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Surface grafting of *Corchorus olitorius* fibre: A green approach for the development of activated bioadsorbent

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ABSTRACT

The present work is an endeavor to prepare lignocellulosic biomass based adsorbent, suitable for removal of organic and inorganic pollutants from industrial effluents. Lignocellulosic *Corchorus olitorius* fibre (jute fibre) surface was grafted with naturally available polyphenol, tannin, preceded by the epoxy-activation of fibre surface with epichlorohydrin under mild condition in an aqueous suspension. The reaction parameters for the modification, viz., concentration of epichlorohydrin and tannin, time, and temperature were optimized. The successful occurrence of surface modification of jute fibre (JF) was characterized and estimated from weight gain percent, elemental analysis, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction, scanning electron and atomic force microscopy, and thermogravimetric analysis. An extensive analysis of deconvoluted FTIR spectra using the Voigt model was utilized to ensure the surface grafting. The microbiological susceptibility study revealed high persistency of JF towards biodegradation after efficient grafting with tannin.

1. Introduction

Recently, cellulosic and lignocellulosic materials have emerged as one of the most significant biopolymers from natural origin with an annual production of approximately 10^{11} tonnes (Heinze & Lebert, 2001). It is reported that the worldwide fibre production in the last two decades increased to 0.8 million ton. The plant fibres are rich in cellulose, hemicellulose, and lignin. Depending upon their composition and physico-mechanical properties they find potential applications in versatile sectors such as textiles, building construction, packaging, furniture, automotive and agricultural industry. Hence, an increasing worldwide utilization of low-cost, renewable and abundantly available natural materials such as lignocellulosic fibres has lead to an extensive research and exploration of such natural resources and their new applications (Brígida, Calado, Gonçalves, & Coelho, 2010). The characteristic of the fibre surface is of great importance since it regulates various properties, e.g., wettability, adhesion, reactivity, biological response, etc. Despite of numerous excellent properties of lignocellulosic materials, accomplishment of chemical modifications are sometimes needed to vary certain properties such as its hydrophilic or hydrophobic character, elasticity, water absorbency, adsorption or ion-exchange capacity, microbiological and thermal degradability (Dahou, Ghemati, Oudia, & Aliouche, 2010). In this context, a host of literature is available on different chemical treatment strategies, which were applied to fibre surface while keeping the native fibre crystalline structure, to bring preferred changes in their properties. The chemical treatments performed to achieve optimized compatibility and wettability of fibres with hydrophobic polymers for natural fibre reinforced composites include etherification, esterification (acetylation and benzoylation), urethane and siloxanes formations, grafting oligoether chains, peroxidization, maleated coupling agents and isocyanate treatment (Ly et al., 2010). Alkylation, acetylation, chelation, specific finishing with quaternary ammonium salts, and grafting with acrylic acid or acylonitrile or biocide molecule of natural fibres to exhibit better dyeability, mechanical strength and antimicrobial activity have been achieved for a significant commercial requirement (Dahou et al., 2010; Liu et al., 2008). Besides these, now-a-days various cellulosic and lignocellulosic materials are drawing considerable attention of many researchers as inexpensive, abundantly available and reusable adsorbent for removal of inorganic and organic pollutants from industrial effluent and groundwater. Vieira et al. (2010) introduced new functionality on lignocellulosic fibre with anhydrides to achieve better adsorption properties for the removal of metal ions, and Alila and Boufi (2009) grafted cellulose with hydrocarbon structures to improve the sorption properties of fibres towards organic pollutants. However, most of these chemical treatments involve a large amount of hazardous materials. The managing and proper disposal of the generated chemical wastes during treatment increases the process cost. Therefore, the efforts for the chemical modification of the natural fibres to alter its surface property should focus on environment friendlier and greener technologies.

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Considering all these facts, in the present investigation JF was chosen as a basic lignocellulosic material onto which surface functionalization was carried out by tannin, a natural polyphenol, in aqueous medium using epichlorohydrin as a cross-linker. Jute, a lignocellulosic bast fibre, is produced from plants in the genus *Corchorus*, spieces *olitorius*. The jute producing countries includes India (mainly West Bengal), Bangladesh, China, and Myanmar. JF contains a stable matrix of cellulose, hemicellulose and lignin, which consists of various active functional groups such as hydroxyl, carbonyl and ether. It is one of the cheapest natural fibres and is second only to cotton, in terms of usage, global consumption, production, and availability. Till date, JF is mainly used as raw material for packaging textiles and non-textiles, wrapping or backing fabrics, making geotextiles and decorative fabrics, reinforcing composite, etc. Currently, a significant effort is being undertaken to explore the possible utilization of this lignocellulosic fibre for the socio-economic development. On the other hand, tannin, which is also a naturally renewable plant extract, has a renowned antimicrobial activity (Erasto, Bojase-Moleta, & Majinda, 2004). Moreover, tannin contains high content of multiple adjacent phenolic hydroxyls in their molecules, which makes them to have a strong adsorbing ability towards different organic and inorganic pollutants (Huang, Liao, & Shi, 2010). Accordingly, the present investigation was done to graft tannin on JF surface followed by the characterization of morphology, thermal stability and surface constituents of grafted and ungrafted JF.

2. Experimental

2.1. Materials

Analytical grade sodium hydroxide (NaOH) and epichlorohydrin were procured from Merck, India. Commercial grade tannin (wattle extract) was purchased from local market. The tannin content of the wattle extract used in this study was determined to be 57% according to the Prussian blue test (Price & Butler, 1977). JF of TD4 grade were collected from Gloster Jute Mill, Howrah, India. The raw JF was thoroughly washed with deionized water to remove any adhering substances and dust; dried in an oven and then cooled and stored in a desiccator.

2.2. Method

2.2.1. Surface functionalization of JF

The surface functionalization of JF was carried out in three steps. In the first step, the JF was pretreated with alkali solution, which activates the fibre surface for further chemical modification by breaking the intra/intermolecular hydrogen bonds between the hydroxyl groups of fibres (Sinha & Rout, 2008). The JF was mercerized with NaOH solution of 1.0% (w/v) at ambient temperature for 0.5 h. The mercerized fibres were then washed with distilled water until free of alkali.

In the second step, the cellulose on the fibre surface was stimulated by incorporation of active epoxy group onto fibre surface using epichlorohydrin. For this purpose, the pretreated JF (1 g) was further suspended in 0.25% (w/v) NaOH solution followed by sequential addition of epichlorohydrin. The mixture was stirred constantly for 2 h at 60 °C temperature. The reaction mixture was then filtered and washed thoroughly with acetone and deionized water.

In the third step, 1 g of epoxy-activated JF was immersed in tannin solution, the pH was adjusted to be 7 and a catalytic amount (0.5 g/L) of sodium borohydride was added to the suspension. Nitrogen gas was purged through the solution with constant stirring at a specified temperature for a specified time. Further, the treated JF was separated by filtration; extensively washed with acetone and deionized water until no colour was observed in the filtrate. The tannin immobilized JF was subsequently vacuum dried, weighed after cooling, and preserved in a desiccator. Finally, tannin immobilized dark brown coloured JF was obtained.

Optimal conditions for tannin grafting were determined by investigating the effect of epichlorohydrin concentration, tannin concentration, temperature and reaction time on weight gain percent and carbon content of tannin grafted JF. The effect of epichlorohydrin concentration on reaction was studied with different epichlorohydrin concentrations (5–30 mL/L) at 60 °C for 6 h and concentration of tannin (5 g/L) was kept constant. The investigation on the effect of tannin concentration was done by treating epoxy-activated JF by 5–25 g/L of tannin with a constant concentration of epichlorohydrin (5 mL/L) at 60 °C temperature for 6 h. Finally, the reaction temperature and time were varied from 20 °C to 80 °C and 2–8 h, respectively, keeping epichlorohydrin and tannin concentration (5 mL/L and 5 g/L, respectively) as constant.

2.3. Characterization

2.3.1. Weight gain percent and quantitative elemental analysis

The weight gain percent (WGP) of chemically modified JF was calculated as,

$$\mathrm{WGP} = \frac{W_f - W_i}{W_i} \times 100 \tag{1}$$

where W_i is the weight (g) of JF before chemical modification and W_f is the weight (g) of chemically modified JF after washing and drying.

The elemental analysis of the JF samples was performed using CHNS analyzer (Euro EA). Each sample was analysed three times and the average value is reported.

2.3.2. Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopic study was performed for unmodified and modified JF, and crude tannin. Analyses were done in a humidity free atmosphere at room temperature by Thermo Nicolet, Nexus 870 spectrophotometer.

FTIR absorption spectra of large biomacromolecules are generally comprised of complex, broad and overlapping peaks. In such cases, explanation of the bands is difficult due to substantial spectral congestion (Stancik & Brauns, 2008). For the purpose of data analysis, the conventional technique is the direct determination of adsorption intensities and peak areas from FTIR spectra by baseline method, which can obligate error (Chen & Huang, 2001). More accurate data interpretation can be facilitated through curve fitting of FTIR absorption spectra. Hence, the FTIR spectra of JF were analysed by an almost exclusive method with the help of Peakfit software. The data were first fitted with a deemed baseline, Linear (D2), and smoothened using Savitsky–Golay algorithm. The Voigt function was then implemented to model IR adsorption peaks and the areas of the concerned peaks of the rigorously fitted curve were evaluated by deconvolution method.

2.3.3. X-ray diffraction analysis (XRD)

X-ray diffraction data of JF samples were collected from an X-ray diffractometer (RIGAKU ULTIMA III) which was operated at 40 kV and 40 mA, using Cu Kα radiation at a scanning speed of 2°/min. The obtained XRD data were analysed with Pearson model by Peakfit software. Crystallinity index and crystallite size of the cellulose molecules in jute were also calculated (Roy et al., 2012).

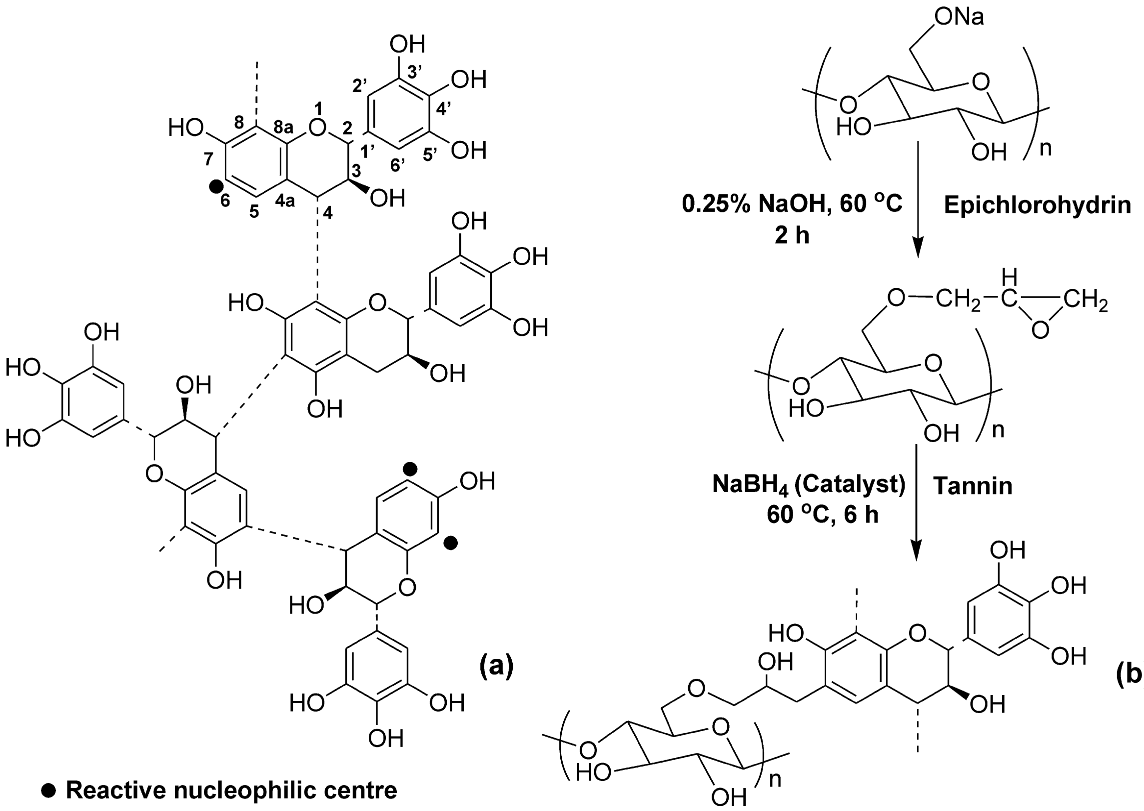

Fig. 1. (a) Branch-chained tetraflavonoid structure of wattle tannin unit and (b) plausible reaction scheme for surface functionalization of jute fibre with tannin.

2.3.4. Solid state ^{13}C cross-polarization magic angle spin nuclear magnetic resonance (CP-MAS NMR) spectroscopy

Solid state ^{13}C-NMR spectra of untreated, pretreated, and treated JF samples were recorded at the magnetic field strength of 7.01 T with cross-polarization magic angle spinning (CP-MAS), on a Bruker AV-300 FT NMR spectrometer. Experimental data were acquired at ambient temperature with 2.5 ms of contact time. The ^{13}C spectra were referenced externally to the chemical shift of methyl group carbons of tetramethylsilane.

2.3.5. Thermal analysis: thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

TGA and DSC of untreated and treated JF were executed using a TG-DTG analyzer (Perkin Elmer Pyris Diamond) and thermal analyzer (DSC200PC) respectively. The TGA and DSC study were done in nitrogen atmosphere with 10 ± 2 mg samples under a flow rate of 100 mL/min at a constant heating rate of 10 °C/min using an alumina crucible with a pinhole.

2.3.6. Scanning electron microscopic (SEM) analysis

The surface morphology of JF samples was investigated to examine the effect of modification upon the fibre surface. Scanning electron micrographs of fibre samples, coated with a thin layer of gold, were taken using SEM (TESCAN Vega$_{\mathrm{LSV}}$).

2.3.7. Atomic force microscopic (AFM) analysis

AFM study of untreated and modified JF were performed using Scanning Probe Microscope (SPM, Multiview-1000$^{\mathrm{TM}}$) in tapping mode to monitor the microstructural changes of fibre surface after chemical treatment. The surface texture parameters (viz., average height, average roughness and root mean square roughness) were determined by SPM image processing software. For AFM measurements the powdered samples were suspended in water and a drop was placed on top of the freshly cleaved mica surface. The water was allowed to evaporate gently overnight under ambient conditions.

2.3.8. Microbiological susceptibility study

The durability of untreated and chemically modified JF was evaluated under microbial exposure by mixed culture method according to IS: 1623 (BIS, 1992) with slight modifications. The specimens were weighed (m_i) and inoculated with a mixed culture of fungi. After 30 and 60 days of incubation the specimens were removed and washed gently. Further, the fibres were dried and weighed (m_f). Microbiological susceptibility of the fibres is reported in terms of weight loss percent (Eq. (2)). Five replicates of experiments were performed.

$$\text{Weight loss}\,(\%) = \frac{m_f - m_i}{m_i} \times 100 \qquad (2)$$

where m_i is the weight (g) of JF before microbial exposure and m_f is the weight (g) of biodegraded JF.

The SEM images of the samples collected after 30 and 60 days of biodegradation were also analysed.

3. Results and discussion

The wattle tannin belongs to the class of condensed tannins which are the polymerized products of flavan-3-ols and/or flavan-3,4-diols and are the polyphenols with molecular weight of 500–3000 Da (Pizzi, 1993). The branch-chained tetraflavonoid structures of wattle tannin have reactive and accessible nucleophilic centers in the 'A' rings (Fig. 1(a)). These centers, particularly the 6th positions on each of the 'A' rings, provide sites for electrophilic aromatic substitution in wattle tannin units (Roux, Ferreira, & Botha, 1980). On the other hand, epichlorohydrin, an electrophile, is capable to react with the —OH groups of cellulose on JF surface as well as can form covalent bond with wattle tannin (Lima

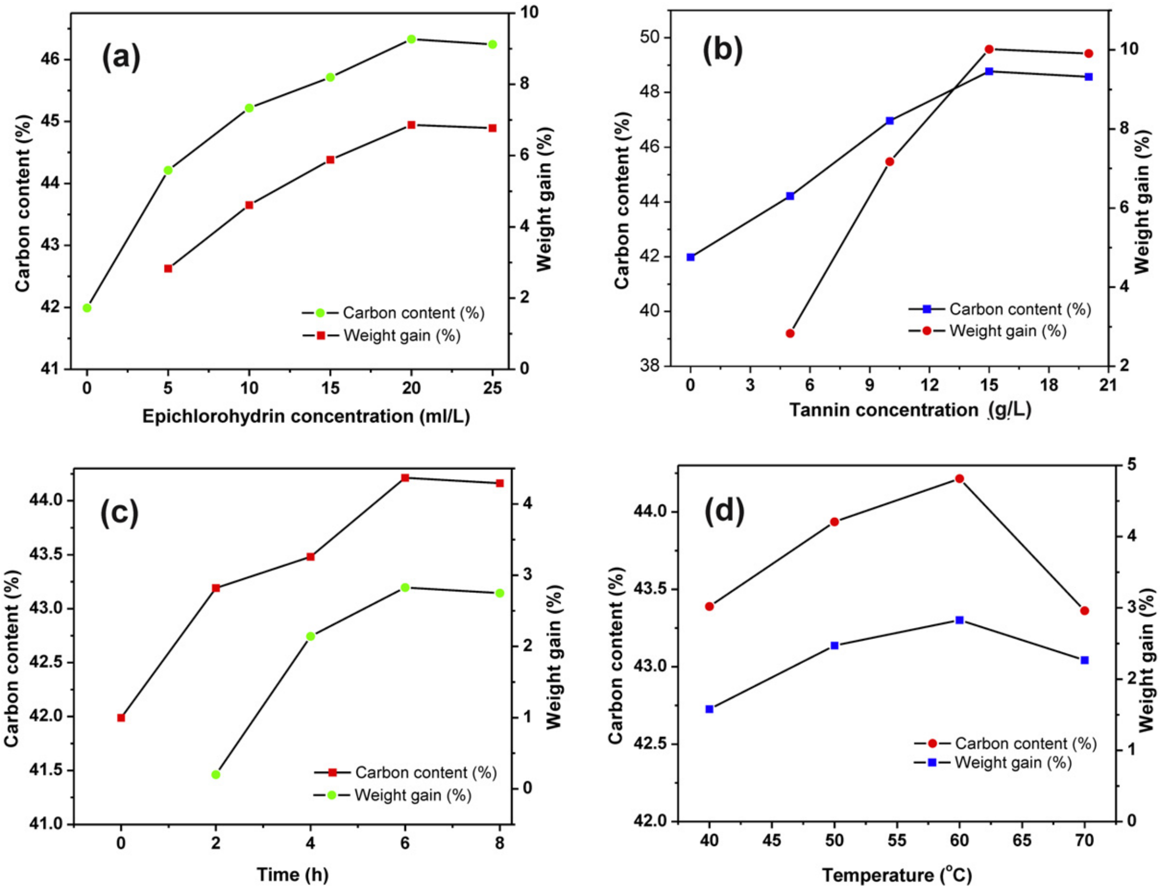

Fig. 2. Effect of (a) epichlorohydrin concentration, (b) tannin concentration, (c) reaction time and (d) temperature on carbon content and weight gain percent of treated jute fibre.

et al., 1998). Thus, tannin immobilized JF can be prepared using epichlorohydrin as a cross-linking agent, as shown in the plausible reaction scheme, Fig. 1(b). The polyfunctional nature of the wattle tannin in terms of uniformly distributed binding sites such as —OH groups in the 'B' ring of each flavonoid unit, allows them to exhibit significant affinity towards various organic and inorganic materials (Huang et al., 2010; Roux et al., 1980). The effective surface modification of JF by tannin, containing polyphenolic functional groups, may endow with the fibres with promising adsorption capacity towards inorganic and organic pollutants and thus provides a suitable alternative adsorbent of potential utility for water purification.

3.1. Weight gain percent and elemental analysis

The carbon content of untreated JF obtained from elemental analysis was 41.98%. To find out the optimum condition for surface grafting of JF with tannin, the effects of epichlorohydrin concentration, tannin concentration, temperature and time on weight gain percent and carbon content were investigated and the consequences of these different reaction parameters on the final surface grafting onto cellulose of JF are discussed below.

3.1.1. Effect of various concentrations of epichlorohydrin

Fig. 2(a) displays the effect of epichlorohydrin concentration on carbon content (wt%) from elemental analysis and weight gain percent of JF after modification by tannin with constant tannin concentration (5 g/L) for 6 h at 60 °C temperature. Both carbon content and weight gain percent of JF enhanced from 44.21% to 46.24% and 2.82% to 6.77%, respectively, as the epichlorohydrin concentration was increased from 5 to 20 mL/L. But further increment in epichlorohydrin concentration did not increase the extent of grafting significantly.

3.1.2. Effect of various concentrations of tannin

The effect of tannin concentration on the surface grafting was studied at constant epichlorohydrin concentration (5 mL/L) for 6 h at a fixed temperature (60 °C) with different tannin concentrations in the range of 5–20 g/L. It was observed that the carbon content and weight gain percent of the grafted JF increased as the concentration of tannin increased and the maximum values (carbon content and weight gain percent were 48.57% and 9.90%, respectively) were obtained at a tannin concentration of 15 g/L. Above 15 g/L of tannin concentration both the carbon content and weight gain of the grafted JF remained almost same (Fig. 2(b)).

3.1.3. Effect of reaction time

The effect of reaction time (2–8 h) on the extent of surface grafting with tannin was studied at a fixed concentration of epichlorohydrin (5 mL/L) and tannin (5 g/L) at 60 °C (Fig. 2(c)). Both carbon content and weight gain of the grafted JF were increased up to 6 h of reaction and remained almost constant when the reaction was further extended for more than 6 h. So, it can be inferred that the reaction equilibrium has been achieved within this period.

3.1.4. Effect of temperature

The effect of temperature on the extent of reaction of tannin with JF is shown in Fig. 2(d), which depicts that at a constant concentration of epichlorohydrin and tannin (5 mL/L and 5 g/L, respectively) and 6 h of reaction time, the carbon content as well as the weight gain percent for tannin treated JF increases with increase in

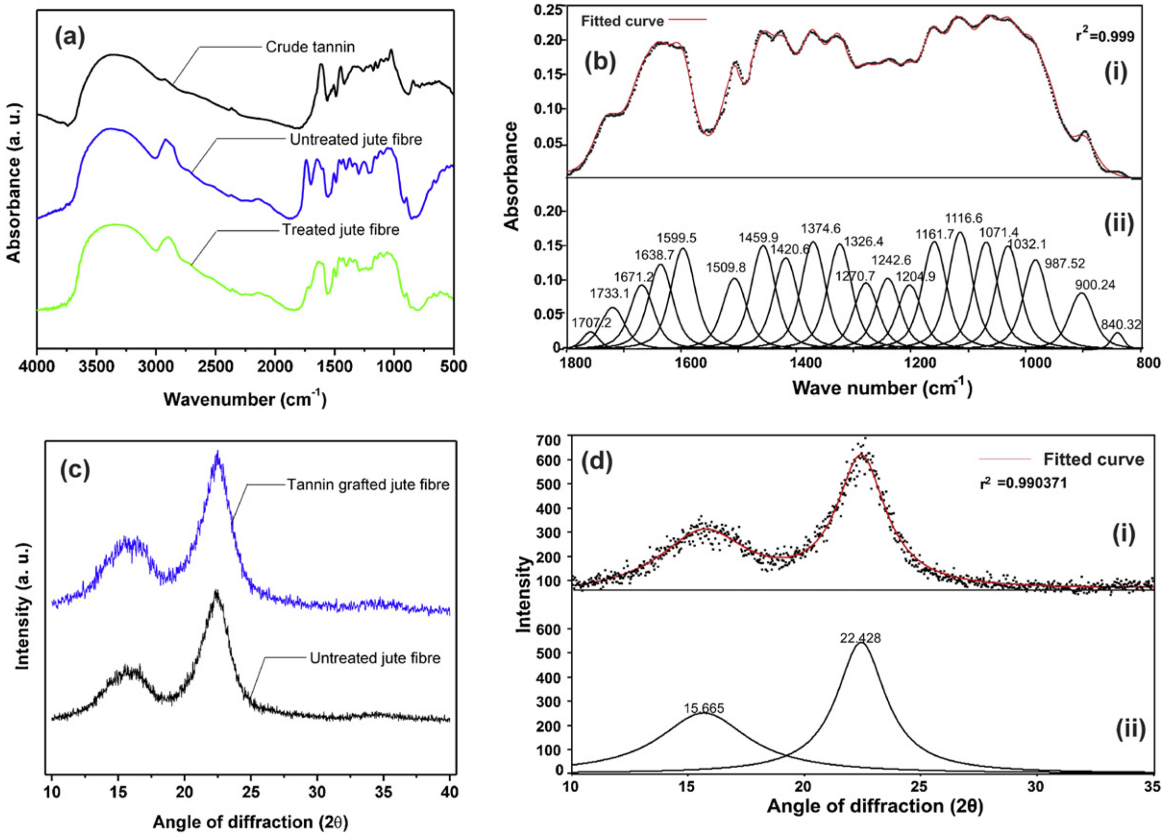

Fig. 3. (a) FTIR spectra of crude Wattle tannin, untreated and tannin grafted jute fibre. (b) (i) Fitting of FTIR absorption spectra of surface modified jute fibre using Voigt function and (ii) corresponding deconvoluted results in the region of 1800–800 cm^{-1}. (c) X-ray diffraction pattern of untreated and tannin grafted jute fibre, and (d) fitting of XRD spectra of surface modified jute fibre using Pearson function.

temperature until it reaches 60 °C. However, as the reaction temperature increased above 60 °C the weight gain percent and carbon content decreased. This may be due to the fact that at higher temperature the epoxy groups get slightly hydrolysed resulting in reduction of extent of surface functionalization of JF with tannin (Liu et al., 2008).

Thus, the maximum extent of functionalization of cellulose in JF with tannin could be achieved by performing the reaction at 60 °C temperature for 6 h with 20 mL/L of epichlorohydrin concentration and 15 g/L of tannin concentration.

3.2. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra recorded for the wattle tannin, untreated and surface functionalized JF are represented in Fig. 3(a). The FTIR spectra of wattle extract showed a broad band in the region of 3600–3010 cm^{-1}, which is due to the characteristic —OH stretching for phenolic or alcoholic group of tannin. The smaller peak at 2927 cm^{-1} is associated with the —CH stretching of the aromatic rings and methylene (—CH_2—) bridges. The peak at 1611 cm^{-1} corresponds to the characteristic elongation of aromatic —C=C— bonds. The deformation vibration of —C—C— bonds in the phenolic group absorbs in the region of 1510–1400 cm^{-1}. The peak at 1454 cm^{-1} may be assigned to —CH_2 bending. The signal at 1345 cm^{-1} is associated with the —OH deformation vibration for phenolic or alcoholic group. The absorption peak at around 1232 cm^{-1} is associated with the —CO stretching of aromatic ring. The antisymmetric —C—O—C— stretching contributes for the peak at 1159 cm^{-1}. The bands in the range of 843–665 cm^{-1} are attributed to the deformation vibrations of the C—H bond in the aromatic rings (Sánchez-Martína, González-Velasco, Beltrán-Heredia, Gragera-Carvajal, & Salguero-Fernández, 2010).

Since the peak at 898 cm^{-1} for β-glucosidic linkage of cellulose in JF is prominent and assumed to be unaffected during chemical treatment, this peak was chosen as internal standard (Rosa et al., 2010). The absorbance areas of the individual bands of the Voigt equation fitted deconvoluted FTIR spectra were normalized with respect to the area of this internal standard peak. The fitting of FTIR absorption spectra of surface modified JF using Voigt model and the corresponding deconvoluted results in the region of 1800–800 cm^{-1} are shown in Fig. 3(b). The possible assignments for different bands of FTIR spectra of JF and corresponding absorbance area ratios (A_ν/A_{898}) are summarized in Table 1a. The characteristic band at 3200–3600 cm^{-1} and 1735 cm^{-1} in the FTIR spectra of JF was attributed to hydrogen bonded —OH stretching and carboxyl and ester group C—O stretching, respectively. The decrement in absorbance area ratio of both of these peaks to that internal standard peak after alkali treatment implies a reduction in inter/intramolecular hydrogen bonding between the hydroxyl groups of cellulose and hemicellulose as well as removal of hemicellulose from JF upon alkali treatment (Roy et al., 2012). After tannin treatment the absorbance peak area ratio for —OH stretching frequency increased. The peak at 2920 cm^{-1} is associated with the —CH stretching in methyl and methylene groups. The increase of intensity ratio of this peak for treated JF might be due to the presence of aromatic —CH/—CH_2— bridging units in tannin which was grafted onto the surface of pretreated JF. The peak area ratio corresponding to aromatic —C=C— stretching at 1600 cm^{-1} is also found to be augmented after tannin grafting from 2.3886 to 3.1345. The partial removal of hemicellulose after pretreatment diminished the area ratio of the peak at 1238 cm^{-1} for C—O stretching

Table 1a
FTIR spectral data and absorbance intensity ratio of untreated, pretreated and tannin modified jute fibres.

Position of bands (cm^{-1})	Possible assignments	Untreated fibre (A_v/A_{898})	Tannin treated fibre (A_v/A_{898})
3350	—OH stretching	19.0699	26.7761
2920	—CH stretching in methyl and methylene	16.7104	20.9759
1735	C—O stretching in carbonyl and unconjugated β-ketone	3.5802	1.4888
1600	Aromatic —C=C— stretching	2.3886	3.1345
1458	—CH_2 bending	1.9942	3.0474
1375	—CH deforming (asymmetric)	2.5744	3.1658
1238	C—O stretching in acetyl group of hemicelluloses/—CO stretching of aromatic ring	2.9845	1.9661
1161	Antisymmetric —C—O—C— stretching	2.8174	3.2415
1031	Aromatic —CH in plane deformation	3.0894	3.5472
840	Aromatic —CH out-of-plane vibration	0.2135	0.6615

of untreated JF. The peak area ratio for asymmetrical —C—O—C— stretching (1161 cm^{-1}) was observed to be enhanced after chemical modification of JF. The absorbance bands at 1452 cm^{-1}, 1374 cm^{-1}, 1035 cm^{-1}, and 840 cm^{-1} of JF are ascribed to —CH_2 bending, —CH asymmetric stretching, aromatic —CH in plane deformation and aromatic —CH out-of-plane vibration, respectively (Ray & Sarkar, 2001). The absorbance area ratios of all of these peaks for asymmetric stretching were found to be increased after immobilization with tannin onto pretreated JF.

3.3. X-ray diffraction analysis (XRD)

The X-ray diffraction patterns of untreated, pretreated, and surface functionalized JF are shown in Fig. 3(c) and (d). The crystallite size and crystallinity index were calculated from the diffractrogram. The removal of amorphous components enhances crystallinity index and crystallite size of JF after alkali treatment from 50.40 to 57.58, but decreases the FWHM of the diffraction peak (Roy et al., 2012). On the other hand, tannin functionalization onto JF decreased both crystallinity index and crystallite size (Table 1b).

3.4. Solid state ^{13}C CPMAS NMR spectroscopy

The solid state ^{13}C CP-MAS NMR spectroscopy was applied for the structural studies of untreated, pretreated and tannin modified JF, and the corresponding spectra are shown in Fig. 4. Since JF is composed of complicated chemical structures of cellulose, hemicellulose and lignin, as main components, the obtained NMR spectra are complicated with many broad signals. In the NMR spectra of raw JFs the most intense peaks that appeared at 61–63 ppm (C6 of cellulose), 70–73 ppm (C2,3,5 of cellulose), 82 ppm (C4 carbon of non-crystalline cellulose), and 86.9 ppm (C4 carbon of crystalline cellulose) confirm the presence of the cellulose units. The sharp and high signal at 103 ppm was the characteristics of the C1 carbon of cellulose. The signals appeared at 19.4 and 170.6 ppm are assigned to the methyl and carboxylic carbons, respectively, in the acetyl groups of hemicellulose, the second major constituent of JF (Fig. 4(a)). The less intense signals of methoxyl and aromatic carbons of lignin in untreated JF resonate at 54.4, 124.4, 126.6, 144.1, and 151.1 ppm. The signals for the carbohydrate of xylans in hemicellulose and the other structural elements of lignin, e.g., CHOH, CH_2OH, and C—O—C groups, remain overlapped by the carbohydrate signals from cellulose and hence, are undistinguishable. After pretreatment of JF with alkali solution no considerable changes were detected in the chemical shifts for the cellulosic carbons. But, the signal at 19.4 ppm for methyl carbon of hemicellulose and some of the signals (124.4, 126.6, 144.1 ppm) for aromatic carbons of lignin were found to be disappeared along with a significant decrement of the signal for the carboxylic carbons in the acetyl groups of hemicellulose (Fig. 4(b)). This implies the partial removal of amorphous hemicellulose and lignin from JF upon pretreatment (Martins, Forato, Mattoso, & Colnago, 2006). However, the most remarkable change after tannin grafting onto pretreated JF surface is the appearance of two signals for aromatic carbons at 142.8 and 146.6 ppm (Fig. 4(c)). On the other hand, it is reported that the ^{13}C NMR of condensed tannins showed signals at 70–90 ppm (C2, C3, and C4), 106–115 ppm (C8, C6, C2′, C5′ and C6′), 150–160 ppm (C5, C7, and C8a), and the typical signals for C3′, C4′ and C5′ around 142–146 ppm (Zhang, Lin, Zhou, Wei, & Chen, 2010). Hence, in Fig. 4(c), the presence of two peaks at 142.8 and 146.6 ppm, may be due to C3′, C4′ and C5′ of tannin unit, strongly supports the successful treatment of JF with tannin. Moreover, in Fig. 4(c), it can also be observed that the peak at 61.6 ppm for C6 of cellulose of untreated and pretreated JF was shifted to 60 ppm by surface functionalization with tannin. This slight upfield shift may be attributed to the participation of the hydroxyl groups at the C6 position of cellulose unit in chemical reaction, which provided clear evidence of surface modification of JF by tannin.

3.5. Thermal analysis: thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

Thermal analysis reflects the reactions that occur at the molecular level of the materials. The TG and DTG curves of the untreated, pretreated and surface functionalized JF are shown in Fig. 5(a). It can be observed from figure that the weight loss profiles of the fibres are characterized by three stages with a prolonged temperature range. The first stage of weight loss provided the broad peak below 100 °C due to the release of structural moisture. In the second step, the decomposition occurred in 229–306 °C temperature range is attributed to the degradation of hemicellulose. Lastly, the major weight loss occurred within the temperature range of 314–383 °C as a consequence of the cellulose combustion process. In the DTG profile of the untreated JF, the shoulder peak due to hemicellulose degradation is observed at about 279.5 °C. The area of

Table 1b
Calculated and observed crystalline parameters from XRD diffractograms of jute fibres.

Jute fibre	Peak position (2θ)	FWHM (2θ)	Area (%)	Intensity (counts/s)	Crystallite size (nm)	CrI (%)
Untreated	15.62	4.23	42.05	232.74	1.88	50.40
	23.36	2.89	57.94	469.23	2.78	
Surface functionalized	15.68	4.48	41.73	247.62	1.79	54.41
	22.43	2.57	58.27	543.20	3.15	

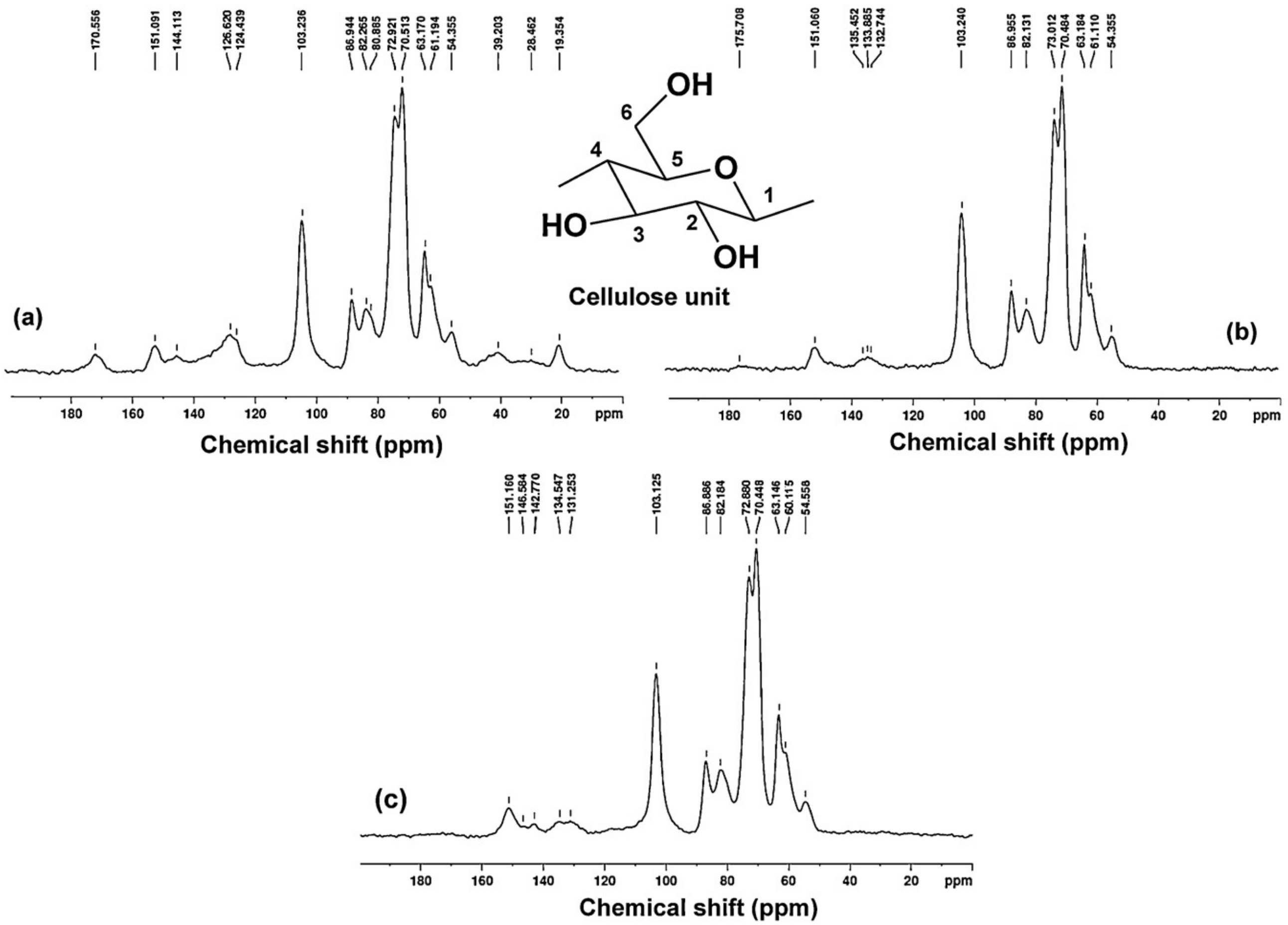

Fig. 4. Solid-state ^{13}C CP-MAS NMR spectra: (a) untreated, (b) pretreated, and (c) tannin modified jute fibre.

hemicellulose degradation peak decreased significantly after pretreatment and chemical modification of JF. The cellulose degradation peak for untreated JF was at 358 °C, which increased slightly for both pretreated and tannin treated JF. The reason for these changes might be the removal of less thermally stable hemicellulose caused by alkali treatment (Sinha & Rout, 2008). The maximum residual char at 600 °C was obtained for tannin treated JF (23.4%), whereas the residual char for untreated JF is 14.9%. This phenomenon strongly supports the surface grafting of tannin onto the JF surface (Serrano, Urruzola, Nemeth, Belafi-Bako, & Labidi, 2011). Thermal degradation profile of the treated fibres is almost same as that of the pretreated fibres. Similar observations were reported by Kabir, Wang, Lau, Cardona, and Aravinthan (2011) for formerly mercerized silane treated hemp fibre.

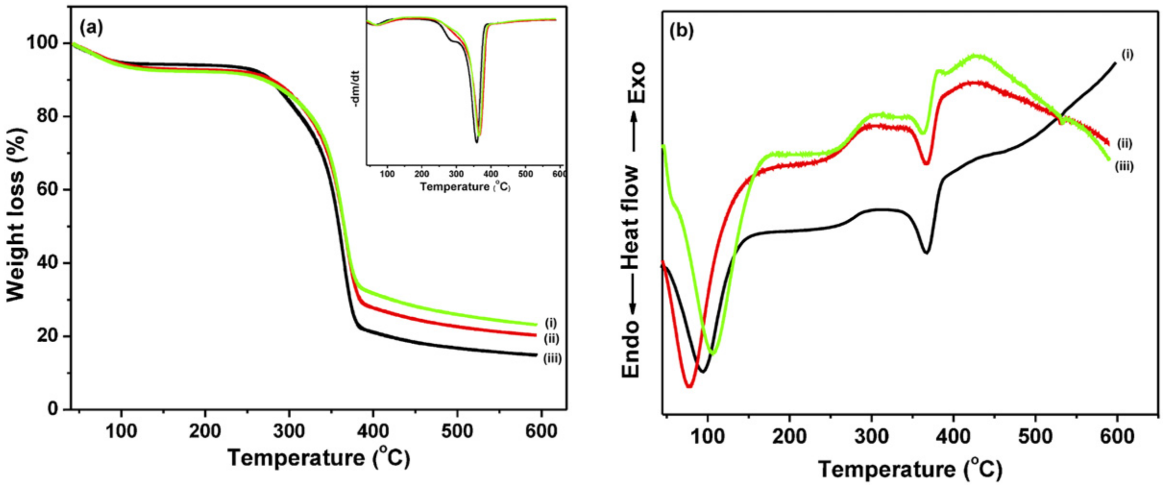

Fig. 5. (a) TG and DTG curves and (b) DSC profiles of the (i) untreated, (ii) pretreated and (iii) surface functionalized jute fibres.

Table 2a
Surface texture parameters of jute fibres from AFM measurements.

Jute fibres	Average roughness (R_a, nm)	Root mean square roughness (R_q, nm)	Average height (H_a, nm)
Untreated	37.2	45.2	119.4
Pretreated	138.5	204.2	514.8
Surface functionalized	142.1	188.4	302.3

Table 2b
Results of DSC analysis of untreated, pretreated and treated jute fibres.

Sample	Peak temperature (°C)	Nature of peak	ΔH (J/g)
Untreated jute fibre	89.8	Endo	131.8
	289	Exo	20.7
	365.3	Endo	32.79
Pretreated jute fibre	72.8	Endo	126.2
	290.3	Exo	16.68
	367.1	Endo	31.68
Tannin treated jute fibre	92.7	Endo	130.1
	292.3	Exo	15.49
	367.1	Endo	20.06
	388.7	Endo	1.62

The DSC curves of the JF are depicted in Fig. 5(b), and the corresponding values of enthalpy change are given in Table 2a. All the JF, viz., untreated, pretreated and chemically treated, in their respective DSC curves exhibited a broad endothermic peak below 100 °C, resulting from structural moisture desorption (Fig. 5(b)). In the DSC curve of the untreated JF, the hemicellulose being the least resistant shows an exothermic peak at 289 °C, while the cellulose being more resistant exhibits an endothermic peak at 365.3 °C (Basak et al., 1993). Both alkali and tannin treated fibres showed the major endothermic peak for cellulose decomposition at 367 °C, the position of which is more than 1.8 °C higher than that of the untreated JF. However, the enthalpy change value for cellulose degradation of chemically treated fibre is smaller than that obtained for the alkali treated fibre though the peak position of both the fibres is almost same (Table 2a). The presence of a new endothermic peak in the DSC plot of tannin treated JF was observed at 388.7 °C. Thus, the reason behind the decrement of peak area for cellulose decomposition and the appearance of the new endothermic peak in the DSC profile of chemically treated JF presumably ascribed to the chemical and morphological changes of JF upon chemical treatment that affects the thermal response of the fibres (Saw, Sarkhel, & Choudhury, 2011).

3.6. Scanning electron microscopic (SEM) analysis

SEM micrographs (Fig. 6(a)–(c)) indicate a significant change in the surface topography of JF after chemical treatment. The surface of raw JF was smooth with multicellular nature, whereas rough surface morphology with fragments and groove like structures was observed due to alkali treatment (Fig. 6(a) and (b)). This phenomenon may be attributed to the leaching of surface impurities, non-cellulosic materials, inorganic substances and waxes (Sinha & Rout, 2008). However, in Fig. 6(c) it can be observed that the surface of tannin treated JF exhibited a lower coarseness as

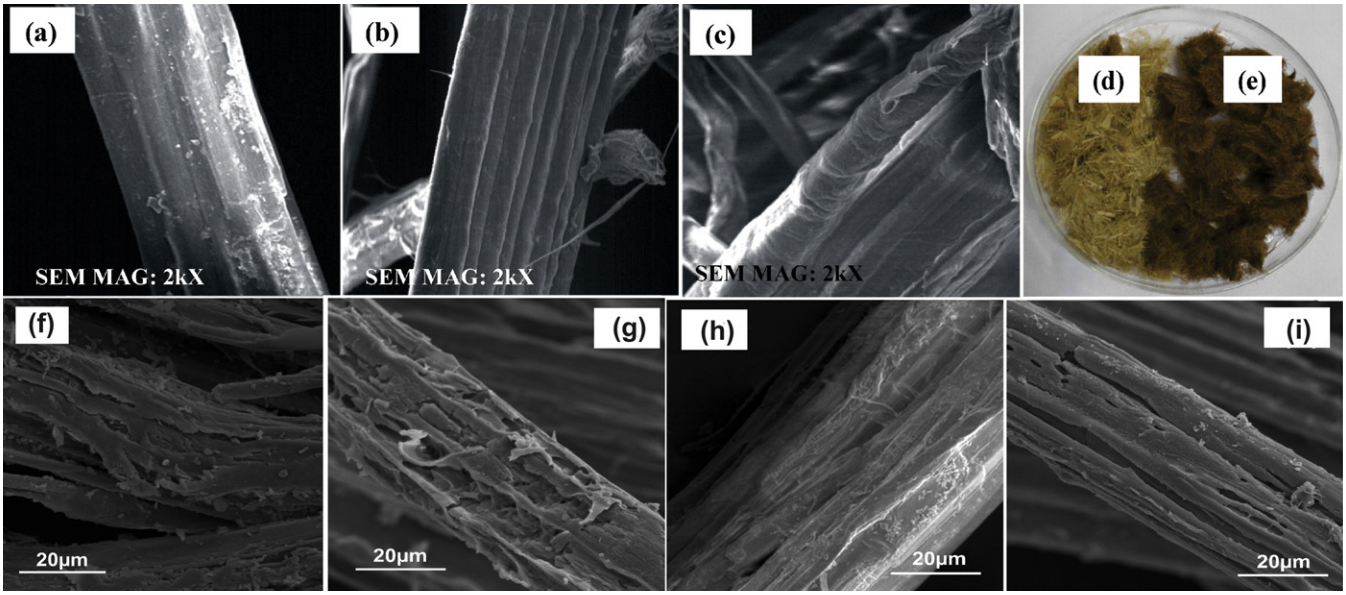

Fig. 6. SEM images of (a) untreated, (b) pretreated and (c) tannin grafted jute fibre; photographs of (d) raw and (e) tannin modified jute fibre. SEM images of untreated jute fibres after (f) 30 days and (g) 60 days of incubation and treated jute fibres after (i) 30 days and (j) 60 days of biodegradation.

compared to the pretreated fibres. This suggests that the tannin was well dispersed onto JF surface. Moreover, it was also observed that the natural golden colour of JF had become dark brown after tannin immobilization upon JF (Fig. 6(d) and (e)).

3.7. Atomic force microscopic (AFM) analysis

The surface texture parameters obtained from the AFM analysis of JF are summarized in Table 2b. The AFM phase image of the untreated JF exhibited an irregular phase with a fine corrugation. The layer of pectin and waxy materials on the surface of untreated JF provides the minimum average surface roughness value of 37.2 nm, compared to the pretreated and chemically modified fibre (Choi, Han, & Lee, 2008). An appreciable increment in surface roughness value of the JF, observed after pretreatment with alkali, was due to the removal of amorphous materials from outer surfaces. Whereas, the tannin treated JF exhibited a decreased root mean square surface roughness value (188 nm) than that of the pretreated fibre, which indicates the successful surface modification of the JF with tannin (Saw et al., 2011). The observations obtained from AFM image analysis supports the results of SEM study.

3.8. Microbiological susceptibility study

The biodegradation study of the JF revealed that the untreated fibre is more prone to microbial attack than that of the treated one. Although the treated JF reached 13.8% and 38.3% degradation after 30 and 60 days of biodegradation with microbes respectively, the weight loss for untreated JF was found to be 23.6% and 50.1% within the same period. The reason for increased resistance of treated JF towards the action of microbes is attributed to the protective ability of polyphenolic tannin, which interferes the extracellular enzymes of micro-organisms resulting disintegration of microbial colonies (Erasto et al., 2004).

Fig. 6(f)–(i) portrays the SEM images of the untreated and treated JF after 30 and 60 days of incubation. These SEM results were also consistent with the biodegradation weight loss data. After 60 days of exposure to microbes, the untreated JF showed a significant biodegradation as evident by the appearance of its severely eroded surface; whereas a minor surface erosion was observed for treated JF compared to the untreated one over the same time period (Fig. 6(f)–(i)).

4. Conclusion

This work represents a feasible and a greener approach for successful grafting of tannin onto JF in aqueous medium, previously activated with epichlorohydrin. The extent of grafting was dependent on epichlorohydrin and tannin concentrations, time, and reaction temperature. The reaction parameters were optimized as the epichlorohydrin concentration of 20 mL/L, the tannin concentration of 15 g/L, the time of 6 h, and the temperature of 60 °C. The surface functionalization of JF with tannin was feasible as evidenced by weight gain percent, elemental analysis, FTIR, XRD, NMR, SEM, AFM, TGA, and DSC study. The microbiological susceptibility study showed that the efficient grafting of tannin made the JF more resistant towards biodegradation. This newly developed approach for surface immobilization of JF with tannin via epichlorohydrin activation, may be considered as a novel, environment friendly, greener technology in the field of research in regard to the (1) utilization of abundantly available, inexpensive, and renewable raw materials such as lignocellulosic JF and tannin, (2) use of water as solvent rather than other toxic organic substances, (3) no generation of hazardous chemical byproducts that must be handled and disposed of appropriately, (4) accomplishment of reaction at 60 °C makes the production cost economized. Moreover, JF being a potential agricultural product, the utilization of jute as adsorbent will promote jute farming industries. Currently, our research group is engaged in exploring the adsorption capacity of these newly developed surface grafted JF with polyphenolic tannin towards inorganic and organic pollutants and thus providing a suitable alternative adsorbent of potential utility for water purification.

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