Journal of Colloid and Interface Science 416 (2014) 205–211

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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Gellan hydrogel as a powerful tool in paper cleaning process: A detailed study

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ARTICLE INFO

Article history:
Received 5 August 2013
Accepted 21 October 2013
Available online 8 November 2013

Keywords:
Paper conservation
Paper morphology cultural heritage
Gellan gum
FTIR
HPLC
SEM
Gel residues

ABSTRACT

Hypothesis: Wet cleaning of ancient papers is one of the most critical steps during a conservation treatment. It is used to improve the optical qualities of a graphic work and remove dust and by-products resulting from cellulose degradation. Nevertheless, washing treatment usually involves a substantial impact on the original morphological structure of paper and can sometimes be dangerous for water sensitive inks and pigments.
Experiments: The use of rigid hydrogel of Gellan gum as an alternative paper cleaning treatment is developed. The application of a rigid hydrogel minimizes damages caused by the use of water, and therefore is much more respectful for the original integrity of ancient paper.
Findings: Gellan hydrogel has been used to clean paper samples belonging to different centuries (from XVI to XIX) and therefore, characterized by a different story in terms of degradation condition and paper composition. Several techniques, such as high-performance liquid chromatography, Fourier transform infrared spectroscopy, scanning electron microscopy and pH measurements, has been employed to assess the effectiveness and safety of the proposed cleaning method.

1. Introduction

Cleaning is one of the most delicate and important steps in paper conservation. It allows the removal of pollution, deposited on paper surfaces and the partial dissolution of organic substances as a result of cellulose degradation [1]. Washing by immersion – in principle – represents the ideal technique because water can uniformly reach paper artifacts [2]. Nevertheless, such a common cleaning treatment presents several disadvantages: (1) water has to be frequently replaced during the treatment; (2) the prolonged contact with water induces swelling of cellulosic fibers, which, in turn, can cause deformation of paper material after drying. This phenomenon complicates the reconstruction of artworks fragments; (3) water induces a good removal of sizing agents like gelatin [3]; (4) modern paper cannot be cleaned by using this method because of its fragility and sensitivity to water.

In the last years, to confront these issues, innovative cleaning methodologies based on the application of suitable hydrogel have been proposed in the cultural heritage field. Due to their high retention power and their viscosity, the penetration of these liquids into the paper sheets can be significantly reduced, therefore minimizing paper fibers swelling [4–7]. However, a complete removal of these gels often requires an abrasive mechanical action (i.e., removal with a brush or by wet cotton swabs), which is often unsafe for the artwork. At the same time, gel residues can induce dangerous microbial growth [8,9]. To overcome this drawbacks, highly rigid and film forming hydrogels may represent a useful alternative [3,5,7,10], as they can be completely and easily removed in one operation after their application, thus minimizing the side effects already presented. In this contest, a new wet cleaning technique based on the use of a rigid hydrogel of Gellan gum has been recently developed [3,6,11]. Gellan gum is a gelling agent widely used in food, biomedicine and pharmaceutical industry. It is a linear anionic heteropolysaccharide produced by *Pseudomonas elodea* and consists of (1,3)-β-D-Glucose, (1,4)-β-D-Glucuronic acid, (1,4)-β-D-Glucose, (1,4)-α-L-Rhamnose, repeating units [12]. In the native polymer two acyl substituents, L-glyceryl at O(2) and acetyl at O(6) are present at the 3-linked glucose and, on average, there is one glyceryl per repeating unit and one acetyl every two repeating units [13]. Deacylated Gellan gum is obtained by alkali treatment of the native polysaccharide. Both native and deacetylated

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0021-9797/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2013.10.062

polymers form hydrogels [12–18] whose sol–gel transition process is temperature dependent [16,17]; in particular, the deacylated polysaccharide, in presence of calcium salts, forms hard and rigid hydrogel with a slow syneresis rate; moreover, it is homogenous, transparent, and stable to pH variations [14,18]. The pH stability assures that the hydrogel can be safety applied to every paper samples whatever its pH value. Due to these properties, Gellan hydrogel has been selected to perform safer wet cleaning treatments on paper artworks. The present paper will then discuss and compare the results obtained by applying the Gellan hydrogel cleaning method and the traditional cleaning technique (i.e. immersion in a deionized water bath) on different paper samples. Tests for fibers identification and analysis to assess the degradation levels of paper samples have been preliminary carried out using high-performance liquid chromatography (HPLC), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and colorimetric analysis.

2. Materials and methods

2.1. Reagents and materials

The analysis was performed on samples of original papers (50 × 60 mm) without ink color (called blank samples) taken from the following printed books dating respectively to the 16th, 17th, 18th, and 19th centuries:

Virgilius Viridarium Illustrium Poetarum, Venetiis MDVII, Discorso sopra l'iscrittione della Colonna Rostrata in Roma MDCXXXV, Theatrum Veritatis et Justitiae, Venetiis MDCCXXXIV, Ettore Fieramosca o la Disfida di Barletta, Losanna, 1862.

Zinc chloride, aluminum chloride, potassium iodide, calcium acetate, calcium chloride and standard organic acids were obtained from Sigma (Sigma–Aldrich, Mo, St. Louis, USA). Iodine was obtained from Carlo Erba Reagenti (Carlo Erba Reagenti srl, Milano, Italy). Gellan gum was sold under the commercial name KELCOGEL® CG-LA Gellan gum product by CP Kelco (Atlanta Georgia, USA). Whatman paper was purchase by GE Healthcare (Italy). All reagents used were of analytical grade and used without further purification. In all cases, in the preparation of water solutions bidistilled water was used (Millipore, Billerica, MA, USA).

2.2. Methods

2.2.1. Gel preparation

The protocols reported by Iannucelli et al. were followed for hydrogel preparation [13,11]. The weight percentage of the polysaccharide and calcium ion in the hydrogels was selected according to literature [12,17,18] and to the results of several tests like the *contact* angle test, [3] performed in our laboratories on all samples to be treated. To prepare the hydrogel an aqueous solution of Gellan (20 g L^{-1}) and calcium acetate (0.40 g L^{-1} = 2.5 mM) was put for almost a minute in the microwave at 600 W (Mars Microwave, CEM Corporation, Matthews, NC, USA) until it boils and become transparent; then it was left to cool at room temperature on a Petri dish.

2.2.2. Gel application procedure

The samples were divided into four groups each one belonging to a specific century, and subsequently split into two sub-homogeneous samples to be treated respectively by immersion in deionized water and by contact with Gellan gum. In the first case, each sample was placed in a Petri dish containing 40 mL of free deionized water at room temperature. In the second case, 40 mL of Gellan hydrogel was applied to the *recto* of each paper samples and covered with a PET film (Mylar®), uniformly pressed to ensure a contact between the gel and the sample. After treatment, the gel was removed very easily with the use of a spatula. The interval time of both cleaning techniques was one hour.

2.3. Paper samples characterization

2.3.1. Paper composition

Paper fibers composition was estimated by exposing them to graff "C" stain [19]. Briefly, graff "C" was prepared by mixing in 52 mL of a $ZnCl_2$ saturated solution, 0.06 mol of $AlCl_3$ and 0.06 mol of $CaCl_2$, 0.64 mmol of I_2 and 1.4 mmol of KI. To analyze paper materials, a drop of graff "C" stain was applied to a very small portion of each sample, previously chopped with the help of a droplet of water. The sample was then placed on a microscope slide and observed on a Zeiss microscope (mod. Axio Scope. A1, Carl Zeiss AG. Oberkochen, GmbH). The presence of proteinaceous sizing agents was investigated by the Bicinconic acid test (BCA test) [21] on fragments of paper samples and following the procedure reported on the Pierce assay kit.

The presence of carbonates as alkaline reserve or due to the original paper manufacture procedure was investigated by the carbonates test. Few droplets of hydrochloric acid and barium hydroxide were added at the same time, on paper samples fragments. The opalescence due to the formation of barium carbonate indicates the presence of this carbonates salt in the samples [22].

2.3.2. Spectroscopic analysis

FTIR spectra were acquired on a Thermo-Nicolet (mod. Nexus 670) instrument (Thermo Scientific Inc., Madison WI), equipped with an attenuated total reflectance (ATR) ZnSe cell for measurement in the 4000–700 cm^{-1} region, at a resolution of 4 cm^{-1}. Spectra were performed by placing the paper samples directly on the ATR cell. A total of 256 scans were collected for each sample.

To determine the presence of degradation products in the paper samples, a deconvolution of FTIR bands region was done following the algorithm described by Calvini and Gorassini [23]. Briefly, fitting was performed in 1400–1900 cm^{-1} region on normalized absorbance spectra by means of a sum of Lorentzian functions using routines written in-house. The constraints imposed on the fitting algorithm were: the number of fitting bands, the range of allowed full width in half maximum (FWHH) and the range of frequency in which the minima are searched, according to the features of expected products of cellulose and lignin oxidation bands described in literature [23–25].

Scanning Electron Microscopy was performed using a FE-SEM, Field Emission Scanning Electron Microscope (SUPRA™ 35, Carl Zeiss SMT, Oberkochen, Germany). Punched samples were previously metalized to allow electronic conduction on the sample surface in order to obtain high quality images without deteriorating the samples or creating any kind of artifacts. The metallization, 1 min at 25 mA, was performed using a sputter coater (EMITECH K550X, Quorum Technologies Ltd., West Sussex, United Kingdom) with a gold target. The detector used was the SE (Second Electron detector) as the interest was mainly focused on the morphology of the paper fibers and on the presence of residues deriving from the cleaning agents; the main operating parameters of the instrument were 10 kV as gun Voltage and a working distance of about 8 mm.

2.3.3. Chromatographic analysis and pH measurements

The HPLC system consisted of a modular CHROMQUEST spectra system from THERMOQUEST (San Joes, CA, USA), equipped with two LC-10AT Vp pumps, Schimadzu UV–VIS spectrometer model (SPD-10AV) detector. A SCL-10A Vp controller operated the HPLC system working under control of software included in the CHROMQUEST module. The chromatographic separation was performed

using a reverse phase C18 stainless steel column (5 μm 150 × 4.6 mm I.D – VYDACTM, W.R. Grace & Co, USA). The composition of the mobile phase was 25 mM phosphate buffer of aqueous solution at pH 2.4 and 1% (v/v) methanol with a flow rate of 0.7 mL min^{-1} and using a detection wavelength equal to λ = 210 nm [26]. Analysis was performed before and after both cleaning treatments (by Gellan hydrogel and washing by immersion in deionized water [2,27]). Each chromatographic analysis was repeated three times in the same day (reproducibility intra-day) and on different days (reproducibility inter-day) for all the samples. The chromatographic analysis was performed on extracts obtained by treating 1 cm^2 of every sample (paper or hydrogel) with 1 mL of distilled water, stirring overnight at room temperature. An anion exchange column (STRATA-SAX Phenomenex, Torrance, CA, USA) was used for the separation and concentration of the acid component of each analyzed sample [28]. In order to determine these contaminants at trace level in paper samples, pre-concentration was necessary prior to chromatography analysis. For this reason, a preliminary purification by solid phase extraction (SPE) cartridge on the water extracts of the paper samples was performed prior HPLC analysis. The SPE method was used for separating, for concentrating and for converting all salts present in the paper samples (as alkaline reserve or paper degradation) in the corresponding acid forms, which are easier to be identified by HPLC. In particular the attention was focused on ascorbic, malic, lactic, oxalic, citric, and succinic acids. pH measurements were carried out before and after both cleaning treatments (Gellan hydrogel and immersion in deionized water) on the same aqueous extract before the STRATA separation, used for chromatographic analysis, [29] by using an Amel Instrument 334-B pH meter with a combined glass electrode Ag/AgCl 6 mm (Amel Instrument, Italy).

3. Results and discussion

3.1. Paper characterization

Paper composition was estimated by exposing paper fibers to graff "C" stain. The paper color obtained after exposure to the stain, is related to the paper composition (which is different from paper deriving from wood pulp or from rag pulp, if the wood pulp is from softwood or hardwood wood and, if the pulp has been bleached or not) [20]. The images obtained for samples belonging to 16th, 17th and 18th centuries (Fig. S1) show that their fibers are orange/red colored, because they mainly consists of cellulose and, therefore, are from rag pulp. The fibers of the samples belonging to 19th century, however, are not only orange/reddish, but also, red/purple colored, indicating the presence of bleached lignin.

SEM images (Fig. 1) show that the morphology of the samples appears different from each other. In the figures of the older papers (16–18th centuries) are clearly visible cellulosic fibers [30], while in those from the 19th century are absent. Moreover, cellulosic fibers in the three older samples are in a well conservation state, as fraying and breakages are not present.

FTIR-ATR is a very useful, non-destructive technique to identify the main component of paper and to evaluate the presence of other compounds [23]. FTIR-ATR spectra of all the samples (Fig. 2) show the typical features of cellulose paper spectrum [23,31]. As a matter of fact, in the region 1500–950 cm^{-1} the characteristic complex pattern of cellulose absorption bands due, for example, to CO and CC stretching, CCH and OCH deformation stretching, COH and HCH bending. A detailed inspection on the IR spectra of samples from different periods reveals that subtle differences between them exist. For example, as shown in Fig. 2 in the spectra of the sample from 16th century, the intensity of the peak at 998 cm^{-1}, is the same of that of main cellulosic peak (1024 cm^{-1}), indicating the presence of starch. Moreover, the peaks at 1415 and 874 cm^{-1}, which appears in the three older samples, reveal the presence of carbonates [32–34] as a result of the retting process with lime which produced an alkaline reserve during paper manufacture process. The spectra of 19th century samples, unlike the others, lack the peaks of gelatin (sizing used before 19th century), normally localized at 1640 and 1580 cm^{-1} [33,34]. Nevertheless, the presence of colophony (the alum–rosin size introduced during the 19th century), cannot be detected by IR measurements [33]. In principle, the presence of wood pulp in paper can be detected by the appearance of two IR peaks at 1505 cm^{-1} and at 807 cm^{-1}, relative to lignin and hemicelluloses, respectively [34,35]. In the FTIR spectra of samples belonging to the 19th century, on which the "graff C" test indicates the presence of lignin, these peaks are not so evident, indicating that probably the amount of wood pulp in these samples is low.

BCA and carbonates tests confirm the presence of gelatin and carbonates in the three older samples. To determine the presence of degradation products on paper, deconvolution of FTIR spectra into several bands has been performed, according to the indications reported in literature [23–25]. On Table 2 the characteristics (peak assignment, mean value and FWHH) of the bands attributed to several compounds that are (or may be) presents on paper samples are indicated; while, in Fig. 3, the deconvolution bands obtained for sample belonging to 17th century, together with the comparison between the spectrum obtained from deconvolution and the experimental one are reported. From the deconvolution bands it is possible to calculate the overall oxidation index (O.I.) [24] and therefore to estimate the oxidation state of cellulose. More in detail, the O.I. is the ratio between the integrals of two IR regions, localized respectively at 1664–1837 cm^{-1} and 1500–1664 cm^{-1}, taking care to avoid band due to bound water, which maximum is at 1639 cm^{-1}. This definition is based on the evidence that bands attributed to carboxyl and carbonyl groups, which represent the final oxidation stage of cellulose, are localized at higher wavenumbers (1745–1710 cm^{-1}) with respect of bands arising from oxidation intermediates (1660–1620 cm^{-1}). Therefore, higher is the O.I., more oxidated is paper. From data reported, the O.I. of studied samples are low (0.20, 0.38, 0.17 and 0.16 for samples of 16th, 17th, 18th and 19th century, respectively), comparable with those obtained for not aged cellulosic material [25]. This evidence indicates that studied samples are, after all, in a good state of preservation and not strong degradation processes are ongoing.

Paper artworks generally contain also several organic acids due to their preparation method, their composition and/or their degradation level. Cellulosic fibers, indeed, degrade when exposed to acid environment in the presence of humidity. In this hydrolysis reaction, cellulose chains are repeatedly split into smaller fragments as long as acidic components are present in paper. In addition, hydrolysis produces acid molecules and thus, paper degradation accelerates. Recently the research group of Library Congress (USA) discovered that the cellulose itself of paper generates several low molecular weight acids, such as acetic, formic, lactic, and oxalic acids [36,37]. Most early papers, made from cotton and linen rags, are still strong and durable, while, papers produced from wood pulps (from the middle of XIX century) are more fragile and sensitive to the acidic hydrolysis due to the presence of lignin and hemicelluloses, more reactive than cellulose. In XIX century, in addition, the alum-rosin agent was introduced as ingredient during paper production; this reagent generates sulfuric acid in the presence of humidity [38]. To slow down degradation, as reported earlier, an alkaline reserve is added during the production of every kind of paper. This reserve is used to neutralize acids present in the paper and as whitening agent [39,40].

To characterize the salt and acidic compounds present in the paper samples under investigation, chromatographic analysis have

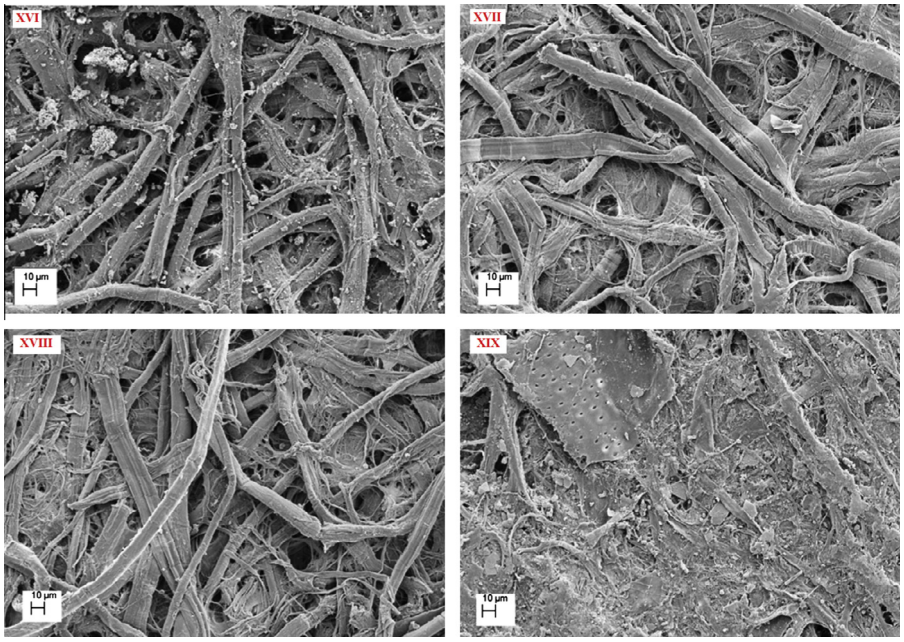

Fig. 1. SEM images of paper samples before any treatments. Paper samples belongs to: XVI, XVII, XVIII and XIX centuries.

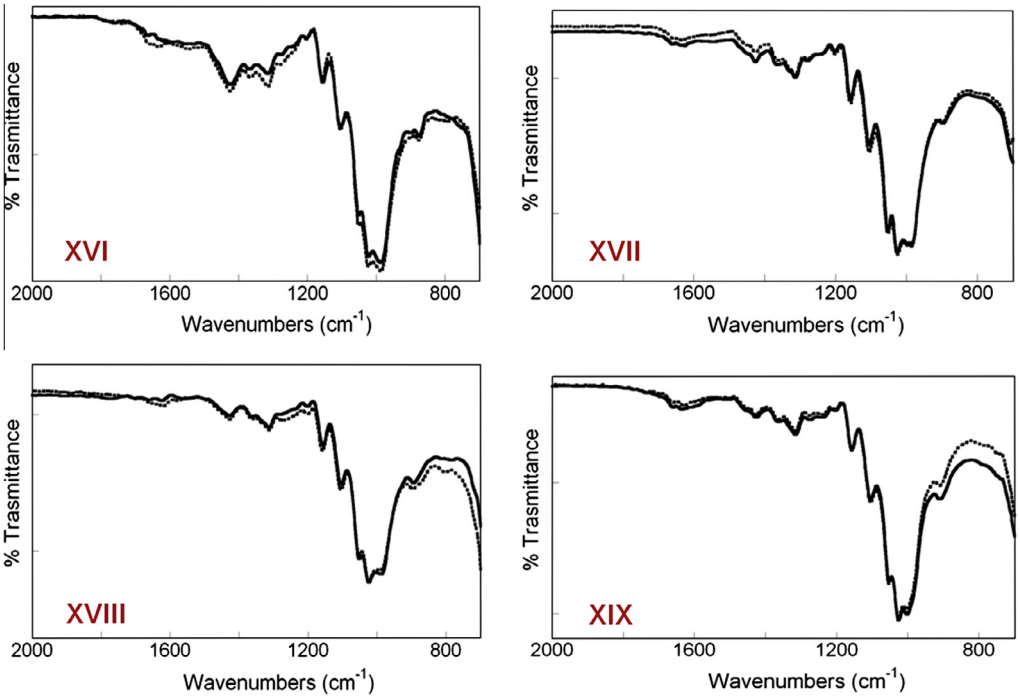

Fig. 2. FTIR spectra of paper samples before (solid line) and after (dashed line) cleaning treatment.

Table 1
pH values before and after cleaning treatments.

	Before	After (cleaning step with gel)	After (traditional clearing step)
XVI	8.5 ± 0.1	9.4 ± 0.2	9.3 ± 0.1
XVII	7.1 ± 0.2	7.6 ± 0.1	7.9 ± 0.2
XVIII	8.6 ± 0.2	9.0 ± 0.2	8.9 ± 0.2
XIX	5.1 ± 0.1	6.4 ± 0.1	5.9 ± 0.1

been carried out following the protocol reported in materials and methods. In particular the attention was focused on ascorbic, malic, lactic, oxalic, citric, succinic acids, present in alkaline reserve and product of spontaneous degradation of cellulose. The

Table 2
Peak assignment and FWHH used for spectra deconvolution [26].

Peak assigned to:	CH2	COH	NH, lignin	Amide II	Water bound	C=CCO	Amide I	C=O Chetonic group	C=O Aldeidic group	COOH
Mean[a]	1430	1460	1517	1546	1640	1657	1675	1726	1736	1743
FWHH[b]	36	61	42	69	88	26	84	47	35	28

[a] Peak values are in a range of 10 cm^{-1}.
[b] Values are allowed to vary in a range of 20 cm^{-1}.

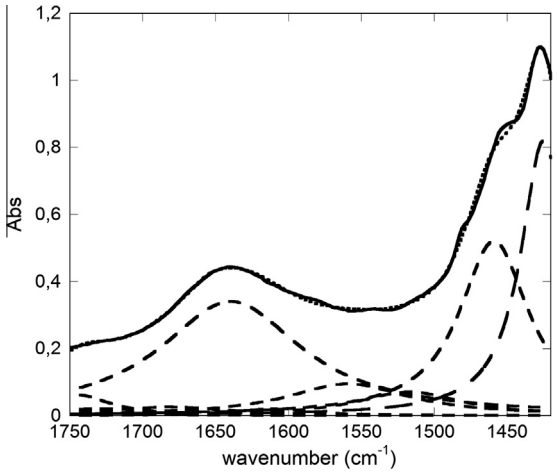

Fig. 3. Deconvolution of Lorentzian functions (*dashed lines*) to the FTIR spectrum of paper sample belonging to the 17th century (*dotted line*); in the figures is reported also the sum of the bands obtained from deconvolution (*solid line*).

chromatographic analysis on samples before cleaning treatment have shown that there are some differences among paper samples belonging to different centuries, with respect to the acidic components. The results have been compared to the chromatogram obtained for standard solution of the selected acids in order to allocate the peaks. All samples showed one peak around 3 min relative to oxalic acid. The chromatograms of the samples of 16th and 17th century (Fig. 4A and C) showed another peak around 8 min, more evident for the sample of 16th century, and less for the 17th century; it could be related to the fractions of the acidic degradation products of gelatin, which has been used mainly in the 16th century. Its attenuation in the chromatogram of the sample relative to the 17th century may be due to a decrease of the amount of gelatin on it, according to literature [1]. The chromatogram of the sample of 17th century showed other two peaks relative to lactic and citric acids (3.5 and 5 min) (Fig. 4B). In the chromatogram of the sample belonging to the 19th century, new peaks appear, at 3.5 min, 5 min, 7.8 min (Fig. 4D). Two of them (3.5 and 5 min), are relative to lactic and citric acids while the other two are due to less polar acid fractions not yet identified by comparing the chromatogram with the one of standard organic acids. These results are in according with the data reported in literature [27,39,40].

pH measurements (Table 1) give information on the amount of acidity present in the paper and so to the preservation state of samples. pH values of the samples belonging to the 16th and

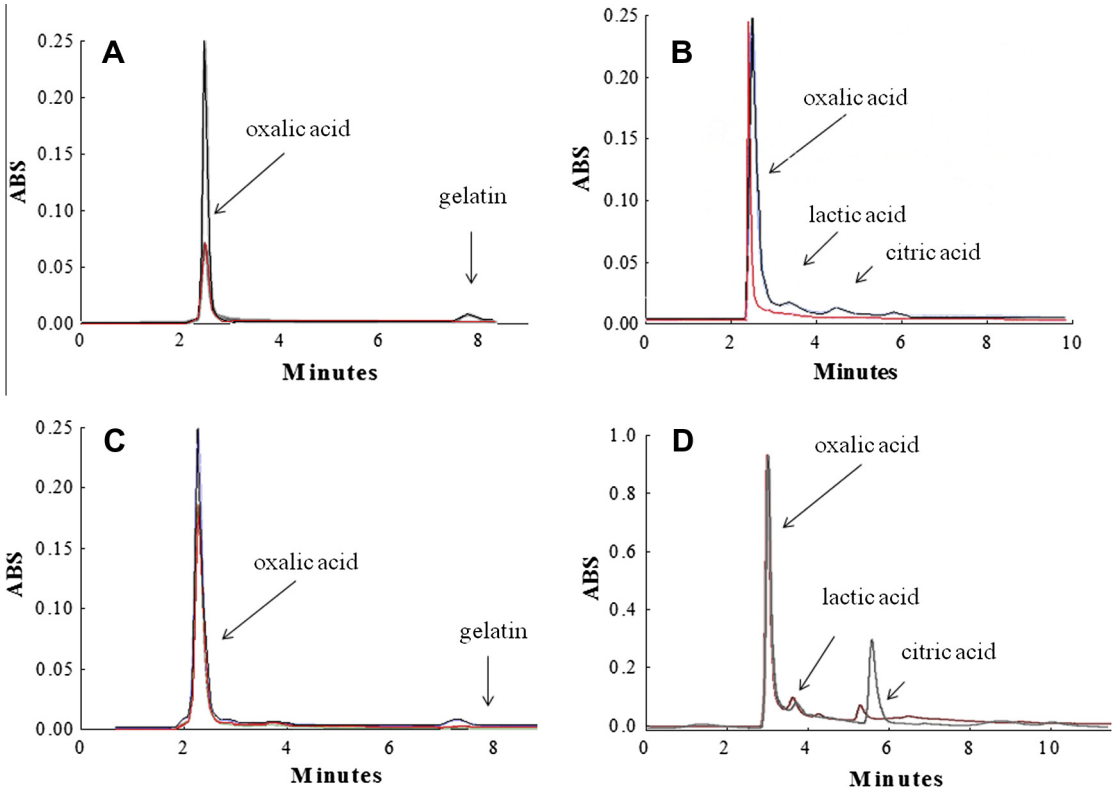

Fig. 4. HPLC measurements on water extracts of paper samples belonging to XVI (A), XVII (B), XVII (C), XIX (D) centuries before (*black line*) and after (*red lines*) Gellan gel treatment. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

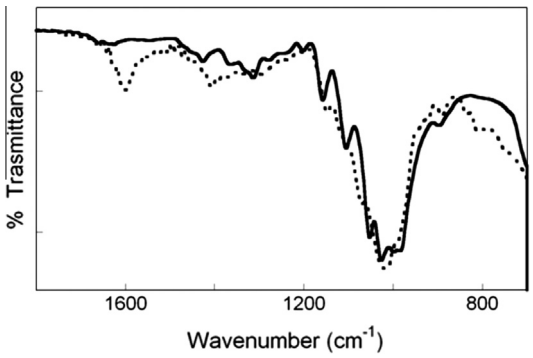

Fig. 5. FTIR-ATR spectra of a paper sample belonging to XVII century (solid line) and of the Gellan gel (dashed line).

18th century are greater than that of the 17th and 19th samples and are consistent with values considered optimum for cellulosic material, that is from 8 to 9 pH units [1,32]; slightly lower pH values obtained with samples of the 17th century indicates that the degradation processes are ongoing. Chromatographic analysis of the 17th century sample, confirmed this result: a relevant amount of acidic components (see above) was revealed. The lower pH value detected in the 19th century paper sample is probably due to the presence of lignin (confirmed by the colorimetric "graff C" test) since the paper of the 19th century sample was obtained from bleached wood pulp.

3.2. Hydrogel application

Gellan hydrogel, due to its properties, could represent, in the paper cleaning procedure, a valid alternative to the traditional method with water. In our work we want to assess the general validity of the proposed cleaning treatment; to this end, we have employed paper samples belonging to different centuries and therefore, are characterized by a different story in terms of degradation condition and paper composition.

As reported in materials and methods, paper samples were divided into two groups and treated respectively by immersion in deionized water and by contact with Gellan hydrogel. After both cleaning treatment, dried samples were analyzed to assess treatment efficiency. FTIR analysis shows that hydrogel applications do not leave residues on paper material. The hydrogel displays a very characteristic IR spectrum, whose peaks are not present in every spectrum of the treated samples, as shown in Fig. 5. The spectra obtained before and after treatment, are indeed comparable, also suggesting that no detectable chemical degradation of cellulose takes place as a result of the hydrogel treatment. SEM images (Fig. 6 showing 17th and 19th century samples) confirm these results as both samples after immersion in water and hydrogel treatment, seem cleaner and no swelling or fraying are present. At the same time, the increase of pH values obtained after both cleaning procedures indicates that acidic components, involved in degradation processes are removed; anyhow it should be noted that the pH values are acidity is lightly higher after Gellan hydrogel cleaning procedure. These results indicate that hydrogel treatment is an efficient cleaning method and does not cause change in the morphology of paper.

Gellan hydrogel is, furthermore, more able to remove pollution and degradation products from paper, with respect to immersion in water, as shown by the comparison between the chromatograms of samples treated with the two methods (Fig. 7). Peaks were only attenuated after the cleaning treatment using water, and have disappeared after Gellan hydrogel treatment. This phenomenon can be explained by taking into account both the diffusive properties of molecules in the hydrogel and the intrinsic nature of it, rich in alcohol groups, capable to interact with the acidic residues on paper. A further identification of acid components in paper samples, removed by the hydrogel during the cleaning step, is obtained by performing HPLC measurements on Gellan hydrogel after extraction procedure (see material and method). The analysis was carried out on the same hydrogel before and after cleaning treatments (data shown only for 16th and 18th centuries, Fig. 7). The comparison of the results with the chromatograms of acid standard solutions confirmed the presence of oxalic, citric, succinic and lactic acids on them, absent in the hydrogel before the cleaning step (not used) and not observed in the chromatograms of paper samples because there acids were present in low concentration (the absorbance of paper samples chromatograms are 10 times higher). The presence of gel residues on paper samples has been investigated by performing HPLC analysis of aqueous extracts of Gellan hydrogel before and after treatment on Whatman paper samples (Fig. S2), as reported in SI section.

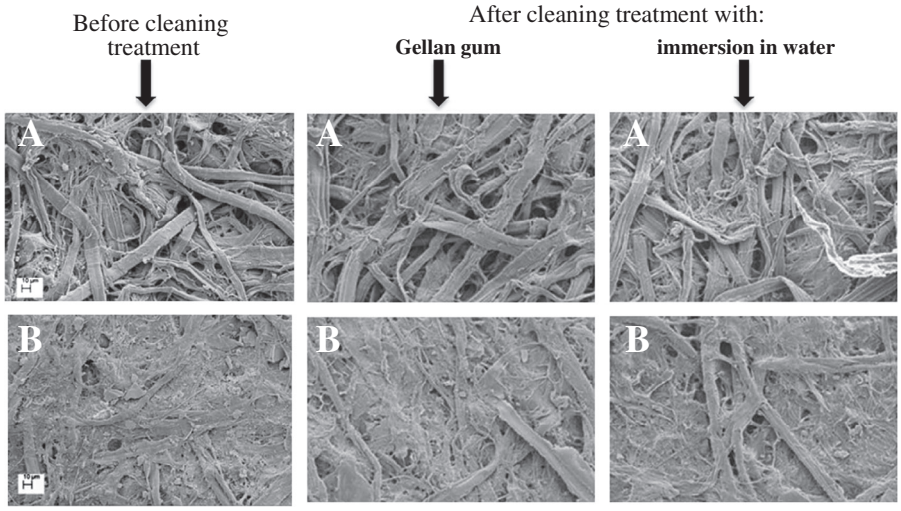

Fig. 6. SEM images of paper samples belonging to XVII (A) and XIX (B) century respectively before cleaning (*left*), after Gellan hydrogel treatment (*middle*) and after immersion in water (*right*).

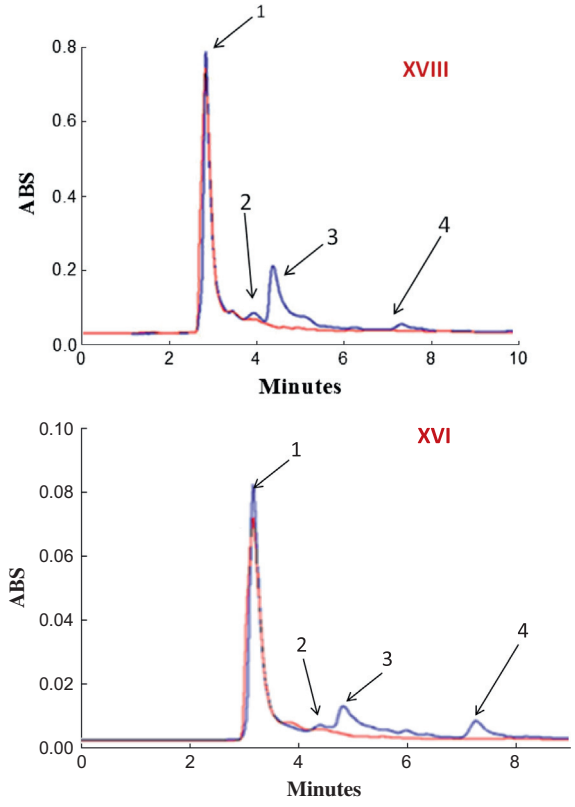

Fig. 7. HPLC chromatograms of water extracts hydrogels used for cleaning step of XVI and XVIII century samples: before any cleaning treatment (blue line), after paper cleaning step (red line). Extracted acid compound: 1- oxalic acid, 2- lactic acid, 3- citric acid, 4- succinic acid. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4. Conclusions

In this study, a new and alternative method for traditional cleaning treatment of paper has been assessed. The proposed system is based on the use of highly rigid hydrogel obtained with the deacylated form of Gellan gum and calcium acetate. Its peculiar rheological and film forming properties make it possible to remove it very easily from paper in one operation, thus avoiding damages and any risk on paper artworks. The proposed cleaning method was tested on different paper samples dating from 16th to 19th centuries and therefore characterized by different ageing and paper properties. The results obtained after pH, HPLC, FTIR-ATR, SEM were then compared with those obtained from of the same paper samples cleaned using the conventional washing procedure (immersion in deionized water). The comparison of the results obtained allowed highlighting and assessing the efficacy of the proposed Gellan gum cleaning method.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2013.10.062.

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