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Fabricating multifunctional nanoparticles bonded to enzymatically oxidized fabrics for their various applications

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An effective procedure for obtaining fragrance finished fabric based on cellulose and chitosan has been developed. The first step involves the formation of oxidized cellulose, which is able to form a schiff's base with the chitosan. In order to maintain the strength of fabric, a novel enzymatic method for oxidation of cellulose is adopted. In the second step, chitosan nanoparticles loaded with the jasmine oil are prepared and coated on the oxidized cellulosic fabric by forming a strong covalent bond. The FTIR analysis proves the formation of cellulose-chitosan composite. Scanning electron microscopic study demonstrates the coating of nanoparticles on the cotton fabrics. The retention capacity of the jasmine oil in the fabric after repeated washings is proved by GC analysis. The cotton fabrics finished by the covalent bonded coating of chitosan nanoparticles loaded with the jasmine fragrance are found to have a better sustained release capability for a longer time as compared to the conventionally entrapped nanoparticles in the fabric.

Keywords: Alcohol dehydrogenase, Cellulose, Chitosan nanoparticles, Fragrance finished textiles, Jasmine

1 Introduction

In recent years, the functional innovative textile products with thermal protection[1], mosquito repellent, vermin proof[2] and long lasting perfumed properties have received much attention. Especially, the long-time fragrance emitting textiles and antibacterial textiles hold the industrial demand. In the traditional fragrance finished textiles, compounded fragrance was added into the textiles during dyeing or finishing processes directly[3]. However, the main compounds of the fragrance are labile and volatile. The most volatile fragrance materials are lost easily during the manufacture processes, storage, repeated washings and use of the perfumes. Therefore, the main focus of fragrance application to textiles lies in its stability. Nowadays, the fast development of microencapsulation techniques has provided slower release of fragrances or flavours, which can deliver them over longer period of time, instead of being instantaneous[2]. Many researchers reported spray-drying[4-8] , coacervation[9-13] and inclusion complexes with cyclodextrins[14]. However, all these techniques still have few disadvantages. Hence, the encapsulation of fragrance with polymeric carrier materials has been explored[15]. At the same time, many researches in the field of biology and medicines also indicated that nanoparticles have sustained release properties[15]. However, the sustained release of fragrance in the finished cotton fabrics depends on the use of adhesive agents in the above researches. As the cotton fibre has the porous reticular structure and the average diameter of the pores on the fibres is about 50 nm, it is difficult for more than 50 nm particles to be fixed on the fibres firmly. Especially when the textile products are washed several times, particles easily get vanished from the fibres[16]. So in this paper enzyme mediating bonding of the nanoparticles to the fabric has been developed, where the formation of strong covalent bond enables the fixing of the nanoparticles firmly to the fabric.

The cotton fabric is composed of cellulose. Cellulose is the most abundant natural polysaccharide and the most important component in plants that makes about 50% of biomass[17]. Chemical modification of polysaccharides is an important approach for preparation of novel materials with improved performance and value-addition[18]. By oxidizing the cellulose, the new functional groups can be bonded to the various chemical compounds.

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Different oxidizing agents like the gaseous oxidizing agent and acid oxidizing agent are in use to oxidize the cellulose molecule . However enzymatic fabric oxidation is a novel oxidation method discussed in this paper. Alcohol dehydrogenase is the enzyme used to improve the strength of the fabric. Alcohol dehydrogenases (ADH) are a group of dehydrogenase enzymes that occur in many organisms and facilitate the interconversion between alcohols and aldehydes or ketones with the reduction of nicotinamide adenine dinucleotide (NAD^+ to NADH)[19]. In yeast and many bacteria, alcohol dehydrogenase plays an important part in fermentation. Pyruvate resulting from glycolysis is converted to acetaldehyde and carbon dioxide, and the acetaldehyde is then reduced to ethanol by an alcohol dehydrogenase called ADH1. Brewer's yeast also has another alcohol dehydrogenase (ADH2), which is evolved out of a duplicate version of the chromosome containing the ADH1 gene. ADH2 is used by the yeast to convert ethanol back into acetaldehyde, and it is expressed only when sugar concentration is low[14].

Chitosan, a natural polysaccharide obtained from crustacean shells and composed of D-glucosamine and N-acetyl-D-glucosamine units linked by (1–4) glycosidic bonds, has attracted great interest in the materials science due to its non-toxicity, biocompatibility, biodegradability and mucoadhesive property[20]. Hence, by using chitosan, ecological aroma textiles can be prepared.

In this work, the chitosan nanoparticles loaded with jasmine fragrance have been prepared via ionic gelation process, where nanoparticles are formed by means of electrostatic interactions between the positively charged chitosan chains and polyanions employed as cross-linkers like tripolyphosphate (TPP)[21]. Tripolyphosphate (TPP) has been popular because it is nontoxic and has the ability to immediately form gel while interacting electrostatically with cationic chitosan. Subsequently, JF-NPs (jasmine fragrance loaded chitosan nanoparticles) are bound to the oxidized cellulosic fabric by a covalent bond. The dispersion and micromorphology of JF-NPs bonded on the aroma finished cotton fabrics are demonstrated via scanning electron microscope (SEM). Fragrance releasing chemical component in JF-NPs remained in the finished cotton fabric has been detected by gas chromatography analysis. The absorption peak of the oxidized cellulose and chitosan-cellulose composite, is investigated by Fourier transform infra-red spectroscopy (FTIR). The tear strength of the fabric with different oxidizing agents are exposed by the tensiometer readings.

2 Materials and Methods

2.1 Materials

Jasmine fragrance oil was purchased from Himalaya Herbs, Andhra Pradesh. India. Chitosan (MW 150 kDa, degree of deacetylation 90%) was purchased from Sigma Aldrich, Germanay. Sodium tripolyphosphate (TPP) and polyoxyethylene (80) sorbitan monolaurate (Tween-80), ADH enzyme were purchased from Sigma Aldrich, Germany, 100% pure cotton fabric has been used throughout the study.

2.2 Methods

Three types of oxidizing agents, viz HNO_3/H_3PO_4–$NaNO_2$, NO_2 and alcohol dehydrogenase (ADH) were used to form a oxy-cellulose.

2.2.1 Acid Oxidation

The process of preparing oxidized cotton fabric by HNO_3/H_3PO_4–$NaNO_2$ was carried out using the process developed by Xua *et al.*[22].

2.2.2 Gaseous Oxidation

Concentrated nitric acid was reduced using metal, such as copper, as shown below.

$$4HNO_{3} + Cu \longrightarrow Cu(NO_3) + 2NO_2 + 2H_2O$$

The nitric acid reacts with the copper metal and produces the nitrogen dioxide gas. This is a yellowish gas and a very good oxidant. The reaction shows a greenish coloured solution of nitric acid (40 mL) and copper (20g), producing the nitrogen dioxide gas. Cotton fabric (60g) was taken and exposed to the NO_2 gas. The fabric was exposed to the NO_2 gas for 30 min, after that washed with the distilled water and dried at 40^0C in oven.

2.2.3 Enzymatic Oxidation

Yeast alcohol dehydrogenase (ADH) is an enzyme of MW 141000, and composed of four apparently identical subunits. ADH is an intracellular enzyme, so the cell disruption methods are to be followed to break the yeast cell (*Saccharomyces cerevisae*)[23]. Yeast cake was taken and grown in 2.5% molasses solution and placed in the shaker for 24 h under aerobic conditions at 30^0C. Now the extract was transferred to anaerobic conditions for the next 24 h and the growth of yeast cells was observed under the microscope. In the anaerobic conditions the ethanol was produced which gets oxidize to acetaldehyde by the ADH2 enzyme, The yeast cell extract was collected by centrifuging the solution at 8000 RPM for 15 min. The supernatant was discarded and the collected cell pellet is found to contain ethanol. This ethanol has to be eliminated to an extent because competitive inhibition occurs between the ethanol and the hydroxyl groups of the cellulose. Hence, the extract was washed thrice with 5mM Phosphate buffer at *p*H 7 until the ethanol no longer appears. Since the ADH enzyme is an intracellular enzyme, the cell disruption is done by the method of sonication for 15 min. This extract was centrifuged at 8000 RPM for 10 min, and the supernatant was collected. To this supernatant, the cellulosic fabric was added and rotated under the shaker for 24 h. The fabric sample was collected, washed and dried with the distilled water for several times to remove the impurities.

The alcohol is converted into aldehyde in the presence of NAD^+ by ADH2 enzyme. This is a reversible reaction where aldehyde was formed by ADH2 and the formation of alcohol i,e ethanol by ADH1 enzyme. This *in vivo* pathway was applied to the in vitro technology to oxidize the cotton fabric. The cellulosic fabric contains alcohol groups which are converted in to aldehyde groups (-CHO) by the ADH2 enzyme.

2.2.4 Determination of Weight Loss

The formation of soluble fragments, as a result of the cellulose chain scission caused by oxidation treatment, was determined by measuring the weight loss of oxidized fabric by applying the direct gravimetric method[24].

2.2.5 Determination of Chemical Groups

The amount of carboxyl groups (COOH) present in the oxidized products was determined according to the procedure as reported by Yackel *et al.*[25]. The aldehyde (CHO) content in oxidized products was determined by the method as described by Saito *et al.*[26]. The amount of carbonyl groups in oxidized bamboo pulp fabric was measured according to the hydroxylamine method[27]. The ketone group content (%w/w) in oxidized fabric sample was determined by subtracting the aldehyde group content from the carbonyl content.

2.3 Tensile Test

The tensile property tests were implemented using ASTM D5035-06 standard test method for breaking force and elongation of textile fabrics (Strip Method). The valid tensile extension zone was kept within the area of 200 - 250 mm. The tests were carried out on the multipurpose material tester Instron 3385 H. The loading speed was 5cm/min and the gage length was 200mm.

2.4 Preparation of JF-NPs

JF-NPs were prepared via ionic gelation method as reported by Calvo *et al.*[28]. Chitosan solution (2.5 mg/mL) was prepared in 1% acetic acid under the ultrasonic treatment at 900 W, 25 kHz for 10 min. Five drops of jasmine oil were dispersed in the chitosan solution to form an o/w emulsion under ultrasonic treatment at 900 W, 25 kHz for 10 min. After that, the *p*H of the emulsion was controlled at 4.5 with 1 mol/L sodium hydroxide aqueous solution. Then 15 mL TPP (0.7 mg/mL) was added drop-wise to 35 mL of the emulsion with stirring at 25^0C, so that the weight ratio of chitosan:TPP was controlled to 3:1. Then, the reaction was allowed to occur for 3 h at the stirring speed of 375 rpm.

2.5 Binding of Chitosan-nanoparticles to Oxidized Fabric

The oxidized cellulosic fabric was immersed in chitosan nanoparticles solution with stirring for up to 3 h at 60^0C. After the treatment, the fabric was washed with deionized water for several times, and soaked in deionized water (400 mL) for 20 h at 37^0C. The resulting fabric was dried at 60^0C during 5 h to produce the composite cellulose-chitosan fabric.

2.6 Washing Conditions for GC Analysis

Each 60 g of cotton fabric, finished by JF-NPs respectively, was mixed with 1600 g water at 40^0C and 3g of commercial detergent then added into the commercial washing machine for washing treatment. During each washing cycle, the perfumed cotton fabrics were washed with 1600 g water at 40^0C under the standardized procedure for 10 min, drained and rinsed with 1600 g water at 25^0C for 5 min and then spun for 2 min. After 20-30 cycles, the sample was dried in the oven with the air current of 0.4 m/s at 40^0C for 1 h (ref. 29).

2.7 Particle Micromorphology

Scanning electron microscopy (SEM) was used to investigate the micromorphology and the diameter of materials to demonstrate whether JF-NPs have been formed, SEM analysis of JF-NPs was done with an SC7620 scanning microscope (Sathyabama University, Chennai, India).

2.8 FTIR Study

Infrared spectra were recorded by using a BOMEM Hartmany & Brayn MB-Series spectrophotometer in the wave number region 4000-400 cm^{-1}. The samples were prepared in the form of pellet, by mixing the grained fabric and potassium bromide. The formation of carboxyl and aldehyde groups in the oxidized cellulose and the preparation of cellulose-chitosan composite was determined by FTIR analysis.

2.9 SEM Study

SEM was performed to analyze the cotton fabric, the cotton fabrics finished by JF-NPs and oxidized cellulose. The finished cotton fabrics were placed on a carbon-coated stub and coated with a thin layer of sputtered gold by Mini Sputter Coater SC7620. The morphology and microstructure of the samples were observed through a scanning electron microscope (Sathyabama University, Chennai, India).

2.10 Gas Chromatography

The volatile components in the JF-NPs bonded fabric and JF-NPs entrapped fabric were observed by using the gas chromatography in order to know about the importance of strong bonding of nanoparticles with fabric. The finished cotton fabric was immersed in pure acetone with ultrasonic treatment so that the nanoparticle was destroyed by swelling CS shell. Finished cotton fabrics (3 g) were cut into small pieces, and then immersed in 150mL of acetone for 3 h. Finally, the fabric was removed and this acetone was injected in to the GC for further analysis. The influence of the washing treatment on the fragrance released from the above cotton fabrics was investigated.

3 Results and Discussion

3.1 Effect of Oxidizing Agents on Oxidation Contents of Cotton Fabric

For obtaining monocarboxy cellulose, the impacts of various oxidation on fabric are assessed by determining the carboxyl group content, weight loss, fabric strength and mechanical properties of fabric samples.

The carboxyl content and weight loss of cellulose oxidized with different oxidizing agents at various ambient temperatures are summarized in Table 1. It is observed that the enzymatic oxidation used in the reaction does not have a significant effect on the weight loss of fabric, and the HNO_3/H_3PO_4–$NaNO_2$ oxidation shows the maximum carboxyl content of 9.75% and a very high weight loss of 17.03%. The oxidation with NO_2 produced the oxy-cellulose with 7.93% carboxyl content, whereas the weight loss of oxidized cellulose is found to be high (about 16.35%). As shown in Table 1, the reaction system of ADH can achieve the oxidize fabric with a high carboxyl content (7.93–9.71%) and in a relatively zero weight loss. These results reveal that the ADH produces oxy-cellulose in high yields with a minimum damage to the strength of the fabric. These data illustrate that the oxy-cellulose by HNO_3/H_3PO_4–$NaNO_2$ and NO_2 mediated oxidation have no aldehyde group and the carbonyl content formed in the oxidized samples is only due to ketone groups. Simultaneously by the ADH oxidation, 8.67% of aldehyde content is present with sodium chlorite treatment and no carboxyl groups due to the conversion of ethanol to acetaldehyde groups by ADH2 enzyme.

3.2 Tensile Strength of various Oxidised Fabrics

Tensiometer is used to study the breaking strength of the material and the time it takes to break. Breaking strength analysis is helpful to select an appropriate oxidation method to oxidize the fabric. The fabrics, oxidized using the three oxidation methods as discussed above, have been taken for the tensile strength analysis. The oxidized fabrics with almost equal strength to the normal fabric have been selected and continued for further steps.

Table 2 shows the strength of oxidized fabrics with different oxidation methods. Compared to the acid and gaseous oxidation, in enzymatic oxidation the

Table 1 — Percentage of carboxyl and aldehyde contents with different oxidation system

Oxidation	Weight loss %	Carboxyl content, %	Carbonyl content, %	Aldehyde content, %
Acid	17.03	9.75	2.68	–
Gaseous	16.35	7.93	1.82	–
Enzymatic	–	–	1.98	8.67
SD, %	±0.68-1.19	±0.14-0.47	±0.11-0.91	±0.13-0.76

Table 2 — Tensile strength analysis of oxidized fabrics with different oxidizing agents

Cotton fabric	Breaking strength, N/cm^2	Elongation-at-break, %	Breaking time, s
Non-oxidized	38.76	16.45	5.02
Acid oxidized	25.43	11.56	1.5
NO_2 oxidized	28.56	13.57	3.45
Enzymatic oxidized	38.45	16.34	5.00
Chitosan- coated enzymatic oxidized	38.76	16.45	5.01

strength of the fabric remains almost the same as the non-oxidized cotton fabric. At higher concentrations of chitosan, chitosan molecules would be greatly available in the proximity of the macrostructure of cotton and fabric surfaces both containing aldehyde groups, thereby leading to Schiff's base formation between aldehyde groups and chitosan amino groups. By increasing the chitosan concentration, the strength of the fabric also increases. Hence, it is concluded that the enzymatic method is the best for the oxidation of cellulose.

3.3 Chitosan Nanoparticle Surface Morphology

The nanoparticles are formed with a mean diameter of 142 nm and spherical in shape (Fig. 1). The molecular chains of chitosan with the rigid crystalline structure are formed with NPs via ionic gelification interactions between the positive charged protonated amino groups on chitosan and the negative charged phosphate groups on TPP by encapsulating the jasmine fragrance on the cotton fabric.

3.4 FTIR Characterization for Oxy-cellulose and Chitosan Coated Oxycellulose

FTIR results are used to characterize the chemical composition of the cotton. Infrared spectroscopy is an effective method for the identification of molecular functional groups, such as methyl (C-H), hydroxyl (O-H), and carbonyl (C=O) groups[30]. Here, the carbonyl and imino bonds are confirmed using FTIR.

FTIR spectra of oxidized fabrics with different oxidizing agents shows a broad peak (3100-3500 cm^{-1}) corresponding to OH group stretching of cellulose. However, these absorption peaks of OH stretching in oxidized fabric gradually become narrower and shifted towards higher wave number position with increase in the oxidation time. For the fabrics oxidized at different oxidation time intervals, a sharp band associated with OH group in-plane bending of cellulose at 1377.1 cm^{-1}, a peak at around 1161.2 cm^{-1} due to C-O-C asymmetric stretching and a little peak at 1030.2 cm^{-1}due to C=O stretching are totally decreased in the intensity. But another sharp band corresponding to CH group bending of cellulose at about 1284.5 cm^{-1} is found very stronger than that of original fabric. Compared to non-oxidized fabric, the infrared spectra of the oxidized fabrics exhibit a sharp characteristic absorption peak at 1739.7 cm^{-1} corresponding to C-O stretching vibration of carbonyl group, whose absorptivity is enhanced with extending oxidation time, consistent with the increase of the carboxyl and aldehyde groups in oxidized fabric.

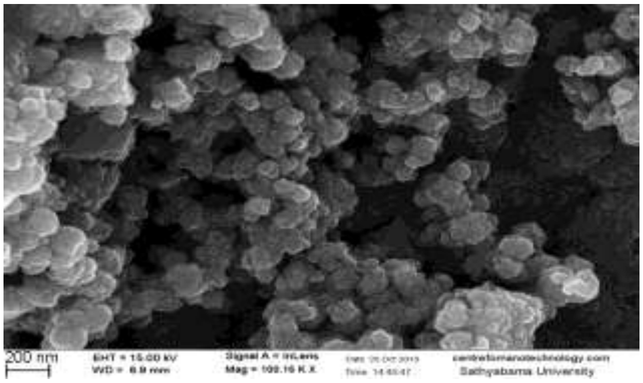

Fig. 1 — SEM image of chitosan nanoparticles

The aldehyde content of the oxy-cellulose reflects not only the oxidative extent of the cellulose fabric oxidized by ADH but also the extent of incorporated chitosan. The amount of bonded chitosan increases with the oxidation time and the concentration of chitosan. Carbonyl peak reduces and the imino peak is appeared, indicating that the chitosan is coated in the oxidized fabric. With the increase in chitosan concentration, the imino peak area increases and the carbonyl peak reduces still more. The chitosan coating is found higher for fabric oxidized by acid oxidation in relation to fabric oxidized by ADH, due to the presence of high carboxyl content through acid oxidation. When the reaction time of oxidant is over 180 min, the chitosan content becomes constant, regardless of the content of carbonyl groups. This phenomenon can be explained by considering the difference in the mechanism, in which the oxidation takes place along with the formation of Schiff's base in the cellulose[31].

Structural changes in the fabric occur during the oxidation and coating can be followed via IC spectrum. The occurrence of the peak in the IC spectrum of the oxidized fabric at about 1730 cm^{-1}, suggests an increase of the carbonyl group content as well as the aldehyde groups. According to Janjic *et al.*[29], it is suggested that the change at 1726 cm^{-1} in the spectrum of the oxidized cellulose agrees with the vibration C=O of the double aldehyde group. In the study of Liu *et al.*[30], where cellulose oxidation also occurred, the increase in the intensity of peak at 1729 cm^{-1} is stated as the evidence for the increase in carbonyl groups. The change in the intensity of spectrum at 1700 cm^{-1} and 1740 cm^{-1} also suggests the change carbonyl groups.

The intensity of the peak is changed at about 1646 cm^{-1} for chitosan coated fabric in relation to the oxidized fabrics, which indicates the incorporation of chitosan in the fabric. Liu *et al.*[30] stated that the peak at 1646 cm^{-1} also suggests the incorporation of chitosan. Besides that, the literature states that after treating oxidized cellulose with chitosan, the distinctive peak in the absorption shifts towards 1716 cm^{-1} , which is characteristic for the C=N double bond. This further suggests that the Schiff's base is formed by reaction between aldehyde group of the oxidized cellulose and the amino group of chitosan. Another study[31] suggests that after treating oxidized cellulose with chitosan, the absorption appears at about 1628 cm^{-1} on the IC spectrum, which is typical for the amino groups.

3.5 Parameters effecting Tensile Strength of Fabric

As shown in Table 3, at higher concentrations, chitosan molecules remain greatly available in the proximity of macrostructure of cotton and fabric surfaces both containing aldehyde groups, thereby leading to Schiff's base formation between aldehyde groups and chitosan amino groups. It is further observed that the values of carbonyl content of the modified fabric decrease substantially by increasing chitosan concentration. This indicates that the carboxyl groups of the modified cotton fabric are involved in chemical reactions with chitosan. Here in this case, the carbonyl groups are masked and their values are decreased by increasing in the chitosan concentration. At higher concentration of the chitosan, the tensile strength of the fabric also increases, these two parameters are proportional to each other.

The tensile strength of the treated fabric has been studied under the following two conditions:

Condition 1–enzymatic oxidized fabric treated with 2% chitosan for 1h at different temperatures

Condition 2–enzymatic oxidized fabric treated with 2% chitosan at 60^0C for different time intervals

By raising the chitosan treatment temperature for 1 h, it adversely affects the tensile strength of the modified fabric. Most probably greater penetration of the highly mobile chitosan at higher temperatures in the fibriller structure of swollen cotton causes rigidity and, in term, decrement in tensile strength. Table 4 shows that the tensile strength decreases from 35.47 N/m^2 to 33.56 N/m^2 when the duration of chitosan treatment increases from 1 h to 3 h. At any event, however, these decrements are considered to be a direct consequence of rigidity conferred on cotton caused by chitosan penetration. As already stated, rigidity is proportionally related to the amount of chitosan on the fabric and the extent of penetration of former in the latter[31].

3.6 SEM Analysi*s*

The coating of oxidized fabric with chitosan has a significant influence on physico-mechanical properties of the obtained bicomponent fabric. Here, chitosan is filled on the rough surface made during the oxidation and thereby enhances the fabrics mechanical properties. These can be seen on the SEM images of the surfaces of the both oxidized [Fig. 2(a)], and chitosan coated fabric [Fig. 2(b)]. The surface of the oxidized fabric is little rough, which is caused by oxidation [Fig. 2(a)], while the surface of chitosan-coated fabric is very smooth, indicating that after treatment with chitosan, the surface of fabric is covered with a layer of chitosan. Also small grains, which are agglomerates of chitosan, can be seen on the surface of chitosan-coated fabric as shown in Fig. 2(b), indicating that the JF-NPs are bonded to the cellulosic fabric.

3.7 GC Studies on Flavour Retention Capacity of Fabric

Flavour can be analyzed either using sensory methods or with analytical instruments such as gas-chromatography (GC). As most flavour compounds are volatile, simplified GC methods may offer an appropriate technique for the separation and characterisation of volatiles in different samples[32]. The jasmine fragrance, encapsulated in the nano-

Table 3 — Effect of chitosan concentration on tensile strength and carbonyl contents of fabric

Chitosan concentration, %	Tensile strength N/m^2	Carbonyl content[a] , Meq/100g of fabric
0	38.45	28.67
0.5	38.47	22.34
1.0	38.57	17.34
1.5	38.67	14.45
2.0	38.76	9.67

[a] Calculated by enzymatic oxidation of cellulose.

Table 4 — Effect of time and temperature of chitosan treatment on tensile strength of the fabric

Time, h	Tensile strength, N/m^2
1	35.47
2	34.35
3	33.56
Temperature, ^{0}C	
40	36.45
60	35.34
80	32.67

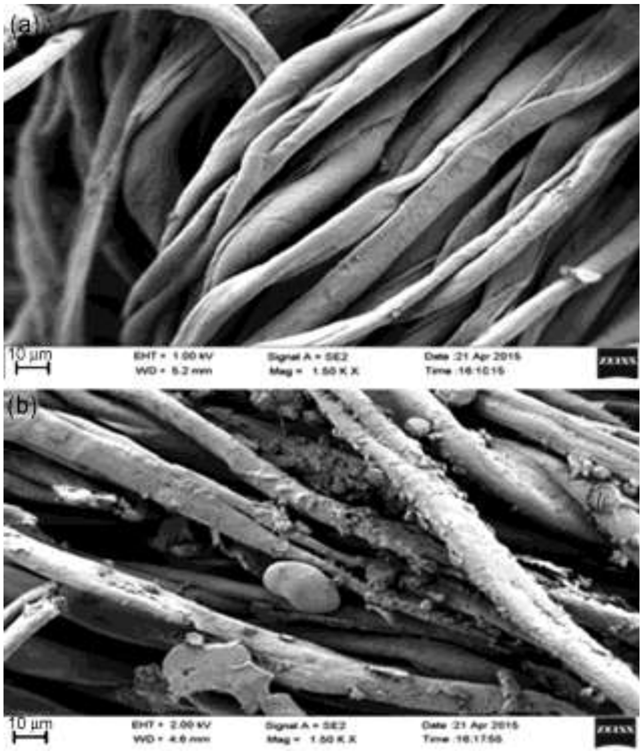

Fig. 2 — SEM images of (a) oxidized cotton fabric and (b) chitosan nanoparticles coated fabric

particles, has been confirmed by the GC analysis. The standard jasmine oil GC analysis is shown in Fig. 3.

The entrapped chitosan nanoparticles to the fabric are prepared as a control to analyse the GC result. The non-oxidized cotton fabrics (50 g) were just immersed in 0.3% JF-NPs solution inorder to entrap the particles (there will be no bond formation as non-oxidized fabric was take) for 2 h under vacuum (100 Pa) at 30^0C. Then, the finished fabrics were dried at 50^0C with the air current rate of 0.4 m/s for 1 h in the oven. The GC analysis proves that the chitosan nanoparticles are encapsulated with the jasmine fragrance and the retention capacity of the fabric bonded with JF-NP, compared to the entrapped JF-NP to the fabric. Jasmone has a boiling point at 146^0C, and the peak at 6.5 min is the largest peak obtained at 146^0C boiling point indicating that the nanoparticles have been encapsulated with the jasmine fragrance. The fabric was subjected to washings for 30 cycles and observed for the presence of the jasmine fragrance. Fabric with the bonded JF-NPs have retained the peak at 6.5 min, whereas the fabric with entrapped JF-NPs has no jasmine flavour left with the fabric. The loss in flavour is due to the vanishing of entrapped nanoparticles from the fabric after repeated

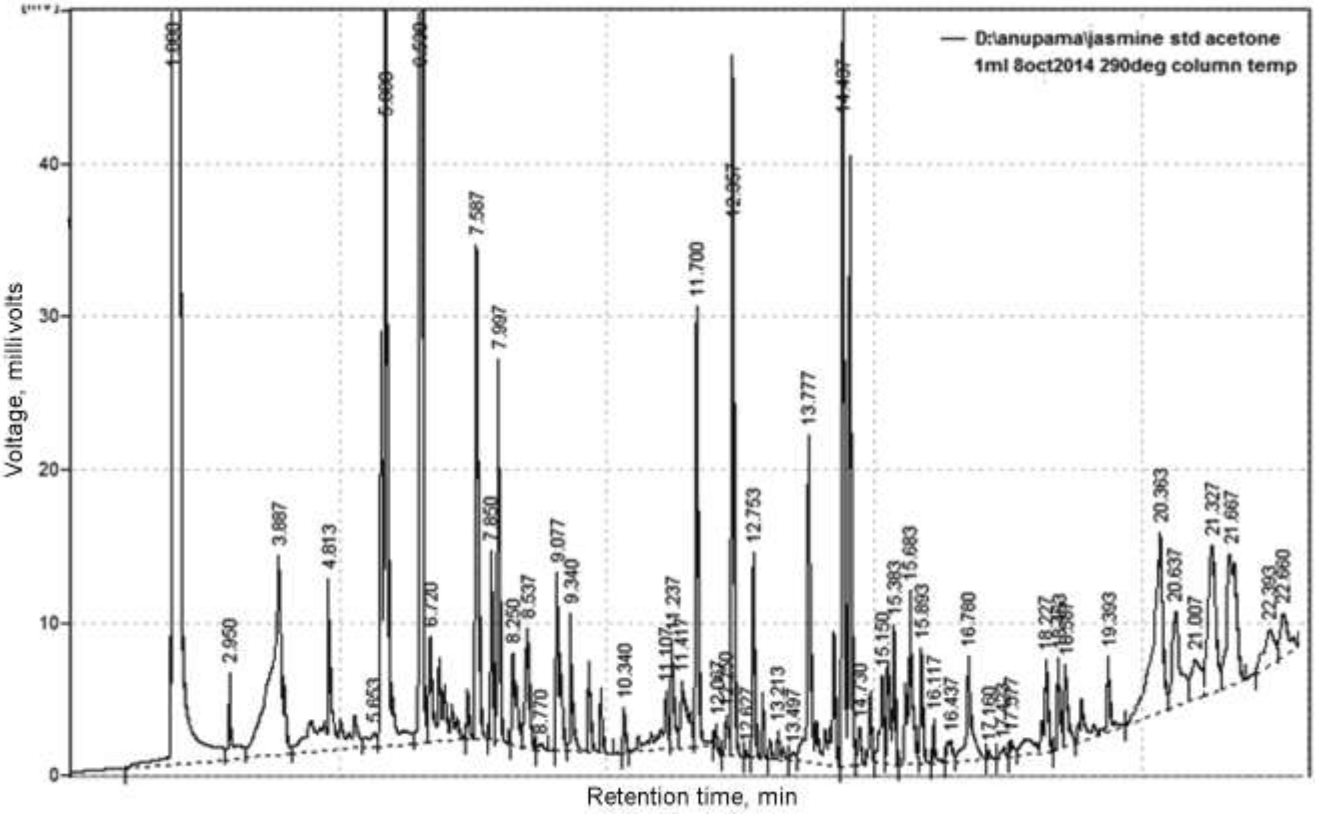

Fig. 3 — GC chromatogram of standard jasmine oil

washings. Nevertheless, the bonded nanoparticles to the fabric by a covalent bond stays in contact with the fabric, so the retention capacity of the bonded nanoparticles is found long-lasting compared to the entrapped nanoparticles.

4 Conclusion

A novel oxidation method has been introduced with an enzyme alcohol dehydrogenase. The *in vivo* pathway of the ADH in the yeast is applied to oxidize the cellulose. Thus, the aldehyde groups are bonded to the amino groups of the chitosan to form an schiff's base. FTIR spectroscopy analysis proves that the fabric is oxidized with a peak at 1720-1750cm^{-1} .The imino group at 1670 cm^{-1} and 1629 cm^{-1} in the spectrum of JF-NPs indicates the interaction between JF-NPs and cotton fabric. .Spherical JF-NPs (142 nm) attained via ionic gelation in emulsion system are observed by the SEM image. SEM also demonstrated the coating of the fragrance particles on the cotton fabric. Washing reduces the amount of fragrance on the entrapped finished cotton fabric, as compared to the bonded fabric with a lasting fragrance for 30 washing cycles. Thus, the strength of fabric is retained, even after the oxidation of cellulose and bonding of chitosan nanoparticles to the fabric, and the fabric exhibits sustained release of the fragrance for a longer time with no loss of nanoparticles through repeated washings. This novel oxidation technology has various applications, such as to prepare mosquito repellent, fragrance enhancing fabrics, etc.

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References

1 Mondal S, *Appl Thermal Eng*, 28 (2008) 1536.
2 Nelson G, *Rev Prog Color*, 321 (2001) 57.
3 Bakkali F, Averbeck S, Averbeck D & Idaomar M, *Food Chem Toxicol*, 46(2) (2008) 446.
4 Anandaraman S & Anne R, *WO Pat 016345* (2004).
5 Millqvist F, *Colloids Surf B*, 31 (2003) 65.
6 Mortenson M A & Reineccius G A, *Flavour Fragr J*, 23 (2008) 392.
7 Mortenson M A & Reineccius G A, *Flavour Fragr J*, 23 (2008) 407.
8 Paetznick D & Reineccius G**,** *Am Chem Soc*, 18 (2009) 272.
9 Yeo Y, Bellas E, Firestone W, Langer R & Kohane DS, *J Agric Food Chem*, 53 (2005) 7518.
10 Soper J C, Yang X G & Josephon DB, Method of encapsulating flavors fragrances by controlled water transport into microcapsules, *US Pat* 6106875, 2000.
11 Jason M E & Kalota DJ, Microencapsulation process by coacervation, *US Pat* 5540927, (1996).
12 Kant A, Linforth RST, Hort J & Taylor AJ, *J Agric Food Chem*, 52 (2004) 2028.
13 Mourtzinos I, Salta F, Yannakopoulou K, Chiou A & Karathanos V T, *J Agric Food Chem,* 55 (2007) 8088.
14 Magenheim B, Levy M Y & Benita S, *Int J Pharma*, 94(1–3) (1993) 115.
15 Li S, Boyter H & Qian L, *J Text Inst*, 96(6) (2005) 437.
16 Janjic S, Kostic M, Skundric P, Lazic B & Praskalo J, *Contemporary Materials*, 3(2) (2012) 215.
17 Schurz J, *Prog Polym Sci*, 424 (1999) 481.
18 Okuma Y, Ito Y & Endo A, *J Ferment Bioeng*, 71 (1991) 309.
19 Roberts G A F, *Chitin Chemistry* (The Macmillan Press, London), 1992.
20 Stoica R & Somoghi R M, *Digest J Nanomater Biostruct*, 8 (2013) 955.
21 Yunhui Xua, Xin Liub, Xuelan Liuc, Jiulong Tana & Hongling Zhuaa, *Carbohydrate Polym*, 111 (2014) 955.
22 Mouillet-Loevenbruck D, Nicolas M, Moulin G & Galzy P, *Ferment Bioeng*, 68 (1989) 404.
23 Yackel E C & Kenyon W O, *J Am Chem Soc*, 64 (1942) 121.
24 Saito T & Isogai A, *Biomacromolecules,* 5 (2004) 1983.
25 Kumar V & Yang T, *Carbohydrate Polym*, 48 (2002) 403.
26 Calvo P, Remunan-Lopez C, Vila-Jato J L & Alonso M J, *Pharma Res*, 14(10) (1997) 1431.
27 Jing Hu, Zuo-Bing Xiao, Ru-Jun Zhou, Shuang-Shuang Ma, Zhen Li & Ming-Xi Wang, *Text Res J*, 81 (19) (2014) 2056.
28 Mohammad shateri-Khalilabad, Mohammad E, Yazdanshenas, Ali Etamadifar, *Arabian J Chem,* 10 (2017) 2355.
29 Janjic S, Kostic M, Skundric P, Lazic B & Praskalo J, *Contemporary Materials*, 3(2) (2012) 215.
30 Liu XD, Nishi N, Tokura S, Sakairi N, *Carbohydrate Polym*, 44 (2001) 233.
31 Strnad S, Sauper O, Jazbec A & StanaKleinschek A, *Text Res J*, 78 (2008) 390.
32 Millqvist F, *Colloids Surf B*, 31 (2003) 65.