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FTIR ANALYSIS FOR THE EVALUATION OF SOME TRIAZOLE FUNGICIDES FOR THE TREATMENT OF WOODEN ARTIFACTS

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ABSTRACT

The Growth of fungi on wooden artifacts is accompanied as a rule by various physic-chemical processes making wood rigid, brittle and deformed. Therefore it is necessary to evaluate some fungicides for the preservation of wooden artifacts in order to eliminate any deformation caused by microorganisms. This study represents an attempt to use some triazole fungicides with different concentrations (propiconazole and tebuconazole) in order to assess the chemical stability of wood damaged by fungi. Fungal ageing over different periods of time was applied by using three species of fungi (*Aspergillus niger*, *Aspergillus flavus* and *Penicillium chrysogenum*), which were collected from different historical buildings in Egypt (such as The Mosque of Sabiile and Koutab Suleiman Agha Selehdar dated back to 1837–1839 AD, The Mosque of El Mouayed Sheikh Al-Mahmoudi dated back to 1415 to 1421 AD etc.), and were identified in previous work. Fourier transform infrared spectroscopy (FTIR) was used to evaluate the fungicides used. The results revealed that it is unfavorable to use propiconazole in the treatment of wood infested by Aspergillus flavus. However, tebuconazole can be used safely to treat wood infested by this fungus. The results also proved that increasing propiconazole and tebuconazole concentrations was needed to achieve acceptable protection against Aspergillus niger. In case of Penicillium chrysogenum, it is noticed from the results that the increased in propiconazole and tebuconazole concentrations is not recommended for treatment and a low concentration (0.25 %) is sufficient to inhibit the fungal effect.

KEYWORDS: Archaeological wood, fungal deterioration, ageing, propiconazole, tebuconazole, FTIR.

1. INTRODUCTION

The main organic macromolecular components of sound wood, which make 90–99% of its weight, are cellulose, hemicelluloses and lignin (Kolar and Rybnicek, 2014). In Egypt, the state of preservation of organic materials such as wood in some locations (Museums, buildings, storerooms and excavation area) is not good because of environmental factors, such as rapid fluctuation in relative humidity and temperature. These conditions are suitable for the growth of fungi in wooden artifacts especially when exposed to relative humidity (RH) over 65% and temperature over 22° C (Abdel-Maksoud, 2002). In addition, the degree of susceptibility of wood to attack by microorganisms depends on the raw material, its method of preparation, and environmental conditions. All these factors should be taken into consideration to understand the biodeterioration process (Valentin, 1996).

Propiconazole (C15H17Cl2N3O2) and tebuconazole (C16H22ClN3O) are organic triazole biocides that are effective against wood decay fungi. They are soluble in some organic solvents. Propiconazole has low solubility in water, but tebuconazole does not dissolve in water. They are stable and leach resistant in wood (Highley, 1999). Triazoles fungicides (Tebuconazole and Propiconazole) were used on archaeological materials (such as paints and wood). They are good fungicides and have stability at high pH-values (Lindner, 2004).

FTIR analysis can be used for different purposes (Moustafa et al., 2017; Amin, 2017; Abdallah et al., 2018; Zidan et al., 2016; Medhat et al., 2015; Abu Dalou et al., 2017). It has been successfully used for detecting and identifying microorganisms. Some studies have shown that discrimination was possible not only at the genus level, but also at the species and strain levels. It also used for the deterimination of wood deterioration (Salman et al., 2010).

In this work, we used the attenuated total reflectance (ATR) Fourier transform infrared (FTIR) radiation in order to follow the changes in wood treated with fungicides used. Jelle and Hovde (2012) noted that the ATR-FTIR technique makes it possible to study materials which are nontransparent to IR adiation in a pristine condition. That is, the extensive, time-consuming, and often cumbersome sample preparation by pressing thin KBr pellets as in traditional FTIR transmittance spectroscopy, which might even change the sample material in question, is avoided. The ATR technique is based on a special reflectance setup where the sample material is pressed directly onto various crystals with high refractive indices. It can be added that the use of FTIR spectroscopic techniques is promising as a valuable tool because of its sensitivity, rapidity, low cost and simplicity.6 Many authors (Bugheanu et al., 2010; Picollo et al., 2011; Gelbrich et al., 2012) have used FTIR for studying biodeteriorated wood or for the evaluation of pesticides.

This study aims to use FTIR for the evaluation of the efficiency of propiconazole and tebuconazole fungicides with low concentrations for the treatment of wooden artifacts.

2. MATERIALS AND METHODS

2.1. FUNGAL STRAINS

Three active strains (Aspergillus niger, Aspergillus flavus, and Penicillium chrysogenum) were isolated and identified by El-Gamal et al. (2016) from different historical locations (Historical Cairo, Egypt) dated back to different times as follow:

- The Mosque of Sabiile and Koutab Suleiman Agha Selehdar (dated back to 1837–1839 AD).
- The Mosque of Abu Haribh (dated back to 1480 and 1481 AD).
- The Mosque of El Musafir Khana (dated back to 1779 AD).
- The Mosque of El Mouayed Sheikh Al-Mahmoudi (dated back to 1415 to 1421 AD).

The infestation of wood samples by the fungi mentioned above before and after treatment with fungicides used at different concentrations for four months was in accordance with El-Gamal et al (2016).

2.2. SAMPLE INCUBATION

According to El-Gamal et al. (2016) fungal cultures were incubated at 28°C for four months. After each incubation period, the wood samples were picked out and cleaned mechanically with a brush to remove mycelia.

2.3. FUNGICIDES USED

Propiconazole ($C_{15}H_{17}Cl_2N_3O_2$), and tebuconazole ($C_{16}H_{22}ClN_3O$) fungicides dissolved in toluene were used in this study. The concentrations used were 0.25% and 0.50%. These fungicides were purchased from Aldrich.

2.4. THE APPLICATION OF FUNGICIDES TO THE WOOD SAMPLES

The application method used was the impregnation technique. The samples were soaked until saturation with fungicide. Upon removal of excess fungicide, the samples were allowed to dry at room temperature, and then were transferred to Petri dishes (El-Gamal et al., 2016).

2.5. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

According to El-Gamal et al. (2016) Fourier transform infrared attenuated total reflection spectroscopy (FTIR-ATR) has been used extensively to investigate adsorption and reactions on surfaces. The infrared spectra were obtained using a JASCO-ATR-FT/IR-6100 Fourier transform infrared spectroscope. ATR crystal was used which represents (2mm/sec). Spectral region ranging from 4000 to 400 cm-1 with 4 cm-1 resolution.

3. RESULTS AND DISCUSSION

Wood samples infested by the three active strains (*Aspergillus flavus*, *Aspergillus niger* and *Penicillium chrysogenum)* were analyzed by FTIR before and after treatment with triazole fungicides used at different concentrations for four months.

3.1. Results of *Aspergillus flavus*

The results obtained from propiconazole and tebuconazole at the concentrations used with *Aspergillus flavus* (Figs. 1 & 2) were as follow:

The band at 3571.5 cm^{-1} to 3647.7 cm^{-1} was assigned to Bonded O-H stretching band of cellulose, hemicellulose & lignin (Owen and Thomas, 1989; Faix, 1992; Pandey, 1999, Ghali, et al., 2012). In infected wood samples, all the frequencies of this band were shifted gradually to higher values by +33.4, +49.1, +65.5 and +76.2 cm^{-1} with the increase of the incubation period compared with that of the control sample indicating the breakdown of some of the hydrogen bonds. This can be explained as *Aspergillus flavus* secreted hydrolytic enzymes that cleaved hydrogen bonds at early stages of infection (Leger, et al., 1997; Mellon, et al., 2017). For treated wood with 0.25 % and 0.50 % propiconazole, it was found that the frequencies decreased compared with that of the infected samples. It can be said that propiconazole deceased the enzyme secretion or inhibited their activities. In the case of wood treated with 0.25 % tebuconazole, the results showed that the broadening of these bands with a decrease in frequency after treatment for 3 and 4 months reflected the formation of more hydrogen bonding and the capability of this low concentration in inhibiting fungal cellulases activity. The same results were obtained at 0.50 % as all the frequencies of the treated samples reflected the positive effect of 0.50 % tebuconazole in inhibiting cellulose hydrolysis.

The band at 1739.5 cm^{-1} was assigned to unconjugated C=O stretching band in ester group of hemicellulose (Ghali, et al., 2012 and Galletti, et al., 2015). It was noticed that infection with *Apergillus flavus* had a role in hemicellulose hydrolysis. This was confirmed by vanishing the band of ester group at 1739.5 cm^{-1} and appearing a new one around 1706 cm^{-1} assignable to acidic carbonyl group. The same results were obtained in all treated samples with propiconazole at the concentrations used except when treated sample with 0.50 % after 4 months of infection. This indicates that both infection by *Aspergillus flavus* and treatment with propiconazole fungicide sharply affected wood hemicellulose and hydrolyzed its ester groups to acidic ones. In case of treatment with 0.25 % tebuconazole, the results showed that the ester group of hemicellulose had disappeared in the samples treated for 1 and 2 months proving complete hydrolysis of these groups to acidic ones. However, the best results on hemicellulose content were obtained when the wood samples were treated with 0.25 % tebuconazole for 3 and 4 months as well as treatment with 0.5 % for all the incubation periods studied except for 3 months. In case of 3 months, unexpected results were obtained as only one band appeared at ≈ 1679 cm^{-1} assignable to a carbonyl group. This may be due to heterogeneity of the sample taken.

The band at 1645.9 cm^{-1} to 1706.7 cm^{-1} was assigned to adsorbed O-H and C=O conjugated stretching band of cellulose (Pandey and Pitman, 2003). A new broad band centered around 1700 cm^{-1} appeared after fungal infection and after treatment with 0.25 % and 0.50 % propiconazole and 0.25 % tebuconazole for 1 and 2 months. This band is assigned as acidic carbonyl group resulting from hydrolysis of the ester group of hemicellulose. Broadening of this band perhaps resulted from O-H bending of absorbed water plus C=O conjugated stretching of some oxidized cellulose. However, in the treatment with tebuconazole at 0.25 % for 3 and 4 months and 0.50 % for all the incubation periods studied except for 3 months as mentioned before, the results clarified the success of tebuconazole in preventing hemicellulose hydrolysis.

The band at 1511.9 cm^{-1} was assigned to Aromatic skeletal vibration in lignin (Pandey and Pitman, 2003 & Ghali, et al., 2012). It was noticed that the disappearing of these bands or decreasing in their intensities after fungal infection indicated decomposition of the aromatic skeleton of lignin. While, the increase in intensities after treatment with both propiconazole and tebuconazole at different concentrations for four months reflected a positive effect of these fungicides on the lignin content.

The bands from 1465.6 cm^{-1} to 1380.7 cm^{-1} were assigned to C-H in plane deformation in carbohydrate and lignin (Pandey and Pitman, 2003 & Shi and Li, 2012). Absence or decrease in absorptions at these wave numbers showed that advanced decay has occurred in cellulose as well as lignin. This indicated

that a depolymerization process has occurred (Achachluei and Vatankhah, 2010). The intensities of these bands increased after treatment with both propiconazole and tebuconazole at different concentrations for four months reflecting the role of these fungicides in protecting cellulose and lignin from decomposition.

The bands from 1284.4 cm^{-1} to 1164.8 cm^{-1} were assigned to asymmetric C-O-C vibration of carbohydrate (Pandey and Pitman, 2003; Zhou, et al., 2009 & Shi and Li, 2012). The band around 1275 cm^{-1} is assigned to syringyl ring and C-O stretching in xylan and hemicellulose. The decrease in intensity of this band in the infected wood after 3 and 4 months suggested a decrease of lignin and adjacent hemicelluloses in the ultrastructure of the wood. However, the intensity of this band increased in the treated samples with 0.25 % and 0.50% of both propiconazole and tebuconazole. This revealed that treatment inhibited the fungal effects and prevented wood decay. Bands in (1164-1183 cm^{-1}) range are related to C–O–C stretching in cellulose and hemicelluloses. The results showed that the intensities of these bands before and after fungal infection were nearly the same. Disappearance of bands in this region (≈1175 cm^{-1}) in treated samples with 0.25% and 0.50% propiconazole indicated advanced breaking of cellulose chains and showed that depolymerization had occurred. Appearing the bands in treated wood with 0.50 % propiconazole after 3 and 4 months may be probably due to new C-O-C linkages in the treated wood resulting from crosslinking reactions which occurred through the formation of ester or ether C-O-C groups. Reyden (1992) revealed that degree of polymerization increased by cross-linking. In case of wood oligomers (depolymerized fragments) there are many hydroxyl groups which the most reactive groups accessible for cross-linking reaction.

However, when treated with 0.25 % and 0.50% tebuconazole, the intensity of these bands increased indicating a positive effect of tebuconazole on cellulose and hemicellulose chains.

We can conclude that treatment with propiconazole in the concentrations used negatively affected hemicellulose content and enhanced cellulose depolymerization and oxidation. However, it protected lignin from fungal decay. So, it is unfavorable to use propiconazole in the treatment of infested wood by *Aspergillus flavus*. However, tebuconazole had a slight effect on all main wood components and can be used safely to treat infested wood by *Aspergillus flavus*.

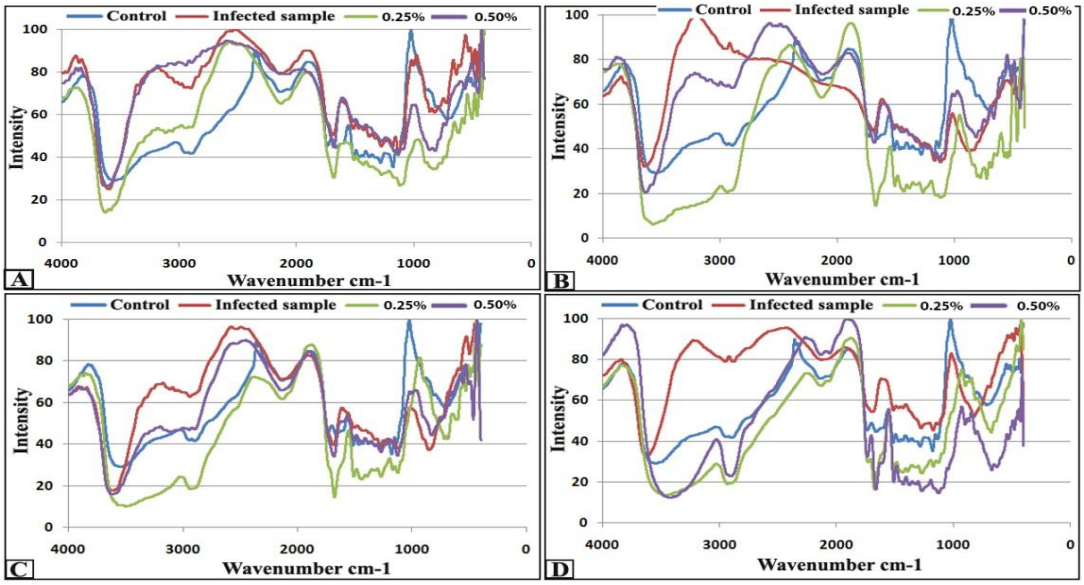

Figure 1. FTIR of treated wood samples with Propiconazole at different concentrations and infected with Aspergillus flavus at different times: (A) after 1 month, (B) after 2 months, (C) after 3 months, (D) after 4 months

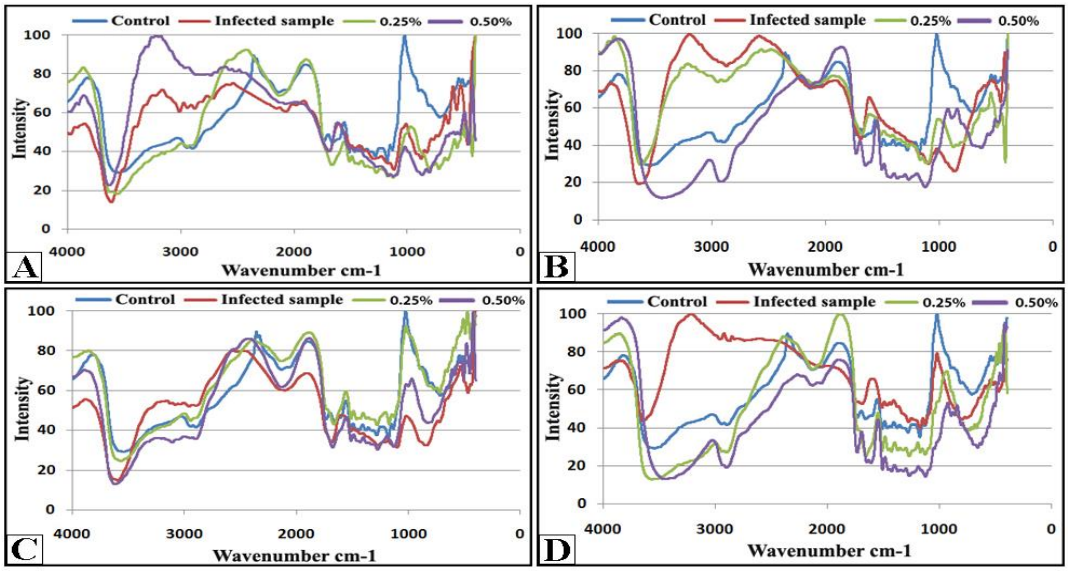

Figure 2. FTIR of treated wood samples with tebuconazole at different concentrations and infected with Aspergillus flavus at different times: (A) after 1 month, (B) after 2 months, (C) after 3 months, (D) after 4 months

3.2. Results of *Aspergillus niger*

The results obtained from propiconazole and tebuconazole at the concentrations used with *Aspergillus niger* (Fig. 3 & 4) were as follows:

The band at 3571.5 cm^{-1} to 3647.7 cm^{-1}: The result showed that all the frequencies of this band in the infected wood samples were shifted to higher values compared with that of the control sample. This was due to the cleaving some hydrogen bonds by the fungal effect. Wood samples treated with propiconazole for 3 and 4 months at 0.25 % concentration and all samples treated at 0.50 % concentration showed a decrease in wave numbers accompanied with an increase in intensities indicating the presence of carboxylic and hydroxyl groups. At the concentrations 0.25 % and 0.50 % tebuconazole, the treated samples after one and two months showed a little change in the frequency and intensity of these bands compared to that of the infected samples indicating the slight effect of this fungicide on *Aspergillus niger*. However, these bands in samples treated for 3 and 4 months broadened and were shifted to lower wave numbers with an increase in their intensities indicating the presence of carboxylic acid and hydroxyl groups. The presence of carboxylic and hydroxyl groups in samples treated by both propiconazole and tebuconazole could result from oxidation reactions on these triazole fungicides by *Aspergillus niger* to form the alcohol monolog, which was further oxidized to form the carboxylic acid analog of them (Obanda and Shupe, 2009).

The band at 1739.5 cm^{-1}: The results showed that infection with *Aspergillus niger* had a clear role in hemicellulose hydrolysis. This was confirmed by decreasing the intensity of the ester band at 1739.5 cm^{-1} and adding a new one around 1700 cm^{-1} assignable to acidic carbonyl group. However, in cases of the samples treated with 0.25 % propiconazole after 1 and 2 months, the intensities slightly increased compared with that of the corresponding infected samples, indicating the slight effect of the fungicide. On the other hand, a sharp increase in intensities by +22.0 and +28.0 % with a shift to a lower wave number 1728.9 cm^{-1} were found in samples treated for 3 and 4 months compared with that of the control sample or those of corresponding infected samples. This sharp increase may be due to the combination between ester carbonyl group of hemicellulose and carboxylic carbonyl group resulting from oxidation of propiconazole (Obanda and Shupe, 2009). At 0.50 %, the results showed the positive effect of treatment with 0.50 % propiconazole on hemicellulose content.

In the case of samples treated with 0.25 % tebuconazole after 1 and 2 months, the intensities of this band decreased compared with that of the corresponding infected samples showing no effect of the fungicide on the fungus. Additionally, the fungicide had a negative effect on hemicellulose content. However, in the treated samples with 0.25 % after 3 and 4 months and all samples treated with 0.50%, the intensities of this band in all treated samples were higher than that of the control sample or those of corresponding infected samples. This result is probably due to ester formation resulting from the reaction between the hydroxyl groups of cellulose or of oxidized tebuconazole and the carboxylic group resulting from final oxidation step of cellulose or tebuconazole in addition to ester groups of remaining hemicellulose.

The bands at 1647.5 cm^{-1} to 1706.7 cm^{-1}: A new broad band appeared in the 1696-1717 cm^{-1} range

after fungal infection and treatment with 0.25 % propiconazole for 1 and 2 months and with 0.25 % and 0.50% tebuconazole. This band is assigned as acidic carbonyl group resulting from hydrolysis of some ester groups of hemicellulose in infected samples or resulting from the oxidation of propiconazole or tebuconazole in treated samples. It was noticed that oxidation of tebuconazole increased with time as is clear from the increasing band intensity by increasing the incubation period.

The band at 1511.9 cm^{-1}: The results showed that the intensity of this band decreased after fungal infection indicated decomposition of the aromatic skeleton of lignin. Treatment with propiconazole showed that, except for the samples treated with 0.25 % for 1 and 2 months, all the intensities of this band increased compared with that of the control and the corresponding infected samples indicating the positive effect of propiconazole on lignin content.

At 0.25 % tebuconazole, the results showed that, except for the samples treated for 3 and 4 months, all the intensities of this band decreased compared with that of the control sample indicating decomposition of the aromatic skeleton of lignin. At 0.50 %, the results showed that all the intensities of these bands increased compared with that of the corresponding infected samples indicating good effect of tebuconazole on the aromatic skeleton of lignin.

The bands from 1465.6 cm^{-1} to 1380.7 cm^{-1}: The results showed that, except for the samples treated with 0.25 % propiconazole or 0.25% tebuconazole for 3 and 4 months, the intensities of these bands in all the infected and other treated samples decreased compared with that of the control sample. However, in treatment with 0.50 % propiconazole, the decrease or absence of absorptions at these wave numbers showed that advanced decay has occurred in cellulose as well as lignin, which indicated that a depolymerization process has occurred. At 0.50% tebuconazole, the results showed that all the intensities of these bands in the treated samples increased compared with that of the infected sample indicating the positive effect of the fungicide.

The bands from 1284.4 cm^{-1} to 1164.8 cm^{-1}: The results showed that the decrease in intensities of the band around 1270 cm^{-1} in the infected wood suggested a decrease of lignin and adjacent hemicelluloses in the ultrastructure of the wood. Disappearance of the bands between 1160 cm^{-1} and 1176 cm^{-1} or decrease in their intensities indicated advanced breaking of cellulose chains and showed that depolymerization had occurred. Except for the samples treated with 0.25 % propiconazole or 0.25 % tebuconazole after 1 and 2 months, the intensity of these bands increased compared with that of the control and the corresponding infected samples. This may result from C-O of hydroxyl and/or C-O of carboxylic groups formed from the fungal oxidation of triazole fungicides. However, at the 0.50 % concentration, the increase in the intensities of all these bands after treatment reflected the positive effect of 0.50 % propiconazole or tebuconazole.

The results proved that increasing propiconazole and tebuconazole concentrations was necessary to achieve acceptable protection against *Aspergillus niger* in spite of oxidation of these fungicides by the fungus especially in low concentration of the fungicide. Positive results were obtained for all the main wood components (cellulose, lignin & hemicellulose) at 0.50 % compared with that at 0.25 %. These results agreed with that obtained by Woo et al. (2010) who stated that low concentrations of triazole impregnated in wood can be degraded by some fungal species.

3.3. Results of *Penicillium chrysogenum*

The results obtained from propiconazole and tebuconazole at the concentrations used with *Penicillium chrysogenum* (Fig. 5 & 6) were as follows:

The band at 3571.5 cm^{-1} to 3647.7 cm^{-1}: at the concentration 0.25 % propiconazole, except for the samples treated for 3 and 4 months, all the frequencies of these bands were shifted to higher wave numbers with the decrease in the intensities compared with that of the control sample indicating breakdown some hydrogen bonds. This probably resulted from the fungal hydrolytic enzymes that cleaved hydrogen bonds in infected samples (Kasana, et al., 2008). This also reflected the slight effect of low concentration of propiconazole. The broadening of this band in the sample treated for 3 and 4 months with increase in its intensity and decrease in frequency compared to corresponding infected sample reflected the formation of more hydroxyl groups with the formation of more hydrogen bonds resulting from propiconazole oxidation. At the 0.50% concentration of propiconazole, except the O-H stretching band of the sample treated for 4 months, few changes were reported in treated samples compared with corresponding infected samples. However, in the sample treated for 4 months the band broadened and the frequency sharply decreased with increased intensity resulting from propiconazole oxidation. All the frequencies of the samples treated at 0.25% and 0.50% tebuconazole were shifted gradually with time to lower wave numbers accompanied with an increase in intensities compared with the control sample and corresponding infected ones. This means the formation more hydroxyl groups and more hydrogen bonds resulting from oxidation of tebuconazole.

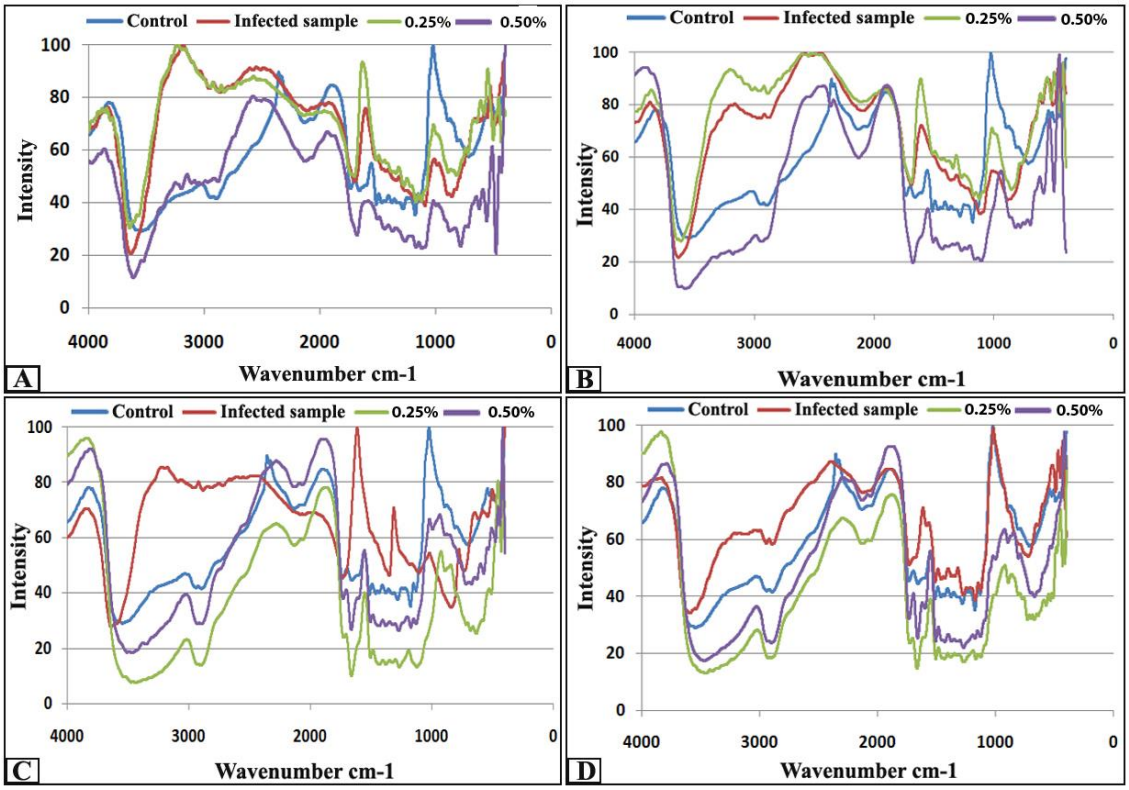

Figure 3. FTIR of treated wood samples with Propiconazole at different concentrations and infected with Aspergillus niger at different times: (A) after 1 month, (B) after 2 months, (C) after 3 months, (D) after 4 months

The band at 1739.5 cm^{-1}: The results showed that the intensities of this band decreased after infection with Penicillium chrysogenum proving the deteriorating effect of this fungus on wood hemicellulose. At 0.25 % propiconazole, the results showed that the intensities of this band increased after treatment compared with that after infection indicating the positive effect of 0.25 % propiconazole on hemicellulose. At 0.50 % propiconazole, the results showed that, except for the sample treated for 4 months, the results showed that the intensities of this band for infected and treated samples were nearly the same and they were lower than that of the control indicating the ineffectiveness of 0.50 % propiconazole on hemicellulose. The results of using tebuconazole with all concentrations used revealed that, except for the sample treated for one month which showed poor effect of tebuconazole, all the other treated samples showed an increase in intensities compared with that of the control sample or those of corresponding infected samples. This is probably due to ester formation resulting from the reaction between the hydroxyl groups of cellulose or of oxidized tebuconazole and the carboxylic group resulting from the final oxidation step of cellulose or tebuconazole combined with ester groups of remaining hemicellulose.

The band at 1664.3 cm^{-1} and 1647.5 cm^{-1}: When propiconazole was used at all concentrations, new bands appeared around 1680 cm^{-1} in all the infected and treated samples, which is attributable to carbonyl stretching conjugated band of oxidized cellulose in addition to carbonyl groups resulting from propiconazole oxidation in treated samples. At 0.25% tebuconazole, in all the treated samples, new bands appeared in (1680 – 1617) cm^{-1}, and at 0.50 %, except the sample treated for four months, all the treated samples showed new bands in the (1680 – 1650) cm^{-1} region as a result of carbonyl stretching conjugated band of oxidized cellulose in addition to carbonyl groups resulting from tebuconazole oxidation. The sample treated for four months showed a strong band at 1725.9 cm^{-1} attributable to carbonyl stretching of carboxylic group of oxidized tebuconazole. Some researchers found that tebuconazole was oxidized by some fungi first to hydroxyl groups, then to carbonyl groups and finally to carboxylic groups (Obanda, 2009; Woo, et al., 2010).

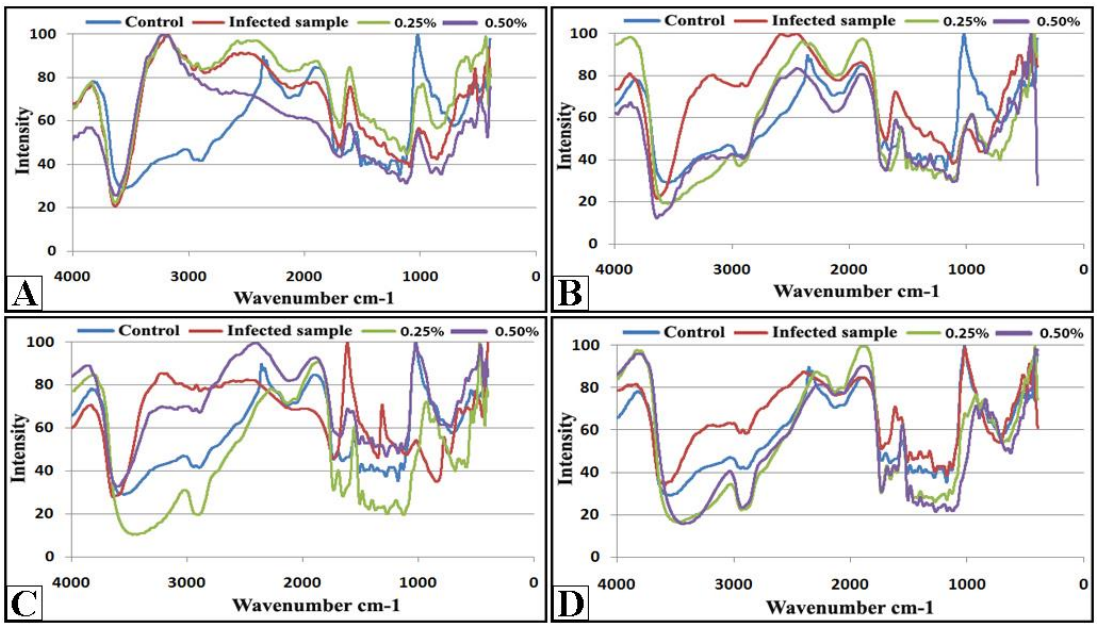

Figure 4. FTIR of treated wood samples with tebuconazole at different concentrations and infected with Aspergillus niger at different times: (A) after 1 month, (B) after 2 months, (C) after 3 months, (D) after 4 months

The band at 1511.9 cm^{-1}: It was found that the intensities of this band decreased after fungal infection indicating the decomposition of the aromatic skeleton of lignin. However, the increase in intensity after treatment with 0.25 % propiconazole reflected the positive effect of the fungicide on lignin content. At 0.50 %, the results showed that the intensities of this band decreased after treatment. These results reflected the decomposition of the aromatic skeleton of lignin. However, when treated with tebuconazole at the concentrations used, it was found that, except for the sample treated sample 0.50 % for one month, the intensities of this band increased after treatment with the fungicide. This reflected the positive effect of tebuconazole on lignin content. The high increase in the intensities of this band compared with that of the control sample indicated that as decay progressed, extensive carbohydrate loss occurred and lignin concentrations increased in the residual wood (Blanchette, 2000; Pandey and Pitman, 2003).

The bands from 1468.5 cm^{-1} to 1381.7 cm^{-1}: The decrease in absorptions at these wave numbers in infected samples showed that advanced decay has occurred in cellulose as well as lignin. This indicated that a depolymerization process had occurred. Treatment with 0.25 % propiconazole protected cellulose and lignin from decomposition. At 0.50 %, the results showed that, except for the sample treated for 4 months, the intensities of these bands for infected and treated samples were lower than that of the control indicating the ineffectiveness of 0.50 % propiconazole on wood components; the depolymerization process occurred. Except for the sample treated with 0.50% tebuconazole for one month, all the intensities of these bands in the other samples treated with tebuconazole increased compared with that of the corresponding infected samples indicating the positive effect of this fungicide on these bands.

The bands from 1284.4 cm^{-1} to 1176.4 cm^{-1}: The decrease in the band intensities around 1275 cm^{-1} in the infected wood samples suggested a decrease of lignin and adjacent hemicelluloses. However, the decrease in the bands intensities in (1165-1186) cm^{-1} in infected samples indicated breaking of cellulose chains, i.e., depolymerization has occurred. Treatment with 0.25 % propiconazole kept wood from decay. At 0.50 %, except for the sample treated for 4 months, the results showed that the intensities of these bands for infected and treated samples were lower than that of the control indicating the ineffectiveness of 0.50 % propiconazole on wood components; the depolymerization process occurred. In samples treated with tebuconazole, the results showed that, except for the sample treated with 0.50% after one month, the intensities of these bands increased compared with that of control and corresponding infected samples. This may result from C-O of hydroxyl and carboxylic groups formed from fungal tebuconazole oxidation plus the positive partial effect of the fungicide on the stability of these bonds.

The above results indicate that the increase in propiconazole and tebuconazole concentrations is not recommended for *Penicillium chrysogenum* treatment and a low concentration (0.25 %) is sufficient to inhibit fungal effect.

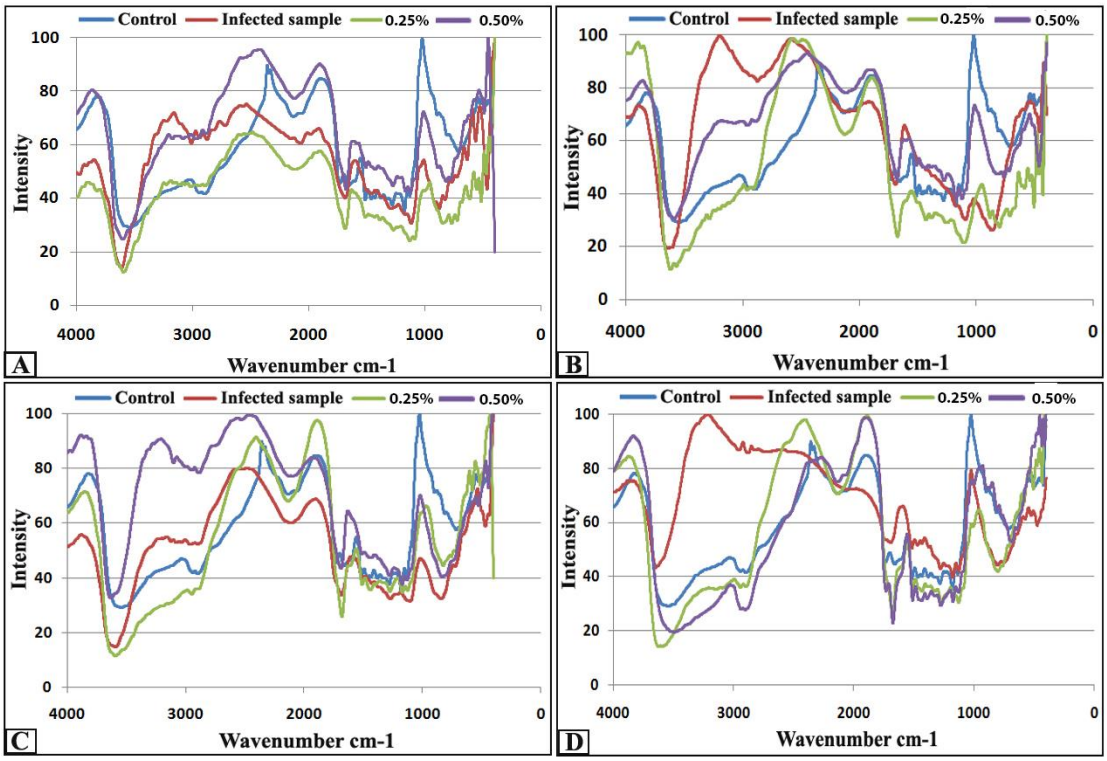

Figure 5. FTIR of treated of treated wood samples with Propiconazole at different concentrations and infected with Penicillium chrysogenum at different times: (A) after 1 month, (B) after 2 months, (C) after 3 months, (D) after 4 months

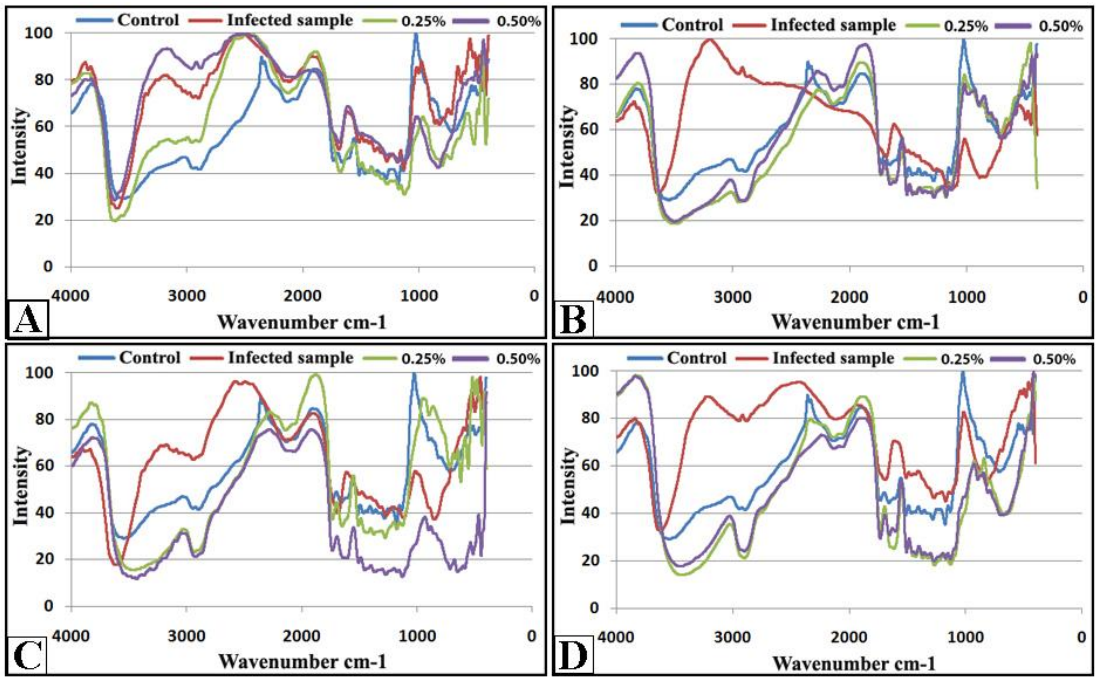

Figure 6. FTIR of treated of treated wood samples with tebuconazole at different concentrations and infected with Penicillium chrysogenum at different times: (A) after 1 month, (B) after 2 months, (C) after 3 months, (D) after 4 months

4. CONCLUSION

We can conclude that treatment with propiconazole in the concentrations used negatively affected hemicellulose content and enhanced cellulose depolymerization and oxidation. However, it protected lignin from fungal decay. So, it is unfavorable to use propiconazole in treatment infested wood by *Aspergillus flavus*. On the contrary, tebuconazole had a slight effect on all main wood components and can be used safely to treat infested wood by *Aspergillus flavus*.

The results also proved that increasing propiconazole and tebuconazole concentrations was necessary to achieve acceptable protection against Aspergillus niger in spite of oxidation of these fungicides by the fungus especially in low concentration of the fungicide. Positive results were obtained in the treatment of wood infected by *Aspergillus niger* and it was safe for all the main wood components (cellulose, lignin & hemicellulose) at 0.50% compared with that at 0.25%. We also observed that the increase in propiconazole and tebuconazole concentrations is not recommended for Penicillium chrysogenum treatment. A low concentration (0.25%) is sufficient to inhibit fungal effect.

Wood samples infested by the three active strains (*Aspergillus flavus*, *Aspergillus niger* and *Penicillium chrysogenum*) were analyzed by FTIR before and after treatment with triazole fungicides used at different concentrations for four months.

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