fibre. The untreated fibre surface is not so smooth, hence the sorption of crude oil is very less.

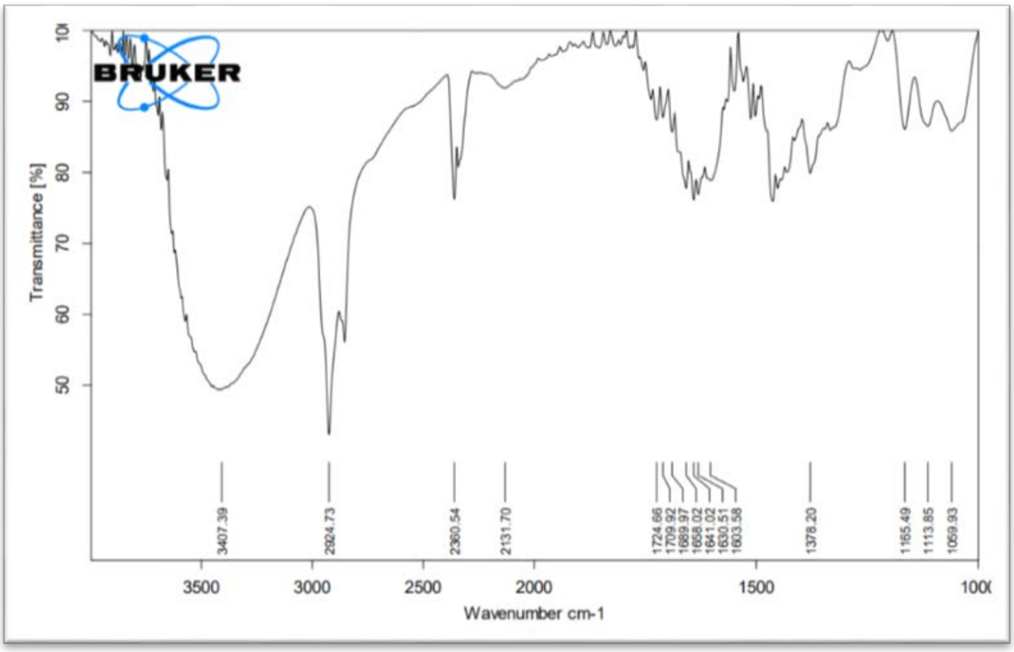
b) FTIR-spectra analysis of untreated and treated fibres after oil sorption

The effect of chemical modification treatment on the oil sorption capacity of Sugarcane bagasse fibres was assessed using Fourier-Transform Infrared Spectroscopy (FTIR). The FTIR spectra of untreated and treated fibres after oil testing are shown in the following Graphs:



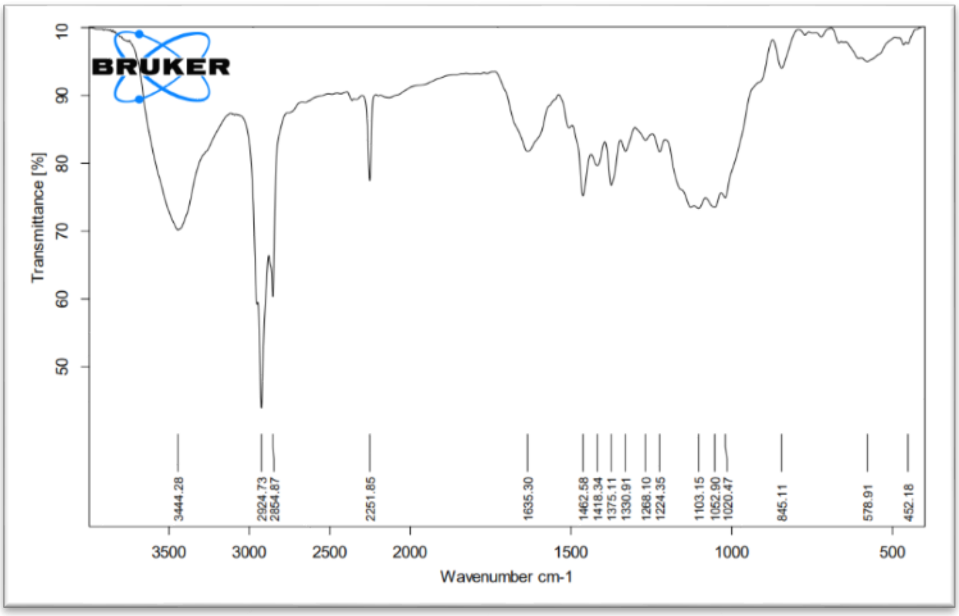
Graph 4.29(a): FTIR spectra of untreated fibre after sorption in Mo

From Graph 4.29(a), the stretching between 2824 cm^{-1} indicated C-H stretching and O-H stretching. C-H and O-H bonds are found in cellulose and lignin. These bonds are also found as inter-polymer linkages between cellulose and hemicellulose, hemicellulose and lignin and cellulose and lignin. The spectra show a broad peak around 3423 cm^{-1}, which is attributed to the O-H group of the fibre. The spectra show a low peak of oil content. Graph 4.29(a) represents the FTIR spectra of untreated Sugarcane bagasse fibre. The transmittance bands around 3423 cm^{-1} and 2899 cm^{-1} are indicative of O-H bond and C-H bond stretching respectively. The peak at 2824 cm^{-1} shows the sorption of oil.



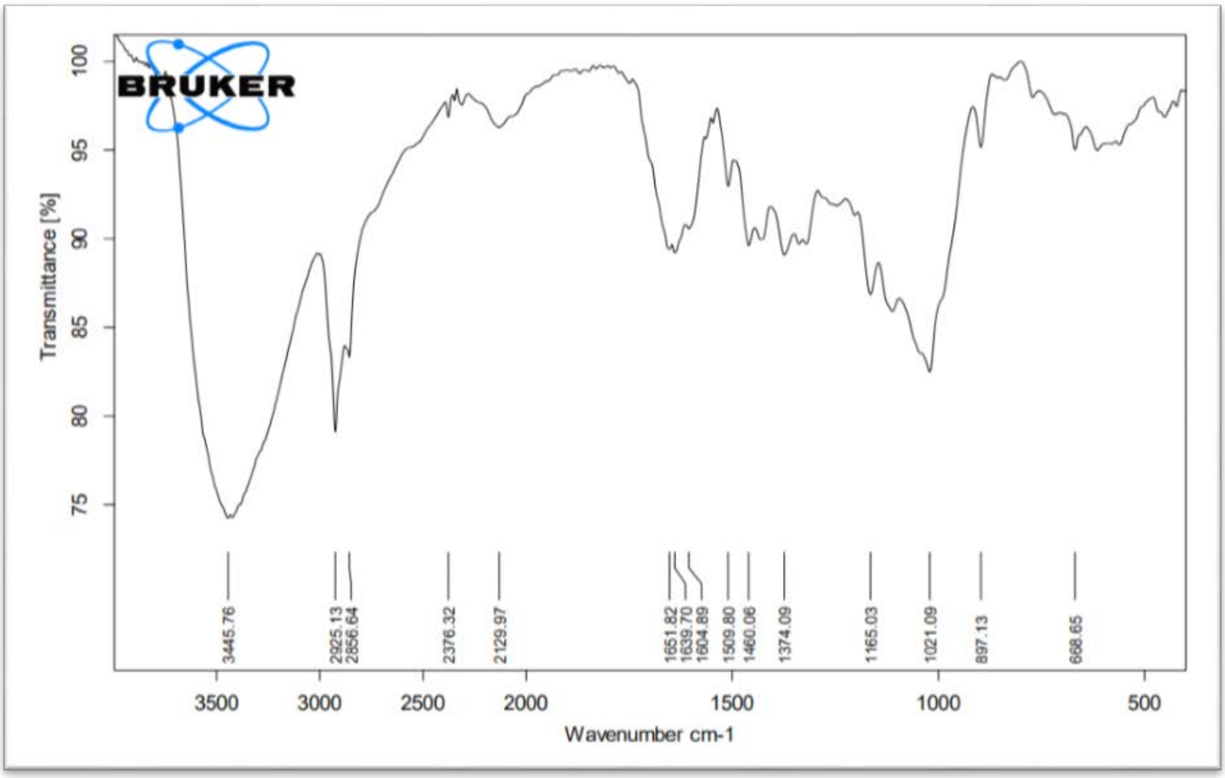
Graph 4.29(b): FTIR spectra of Acetylated fibre after sorption in Mo

The peak at 1500 cm^{-1} indicates for introduction of an acetyl group as shown in Graph 4.29. The absorbance band at 1657-1723 cm^{-1} shows the presence of an amide group. The broadening and reduction in the intensity of the peak for O-H stretching (Graph 4.29) prove that some of the O-H groups are utilised by other reactors which is Acetylation in this case. The ester band appearing between 1723 cm^{-1} - 1641 cm^{-1} (carbonyl C=O stretching of ester) provides evidence of Acetylation of the cellulose. The presence of oil content peak proves the presence of oil in fibre.



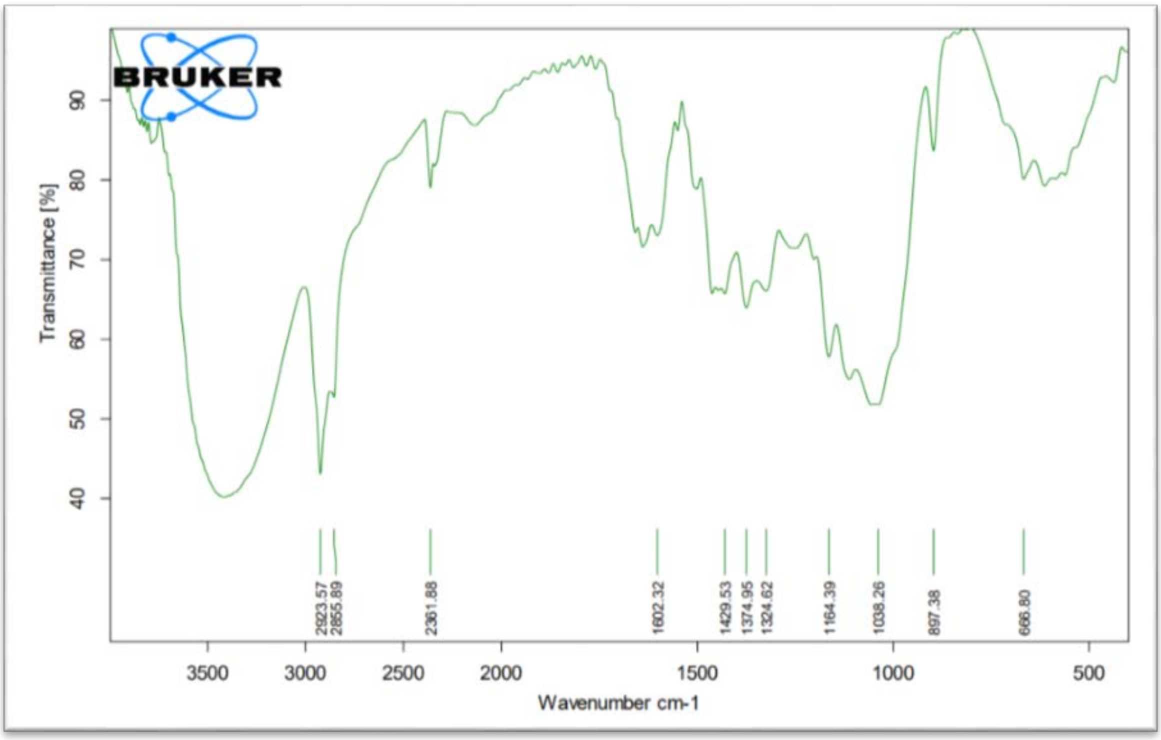
Graph 4.29(c): FTIR spectra of Cyanoethylated fibre after sorption in Mo

In the FTIR spectra of Cyanoethylated fibre after sorption shown in Graph 4.29(a), a strong transmittance band appeared at 2251 cm^{-1} for the nitrile group (−C≡N) is appeared which confirms successful Cyanoethylation of the fibre. Also, the increased intensity of the transmittance band at around 2888 cm^{-1} for the CH_2 group is increased, which also provides proof of Cyanoethylation. The transmittance band appeared at 2854 cm^{-1} for oil peak which confirms sorption of motor oil in fibre.

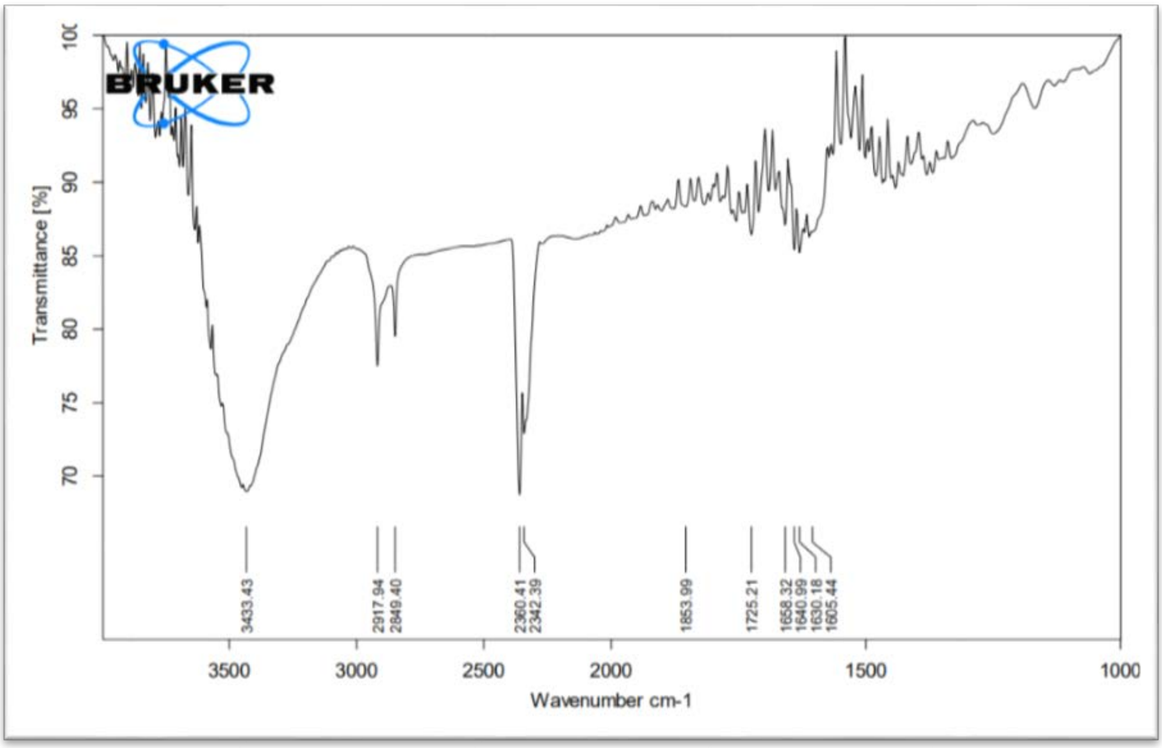


Graph 4.29(d): FTIR spectra of Enzyme treated fibre sorption in Mo

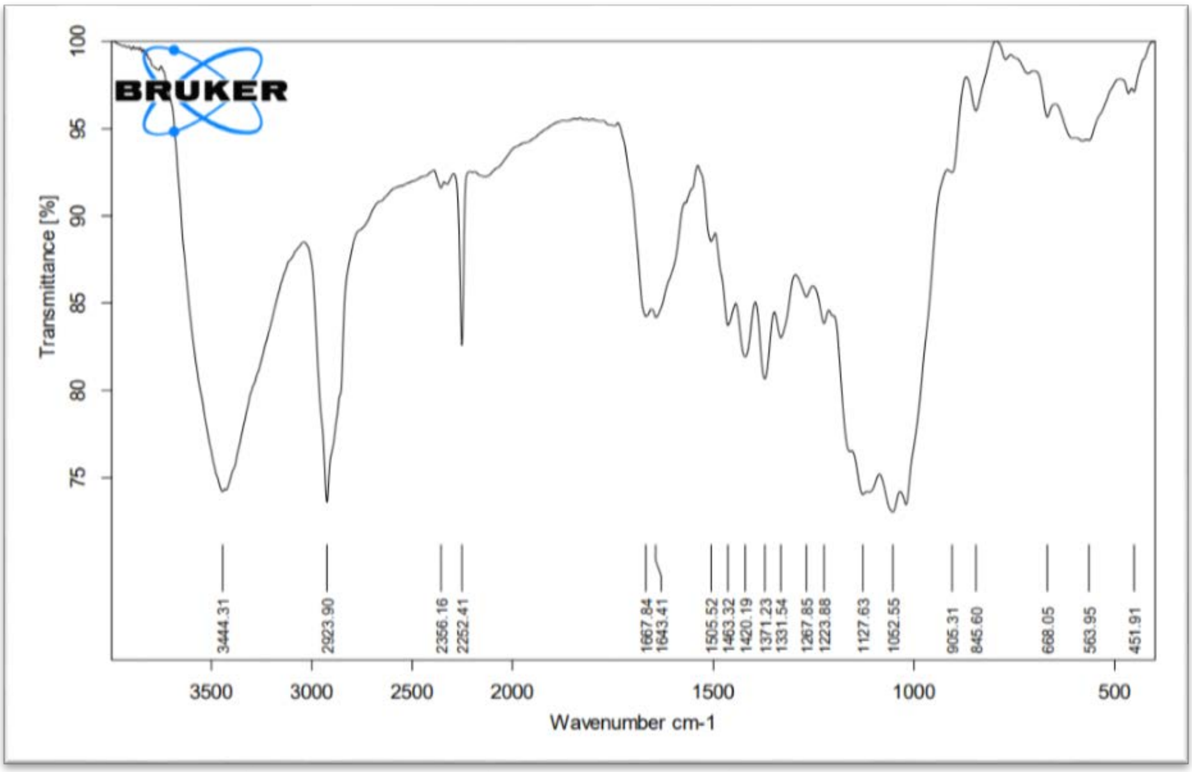
The FTIR spectra of Enzyme-treated fibre after sorption are shown in Graph 4.29(d), it shows the spectra same as the enzyme-treated which represents the softness of the fibre. The transmittance band appeared between 2854 cm^{-1} - 2856 cm^{-1} for the oil peak which confirms the sorption of oil in fibre.



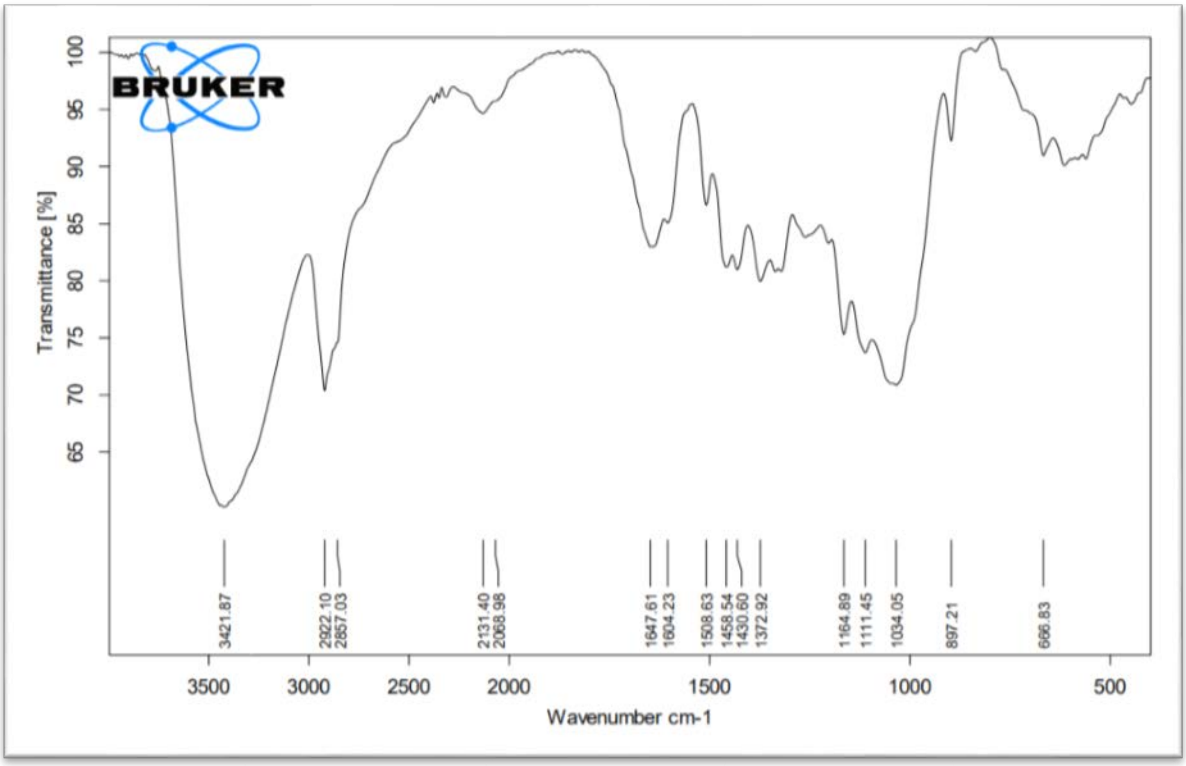
Graph 4.30(a): FTIR spectra of untreated fibre sorption in LvCo



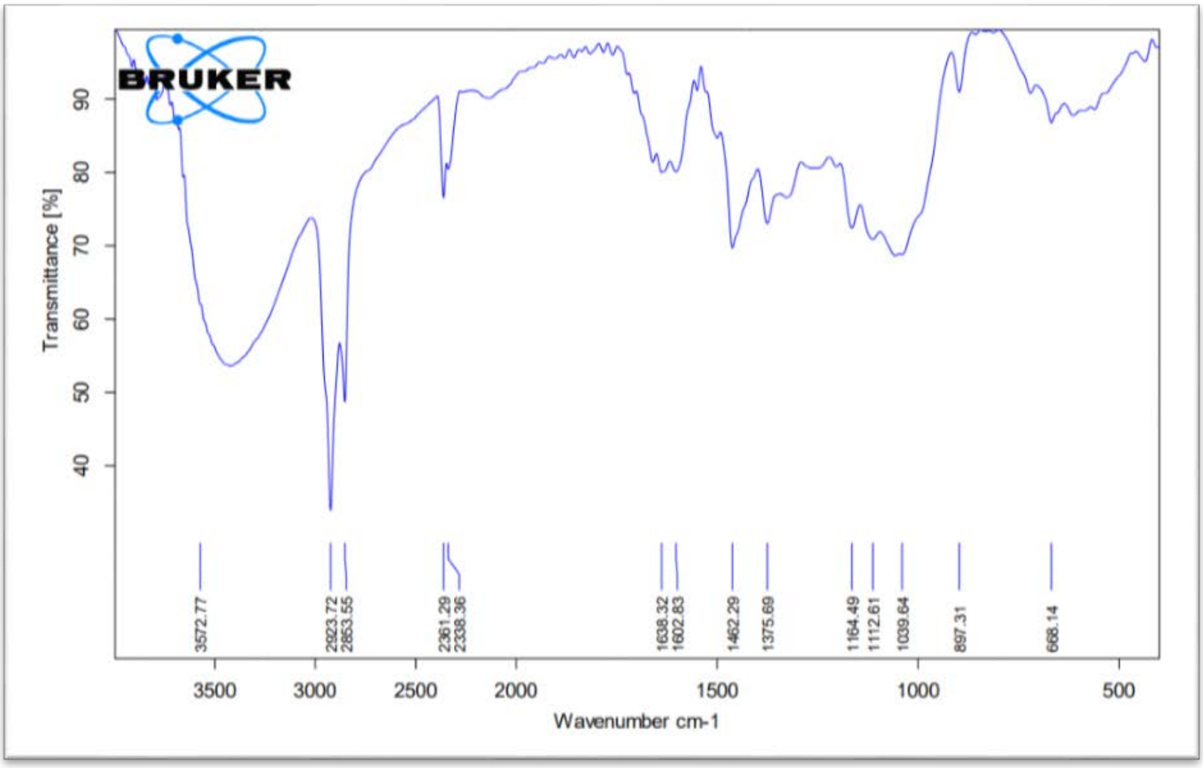
Graph 4.30(b): FTIR spectra of Acetylated fibre sorption in LvCo



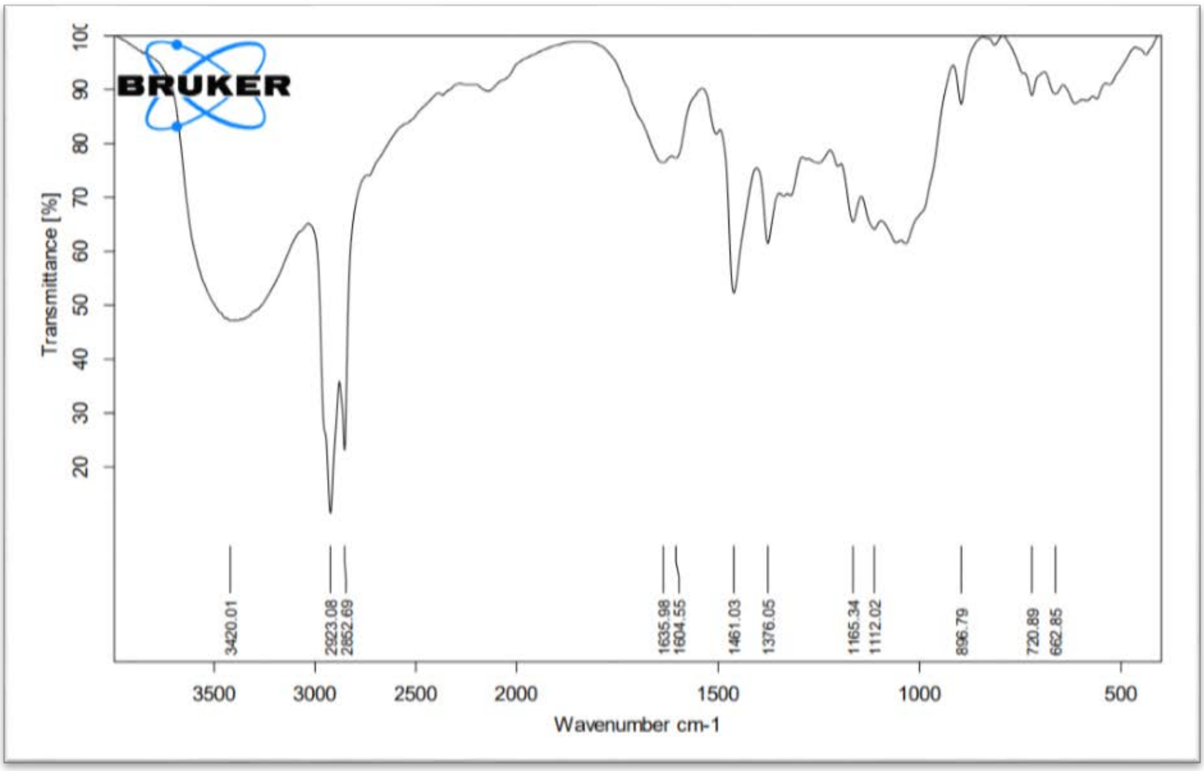
Graph 4.30(c): FTIR spectra of Cyanoethylated fibre sorption in LvCo



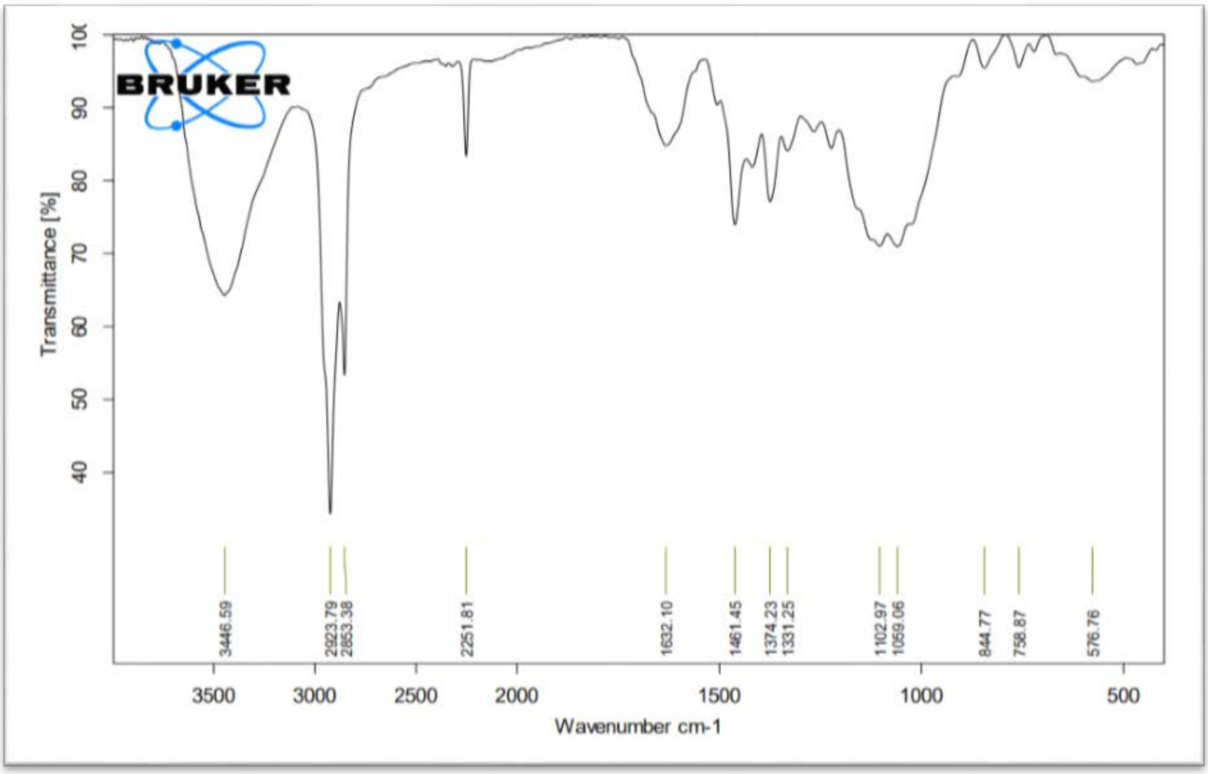
Graph 4.30(d): FTIR spectra of Enzyme treated fibre sorption in LvCo



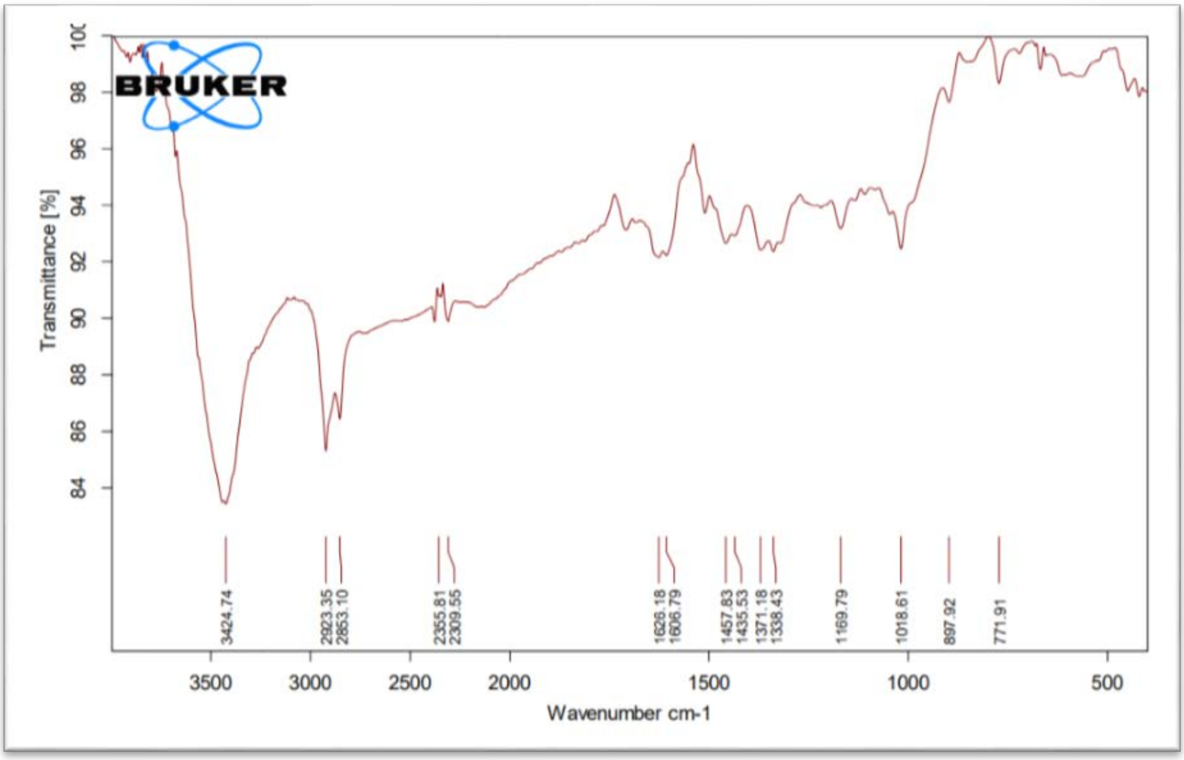
Graph 4.31(a): FTIR spectra of untreated fibre sorption in HvCo



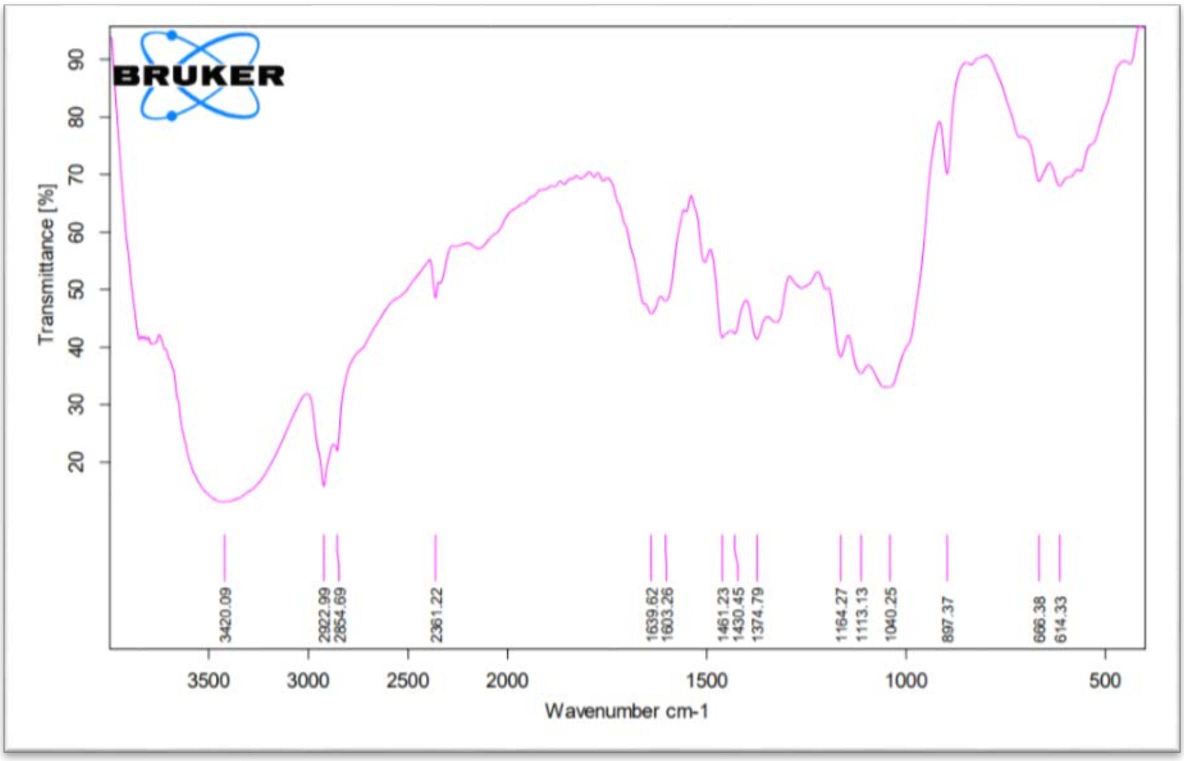
Graph 4.31(b): FTIR spectra of Acetylated fibre sorption in HvCo



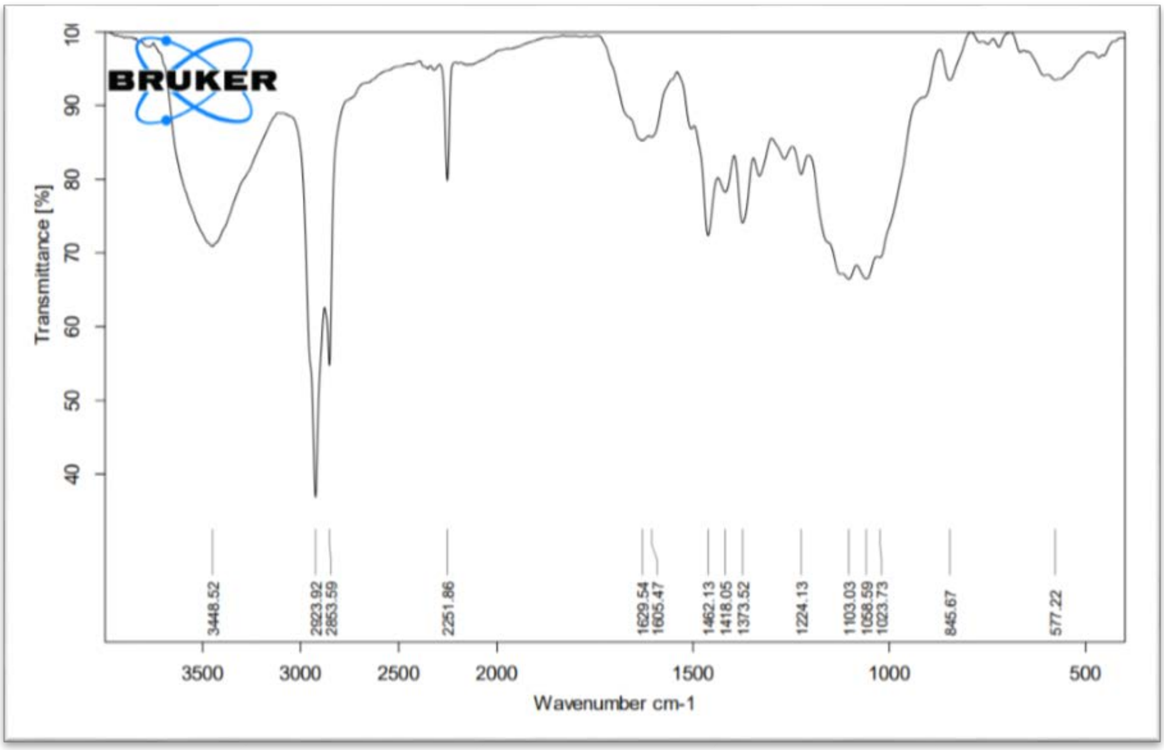
Graph 4.31(c): FTIR spectra of Cyanoethylated fibre sorption in HvCo



Graph 4.31(d): FTIR spectra of Enzyme treated fibre sorption in HvCo



Graph 4.32(a): FTIR spectra of untreated fibre sorption in HvCoW



Graph 4.32(b): FTIR spectra of Cyanoethylated fibre sorption in HvCoW

The FTIR spectra for Sugarcane bagasse fibre untreated and treated, were taken after sorption in different oils viz. Mo, LvCo and HvCo. All the spectra shows the oil typically contains 75-80% aliphatic hydrocarbons and the residual amount of aromatic hydrocarbons. The strong transmittance spectrum of 2924 cm^{-1} indicates the presence of oil in the fibre. The Cyanoethylated fibre FTIR spectra shows a strong transmittance spectrum at 2923 cm^{-1} band which represents more sorption of oil. Due to high viscosity, in HvCo the spectra represent higher sorption of oil (Graph4.31 c). Untreated sugarcane bagasse fibre also shows some amount of sorption in the spectra due to the inherent property of the fibre. The FTIR spectra of enzyme-treated fibres after oil sorption show mid-peak sorption for LvCo (Graph 4.30 d) compared to HvCo (Graph 4.31 d). The Acetylated fibre spectra show a low peak for oil in LvCo (Graph 4.30 b) compared to the high peak for oil sorption present in HvCo (Graph 4.31 b).

From the above results and discussion, It was concluded that Sugarcane bagasse fibres were successfully extracted and modified with two chemical treatments and an enzymatic treatment. The chemical treatment: Acetylation using acetic anhydride in the presence of $HClO_4$ as catalysts and Cyanoethylation using acrylonitrile. The fibres were also modified with Enzymatic treatment using two enzymes viz. cellulose and pectinase. The modification was characterised by the FTIR spectra and SEM analysis. Maximum oil sorption was achieved at around 23.72 g/g for Cyanoethylated fibre using a 5% concentration of NaOH at 55℃ temperature for 60 minutes. Enzymatic treatment resulted in 21.32 g/g oil sorption for Sugarcane bagasse sample with 4% enzyme concentration at 70℃ temperature for 60 minutes. Acetylated treatment resulted in 19.07 g/g oil sorption using 1% perchloric acid at 30℃ temperature for 30 minutes. The recovery of oil from the chemically modified fibre was high compared to untreated fibres. The recovery of oil from Enzyme-treated, Cyanoethylated and Acetylated fibre samples was about 74%, 73% and 69 % respectively.

It was found that the chemically modified samples can also be reused conveniently at least 3 times. In addition to oil sorption, the higher sinking time of chemically modified fibres in water further confirmed the chemical modification. Cyanoethylated, Enzymatic and Acetylated Non-woven from waste Sugarcane bagasse fibre, therefore, can be suitably used for oil spill cleanup applications. The outcome of this study suggested that it is possible to replace fully or partially synthetic oil sorbents with chemically modified Sugarcane bagasse fibre for oil spill cleanup application which comes with other advantages like waste management of waste Sugarcane bagasse and better biodegradability.