The Effect of Carvacrol and Carvone Treatments on the Cedar Wood SurfacePhysico-chemical Properties

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Abstract— The contact angle method was used in this study to investigate the impact of the cedar wood surface treatment by two essentials oil components on its physicochemical properties.Thus, the hydrophobicity and the Lewis acid/base components were evaluated before and after the treatment of the cedar wood with carvacrol and the carvone. The obtained results revealed that the cedar wood showed the initial characteristics of hydrophobic surfaces ($\theta w = 89 \pm 0.12°$; $\Delta Giwi = -67.93$ mJ/m^2) with low electron Donor and Acceptor properties ($\gamma^- = 0.28 \pm 0.06$ mJ/m^2; $\gamma^+ = 3.03 \pm 0.2$ mJ/m^2). After 15 min of treatment with carvacrol, the surface became hydrophilic ($\theta w = 42.2 \pm 0.3°$; $\Delta Giwi = 11.29$ mJ/m^2), the electron acceptor character is canceled ($\gamma^+ = 0.18 \pm 0.08$ mJ/m^2) while the electron donor component increased considerably ($\gamma^- = 36.82 \pm 0.93$ mJ/m^2). However, the treatment of the cedar wood by carvone allowed to notice that the surface remained hydrophobic ($\theta w = 39.8 \pm 0.3°$; $\Delta Giwi = -5.31$ mJ/m^2) but also with a strong increase of the electron donor character ($\gamma^- = 29.11 \pm 0.43$ mJ/m^2) compared with the controls samples. This study contributes to demonstrate the significant impact of these essential oil components on the initial physicochemical properties of cedar wood.

Index Terms—Carvacrol, Carvone, Cedar wood, Contact Angle, Physico-chemical properties, Surface treatment, Wood.

1 Introduction

Different parts of plants are used for centuries in traditional medicine, such as the leaves, bark or roots. The bioactive properties of these plants are mainly due to their content of different molecules such as flavonoids, tannins, alkaloids and phenols [1],[2]. In recent decades, several studies have reported the extraordinary antibacterial or antifungal potential of essential oils and their main components testedagainst many microorganisms on planktonic [3],[4], [5] or sessile [6], [7], [8]forms.

The microorganisms (bacteria and fungi) are able to adhere to different materials, including wood, grow and eventually weaken their structure. Indeed, wood which is widely used in the manufacturing of furniture, in food-processing industries, or in the constructions of houses , is very exposed to the risks of biodegradation by the microorganisms [9].In fact, the lignocellulosic nature of the wood as well as its heterogeneous composition and its important hygroscopicity make it vulnerable to the attacks of microorganisms. This implies the necessity to treat the wood surface in order to preserve it from this microbial degradation.

The importance of the physicochemical properties of material surfaces on initial cell adhesion have also reported in literature[10], [11], [12]. Thus, the physicochemical interactions of Van der Waals type, the electrons donor / acceptor characteristics of the surface energy as well as the hydrophobicity govern the first step of the microorganisms adhesion on the materials surfaces including wood.

However, Although several researches were conducted on the surface treatment by various methods such as the treatment by plasma[13], [14], heat[15], fatty acids [16], plant triglycerides[17], copper amine [18] and many other molecules, but to our knowledge, no study has already shown the impact of the essential oil components on the wooden surface physicochemical properties.

Therefore, this present investigation has for main purpose to study the effect of two essential oil components that are carvacrol and carvone on the cedar wood surface physicochemical properties using the contact angle measurement.

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2 Materials and Methods

2.1 Preparation ofthe Cedar Wood Surface

The substrate used in our study is the cedar wood (Cedrus atlantica) which is widely used in the construction of houses in the old medina of Fez. The cedar wood was cut into pieces which had the following dimensions: length = 3 cm, thickness = 0.4 cm and width = 1 cm. The roughness of the wood pieces was set in a range from 0.8 to 1µm by using a rugosimeter (Model : Mitutoyo Sj 301). Then, each piece of wood was washed six times with distilled water and then autoclaved at 120 ° C for 15 min.

2.2 Essential Oil Components

The effect of essential oil components on the physicochemical surface properties of cedar wood was evaluated using carvacrol (≥97.0% pure) and carvone (≥99% de pure) purchased from Sigma-Aldrich.

2.3 Cedar WoodSurface Treatment

On the cedar wood surface samples, prepared such as mentioned above, a volume of 10 µl of essential oil components was deposited for 15 min. After a good drying and adsorption of the essential oil components tested at room temperature, the contact angles measurements were directly performed.

2.4 Measurements of contact angles and calculation of the physicochemical characteristics

The surface properties of the cedar wood were characterized by the sessile drop technique [19]. Three measurements of contact angles were made on each wood samples using two polar liquids (water and formamide) and one apolar liquid (diiodomethane) with known energy characteristics (Table 1). All parameters of the physico-chemical characteristics of the surface (The surface free energy (ΔGiwi) of substrates, the Lifshitz-van der Waals component (γ^{LW}), electron donor or Lewis base (γ^{-}) and electron acceptor or Lewis acid (γ^{+})) were calculated by the equation of Young [20]:

$$\gamma_L(\mathrm{Cos}\theta + 1) = 2(\gamma_S^{LW}\gamma_L^{LW})^{1/2} + 2(\gamma_S^{+}\gamma_L^{-})^{1/2} + 2(\gamma_S^{-}\gamma_L^{+})^{1/2} \quad (1)$$

Where the terms (S) and (L) denote solid surface and liquid phases respectively.

The Lewis acid-base component (γ_S^{AB}) is obtained by:

$$\gamma_S^{AB} = 2(\gamma_S^{-}\gamma_S^{+})^{1/2} \quad (2)$$

And the samples degree of hydrophobicity was evaluated through contact angle measurements and by the approach of Van Oss and al. [20]. According to this approach, the degree of hydrophobicity of a given material (i) is expressed as the free energy of interaction between two entities of that material when immersed in water (w): ΔGiwi. This latter is evaluated through the surface tension components of the interacting entities, according to the following formula:

$$\Delta\mathrm{Giwi} = -2\gamma_{iw} = -2\left[\left((\gamma_i^{LW})^{1/2} - (\gamma_w^{LW})^{1/2}\right)^2 + 2\left((\gamma_i^{+}\gamma_i^{-})^{\frac{1}{2}} + (\gamma_w^{+}\gamma_w^{-})^{\frac{1}{2}} - (\gamma_i^{+}\gamma_w^{-})^{\frac{1}{2}} - (\gamma_w^{+}\gamma_i^{-})^{\frac{1}{2}}\right)\right] \quad (3)$$

Table 1: Surface tension properties of pure liquid used to measure contact angles [21], [22], [23].

Liquids	Surface Energy parameters (mJ/m²)		
	γ^{LW}	γ^{+}	γ^{-}
Water (H_2O)	21.8	25.5	25.5
Formamide (CH_3NO)	39	2.3	39.6
Diiodomethane(CH_2I_2)	50.5	0	0

3 Results and Discussion:

3.1 The initial physicochemical surface properties of the cedar wood

The physicochemical characterization of the cedar wood surface untreated and treated by the essential oil components (carvacrol and carvone) has been carried out by the sessile drop technique. Hydrophobicity, surface energy as well as the electron donor/acceptor characters were evaluated with the contact angle data and calculations were done using the approach of Van Oss [21].

According to Vogler [24] and Van Oss [21], when the value of the watercontact angle exceeds 65 °, the surfaces are characterized as hydrophobic and hydrophilic when inversely the value of the contact angle of water is less than 65 °. Moreover a positive value of the surface free energy (ΔGiwi) means that the surface is hydrophilic and a negative value indicates that it is hydrophobic.

The surface free energy gives a quantitative indication of the surface substrate hydrophobicity; while the contact angle with water permits a qualitative assessment of hydrophobicity.

Table 2 include the results of contact angles measurements with the three pure liquids and components of Lifshitz-Van der Waals (γ^{LW}), electrons donor (γ^{-}) and electron acceptor (γ^{+}) obtained by calculation based on the equation of Young[21], for the cedar wood surface before and after treatment with carvacrol and carvone, and this in order to better observe the wood surface physical chemistry modifications throughout 15min of treatment time.

Table 2: Contact angle measurements of cedar wood surfaces untreated (control) and treated with carvacrol and carvone for 15min.

	Liquids contact angles (°)			Surface Energy parameters (mJ/m²)			
	θ_W	θ_F	θ_D	γ^{LW}	γ^{+}	γ^{-}	ΔGiwi
Untreated wood	89±0.12	38.5±1	28.9±0.7	44.55±0.3	3.03±0.2	0.28±0.06	-67.93
Treated with Carvacrol	42.2±0.3	34.7±0.7	31±1.38	43.68±0.1	0.18±0.08	36.82±0.93	11.29
Treated with Carvone	39.8±0.3	10.6±2	14.4±1.6	49.1±0.4	0.85±0.11	29.11±0.43	-5.31

Thus, as it can be seen in table 2, the value of the surface free energy obtained for the untreated cedar wood was negative (ΔGiwi= -67.93 mJ/m²); in fact, this was indicative of the cedar surface hydrophobic character. The value of the water contact angle also showed that the surface of the untreated cedar wood was hydrophobic with a high value (θw = 89±0.12°) (Table 2).

Similar results to ours on the physicochemical surface properties of wood were reported in several works. Indeed, Sadiki et al. [25] and De Meijer et al. [26] have reported a hydrophobicity of the wood with values of (θw = 86±0.2°; ΔGiwi = -81.98 mJ/m²) and (θw = 69±2°; ΔGiwi < 0 mJ/m²) respectively.We also reported the hydrophobicity of cedar wood in our recent work [27] which concern the evolution of physicochemical surface properties following the *Penicillium expansum*spores adhesion with contact time. Indeed, the hydrophobicity of these samples was very pronounced (θw = 118.5±4.32°; ΔGiwi = -6.29 mJ/m²) compared to those of this study.

The results of the Lewis acid/base components before and after treatment are also reported in Table 2. The electron-donor character of the cedar surface was lower (γ^- = 0.28±0.06 mJ/m²) than the electron acceptor (γ^+ = 3.03±0.2 mJ/m²) and the Lifshitz van der Waals component was 44.55±0.3 mJ/m².

These results of the initial Lewis acid/base properties are partially consistent with those of El Abed et al. [28] and De Meijer et al. [26] who also showed a low electron donor-acceptor values of the wood surfaces and relatively close (γ^- = 5.5 mJ/m²; γ^+ = 0 mJ/m²) and (γ^- = 4.7 mJ/m²; γ^+ = 1.7 mJ/m²) respectively. However, unlike our results, their electron donor characters were slightly higher than the electron acceptors.

Therefore, according to the obtained results in this study, the cedar wood has a hydrophobic surface and very low acid-base components although slightly more acidic.

3.2 Impact of Carvacrol and Carvone Treatments on the Wettability of Cedar Wood Surface

To study the impact of the treatment by carvacrol and carvone on the cedarsurface properties, the different physicochemical parameters (free surface energy, hydrophobicity and electron Donor/Acceptor characters) were evaluated after 15 minutes of treatment; and the volume of essential oil components used in this study was 10µl. The observed results revealed that the initial cedarsurface properties were significantly modified after the treatment .

Thus, the obtained results of the surface properties allowed to notice that after 15 min of treatment with carvacrol, the cedar surface lost its hydrophobic properties both qualitatively and quantitatively. However, although there was a qualitative change of hydrophobicity by the important decrease of the water contact angle on the treated surface by carvone, thefree surface energy valueshown that the hydrophobic character of the cedar surface remains after the treatment.

Indeed, the values of the water contact angles for the treated surface with carvacrol indicated θw = 42.2 ° while that treated with carvone showed θw = 39.8 °: what reflected a qualitative hydrophilicity for both treatments. However, the results of the free energies calculations of the two surfaces clearly showed that only the surfaces of the treated samples by carvone remained hydrophobic (ΔGiwi = -5.31 mJ/m²) when those treated by carvacrol became quantitatively hydrophilic (ΔGiwi = 11.29 mJ/m²).

We have reported partially similar results in our recent works [25] on the treatment of the cedar surface by the *Thymus vulgaris* extracts obtained by maceration and ultrasound, where significant changes in surface properties were observed. Indeed, after treatment by both extracts, the cedar wood which initially hydrophobic became highly hydrophilic with values of water contact angles of 29.7° and 18.2° and surface free energy of 17.78 and 30.62mJ/m² for treated surface respectively by the extracts obtained by maceration and ultrasound. However, contrary to the results presented in this study, Gerardin and al. [15] found that the hydrophobicity of the pine and beech woods were strengthened from θw = 55.4 to 81.3° and from 54.5 to 69.4° respectively after the heat treatment.

Following the same logic, Hakkou et al. [29] also reported a sudden increase in the value of the water contact angles from zero to 90°, when the beech wood is treated at a temperature between 130 and 160°C. Thus, beech wood loses its natural hydrophilicity and becomes hydrophobic due to the heat treatment.

The modification of the surface properties is a function of the material as well as the treatment to which it is subjected. Thus, the silicone surface treatment by plasma as a function of time showed a considerable increase of the surfacehydrophilicity[30]. Indeed, the authors have shown that the value of the water contact angle decreases from 72 ° to a value lower than 5 ° to the plasma treated samples.

These modifications of the surface properties observed in this study were due to the chemical composition of the two essential oils components used for the treatment of the cedar samples. The surfaces having become hydrophilic after treatment with carvacrol, this could be explained by the presence of hydroxyl group which more hydrophilic, through the hydrogen bonding, compared to the ketone function present on carvone.

3.3 Surface Energy Components of Treated Wood Surfaces

On the other hand, the treatment of the cedar surface by the essential oil components has favored a significant increase of the cedar wood electron donor character (Table 2). Indeed, after 15 min of treatment, the value of the Lewis acid component relative to the electron donor parameter (γ^-) was higly increased from 0.28±0.06 for untreated wood to 36.82±0.93 mJ/m²and 29.11±0.43

$mJ/m^2$for thetreated surfaces by carvacrol and carvone respectively.

However, the value of the electron acceptor character (γ^+) has considerably decreased from 3.03±0.2 $mJ/m^2$for untreated wood to 0.18±0.08 mJ/m^2 and 0.85±0.11 respectively as mentionned above. In what concerns the Van der Waals component (γ^{LW}), the results showed that the values are maintained approximately constant throughout the experiment (Table 2).

Our previous study [25] on cedar wood treatment with plant extracts, quoted above, had also reported very similar results. Thus, for both Thymus vulgaris extracts obtained by maceration and ultrasound, the surfaces of the treated samples showed a decrease in the electron acceptor character for the treatment by the first extract (γ^+=0.15±0.01 mJ/m^2) when the value of this parameter following treatment with the second extract did not change (γ^+=2.03±0.02 mJ/m^2) compared to the control (γ^+=2.03±0.04 mJ/m^2). However, these extracts being rich in polyphenols induced a significant increase of the electron donor component of the surface treated by both treatments (γ^- =44.76±0.3 et γ^- =53.80±0.3 mJ/m^2 respectively according to the previous order). The untreated cedar showedalmost zero value (γ^-=0.02±0.01 mJ/m^2).

We had already described, above, the involvement of the hydrogen atoms of the hydroxyls groups in the increase of the hydrophilicity of the treated surface by carvacrol. However, the analysis of the Lewis acid/base parametersresults reported in Table 2 suggests that changes in these properties would be due to electron pairs of the oxygen atoms, what allowed to strengthen the electron donor character of the wood surface treated with the two essential oils components.

Previous works reported by Jiang et al. [18], on the surface treatment of northern red oak but with chemical compounds, showed partially similar results to ours. Indeed, the authors indicated that the value of the electron donor character of the Northern red oak surface were 11 times greater than (γ^- = 11.0 mJ/m^2) than that of untreated wood (γ^- = 0.9 mJ/m^2) by the solution of copper ethanolamine (0.4 wt%). However, contrary to our results, they also indicated that the value of the electron acceptor character was almost 7 times (6.8) (γ^+ = 6.8 mJ/m^2) greater than that of the control (γ^+ = 0.7 mJ/m^2) for the same treatment.

Besides the treatment of surfaces by various molecules or substances which can significantly influence the surface properties of materials, the physical parameters such as pH may also influence very significantly the adhesive behavior of microorganisms on surfaces.

4 CONCLUSION

The physico-chemical properties which govern the interactions between surfaces were evaluated in this study by the contact angle method before and after the treatment of the cedar wood samples by two components of essential oil. Thus, under the conditions of this study, the obtained results showed that the surface treatment by carvacrol and carvone have significantly influenced the hydrophilic/hydrophobic character as well as the electron donor parameter of the cedar surface. Although these surface properties have evolved according to the chemical composition of molecules used, their use could allow to reduce or to inhibit the adhesion of microorganisms responsible of the woodbiodegradation.

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