

Experimental Study on the Water Absorption and Surface Characteristics of Alkali Treated Pineapple Leaf Fibre and Coconut Husk Fibre

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Abstract

Environment sustainability, depletion of raw materials, high consumption of energy during the stage of material processing, and high cost of raw & semi-finished materials are the major problems facing by industries in present days. To get rid of all these problems, scientists have focussed their attention towards the employment of agricultural residue, and plant waste fibres. The significant factor which affects the effective utilization of natural fibres in composite is interfacial adhesion between fibre and matrix polymer. Due to the presence of hydroxyl and polar groups in various constituents of cellulosic fibres, the moisture sorption is quite high which leads to dimensional instability, poor stress transfer from matrix to resin, and fibre pull out at low load conditions. Therefore, it becomes necessary to reduce hydrophilicity of natural fibres by appropriate chemical treatment which results the high strength, fracture resistant bio-composite material. In this work, experimental investigation was done to understand the water up-take behaviour of pineapple leaf fibre and coconut husk fibre. The influence of alkali treatment (NaOH) on the surface chemistry and water sorption *i.e.* swelling behaviour of natural fibres has been carried out. Surface characterization of fibres (PALF and COIR) has done by using FTIR and SEM. The results indicate that the alkali treated fibres are more roughen with regularly placed pin holes than untreated fibre due to the removal of hemicellulose, binder lignin, and waxy substances. Changes in the peaks at 1745, 1525, and 1250 cm^{-1} in FTIR spectra also confirmed the partial removal of hemicellulose and lignin. The water absorption study on alkali treated PALF and COIR shown that the alkali treated fibres absorbs more water than raw fibres. The 4% NaOH treated COIR and 8% NaOH treated PALF absorbs (5-8%) and (9-15%) more water than untreated fibres respectively.

Keywords: Pineapple leaf fibres (PALF); Coconut husk fibres (COIR); Alkali treatment; Hydrophilic nature; Water absorption; Surface morphology.

INTRODUCTION

Increasing concern about environment, depletion of petroleum reserves, high energy consumption, global warming, and high cost of raw materials etc. gives the acceleration towards lignocellulosic materials. Lignocellulosic materials include agricultural residue, grasses, wood, water plants, and plant

waste fibres such as banana, sisal, jute, hemp, coir, pineapple leaf fibre, kenaf, flax etc. The current major applications of natural fibres are in automobile, packaging, building and construction, railway coach interiors, storage devices, and partition wall cabinets etc. are due to their wide varieties of advantageous properties like light weight (low density), cheaper source, good specific strength and modulus, biodegradability, high degree of flexibility, non-carcinogenic, and absence of health hazards. Moreover, the abundant and easy availability of huge and wide range of natural fibres is the main cause to select as a raw material in industries. It has been found that scientists and technologists are doing lot of efforts to utilize natural fibres in value added applications. In modern days, natural fibres and agricultural biomass are highly used as reinforcement filler in composite material. This was because of good electrical resistance, acoustic and thermal insulating properties, and high resistance to fracture.

Among all the natural fibre materials, pineapple leaf fibre (PALF) and coconut husk fibre (COIR) seems to be an outstanding material because they are abundantly available in Asia, inexpensive, and eco-friendly in nature. Pineapple leaf fibre and coconut husk fibre are waste material in agriculture sector, which has potential to replace synthetic fibres. PALF can obtain from leaves of pineapple fruit and COIR from the husk of Coconut fruit. The chemical composition of PALF and COIR is mentioned in Table 1.

Table 1. Chemical composition of pineapple leaf fiber and coir fiber [1]

Sr. No	Fiber	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Pectin (%)
1	PALF	70-82	18.8	5-12.7	1.1
2	COIR	32-43	0.15-0.25	40-45	3-4

PALF is highly accepted for making of biocomposite material because of its high tensile strength and modulus, high creep resistance, good strength by weight ratio, and good flexural properties. In spite of large profitable properties, PALF and COIR have poor resistance to moisture, low thermal stability, and poor dimensional stability. For effective utilization of these fibres in composite material, it is highly required to

reduce hydrophilicity, and increase thermal stability of natural fibres by chemical treatment. Frederick *et al.* (2004) reported that COIR fibre is more durable than other natural fibres. This was due to the presence of high lignin content in COIR fibre [2]. Lignin has the least water sorption property as compared to other natural fibre components. The hydrophilic nature of natural fibres can have undesirable effect on the effective stress transfer from matrix to the fibre (Srinivasa *et al.* 2011) [3]. Therefore, to make a high performance biocomposite material, it is necessary to modify the surface of natural fibres by chemical treatments i.e. alkali treatment, acetylation, methylation, permanganate treatment, cyanoethylation, and grafting of acrylonitrile monomer onto dewaxed PALF [4]. Among the methods, mercerization or alkaline treatment is a cost effective, mostly used surface modification technique in order to improve fibre-resin interfacial bonding [5]. Surface impurities and fibre components such as pectin, waxy substance, lignin, and hemicellulose are partially removed after alkaline treatment which results the better interfacial adhesion between fibre and resin. Currently, there is no work on the water uptake behaviour of pineapple leaf fibre and coconut husk fibre. Therefore in this study, an experimental investigation was done to understand, estimate, and compare the water absorption of untreated and alkali treated PALF and COIR. Moreover, the effect of alkali treatment on surface chemistry of PALF and COIR was studied by FTIR and SEM analysis.

MATERIALS AND METHODS

Materials

Two different types of lignocellulosic fibres were used in this study, viz., coconut (*Coco- nucifera*) husk fibre (COIR), and pineapple (*Ananas comosus*) leaf fibre (PALF). Pineapple leaf fibre (PALF) and coconut husk fibre (COIR) were obtained from Go Green Products, Chennai, India. The average density of COIR and PALF was equal to 1.32 g/cm³ and 0.98 g/cm³ respectively. The moisture content in coir and pineapple leaf fibre ranged from 7-8% and 10-11% respectively. Sodium hydroxide (NaOH) used for alkaline treatment was of laboratory reagent (LR) grade and obtained from local supplier.

Alkali treatment of fibres

Pineapple leaf fibre and coir fibre were soaked in various concentrations (2%, 4%, 6%, 8%, and 10%) of alkaline (NaOH) solutions for 24 hrs at 25 °C, followed by washing with deionized water (until the pH was reached 7), and drying in oven at 60 °C for 24 hrs (until the constant weight was maintained). The untreated PALF and COIR fibres were also washed in deionized water and dried at 60 °C for 24 hrs.

Fourier-Transform Infrared Spectroscopy (FTIR)

Fourier-transform infrared spectroscopy, model Perkin Elmer 2000 was used to analyze the surface chemical composition of untreated and treated pineapple leaf fibre and coir fibre. FTIR spectra were analyzed with an infrared spectrophotometer in the range 4000 cm⁻¹ to 400 cm⁻¹. FTIR of both untreated and alkali treated COIR and PALF had done in Analytical Instrumentation Laboratory, CSIR-CSIO Chandigarh, India.

Morphological study

Scanning electron microscopic (SEM) images of untreated and alkali treated pineapple leaf fibre and coconut husk fibre were obtained by using a scanning electron microscope (FE-SEM, Hitachi 4300) at the accelerating voltage of 10 kV in Analytical Instrumentation Laboratory, CSIR-CSIO Chandigarh, India.

Water absorption measurement

Water absorption measurement on untreated and alkali-treated PALF and COIR fibre was done in various water samples such as distilled water, river water, and hand-pump water. The pH of water samples were distilled water: 7.0, river water: 7.67, hand-pump water: 7.42. The samples were prepared from bundle of individual fibers (5g) bound together and kept inside the beaker containing various source of water at room temperature (25 °C). The weight of the fibers was measured after every 12 hrs and the moisture content was calculated by weight difference,

$$MC = \frac{m_a - m_d}{m_a} \times 100$$

Where MC is the moisture content, m_a is the mass of the sample after exposure to moisture, and m_d is the mass of the dry sample.

RESULTS AND DISCUSSION

Fourier-Transform Infrared Spectroscopy (FTIR)

Figs. 1 and 2 shows the FTIR spectra of untreated and alkali treated coir fibers and pineapple leaf fibers respectively. It is clearly evident that surface chemistry of COIR and PALF was changed after alkaline treatment. The increase in intensity around 3300 cm⁻¹ and 1000 cm⁻¹ corresponds to the higher accessibility of -OH functional group after alkaline treatment. This was due to the removal of waxy and gummy substance. The increase in peak intensity at around 1600-1650 cm⁻¹ and 1250 cm⁻¹ after alkaline treatment also confirmed the removal of wax, adhesives, pectin, and gummy substance from the fiber surface. The absorption peak at 1745 cm⁻¹ is related with

C=O stretch observed in raw fibers (PALF and COIR) but disappears after NaOH treatment. This was attributed to the removal of hemicellulose.

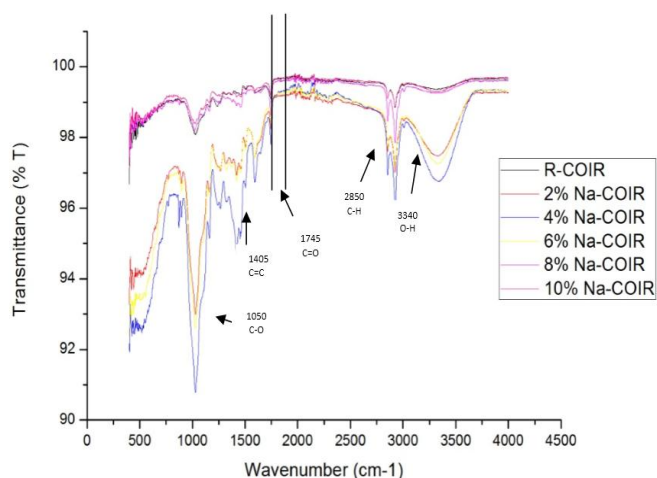


Figure 1. IR spectra of untreated and alkali treated coir fiber

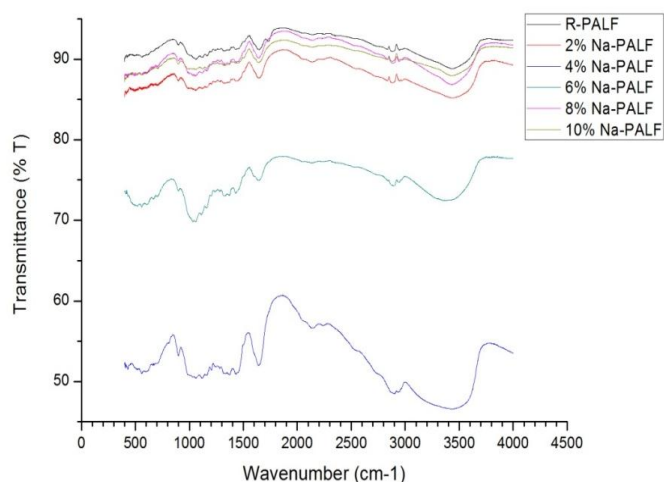


Figure 2. IR spectra of untreated and alkali treated pineapple leaf fiber

The IR spectra for raw pineapple and coconut husk fibers are shown in Fig. 3. It was observed that pineapple leaf fibers consist large amount of hydroxyl (-OH) group than COIR fibers. The broad peak in the region 3200-3500 cm^{-1} attributed to the vibration of -OH group. This O-H group provide active sites for fiber-matrix adhesion. The peak at 1244 cm^{-1} is much smaller in PALF than COIR. This peak corresponds to C=O stretch of the acetyl group of lignin.

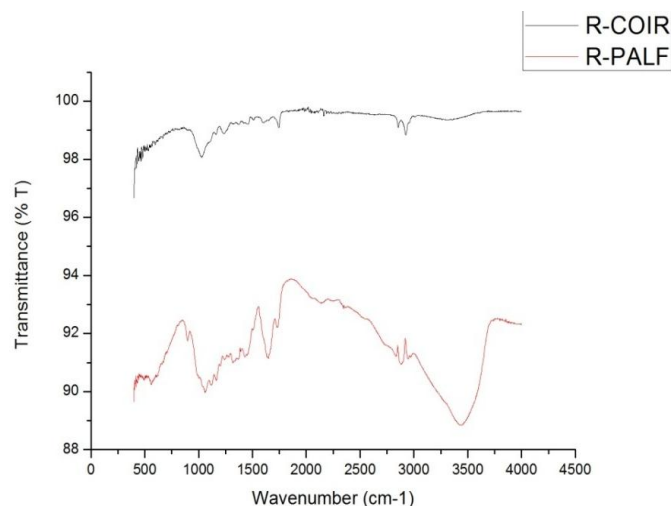
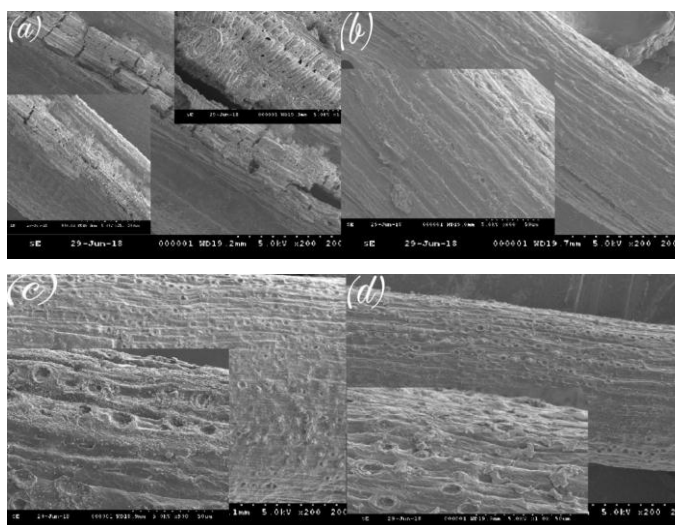


Figure 3. IR spectra of coir fiber and pineapple leaf fiber

Fibre Surface Morphology; SEM Analysis

Surface morphology of COIR fibres (untreated and alkali treated) was shown in Fig. 4 (a)-(f). The untreated COIR fibre display “rotten-wood” like appearance in which many holes, and cavities are present. The SEM micrograph shown in left bottom of Fig. 4 (a), shows network like structure that contains longitudinally oriented unit cells held together by binder lignin and fatty-waxy substances. Fig.4 (b) clearly shows that the surface topography of 2% NaOH treated COIR fibre is much smoother than untreated (raw) COIR fibre. It seems that the fibre surface being roughen again with regularly placed pin holes upon modification by high concentrated alkali solution [Fig. 4 (c)-(f)]. This might be due to the partial removal of wax, surface impurities, and fatty deposits. Similar results have also been reported by Bismarck *et al.* (2001) [6], Prasad *et al.* (1983) [7], Mwaikambo *et al.* (2002) [8].



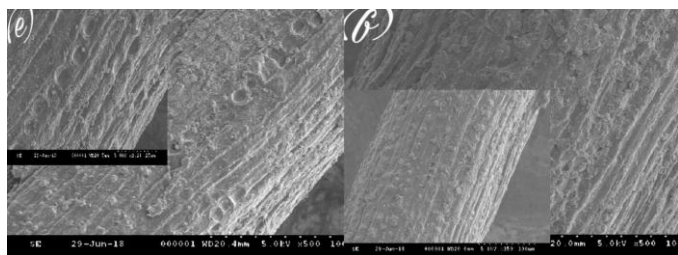


Figure 4. (a) Untreated COIR fibre, plane view (X200), and magnified plane view (X1200). (b) 2% NaOH treated COIR fibre, plane view (X200), and magnified plane view (X400). (c) 4% NaOH treated COIR fibre, plane view (X200), and magnified plane view (X900). (d) 6% NaOH treated COIR fibre, plane view (X200), and magnified plane view (X1000). (e) 8% NaOH treated COIR fibre, plane view (X500), and magnified plane view (X1200). (f) 10% NaOH treated COIR fibre, plane view (X350), and magnified plane view (X500).

Comparing the morphology of COIR fibres with PALF fibres [Fig. 5 (a)-(e)] revealed that pineapple leaf fibres are much smoother and continuous than coir fibres. As compared to COIR fibres, surface morphology of PALF shows no pinholes. Again, we can observe from Fig. 5 that the alkali treated PALF has higher degree of roughness due to the partial removal of hemicellulose and binder lignin. Previous works [Ramadevi *et al.* (2012), Sgriccia *et al.* (2008)] have also reported the similar effect [9-10]. Fig. 5 (c)-(f) clearly shows that defibrillation increased and cracks were developed in pineapple leaf fibers after alkaline treatment. This was also because of partial removal of hemicellulose and lignin.

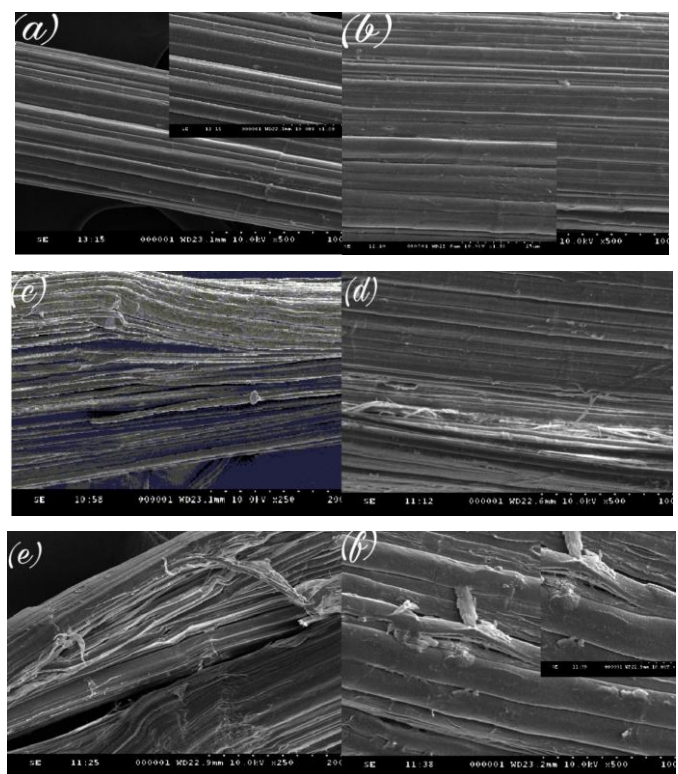


Figure 5. (a) Untreated PALF fibre, plane view (X500), and magnified view (X1000). (b) 2% NaOH treated PALF fibre, plane view (X500), and magnified plane view (X1300). (c) 4% NaOH treated PALF fibre, plane view (X500), and magnified plane view (X1300). (d) 6% NaOH treated PALF fibre, plane view (X500), and magnified plane view (X1300). (e) 8% NaOH treated PALF fibre, plane view (X500), and magnified plane view (X1300). (f) 10% NaOH treated PALF fibre, plane view (X500), and magnified plane view (X1300).

NaOH treated PALF fibre, plane view (X250). (d) 6% NaOH treated PALF fibre, plane view (X500). (e) 8% NaOH treated PALF fibre, plane view (X250). (f) 10% NaOH treated PALF fibre, plane view (X500), and magnified plane view (X1000).

Water Absorption Measurement

The main barrier against the selection of lignocellulosic materials in engineering applications is its moisture sorption ability. The moisture absorption by cellulosic fibres leads to swelling of material, dimensional change, reduction in rigidity of cell wall, and poor strength & stiffness. In moisture sorption process; hemicellulose, non crystalline cellulose, lignin, and surface morphology of fibre plays an important role. To make first choice of lignocellulosic materials, it is greatly required to understand, estimate, and overcome the water uptake behaviour of natural fibres. To measure the water absorption of COIR and PALF fibres, the bundle of fibres were immersed in a container containing various source of water (River water, Distilled water, and Hand-Pump water). After every 12 hours, the fibres were taken out and mopped the excess water on the fibre surface before weighing. For better estimation and comparison of the water absorption of untreated and alkali treated PALF and COIR fibre, it is very important to prepare fibre bundles in the same manner. Four replicates were tested and their mean was presented as a result. The observations on the water absorption of untreated COIR and PALF fibres showed that PALF absorb more water (7.8%) than COIR fibre in distilled water (Fig. 6). It was due to the lower O/C ratio in COIR fibre than PALF fibre.

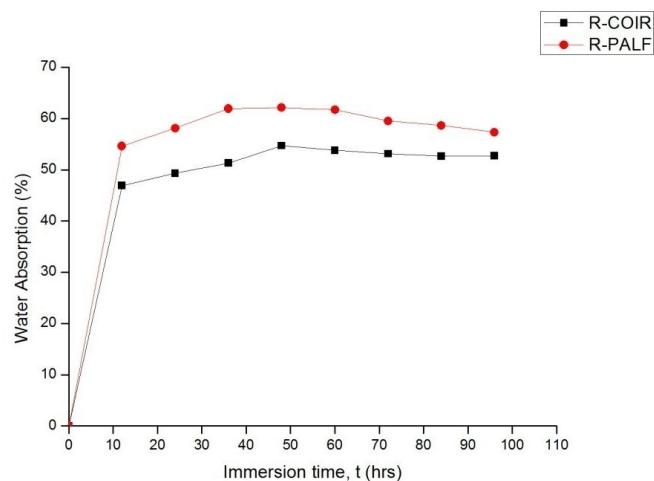


Figure 6. Comparison of water absorption by COIR and PALF fibre in distilled water.

Bessadok *et al.* (2007) reported that, when water concentration exceeds threshold limit, a significant swelling of natural fibers takes place. This was due to the linkage of water molecules to the network of polymer via hydrogen bonds [11]. The untreated COIR fibre absorbs more water in river water (60.6%) than distilled water (54.68%) and hand-pump water (52.76%). Similarly, PALF fibre absorbs more water in distilled water (62.99%) than hand-pump water

(59.6%) and river water (62%). The water absorption by fibres is attributed to the presence of free hydroxyl and polar group in amorphous and crystalline surface of fibre; presence of hollow cavity called lumen; and capillary action of micro pores, cavity, crevices, and holes in fibre surface. Figs. 7-9 clearly show the effect of immersion time (t) on water absorption of raw and alkali treated COIR fibre. In both cases (untreated and alkali treated fibre), the moisture sorption is a two step process. In 1st step fibre absorbs water up to saturation level due to the capillary effect and in 2nd step a decrease in the water absorption due to hydro-elastic property of fibre. We can also observe from Figs. 10-12 that capillary and water diffusion action is more pronounced in alkali treated fibres than untreated one. This was due to the fibre surface modification (changes of pore diameter and contact angle) after alkaline treatment of fibres. Alkaline treatment of fibres with various concentrations (2%, 4%, 6%, 8%, and 10%) influence capillary rise heights and capillary diffusion coefficients.

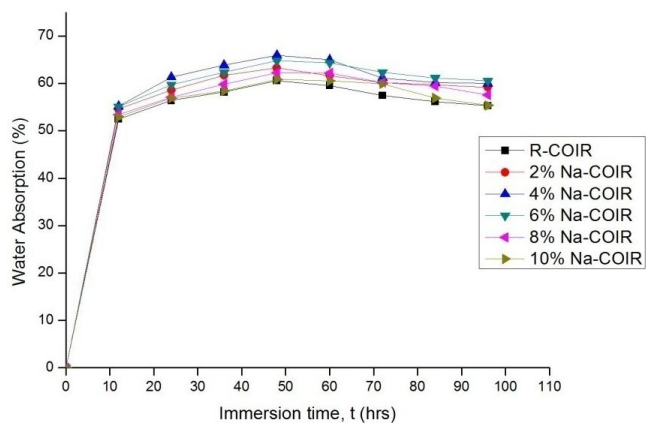


Figure 7. Effect of immersion time on water absorption of untreated and alkali treated COIR fibre in river water.

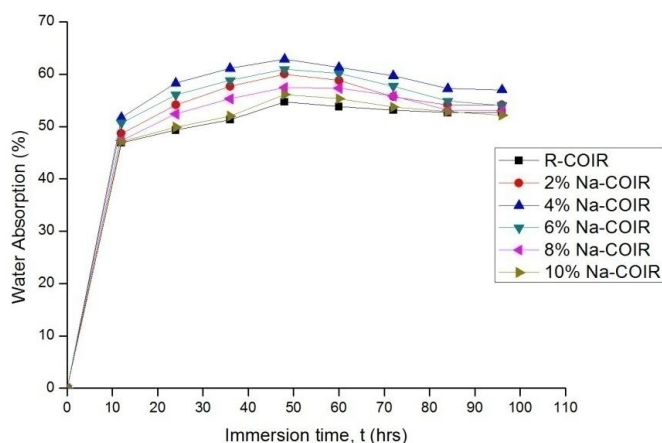


Figure 8. Effect of immersion time on water absorption of untreated and alkali treated COIR fibre in distilled water.

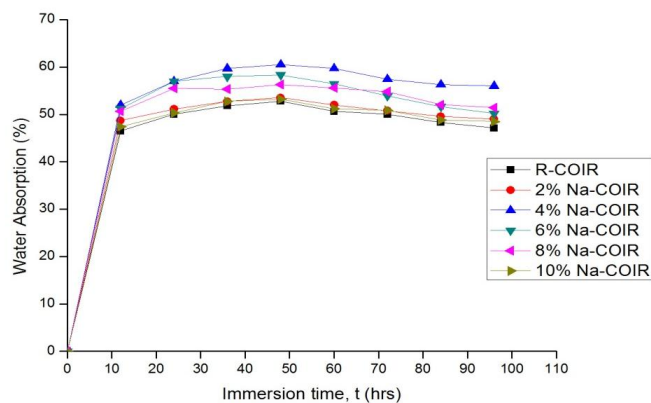


Figure 9. Effect of immersion time on water absorption of untreated and alkali treated COIR fibre in hand-pump water.

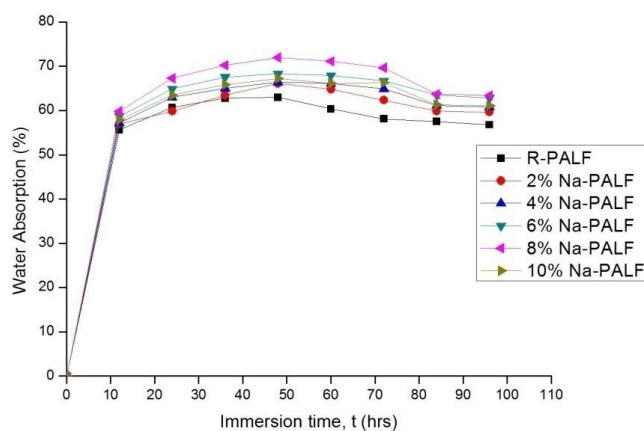


Figure 10. Effect of immersion time on water absorption of untreated and alkali treated PALF fibre in river water.

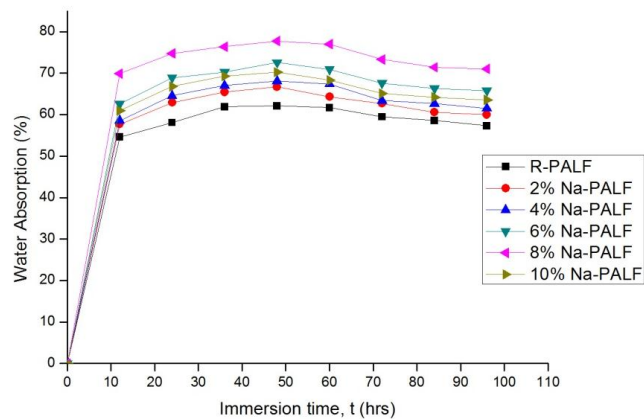


Figure 11. Effect of immersion time on water absorption of untreated and alkali treated PALF fibre in distilled water.

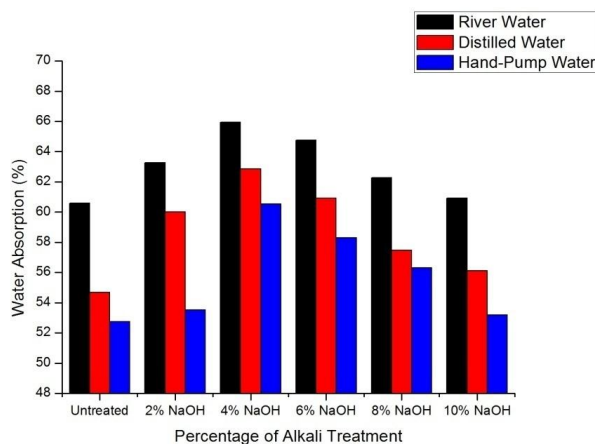
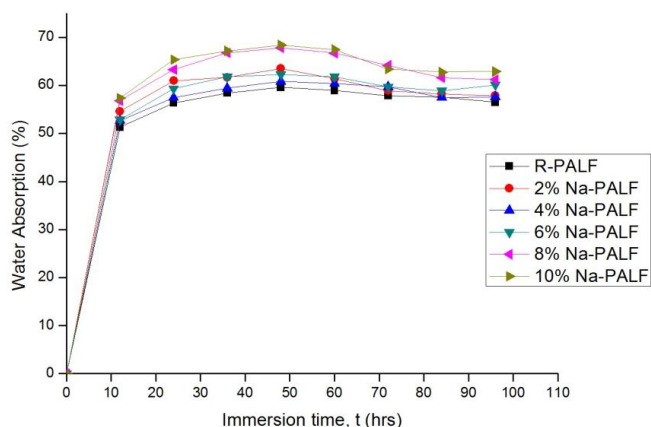


Figure 12. Effect of immersion time on water absorption of untreated and alkali treated PALF fibre in hand-pump water.

Figure 13. Effect of alkali-treatment on water absorption of COIR fibre.

Fig. 13 and 14 depicts the effect of alkali treatment on water absorption of COIR and PALF fibre respectively. It was observed that moisture sorption of fibres (PALF and COIR) were increased upon alkali treatment, which agrees with previous works (Rong *et al.* (2001), Bal *et al.* (2004), Nabi and Jog *et al.* (1999). This improvement was due to the partial removal of hemicellulose and lignin [12-14]. Bismarck *et al.* (2001) also reported the de-waxing and higher accessibility of active functional group in sisal fiber surface after alkali treatment [6]. Pejic *et al.* (2008) reported that hemicelluloses removal increases the moisture sorption and lignin removal increases the water retention ability of hemp fibre [15]. Literature studies (Buschle Diller *et al.* 1999; Wang *et al.* 2003; Kostic *et al.* 2008) concluded that non-cellulosic components (hemicellulose, lignin, pectin and waxes) negatively affect fibre processing and fibre properties (sorption property, evenness, and elasticity) [16-18]. It was observed that 4% NaOH treated COIR fibre shows maximum water uptake in all water samples [river (65.95%), distilled (62.86%), and hand-pump water (60.53%)]. The pineapple leaf fibre treated with 8% NaOH shown maximum water absorption in river (71.96%) and distilled water (77.72%); and treated with 10% NaOH shown maximum water absorption in hand-pump water (68.4%). The obtained results showed that alkaline treatment removed the pectinous gum, lignin, and hemicellulose which results faster liquid penetration in small, interconnected and uniformly distributed pores [Fig. 4 (c)-(f)]. Celino *et al.* (2014) described that heterogeneous morphologies, hydrogen bonding, and voids within the polymer are certain sites for diffusion of water [19]. The water penetration inside the fibre breaks the secondary bonds between cellulose macromolecules and formed hydrogen bonds with hydroxyl group of the polymer (cellulose) which results fibres swelling, defibrillation, close smaller pores, and reduce capillary spaces into the fibre.

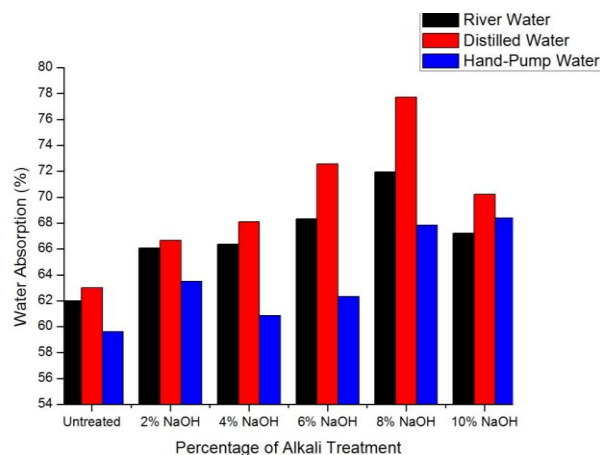


Figure 14. Effect of alkali-treatment on water absorption of PALF fibre.

CONCLUSION

We have performed the experiments to study the alkali treatment effects on surface morphology and water absorption behaviour of pineapple leaf fibre and coconut husk fibre. FTIR and SEM micrograph shows the removal of hemicellulose and binder lignin after alkali treatment. The surface of COIR fibre display many pin-holes than PALF. Defibrillation, surface cracks, porosity, and high serrated surface were produced after alkali treatment due to the partial removal of waxes and fatty substances.

PALF is more hydrophilic than COIR fibre. This was due to the presence of more holocellulose in PALF fibre. The water up-take behaviour is greatly influenced by chemical modifications. All alkali treated fibres absorb more water than untreated fibres. The 4% NaOH treated COIR and 8% NaOH treated PALF absorbs (5-8%) and (9-15%) more water than untreated fibres respectively. The capillary and water diffusion action is more pronounced in alkali treated fibres.

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