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THE EFFECT OF CARBOGEL POULTICES ON PINE WOOD

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Abstract:
Carbogel, a "polyacrylic acid", has been applied for cleaning different materials in the field of archaeological conservation, but it was rarely applied on wooden artifacts, and its effect on wood has not been assessed. Therefore the aim of this paper is to study the effects of carbogel poultices on one type of wood, namely pine wood, a softwood commonly used in many countries around the world throughout history. Three different Carbogel poultices were prepared by mixing in: distilled water, water and ethyl alcohol and water and acetone. Wood samples were covered with the different carbogel mixtures for 5, 15 and 30 minutes. To assess the long term effect of Carbogel on the treated wood, samples were exposed to accelerated heat ageing and humidity. Infrared spectroscopy analyses of treated and aged wood were conducted to study the effect of the poultices on wood components. Color change measurements and visual examination using a digital microscope were recorded. The results obtained indicated that carbogel can be safely applied in cleaning wooden artifacts made of softwoods, because its effect on wood components is minute and color change is negligible.

1. Introduction

Cleaning materials and/or techniques have always been applied to remove a "foreign matter" from the surface of the artifact. During cleaning of artifacts, there is always the risk of exposing wood to additional deteriorating agents, because every known cleaning technique, whether it is chemical or mechanical, has its disadvantages. Therefore different kinds of organogels and hydrogels have been introduced, proposed and tested for different applications in the conservation of cultural heritage artifacts [1]. Since the 1980$_s$ gel-based aqueous cleaning methods, which include organic solvent gels that offered many advantages over pure organic solvents and solvent mixtures have been known to conservators [2]. Gel systems improved the traditional cleaning methods giving at the same time both the minimization of the environmental impact and the optimization of the cleaning performance [3]. Carbogel, which is composed of polyacrylic acid [4], has been approved as an environmentally friendly material used at different temperatures [5,6]. Preparation of the gel material is by simple addition of water [7]; and its viscosity can vary depending on the ratio of water added, ranging from 0.5% to 4% weight of carbogel in water solutions [8]. Mixing is preferred at room temperature using a mixer to obtain a high viscosity gel [9]. Its method of application, when used for cleaning different artifacts is often determined by the condition of the object to be treated, the pH and the physical properties of the gel itself. To assess whether or not carbogel would affect wood chemically or change its physical appearance, the experiments conducted in this paper aim to evaluate the "direct effect" of three different carbogel poultices applied on pine wood surfaces for three different periods of exposure time, without adding any stains or layers of dirt, dust etc…, which could act as a barrier between the wood and the poultice, and cause confusion during investigation and interpretation of analysis. The ability of carbogel to clean a surface and remove foreign matter has been proven and discussed in previous research, and is beyond the scope of this paper.

1.1. Physical and chemical properties of carbogel

Carbogel, a polyacrylic acid gel, is a low toxic environmentally friendly product, with a pH value of 7. It is considered safer than some of the alkaline substances sometimes used in cleaning wooden artifacts. Carbogel does not absorb cold water, and it is necessary to dissolve it in warm water at a temperature ranging between 30-35 °C. When carbogel is added to water the swelling of the grains is observed, and by increasing the amount of water gradually, it increases in volume indicating its ability to continue absorbing water. It could be considered relatively economic; because one gram carbogel mixed in 100 ml water is sufficient to cover an area of 20×15 cm. Carbogel is available in the form of white odorless powder, which consists of a three-dimensional network within the liquid phase. The gel used in this research is a CTS product and according to the data sheet the following details were mentioned: *steam pressure*: <10.0 Pa at 20 °C, *virtual density*: 0.66 g/cm^3, *thermal decomposition*: stable under normal use conditions, decomposition at more than 200 °C [10]. According to literature cleaning has been applied by using a gel poultice [11] to remove soot from external surfaces [12], it was used successfully in removing nitrate spots [13], and by adding silica good results in cleaning operations were obtained [14]. When adding other chemicals to carbogel, it gave a good result, as well as maintaining partially anaerobic conditions [15]. Carbogel can be applied on wood directly and/or on wood carrying a plaster layer, which was commonly used as a preparation layer beneath a colored layer. Carbogel was efficient for sulfate removal from surfaces [16] and was used to remove only a small percentage of undesired salts [17]. Its film forming properties make it possible to easily remove it from wood in one step [18]. In this study the poultices were layered on top of the surface of wood samples in the following order: **1)** Cotton gauze on the wood surface. **2)** Carbogel layer. **3)** Cotton gauze, used for distribution of the gel when slight pressure is exerted. **4)** Polyethylene sheet, for prevention of evaporation of either water or solvent.

2. Materials and methods

2.1. Wood samples and poultices

Ten samples from pine wood were prepared for the experimental part. Ethyl alcohol, acetone and distilled water (pH= 6.8) were used to form the following carbogel mixtures for the application on the wood samples: ***)** 3 g. carbogel dissolved in 50 ml. distilled water + 50 ml. pure acetone. ***)** 3 g. carbogel in 50 ml. distilled water + 50 ml. pure ethyl alcohol. ***)** 3 g. carbogel dissolved in 100 ml. distilled water as in fig. (1). The poultices were placed on the wood samples for different periods of time (5 minutes - 15 min. - 30 min.), tab. (1), putting into consideration the longer the exposure time, the higher the amount of the solvent released by the gel, and the higher the risk of its interaction with the surface [19].

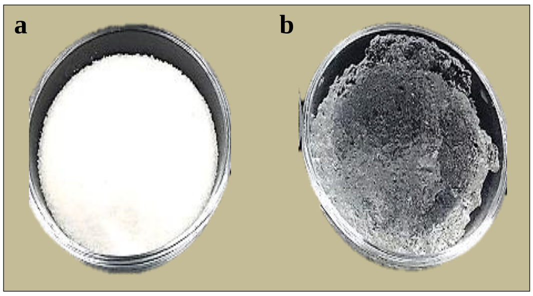


Figure (1) Shows **a.** carbogel before mixing with water, **b.** carbogel after mixing with water forming a gel prior to its addition to the poultice

Table (1) Numbering of experimental pine wood samples

Samples exposed to accelerated ageing	**Symbol**
Standard untreated sample	ST
Carbogel and acetone treated sample for 5 minutes	A1
Carbogel and acetone treated sample for 15 minutes	A2
Carbogel and acetone treated sample for 30 minutes	A3
Carbogel and ethyl alcohol treated sample for 5 minutes	E1
Carbogel and ethyl alcohol treated sample for 15 minutes	E2
Carbogel and ethyl alcohol treated sample for 30 minutes	E3
Carbogel and water treated sample for 5 minutes	W1
Carbogel and water treated sample for 15 minutes	W2
Carbogel and water treated sample for 30 minutes	W3

2.2. Evaluation methods of carbogel as a cleaning material

2.2.1. pH measurements

2 g. of carbogel were added to 50 ml. warm distilled water, and then left covered for 30 minutes, before measuring the pH of the carbogel using pH meter D11. In distilled water the pH measured (7.1), in alcohol and water the pH was (6.9), in acetone and water the pH was (7.0), indicating that the gel is neutral when dissolved in different solutions [20].

2.2.2. Accelerated heat aging

For more than a year in normal conditions, preliminary experimental samples showed negligible signs of deterioration after their treatment with carbogel. To study the long term effect of the treatment on all treated samples it was necessary to conduct accelerated ageing according to the "*Standard Specification for Aging: Standard for wood pulp paper BS 6388-3:1996 - ISO 5630-3:1996, Paper and board- Accelerated ageing*". Samples were exposed to moist heat treatment at 80˚C and 65% relative humidity for a period of 120 hours continuously in an oven (BINDER 924030000200), Serial Number: 1990/22 -Code: NIS-PMTL-NIS-11 at the National Institute for Standards (NRC) in Giza, Egypt. According to references this ageing process is an equivalent of 25 years of ageing in normal conditions [21-23]. Figures (2-a, b, c) show the wood samples before and after application of the gel, and after exposure to accelerated ageing.

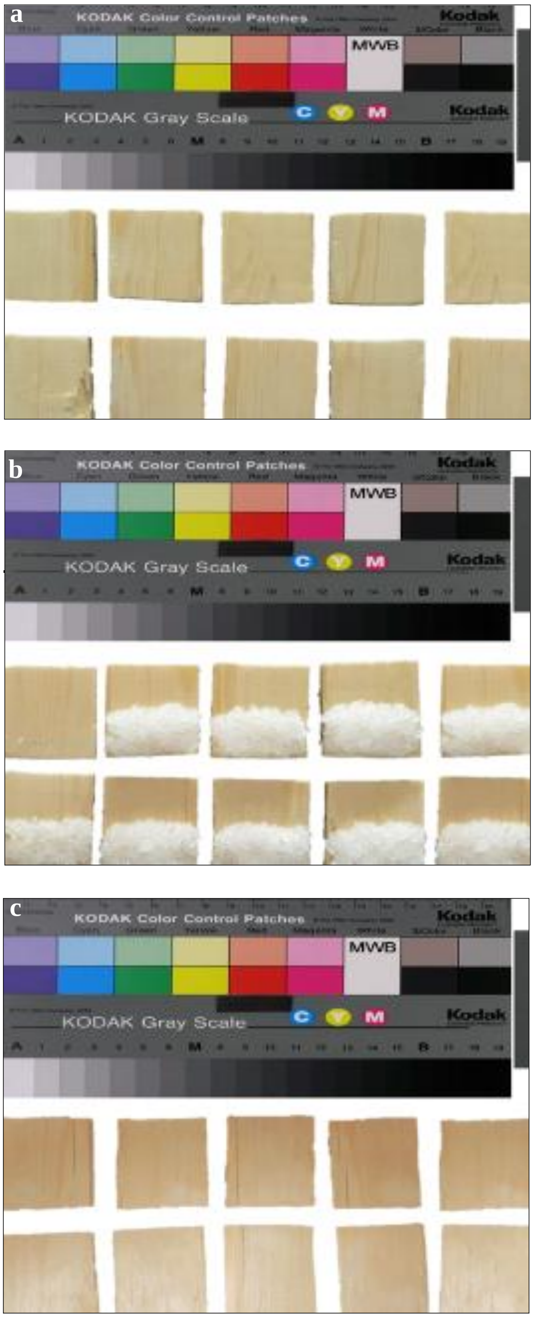


Figure (2) Shows Pine samples **a**. before treatment, **b**. during treatment, **c**. after treatment and ageing

2.2.3. FT-IR analysis of the treated pine wood samples

FTIR spectra of wood samples were measured with a Nicolet 380 FT-IR Spectrometer, at the National Institute for Standards (NRC) in Giza, Egypt; in the frequency range of 4000 - 400 cm^{-1} in transmission mode using the potassium bromide pellet technique, where the weight of the wooden sample in potassium bromide is 0.002 g and the weight of the potassium bromide tablet is supplemented to 0.2 g. Peak heights and width of absorption bands were measured by Essential FTIR program software (version 350_071).

2.2.4. Microscopic examination

A digital microscope, Model; USB S02, Cooling Tech 50X to 500X optical zoom, was used to evaluate the treated samples after treatment and exposure to the accelerated aging processes.

2.2.5. Colorimetric measurement

Color change was measured with Optimatch 3100® SDL Company using the CIE lab system [24] for the assessment of chromatic changes that occur to samples treated after aging to select the most appropriate in terms of optical properties after cleaning.

3. Results

3.1. *FTIR analysis*

3.1.1. Pine samples treated with acetone

Few changes occurred in the spectra of samples A1 and A2, but a clear decrease was recorded in the C-O stretching intensity at (1000-1210). Stronger changes were noticed in A3 spectrum, especially in the decrease O-H stretching broadening at (3300-3450), which could be due to the high volatility of acetone, thereby reducing the moisture content of the wood after a long exposure period, and an increase of C-O stretching intensity at (1000-1210) in the A3 sample. The increase of C=O at 1652 indicates the oxidation of cellulose due to reduction of the moisture content of the wood after a long period of exposure, fig. (3-a).

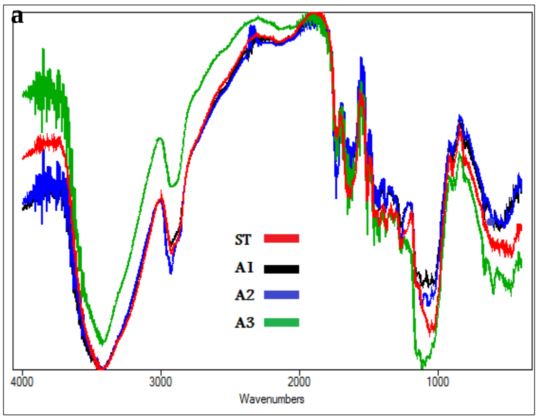


Figure (3-a) Shows FTIR spectra for samples treated with acetone.

3.1.2. Pine samples treated with ethyl alcohol

Changes were different in comparison to the acetone samples; in E1 spectrum, a decrease of O-H stretching intensity at (3300-3450) and a strong increase and shift in C-O stretching intensity at (1000-1210) was noticeable. In E2 and E3, a negligible decrease of O-H stretching broadening at (3300-3450) and a relatively clear decrease in C-O stretching intensity at (1000-1210) was recorded indicating that the effect of alcohol varied with different exposure times. The spectra of the treated samples indicate that a slight change occurred in the moisture content of wood, and these changes vary with the increase of exposure time. Another very clear decrease is noticed in the C-O-C stretching and C-H deformation at around (850-880) in the samples E2 and E3, fig. (3-b).

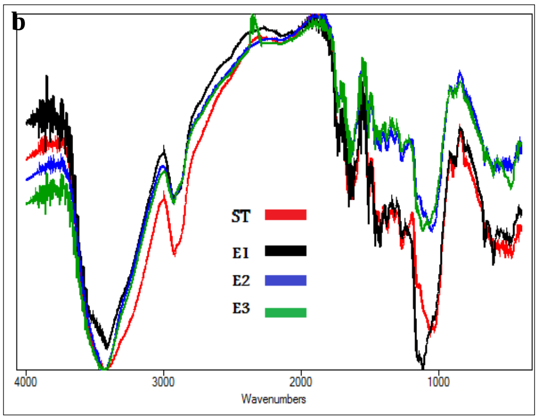


Figure (3-b) Shows FTIR spectra for samples treated with ethyl alcohol.

3.1.3. Pine samples treated with water

Slight changes occurred: O-H stretching intensity at (3300-3450) was almost negligible in all three samples treated with water and a decrease in C-O stretching at (1000-1210) is noted in all samples, yet it was most prominent in W2. A very clear decrease is noticed in the C-O-C stretching and C-H deformation at around (850-880) in the samples W2 and W3, similar to the decrease that occurred in the ethanol samples E2 and E3, indicating an effect of water on cellulose, fig. (3-c).

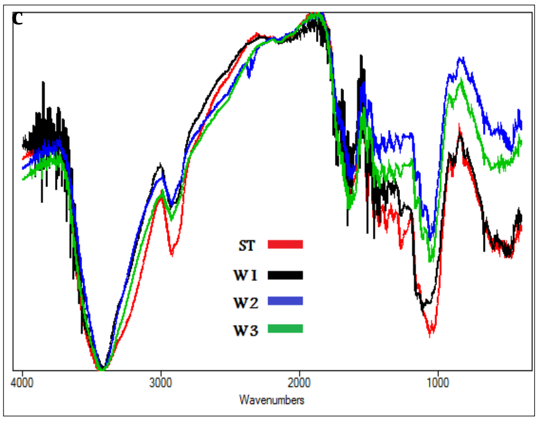
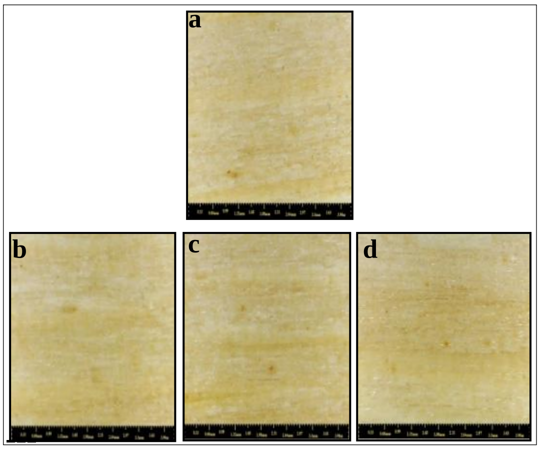


Figure (3-c) Shows FTIR spectra for samples treated with water.

3.2. *Microscopic examination*

Minute changes, which were not noticeable to the naked eye and barely noticeable during microscopic examination, occurred on the surface of the wood samples, and there was no change in the topography of the treated surface as in fig. (4); carbogel remains were easily removable with a soft, dry cloth or brush.



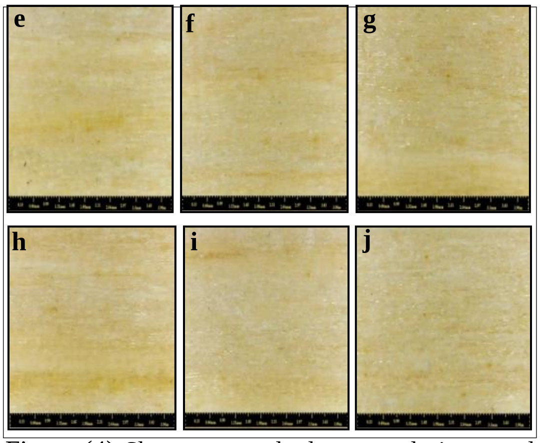


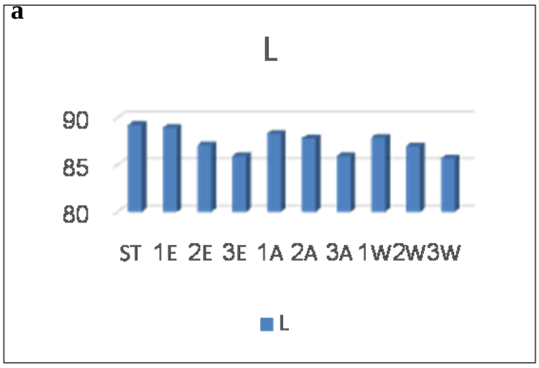
Figure (4) Shows **a.** standard untreated pine wood sample; very slight remains of carbogel in samples: **b.**, **c.** and **d.** treated with ethyl alcohol for 5, 15 and 30 min. respectively; **e.**, **f.** and **g.** treated with acetone for 5, 15 and 30 min. respectively, **h.**, **i.** and **j.** treated with water for 5, 15 and 30 min. respectively.

3.3. *Colorimetric measurement*

Samples treated with carbogel mixed with alcohol and water for 5 minutes showed the lowest chromatic change in the value of (ΔE), while samples treated with Carbogel diluted in acetone and water for 30 minutes gave the highest chromatic change as in tab. (2) and fig. (5).

Table (2) Colorimetric measurements of treated samples;

Sample	L	A	B	ΔE
ST	89.24	8.56	36.89	---
E1	88.96	9.02	37.23	0.37
E2	87.09	8.89	36.93	1.39
E3	85.93	8.03	39.65	2.46
A1	88.32	8.96	40.05	1.30
A2	87.80	8.65	39.69	1.41
A3	85.93	7.86	40.89	2.76
W1	87.89	8.06	36.96	0.94
W2	86.98	8.96	35.95	1.54
W3	85.69	8.09	34.83	2.41



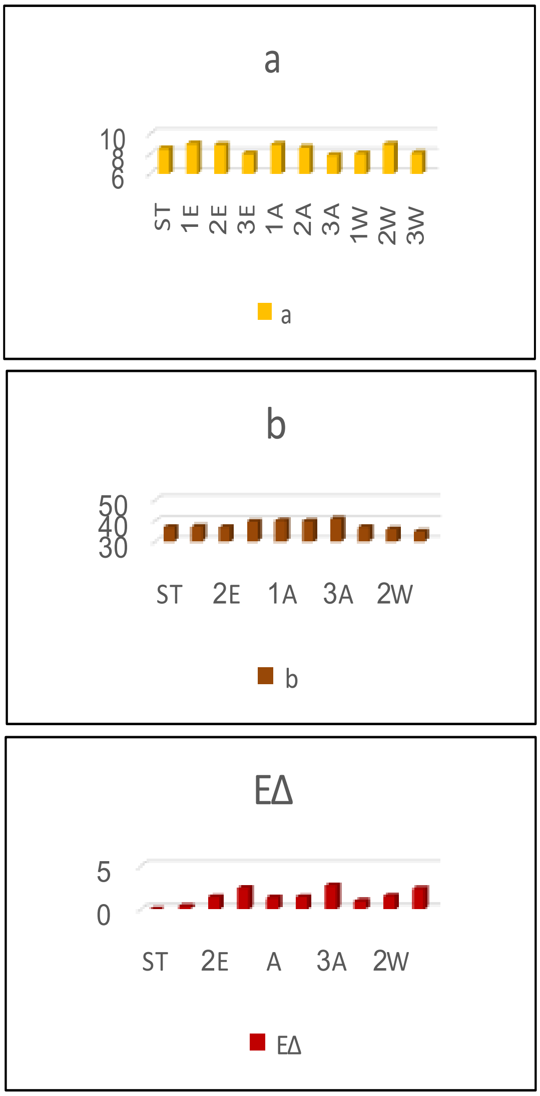


Figure (5) Shows (L) and (a) values of the treated samples compared to the standard sample, show a slight increase or decrease in all the samples, and a slightly stronger increase in the (b) value of the samples treated with acetone and ethyl alcohol. (ΔE) graph shows the total color change values of the treated samples compared to the standard sample.

4. Discussion

It is not clear why gel systems were not a common choice in the past in the process of wood cleaning, and references rarely mention its application on both archaeological wood and polychrome wood, although it had proved to be efficient for sulfate removal from encrusted marble [16]. It was also used in the cleaning of wall paintings [9], and its use allowed removal of black crusts of one of the frescoes in the monumental cemetery of Pisa [6]. In two different studies, carbogel was compared with other materials. In the first study the result of the cleaning process using Agar gelling agent was much poorer than the one performed with carbogel [5], and in the second study carbogel proved to be superior to both sepiolite and hydrobiogel-97 [17]. To assess the application of carbogel on wood, it was used in this experimental study in the form of a poultice, where it was dissolved with distilled water, a mixture of distilled water and acetone and a mixture of distilled water and ethyl alcohol. The poultices were applied for different periods of time, i.e. 5, 15 and 30 minutes, giving good results without causing any deterioration to the surface. In the visual examination traces of carbogel on the surface were evident, but they were easily removed mechanically at the end of the treatment. Microscopic examination showed there was no change in the topography of the treated surface. Chromatic change of samples treated with carbogel indicated that a gradual change occurred in relation to longer exposure periods; therefore treatments should not exceed a period of 30 minutes. The results indicated a slight decrease in the L value in all of the samples; wood treated with carbogel and water for 30 min. gave the highest chromatic change. The samples that were treated with either carbogel and acetone or carbogel with ethyl alcohol for 15 min. and 30 min. showed a gradual decrease in chromatic change in relation to increase of exposure time in the (a) value, yet an increase was noticed in the sample that was treated with carbogel and water for 15 min., which is confirmed by the increase in C-O stretching broadening at (1000-1210) in the FTIR spectra of the same sample. The (b) value of the samples treated with carbogel and ethyl alcohol and carbogel with acetone increased in all three cases, yet there was a relative decrease during the 15 min. of exposure. In the samples treated with water a gradual decrease occurred relative to longer periods of exposure. (ΔE) calculations showed that slight color changes occurred and increased with time, but none of the results exceeded the value of 3. The strongest change was recorded in the sample treated for 30 min. with acetone, which can be explained by the result obtained from the FTIR analysis where the increase of C=O at 1652 indicates the oxidation of cellulose. From the FTIR spectra of the samples it is evident that there is a clear "opposite" relationship between the changes in intensities of O-H stretching at (3300-3450) and C-O stretching at (1000-1210) in the samples treated with acetone and ethyl alcohol. A clear increase in one of the bands would result in a clear decrease in the other band and vice versa. In the samples that had been treated with water this relationship was not clear, because there was minimal change in the intensities of O-H stretching at (3300-3450) and a decrease in all three exposure periods in the C-O stretching at (1000-1210). The slight changes that occurred in the moisture content of wood with the increase of exposure time may be due to the fact that the carbogel itself absorbs some of the water from the wood, which means that the gel can have a drying effect, if left for long periods of time on wood, especially when mixed with acetone or ethyl alcohol. To find a definite explanation for these changes is extremely difficult, because both acetone and ethyl alcohol were mixed with distilled water (ratio 1:1) during the preparatory steps of the gel. The effect of water will always be present in all samples, just with different ratios or percentages and there is no way in avoiding this, because carbogel has to be diluted in water.

5. Conclusion

The use of carbogel has its advantages in cleaning different materials according to literature. Different exposure times and the addition of solvents, such as acetone and alcohol, can effectively remove different types of foreign deposits that accumulate with time on wooden artifacts. In this experimental study there was almost no negative effect on the chemical composition of cellulose, hemicelluloses and lignin in the pine wood samples that were treated for periods that lasted as long as 30 minutes. The main bands of lignin in all cases were not affected, and only some of the cellulose bands were affected by the presence of water. A change in moisture content was noticeable in all samples treated with carbogel mixed with acetone and ethyl alcohol. The treated wood surface was not affected and color change was minimal. Yet the reapplication of the poultice or a prolonged application may lead to negative results, depending on the state of the artifact and type of dirt accumulations on the surface of an object. The wood samples exposed to the poultices that were mixed with acetone for 30 minutes gave the worst results, and as an outcome of this experimental study it has been proven that carbogel can be applied for cleaning wooden artifacts for 5 to 15 minutes. In cases where the poultice is applied for 30 minutes conservators need to monitor both the color of the poultice and the surface of the artifact. Due to the water absorption properties, that were obvious after 30 minutes of exposure of the carbogel poultice, caution is necessary in cases where wood is extremely dry or has low moisture content. Future research can be conducted on studying the effects of carbogel on other types of wood and on the changes in the moisture content of wood after applying carbogel for different periods of time using different solvents.

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