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EFFECTS OF INNOVATIVE GREEN CHEMICAL TREATMENTS ON PAPER. CAN THEY HELP IN PRESERVATION?

Ruggero CAMINITI, Luigi CAMPANELLA*,
Susanne Heidi PLATTNER, Eleonora SCARPELLINI

Sapienza University of Rome, Department of Chemistry, Piazzale A. Moro 5, 00185 Rome (Italy)

Abstract

Increasing attention is paid to sustainability in conservation. Among all the kinds of objects those ones made of paper (e.g. documents, books, artworks) present the important problem of their increasing brittleness due to the inherently acid nature of many modern papers; research for sustainable restoration materials and methods in this field is particularly needed. Our contribution relies in the preparation of innovative materials and in the exploitation of their effects on paper for application in restoration. A research line regards paper consolidation and we extracted and tested the polysaccharide fraction from the cyanobacterium Arthrospira maxima for this purpose. Another research approach focuses on green ionic liquids; these not-toxic compounds, which can help in cleaning operations, are synthesized and their effect on paper explored; here a cholin-glycine based one is considered. Testing was carried out on plain paper samples (pure cellulose) subjected to accelerated aging (dry heat at 105°C) in order to consider stress response of treated samples. Treatment effects were evaluated with regard to pH and colour changes, FTIR spectra and mechanical behavior (folding endurance). While this latter gave interesting contrasting responses to that one by ionic liquid treatment, clear positive results were obtained for restoration with the polysaccharide extract.

Keywords: *Paper; Cleaning; Consolidation; Ionic liquid; Cholin-glycine; Polysaccharide extract; Arthrospira maxima*

Introduction

Increasing attention is paid in the field of Cultural Heritage conservation to sustainability, inviting researchers to look for innovation of traditional working materials and methods in order to reduce or avoid possible damages to health & safety and environment. Conservators-restorers or similar staff (e.g. visual artists, museum workers) are exposed to a series of hazards (e.g. contact with biocides, solvents, organic dust including endotoxins, moulds and mites) but few data are available regarding their health [1] enhancing the problem of the inadequate consideration of health and safety risks; so, while the importance of Cultural Heritage for Europe was recently stressed to be central [2], the problems of the related professionals are not considered in term of safety and health. Protection of professionals from working hazards occurs through personal protective equipment (PPE), installation of air purification systems and fume extractors in museums and laboratories, for care and preservation intervention are safer for health then the use of any chemical reagent and the costs for chemical

* Corresponding author: luigi.campanella@uniroma1.it

waste disposal are reduced, as well, resulting as the best option for both workers and the environment. This goal can be achieved by proposing adequate alternative materials and methods of intervention instead of the traditional ones but the way from the research to the real restoration laboratory is a long one, considering the precious nature of objects to be treated.

This work can be located in the first phase of this innovation action and regards the synthesis/extraction of innovative materials for paper conservation, tested on plain filter paper; specifically changes in pH, colour, FTIR spectra and mechanical behavior (folding endurance) were monitored. Restoration interventions on paper artifacts can be rather complex due to the composite nature of the material itself and the possible interaction with inks and pigments. Paper's main component is cellulose, but additives are needed to ensure strength to the final product and to prevent ink from diffusing around the typed words. During natural aging, paper undergoes colour changes and becomes brittle. This is mainly due to the degradation of cellulose, which suffers acid-catalysed hydrolysis and oxidation in a mixed mechanism [3-5], where the reactions are autocatalytically accelerated by protons and by reactive oxygen species.

Current paper preservation is thus based, overall, on deacidification-treatments and physical reinforcement. While much work was spent on paper dacidification to contrast the inherent cause of decay, these treatments do not recover the lost physical-mechanical properties. Consolidation of brittle paper either acidic or not is faced in different manner, but in general two approaches can be identified: reinforcement by lamination (inclusion of the brittle sheet between two sheets of consolidator) or by application of a consolidating agent among which solutions of cellulose ethers in water are often applied, mainly methyl-cellulose. It is a not toxic, not allergenic chemical compound, which is widely accepted by stakeholders [6]; however, its synthesis requires the use of the carcinogen Chloromethane. Several workers aim to identify efficient and chemically stable alternative synthetic compounds [7], but also natural matrices such as the traditional Japanese adhesive Funori, recently discovered by the Western conservator-restorer community [8-9] and bacterial cellulose [10]. A previous study in our laboratory showed positive results for the paper reinforcing activity of stimulated *Arthrospira* (Spirulina) [11], an easily cultivable microalga; however the treatment protocol was difficult to be proposed to conservators and the reinforcement activity was investigated by a non conventional method, so that we decided to follow a more traditional testing protocol and to focus on the polysaccharide extract with the aim to understand the mere effect of this component, which had shown also antioxidant properties [12]. For this purpose we used a specific extraction protocol starting this time from pure *Arthrospira maxima* powder, a widely used nutritional supplement. An aqueous solution of this extract was used for testing on paper.

Apart from consolidating media and so passing to other aspect conservators often use solvents for removal of adhesives or cleaning interventions due to paper discolouration and staining. Many organic solvents are associated with serious health risks for the worker and cause environmental problems for waste disposal, too. Over past decades ionic liquids (ILs) have been considered promising alternatives to traditional organic solvents for industrial applications due to interesting properties like low flammability, chemical and thermal stability, excellent solvation potential and negligible low vapour pressure. For applications to Cultural Heritage conservation these compounds were scarcely investigated; some evidence was found in literature with different application purposes [13-18], but referring to compounds of previous generations which generally cannot be considered green anymore [19]. In fact only ILs of the currently studied fourth generation can be considered green and not toxic. We refer to compounds prepared from renewable sources such as cholin hydroxide and amino-acids. ILs containing biocompatible cholinium as a cation and amino acids as anions are synthesized as only byproduct via a simple neutralization reaction, with water. We prepared such an IL based on cholin and glycine and applied it as solvent in paper cleaning interventions looking any eventual side effect contrasting with the use in the real operative restoration.

Experimental

Polysaccharide extraction and treatment solution preparation

Starting from a commercial Spirulina (*Arthrospira maxima*) powder product (Laboratori Biokyma S.R.L.), controlled for botanic identification, the polysaccharide (PS) extract was obtained (see Fig. 1) following a procedure described in literature [20]; Extraction steps include boiling in water, centrifugation and purification steps (protein precipitation and dialysis). The polysaccharide nature of the final extract, a white solid of cotton-like appearance, was confirmed by a spectrophotometric test [21]. The solid is easily soluble in water so that solutions of it in distilled water were prepared (1 or 2% of extract) for testing on paper; calcium hydroxide was added to ensure an optimum pH value of 8.0 (generally the range 7.5-8.5 is suggested) for paper treatment.

Fig. 1. Raw material (left) and solid extract (right): from commercially available dry Spirulina powder a polysaccharide extract was obtained and the effects of its aqueous solution was tested on paper in order to record its effects.

Ionic liquid preparation

For testing on paper we have chosen an IL composed by choline as cation and glycine as anion ([Ch][Gly]), prepared in water via a simple potentiometric titration between choline hydroxide and the amino-acid our choice was based primarily on the more paper compatible pH value of aqueous solutions of this IL compared to those ones prepared with other amino-acids. The nature of the obtained [22] compound was confirmed by NMR analysis.

Paper samples

The samples used in this study were cut from commercial Whatman filter paper n°1 (pure cellulose, 87g/m^2). This type of paper allows us to monitor the compound's action just on a cellulose matrix, free from sizing agents or other typical paper additives.

Accelerated aging

A wide variety of accelerated aging techniques is described in literature and some of them have become standard methods. Considering all the experimental parameters described as useful with their control for promoting aging [23] and also with our equipment available, we have chosen ISO 5630-1 method, where paper is exposed to dry heat at 105°C. Aging times up to 44 days were explored, but we concentrated mainly on 11 days because sufficient to produce significant changes of almost all considered aspects.

pH measurements

pH measurements are typically carried out in paper conservation studies for evaluation and monitoring of acidity, as considered at the same time source and result of aging process: really deterioration processes induce oxidation of paper components that is enhanced by acidity as able to increase oxidation potential of oxygen and that on its term increase acidity due to the autoxidation of the terminal groups of the chain fraction. This means that final oxidation products are acidic and favour cellulose chain hydrolysis which induces paper brittleness. Thus pH of paper is an important indicator for its integrity state. For pH determination we used the traditional cold extraction method Tappi 509.

Colour measurements

Colour changes typically occur on paper with aging due to oxidation processes that induce the formation of chromophores or they result from application of products, e.g. consolidating compounds. These changes are generally undesired but tolerated at a certain extent. For their determination we used a portable spectrophotocolourimeter (MINOLTA, 2600d), which allows determination of reflectance curves in the visible light region compared to a white standard (White calibration plate CM-A145) as well as of colour coordinates L*a*b* with reference to the CIE system. These coordinates, which identify objectively colours, allow also computation of the colour difference indicator ΔE*, according to the commonly used equation:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

A ΔE* value of 1 means that there is almost no perceptible difference while noticeable colour differences have ΔE* values above 2 [24-29].

Folding endurance

As stated above during aging paper becomes more brittle and this brittleness is measurable by mechanical tests, among which the folding endurance determination that is commonly adopted in conservation studies as it approaches better than others the stimulus applied to paper when handling a book for reading [30]. The number of double folds of the sample before break-down can provide a statement on how brittle or strong is paper. A reason of uncertainty is the dispersion of results (expressed by large standard deviations), therefore many measurement have to be carried out (we computed averages from 15 repeated measurements, all in longitudinal fiber direction with an applied load of 1kg and stripe dimension of 1.5 x 10.5cm) consuming a certain amount of material. Because of the risk that variation among differently treated samples may not be significant and considering that the consolidating capacity was the most interesting feature for the polysaccharide extract, we decided to apply a 2% solution of the extract to the paper sample. Other paper samples were instead treated with a 0.01M ionic liquid solution. In this way we could determine the combined effect on paper of the pre-treatment + aging. A potential restoring capacity of the polysaccharide extract and of the choline-amino acid based ionic liquid was also explored, as it would occur in case of real conservation interventions. In fact we tested also post-treated samples which were firstly aged and then worked with the two compounds.

FTIR Spectra

The chemical modifications occurring during aging of paper can be recorded by changes of IR vibration patterns measured by FTIR spectroscopy, but in order to avoid the coverage of an interesting spectral zone (1600-1750cm^{-1}) showing carbonyl and carboxyl vibrations by bending vibrations of water molecules particular experimental conditions are required; for instance substituting the free H_2O by D_2O or using a conditioned chamber for the desorbing of water from paper [31, 32]. Initially we tried working with a FTIR-ATR-instrument without an adequate sample chamber, but as expected results were unsatisfactory, so we passed to an Interferometer FTIR Bruker IFS 66v/S equipped with a sample chamber allowing spectra acquisition under vacuum achieved with a vacuum pump (UHV PFEIFFER) that reaches 0.0001mBar. For the measurements samples were left in the chamber over night for complete water desorption and in the morning spectra were registered by specular angle reflectance measurements and absorbance was computed according to the assumption that paper is a Lambertian surface [33]. This procedure worked well: intensity variations within the same sample were minimized and comparison of intensity variations of differently treated samples is possible and significant.

Results and Discussions

pH – effect of aging and treatments

The pH changes of *untreated* paper samples aged up to 11 days were not significant compared to unaged ones because variations were smaller than the method's uncertainty (0.2 pH units). We expected acidification to occur, but this was not the case. Clearly pure cellulose filter paper is free from typical paper additives which commonly coadjuvate acidification; further it is stated that hydrolysis is the main degradation route in case of thermal aging even under dry conditions [34, 35]. No significant differences in terms of pH values were found for samples treated with a 0.01M aqueous solution of the Cholin-Glycine IL or a 1% solution of the polysaccharide extract as well, compared to untreated samples of the same simulated "age".

Colour – effect of aging and treatments

The spectrophotometric measurements of reflectance curves in the visible light region and the determination of the CIE L*a*b* coordinates and ΔE* values allowed monitoring of the optical changes induced by aging and treatment. From (Fig. 2) it can be seen that aging induced a progressive reflectance reduction in both treated and untreated samples due to the build-up of chromophores which absorb light primarily in the lower wavelength region, e.g. [36].

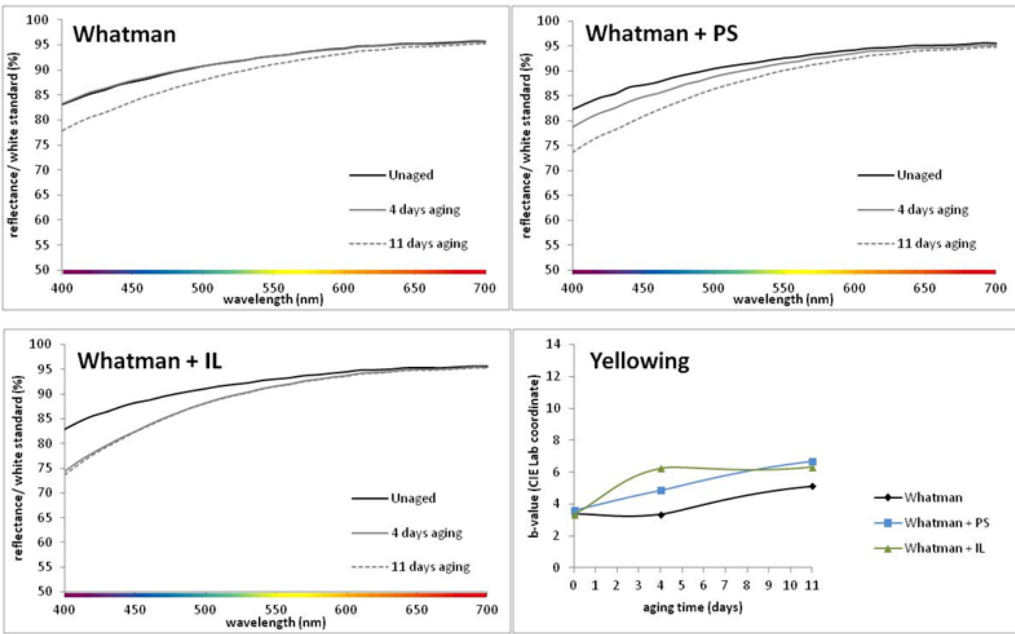

Fig. 2. Spectrocolourmetric data of Whatman filter paper samples: untreated (Whatman), treated with a 1% aqueous solution of the *Arthrospira maxima* polysaccharide extract (Whatman + PS) or a 0.01M aqueous solution of the Ionic Liquid (Whatman + IL) composed by cholin and glycine. Reflectance curves in the visible light range (% values compared to a white standard) and b-values of the CIE L*a*b*colour coordinates are shown (Yellowing) for both unaged and artificially aged samples (4 and 11 days dry aging at 105°C).

These changes are perceived by the human eye as yellowing, which is clearly expressed by the increasing b-value of the CIE L*a*b* colour coordinates. On unaged samples our test materials induce both minimal optical changes, expressed by a ΔE* of 0.2 (see Table 1). Typically with aging the treated samples appear slightly more yellow (but with different kinetics of the yellowing process), because also the compounds used for the treatment undergo yellowing; however, for both treatments the resulting colour differences (ΔE*) after 11 days of dry aging are smaller than 2 (1.6 and 1.3 respectively for the polysaccharide extract and the IL treated samples), which can be considered a benchmark value for noticeable colour differences.

Table 1. Colour differences (ΔE*) of Whatman filter paper samples treated with a 1% aqueous solution of the *Arthrospira maxima* polysaccharide extract (PS) or a 0.01M aqueous solution of the Ionic Liquid (IL) composed by cholin and glycine. Values refer to both unaged and artificially aged samples (4 and 11 days of dry aging at 105°C).

	Colour difference (ΔE*) compared to untreated sample of the same "age"
Whatman + PS	0.2
Whatman + PS (4 days accelerated aging)	1.6
Whatman + PS (11 days accelerated aging)	1.6
Whatman + IL	0.2
Whatman + IL (4 days accelerated aging)	3.0
Whatman + IL (11 days accelerated aging)	1.3

Folding endurance – effect of aging and treatment

The results of the folding endurance test are shown in (Fig. 3): the polysaccharide solution in all cases increased significantly the double fold number for both unaged and aged samples. This means that application of this carbohydrate material increases paper strength (increase of the average double fold number from 13.7 to 24.9 for unaged samples) and, with reference to aging, protects samples to some extent from their natural tendency to become brittle and it is capable to restore paper that lost its strength due to aging mechanisms.

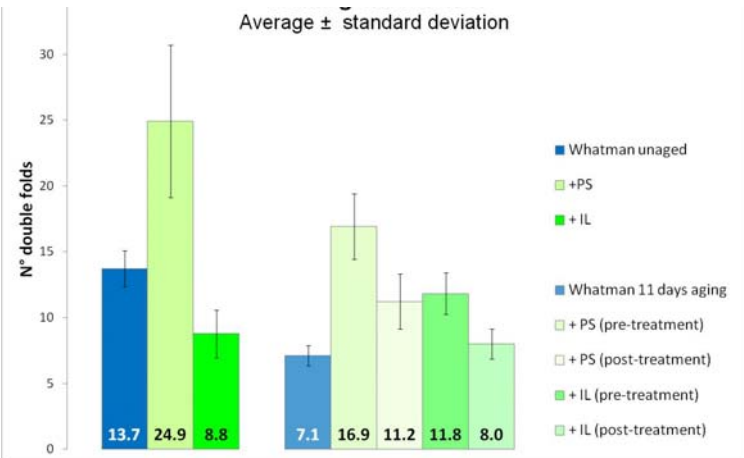

Fig. 3. Folding endurance test of Whatman filter paper samples: untreated (Whatman), treated with a 2% aqueous solution of the *Arthrospira maxima* polysaccharide extract (+ PS) or a 0.01M aqueous solution of the Ionic Liquid (+ IL) composed by cholin and glycine before (pre-treatment) or after (post-treatment) aging (11 days dry aging at 105°C).

The treatment of samples with the ionic liquid induced interesting changes in the double fold number: while for unaged samples this number dropped, no significant changes occurred for post-treated samples, while a pre-treatment increased this number. The reason for this behavior is not clear; it is plausible that, when the ionic liquid on the paper is subjected to aging, some reactions which increase the mechanical strength of paper occur, but this hypothesis does not explain why the double-fold number of aged post-treated samples does not drop.

FTIR Spectra- effect of aging and treatment

The changes in the IR vibrational patterns of cellulose and paper described in literature are subsequent changes of bands cited as sensitive to aging because of crystallinity changes [37-41] and to the band broadening [39] or profile and intensity changes in the carbonyl-carboxyl region (1600-1750cm^{-1}) [31, 32]. Results of our FTIR-reflection measurements induced by dry aging on the untreated paper samples are shown in (Fig. 4).

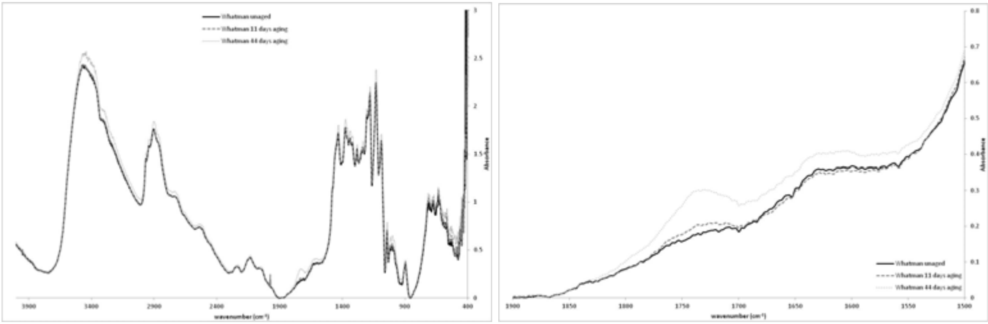

Fig. 4. FTIR reflection spectra of untreated Whatman filter paper unaged and aged (11, 44 days at 105°C). On the right, zoom of the spectrum on the carbonyl-carboxyl vibration region

While the differences between the unaged and 11 days aged samples are hardly seen without zooming except for the 1600-1750cm^{-1} region, if artificial aging is extended to 44 days, spectral changes become macroscopically more evident (most band intensities grow), indeed, at this stage, paper has become very brittle (it is confirmed by the folding endurance test where we found that the 44 days aged samples break down after one double fold) and it seems reasonable to refer to a less extreme situation and therefore to concentrate on 11 days aged samples. With reference to these ones at the current state of data elaboration we could not find any clear correlation of our spectral data with the band intensity changes related to crystallinity changes and described as aging sensitive in literature, but we are currently working to clear this part. We can probably confirm band broadening for the 900cm^{-1} band with aging, as indicated in literature (see Fig. 5).

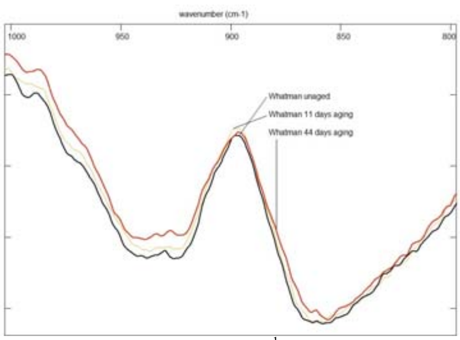

Fig. 5. Details of the band at 900cm^{-1} of FTIR reflection spectra of untreated Whatman filter paper unaged and aged (11, 44 days at 105°C). Band broadening is reported in literature as consequence of a more disordered structure

The measurements under vacuum allow us to monitoring the band growth in the carbonyl-carboxyl region, the growth of these cromophore groups was also detected by our colour measurements showing significant yellowing after 11 days aging (in Fig. 2). These considerations apply also to the treated (with aqueous solutions of 1% Arthrospira maxima polysaccharide extract or 0.01M ionic liquid) unaged and aged (11 days) samples; related spectra are shown in (Fig. 6) and (Fig. 7) respectively.

With reference to (Fig. 6 - polysaccharide extract), one can observe that the treated (unaged and aged) paper samples follow tightly the profile of the related untreated ones in the fingerprint region, while significant profile changes occur in the carbonyl-carboxyl region where band intensities are higher compared to untreated samples; a proteinaceous residue can be hypothized (band around $1600cm^{-1}$); in the $1600-1750cm^{-1}$ region the profile changes induced by aging (mainly growth of bands with wavenumber above $1700cm^{-1}$, reconcilable with the carboxyl contribute) are parallel to those ones observed on the untreated samples, underlining the chemical similarity of the applied material with cellulose. If the bands growing with aging in the carbonyl-carboxyl region can be assigned to the carboxyl component, why isn't it reflected in the pH measurements? This may be either due to the cold extraction method or to the acidic component, successfully neutralized by addition of calcium hydroxide to the treatment solution.

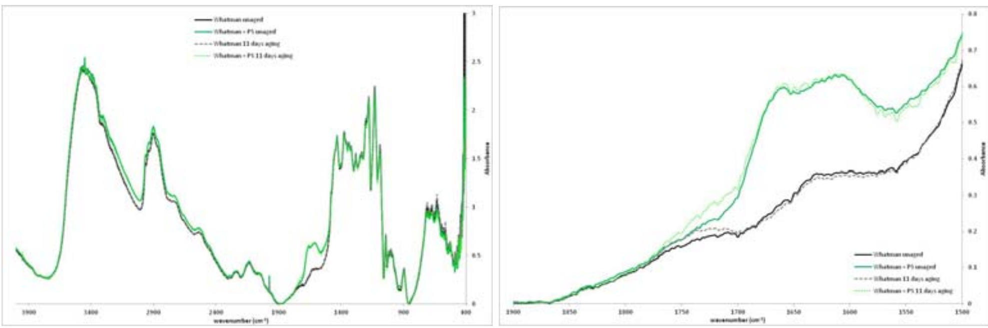

Fig. 6. FTIR reflection spectra of Whatman filter paper either untreated (Whatman) or treated with a 1% aqueous solution of the *Arthrospira maxima* polysaccharide extract (Whatman + PS), before (unaged) and after accelerated aging (11 days aging) 105°C. On the right, zoom on the carbonyl-carboxyl vibration region.

Referring to (Fig. 7) one can observe several band intensity changes (growth) for the ionic liquid treated samples already in the fingerprint region and these band intensity changes are amplified for the aged sample.

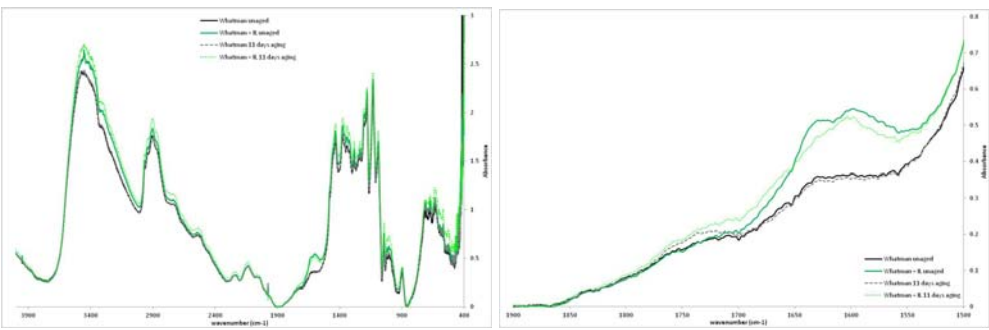

Fig. 7. FTIR reflection spectra of Whatman filter paper either untreated (Whatman) or treated with a 0.01M aqueous solution of ionic liquid (Whatman+IL), before (unaged) and after accelerated aging (11 days aging) 105°C. On the right, zoom on the carbonyl-carboxyl vibration region.

Focusing on the carbonyl-carboxyl region one may assign $1600cm^{-1}$ band to amino-acid component; with reference to aging profile, changes of ionic liquid treated samples induced by aging are more pronounced because together with the typically growing bands above $1700cm^{-1}$

(less relevant than for polysaccharide extract treated sample) the band at 1630cm^{-1}, specific for the ionic liquid treated samples, disappears after 11 days aging.

Conclusions

The aim of the presented research is the exploitation of innovative materials for sustainable restoration on paper artefacts. This study considered two different restoring materials, a polysaccharide extract of the cianobacterium *Arthrospira maxima* with potential application in paper consolidating treatments and a not-toxic fourth generation ionic liquid synthesized by the renewable feedstocks cholin and glycine via a neutralization reaction for application opportunities in cleaning operations as ionic liquids have always been considered interesting alternatives to conventional solvents. For both materials their effects on filter paper samples were investigated for changes in pH, colour, folding endurance and FTIR-spectra. In order to take into account also response to stress samples were also subjected to dry aging at 105°C. With reference to the adopted monitoring methods we observed:

- pH measurements did not allow detection of significant changes; if this is due to the applied method or to the chosen type of paper (pure cellulose filter paper, resistant to chemical changes) or to the type of aging is not clear;
- colour and folding endurance measurements fulfilled their scope;
- acquisition and data analysis of FTIR spectra of paper were more complex than expected; firstly the need of a suitable instrumentation is confirmed (otherwise results are very confusing and the significant carbonyl-carboxyl region cannot be observed properly); also data discussion requires expertise because profile shape changes are not macroscopic and any data elaboration (e.g. blank subtraction) must be performed with care.

Referring to the effects of the tested materials: the polysaccharide extract of *Arthrospira maxima* applied in aqueous solution, pH corrected with $Ca(OH)_2$, has shown significant paper consolidating capacity; the folding number for both unaged and aged pre-treated samples was doubled by an application of a polysaccharide 2% solution. Undesired colour difference ΔE^* was negligible for the unaged sample and after a 11 days aging ΔE^* was 1.6 and thus lower than the commonly considered threshold value 2. FTIR spectra are currently still under examination, but we can state that as expected polysaccharide extract induces very slight spectral changes and it seems not to modify substantially the typical response of paper to aging. However, certain intensity increases in the region 1700-1750 cm^{-1}, which may be related to carboxyl bands, suggest caution, although no pH changes could be detected (but this may be due to sensitivity problems as stated above). Further any natural product may attract microorganisms, possibly hazardous to paper and this aspect was not yet investigated. When the ionic liquid is applied to paper as a potential solvent and not completely removed afterwards, the possible consequences are changes in colour (yellowing) and in the mechanical properties of treated papers. This aspect which is reflected in contrasting and interesting results in the folding endurance test must be further investigated. FTIR spectra of treated papers show increased absorption intensity for many cellulose bands, which is amplified in case of aging. Further discussion of the information possibly obtained by FTIR spectra is opportune before complete data elaboration. The authors are thankful to any suggestion and contribute on this side.

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FTIR reflection spectra were carried out in kind collaboration with Dr. M.Ortolani from the Physics Department of Sapienza University in Rome, Italy.

References

[1] V.M. Varnai, J. Macan, A. Ljubicić Calusić, L. Prester, B. Kanceljak Macan, *Upper respiratory impairment in restorers of cultural heritage*, **Occupational Medicine, 61**(1), 2011, pp. 45-52.

[2] * * *, **Proceedings of the 6th Conference of Ministers Responsible for Cultural Heritage** (22-24 April 2015), Belgian Chairmanship of the Committee of Ministers of the Council of Europe https://rm.coe.int/CoERMPublicCommonSearchServices/DisplayDCTMContent?documentId=09000016802f8129 [accessed on 24 june 2015].

[3] M. Strlič, J. Kolár, *Evaluating and enhancing paper stability - the needs and recent trends*, **Proceedings of the 5th EC Conference 'Cultural Heritage Research: A pan-European Challenge' PANEURO**, 16th-18th May 2002, Cracow, Poland, pp. 79-86.

[4] S. Margutti, G. Conio, P. Calvini, E. Pedemonte, *Hydrolytic and Oxidative Degradation of Paper*, **Restaurator, 22(**2), 2001, pp. 67-83.

[5] M.C. Sistach, N. Ferrer, M.T. Romeo, *Fourier Transform Infrared Spectroscopy Applied to the Analysis of Ancient Manuscripts*, **Restaurator, 19**(4), 1998, pp. 173-186.

[6] R.L. Feller, M. Wilt, **Evaluation of Cellulose Ethers for Conservation**, Getty Conservation Institute, 1990.

[7] E. Ardelean, E. Bobu, G. Niculescu, C. Groza, *Effects of different consolidation additives on ageing behaviour of archived document paper*, **Cellulose Chemistry and Technology**, **45**(1-2), 2011, pp. 97-103.

[8] F. Michel, T. Geiger, A. Reichlin, G. Teoh-Sapkota, *Funori, ein japanisches Festigungsmittel für matte Malerei*, **Zeitschrift für Kunsttechnologie und Konservierung, 16**, 2002, pp. 257-275.

[9] W. Liszewska, *Japanese Polysaccharide Adhesives. Wheat Starch and Funori in Theory and Practical Conservation Treatments*, **Journal of Paper Conservation, 6**(4), 2005, pp. 23-30.

[10] H. Rosa, A. Strzelczyk, E. Jabłońska, T. Kozielec, J. Karbowska Berent, *Study of the Adaptation of Bio Cellulose Nano-Fibers for the Restoration of Historical Paper, Parchment and Textiles*, **New Approaches to Book and Paper Conservation-Restoration**, Verlag Berger, Horn, 2011, pp. 629–638.

[11] L. Campanella, C. Costanza, A. De Lera, *Riparazione di Carta Invecchiata Artificialmente e Fotodegradata*, **Proceedings of AIAr, Convegno nazionale sistemi biologici e beni culturali**, 6th-7th October 2009, Palermo, Italy, p. 278.

[12] Zhou Zhi-gang, Liu Zhi-li, Liu Xue-xian, *Study on the Isolation, Purification and Antioxidation Properties of Polysaccharides from Spirulina maxima*, **Journal of Integrative Plant Biology, 39**(1), 1997, pp. 77-81.

[13] G. Ceres, V. Conte, V. Mirruzzo, J. Kolar, M. Strlic, *Imidazolium-Based Ionic Liquids for the Efficient Treatment of Iron Gall Inked Papers*, **ChemSusChem, 1**, 2008, pp. 921-926.

[14] M.F. Pacheco, A.I. Pereira, L.C. Branco, A.J. Parola, *Varnish removal from paintings using ionic liquids*, **Journal of Materials Chemistry A, 1**, 2013, pp. 7016-7018.
[15] J. Pernak, N. Jankowska, F. Walkiewicz, A. Jankowska, *The use of ionic liquids in strategies for saving and preserving cultural artifacts*, **Polish Journal of Chemistry, 82**, 2008, pp. 2227– 2230.
[16] G. Giovannelli, L. D'Urzo, G. Maggiulli, S. Natali, C. Pliara, I. Sgura, B. Bozzini, *Cathodic chloride extraction treatment of a late bronze-age artifact affected by bronze disease in room-temperature ionic-liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI-TFSI),* **Journal Solid State Electrochemistry, 14**(3), 2009, pp. 479-494.
[17] M. Seter, M.J. Thomson, J. Stoimenovski, D.R. MacFarlane, M. Forsyth, *Dual active ionic liquids and organic salts for inhibition of microbially influenced Corrosion*, **Chemical Communications**, **48**, 2012, pp. 5983–5985.
[18] C.L. Cortes Pereira, *Application of ionic liquids and enzymes for the removal of proteinaceous layers from polychrome of works of art and evaluation of the cleaning effectiveness*, **PhD Thesis** in Conservação e Restauro especialização em Pintura pela Universidade Católica do Porto – Escola das Artes, University of Lisbona, 2012.
[19] M. Cvjetko Bubalo, K. Radošević, I. Radojčić Redovniković, J. Halambek, V.G. Srček, *A brief overview of the potential environmental hazards of ionic liquids*, **Ecotoxicology and Environmental Safety, 99**, 2014, pp. 1-12.
[20] T. Hayashi, K. Hayashi, *Calcium Spirulan, an inhibitor of enveloped virus replication, from a blue-green alga, Spirulina platensis*, **Journal of Natural Products, 59**, 1996, pp. 83-87.
[21] Q. Jiao, Q. Liu, *Simple Spectrophotometric method for the estimation of algal polysaccharide concentrations*, **Journal of Agricultural and Food Chemistry, 47**, 1999, pp. 996-998.
[22] S. De Santis, G. Masci, F. Casciotta, R. Caminiti, E. Scarpellini, M. Campetella, L. Gontrani, *Cholinium-amino acid based ionic liquids: A new method of synthesis and physico-chemical characterization*, **Physical Chemistry Chemical Physics**, **17**(32)**,** 2015, pp. 20687-20698.
[23] H. Bansa, *Accelerated Ageing of Paper: Some Ideas on its Practical Benefit*, **Restaurator, 23**(2), 2002, pp. 106–117.
[24] J. Schanda, **Colorimetry**, Wiley-Interscience John Wiley & Sons Inc., 2007, p. 56.
[25] G.V. Atodiresei, I.G. Sandu, E.A. Tulbure, V. Vasilache, R. Butnaru, *Chromatic characterization in CieLab system for natural dyed materials, prior activation in atmospheric plasma type DBD,* **Revista de Chimie** (Bucharest), **64**(2), 2013, pp. 165-169.
[26] A. Bailao, M. San Andres, A. Calvo, *Colorimetric analysis of two watercolours used in retouching*, **International Journal of Conservation Science, 5**(3), 2014, pp. 329-342.
[27] R.R.A, Hassan, *A "Tafsir Al Khazen" manuscript (17th century ad). A technical study,* **International Journal of Conservation Science, 6**(3), 2015, pp. 369-382.
[28] T. Lech, A. Ziembinska-Buczynska, N. Krupa, *Analysis of Microflora Present on Historical Textiles with the Use of Molecular Techniques,* **International Journal of Conservation Science, 6**(2), 2015, pp. 137-144.
[29] O**.** Abdel-Kareem, *Preparation of Experimental Deteriorated Dyed Textile Samples Simulated to Ancient Ones,* **International Journal of Conservation Science, 6**(2), 2015, pp. 151-164.

[30] D. van der Reyden, *Recent scientific research in paper conservation*, **Journal of the American Institute for Conservation, 31**(1), 1992, pp.117-138.

[31] M. Ali, A.M. Emsley, H. Herman, R.J. Heywood, *Spectroscopic studies of the ageing of cellulosic paper*, **Polymer, 42**(7), 2001, pp. 2893–2900.

[32] J. Łojewska, A. Lubańska, T. Łojewski, P. Miśkowiec, L. Marian Proniewicz, *Kinetic approach to degradation of paper. In situ FTIR transmission studies on hydrolysis and oxidation*, **e-Preservation Science, 2**, 2005, pp. 1-12.

[33] M. Ortolani, J.S. Lee, U. Schade, H.-W. Hübers, *Surface roughness effects on the terahertz reflectance of pure explosive materials*, **Applied Physics Letters, 93**(8), 2008, 081906.

[34] P.M. Whitmore, J. Bogaard, *Determination of the Cellulose Scission Route in the Hydrolytic and Oxidative Degradation of Paper*, **Restaurator, 15**, 1994, pp. 26-45.

[35] D. Erhardt, C.S. Tumosa, M.F. Mecklenburg, *Material consequences of the aging of paper,* **Proceedings of the 12th Triennial Meeting**, 29th August – 3th September 1999, Lyon, pp. 501-506.

[36] T. Łojewski, P. Mis´kowiec, M. Missori, A. Lubanska, L.M. Proniewicz, J. Łojewska, *FTIR and UV/vis as methods for evaluation of oxidative degradation of model paper: DFT approach for carbonyl vibrations*, **Carbohydrate Polymers, 82**, 2010, pp. 370–375.

[37] R.T. O'Connor, E.F. DuPre, D. Mitcham, *Applications of IR adsorption spectroscopy to investigations of cottons and modified cottons*, **Textile Research Journal**, **28**, 1958, pp. 82-92.

[38] M. Nelson, R. O'Connor, *Relation of certain infra-red bands to cellulose crystallinity*, **Journal of Applied Polymer Science**, **8**, 1964, pp. 1325-1341.

[39] D. Fengel, *Characterisation of cellulose by deconvoluting the OH valency range in FTIR spectra*, **Holzforschung, 46**, 1992, pp. 283-288.

[40] L.M. Proniewicz, C. Paluszkiewicz, A. Wesełucha-Birczyńska, H. Majcherczyk, A. Barańskia, A. Konieczna, *FT-IR and FT-Raman study of hydrothermally degradated cellulose*, **Journal of Molecular Structure, 596(**1–3), 2001, pp. 163–169.

[41] M. Ali, A.M. Emsley, H. Herman, R.J. Heywood, *Spectroscopic studies of the ageing of cellulosic paper*, **Polymer, 42**(7), 2001, pp. 2893–2900.

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