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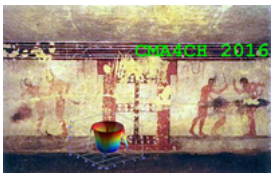

Algae Extracts for Restoration and Conservation of Paper

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Abstract

Ageing is an irreversible process that deteriorates the mechanical and chemical properties of paper. Paper becomes brittle due to the influence of internal and external factors. The most important internal factors are established during the manufacture of the paper and include the kind and quality of the fibers, sizing materials, coatings, the presence of acidic and metallic compounds and other components of the sheets. The external factors are related to the deleterious influence of the storage conditions or use, such as temperature and humidity, light, air pollutants, microbial attack, atmospheric oxidation, etc.

The strength of brittle paper can be improved by conservation treatment mainly based on two approaches: lamination (inclusion of the brittle sheet between two sheets of consolidator) or application of a consolidating liquid such as aqueous solutions of cellulose ethers, synthetic or natural products. Our proposal looks at natural products application to brittle paper but in a very innovative approach.

Introduction

During natural ageing, 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 [1] 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 even if the consolidation by lamination or application of consolidating solutions which are generally the less costly and more rapid option, are used as alternatives. Solutions of cellulose ethers in water are often applied, mainly methyl-cellulose because it is not toxic, not allergenic and then well accepted by the stakeholders [2]; however, its synthesis requires the usage of hazardous reactants, among which the carcinogen Chloromethane. Several workers aim to identify efficient and chemically stable alternative synthetic products [3], while an other alternative is the usage of natural products. Polysaccharides contained in or produced (intra- or extracellularly) by algae and cyanobacteria for nutrition and/or defense are currently hot topics in research, because of their peculiar properties, longing from antiviral to antifungal to antioxidant [4]. Some of these substances have already found application in the restoration of paper, for instance due to gelling attitude (gels are used for cleaning or deacidification treatments; e.g. Agar agar from Gelidium, Gracilaria, Gelidiella, Pterocladia or Sphaerococcus or Gellan produced by Pseudomonas) or adhesive characteristic (e.g. Funori, extracted from Gloiopeltis, has recently entered European Conservation laboratories and is mainly a mixture of sulphated polysaccharides, lipids, proteins and salts [5]).

Starting from our previous experiments with the micro-alga/cyanobacterium Arthrospira [6], we have recently focused our research efforts on the polysaccharide extract of Arthrospira maxima, which owns also a potentially interesting antioxidant capacity, in order to explore its effect on paper both aged and unaged. Interest on the polysaccharide extract is based on its chemical affinity to the polysaccharide cellulose in paper. Chemical interaction can occur because all polysaccharides have a high number of hydroxyl groups and H-bridges can be built up between the polysaccharides constituting the paper fibers and those ones of the aqueous solution of the algae-extract applied on the paper. Further H-bridges can build up with carbonyl groups of cellulose and also real chemical bonds can occur with the carboxyl groups of cellulose, forming esters. Both carbonyl and carboxyl groups in cellulose are due to oxidation processes occurring during ageing.

Materials & Methods

Starting from commercial dry powder of Arthrospira maxima (kindly furnished by prof. M.Nicoletti, Botany Dept of "Sapienza" University), the polysaccharide fraction was extracted, purified (with a yield of about 1%) and used as consolidator.

Folding endurance test, colorimetric, pH and FTIR-AR measures were performed in order to evaluate changing in the mechanical and chemical properties of Whatmann paper, as such and after 11 days aging in oven, with and without treatment with the algae extract.

Table 1; Folding endurance averages on 12 measures obtained for all the tested samples.

	no-aged (na)	Aged (a)	(a-na)
Untreated (ut)	13.1±2.5	2.3±0.5	-10.8
Treated (t)	14.3±2.8	4.3±0.5	-10.0
t-ut	1.2	2.0	

Results

Table 1 evidences a higher folding endurance for both the aged and no-aged consolidated samples; a lower decrease, due to the aging, can be also seen for the consolidated paper.

The pH of the treated paper resulted higher than the untreated one while a no significant improvement was observed for the aging effect.

The treatment causes a no significant chromatic change while, as common for most of the consolidators, a quicker yellowing occurs on treated samples.

The treatment with the algal extract provokes an increase of the intensity in the bands relating to the "fingerprint" zone of the cellulose (bands related to typical carbohydrate vibration), but also in other areas there are small spectral differences (see Fig. 1). Considering the variations in intensity of some bands (as an example the one at 900 cm^{-1}) such as aging indicators, it seems fair to assume that the preventive treatment with algal extract has had a positive effect on the aging of the paper.

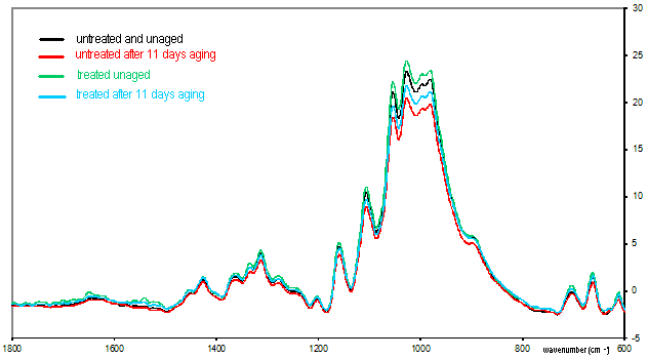

Fig. 1; FTIR-AR spectra of all the analyzed samples

Conclusions

Surely the use of a highly purified polysaccharide fraction of algae is a new interesting approach for a consolidation treatment of paper.

Results obtained using the Arthrospira maxima extract encourage to deepen the research. Different experimental conditions as well as the effect of a longer aging time must be tested.

References

1) S. Margutti, G. Conio, P. Calvini, E. Pedemonte "Hydrolytic and Oxidative Degradation of Paper", *Restaurator*, 2001, 22 (2), 67-83.
2) M.C. Sistach, N. Ferrer, M.T. Romeo "Fourier Transform Infrared Spectroscopy Applied to the Analysis of Ancient Manuscripts", *Restaurator*, 1998, 19 (4), 173-186.
3) E. Ardelean, E. Bobu, GH. Niculescu, C. Groza "Effects of different consolidation additives on ageing behaviour of archived document paper", *Cellulose Chem. Technol.*, 2011, 45 (1-2), 97-103.
4) H. M. Amaro, A. C. Guedes, F. X. Malcata (2011) "Antimicrobial activities of microalgae: an invited review", in: Science against Microbial Pathogens: Communicating Current Research and Technological Advances, ed. A.Mendez-Vilas, FORMATEX Microbiology Series N° 3, vol. 2, 1272-1280.
5) K. Izumi "Chemical Heterogeneity of Anhydrogalactose Containing Polysaccharides from Gloiopeltis furcata", *Agricultural and Biological Chemistry*, 1971, 35, 633-657.
6) L. Campanella, C. Costanza, A. De Lera, "Riparazione di Carta Invecchiata Artificialmente e Fotodegrata", congress comunication at AIAr, Convegno nazionale sistemi biologici e beni culturali, Palermo, 6-7 October 2009.