AROMATHERAPEUTIC CHARACTERISTICS OF COTTON FABRICS TREATED WITH ROSEMARY ESSENTIAL OIL

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The paper targets the production of textile fabrics with aromatic and antimicrobial properties by applying a chitosan film containing rosemary essential oil, at the surface level. The release in time of the essential rosemary oil was confirmed by colour and odour qualitative tests. The mechanical and comfort indices were also determined (rigidity, hydrophilic and hygroscopic characteristics), as well as the antibacterial properties. Another objective of the paper is to establish the kinetic model for the controlled release of the essential oil mechanism.

Keywords: rosemary essential oil, chitosan, cotton fabric, antimicrobial activity, mechanical and comfort indices

INTRODUCTION

The specialty literature records the present concerns on the acquisition of textile materials with antimicrobial properties, obtained by the application of polymers, quaternary ammonium salts, N-Halamine polymers and metallic compounds.[1-5]

A large amount of recent researches focus on biodegradable and biocompatible products with potential applications in the pharmaceutical domain.[6-8] Among them, the biologically active compounds isolated from plants present particular interest. The use of essential oils in the food industry, microbiology or as pharmaceutical products is based on their antibacterial and antifungal properties. Rosemary oil is widely used in the cosmetic industry, due to its aromatic, anti-inflammatory and antimicrobial behaviour.[9-10] Essential oils are less frequently used in the textile industry. As known, essential oils are adsorbed by the skin from the textile fabric through a mechanism of controlled release.[11]

The aim of the present paper is to study the therapeutic effect of textile materials treated with rosemary essential oil and to establish the kinetic model for the controlled release of the essential oil mechanism. The fixation of the biologically active compound on the textile support was obtained by the utilization of poly(sacharides). The combination of the two natural compounds created a unique system with improved antimicrobial properties. The treated samples were characterised by IR spectroscopy, comfort indices (stiffness, hydrophilic and hygroscopic characteristics), as well as by sensory evaluations. The antimicrobial activity of the material treated with rosemary oil was tested against both gram-positive and gram-negative bacteria.

EXPERIMENTAL

Materials

Rosemary essential oils (extract of the *Rosmarinus officinalis Linne* species) were pur-

chased from Fares SA Romania. Chitosan (molecular weight: 100,000-300,000; degree of deacetylation: 85) was obtained from Fluka Chemie GmbH, Switzerland, while Tween 80 was supplied by Merck, Germany.

Commercial scoured and bleached 100% cotton fabrics were used in the experiment.

Chitosan emulsion

The chitosan solution was obtained by dissolving chitosan in a 1% acetic acid solution (to assure the complete dissolution of chitosan), which was then stirred for 24 h at room temperature, filtered for removing impurities and sterilized at 121 °C for 15 min. An essential oil/Tween 80 emulsion was added to the previously prepared solution, under stirring for 10 min at room temperature. The composition of the emulsions for the different treatments is given in Table 1.

Table 1
Treatment variants

Concentration of treating compounds			
Treatment variants	Essential oil, % (w/v)	Chitosan, % (w/v)	Tween 80, % (w/v)
V.1.	0.23	0.225	1.0
V.2.	0.45	0.225	1.0
V.3.	0.90	0.225	1.0
V.4.	1.35	0.225	1.0
V.5.	0.90	0.100	1.0
V.6.	0.90	0.175	1.0
V.7.	0.90	0.250	0.5
V.8.	0.90	0.250	2.0

Applying chitosan to cotton fabric

100% cotton fabrics (0.8 g) were padded twice with the chitosan dispersion (V.1.-V.8.) to a wet pick-up of 110%. The padded fabrics were dried at 60 °C for 30 min.

FTIR analyses

The chemical changes occurring at the surface of cotton fibres, as a result of chitosan and essential oil treatments, were recorded by FTIR–ATR spectroscopy. The FTIR spectra were recorded on a FTS 2000 Digilab spectrophotometer, over the 4000-250 cm^{-1} range, at a resolution of 4 cm^{-1}, with a special Merlin Digilab programme.

Study of essential oil release capacity

A known amount of 100% cotton tissue, treated according to Table 1, was introduced into a known volume of 0.3% (w/v) Tween 80 solution and maintained under stirring at 30 °C. At previously established periods, 5 mL of sample were withdrawn, filtered and analysed by photocolorimetry. To maintain a constant solution volume, 5 mL of Tween 80 (0.3%) were added after each withdrawal.

The absorbance values of the withdrawn samples were determined at 260 nm on a UV-VIS Camspec M 501 Single beam Scanning spectrophotometer. The unknown oil concentration was calculated with a previously measured calibration curve.

Sensory evaluation

Sensory evaluation was tested on a group of 10 subjects (persons with ages between 20 and 30 years). The samples treated with rosemary essential oils (variants V.1-V.4) were stored at room temperature and smelled every five days (under the same conditions).

Colour measurements

The release of rosemary essential oils over time was qualitatively evidenced by chromatic measurements. Thus, the samples treated with essential oil were coloured with Sudan Red (C.I. Solvent Red I), dissolved in chloroform (2 g/L) through impregnation, then squeezed and dried at room temperature. The colour of the samples was assessed on a Spectraflash 300® of DATACOLOR® spectrophotometer. The colour differences (ΔE) between untreated and treated samples were calculated with a Micromath 2000® programme.

Comfort indices

The change of the surface characteristics of 100% cotton textile material treated with rosemary essential oil was determined by the measurement of comfort indices, such as

hygroscopicity and stiffness [STAS 12749-89; STAS 9005-79; SR ISO 2313-97].

Antimicrobial testing

The sensitiveness of *Staphylococcus Aureus* (ATCC–6538) and of the *Escherichia coli* (ATCC–10536) bacteria to rosemary essential oil was tested *in vitro* under optimum and standard conditions of inoculation (lawn culture, inoculum, incubation time, etc).[12] To this end, the Kirby-Bauer disc diffusion method was applied.[13]

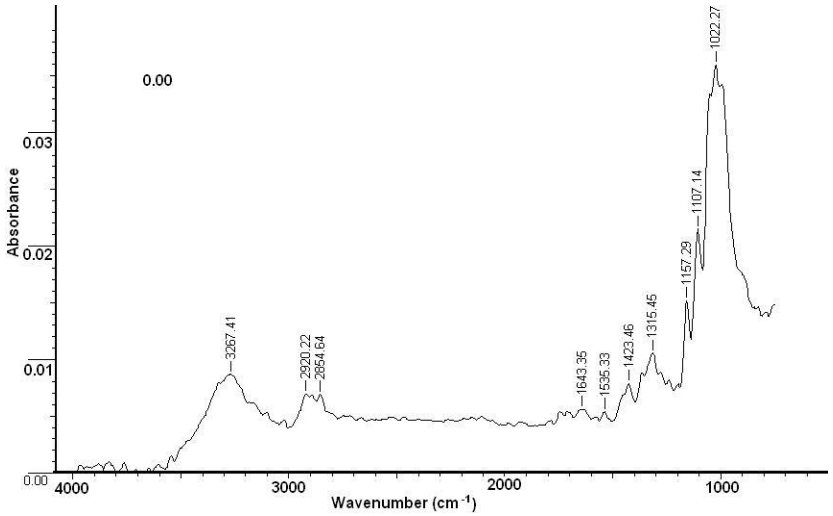
After placing the untreated and treated woven circular samples on a solid surface with a bacterial culture, the active antimicrobial substance was diffused within the environment, a constant decrease of the concentration gradient from the sample centre toward its edges being noticed. After 24 h of incubation at 37 °C, two distinct areas could be observed: one in which the microbial growth was restricted by the high concentrations of the antimicrobial substance and another in which oil concentration was too low to restrict growth.

RESULTS

Surface characterisation

The presence of a chitosan film on the cotton textile support was confirmed by FTIR analyses (Fig. 1). The chemical interactions between the chitosan film and the cotton fibre are evidenced by the change of the peaks from the characteristic spectra (Table 2).

The shifting of the peaks from 3267.41 cm^{-1} to 3271.26 cm^{-1} is due to the insertion of the NH_2 groups involved in the formation of hydrogen bonds from chitosan.



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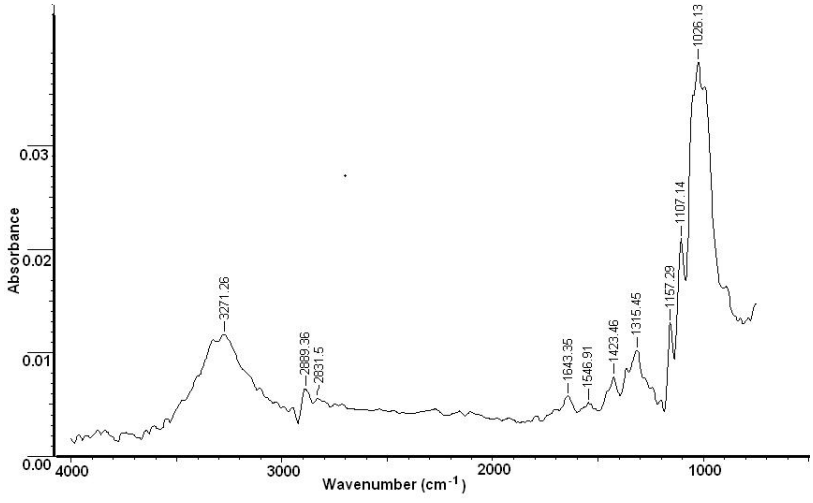

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Figure 1: FTIR spectra of cotton (a) and cotton+chitosan film (b)

Table 2
Characteristic peaks of functional groups

Groups	Type of vibration	IR vibration frequency, cm^{-1}	
		Cotton	Chitosan film
ν_{OH} (associated OH)	stretching vibration	3267.41	3271.26
ν_{CH}	asymmetric stretching vibration	2920.22	2889.36
ν_{CH}	symmetric stretching vibration	2854.64	2831.6
$\nu_{C=O}$ (CHO)	stretching vibration	1643.36	1643.36
ν_{NH}	wagging vibration	1535.33	1546.91
ν_{OH} (COOH)	wagging vibration	1423.46	1423.46
$\nu_{OH \text{ or } CH2}$	wagging vibration	1316.46	1315.45
ν_{C-O} (C-O-C)	stretching vibration	1157.29	1157.29
ν_{OH} (R_2CH-OH)	stretching vibration	1107.14	1107.14
ν_{C-O} (CH_2-OH)	stretching vibration	1022.27	1026.13

The shifting of the peaks from 2920.22 and 2854.64 to 2889.36 and 2831.6, respectively, is attributed to the overlapping of the CH=O and CH stretching vibrations from cotton and chitosan, while the change of vibration frequency from 1535.33 to 1546.91 can be explained by the formation of hydrogen bonds.

Controlled release kinetics of rosemary essential oil

The results obtained on the controlled release kinetics of rosemary essential oil *versus* nature and concentration of components from the chitosan film on the textile support are shown in Figures 2-4.

The results evidence a decrease in the rosemary oil release capacity with the increase in chitosan concentration, which could be explained by the fact that higher amounts of chitosan reduce the intermolecular spaces, causing a more difficult release of the essential oil from the chitosan film. As for the Tween 80 concentration, it had been observed that, with its increase, the amount of the released essential oil decreased, as due to the interactions between the hydrophilic groups of the Tween 80 non-ionic agent and those of chitosan, on the one hand, and to the interactions between the Tween 80 hydrophobic groups and those of the essential oil compounds, on the other hand.

The release mechanism for the biologically active compound from the chitosan film is primarily based on the diffusion process of the oil molecules, the dimensions of which are relatively small compared to those of the polymers. To check whether the controlled release follows a Fickian model, the authors started from the kinetic equation describing the amount of biological compound released in time: [11]

$$M_t / M_\infty = k \cdot t^n \quad (1)$$

where:

M_t – amount of biologically active compound released at time t;

M_∞ – amount of biologically active compound released at equilibrium;

k – constant regarding the release rate;

n – process order.

The linearization of this equation through logarithmation allowed the graphical determination of constants k and n. The values obtained are shown in Table 3.

The kinetic curves evidence two stages for the release of the biologically active compound (the former – from 0 to 3 h, the latter – from 3 to 6 h). The experimental value of the release exponent for the first stage indicates the diffusion of solvent through the chitosan matrix. Therefore, the release of the biologically active compound follows a Fickian diffusion mechanism.

For the next time period (3-6 h), the value of the release coefficient indicates a non-Fickian mechanism ($0.5 < n < 1$). In this case, the release of the active compound is controlled both by Fickian diffusion and by the relaxation process of the matrix. For $n > 1$, a mixed release mechanism occurs (non-Fickian, zero-order release).

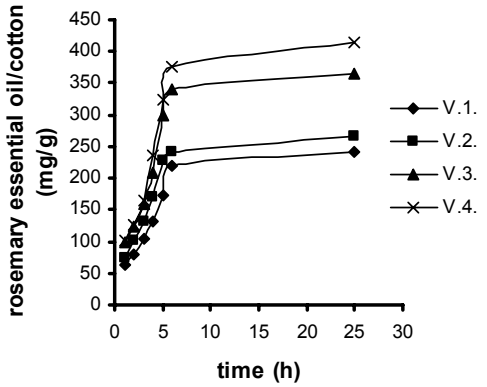

Figure 2: Effect of essential oil load on controlled release kinetics

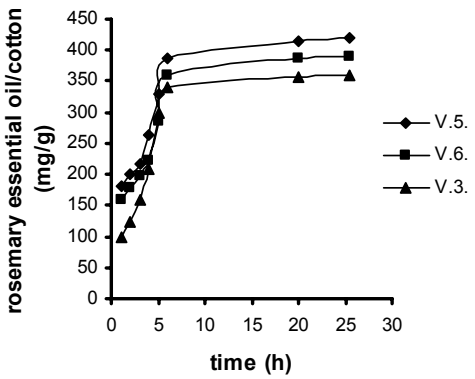

Figure 3: Effect of chitosan load on release kinetics

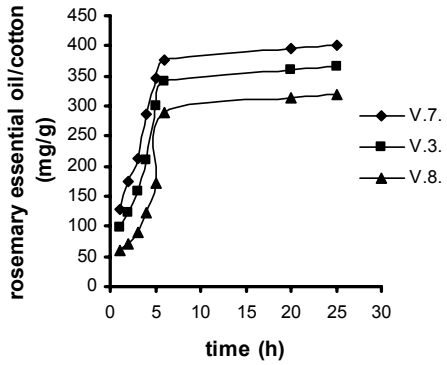

Figure 4: Effect of Tween 80 concentration on controlled release kinetics

Table 3
Kinetic parameters

Treatment variants	Kinetic parameters					
	0-3 h			3-6 h		
	k	R^2	n	k	R^2	n
V.1.	1.3693	0.9638	0.4553	2.0234	0.9889	1.0568
V.2.	1.2895	0.9946	0.5134	1.72	0.9726	0.9271
V.3.	1.3322	0.9695	0.4291	2.099	0.9834	1.1457
V.4.	1.4355	0.9548	0.4279	2.2713	0.993	1.2312
V.5.	0.8486	0.995	0.1719	1.5912	0.9912	0.8367
V.6.	0.9128	0.9847	0.1885	1.7047	0.9478	0.872
V.7.	1.1408	0.9985	0.4538	1.5303	0.9788	0.8389
V.8.	1.3485	0.9695	0.4291	2.1153	0.9834	1.1457

Sensory testing

The mean values of the experimental results obtained after the sensorial evaluation of the treated samples (variants I-IV) are showed in Table 4.

From the experimental data, one can conclude that the scent intensity of the rosemary essential oil-treated samples increases with treatment concentration. The smell strongly persists for 15 days and then begins to gradually decrease.

Colour measurements

The results on the colour differences recorded between the samples treated with rosemary essential oil and the untreated ones (V.1.-V.4.), after staining both types of samples with Sudan Red, are shown in Figure 5.

The results obtained confirmed the release in time of the rosemary essential oil. A controlled release leads to a decrease in oil concentration on the textile material, causing

the increase of the ΔE values for the samples coloured with the Sudan Red lyophilic dye.

Comfort indices

The values obtained for the comfort indices are shown in Table 5.

The analysis of the experimental data shows that the samples treated only with chitosan evidence a higher hygroscopicity than that of the untreated samples, as due to the presence of the hydroxyl and aminic groups from chitosan, which provide the active centres for humidity sorption.

The presence of a Tween 80 emulsifier (polyoxyethylene (20) sorbitan monooleate) in the chitosan film leads to an increase in the hygroscopicity of the treated fabric, due to its hydrophilic groups. The incorporation of rosemary essential oil into the chitosan film decreases the water vapour permeability.

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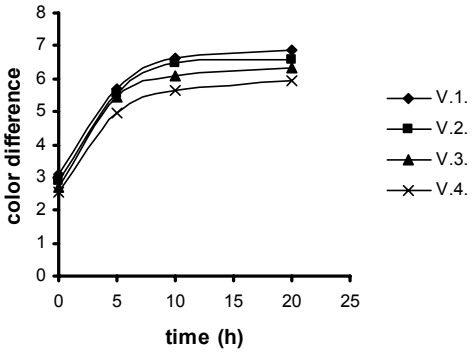

Figure 5: Variation of colour differences over time for the samples treated with rosemary essential oil

Table 4
Sensorial evaluation of scent intensity

Treatment variants	Odour intensity*						
	1 day	5 days	10 days	15 days	20 days	25 days	30 days
V.1.	++	++	++	++	++	+	+
V.2.	++++	++++	++++	++++	+++	++	+
V.3.	+++++	+++++	+++++	++++	+++	++	+
V.4.	++++++	++++++	++++++	+++++	++++	+++	++

* very very strong ++++++ ; very strong +++++ ; strong ++++; common +++; weak ++; very weak +

Table 5
The effect of treating agents on comfort indices

Concentration of components (%)			Hygroscopicity (%)	Hygroscopicity index ($g/m^2 \cdot h$)	Stiffness (mm)
Chitosan	Tween 80	Rosemary essential oil			
0	0	0	12.61	11.715	4.0
0.225	0	0	11.94	14.208	7.0
0.225	1	0	13.88	12.161	6.0
0.225	1	0.23	12.32	12.726	5.8
0.225	1	0.45	12.82	12.696	5.6
0.225	1	0.90	13.10	12.587	5.2
0.225	1	1.35	13.26	12.557	4.6

As to the stiffness of the treated samples, a decrease in stiffness with the increase in essential oil concentration may be observed. Consequently, besides the improvement of the antimicrobial characteristics, the essential oil is also an emollient (reducing the fabric rigidity induced by chitosan).

Antimicrobial analysis

Assessment of the sensitiveness/ resistance of the tested microorganism has been established according to the diameter of the inhibition zone: the larger the diameter, the more sensitive the germ is.[14] The analysis of the data shown in Table 5, as well as the photos from Figures 6 and 7, confirm the bactericidal action of the tested rosemary oil, manifested in the case of both gram-positive (*Staphylococcus Aureus* ATCC-6538) and gram-negative (*Escherichia coli* ATCC-10536) bacteria.

The different sensitiveness of the two bacterial species to the tested oils could be correlated with the ultrastructure of the cellular wall, which is different in gram-positive and gram-negative bacteria.

Table 6
Inhibition area diameters (mm) for rosemary oil-treated material

Treatment variants	Microorganism test	Diameter of inhibition zone (mm)
V.1.	*Staphylococcus aureus*	23
	Escherichia coli	25
V.3.	*Staphylococcus aureus*	26
	Escherichia coli	29

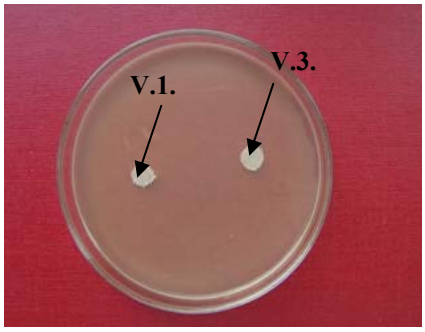

Figure 6: Inhibition zone of *Staphylococcus Aureus* bacterium on essential oil-treated cotton fabric

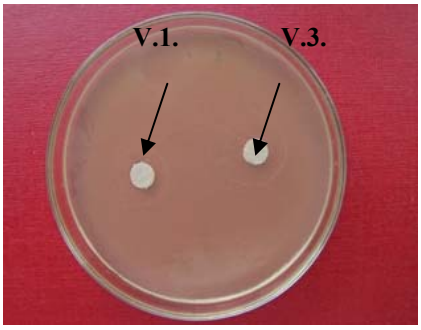

Figure 7: Inhibition zone of *Escherichia coli* bacterium on essential oil-treated cotton fabric

CONCLUSIONS

Materials with aromatherapeutic properties are obtained by the treatment of cotton fabrics with rosemary essential oil, in the presence of chitosan. FTIR analysis confirmed the presence of the essential oil on the textile material surface. Chromatic measurements confirmed the controlled release of the rosemary oil. The samples treated with rosemary essential oil present maximum smell intensity in the first 15 days. The antimicrobial activity of the material treated with rosemary oil was tested for *Staphylococcus aureus* and *Escherichia coli* bacteria.

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