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Antibacterial polyester fabrics via diffusion process using active bio-based agents from essential oils

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ABSTRACT

Antimicrobial products such as silver nanoparticles and QACs - Quaternary ammonium compounds, used to produce antibacterial textiles, are being targeted due to environmental concerns. Most of the active antibacterial molecules from essential oils are small molecules with a solubility parameter (δ) close to that of polyester –PET-poly(ethylene terephtalate) ($\delta = 21.9\ MPa^{1/2}$ at 129.4 °C), and can therefore be potentially used to functionalize polyester fabrics using diffusion process. The aim of this paper was to explore the diffusion process to produce antibacterial polyester textiles using active agent(s) from essential oils.

Diffusion process was explored at high temperature (130 °C) and pressure, to functionalize polyester fabric (PET) with five different bio-based antimicrobial agents isolated from essential oils. Thymol, geraniol, cinnamaldehyde, ortho-vanillin and para-vanillin, were selected based on their solubility parameter (in the range of 19 to 25 $MPa^{1/2}$), and small their molecular size (molecular weight < 155 g/mol).

Both quantitative and qualitative tests were used to analyze antibacterial activity of the functionalized polyester fabrics. Quantitative absorption method (ISO20743) showed that most of the functionalized polyester textiles exhibit antibacterial activity towards gram positive (*Staphylococcus aureus*) and gram negative (*Klebsiella pneumoniae*) bacteria, though no inhibition zone was observed with the qualitative agar diffusion method. Spectrophotometric analysis of the functionalized fabrics confirmed the diffusion of the active agents inside the PET fibers in between macromolecular chains, as PET fibers became pale yellow.

Antibacterial polyester fabrics functionalized with O-vanillin and cinnamaldehyde exhibited good wash durability.

Thermogravimetric analysis showed that most of the active agents (except thymol), have maximum stability temperature (< 5% weight loss) higher than the diffusion temperature (130 °C) used. Some degradation products may be formed, which may also diffuse inside the PET fiber, but further studies need to be considered in future.

The toxicity issue is also discussed with the view of using the antibacterial polyester textiles for outdoor applications.

1. Introduction

Antimicrobial textiles can be found in many fields such as hospitals, to limit the spread of diseases and for wound healing or even in apparel or sportswear for odor control, but their application can also be extended to other applications such as textiles for architecture. Commercial antimicrobial products have already been developed, but some of the most efficient compounds such as silver nanoparticles, triclosan, and quartenary ammonium compounds (QACs) are targeted due to the environmental concerns (regulation 528/2012) (Boholm and Arvidsson, 2014; Panyala et al., 2008; Zhang et al., 2015). Indeed REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) is a regulation of the European Union, adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals, while enhancing the competitiveness of the EU chemicals industry. This regulation highlighted the fact that silver nanoparticles, triclosan, and quartenary ammonium compounds (QACs) used for antibacterial textiles, are toxic especially for aquatic life with

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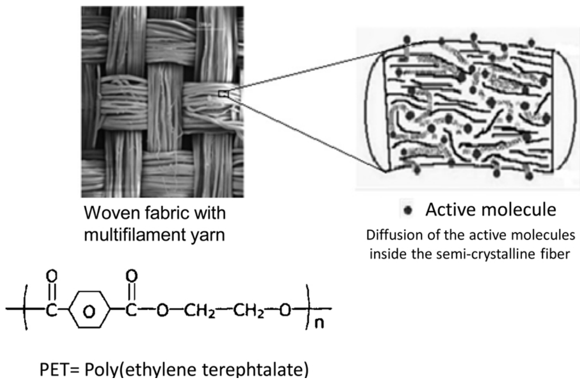


Fig. 1. Polyester –PET made of woven multifilament yarn and, the diffusion of active molecules inside the semi-crystalline PET fiber.

long lasting effect. Thus, new biocide is needed in order to replace the actual ones. (European Chemicals Agency, 2019, http://echa.europa.eu/, 07/2018; Marambio-Jones and Hoek, 2010; Zhang et al., 2015)

Polyester fiber made of poly(ethylene terephthalate)-PET (Fig. 1), is an important synthetic fiber holding the highest market share (> 50%) in textile industry, used for apparel, medical and architectural applications. Functionalization of such fabrics with bio-based renewable antibacterial molecules will help to improve environmental issues.

Essential oils are natural bio-based multicomponent products containing active agent(s) responsible for fragrances (Buchbauer and Jirovetz, 1994) but also antibacterial activity. In literature, different essential oils have been shown to exhibit antibacterial activity against a broad range of microorganisms. Various types of bacteria have been tested such as *Escherichia coli*, *Klebsiella pneumoniae*, or *Pseudomonas aeruginosa* (gram negative) but also *Bacillus subtilis* and *Staphylococcus aureus (*gram positive) at different concentrations. Growth of all these bacteria were evaluated in presence of cinnamon, clove, geranium, lemon, lime, orange and rosemary oils and a significant inhibitory effect was exhibited (Nazzaro et al., 2013. Some essential oils are known to be also effective against fungi (Xie et al., 2017), (Abbaszadeh et al., 2014).

Cinnamon, clove and lime oils were found to be inhibit growth of both gram-positive and gram-negative bacteria (Prabuseenivasan et al., 2006). (Shelef, 1984)

Essential oils are mostly used for food applications, and used to a lesser extent to produce antibacterial textiles. Some essential oils have been immobilized on the textile fiber surface using microcapsules which break to release the essential oil (Boh and Knez, 2006). Nanocapsules such as cyclodextrins (Martel et al., 2002) and textile chemical finishings (Sayed et al., 2017) have been used to functionalize textiles with essential oils. The functionality of such textiles is non-lasting as the microcapsules/nanocapsules and the finishings lose all their contents after few washes. Moreover, extra chemicals are necessary for immobilization of the essential oil to the textile. In this paper, the aim was to explore diffusion process using exhaustion method to functionalize polyester-PET fabrics with active agent(s) from essential oils to produce antibacterial polyester textiles. Indeed, the diffusion method used to functionalize the PET fiber with the active agents, is similar to dyeing, and it can be decomposed into different steps. First, the active molecules which are in dispersion form in the aqueous medium migrate towards the fiber and sorb on the fiber surface to form a boundary layer and then, the sorbed molecules biomolecules diffuse progressively inside the fiber (Fig. 2).

Exhaustion method has been successfully used to functionalize wool fabrics with natural dyes from green tea, madder, turmeric, and Chinese gall to produce antibacterial wool fabrics (Ghaheh et al., 2014; Zhang et al., 2014). Recent papers published by our team showed that diffusion method can be appropriate to obtain antibacterial polyester textiles, using curcumin (Kerkeni et al., 2011) and madder (Agnhage et al., 2017). Our previous work also showed that ortho-vanillin can act as carrier to improve dye diffusion inside PET fiber during polyester fabric dyeing (Pasquet et al., 2013). The challenge is to achieve relevant results namely a strong antibacterial activity for the PET fabric, using different active agents from different essential oils.

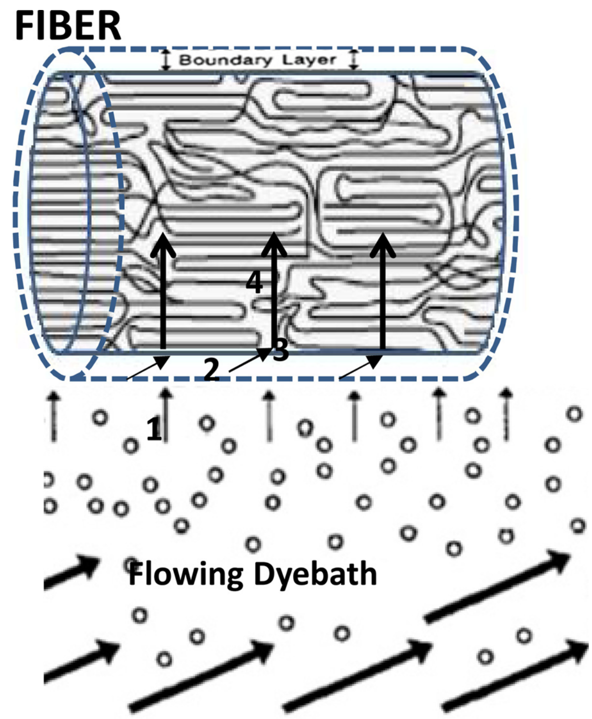


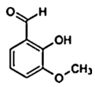
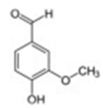
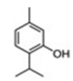
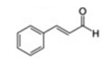
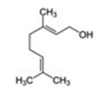
Fig. 2. Steps of the diffusion process: Diffusion of dye or active molecule from the waterbath (1) through the diffusional layer (2), followed by sorption onto the fiber surface (3) and diffusion into the fiber interior (4).

Most of the active antibacterial molecules from essential oils are small molecules with a solubility parameter close to that of polyester–PET fabrics. This means that, they can be potentially used to functionalize polyester fabrics using diffusion process used generally to dye polyester fabrics (Roy Choudhury, 2011). Indeed, concerning transport of molecules through PET fibers, Slark et al. specify that this transport is function of both diffusivity and solubility of the molecule inside the PET fiber (Slark and Hadgett, 1999). Solubility parameter of the active antibacterial molecule must be very close to that of the polyester-PET to allow the diffusion of the antibacterial molecules inside the PET fiber. Thus molecules with solubility parameter close to that of PET ($\delta = 21.9\ MPa^{1/2}$ at 129.4 °C) (Slark and Hadgett, 1999), can potentially diffuse inside the PET fiber (see Fig. 1).

Diffusion process (see Fig. 2) can take place only at high temperature (above the glass transition temperature of PET-polyester fabric) which allows mobility of PET polymer chains in the amorphous regions of the fiber, and the creation of spaces between the macromolecular chains, allowing molecules of small size to diffuse rapidly inside the fiber. Experiments carried in our laboratory using DSC- Differential scanning calorimetry, confirmed that the polyester fabric used has a Tg (glass transition temperature) of 80 °C, a value similar to that used by Slark et al. in their studies on polyester fabrics dyeing (Slark and Hadgett, 1999).

Five different antibacterial compounds were tested: thymol, geraniol, cinnamaldehyde, ortho-vanillin, para-vanillin, which are pure extract of active component in essential oils (Burt, 2004). These compounds present antibacterial (Shelef, 1984) and antifungal activities (Abbaszadeh et al., 2014). They were solubilized in aqueous medium before being used for PET fiber functionalization by diffusion method at 130 °C under high pressure conditions (HTHP). The quantitative

Table 1
List of the selected active agents from essential oils, with their name, chemical formula (*All data were obtained from pubchem web site: open chemistry database*).

	0rtho-Vanillin	Para-Vanillin	Thymol	Trans Cinnamaldehyde	Geraniol
Natural Origin-CROP	 Vanilla	 Vanilla	 Thyme	 Cinnamon	 Rose, Geranium,
Physical state at RTP	powder	powder	powder	liquid	liquid
Color in aq. solution	Bright yellow	Colorless	Colorless	yellow	colorless
Cas Number	148-53-8	121-33-5	89-83-8	104-55-2	106-24-1
Chemical structure					
IUPAC name	2-hydroxy-3-methoxybenzaldehyde	3-hydroxy-4-methoxybenzaldehyde	5-methyl-2-(propan-2-yl)phenol	trans-3-Phenyl-2-propenal	trans-3,7-dimethylocta-2,6-octadien-1-ol
Molecular Weight g/mol	152	152	150	132	154
Vapor pressure (mm Hg) at 25 °C	6. 10^{-3}	2. 10^{-3}	1.6. 10^{-2}	2.89. 10^{-2}	3. 10^{-2}
TPSA*	35.5	46.5	20.2	17.1	20.2

(All data were obtained from pubchem web site: open chemistry database).
* TPSA = Topological polar surface area.

antibacterial absorption method and agar diffusion test (Balouiri et al., 2016) were used to test activity of the functionalized textiles against gram positive (*Staphylococcus aureus*) and gram negative (*Klebsiella pneumoniae*) bacteria.

2. Materials and methods

2.1. PET fabric

A 100% polyester (PET-poly(ethylene terephtalate) twill woven fabric of density 180 g/m^2 was used. The fabric was made from multi-filament yarn, each filament having a diameter of 15 µm (see Fig. 1). The polyester fabric was cleaned to remove impurities using Soxhlet method with petrol ether, then with ethanol. Then the samples were rinsed in three different water-baths with distilled water, before being dried and ready for use.

2.2. Active agents from essential oils used

Five bio-based molecules found in renewable natural products were selected (Table 1). Ortho-vanillin and para-vanillin are the most important component of vanilla aroma. Cinnamaldehyde is the principal component (90%) of cinnamon oil, and thymol is the essential component of thyme oil. Geraniol is the primary part of rose oil but it also occurs in small quantities in geranium, lemon, and many other essential oils. Ortho-vanillin, cinnamaldehyde, and geraniol were obtained from Sigma Aldrich while para-vanillin and thymol were purchased from Acros Organics and Laboranor.

The chemical formula, the CAS number, the color in aqueous solution, the vapor pressure at 25 °C, and other data were obtained from an open chemistry database (Pubchem web site), see Table 1.

Qualitative antibacterial test carried on agar-plate showed that all active agents used alone, showed antibacterial behavior against *Staphyloccoccus aureus*, with the appearance of more or less important inhibition zones (see Fig. 3).

2.3. Calculation of solubility parameters of the active agents used

The total solubility parameter of each active agent 'δ_t' called the Hildebrand solubility parameter was calculated from Hansen solubility parameters (HSP). Charles Hansen has established that the solubility parameter of a solvent or polymer is the result of the contribution of three types of interactions: dispersion forces (δ_d), polar interactions (δ_p) and hydrogen bonds(δ_h) (Hansen, 2007; The HSP values of all active agents except Geraniol, were obtained from the web-based solubility parameter data base which considers the HSP values (Abbott, 2018) and that of the Geraniol from a past published paper (Paseta et al., 2016). The Hildebrand solubility parameter δ_t was calculated using Eq. (1).

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{1}$$

Table 2 gives more detailed values of the HSP and the Hildebrand solubility parameter calculated from the HSP values.

The Hildebrand solubility calculated from HSP (Hansen, 2007) for PET is given in Table 2 (δ_t = 21.4 MPa$^{1/2}$) and is close to that predicted by Slark (Slark and Hadgett, 1999), that is δ = 21.9 MPa$^{1/2}$ at 129.4 °C for polyester fiber based fabrics. Indeed it has been shown that temperature variation influences very slightly the solubility parameter of polymers (Hansen, 2007).

2.4. Functionalization using diffusion method by exhaustion procedure

The diffusion procedures were performed in accordance with the general dyeing method using the diffusion method in a HTHP (High Temperature and High Pressure) Beaker Dyeing Machine, at 130 °C and a liquor ratio of 1:20, with a ratio of active agent with respect to fiber weight (o.w.f) of 10% (i.e. 10 g of active agent for 100 g of fabric).

5 g of polyester fabric was placed in a 200 ml beaker containing 100 ml of aqueous 1% ethanol-water solution with 0.5 g of active agent. The temperature of the exhaustion bath was then gradually raised (about 2 °C/min) to about 130 °C, and was kept constant at this temperature for about 45 min. The bath was cooled and the fabric was squeezed, rinsed thoroughly with hot water and air dried. No surfactant was added in the diffusion bath.

2.5. Antibacterial tests

Two different antibacterial tests were carried out. The agar diffusion test (ISO20645:2004) and the absorption method (ISO20743:2003) were performed using two different bacteria: a gram positive (*Staphyloccocus aureus* - ATCC 6538) and a gram negative bacterium (*Klebsiella pneumoniae* -ATCC4352).

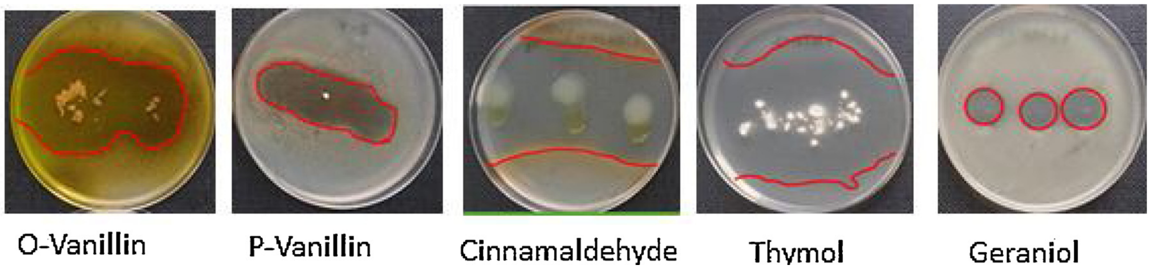


Fig. 3. Qualitative bacterial inhibition zones observed (after 24 h) when small quantities of each pure active agent was placed on an agar dish plated with *S. Aureus* bacteria.

Table 2
Partial Hansen solubility parameters, and the total Hildebrand solubility δ_t parameter of active agents compared to PET polymer.

Solubility parameter In $MPa^{1/2}$	δ_d	δ_p	δ_h	δ_t
0-Vanillin	19.4	9.8	11.2	**23.8**
P-Vanillin	18.6	10.6	13.8	**25.4**
Cinnamaldehyde	19.4	12.4	6.2	**23.4**
Thymol	19	4.5	10.8	**22.3**
Geraniol	16.9	4.16	7.61	**19**
PET	**18.2**	**7.3**	**7.9**	**21.4**

2.5.1. Agar diffusion test (ISO20645:2004)

The level of antibacterial activity is assessed by examining the extent of bacterial growth in the contact zone between the agar and the fabric specimen and, if present, the extent of the inhibition zone around the specimen. 10 (± 1) mL of nutritive agar medium were poured on Petri dishes. Inoculums of bacteria (0.5 ± 0.1) mL with a bacterial culture of 1–5 × 10^8 CFU/mL were then poured on the agar media. Circular textiles sample of $10cm^2$ were then placed on the surface. To maintain good contact, if necessary, a sterilized inox ring was placed on the surface of the textile sample to guarantee good contact between the fabric and the agar. Immediately after placing textile samples on the agar, petri dishes were placed in incubation for 24 h at 37 (± 1) °C. The inhibition zone was measured. The halo is the zone free from bacteria near the sample edges. Contact zone under the tested textile sample was analyzed visually to check whether bacteria growth occurred or not.

2.5.2. Absorption method (ISO 20743:2003)

This test is used to quantitatively measure the antimicrobial activity of textile samples. The treated and untreated PET samples were cut in small pieces (of 0.4 g) and placed in a glass vial. Six test samples in individual vials plus six separate vials of control samples (untreated samples) constitute one test. Each sample and each control sample were inoculated with 200 µl of bacterial suspension adjusted to 1–3 × 10^5 CFU/mL.

Directly after inoculation (0 contact time), an extraction of the bacteria present on three of the six samples of each series was performed, and bacterial count was determined using the plate count method. Then, other vials were incubated at 37 °C during 24 h, after which the bacterial count was performed. For each trial the number of “viable” active bacteria was calculated and then expressed in “log”.

The growth value and the activity values were then computed. We proceed as follows:

$$F = C_t – C_0 \tag{2}$$

Where, F is the growth value on the control sample, C_t is the common logarithm of the arithmetic average of the numbers of bacteria obtained from three test control specimens after 24 h incubation. C_0 is the common logarithm of the arithmetic average of the numbers of bacteria obtained from three control specimens immediately after inoculation (0 contact time).

The test is judged to be effective, when the growth value is ≥1 and when the difference in extremes for the three controls immediately after inoculation as well as after incubation is ≤1 log10.

The calculation of the activity values is obtained according to the following formula:

$$A = (C_t - C_0) - (T_t - T_0) = F\text{-}G \tag{3}$$

Where, A is the antibacterial activity value, F is the growth value on the control fabric (F = C_t–C_0), G is the growth value on the antibacterial treated sample (G = T_t–T_0), T_t is the common logarithm of the arithmetic average of the numbers of bacteria obtained from three antibacterial testing specimens after 24 h incubation, and finally T_0 is the common logarithm of the arithmetic average of the numbers of bacteria obtained from three antibacterial testing specimens immediately after inoculation.

The obtained value for the antibacterial activity (A) can be exploited by the following way:

- If A > 3, the antibacterial activity is strong
- If 2 < A < 3, a significant antibacterial activity is detected
- If A < 2, the antibacterial activity is insufficient.

2.6. Spectrophotometric analysis of fabric sample

Reflectance of the functionalized samples “R” was measured with a Konica-Minolta CM3610 A spectrophotometer for wavelength-λ varying from 360 nm to 700 nm). Relative color strengths “K/S” were automatically calculated from the reflectance values by the software using the Kubelka-Munk Eq. (1) (Kerkeni et al., 2011). K/S value is directly related to the color yield of the fabrics:

$$\frac{K}{S}(\lambda) = \frac{(1 - R(\lambda))^2}{2R(\lambda)} \tag{1}$$

where, K refers to coefficient of absorption, S is the coefficient of scatter, and R is fractional reflectance.

2.7. Thermal stability analysis

As the diffusion process was carried at high temperature-130 °C, there is possibility of thermal degradation of the active agents (Turek and Stintzing, 2013; Olmedo et al., 2015). The thermal stability of the tested compounds was tested using Thermogravimetric Analysis (TGA) which was carried out on a TA 2050 Instrument under atmospheric air. This method has already been used by researchers to assess the thermal stability of vanillin (Kayaci and Uyar, 2011). For each experiment, a sample of approximately 10 mg was used. A heating rate of 10 °C min^{-1} was applied, and the temperature was raised from 20 to 700 °C. Maximum stability temperature was determined at 5% loss of initial mass.

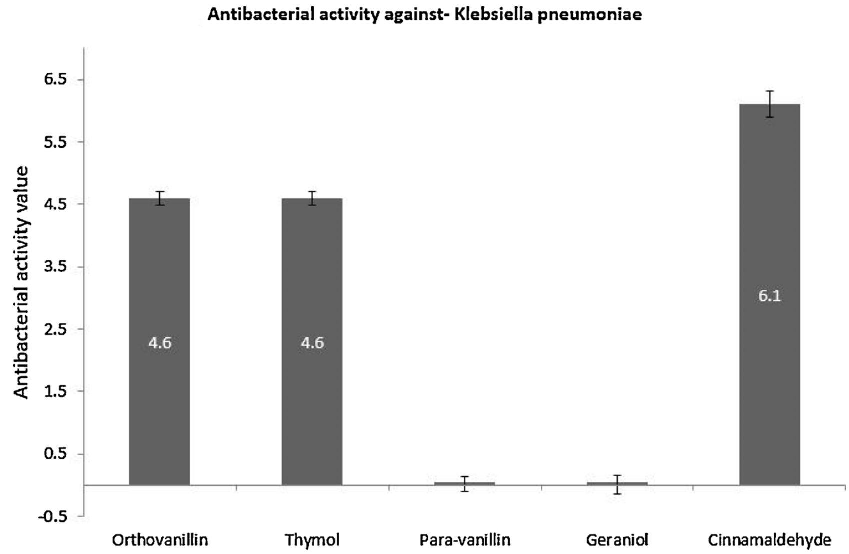


Fig. 4. Antibacterial activity quantitative (ISO20743) against *Klebsiella pneumoniaee*.

3. Experimental results

3.1. Antibacterial tests

3.1.1. Results of the agar diffusion test (ISO20645:2004)

None of the PET functionalized with one of the five active agents showed an inhibition zone against *Klebsiella pneumoniae and Staphylococcus aureus* bacteria. However, beneath the textile samples, no bacterial colony could be observed. We can conclude that bacteria which have a direct contact with the functionalized textile samples die. However, since no inhibition zone was seen, it can be concluded that the bio-active agent did not diffuse away from the textile into the aqueous medium of the agar-plate.

3.1.2. Results of the antibacterial absorption method (ISO20743:2003)

Fig. 4 shows the antimicrobial activity of functionalized PET fabrics against *Klebsiella pneumoniae* bacteria. Functionalization with thymol, cinnamaldehyde and ortho-vanillin yield PET fabrics with very good antimicrobial activity (A > 3), as average 'A' values are 4.6, 6.1 and 4.6, respectively.

PET fabrics functionalized with ortho-vanillin and thymol, have high antibacterial activity value against *Staphylococcus aureus* (see Fig. 5). With thymol, the antibacterial activity is the highest (A > 3). Cinnamaldehyde and geraniol yield a small level of antibacterial activity against this bacterium.

On the overall, PET fabrics functionalized with ortho-vanillin and thymol, have very good antibacterial activity against *Staphylococcus aureus* (gram +) and *Klebsiella pneumoniae* (gram-), while the cinnamaldehyde has very good activity against *Klebsiella pneumoniae* only.

3.2. Spectral analysis of the functionalized polyester fabrics

Further analyses of the functionalized fabrics were carried using spectrophotometry, and the washfastness of the textile samples was evaluated.

Fig. 6 represents the a* and b* coordinates in the CIELab color space, of the samples functionalized with 10% of each bio-based active agent. These were obtained using spectrophotometric analysis.

The a* axis represents the green–red component, with negative values for the green component. The b* axis represents the blue–yellow component, with positive values for the yellow component.

Cinnamaldehyde induces only a very pale yellow coloration of the fabric; ortho-vanillin yields the strongest yellow coloration.

Fig. 7 shows the K/S_{max} (at λ = 400 nm-yellow) values of each

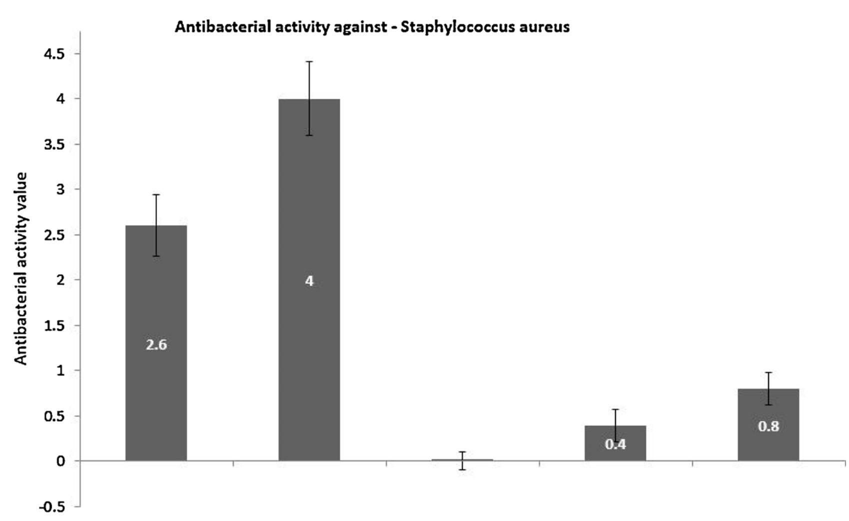


Fig. 5. Antibacterial activity against *Staphylococcus Aureus*.

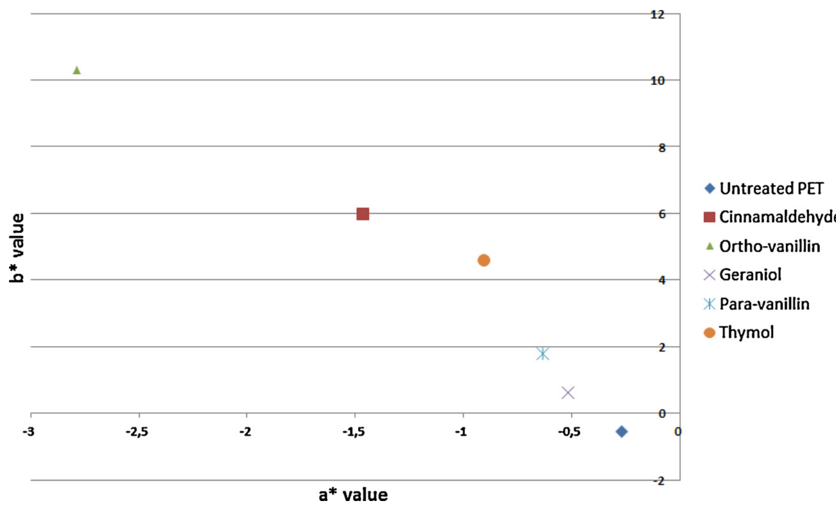


Fig. 6. Coordinates of the functionalized samples in the CIE Color space.

functionalized PET using the five different products. Increased K/S values of the functionalized PET fabric compared to the blank PET fabric (K/S = 0) confirm uptake of the active agents especially in the case of ortho-vanillin and cinnamaldehyde. Geraniol, thymol and para-vanillin are colorless products but yield very pale yellow color in the functionalized PET.

When the K/S curves of the PET fabrics functionalized with ortho-vanillin and cinnamaldehyde are compared (Fig. 8), K/S values appear to be high for the functionalized PET, in the wavelength region from 360 nm to 400 nm, which is the UV A region. The untreated blank PET showed very little absorption in this UV A region.

In the case of thymol, geraniol or para-vanillin, K/S values in the UV A region are smaller for the functionalized fabric, but they are above that of the untreated blank PET (K/S = 0.5). This confirms the presence of additional molecules inside the PET fiber (Fig. 9).

3.2.1. Analysis after removal of surface physi-sorbed molecules

In order to determine whether the active molecule actually diffuses inside the core of the fiber or whether it stays at the fiber surface, spectrophotometric analyses of functionalized PET fabrics were carried before and after the elimination of surface-sorbed molecules using an ethanol rinse. Indeed, experimentally, ethanol (δ = 26 $MPa^{1/2}$) was found to be a good solvent for active molecules used but it is not a solvent of PET polymer. Spectrophotometric measurements were performed on samples functionalized using ortho-vanillin and cinnamaldehyde, before and after ethanol rinse. These two samples were selected since they were colored yellow and could be readily analyzed using spectrophotometry.

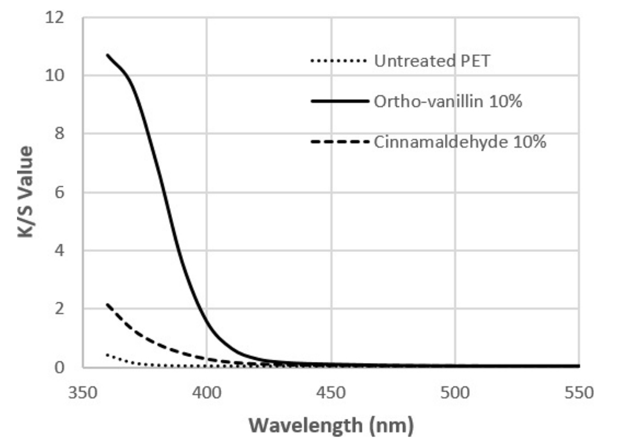


Fig. 8. K/S absorption values with respect to wavelength for the PET fabrics functionalized with cinnamaldehyde and ortho-vanillin, measured by spectrophotometer (KONICA MINOLTA).

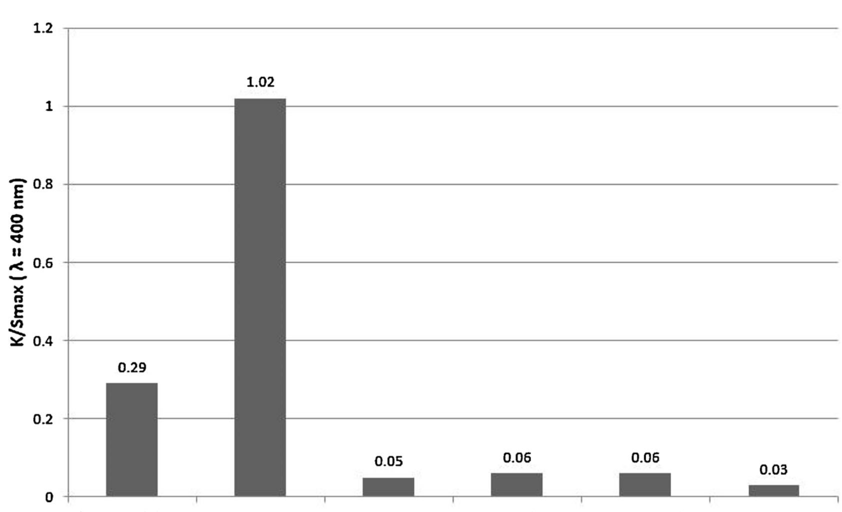


Fig. 7. K/S_{max} (at λ = 400 nm) value of treated PET with the different active agents.

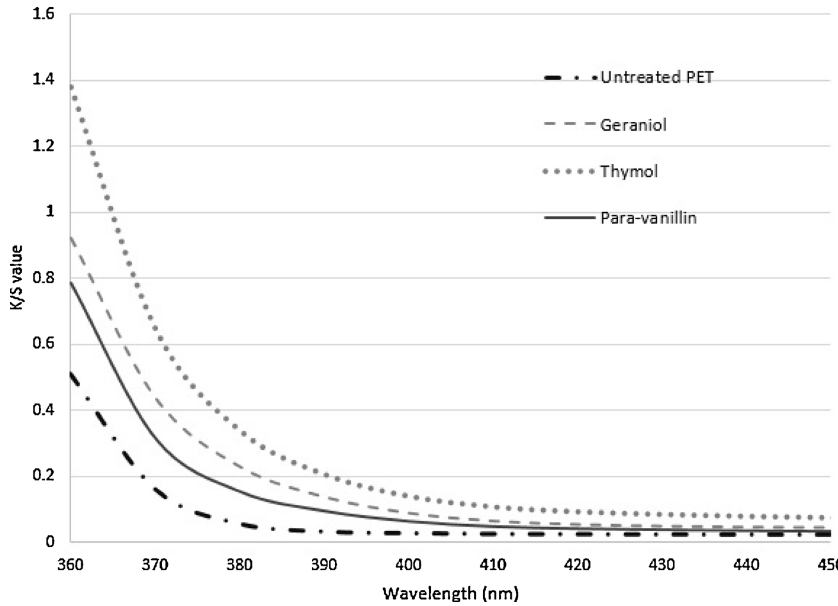


Fig. 9. K/S values for the para-vanillin, thymol and geraniol treated polyester fabrics (λ varying from 360 nm to 450 nm).

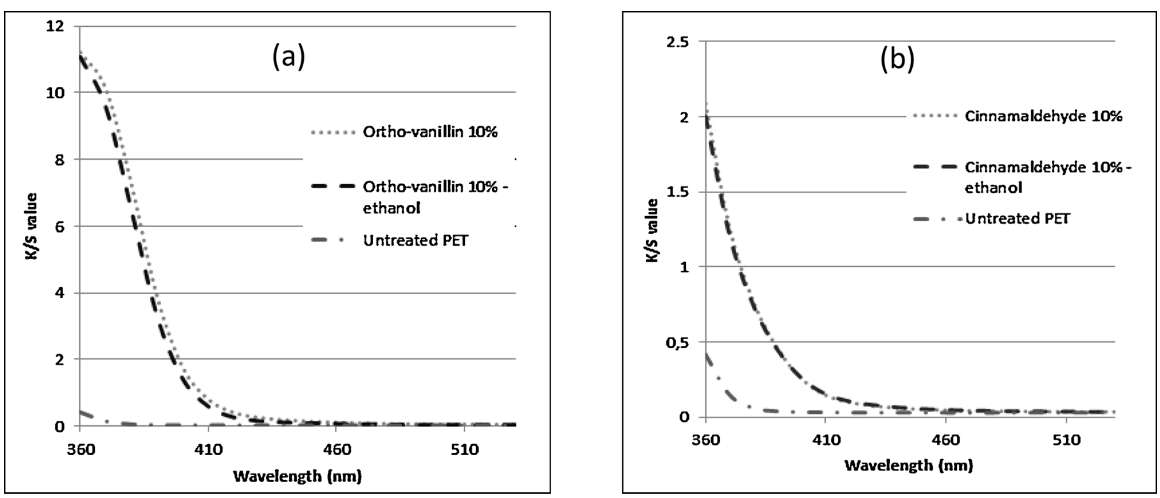


Fig. 10. K/S values (for λ: 360 nm to 450 nm) of the functionalized polyester sample before and after ethanol rinse to remove physi-sorbed active agents, for ortho-vanillin (a) and for cinnamaldehyde (b).

Fig. 10 shows K/S values (for λ : 360 nm to 450 nm) of the functionalized polyester sample before and after ethanol rinse to remove physi-sorbed active agents, for 10% ortho-vanillin (a) and for 10% cinnamaldehyde (b).

The spectrophotometric curves before and after ethanol wash were quite close for both ortho-vanillin and cinnamaldehyde, which leads us to the conclusion that the quantity of surface-sorbed bioactive molecules is very small, and that most of the molecules diffuse inside the PET fiber.

3.2.2. Wash Durability of the functionalized samples

Wash durability of the functionalized PET fabrics was evaluated using washing baths at 30 °C, for 1 h and 3 h.

Samples functionalized with cinnamaldehyde and ortho-vanillin, were tested and they showed good durability to washing (see Fig. 11). Very small decrease in K/S is observed after washing, and this indicates that molecules which are immobilized in the core of the fiber are not readily released during the 3 h washing.

In the case of thymol, geraniol and para-vanillin, spectrophotometric analysis of the functionalized fabrics, carried in the visible region (350 nm–700 nm) revealed to be an inconvenient method, since these products did not absorb in this wavelength range. Further analysis will be made in future.

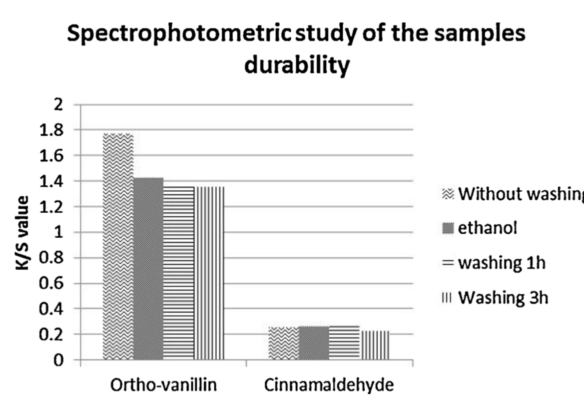


Fig. 11. K/S values at 400 nm for PET functionalized with cinnamaldehyde and ortho-vanillin after ethanol rinse and 3 h washing.

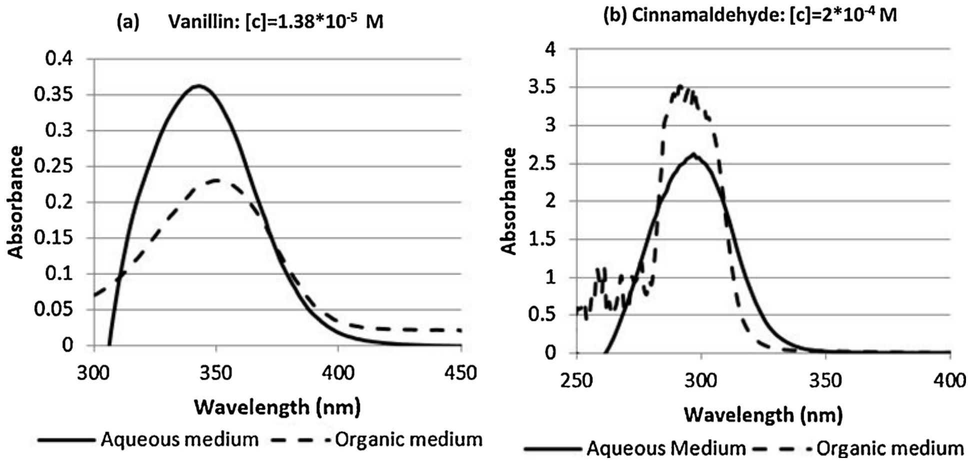


Fig. 12. UV/Visible spectral curves of ortho-vanillin (a) and cinnamaldehyde (b) in aqueous (water) and organic medium (toluene).

3.3. Spectral analysis of the functionalized polyester fabrics and of active agents in solvents

The spectral curves obtained by spectrophotometric analysis of textile samples functionalized with ortho-vanillin and cinnamaldehyde were compared with spectral curves of each of the active agents in aqueous medium (water) and in an organic solvent (toluene) obtained using a UV/visible spectrophotometer (see Fig. 12a and b). Water has indeed a very high solubility parameter (δ = 47.8 $MPa^{1/2}$) compared to PET. Since PET polymer is an aromatic polymer, an aromatic solvent such as toluene was selected, having solubility parameter (δ = 17.3 $MPa^{1/2}$) closer to that of the PET polymer. For ortho-vanillin, similar spectral curves are observed for the polyester functionalized fabric and for ortho-vanillin in organic medium. In the case of cinnemaldehyde, the spectral curve of the functionalized fabric did not seem to be correlated to that of cinnemaldehyde in the organic or aqueous medium. Two reasons may explain this deviation. Either specific interaction between PET macromolecules bearing aromatic ring and the cinnemaldehyde would cause the shift in the absorption peak observed in the functionalized PET fabric, or the molecules present in the fiber are not that of cinnamaldehyde. As high temperature diffusion process is used for functionalization, it is probable that some of the active agents may de degraded, and degradation products may be present in the PET fiber.

3.4. Thermogravimetric analysis

TGA thermographs obtained on a TA 2050 Instrument under atmospheric air, are shown for the different active agents (Thymol, Cinnamaldehyde, Geraniol) in Fig. 13. Mass loss as a function of temperature is related to thermal degradation of the product. Table 3 shows the temperature range of degradation of each active agent (determined by TGA). The maximum stability temperature was determined at 5% loss of initial mass using thermographs of each active agent. Except thymol, all other active agents have maximum stability temperature above 130 °C (used for diffusion process). Chemical conversion or degradation of active agents may occur on increasing temperature, which would lead to mass losses. However, only detailed analysis such as HPLC can help to have more precise analysis of degradation products. Based on these results, it is probable that degradation products may be formed, especially in the case of thymol, which may probably diffuse inside the polyester fiber, too. This diffusion is of course governed by the solubility parameter of the degradation products.

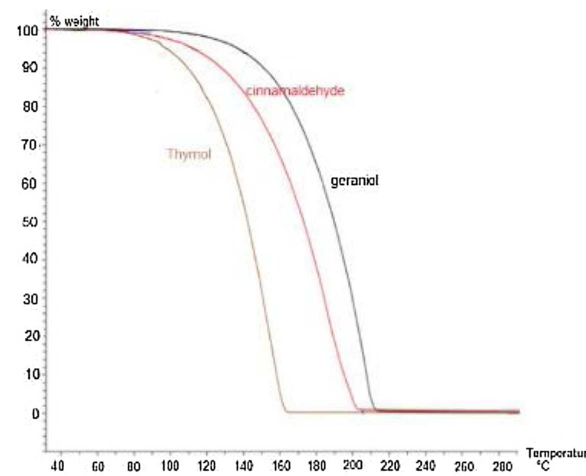


Fig. 13. TGA Thermographs of thymol, cinnamaldehyde and geraniol (Fig. 13).

Table 3
Thermal stability of the active agents determined from TGA thermographs (Fig. 13).

Active agent	Temperature range of degradation	Max. stability Temperature (at 5% mass loss)
0-Vanillin	80 °C–200 °C	142 °C
P-Vanillin	80 °C–200 °C	162 °C
Cinnamaldehyde	80 °C–160 °C	115 °C
Thymol	80 °C–200 °C	136 °C
Geraniol	80 °C–215 °C	153 °C

4. Discussion

4.1. Selection of antibacterial agent

Conventional antibacterial agents, in particular silver particles and quaternary ammonium compounds are very toxic for the aquatic life and aquatic environment with long lasting effects and it is necessary to replace them by some more eco-friendly agents. The different selected antibacterial molecules are bio-based and renewable (nazzaro, Marchese, Xie, Prabuseenisan. They come from natural resources such as vanilla, cinnamon, thyme and rose. As they come from renewable resources, they can potentially lead to reduced environmental impact and can serve as interesting alternatives to standard antibacterial or antifungal agents used to produce antimicrobial textiles.

However these bio-based agents are not all exempt from toxicity

Table 4
Toxicity issue of each active agent.

	 Corrosive to metals Skin corrosion Serious eye damage	 Acute toxicity Skin and eye irritation Skin sensitisation	 Hazardous to the aquatic environment: -Acute hazard -Chronic hazard
Ortho-Vanillin	x	x	
Para-Vanillin		x	
Thymol	x	x	x
Cinnamaldehyde		x	
Geraniol	x	x	
Silver (Ag+)			x Very toxic to aquatic life with long lasting effects

issues. Table 4 summarizes the toxicity concerns obtained from ECHA web site for each of the different products used (European Chemicals Agency, 2019, http://echa.europa.eu/, 07/2018). While silver substance is very toxic and hazardous to aquatic life with long term (chronic) and short term (acute) effect, almost all of the active agents from essential oils may pose problems relative to handling of products, causing skin and eye irritation. Both silver and thymol exhibit chronic aquatic toxicity which corresponds to the development of adverse effects as a result of long term exposure. However, both ortho-vanillin and cinnamaldehyde seem to be nonhazardous for the environment, and they can be used safely for architectural textiles (since they are not in contact with the skin).

While microencapsulation (Boh and Knez, 2006)., nanoencapsulation (with cyclodextrins) (Martel et al., 2002) and finishing (Sayed et al., 2017) have been used as methods to functionalize textile with essential oils, it is shown in this study that no additional chemical agent is required to functionalize PET fabric with active agents from essential oils, using diffusion method. It is shown here that polyester fabrics functionalized with ortho-vanillin or thymol have very good antibacterial activity against both (gram+) *Staphylococcus aureus* and (gram-) *Klebsiella pneumoniae* while cinnamaldehyde functionalized PET fabric has very good activity against the gram - *Klebsiella pneumoniae* only. The antibacterial textiles obtained by the diffusion method have also good wash fastness.

Diffusion inside the PET fiber, of active agent molecules from essential oils depends on the solubility parameter of the molecules but also on their size. Using Hansen solubility parameters the Hildebrand solubility parameter of all active agents were calculated here, and these were found to be close to that of PET polymer. The molecular weight of the active agents ranged from 131 to 152 g/mol indicating their small size (see Table 1). Increasing temperature to 130 °C, which is above the glass transition temperature of the polyester fabric (80 °C), allows mobility of macromolecular PET chains while affinity of the active agent with the PET improves interaction between the active molecule and PET polymer. There is diffusion of the active agent inside the PET fiber, and spreading of molecules of the active agent between macromolecular polyethylene terephthalate chains thereof. Our experiments, particularly the spectrophotometric results, show that in the case of yellow colored active agents (ortho-vanillin and cinnamaldehyde), yellow coloration of the PET fabric (with λ_{max} = 400 nm) occurs, which confirms the uptake of the active agent or their degradation products by the PET fiber. Experiments show that this yellow coloration intensity is maintained even after removal of fiber surface sorbed active agents using ethanol. When samples were subjected to washing with water, very slight difference in K/S values shows that the antibacterial textiles have good wash fastness.

Rinsing with ethanol removes the surface-sorbed molecules only. The quantity of such physi-sorbed molecule is very low, showing that diffusion time used in the method was proper to allow the molecules to diffuse efficiently inside the fiber. The macromolecular chains of PET form a semi-crystalline fiber which is hydrophobic (water contact angle = 80°). Moreover since water has a solubility parameter (δ = 47.8 $MPa^{1/2}$) much higher than that of PET (δ = 21.9 $MPa^{1/2}$), it does not penetrate in between the macromolecular PET chains when washing at temperature (30 °C) below the glass transition temperature of PET.

Thermogravimetric analysis shows that most of the active agents (except thymol), have maximum stability temperature higher than 130 °C (diffusion temperature). In the case of thymol the antibacterial polyester textile may contain degradation products of thymol which are also antibacterial. However, only further investigations would enable to obtain more precise information. Geraniol seems to have the highest thermal stability but does not yield any antibacterial textile. It's probable that its non-aromatic (aliphatic) nature would reduce its interactions with the aromatic chains of PET. Moreover, the Hansen dispersive parameter of Geraniol (δ_d) greatly differs from that of PET, when compared to values of other active agents. This would decrease the amount of geraniol bound to PET, and yield a geraniol-functionalized polyester with reduced antibacterial activity.

Furthermore, compared to ortho-vanillin, the para-vanillin does not yield any antibacterial textile though it is inherently antibacterial. Both vanillins used in the study are aromatic compounds, and have almost similar dispersive Hansen parameter (δ_d) and similar range of vapor pressure (Table 1). The Hansen parameters (δ_h) and (δp) of p-vanillin are higher than that of o-vanillin, as the hydroxyl group in p-vanillin is in para-position and thus more readily prone to interactions of hydrogen type bondings. The TPSA which is the "Topological polar surface area" was then compared. The TPSA is a parameter used in drug design to predict their bioavailability through intestinal absorption or cell permeability (Bytheway et al., 2008). The TPSA values which can be computed by complex softwares are available on '*pubchem* data base, are presented in Table 1 for all active agents used in this study. This TPSA value is much higher for the p-vanillin than o-vanillin, and so the much higher polar surface area of p-vanillin would explain its lower interaction with the hydrophobic nonpolar PET. Hence the functionalized PET would probably contain little amount of p-vanillin, and exhibit nearly no antibacterial activity.

Essential oils are known for their antibacterial activity but they also have specific fragrance. This fragrance is responsible for their limited use in certain applications, but makes them also suitable for use in Aromatherapy (Buchbauer and Jirovetz, 1994). Data shown in Table 1, show that the vapor pressure, and hence the volatility of cinnamaldehyde, thymol and geraniol, are around ten times higher than that of both vanillins. As far as fragrance of all functionalized polyester fabrics is concerned, only a slight aromatic smell could be detected by a panel of students. They estimated that the aroma on textiles was bearable and quite pleasant. Most probably, the molecules of each active agent are entrapped in between the macromolecular chains of PET, which reduces greatly their volatility, and their rate of diffusion in the gaseous form to the environment. Fragrance is reduced but the quantity of active agent which diffuses outside the fiber in conditions of the antibacterial test, maintains a certain degree of antibacterial activity in the case of polyester fabric functionalised with thymol, cinnamaldehyde and o-vanillin.

Both ortho-vanillin and cinnamaldehyde seem to be nonhazardous for the environment, and they can be used safely for architectural textiles (since they are not in contact with the skin). However, ortho-vanillin seems more interesting because of its antibacterial activity against both gram positive and gram negative bacteria. However, precautions have to be taken while manipulating these products.

5. Conclusion

Taking into account the environmental issues of today, bio-based products such as active agent from essential oils are a promising alternative for antibacterial properties even for the textile industry. The diffusion method by exhaustion procedure proved to be an effective way of functionalization of polyester fabrics with these bio-sourced products. Thymol, cinnamaldehyde and ortho-vanillin are more effective ingredients than geraniol, and para-vanillin, to yield polyester fabric with antibacterial activity against *Staphyloccocus aureus* (Gram positive) and the *Klebsiella pneumoniae* (Gram negative). From toxicity and ecotoxicity point of view, the ortho-vanillin and cinnamaldehyde would be the best alternatives though ortho-vanillin yields the best antibacterial activity. The resulting bio-based functionalized polyester is multifunctional, with added coloration and fragrance using a one-shot diffusion process. Thermal degradation observed for certain active agents should be better studied in order to apply this method. This study however opens the perspective of use of other crop based essential oils to yield antibacterial textiles.

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