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Ftir Analysis On Tci And $A_{c=O}/A_{oh}$ Of Dc Air Plasma, Citric Acid And Tetradecanoic Acid Treated Cotton Cellulose

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Abstract. Cotton fabric was treated with DC air plasma, citric acid and neem oil vapour to produce efficient antimicrobial fabric that is wash durable. This work deals with a detailed study on the structural changes in the cotton cellulose due to the air plasma, citric acid and neem oil vapour by analyzing the changes in the ATR-FTIR spectrum of the sample after each treatment. It was identified through the spectral analysis that the oxidation of cellulose due to air plasma treatment, thereby increasing accessible OH sites and –I effect due to citric acid treatment were responsible for the two properties respectively

Keywords. Cotton cellulose; DC air plasma treatment; Citric acid treatment; Antimicrobial fabric; Wash durability.

INTRODUCTION

The durability of the antimicrobial polymer substrate becomes an important criterion for it to be saleable in the market. To improve the durability, polycarboxylic acids, only those with three or more carboxyl groups are effective as crosslinking agents such as citric acid and 1,2,3,4-butanetetracarboxylic acid etc., [1,2,3]. Polycarboxylic acids are inexpensive and non-toxic and have been used to improve the performance properties of cellulose like improved crease recovery behaviour, durable press finish property, retention of strength, whiteness of the fabric and dimensional stability [4].

Sandra Bischof Vukušić et.al, reported that when cotton textile is modified with citric acid it acts as an efficient antibacterial agent for prevention of nosocomial infections [5]. Qinghui Mao et.al., reported that citric acid treated cotton fabric produces carboxyl groups (active sites) on the fabric surface [6]. P.Wasuja et.al., studied the improvement of wrinkle recovery on cotton fabric using citric acid with nano sized -TiO_2 as co-catalyst [7].

Several researchers have worked on improving the antimicrobial activity of cotton fabric using antimicrobial finishes but the finish was not durable. To improve the durability and antimicrobial finish of cotton fabric antimicrobial agent has been cross linked with citric acid by means of the conventional pad-dry-cure process [8,9,10,11]. It has been established that the polycarboxylic acid reacts with cotton to form crosslinks through ester linkages and this fact was first investigated in the 1960's [12,13,14,15]. Debasish Das reported that most of the natural compounds have −OH groups in their structure and can be esterified with a nonpolymeric polycarboxylic acid such as citric acid [16].

Charles Q. Yang reported the cross linking mechanism of cotton cellulosic hydroxyl groups combined with citric acid anhydride to form ester with the help of FTIR analysis [17] and N.M.Morris et.al., determined the degree of esterification involved in the process [18].

But there are no investigations reported till date related to the effect of cross linking agent on the structural and crystallinity changes encountered in the cotton fiber. So in the current work, for the first time we have carried out a systematic ATR-FTIR analysis to understand the effect of citric acid treatment on inter and intramolecular hydrogen bonding system of cellulose and in turn its effect on the degree of crystallinity.

Due to the presence of the electrons and the atomic and molecular species in plasma, the plasma treatment can be effectively used for surface modification of textile substrates without altering the bulk property [19]. Hence in this work in addition, we have investigated the synergistic effect of plasma and citric acid in improving the wash durability of the antimicrobial efficacy of the neem oil vapour treated sample through ATR-FTIR analysis.

MATERIALS

Fabric

The cotton fabric was purchased from M/S, Ranjana stores, Coimbatore. The fabric used in the present work was a 100% pure, finished, plain weave Ne 22's warp count and Ne 19's weft count with an EPI and PPI of 68 x 55, surface mass of 160 GSM and thickness of 0.36 mm.

Neem oil

Neem oil (100% pure) was purchased from Beros Enterprises, Coimbatore. The oil has been prepared using traditional indian cold press technique. The neem oil was used to impart antimicrobial finish to the fabric. Neem (Azadirachta indica) oils have essential fatty acid which is responsible for antimicrobial effect. When neem oil is heated, the bioactive compounds are liberated at their characteristic vaporization temperature. Cotton fabric treated with the vapours of neem oil at 150˚C shows antimicrobial activity. To identify the components, present in the neem oil, it was subjected to GC-MS analysis. It was found that vapours evaporated at 150˚C contain tetradecanoic acid.

Tetradecanoic acid also called as Myristic acid is a long chain saturated fatty acid with the molecular formula $CH_3(CH_2)_{12}COOH$. Among the fatty acids, tetradecanoic acid possesses to have potential antibacterial and antifungal activity [20,21].

Citric acid

Citric acid is used as a cross linking agent to increase the durability of antimicrobial finish when applied on the fabric. Citric acid has been used for a long time as a cross-linking agent in various kinds of cellulosic fibers in paper and textile technologies [22, 23].

The molecular formula of citric acid (Figure 1) is $C_6H_8O_7$.

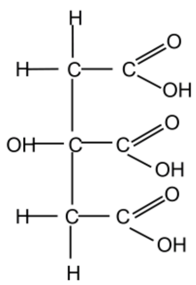

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Figure 1. Structure of citric acid

EXPERIMENTAL METHODS

DC air plasma treatment

Cotton fabric was treated with neem oil vapours to impart antimicrobial activity. To improve the antimicrobial efficacy, DC air plasma treatment was given to the procured cotton fabric prior to neem oil vapour treatment. During the plasma treatment, the fabric was allowed to float at a distance of 2cm between the cathode and anode. The fabric was exposed to plasma produced at a DC current of 25 mA for duration of 15 minutes maintained at a pressure of 0.5 millibar. The plasma treated fabric was processed with the vapours of neem oil maintained at 150°C for an hour.

Citric acid treatment

To increase the wash durability of the samples the control fabric sample and plasma pretreated sample was treated with citric acid (8% on weight of the fabric) as the binder. The citric acid treated samples were cured at 80^{o}C for 30 minutes and then shadow dried.

Assessment of Antimicrobial activity

To analyze the antibacterial activity of the sample, the samples were subjected to Agar Diffusion test (SN 195920) [24]. In this study, two bacteria, S. aureus (gram positive bacteria) and E. coli (negative bacteria) were used as test organisms.

Agar Diffusion Test (SN 195920)

The sample was subjected to Agar Diffusion test [24] to assess the antimicrobial activity.Sterile AATCC bacteriostasis agar was dispensed in sterile petri dish and 24 hours broth cultures of *Staphylococcus aureus* (ATCC 6538), a Gram-positive organism and *Escherichia coli* (ATCC 8739) a Gram-negative organism was used as inoculums. The test organisms were coated over the surface of the agar plate using a sterile cotton swab. A sample of 2cm diameter was gently pressed in the centre of the mat culture. The plate was incubated at 37^{o}C for 18-24 hours. After incubation, a clear space along the sides of the test material was observed. The diameter of this zone was reported and measured as zone of inhibition.

Wash Durability Test (IS: 687-1979)

The durability of the finish was assessed using wash durability test. Washing was carried out as per test no: 1 of IS: 687-1979 by using a neutral soap (5gpl) at 40^{o}C $\pm$ 2^{o}C for 30 minutes, keeping the material: liquor ratio at 1:50, followed by rinsing, washing and drying [25] After drying, the test samples were assessed for antimicrobial activity using AATCC 100 procedure up to 30 laundering cycles.

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Assessment of wash durability- Quantitative Bacterial Reduction Test (AATCC test method 100-2004)

Wash durability of the samples were assessed based on the results of Quantitative Bacterial Reduction Test [24]. This test provides a quantitative procedure for the evaluation of the degree of the antimicrobial activity. Fabric samples of diameter 4.8 ± 0.1cm were inoculated with the 0.1 ml of test organisms (*Staphylococcus aureus* (ATCC 6538), a Gram-positive organism and *Escherichia coli* (ATCC 8739), a Gram-negative organism). The fabric samples loaded with the organisms were shaked in known amount of ATCC Bacteriostasis Broth over contact period of 24 hrs at room temperature for all the samples. 0.1ml from the diluted solution were spread plated on to the sterile AATCC Bacteriostasis agar plates and incubated at 37^{o}C for 24 hours. Colonies of bacteria recovered on the agar plate were counted and the percentage reduction on bacteria colonies (R) was calculated using the equation 2.

$$R = \frac{(B - A)}{B} X100 \tag{2}$$

Where R is the percentage reduction, where A is the number of bacterial colonies from treated specimen after inoculation over 24 hours contact period and B is the number of bacterial colonies from untreated control specimen after inoculation over 24 hours contact time.

Gas chromatography-mass spectroscopy (GCMS) analysis

GC-MS analysis was carried out for Azadirachta Indica neem seed oil using [THERMO GC - TRACE ULTRA VER: 5.0, THERMO MS DSQ II].

ATR-FTIR Spectroscopy

The increase in antimicrobial activity and durability of the fabric due to the plasma and citric acid treatments were analyzed using ATR-FTIR spectra. The spectra were recorded using a Perkin Elmer (Spectrum100) FTIR spectrometer in the range of 4000–500 cm^{-1} with a resolution of 1 cm^{-1}.

RESULTS AND DISCUSSIONS

Effect of Plasma treatment on antimicrobial efficacy

Cotton fabric (**C**) and DC air plasma treated cotton fabric (P) were treated with vapors of neem oil maintained at 150°C for one hour. The antimicrobial efficacy of the treated samples was tested and the results of the agar diffusion assay are presented in the Table 1. The results reveal that plasma pretreatment has improved the antimicrobial efficacy.

Table 1. Antibacterial activity of Neem oil vapour treated cotton fabric against S.aureus and E.coli

Fabric	Antibacterial activity

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	Zone of inhibition in mm	
	S aureus	***E coli***
Neem oil vapour treated cotton fabric (**CN**)	Suppressed	Nil
Plasma and Neem oil vapour treated cotton fabric (**PN**)	32	28

A detailed ATR-FTIR analysis on this has been carried out and the reaction mechanism leading to an increase in antimicrobial activity of the plasma and neem oil vapour treated cotton fabric has been reported in our earlier work [26]. The studies revealed that impingement of plasma particles on the fabric has resulted in oxidation of cotton cellulose which has led to decrease in crystallinity from 84.7% to 81.1 % thereby increasing the accessible OH sites. On subsequent treatment with the vapour, tetradecanoic acid present in the vapour (Table 2 and Figure 2) formed heterogeneous ester bonds with these hydroxyl groups and hence an increase in antimicrobial activity.

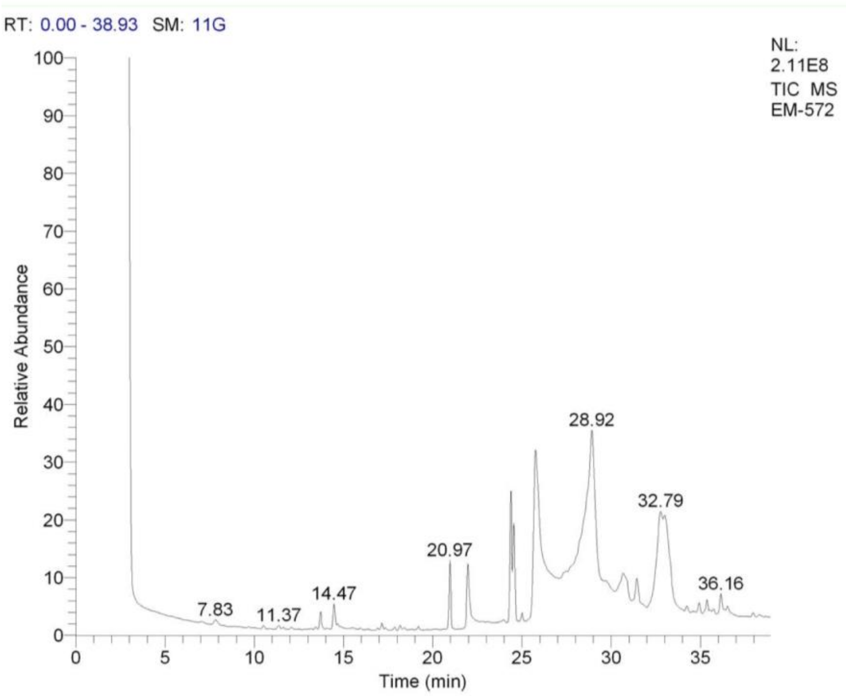

Figure 2 Gas Chromatogram of neem oil

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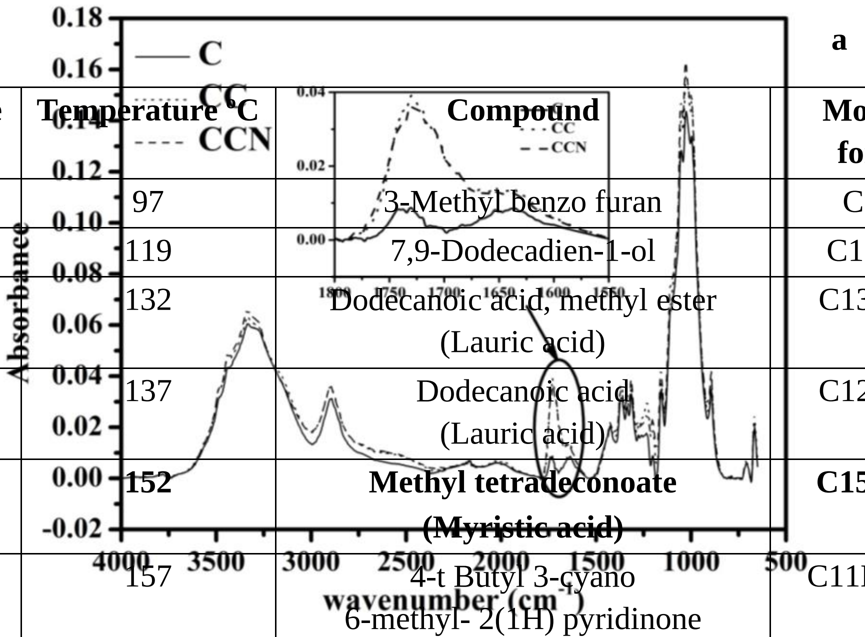
Table 2 Compounds eluted from neem oil at different temperatures

Retention time	Temperature °C	Compound	Molecular formula
7.83	97	3-Methyl benzo furan	C9H8O
11.37	119	7,9-Dodecadien-1-ol	C12H22O
13.72	132	Dodecanoic acid, methyl ester (Lauric acid)	C13H26O2
14.47	137	Dodecanoic acid (Lauric acid)	C12H24O2
17.16	**152**	**Methyl tetradeconoate (Myristic acid)**	**C15H30O2**
17.87	157	4-t Butyl 3-cyano 6-methyl- 2(1H) pyridinone	C11H14N2O
18.16	160	Tridecanoic acid	C13H26O2
20.97	175	Hexadecanoic acid, Methyl ester	C17H34O2
21.97	181	Hexadecanoic acid	C16H32O2

Having made a detailed analysis on the enhancement of antimicrobial efficacy due to DC air plasma pre-treatment, the durability of the finish was assessed using wash durability test. It was observed that the antimicrobial activity of plasma and neem oil vapour treated fabric was completely lost after the fifth wash. This is attributed to the weak heterogeneous ester bond formed between the OH of cotton cellulose and the COOH of tetradecanoic acid due to electron releasing (+I effect) effect of long alkyl chain attached to the carboxyl acid group.

To improve the durability, citric acid was used as a binding agent. Initially the control sample was treated with citric acid and was subjected to ATR-FTIR analysis. Figure 3 shows the ATR-FTIR spectrum of cotton fabric and the same treated with citric acid.



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	Absorption ratio, TCI, HBI and Stretching frequency with

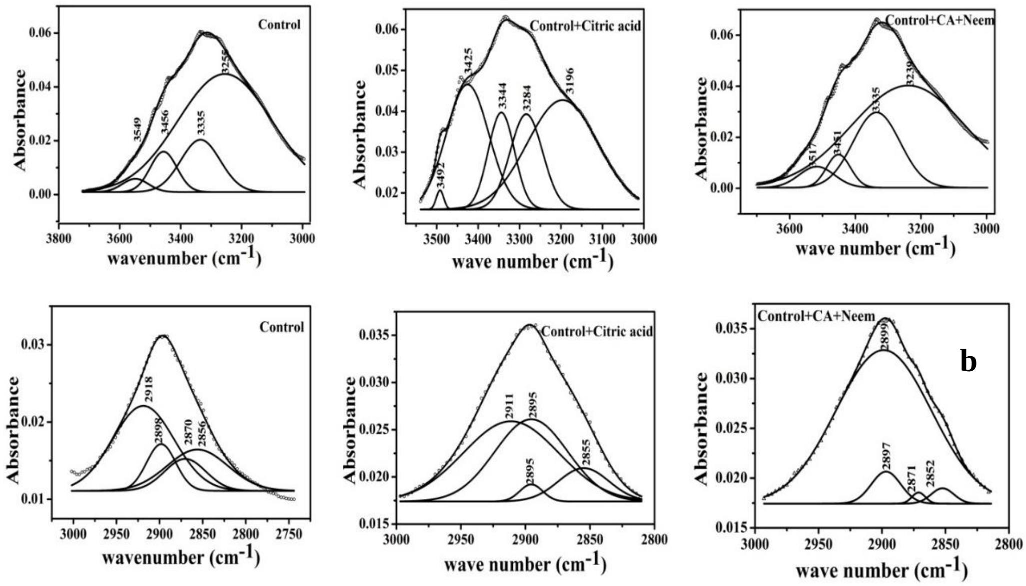

Figure 3. a)ATR-FTIR spectra of the samples C, CC, CCN b) Deconvoluted images

Table 3. Absorption ratio and stretching frequency with peak area

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	peak area				
	C	CC	CCN	P	PCN
Absorption ratio	0.1443	0.614	0.5403	0.7367	1.108
TCI	0.8125	0.7461	0.5942	0.5601	0.4820
Stretching frequency of peak area (C=O)	1740 cm^{-1} (0.143)	1742 cm^{-1} (0.2413)	1745 cm^{-1} (0.202)	1744 cm^{-1} (0.583)	1743 cm^{-1} (0.957)
Stretching frequency of peak area (C-O)	1230 cm^{-1} (0.272)	1237 cm^{-1} (0.692)	1237 cm^{-1} (0.510)	1231 cm^{-1} (0.209)	1232 cm^{-1} (0.443)

Control (C), Control Neem (CN), Plasma (P), Plasma+Neem (PN), Control+Citric acid (CC), Control+Citric acid+Neem (CCN), Plasma+Citric acid+Neem (PCN)

It can be observed that the peak at 1730 cm^{-1} and 1230 cm^{-1} corresponding to C=O stretching and C-O stretching in the cotton cellulose has been shifted to 1742 cm^{-1}, 1237cm^{-1} indicating the formation of ester. The values of absorption ratio ($A_{c=o}/A_{OH}$), peak area (C=O and C-O stretching of ester) and Total crystallinity index TCI) are presented in Table 3. The increase in peak area as well as absorption ratio implies that more free OH groups of cellulose are consumed for esterification process thus forming cross links between two parallel cellulose chains [27] which is presented in Figure 3. This inturn affects the hydrogen bonding system.

The peak at 3456 cm^{-1} and 3335cm^{-1} corresponds to O(2)H stretching and O(3)H stretching respectively which are involved in intramolecular hydrogen bonding with O(6) and O(5) of the same chain. After citric acid treatment, these two peaks are shifted to 3425 cm^{-1} and 3344 cm^{-1} disclosing the weakening of O(2)H and strengthening of O(3)H bonds leading to strengthening and weakening of O(2)H···O(6) and O(3)H···O(5) intramolecular hydrogen bonds respectively. Lengthening and shortening of hydrogen bond is expected to affect the C-O-C glycosidic linkage. However, peak corresponding to C-O-C glycosidic linkage (1158 cm^{-1}) doesn't undergo any shift. This is because peak corresponding to O(6)H stretching has been shifted from 3255cm^{-1} to 3283 cm^{-1} denoting the strengthening of O(6)H bond that lead to the weakening of O(6)H···O(3) intermolecular hydrogen bond. Also the peak at 2898cm^{-1}corresponding to CH_2 stretching shifts to 2895 cm^{-1} indicating a rotation about C_6H_2 [28]. The combined effect of shortening of O(2)H···O(6) intramolecular hydrogen bond and O(6) stretching as well as lengthening of O(6)H···O(3) intermolecular hydrogen bond and rotation about C_6-C_5 counter balances the elongation of O(3)H···O(5).

The shift in peak at 2919cm^{-1} to 2911cm^{-1} indicates the weakening of ring C-H stretching thereby resulting in the strengthening of intersheet hydrogen bonds. The changes in the hydrogen bonds lead to a lattice strain thus decreasing the degree of crystallinity of the citric acid treated sample. A decrease in Total crystalline index (TCI) value of citric acid treated sample shows that more number of accessible OH reactive sites has been generated.

When the citric acid treated fabric is subsequently treated with neem oil vapour, the tetradecanoic acid reacts with free hydroxyl groups present in the amorphous regions of the cellulose and the hydroxyl groups of citric acid as well, to form ester linkages. Comparison

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between the peaks pertaining to C=O stretching (1750 cm^{-1}- 1720 cm^{-1}), C-O stretching (1250 cm^{-1}- 1200 cm^{-1}) of esters formed in CC and CCN samples (Figure 3), and data pertaining to the corresponding peak area and absorption ratio (Table 3), uncovers an increase in ester concentration.

Wash durability of sample was measured by the standard test, and was observed that the fabric was able to retain the antimicrobial property to commercial standards for nearly 30 washes (Table 4). When the cotton cellulose is treated with citric acid, the glucose chains are linked to citric acid molecules through ester bonds which is strong when compared to ester bond formed between cotton cellulose and tetradecanoic acid. This is ascribed to the electron withdrawing effect (-I effect) of the carbon atom of citric acid attached to ester forming carboxylic acid. On subsequent treatment with tetradecanoic acid from the vapour, the ester bond is formed between the HO-C=O and the –OH attached to the centre carbon of citric acid (Figure 4) which is stronger than the previous type due to higher electron withdrawing effect (-I effect) of centre carbon than the second and fourth carbon atom in the citric acid chain.

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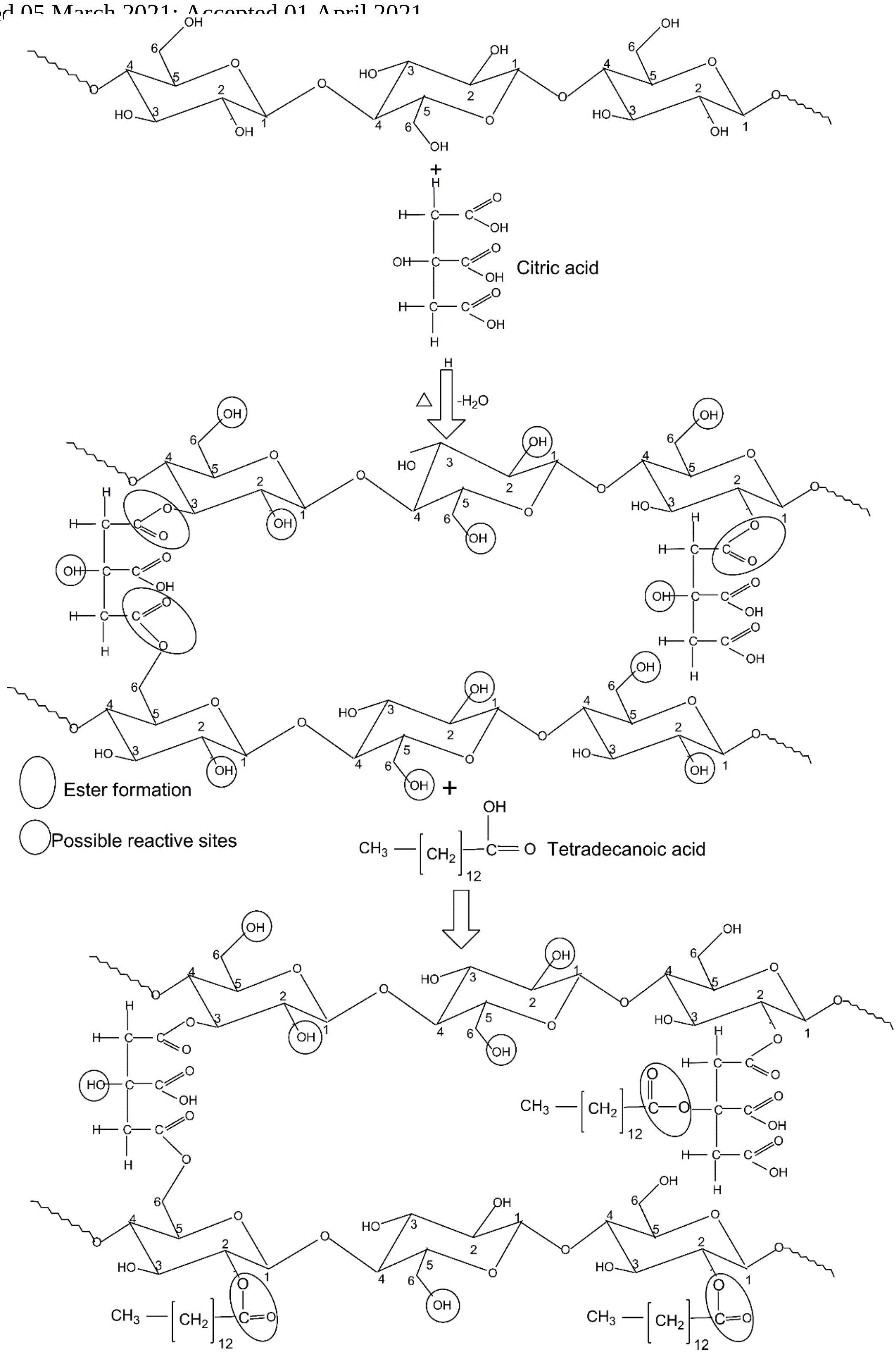

Figure 4. Reaction between Cellulose, Citric acid and Tetradecanoic acid

The reaction explained above, further distracts the hydrogen bonding system in the crystalline region of the cellulose structure. It can be inferred from IR analysis (Figure 3) that the inclusion of tetradecanoic acid in to cellulose and citric acid network affects the intramolecular, intermolecular and intersheet hydrogen bonding. The stretching vibration of

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OH in intramolecular hydrogen bonding peaks pertaining to O(2)H···O6 shifts from 3425cm^{-1} to 3451cm^{-1} and O(3)H···O(5) shifts from 3344cm^{-1} to 3335cm^{-1} which infers the weakening of intramolecular hydrogen bonding with O6 and strengthening of intramolecular hydrogen bonding with O5. Further, the intermolecular hydrogen bonding strengthens as the OH stretching frequency decreases from 3283cm^{-1} to 3239 cm^{-1}. The observed hydrogen bond changes due to the inclusion of tetradecanoic acid in the CC network were exactly the inverse of what happened in the CC network. However, this inverse effect too did not affect the C-O-C glycosidic bond. Further, the increase in frequency of C_6H_2 stretching from 2895cm^{-1} to 2897cm^{-1} due to tetradecanoic acid treatment would result in the rotation about C_5-C_6 covalent bond which counter balances the rotation of C_5-C_6 covalent bond due to citric acid treatment. The stretching frequency of ring C-H decreases from 2855 cm^{-1} to 2852 cm^{-1} indicating the strengthening of the inter sheet hydrogen bond while there was no change in intersheet bonding due to citric acid treatment. When compared to CC, the decrease in TCI value of CCN (Table 3) reveal, that these changes have strained the cellulose chains and has lead to the cleavage of hydrogen bonds.

Synergistic effect of plasma and citric acid treatment

An attempt was also made to study the synergistic effect of plasma and citric acid treatment on the wash durability. Table 4 shows that the plasma treatment prior to citric acid and tetradecanoic acid is even more effective in improving the wash durability of the sample.

Table 4. Wash durability of plasma, citric acid and neem oil vapour treated cotton fabric

	Wash durability Test			
No of laundering cycles	**Bacterial Reduction (%)**			
	Fabric treated with citric acid and neem oil vapour (CCN)		**Fabric treated with plasma, citric acid and neem oil vapour (PCN)**	
	S aureus	***E coli***	***S aureus***	***E coli***
5	100	97.5	100	98
10	98.6	96	99	97
15	90.3	89.8	95	91
20	88.3	83.6	92	86
25	85.2	80	89	84
30	78	65	86	81

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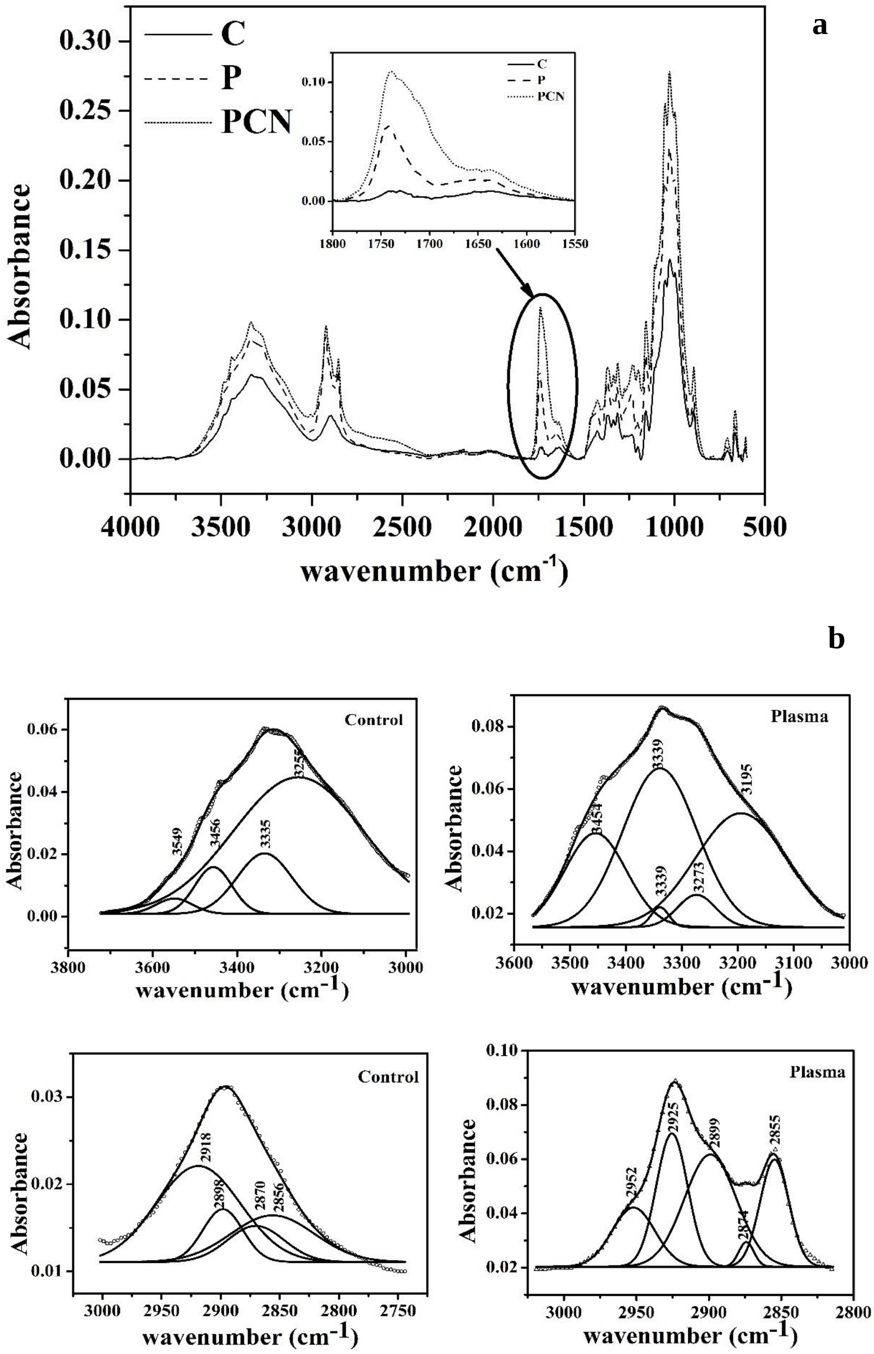

Figure 5. a)ATR-FTIR spectrum of control, plasma, PCN treated sample

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b) Deconvoluted images

The systematic ATR-FTIR analysis (Figure 5) carried out on PCN sample discloses the following facts.

As mentioned earlier, during the plasma treatment the energetic plasma particles impinge on the cellulose molecule oxidizes the sample and also alters the crystallinity which are evident from the following observations. The shift in peak from 3335 cm^{-1} to 3339cm^{-1} which corresponds to OH stretching in O(3)H···O(5) intramolecular hydrogen bonding and increase in OH stretching frequency of intermolecular hydrogen bond O(6)H···O(3) from 3255 cm^{-1} to 3273 cm^{-1} implies the weakening of intra and inter molecular hydrogen bonding with O5 and O3. The peak pertaining to OH stretching in intramolecular hydrogen bonded O(2)H···O(6) decreases from 3456 cm^{-1} to 3454 cm^{-1} which reflects as the strengthening of intramolecular hydrogen bonding with O6 and provides the stiffness to the cellulose chain. Further stretching frequency of ring CH increases from 2918 cm^{-1} to 2925 cm^{-1} which in turn weaken the inter sheet hydrogen bond. The peak corresponding to C_6H_2 stretching doesn't undergo any shift in frequency. These changes introduce a strain in the lattice of crystalline region of cellulose which is reflected as a decrease in TCI value (Table 3). Hence more number of free hydroxyl groups is generated and are available for citric acid treatment.

On subsequent treatment with the citric acid and neem oil vapour, the free accessible OH groups react with citric acid to form ester bonds which results in the additional α hydroxyl group of citric acid available for the tetradecanoic acid to react and form a strong ester bond thereby improving the antimicrobial efficacy and wash durability. The presence of C=O and C-O stretching vibration of esters was confirmed by analyzing the area of the peaks in the region between 1750 cm^{-1}- 1720 cm^{-1}, 1250 cm^{-1}- 1200 cm^{-1} respectively. It can be inferred from Table 3, that there is an increase in area of the peaks and absorption ratio ($A_{c=o}/A_{OH}$) after neem treatment when compared to CCN thus confirming the formation of higher concentration of esters.

CONCLUSION

Wash durability of neem oil vapor treated cotton fabric was enhanced using citric acid as a binding agent. The citric acid molecule that enters the cellulose network (CC network) forms strong ester linkages with free hydroxyl groups of cellulose which is confirmed through the C=O and C-O peak area values and $A_{C=O}/A_{OH}$ ratio calculated using ATR-FTIR spectrum. These ester linkages are stronger due to -I effect. Furthermore, the treatment also has weakened the O3H—O5 intramolecular hydrogen bond and O6H—O3 intermolecular hydrogen bond and has strengthened the O2H—O6 intramolecular hydrogen bond. Also, decrease in stretching frequency of C_6H_2 causes the rotation of C_5-C_6 covalent bond. These effects thus induce strain in the cellulose lattice and affect the crystallinity thereby decreasing the TCI value. When tetradecanoic acid is introduced in the CC network (CCN) an inverse effect is observed in the hydrogen bond system and additionally it also affects the intersheet hydrogen bond. Also, the ester formed between free OH in cellulose / OH in citric acid and carboxyl group of the acid has been ascertained through C-O peak area values and $A_{C=O}/A_{OH}$ ratio. However, the ester formed between OH in citric acid and carboxyl group of the acid is strong due to -I effect whereas the ester formed between free OH in cellulose and carboxyl group of the acid is weak due to +I effect and hence it is responsible for the initial antimicrobial effect. Hence, the strong ester formed between OH in citric acid and carboxyl group of the acid contributes to the durability of the antimicrobial effect. When the fabric is subjected to DC air plasma surface activation prior to citric acid and neem vapour treatment, the plasma particles that bombard on the fabric surface affects the hydrogen bonds by supporting hydrogen bond cleavage and promotes generation of free OH which has been substantiated through ATR-FTIR studies. Thus, the synergistic effect of DC air plasma and citric acid treatments gives way to higher concentration of strong ester formed thereby further enhancing the wash durability of antimicrobial activity.

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