Microchemical Journal 138 (2018) 369–378

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Interdisciplinary approach to develop a disposable real time monitoring tool for the cleaning of graphic artworks. Application on "le Nozze di Psiche"

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ARTICLE INFO

Article history:
Received 31 August 2017
Received in revised form 27 December 2017
Accepted 12 January 2018
Available online 3 February 2018

Keywords:
Disposable monitoring tool
Electrochemical biosensors
Gellan gel
Glues
Non-invasive reflectance spectroscopy

ABSTRACT

Disposable non-invasive and compatible real time monitoring tool was developed in order to follow the cleaning process of paper artwork directly *in situ*. This tool was based on a biocompatible cleaning hydrogel coupled with flow electrochemical diagnostic tool, suitable to verify *in situ* and in a simple way the assessment of degradation of artwork and the efficiency of cleaning process. In this paper, the results obtained by applying this tool on a great format artwork with a lining as support, "Le Nozze di Psiche", engraved by Diana Scultori, printed in 1613, are reported. This opera was affected by a structural and chromatic deterioration due to a strong oxidative degradation. Such deterioration was probably accelerated by the adhesive (a mixture of starch paste and animal glue) used in a previous lining intervention. In this case, the cleaning agents used are rigid hydrogels of Gellan gum, modified with hydrolytic enzymes. By using the flow sampling system, all materials removed by the gel was carried up to a thin layer cell containing a selective electrochemical biosensors, suitable to monitor both treatments, the cleaning process and the removal of lining. These were monitored, allowing understanding when both processes were completed, thus avoiding lengthy and unnecessary cleaning applications. The effectiveness of cleaning with Gellan gel was assessed quantitatively by using non-invasive optical reflectance spectroscopy by a portable instrumentation, elaborating data with an improved version of the Kubelka-Munk theory in order to recover the absorption coefficient of the cellulose fibers of "Le Nozze di Psiche". The concentration of oxidized groups acting as chromophores was obtained by comparing the experimental optical absorption spectra to those simulated computationally by using TDDFT-based calculations. By following the cleaning with Gellan gel the results indicate a large decrease of the concentration of degradation product of cellulose. Moreover, chromatographic analysis were carried out in order to evaluate the amount of acid compound, produced during the aging and present on the graphic artwork, using the Gellan gel after cleaning step. The results obtained from the restoration of "Le Nozze di Psiche" have allowed the restorers to evaluate innovative methods for cleaning treatment of paper artworks with a highly specialized scientific-diagnostic approach.

1. Introduction

Wet cleaning of ancient papers is one of the most delicate and important steps in a conservation process. Due to inherent fragility of ancient paper artworks, the cleaning of these artifacts is a very difficult task because it can cause several damages, such as loss of mechanical properties, inks or pigments fading and fibers weakening of fibers. At the same time, washing treatment improves the optical quality of a graphic work and can effectively slow down degradation processes, promoting the removal of polluting and organic substances resulting from artwork aging. In the last years, several efforts have been done to identify different, less invasive and effective cleaning methods able to preserve original paper features. In this contest, for example, dry cleaning strategies involving mechanical abrasion through microblasting techniques [1] or laser ablation [2, 3] have been developed, so as the introduction of new chemical products like sprayable solutions of sodium

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https://doi.org/10.1016/j.microc.2018.01.022
0026-265X/

hydroxide nanoparticle, able to raise the pH of acid papers, or gel-based material [4–9].

Wet cleaning of ancient papers is usually performed by means of a water bath could be harmful due to fibers swelling, gelatin size partial removal and finally instability of graphic media. Recently, to overcome these drawbacks, cleaning methodologies based on the application of suitable hydrogels have been proposed. The application of rigid, retentive hydrogels reduces water uptake of the paper, more respectful of the original integrity of the artwork. In this context, a valid alternative to traditional paper washing by immersion is represented by Gellan gel, as pointed out in a previous work [5]. Moreover, Gellan gel could be easily loaded with hydrolytic enzymes in order to facilitate the removal of unwanted and/or dangerous materials from paper artwork like old and deteriorated adhesives that, after the enzymatic reactions, could be easily removed from the paper and absorbed by the gel. The efficiency of Gellan gel loaded with enzymes as a cleaning agent was demonstrated by Mazzuca et al. [10, 11]. However, an unresolved problem related to the duration of the cleaning was still pending: the possibility to clearly identify the treatment end in order to optimize its effectiveness and minimize the risk of damages for both paper support and graphic media. Thus, a new system that combines the cleaning Gellan gel with an electrochemical biosensor has been developed. The selected biosensor can detect specific products removed by the gel from the paper, so allowing conservators to finally understand the correct treatment duration. The system is a device tool to monitor *in situ*, in a very simple and relatively cheap way, the degradation state and the efficiency of the cleaning process of the paper artworks. The cleaning process can be monitored in real time, directly on the treated surface, by a flow sampling system, assembled on the hydrogel and connected to ad hoc designed electrochemical sensors. 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 [12]. A previous paper describes the application of this new cleaning and diagnostic tool, in a prototype version, applied for the cleaning of one page of the "Breviarium Romanum ad usum Fratrum Minorum" (1738) [13]. The results obtained demonstrated that these electrochemical devices have great potential for the detection and the evaluation of unwanted substances during cleaning treatments.

In this paper, the results obtained with an improved and implemented version of the developed device, able to monitor both cellulose degradation by-products and particles of hydrolyzed adhesive, used to line the paper artwork in the past, are reported. The removal of old adhesives, used to line the *verso* of the artworks, without causing any damage to them is a very important goal in paper conservation, because deteriorated adhesives normally undergo structural transformations that promote and accelerate the chemical degradation processes of the paper artwork itself. In the case study here presented, the cleaning Gellan gel was loaded with hydrolytic enzymes (a protease to remove animal glue and an amylases to remove starch paste) that hydrolyze adhesive glue polymers into smaller fragments that could be easily solubilized and absorbed by the gel. In detail, a two-flow way diagnostic tool was assembled; the first way is used for monitoring the cleaning treatment of the artwork, able to directly analyse cellulose degradation by-products or dust. The second way is used to monitor the removal of the products of the enzymatic reactions on the adhesives during the application of the enzymatic Gellan gels. Along this second flow way, a bioreactor was put in line with the flow tube (between the sampling plate and the electrochemical biosensor) in order to transform the enzymatic products in an analyte, easily detectable by the electrochemical biosensor. This tool, so modified and optimized, was applied for the cleaning treatment of a large format engraving entitled "Le Nozze di Psiche", edited in 1613. The print (Fig. 1), restored at the Istituto Centrale per il Restauro e la Conservazione del Patrimonio Archivistico e Librario (ICRCPAL), consists of three sheets, corresponding to three copper plates (total width: 1125 mm; height: 373 mm). The artwork showed evident chromatic and structural deterioration, and left dark stains scattered throughout the *verso* of the paper caused by cellulose oxidative degradation and microbial attacks. Moreover, in the past, this artwork was reinforced with a lining using an adhesive mix of paste and glue. The natural aging of the adhesive mix contributed significantly to artwork degradation. The removal of the lining was therefore necessary.

The association of enzymatic Gellan gel with a monitoring system, connected to an electrochemical sensor, allowed the conservators to follow the cleaning activity during all the wet cleaning treatments, monitoring in real time the products resulting from cellulose degradation and from hydrolytic enzymatic activity. Electrochemical biosensors represent an interesting approach offering the possibility to combine the analytical capability of the electrochemical techniques with the specificity of recognition process. This tool represents therefore a cheap, real-time and on-site diagnostic tool for paper artworks. In particular, to assess the potentiality of this tool, the amount of glucose absorbed by the gel during time was monitored, because glucose is the final product of endogenous paper degradation due to the hydrolysis of cellulose (a structural component of paper-based materials) and the final product of the starch glue degradation [14]. To this end, a glucose biosensor, in which glucose is amperometrically detected after the enzymatic conversion of H_2O_2 by glucose oxidase (GOx), was used.

The variation of the optical properties of paper was analyzed through the quantification of the chromophores, which caused the oxidation of cellulose chain. These chemical species (aldehydes, ketons and diketons) characterized by carbonyl group, in a second oxidative stage form carboxyl groups can cause acidity increase in the paper. Furthermore, they absorb the higher energy band of visible light, corresponding to violet and blue, and largely scatter the yellow and red portion, thereby producing the characteristics yellow-brown hue. Interestingly, simulations performed with carboxyl groups showed instead no absorption bands in the UV-Vis range up to 258 nm (4.8 eV) and therefore no contribution to paper yellowing.

Therefore the effectiveness of cleaning with Gellan gel was assessed quantitatively by using non-invasive reflectance spectroscopy in the ultraviolet-visible-near infrared (UV–Vis–NIR) spectral regions. This approach is based on an improved version of the Kubelka-Munk theory for recovering the absorption coefficient of cellulose fibers from reflectance measurements [15].

Experimental absorptions spectra in the UV–Vis_NIR were compared to theoretical absorptions of aldehydes, ketons and diketons obtained by *ab-initio* computational simulations based on the Time-Dependent Density Functional Theory (TDDFT). In this way the concentration of oxidized groups acting as chromophores and inducing yellowing in paper were evaluated [16, 17].

At the same time, the gel, used for the cleaning process was analyzed by High Performance Liquid Chromatography (HPLC), in the same point of the artwork where the reflectance measurements were carried out. Results indicate a large decrease of their concentration following the restoration.

2. Experimental

2.1. Chemicals

The analysis was performed on "Le Nozze di Psiche", engraved by Diana Scultori in 1575 and printed in 1613.

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*), a-*glucosidase* (EC 3.2.1.20), glutaraldehyde (GAD, 25% v/v aqueous solution), *Proteinase K* from *Tritirachium album* [EC-3.4.21.64, ≥30 U/mg], *α-Amylase* [EC-232−560−9; 30,500 U/mL], calcium acetate, calcium chloride