Effect of Alkali Treatment on *Saharan aloe vera cactus* Fibre Properties and Optimization of Process by Response Surface Methodology

GOBI NALLATHAMBI AND BHARGAVI RAM THIMMIAH*

Department of Textile Technology, Anna University, Chennai 600 025, Tamil nadu, India

ABSTRACT

The aim of this study is to optimize the process parameters of alkali treated Saharan aloe vera cactus *fibres using of Box-behnken experimental design. The* Saharan aloe vera cactus *fibres were treated with different concentration of NaOH, soaking time and temperature which affect the properties of fibres and plays main role in removal of lignin, hemicellulose, pectin and wax content. The chemical composition of untreated and treated fibres was analyzed by standard methods. XRD result shows the improvement in the crystallinity index of fibres due to alkali treatment. ATR-FTIR analysis shows that hemicellulose and lignin were decreased in all alkali treated fibres. SEM micrographs show the surface roughness in alkali treated fibres. Mechanical properties for the treated and untreated fibres were tested and analysed through single fibre tensile strength tester. TGA proves that thermal stability and decomposition temperature were increased for alkali treated fibres.*

KEYWORDS : *Natural fibre, Crystallinity, Bio-degradable, Amorphous, Chemical composition.*

INTRODUCTION

In recent years much attention has been directed towards the utilization of bio-degradable natural fibre for several applications like waste water treatment, bio medical, food packaging and automobiles[1,2]. Many researchers have focused their interest towards usage of natural fibre due to its unique properties like biodegradability, low cost, free from corrosion and high mechanical properties. The natural cellulosic fibres are consists of both highly ordered polymer molecular chains which forms crystallites and randomly ordered amorphous region[3,4]. The chemical composition

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Correspondence author e-mail: bhargavithimmiah@gmail.com
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of ligno cellulosic material depends on the age, origin and pre-processing step of the plant.

Surface treatment of cellulosic fibre can remove the amorphous lignocellulosic materials from its structure. There are many surface treatments with alkalis like peroxide treatment, bleaching and permanganate treatment. Alkali treatment is most widely used technique to remove amorphous ligno cellulosic contents as well as change in mechanical properties. The alkali treatment of fibre results an increase in the crystalline cellulose content, which leads to improved mechanical strength of the fibre [5].

Several works are reported on natural fibres such as coir [6], kenaf [7], Thespesia lampas[8], hemp [9] and bamboo for physical and chemical properties, and also its applications[10]. According to Muhammad Khusairy et al. [11], chemical treatment can improve the adhesion interface of jute and kenaf fibres due to the increase insurface roughness of fibres. Crystallinity of the fibre was increased due to removal of less ordered amorphous materials and other compositions, and alkali treatment causes rougher surface and increases the voids. Govardhan Goud et al. [12]., studied about the mechanical properties of alkali treated *Roystonea regia* (royal palm) and results showed that alkali treated natural-fibre-reinforced epoxy composites reveals good mechanical strength. Dipa Ray et al. [13]., observed that the mechanical strength of the fibres varies for 5 % NaOH treatment with different treatment timings and they optimized the reaction time based on the mechanical properties of the fibre. S. S. Saravanakumar et al. [14]., investigated physico-chemical properties of *Prosopis juliflora* fibre. They reported that the optimal concentration of 5 % NaOH and soaking time of 60 minutes is enough to achieve better mechanical properties. The alkali treatment of coir fibre shows improvement in tensile strength[15].

Now-a-days there is a surge in industrial demand for natural cellulose fibre and *Saharan aloe vera cactus* fibre (one of the natural fibres which has high cellulosic content). The fibre is extracted from leaves and it belongs to Agavoideae family. The Saharan aloe vera cactus fibre is a longest fibre and highly porous in nature. The strength and cellulose content of the fibre are also high. So, the fibre can be used in many applications such as waste water treatment industry, bio-polymer applications, automobile industries, electronics and composite industries. As of now, applications of such fibre products are in tablemats, cots, window curtains etc. A.N.Balaji[16] reported about the physico-chemical and mechanical properties of raw and alkali treated fibre *Saharan aloe vera cactus*. The fibres are soaked in 5 % of NaOH for a period of 60 minutes. The results were observed as the partially removal of lignocellulosic materials. In alkali treatment, each process parameter influences the physical properties of fibres. Hence, the optimization of alkali treatment required to identify the optimized process parameters to get required fibre properties. Although variety of natural fibre has been treated and analyzed in different NaOH concentration, process time and process temperature,the alkali treatment of Saharan aloe vera cactus fibre has not been reported to date.

So the aim of this research is to treat the *Saharan aloe vera cactus* fibre by alkali with three different process parameters such as concentration of NaOH, treatment time and treatment temperature as independent variables. An experiment was design with three levels as three variables by box-behnken method. The properties of raw and alkali treated *Saharan aloe vera cactus* fibre was characterized by X-ray diffraction (XRD), Attenuated total reflection-Fourier-transform infrared spectroscopy (ATR-FTIR), Thermo gravimetric analysis (TGA), Scanning Electron Microscope (SEM), and tensile strength. The optimized process parameters were identified for better mechanical properties by an optimum alkali treatment condition.

EXPERIMENTAL

Fibre extraction

The *Saharan aloe vera cactus* leaves were collected from in and around Coimbatore. The long spiky leaves were crushed and soaked in distilled water for 1 week. Then, the fibres were separated. Extracted fibres were washed in distilled water to remove adhering pulpy region. The fibres were dried under shadow for one week. The fibres were again dried in sunlight for 1 week to remove excess moisture. The extracted fibres were shown in Fig. 1. Sodium hydroxide (NaOH) pellets were purchased from Sisco research laboratory's Pvt ltd, India with analytical grade.

Analysis of Chemical Composition

Chemical composition of the fibre can be determined by Chesson Datta method [5]. 1 g of fibre (A) was heated in 150 ml of distilled water at temperature of 90-100°C for 1 hour. The fibres were filtered and

Fig. 1. Extracted Saharan aleo vera cactus fibre.

washed in hot water. The fibre was dried in oven until its weight remained constant (B). The dry fibre (B) was mixed with 150 ml of 1 N sulphuric acid and heated at temperature of 90-100°C for 1 hour. The fibre was filtered and washed in hot water and dried (C). Dry fibre (C) was then soaked in10 ml of 72 % H_2SO_4 at room temperature for 4 hours. The residue (C) was added to a mixture of 150 ml of 1 N H_2SO_4 and refluxed at a temperature of 90-100°C for 1 hour. The residue was filtered and washed with distilled water and heated in an oven at 105°C and weighed to constant weight (D). Finally, the filtrate (D) is converted to ashes using heat and weighed (E). The percentage of hemicellulose (H_c), cellulose (S_c), and lignin (L_c) are calculated using the following equation:

$$H_C = \frac{B - C}{A} \times 100 \quad (1)$$

$$S_C = \frac{C - D}{A} \times 100 \quad (2)$$

$$L_C = \frac{D - E}{A} \times 100 \quad (3)$$

Box-Behnken experimental design

Box-behnken design was used to design the experimental plan with three levels and three variables[17]. In this experimental plan concentration of NaOH, treatment time and treatment temperature are selected as independent variables to carry out the alkali treatment process[18,19]. The experimental plan with independent variables was shown in Table 1. The advantage of three factorial experimental design is to being rotatable which means fitted model evaluates the response with equal precision at all points in the factor space that are equidistant from the centre[20]. The polynomial regression equation coefficient shows relationship between proper response and factors affecting the response, which is given in equation (4).

$$Y = B_0 + b_i X_i + b_{ij} X_i^2 + b_{ij} X_i X_i \quad (4)$$

Where b_0, b_i, and b_{ij} are the regression equation coefficients, i and j are the independent variables and Y is the response of the independent variable.

Alkali treatment

The Saharan aloe vera cactus fibres were treated with alkali as per the experimental plan shown in Table 2. Fifteen different experiments were conducted and fibres were characterized.

TABLE 1. Experimental plan for alkali treatment

Independent Variables	Levels of Box behnken		
	-1	0	1
Concentration of NaOH, % (X_1)	5	10	15
Reaction time, h (X_2)	1	2	3
Reaction temperature, °C (X_3)	40	60	80

2. Fibre characterization

The diameter of *Saharan aloe vera cactus* fibres was measured by optical microscope at magnification of 10 X, Labomed LX-300 model. Twenty single fibres were measured and average of diameter of the fibre was calculated. Crystallinity Index (CI) of the treated and untreated *Saharan aloe vera cactus* fibres were or (fibre was) examined by X-ray diffraction studies using Cu-Kα radiation (λ = 1.5405 Å). All the samples were recorded in a 2θ range between 10°and 80° with measuring speed of 1° min^{-1}. The crystallinity index was calculated using equation (*5*).

$$CrI\ (\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (5)$$

The infrared spectra of treated and untreated fibres were analyzed by Bruker alpha diamond crystal

TABLE 2. Box behnken experimental design for three independent variables with observed values.

Exp. Run	Concentration of NaOH, %	Time, h	Temperature, ℃	Tenacity, cN/tex	Crystallinity Index, %
Untreated *Saharan aloe vera cactus* fibre				17.6697	56.01
1	5	1	60	15.3974	62.73
2	5	3	60	26.5869	70.27
3	5	2	40	15.9380	68.78
4	5	2	80	18.3785	65.61
5	10	1	40	23.6161	56.78
6	10	3	40	23.4527	56.60
7	10	1	80	13.269	54.35
8	10	3	80	9.2832	51.16
9	15	1	60	16.8869	51.66
10	15	3	60	7.8087	52.79
11	15	2	40	12.0715	54.80
12	15	2	80	8.6443	51.85
13	10	2	60	20.4619	54.08
14	10	2	60	19.6866	54.20
15	10	2	60	19.7823	54.55

Attenuated Total Reflection (ATR) with a scan region of 4000–500 cm^{-1} at the atmospheric condition.The surface morphology of treated and untreated fibre was determined using Scanning Electron Microscopy (SEM) (HITACH S-3400 N) with a field emission gun operated at 25 kV.Thermal stability of the treated and untreated fibre was characterized by *Thermo gravimetric Analysis* (*TGA*) with type of Q-50 (TA instruments Ins, US). Tensile strength of the treated and untreated fibre was tested as per the ASTM standard (D-3822-01) using Instron. The gauge length was set as 50 mm and the fibre tenacity and elongation were measured.

3. RESULTS AND DISCUSSION

Fibre charac*teristics*

The untreated fibre diameter was measured as 11.68 micron and the alkali treated fibre diameters were measured in the range of 6-7 microns. The alkali treatment removes the amorphous content from the fibres and brings down the diameter approximately 50 % lower than the untreated fibre. The experiments were carried out to determine the chemical composition of fibre by alkali treatment and results have been given in Table 3.The chemical composition of the fibre clearly shows that the proportion of cellulose content has been increased due to the removal of other components. The percentages of chemical composition of each sample may vary based on process parameters. The maximum proportion of amorphous cellulose and other components were removed by 5% NaOH treatment. In the given range, the treatment time

and temperature was maintained as maximum (3h & 80°C) at the NaOH concentration of 10% which results lowest crystallinity value as 51.16%. However, the lowest hydrolysis in lignin and hemicellulose than cellulose was observed at the concentration of 15% NaOH treated fibres [21].

TABLE 3. Chemical composition analysis for untreated and treated *Saharan aloe vera cactus*

Saharan aloe vera cactus fibre	Q- Cellulose, Wt. %	Hemicellulose, Wt. %	Lignin, Wt. %
Untreated	67.52	13.05	10.63
Exp 1	84.86	3.99	1.51
Exp 2	86.81	4.16	1.74
Exp 3	85.41	3.52	1.42
Exp 4	86.02	5.88	0.99
Exp 5	83.09	3.47	1.13
Exp 6	79.27	2.16	2.00
Exp 7	81.49	5.44	2.1
Exp 8	71.75	3.87	1.68
Exp 9	72.94	4.93	4.13
Exp 10	68.91	5.19	9.83
Exp 11	69.22	6.12	9.79
Exp 12	68.88	4.99	9.05
Exp 13	82.36	3.87	1.12
Exp 14	82.71	3.12	1.71
Exp 15	82.98	3.45	1.99

ATR-FTIR Analysis

The FTIR-ATR spectra of untreated and alkali treated Saharan aloe vera cacus fibre are shown in Figure 2. From the ATR-FTIR spectra it was observed that the peaks at 1735 cm^{-1} corresponds to hemi cellulose that are due to stretching vibration of C=O and 1245 cm^{-1} peak appeared due to stretching vibration of acetyl group of lignin in untreated fibres[22]. The finger print region of cellulose also detected at 1433, 1368, 1322, 1159, 1108, 1080, 1024 and 893 cm^{-1}. All treated fibres exhibits broad and strong band at 3328 cm^{-1} due to more -OH groups. The intensity variations found at 3328 cm^{-1} due to reduction of hydrogen bonding in cellulosic hydroxyl groups.The breakdown of ester or ether bond results,increase inintensity at 3328 cm^{-1} which creates free OH-groups in alkali treated fibres[21]. The characteristic peaks of lignin and hemicellulose disappeared while increasing the alkali concentration for the

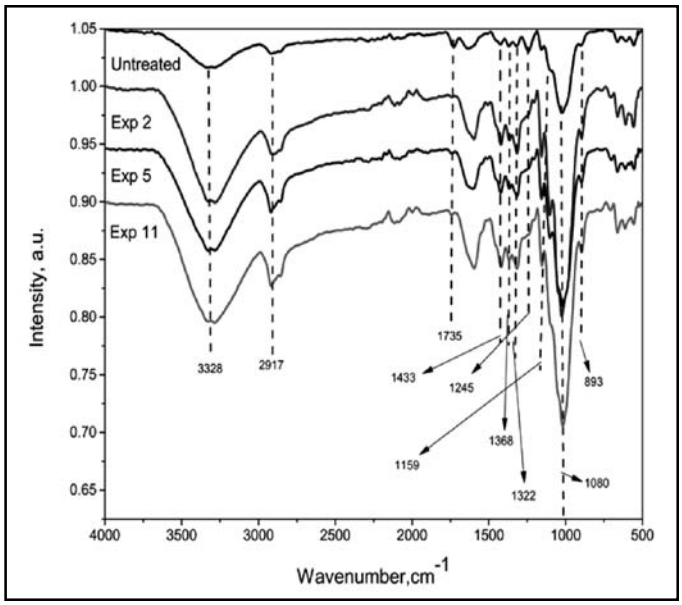

Fig. 2. ATR-FTIR spectra of untreated and alkali treated *Saharan aloe vera cactus* fibre.

treatment of fibres which is supported by Table 3. The intensity of cellulose peaks found to be high due to removal of lignin and hemicellulose materials, which clearly indicates the increase in proportion of cellulose than untreated fibre.

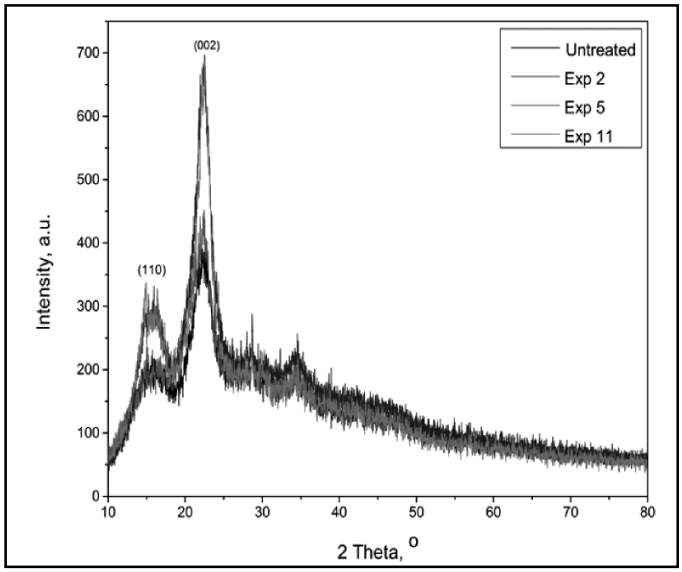

Fig. 3. Shows the XRD patterns of treated and untreated fibre

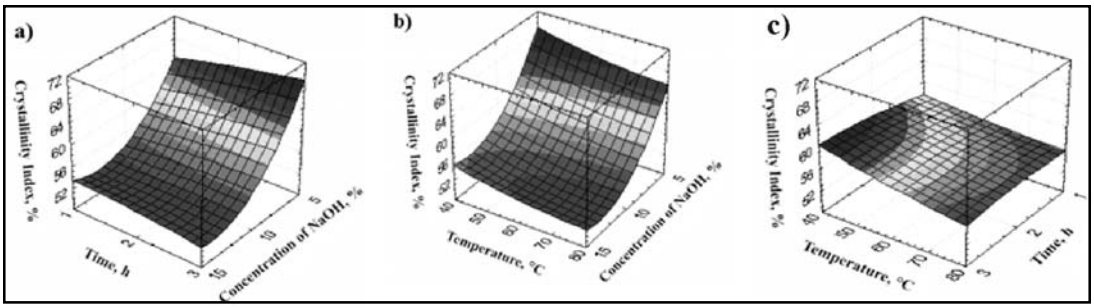

Fig. 4. 4a) Effect of concentration of NaOH and treatment time on Crystallinity Index. 4b) Effect of concentration of NaOH and treatment temperature on Crystallinity Index. 4c) Effect of treatment time and treatment temperature on Crystallinity Index.

The effect of concentration of NaOH, treatment temperature and treatment time on crystallinity index was graphically represented in Fig. 4. The crystallinity index is more at 5 % NaOH and at lower temperature as 40°C. Further increase in concentration of NaOH and treatment temperature reduces the crystallinity indexdue to degradation of the structure of the cellulose and also it weakens the fibre. While comparing the effect of treatment time and temperature, increasing time from 1 to 2 hours slightly increases the crtstallinity index. Increasing the soaking time of fibre from 2 to 3 hours can cause hydrolytic cleavage of cellulose glycosidic bonds which reduces the crystallinity index. The result shows that NaOH concentration of 5 %, treatment time as 2 hours and treatment temperature as 40°C are the optimum process parameters for highest crystallinity index.

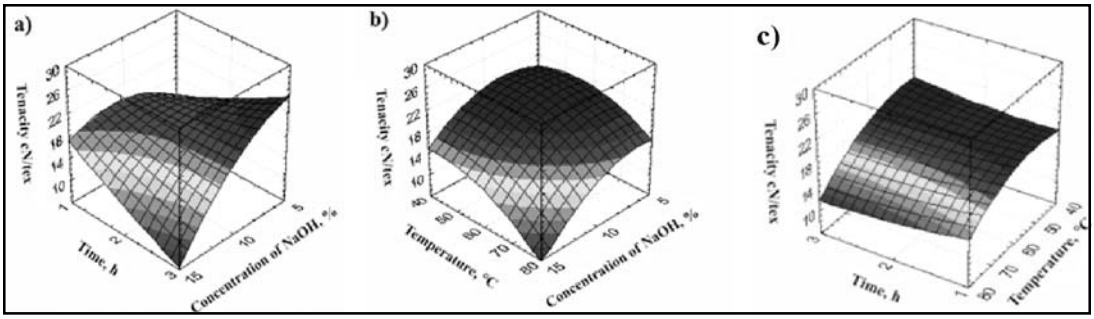

Fig. 5. 5a) Effect of concentration of NaOH and treatment time on tenacity. 5b) Effect of concentration of NaOH and treatment temperature on tenacity. 5c) Effect of treatment time and treatment temperature on tenacity.

The effect of concentration of NaOH, treatment time and treatment temperature on tenacity was shown in Fig. 5. At the time of one hour, with higher concentration of NaOH and lower treatment temperature increases tenacity of fibre as shown in Fig. 5b. On the whole alkali treatment of *Saharan aloe vera cactus* fibre gives higher tenacity due to an increase in crystallinity index by the removal of lignin and hemi cellulose[29]. However, at higher NaOH concentration, treatment time and temperature result in the degradation of cellulose structure which reduces the tenacity of fibres. Regression analysis was carried out for crystallinity index and tenacity [30, 31]. The regression equations are shown in Table 4. Increasing the soaking time of fibre can cause hydrolytic cleavage of cellulose glycosidic bonds.

TABLE 4. Regression equation.

S. No.	Property	Regression equations	'R²' Value	'F' Value
1	Crystallinity Index, %	$54.2767+ (-7.0363X_1) + (0.6625X_2) + (1.7488X_3)-(5.3117X_1X_1) +(-0.2258X_2X_2)-(0.6717X_3X_3)-(-1.6025X_1X_2)-(0.0550\ X_1X_3)-(-0.7525X_2X_3)$.	96.7	16.12
2	Tenacity, cN/tex	$34.4925+(1.64517X_1)+(23.0121X_2)+(0.336938X_3)-(0.0564833X_1X_1)-(3.62958X_2X_2)-(0.00242396X_3X_3)-(0.521X_1X_2)+(0.0065X_1X_3)-(0.066625X_2X_3)$.	83.5	141.41

Thermal Stability

The thermal stability of untreated and alkali treated *Saharan aloe vera cactus* fibre was investigated by TGA analysis. The weight loss of untreated and treated fibre as a function of temperature is shown in Fig. 6. The weight loss

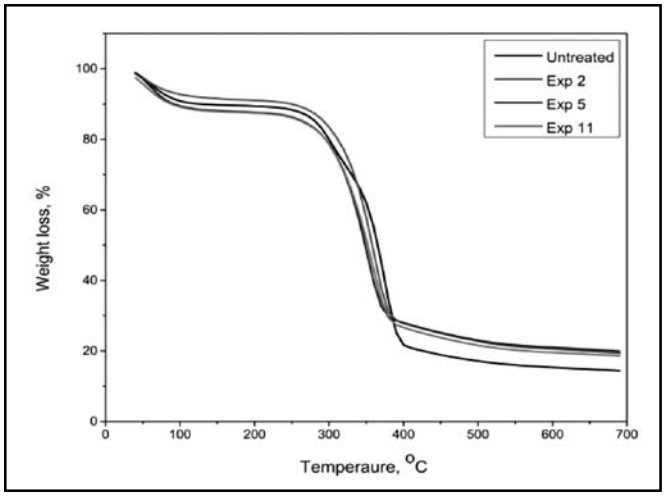

Fig. 6. Thermal analysis of untreated and treated *Saharan aloe vera cactus* fibre.

occurs in three stages[32]. First stage of weight loss occurs between room temperature and 100°C due to evaporation of moisture content. The percentage of weight loss varies from 2.88 % to 12.55 % based on the independent variables of the alkali treatment process. The second stage of degradation process occurs around 250°C due to thermal de-polymerization of hemicellulose and a small amount of lignin with weight loss about 9 % to 18 %[33, 34]. The final major weight loss was observed at 387°C due to degradation of cellulose and the percentage of weight loss about 60 to 70 %. Thermal stability is increased for alkali treated fibre compared tountreated fibres due to removal of hemi cellulose.

Scanning Electron Microscope (SEM)

he surface morphology of untreated and treated fibre is shown in Fig. 7. Fig. 7a shows smoother surface due to waxy substances and also lignin and hemi cellulose contents[35]. Porous and hollow nature of the *Saharan aloe vera cactus* fibre is also observed (Fig. 7b). Fig. 7c exhibits more striations on its surface due to removal of lignin and hemi cellulose by alkali treatment of 5 % NaOH. Fig. 7d shows more striations, split-ups and pores on the surface of fibres due to damage of the structure of the fibre by 15 % NaOH treatment.

4. CONCLUSION

Saharan aloe vera cactus fibre was treated with alkali by varying the concentration of NaOH, treatment time and temperature. The effect of alkali treatment of such *fibre* was analysed for various properties. The chemical composition of alkali treated fibre varies due to the removal of lignin, hemicellulose, pectin and wax content. As a result, the proportion of

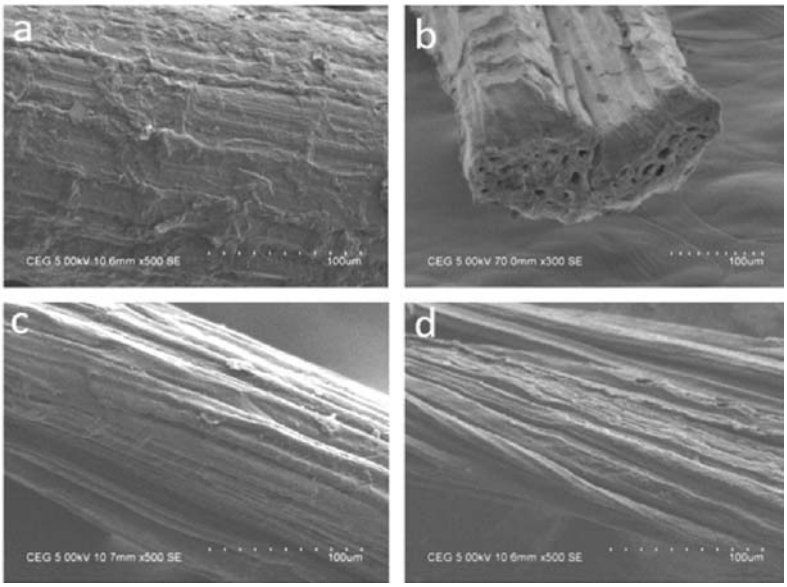

Fig. 7. SEM images of a) untreated fibre, b) cross section of untreated fibre, c) Fibre treated with 5 % concentration of NaOH for 2 hr at 80°C (Exp 4), d) Fibre treated with 15 % concentration of NaOH for 2 hr at 80°C (Exp 12).

crystalline cellulose was increased. X-Ray Diffraction studies reveal that the higher concentration of NaOH, treatment temperature and time reduces the crystallinity index due to hydrolysis of cellulose. The observed tenacity of treated fibre proves that increasing the NaOH concentration, temperature and time leads to degradation of fibre which reduces the tenacity. The removal of amorphous materials was observed as by ATR-FTIR peaks. Thermal stability was increased for alkali treated fibre due to the higher proportion of crystallinity. Based on the findings, the highest hydrolysis of cellulose occurs at process parameters of 15 % NaOH concentration, 3 h and 80°C. It was observed that the treatment of fibres by 5 % NaOH with the treatment time of 3 hours at 60°C gives higher crystallinity index and tenacity.

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