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Multi-function Gellan Gum Hydrogel for Heritage Paper Cleaning

Asmaa M. Rushdy[a], Wafika N. Wahba[b], Sawsan Dacrory[c], Samir Kamel[c]

[a]*Manuscripts Department, Islamic Art Museum, Cairo, Egypt*

[b]*Conservation Department, Faculty of Archaeology, Cairo University, Giza, Egypt*

[c]*Cellulose and Paper Department, National Research Center, El Bohooth St., Dokki, Giza, Egypt*

Abstract

Treatment of historical paper with gels has become a familiar new method used in many conservation labs in museums, libraries, and archives. So, this study evaluates gellan gum with and without loading multifunction materials such as Ethylenediamine tetraacetic acid (EDTA), sodium dithionite, and nano calcium carbonate. Investigation and analysis were used to characterize the hydrogels, such as swelling, scanning electron microscopy (SEM) with EDX analysis, X-ray diffraction analysis (XRD), thermal gravimetric analysis (TGA), and attenuated total reflection analysis (ATR). The historical papers were treated with hydrogels, and photography and digital microscope investigations were used to detect the change in the surface. Also, tensile strength, pH measurements, ATR analysis, and color change of the historical paper before and after treatment by hydrogels were studied. It was found that the multifunction gellan gum hydrogels improved the mechanical and chemical properties of the historical paper.

Keywords: Hydrogel, Gellan gum, Multi-Function Hydrogel, Paper Conservations

1. Introduction

Since time immemorial, the historical paper has contributed to codifying and transmitting many sciences, arts, and literature from different civilizations and cultures. These old papers often suffer from some manifestations of damage, the most important of which are various stains and visually distorted ones, in addition to acidity and oxidation, which may cause darkening, yellowing, and chemical damage. Therefore, the science of conservation and preservation has received significant attention from all countries, and everyone seeks to develop it and update its materials and tools. So, in recent years, modern alternative methods have appeared to the traditional methods, which use liquids, solvents, bleaching materials, or enzymes [1]. One of these modern methods is the use of gel poultice. Gels can be divided into two major categories, depending on the nature of their bonds: physical and chemical gels. Physical gels are formed by electrostatic interactions between polymeric chains, polysaccharide-based gels (e.g., agar-agar or gellan gum) are, at present, one of the most promising tools used by conservators with the intent of retaining the cleaning agent. Chemical gels are, on the other hand, characterized by the presence of covalent bonds. They have a specific shape given during synthesis and have strong gel cohesion; they are more versatile. All kinds share the idea of forming a gel based on developing a rigid form of materials instead of a liquid form, and it is relatively stable at a specific temperature, using another auxiliary substance from cross-links. The gel comprises a monomer, a cross-linker, and a liquid medium [2]. Since 2003, the ICRCPAL library for conserving library materials in Rome has developed and implemented a new method for cleaning paper artworks using semi-rigid gel based on hydrogel obtained from gellan gum [3]. Gellan gum is a crystalline substance widely used in various fields of production, such as the food industry and the biomedical and pharmaceutical industries, in biological and microbiological research. Consists of a

*Corresponding author e-mail: sdmali82@yahoo.com

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linear anionic heteropolysaccharide produced by pseudomonas elodea and consists of (1,3)-ß-D-Glucose, (1,4) -ß-D-glucuronic acid, (1,4)-ß-D-glucose, (1-4)-α-L-rhamnose, repeating units. 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 deacylated. It is obtained by alkali treatment of the native polysaccharide. In particular, in the presence of calcium salts, the deacylated polysaccharide forms stiff and rigid hydrogel with a slow syneresis rate. The gelation process involves two separate thermo-reversible steps. Molecules of gellan gel are in a disordered coil (single chain) upon heating in aqueous solutions. The molecules transform into an ordered double-helical conformation upon subsequent cooling, followed by associations between the helices through weak interactions, such as hydrogen bonds and Van der Waals forces. Finally, produce a gel with a molecular weight equal to 2-3x10^5 Daltons. A three-dimensional network gel made in this way can be kept in the fridge for 1–2 weeks [4]. Gellan gels are stable at a wide range of pH, which can gelify the deacidifying agent and reducing agent for deacidification and reductive bleaching processes. It is more transparent than agar; it does not leave residues on the paper. The rigid gel obtained from gellan is more effective in water retention at low concentrations of 1-2%. It found its efficacy in controlling volume and water release timing to paper during aqueous treatment [5]. It also absorbs the water-soluble decomposition products present on the paper. It has a very high degree of flexibility, homogeneity, and transparency, is very stable at elevated temperatures, and can be applied and removed in a fairly simple, one-step, one-body alternative to traditional methods, such as using water, water mixed with ethanol, or enzymes [6]. Gellan hydrogel with electrochemical biosensors gives the possibility to verify the degradation conditions of the paper artworks and to clean them efficiently, monitoring the removal process of pollution and degradation products [7]. Also, it has been successfully used for the removal of old adhesives like starch [8], animal glue, and gelatins by loading enzymes [9], removal of stain reduction on a silver gelatin photograph, reductive bleaching gel by loading borane tert-butyl amine complex and for deacidification adding calcium propionate. So, it can be integrated with other ingredients, like surfact¬ants, chelators and enzymes that can produce tailor-made rigid gels for specific cleaning applications [10]. The compound was tolerated on the hydrogel to give it more characteristics that make it more capable of cleaning, treating acidity, and thus the mechanical and chemical strengthening of the paper. A compound consisting of EDTA was chosen as an example of a chelating agent [11, 12], and sodium dionith as a reducing agent, which are used to remove iron stains and impurities in paper holdings [13, 14]. Nano calcium carbonate is added to them as a basic buffer, stabilizes the pH, leaves an alkaline residue for future protection, and is used in paper deacidification treatments in many scientific researches [15]. This study aims to evaluate and compare the effect of gellan gum and multifunction gellan gum hydrogels on the treatment of historical paper.

1. Materials and methods

1.1. Materials

Gellan gum (G) was purchased from (B&V Laboratory Chemicals Italy). Ethylenediamine tetraacetic acid (EDTA), sodium dithionite (SDT), and calcium acetate were purchased from SDFCL, 248, Worli Road, Mumbai-30, India. Nano calcium carbonate was prepared by a mechanical method using ceramic ball mill in our lab, and then sonicated using HIELS CHER Ultrasonics GmbH, model UP400S, with Vibra cell vcx600 three times for 3 min.

Naturally aged PARIS paper from a printed book (MEMOIRES DE MISTRISS HUTCHINSON) dating back to 1823 A.D. was used. The samples have natural aging of about 200 years. After treatment by hydrogels, half of the samples were aged in an oven Heraeus type 5042 Kotter manual hanigsen w-Germany set at 80 ± 2 ^oC and 65 % (R.H.) relative humidity for a period of 10 days = 240 h, selected to be equivalent to 50 years of natural aging. The aging procedure was in conformance with the ISO 5630-3: 1996 standard [16, 17].

1.2. Hydrogels preparation

The gellan gum hydrogel (GH) was prepared by adding an aqueous solution of calcium acetate (0.40g/L) to an aqueous solution of gellan gum (20g/L) with continued stirring. The homogenous

solution was microwaved (Microwave Oven CAIRA CA-MW1134 1500W, China) at 600 W for 2 min [18, 19]. To prepare multifunction gellan gum hydrogel (GHM), 10 % (wt/wt) multifunction material (EDTA, SDT, or $NCaCO_3$) was loaded into the homogenous solution and microwaved for 3 min. The solution was poured into a heat-resistant tray or Petri dish while still hot and runny and cooled to room temperature to form a hydrogel film. The dimensions of the hydrogel pieces were 2 x 3 cm and 0.5 cm in height (Fig. 1).

1.3. Hydrogel characterization

1.3.1. Swelling (water uptake)

The swelling behavior was measured gravimetrically, as described in previous work in a typical swelling experiment. A definite-weight hydrogel sample was immersed in a distilled water solution and allowed to swell for a definite time. After that, the hydrogel was removed from the water and put between two filter papers to remove excess water; then, the swollen hydrogel was weighed, and the swelling degree of hydrogel was determined as a function of time as follows:

$$\text{Swelling degree (\%)} = \frac{m_t - m_o}{m_o} X\ 100$$

Where m_o and m_t are the weight of the dry and swollen hydrogels at time t, respectively.

Fig. 1. Schematic preparation of gellan gum (GH) and multi-function gellan gum (GHM) hydrogels.

1.3.2. Scanning electron microscopy with energy dispersive electron spectroscopy (SEM- EDX)

The surface morphology of hydrogels was analyzed, and images were recorded using FEI IN SPECTS Company, Philips, Holland environmental scanning (SEM) without coating with an accelerating voltage of 10–15 kV. The elemental constitution of hydrogels was studied using the non-destructive energy dispersive X-ray (EDX) unit attached to SEM.

1.3.3. Transmission electron microscope (TEM)

The particle size of prepared N $CaCO_3$ was studied by imaging at 100 000× magnification and an acceleration voltage of 120 kV using a STA6000, Perkin Elmer (USA).

1.3.4. Thermal gravimetric analysis (TGA)

The thermal stability was conducted by a TG-DSC 1200^{O}C Thermo-Microbalance (SETARAM Labsys Evo gas option, Germany) from 25 to 800°C under nitrogen at 10 °C/min heating rate.

1.3.5. X-ray diffraction analysis (XRD)

The XRD patterns of hydrogels were investigated using a Diano X-ray diffractometer using a CuKα radiation source (λ=0.15418 nm) energized at 45 kV. The diffraction angle range 2θ was ranged from 10 to 70° in reflection mode.

1.3.6. Attenuated total reflection analysis (ATR)

The ATR spectra of hydrogels were determined by (Bruker 1238 2310 Platinum ATR diamond cell) Model: Alpha, PN: 1003271\07, SN: 104633, Made in Germany in the range of 4000 - 600 cm^{-1} with a resolution of 4 cm^{-1}. The spectra were collected by placing the samples directly on the ATR cell.

1.4. Paper model preparation and treatment process

Three stains were applied on paper samples without ink, tidelines were using drops of water randomly to paper samples and then left the samples to dry at room temperature. Iron pieces were put onto wet blotting paper for rust stains and kept at room temperature for about 72 hours. The iron pieces corroded slowly and emitted a yellowish-orange color throughout the paper fibers. The stained blotting paper was then used to produce rust stains in paper by contact and absorption. Paper samples were kept in between two sheets of rust-stained blotting paper and maintained under wet conditions at room temperature for about 72 hours. Foxing is the term that describes the stains, spots, and blotches on old papers or documents. These phenomena may be formed by the oxidation of iron compounds in paper and derived from water or reagents involved in paper production or iron elements in paper-production machines [20, 21]. The prepared hydrogels were put on the paper stain samples for approximately 2 hours.

1.5. Paper samples characterization

1.5.1. Photography and digital microscope investigations

For photography and digital microscope investigations, a camera (Nikon D 3200 24.2 MP CMOS Digital SLR Made in Thailand) was used to take some photo snapshots with an aperture of F / 4.5, the shutter 1/40, and IOS 100 for paper stain samples before and after treatment with GH and GHM. A portable USB digital microscope (model PZ0I, Shenzhen Super Eyes Co., Ltd, Guangdong, Made in China) was used to investigate the surface of the paper samples before and after treatments.

2.5.2. Tensile strength measurements

The paper samples were conditioned for 24 hours in a standard atmosphere (at 23°C and 50% relative humidity) before testing for tensile strength according to IOS 1928-2 (2008). Tensile testing was carried out on 15 mm wide strips between jaws set 100 mm apart [22], using a The paper samples were conditioned for 24 hours in a standard atmosphere (at 23°C and 50% relative humidity) before testing for tensile strength according to IOS 1928-2 (2008). Tensile testing was carried out on 15 mm wide strips between jaws set 100 mm apart. The measurement was repeated in triplicate for each sample.

2.5.3. pH measurements

The pH was performed on hydrogel samples according to the TAPPI method (TAPPI T 509 om-11) [23]. The pH values were measured directly, with the help of a drop of water on samples, and left for 2 minutes to allow the extraction of both acidic and basic substances contained in the paper. After this period, the pH was measured using (Adwa AD 1030 pH/mV & Temperature Meter) with a flat surface glass electrode, made in Romania, between pH 4.01and 7.01 at 20 ^{o}C.

2.5.4. Color change measurements

The measurement was made using Ultra Scan PRO Hunter Lab D65, 10 A. Before hydrogel treatment, each stain on the paper samples was measured and taken as a standard sample. Then, the color changes caused by hydrogels and the effect of accelerated aging were compared by drawing an 8 mm diameter circle on the stains to identify the analysis location. Data were interpreted using the color space L*a*b*, the L* - scale measures lightness, and varies from 0 (black) to 100 (perfect white). The a* - scale measures red-green; +a* means more red, -a* measures green; the b* - scale measures yellow-blue; +b* means more yellow, -b* more blue, and the global color variation was assessed by calculating the ΔE following CIE 2000.

Each ΔE value was interpreted as follows: 0-1(color difference undetectable by a human eye), 1–3 (slight color difference between two samples), 3-6 (perceivable difference), or > 6 (significant difference) [24].

3.Results and discussions

3.1. Hydrogel preparation

Gellan hydrogels have recently been used in paper cleaning processes due to their stability, biocompatibility, and biodegradability. It is a polysaccharide polymer with many hydroxyl groups, so it can form hydrogen bonds easily when exposed to mild temperatures. In the presence of calcium salts, it forms hard and rigid hydrogel due to calcium ions interpenetration in its matrix by the physical crosslinking process [25].

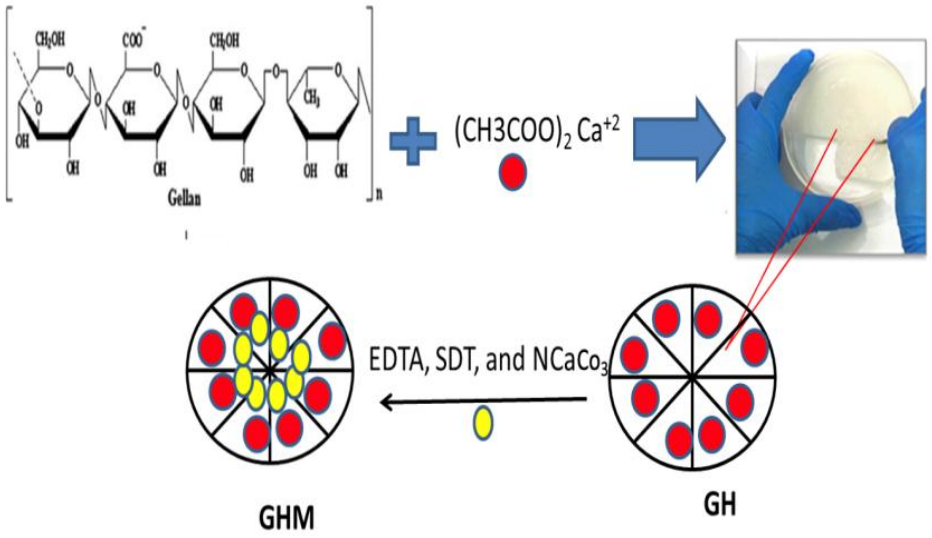

Fig. 2. Possible hydrogel formation.

3.2. Hydrogels characterization

3.2.1. Swelling studies of hydrogels

(Fig. 3) illustrates the effect of time (1-6 hours) on the swelling properties of the prepared hydrogels, GH and GHM. Increasing the time, the swelling properties of hydrogels increased up to 4 hours, then decreased as the time increased. The optimum degree of swelling of hydrogels occurred after 4 hours; this can be referred to as the instability of the hydrogels for a long time and loss of a degree of binding. There is a gradual increase in the superiority of the GHM compared to the GH at the same time of swelling; this confirms the improvement in hydrogel by loading multifunction materials onto GH.

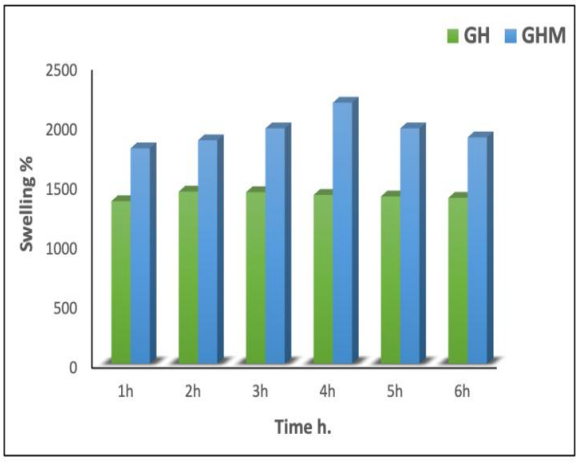

Fig. 3. Effect of time on the swilling of GH and GHM.

3.2.2. Surface morphology by scanning electron microscopy (SEM) and elemental analysis (EDX)

The morphological features of GH and GHM were studied by SEM and illustrated in **(**Fig. 4)**.** The surface of GH appears as multilayers stacked on each other. In contrast, GHM appears as multilayers in more homogeneous with a light spot on its surface due to the loading of multifunctional materials such as Na, Ca, and S. Both GH and GHM have interstitial spaces, which help absorb the damaged materials from the surface of artworks. The EDX analysis confirmed that the hydrogels consist of natural materials represented by the two elements C and O, with Ca as a crosslinker. The EDX analysis also confirmed the loading of multifunctional materials as the percentage of Ca in GHM is higher than in GH. Also, Na and S are absent in GH and appear in GHM. The TEM analysis also revealed that the $CaCO_3$ was formed in the spherical nanoparticals [26].

3.2.3. Thermogravimetric analysis (TGA)

(Fig. 5a) shows the thermal stability of prepared hydrogels. The degradation process of GH and GHM occurs in many steps. The first step was up to 150 °C, where moisture was removed, followed by small stability up to 200 °C, with weight loss of 5 and 7 mg (~ 14 and 20%) for GH and GHM, respectively. The second step was up to 300 °C, where the pyrolysis occurred with a loss in weight of ~ 50 %, followed by slight stability at 700 °C in GH more than GHM.

The residue was 25 and 10 mg for GH and GHM, respectively[27].

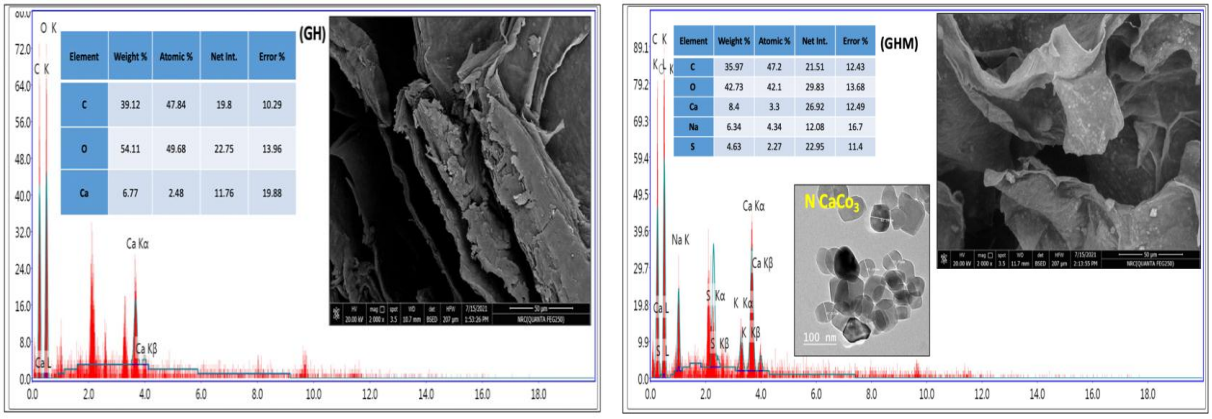

Fig. 4. SEM images and EDX analysis of GH and GHM.

3.2.4. X-ray diffraction

In this work, the XRD studies were performed with the GH and GHM hydrogels (**Figure 5b**). The XRD patterns of both hydrogels showed peaks and a wide amorphous halo, indicating a typical behavior of semicrystalline polymers with low crystallinity degrees. The intensity of peaks was decreased by adding the multifunction materials to GH. Also, a peak appeared around 30, attributed to Ca's presence [32,33].

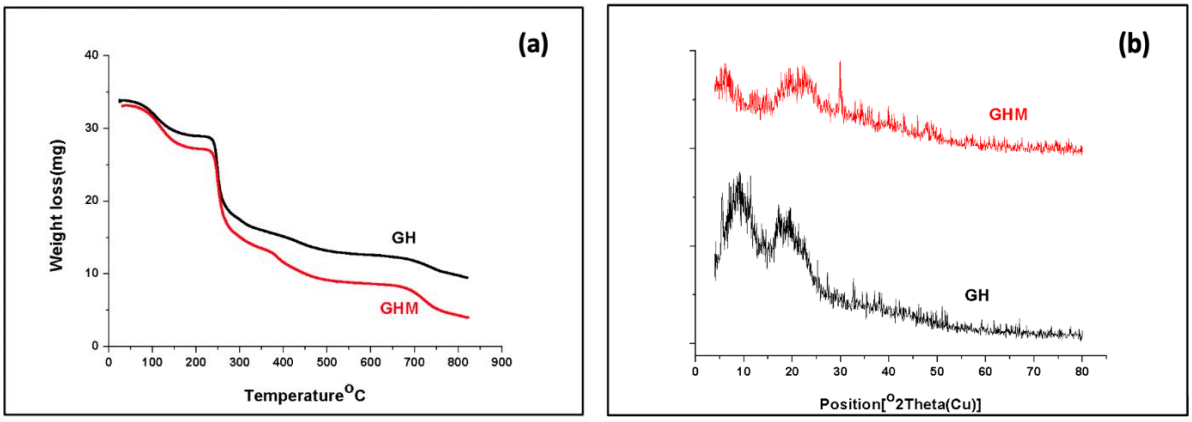

Fig. 5. (a) TGA analysis and (b) XRD of GH and GHM.

3.2.5. Attenuated total reflection analysis (ATR)

The ATR spectra of pure gellan gum (G) and hydrogels (GH and GHM) shown in Fig. 6 show that the pure gellan gum (G) and hydrogels (GH and GHM) present characteristic peaks at around 2929, 1620, and 1069 cm^{-1}. The band corresponded to C-H vibrations at approximately 2929 cm^{-1}, C=O stretching peaks around 1620 cm^{-1}, while the strong band at around 1069 cm^{-1} was attributed to the C-O-C stretching. The fingerprint region of G, GH, and GHM at 1500-700 cm^{-1} contains the absorptions of the individual bonds between carbon and non-hydrogen atoms such as C-C, C-N, C-O, and others. The characteristic peaks of G localized at 1597, 1402, and 1021 cm^{-1}, GH 1599, 1408, and 1024 cm^{-1}, and GHM 1581, 1408, and 1026 cm^{-1} [28].

3.3. Paper samples characterization

3.3.1. Photography and digital microscope investigations

Photo snapshots were taken for stain samples before and after treatment with GH and GHM. The results are shown in **(**Fig. 7a**.)** to confirm the results, images of paper samples taken by digital microscope are shown in **(**Fig. 7b**.)** It was revealed through photographic and morphological surface investigations with a digital microscope of paper samples treated with hydrogels; complete cleaning of tideline and rust stains occurred clearly and in a large proportion, while the foxing stains still have traces on the surface of the treated paper. After treatment, the treated gellan hydrogels did not leave any traces of hydrogel residue on the paper surface.

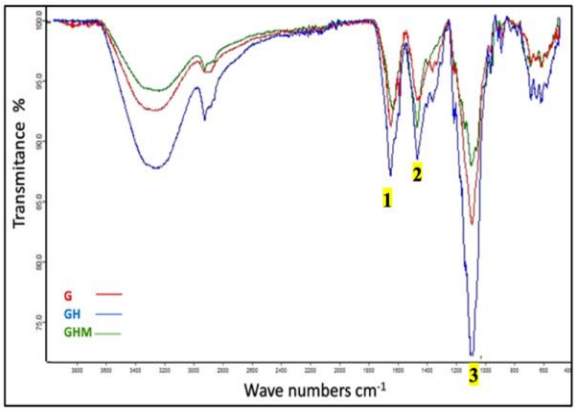

Fig. 6. ATR analysis of G, GH, and GHM.

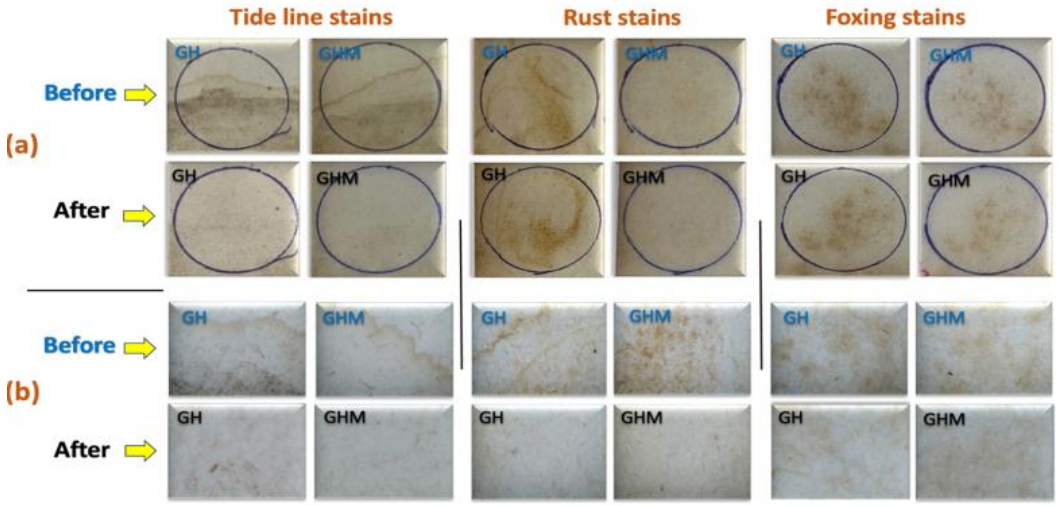

Fig. 7. (a) Photography and (b) Digital microscope images (Zoom 40 X) of paper samples before and after treatment by GH and GHM.

3.3.2. Tensile strength measurements

The effect of the cleaning process using gellan hydrogels on the mechanical properties of papers was studied by measuring the tensile strength and elongation ratio of paper samples treated with gellan gum hydrogels before and after accelerated wet thermal aging **(**Fig. 8**)**. It was found that the treatment by GHM improved the tensile strength and elongation ratio of treated papers by approximately 10% more than GH. Aging of untreated and treated papers decreased their mechanical properties with the keeping of treatment by GHM was more effect than by GH.

3.3.3. pH measurements

GH may be more sensitive to pH changes; G also has carboxylic acids, so the pH effect on the gel's network will be substantially different. Also, gellan hydrogels contain calcium acetate as a cross-linker. Ultimately, the removal of adsorbed chemical compounds from paper depends on physical interactions (gel cross-linking, porosity) and chemical interactions such as hydrogen bonding and electrostatic effects between the adsorbate, the gel (both matrix and solution), and the paper [29]. Table 1 shows data on the surface pH of untreated and treated samples by GH and GHM. Increasing pH values after cleaning indicates that acidic components involved in degradation processes were removed. This proves that gellan hydrogels, GH and GHM, are efficient cleaning materials.

3.3.4. Color Change Measurements

Table 2 shows the color change of the stained paper before and after treatment by GH and GHM. ΔE displays the difference as a single value for color and lightness. ΔE values of 4 and over will normally be visible to the average person, while those of 2 and over may be visible to an experienced observer [30, 31]. GHM was more effective in removing stains, especially rust and tideline stains.

Table 1. pH of untreated and treated paper samples by GH and GHM.

Hydrogels	Blank	GH	GHM
	Before Aging		
tideline	5.23±2	6.61±2	6.74±2
Rust	5.34±2	6.61±2	6.90±2
Foxing	5.20±2	6.32±2	6.66±2
	After Aging		
tideline	5.21±2	6.56±2	6. 61±2
Rust	5.25±2	6.37±2	6.52±2
Foxing	5.04±2	6.15±2	6.25±2

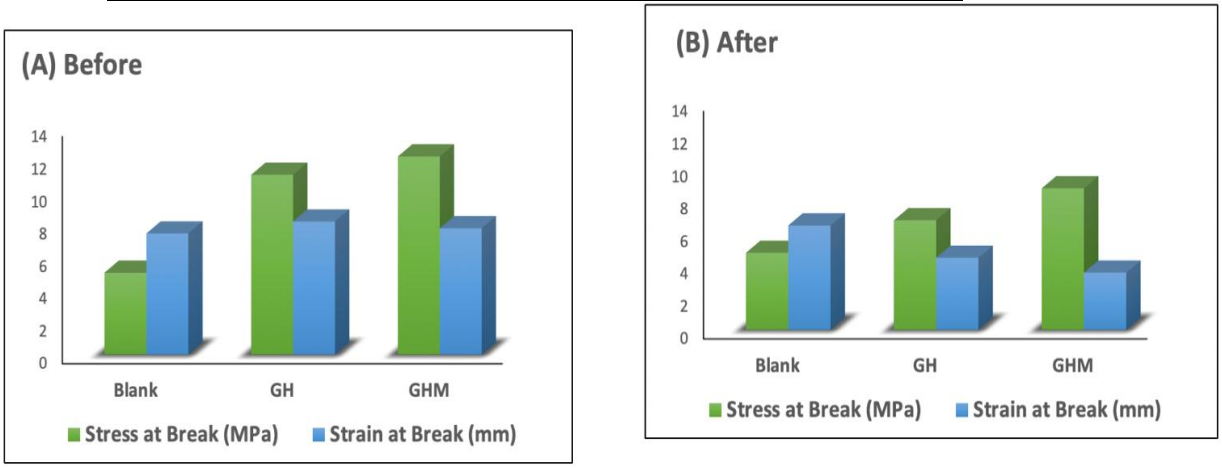

Fig. 8. Tensile strength of treated paper samples before (A) and after (B) aging.

Table 2. The effect of color changes on stains samples before and after treatment by GH and GHM.

	L	a	b	ΔL	Δa	Δb	ΔE
Standard	79.99	-31.78	2.79	----	----	----	----
Tideline stains	73.99	-32.17	3.61	----	----	----	----
GH	80.10	-28.67	3.27	6.12	3.49	-0.33	6.3
GHM	81.21	-28.10	3.49	7.23	4.07	-0.12	7.4
Rust stains	65.31	-6.77	12.72	----	----	----	----
GH	79.09	-22.06	5.51	13.78	-15.29	-7.20	19.0
GHM	81.48	-24.25	4.77	16.17	-17.48	-7.95	21.9
Foxing stains	72.38	-17.18	6.94	----	----	----	----
GH	76.52	-14.62	6.20	4.14	2.56	-0.74	4.4
GHM	78.18	-18.45	4.79	5.80	-1.27	-2.15	6.1

4. Conclusion

In this study, the loading of multi-functional substances such as a chelating agent (EDTA), a reducing agent (SDT), and a basic buffer (Nano calcium carbonate) onto a gellan gum hydrogel (GH) was performed to evaluate its effect on the treatments of historical paper as a multifunctions cleaning material such as deacidification and consolidation. It was found that the loading of these materials improved the hydrogel's properties, increasing cohesion and homogeneity. In this way, it is possible to use the treatment materials easily instead of the traditional methods of immersion and spraying that lead to damage to the treated historical paper, human health, and the environment. The treatment of stained paper by the prepared hydrogels improved its optical, mechanical, and chemical properties. Also, these materials removed the stains without leaving any traces on the paper's surface, decreased the paper's acidity, and strengthened it. In addition, these materials could be easily removed after paper treatment, reused, safe, and do not cause any future damage to the historical paper.

Conflicts of interest

There are no conflicts to declare.

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References

[1] Micheli, L., et al., Development of a diagnostic and cleaning tool for paper artworks: a case of study. Microchemical Journal, 126, 32-41 (2016).
[2] Domingues, J.A., et al., Innovative hydrogels based on semi-interpenetrating p (HEMA)/PVP networks for the cleaning of water-sensitive cultural heritage artifacts. Langmuir, 29 (8), 2746-2755(2013).
[3] Di Vito, M., et al., Hydrolates and gellan: An eco-innovative synergy for safe cleaning of paper artworks. Studies in Conservation, 63(1), 13-23 (2018).
[4] Iannuccelli, S. and S. Sotgiu, Wet treatments of works of art on paper with rigid gellan gels. The book and paper group annual, 29(2010), 25-39 (2010).
[5] Kanth, A. and S.C. Pandey, Optimizing the rigidity of gellan and agar gels for cleaning sensitive acrylic emulsion painted surfaces. International Journal of Conservation Science, 9 (3) (2018).
[6] Petrella, G., et al., A new sustainable and innovative work for paper artworks cleaning process: Gellan hydrogel combined with hydrolytic enzymes. International Journal of Conservation Science,. 7(SpecialIssue1), 273-280 (2016).
[7] Micheli, L., et al., New strategy for the cleaning of paper artworks: a smart combination of gels and biosensors. Advances in Chemistry, 2014, 1-10(2014).
[8] Mazzuca, C., et al., Cleaning of paper artworks: development of an efficient gel-based material able to remove starch paste. ACS Applied Materials & Interfaces,. 6(19), 16519-16528(2014).
[9] Casoli, A., et al., Analytical evaluation, by GC/MS, of gelatine removal from ancient papers induced by wet cleaning: A comparison between immersion treatment and application of rigid Gellan gum gel. Microchemical Journal,. 117, 61-67(2014).
[10] Maheux, A.F., Cross-disciplinary uses for gellan gum in conservation. The Book and Paper Group Annual, 34, 69-79(2015).
[11] Burgess, H., The use of chelating agents in conservation treatments. The Paper Conservator,. 15(1), 36-44(1991).
[12] Suryawanshi, D. and S. Bisaria, Removing metallic stains from paper objects using chelating agent EDTA. (2005).
[13] Selwyn, L. and S. Tse, The chemistry of sodium dithionite and its use in conservation. Studies in Conservation,. 53(sup2), 61-73(2008).
[14] Irwin, S., A comparison of the use of sodium metabisulfite and sodium dithionite for removing rust stains from paper. The book and paper group annual, 30(37),37-46(2011).
[15] Malešič, J., et al., Nano calcium carbonate versus nano calcium hydroxide in alcohols as a deacidification medium for lignocellulosic paper. Heritage Science,. 7, 1-14(2019).
[16] Kamińska, A., et al., Colorimetric study of the post-processing effect due to pulsed laser cleaning of paper. Optica Applicata, 34(1), 121-132(2004).
[17] Pentzien, S., A. Conradi, and J. Krüger, The influence of paper type and state of degradation on laser cleaning of artificially soiled paper. Lasers in the Conservation of Artworks VIII, 59-65(2011).
[18] De Filpo, G., et al., Gellan gum hybrid hydrogels for the cleaning of paper artworks contaminated with Aspergillus versicolor. Cellulose,. 23, 3265-3279(2016).
[19] Zidan, Y., et al., A comparative study to evaluate conventional and nonconventional cleaning treatments of cellulosic paper supports. Mediterranean Archaeology & Archaeometry, 17(3) (2017).
[20] Łojewska, J., et al., FTIR in situ transmission studies on the kinetics of paper degradation via hydrolytic and oxidative reaction paths. Applied Physics A, 83,597-603(2006).
[21] Szulc, J., et al., Analysis of paper foxing by newly available omics techniques. International Biodeterioration & Biodegradation, 132, 157-165(2018).

[22] Tappi, T., Tensile properties of paper and paperboard (using constant rate of elongation apparatus). Technical Association of the Pulp and Paper Industry: Peachtree Corners, GE, USA, (2001).
[23] TAPPI, T., 509 om-02. Hydrogen Ion Concentration (pH) of Paper Extracts (Cold Extraction Method). TAPPI: Atlanta, GA, USA, (2002).
[24] Đorđević, D., A. Hladnik, and A. Javoršek, Performance of five chromatic adaptation transforms using large number of color patches. Acta graphica: znanstveni časopis za tiskarstvo i grafičke komunikacije, 20(1-4), 9-19(2009).
[25] Coutinho, D.F., et al., Modified Gellan Gum hydrogels with tunable physical and mechanical properties. Biomaterials, 31(29), 7494-7502(2010).
[26] de Oliveira Cardoso, V.M., et al., Development and characterization of cross-linked gellan gum and retrograded starch blend hydrogels for drug delivery applications. Journal of the Mechanical Behavior of Biomedical Materials, 65,317-333(2017).
[27] Karthika, J. and B. Vishalakshi, Novel stimuli responsive gellan gum-graft-poly (DMAEMA) hydrogel as adsorbent for anionic dye. International journal of biological macromolecules, 81, 648-655(2015).
[28] Mazzuca, C., et al., Gellan hydrogel as a powerful tool in paper cleaning process: A detailed study. Journal of colloid and interface science, 416, 205-211(2014).
[29] Barrulas, R.V., et al., Cleaning fungal stains on paper with hydrogels: The effect of pH control. International Biodeterioration & Biodegradation, 152,104996(2020).
[30] Baldevbhai, P.J. and R. Anand, Color image segmentation for medical images using L* a* b* color space. IOSR Journal of Electronics and Communication Engineering, 1(2), 24-45(2012).
[31] Mirjalili, F., et al., Color-difference formula for evaluating color pairs with no separation: ΔE NS. JOSA A, 36(5), 789-799(2019).
[32] Dacrory,S., etal.,Cyanoethylcellulose/BaTiO3/GO flexible films with electroconductive properties.ECS Journal of Solid State Science and Technology, 10(8) (2021).
[33] Fahim, A.M. et al.,Development of semiconductive foams based on cellulose-benzenesulfonate/CuFe2O4- nanoparticles and theoretical studies with DFT/ B3PW91/LANDZ2 basis set.Journal of Molecular Structure, 1247(2022).