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Development of a diagnostic and cleaning tool for paper artworks: a case of study☆

Laura Micheli [a,b,*], Claudia Mazzuca [a], Antonio Palleschi [a], Giuseppe Palleschi [a,b]

[a] Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata", Via della Ricerca Scientifica snc, 00133 Rome, Italy
[b] Consorzio Interuniversitario Biostrutture e Biosistemi "INBB", Viale Medaglie d'Oro 305, 00136 Rome, Italy

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ABSTRACT

Wet cleaning of ancient papers is one of the most delicate and important steps in a restoration process. It allows to improve the optical quality of a graphic work as the removal of pollution and of organic substances resulting from cellulose degradation. Nevertheless, washing by immersion – the traditional process – usually involves a substantial impact on the original morphological structure of paper and could be dangerous for water sensitive inks and pigments. Furthermore it is very important that the time of the cleaning process is optimized in order to remove all contaminants, thus minimizing invasive treatments and time costs.

In this contest, we have developed an innovative and non-invasive cleaning and diagnostic tools, based on a hydrogels combined with electrochemical sensor, suitable to verify in situ and in a simple way the paper degradation progress, and the efficiency of cleaning treatment.

More in detail, the wet cleaning technique is based on the use of a rigid hydrogel of Gellan gum. This gel is able to gradually release the water and also to absorb the water-soluble degradation products present on the paper. Moreover, it is rigid and therefore its application and removal are fairly simple, not leaving residues on the paper surface after treatment. It could be easily combined with selective electrochemical biosensors, suitable to monitor the cleaning process. Using this new tool (a biocompatible hydrogel and an electrochemical sensor) it is possible to know when the cleanup process is completed, avoiding lengthy and sometimes unnecessary cleaning material applications.

Here we report the results obtained by applying the proposed system to the "*Breviarium Romanum ad usum Fratrum Minorum*", a breviary of the 18th century, highlighting the advantage and the potentiality of this new tool with respect to the traditional old paper cleaning methodology. To perform a complete characterization of the proposed system, several invasive and non-invasive techniques, such as spectroscopy, scanning electron microscopy, high-performance liquid chromatography analysis and pH measurements have been used.

1. Introduction

Paper is one of the most important vehicles of Cultural Heritage and therefore its preservation is extremely important. It is a multi-component material, and its overall behavior (chemical and mechanical properties, stability, degradation, etc.) is strongly dependent upon the nature, origin, and characteristic of components as well as upon their interaction. The aging of cellulose-based paper artifacts reduces their mechanism properties and deteriorates their optical quality [1–3].

For example, in the presence of moisture, acids from the environment (e.g., air pollution, poor-quality enclosures), or from the paper itself (e.g., from the raw materials, manufacturing process, deterioration products), repeatedly cut the glucosidic chains into shorter ones [2,4–7].

For all of these reasons and for its fragile and complex structure, paper based artwork is probably one of the most difficult media on which to test degradation state and to restore.

In this contest, critical steps, during the restoration of paper material, to avoid irreversible damages, are the cleaning of the sheets, the pH change and the glue removal. The "standard" cleaning techniques involve washing steps with solvents (organic or aqueous) that can cause problems such as swelling and dissolution of some components. The duration of the cleaning procedure is also a very important parameter to be taken into account in order to remove all pollution and degradation products [8–10]. To solve some of the problems faced by restorers during wet cleaning, in the last years innovative cleaning methodologies have been proposed based on application of suitable hydrogels, easily removable after their application [11–13]. Their characteristics render them suitable for a combination with selective electrochemical biosensors, giving the possibility to monitor the degradation conditions of the

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* Corresponding author.
E-mail address: laura.micheli@uniroma2.it (L. Micheli).

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paper artworks and the gel cleaning efficacy [14]. One of the proposed gels is Gellan hydrogel, made up of Gellan gum and calcium salts [12,14,15]. Gellan gum is a linear anionic hetero-polysaccharide produced by *Pseudomonas elodea*, with a repeating unit of D-Glucose(β 1,4)-D-Glucuronic acid(β 1,4)-D-Glucose(β 1,4)-L-Rhamnose(α 1,3). In the presence of calcium ions, it forms hard and rigid hydrogels that are homogenous, transparent, and stable to pH variations [16]. In a recent paper [18], we have showed that Gellan hydrogel can be applied on a paper sheet and removed from it as one body, not leaving residues, moreover it is able to release water in a controlled manner [12,17,18].

However, an open question for the restorer is the gel application time to obtain a complete cleaning (the protocol used by restorers indicates 1 h, but the optimum cleaning time depends on paper characteristics) [13,15]. In principle, the extent of the cleaning process as a function of time could be determined by performing, at fixed time intervals, diagnostic experiments. In this contest, to simplify the procedure reported above, we have developed a suitable sensor to monitor, in real time, during the gel application, the extent of the cleaning, thus avoiding stopping the process to perform diagnostic investigations. Furthermore, online measurements can be advantageously coupled with Gellan gel using a flow sampling system, able of continuously removing degradation products and pollution absorbed by the gel during the cleaning of the paper samples.

The integration of electrochemical biosensors with this flow sampling system is highly desirable, not only because it simplifies the process handling, but also because measurements become more robust and operator independent [19]. Electrochemical biosensors represent an interesting approach offering the possibility to combine the analytical capability of the electrochemical techniques with the specificity of recognition process. The selectivity of these devices can be designed immobilizing a specific biologically active compound, such as an enzyme, at the surface of an electrode to convert the effects of the biological process into a quantitative electric response. Enzyme based electrochemical biosensors have been widely used in health care, food safety and environmental monitoring [20–23]. Many of these biosensors are also potentially useful for applications in Cultural Heritage area, for monitoring, identification and/or characterization of several important materials such as paper, paintings, textiles or glass [14].

The Gellan gel could be easily combined with selective electrochemical biosensors, suitable to monitor the cleaning process. Therefore, combining the biocompatible Gellan hydrogel and electrochemical sensors, we obtained a new tool for diagnostic and cleaning use. In this way, it is possible to know when the cleanup process will be completed, avoiding lengthy and sometimes unnecessary cleaning material applications.

In this work, we investigated the application of a non invasive tool, based on flow amperometric biosensor within a sampling plate, to determine in an indirect way, the cleaning efficiency of Gellan gel. In detail, to assess the potentiality of this tool, we have used it to monitor the amount of glucose absorbed by the gel during time, because glucose is the final product of endogenous paper degradation due to the hydrolysis of cellulose (a structural component of paper-based materials) [24,25]. To this end, we have used a glucose biosensor in which glucose is amperometrically detected after the enzymatic conversion of H_2O_2 by glucose oxidase (GOx).

Here, we report the results obtained by applying the proposed system during the cleaning process of the "*Breviarium Romanum ad usum Fratrum Minorum*" (Fig. 1), a breviary of the 18th century. To highlight the advantages and the potentiality of this new tool, we have compared the results obtained using our proposed systems with the traditional old paper cleaning methodologies. The application of several spectroscopic techniques such as scanning electron microscopy (SEM), high-performance liquid chromatography (HPLC) and pH measurements have been used to characterize the sheets of *Breviarium* before and after cleaning, assessing the validity of the proposed method.

2. Experimental

2.1. Chemicals

The analysis was performed on pages of the *Breviarium* of regular use at the Capuchin friars. The pages were accurately chosen in order to work on both black and red ink.

Gellan gum was sold under the commercial name KELCOGEL® CG-LA product by CP Kelco (Atlanta Georgia, USA). Albet paper (DP 400-125 — LabScience www.ictsl.net) was purchase by GE Healthcare (Italy). The methanol was of HPLC grade and where purchased by Sigma-Aldrich (Sigma-Aldrich, Mo, St. Louis, USA). Glucose oxidase (GOx, EC 1.1.3.4, type II, 15,500 U\g, from *Aspergillus Niger*), D (+)-glucose monohydrate, glutaraldehyde (GAD, 25% v\v aqueous solution) were from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO, USA). Nafion® 5% (v\v) solution was from Carlo Erba (Carlo Erba Reagenti-Italy).

All reagents were of analytical grade and used without further purification. (SIGMA-Aldich, USA). In all cases, in the preparation of buffer solutions bidistillated water was used (Millipore, Billerica, MA, USA).

2.2. Apparatus and protocols

2.2.1. Sampling and monitoring system coupled with the electrochemical biosensor

A system that combines a gel with a biosensor specific for degradation products is a very useful procedure to determine, at same time, the degradation extent of paper and the time needed to remove all of by-products and pollution, and thus to clean it reducing the time costs and the risks of damages.

Fig. 1. *Breviarium Romanum ad usum fratrum minorum*. Frontispiece before (left) and after (right) cleaning procedure.