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Facile Multifunction Biopolymer Hydrogels for the Potential Treatment of Historical Paper

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Abstract
Old historical paper is one of the most important materials that carry nations' sciences, arts, features and lives throughout the ages. So, this study aims to find an eco-friendly method for treating historical papers with improving their physical and chemical properties. Hydrogels were prepared from Tylose MH 300 and Funori using calcium acetate as a crosslinker. In addition, multifunction materials such as EDTA, Sodium Dithionite, and Nano Calcium Carbonate were loaded onto Tylose and Funori to get multifunction hydrogels. The Tylose, Funori, and their multifunction hydrogels were used to clean historical papers against tidelines, rust, and foxing strains. The swellability, TGA, ATR, XRD analysis, and SEM with EDX analysis were used to characterize the prepared hydrogels. The photography, digital microscope, pH, color change, and ATR analysis were used to investigate the cleaning efficiencies of hydrogels. The results indicated that the Funori hydrogels are preferred over Tylose in cleaning the paper stains, and the loading cleaning agents improved the hydrogel efficiency.

Keywords: Conservations, Hydrogels, Funori, Tylose, Cleaning, Paper.

Introduction:

The paper is one of the most important cultural heritage collectibles, so its preservation is critical. It is a multi-component material, and its overall behavior, such as chemical and mechanical proprieties, stability, degradation, etc., strongly depends upon the components' nature, origin, and characteristics and their interaction. Many kinds of damage are found on old and modern paper-based documents, books, and archival materials. Dirt and stains are among the strongest phenomena that cause paper damage and deformation, in addition to extending the impact on the properties of paper mechanically and chemically. So, cleaning ancient papers is one of the most delicate and important steps in a conservation process. It improves the optical quality of graphic work by removing pollution and organic substances resulting from cellulose degradation (Micheli, Mazzuca, Palleschi, & Palleschi, 2016). The standard cleaning techniques involve immersing paper sheets in a water bath, using organic solvents, bleaching agents, enzymes, and laser ablation. However, all of these methods have drawbacks due to their toxicity, induced fiber weakening, loss of mechanical properties, changing the paper morphology such as pigments or ink fading (Moropoulou & Zervos, 2003), difficulty in controlling the cleaning process, and alteration of cellulose fibers due to chemical and mechanical damaging (Henniges & Potthast, 2009). Therefore, there is a need for a solution that effectively removes the stains without damaging the paper document or artwork in a non-toxic, environmentally friendly, and easy-to-apply manner. In recent years, efforts have been made to determine several new methods for treating historical paper in many libraries, museums, and stores, for example, dry cleaning methodologies like hydrogels, Laser (Arif & Kautek, 2015) and cold plasma (Pawlat, Terebun, Kwiatkowski, & Diatczyk, 2016).

Hydrogels are 3D materials that control the liquid diffusion and the amount of water released into paper during treatment. Moreover, it can absorb the pollutant compounds from the paper surface and clean the artwork while minimizing the damage (Dacrory et al., 2018). At the same time, cleaning hydrogels is a cheap and easy-to-use method (Li et al., 2021) and does not require equipment like a

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suction table or capillary washing unit. Its physio-chemical characteristics must not alter or damage the morphology of paper samples and any chemical interaction with the substrate; its monolithic rigid structure and viscoelasticity allow easy handling without risk of fragmentation (Dacrory, Kamal, & Kamel, 2021). So, hydrogels are particularly suitable for use in the field of heritage conservation. Various polysaccharides, such as Tylose MH 300 (Methyl hydroxyl ethyl cellulose) and Funori, have prepared of hydrogels. The bond interaction in the hydrogel is physical via electrostatic interactions between polymeric chains, so they are usually viscous systems, respond to heat, and are disrupted by mechanical forces or chemically attributed to the presence of covalent bonds depending on the components (monomer, cross-linker, liquid medium, etc.). In this case, hydrogels have a specific shape given during synthesis with good mechanical properties and strong cohesion (Domingues et al., 2013). Tylose is a material of vegetable origin, cellulose, and contains a small amount of ethyl hydroxyl, which raises the degree of its transformation into a gel from 50: 70 °C. It was used in the old treatments as one of the alternatives to the paper washing process, based on the principle of the gelification of the water with adhesive substances, which can modify the surface properties of water that gives the solvent an increase in size (Iannuccelli & Sotgiu, 2010).

In comparison, Funori is a polysaccharide extracted from the red algae Gloiopeltis species on rocks in Japan and is produced year-round (Geiger & Michel, 2005). It has been characterized as a chemically heterogeneous polysaccharide with the repeating unit of G6S-LA (b-Dgalactose-6-sulfate e 3,6-anhydro-a-L-galactose) diad (b-D-galactose-6-sulfate e3,6-anhydro-a-Lgalactose) diad; a diad being a sequence in which two constitutional units are continuing (Harrold & Wyszomirska-Noga, 2015). It was first recorded in Japan in 1673 as a sizing for textiles and papers. It is also used in treatments for canvas (Llamas & San Pedro, 2014; Poulis et al., 2022), papyrus (Menei, 2015), and wall paintings. It is characterized by not producing any trace on the surface after its application and drying, it does not change the color of the surface, it can be easily removed after aging, unlike many organic materials that appear yellow with time, and it becomes more transparent when exposed to this ultraviolet light (Fan, 2012), in addition to their chemical affinity.

On the other hand, chelating agents can be defined as organic compounds which complex or sequester metal ions. In paper conservation, chelating agents are used to remove iron stains and stabilize bleach solutions. One of the chelating agents is Ethylene Diamine Tetra-acetic Acid (EDTA), which is a widespread chelating agent; it might be considered dangerous to treat paper in an acidic solution, so prefer to modify it by adding alkali (Suryawanshi & Bisaria, 2005). Sodium Dithionite is a reductant agent; it was explored to effectively remove rust iron stains from paper. However, its use presents significant hurdles related to cost, transit, and safety (Irwin, 2011). Mixtures of Sodium Dithionite and a Chelating agent have sometimes been recommended to remove iron stains faster than sodium dithionite alone (Burgess, 1991). To reduce the pH, Nano Calcium Carbonate salt can help raise the pH values of the materials used in the treatments and cleaning of paper stains so that they do not negatively affect and damage paper particles and fibers.

According to the above research, this work aimed to use Tylose MH 300 and Funori with/without multifunction materials such as EDTA, Sodium Dithionite, and Nano Calcium Carbonate loaded as cleaning agents into the hydrogel. SEM, EDX, TGA, XRD, and ATR have investigated and analyzed the prepared hydrogels. Photography, digital microscope, tensile strength, ATR analysis, pH, and color change were used to investigate the changes in the cleaned paper from strains.

2. Materials and Methods

2.1. Materials

Naturally aged PARIS paper from a printed book (MEMOIRES DE MISTRISS HUTCHINSON) dating back to 1823 A.D was used. Tylose MH 300 was purchased from CTS Company Italy. Japanese Funori alga was imported from Japan by the Arts conservation company Egypt. Ethylene Diamine Tetraacetic Acid (EDTA), Sodium Dithionite, and Nano Calcium Carbonate were purchased from SDFCL, 248, Worli Road, Mumbai-30, India. Nano Calcium Carbonate suspension was prepared by the mechanical method in the lab. All chemicals and reagents used in this study were performed in analytical grad without any further purification.

2.2. Hydrogels preparation

Tylose and Funori hydrogels have been prepared using calcium acetate as a cross-linker. *In* brief, 3.75 mL of aqueous calcium acetate solution (40 g/ L) was added to Tylose and Funori aqueous solutions (5 g/ 100 mL H_2O) with continuous stirring to obtain a homogenous solution, the pH ~ 7.5. The mixture was microwaved in a domestic microwave at 600 W for 6 min, poured into a Petri dish (9 cm), dry at room temperature, and hydrogels cut to 2 × 3 × 0.5 cm for storing to be used. The produced hydrogels were coded as TH and FH related to Tylose and Funori, respectively.

The modified hydrogels were prepared by loading 0.5 g cleaning agents (ethylene diamine tetraacetic acid (EDTA), sodium dithionite, and nano calcium carbonate) to the Tylose or Funori/ calcium acetate solution, the pH ~ 7.2, followed by microwaving as in previous. The produced hydrogels were coded as THM and FHM for Tylose/ cleaning agents and Funori/ cleaning agents modified hydrogels, respectively.

2.3. Hydrogels characterization

Thermal gravimetric analysis (TGA) was conducted on a TG-DSC 1200OC Thermo-Microbalance (SITARAM Labsys Evo gas option, Germany); temperatures ranged between 25 - 800 °C under a nitrogen atmosphere.

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

Attenuated total reflection analysis (ATR) was used to know the chemical characterization and changes in the hydrogel samples due to loading the treatment materials. Instrument (Bruker 1238 2310 Platinum ATR diamond cell) Model: Alpha, PN: 1003271\07, SN: 104633, Made in Germany, for measurement in the 4000 - 600 cm^{-1} region, at a resolution of 4 cm^{-1} (Librando, Minniti, & Lorusso, 2011). Spectra were collected by placing the dry gel samples directly on the ATR cell.

Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray spectroscopy (EDX) analysis were taken using FEI IN SPECTS Company, Philips, Holland, environmental scanning without coating. SEM was used to investigate the surface morphology of the hydrogels. EDX was used for analyzing the elemental constitution of the hydrogel samples.

Transmission electron microscope (TEM) at 100 000× magnification and an acceleration voltage of 120 kV using An STA6000, Perkin Elmer (USA).

Swelling (water uptake) was measured gravimetrically, as described in previous work (Dacrory, Hashem, & Kamel, 2022). In a typical swelling experiment, a definite-weight of hydrogel sample was immersed in 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.

The swelling degree percentage of hydrogel was determined as a function of time as following:

$$Swelling\ degree\ \% = \frac{m_t - m_o}{m_o} \times 100$$

where m_t and m_o are the weights of the swollen and dry hydrogel.

2.4. Preparation of strain papers

Small pieces of book paper samples without ink were cut, and three stains were performed as follows:

(a) Tidelines were performed by randomly applying water drops to paper samples and then left to dry at room temperature.

(b) **Rust stains** were created by putting iron pieces onto wet blotting paper and kept at room temperature for about 72 h. The iron powder corroded slowly and emitted yellowish-orange color throughout the paper fibers. The stained blotting paper was then used to produce rust stains in the paper by contact and absorption. Paper samples were kept between two sheets of rust-stained blotting paper and maintained at room temperature for about 72 h under wet conditions followed by drying the rust-stained paper for a week.

(c) Foxing strains is the term that describes the stains, spots, and blotches on old papers or documents (Choi, 2007).

2.5. Treatment of strains with hydrogels

The pieces of the prepared hydrogels were put on the stain and covered with transparent polyethylene to avoid fast drying. After 2 h the hydrogel was removed, and the paper sample was dried at room temperature.

2.6. Historical paper aging

Book paper samples have natural aging of about 200 years, in addition to the accelerated aging after treatments in the oven Heraeus type 5042 Kotter manual hanigsen w- Germany set at 80 ±2□C and 65 % (RH) relative humidity for a period of 10 days, selected to be equivalent to 50 years of natural aging. The aging procedure conformed with the ISO 5630-3: 1996 standard (Arias et al.,2013)

2.7. Papers characterization

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 stains before and after treatment with hydrogels. A portable USB digital microscope (model PZ0I, Shenzhen Super Eyes Co., Ltd, Guangdong, made in China) was used to investigate the paper's surface before and after the treatments.

Mechanical properties of the stain papers before and after treatments were measured by conditioning them for 24 h in a standard atmosphere (at 23 °C and 50% relative humidity) according to IOS 1928-2 (2008) (ISO & STANDARD, 1924) using a Lloyd instrument (Lloyd Instruments, West Sussex, United Kingdom) with a 5-N load cell at room temperature.

pH measurement was performed on paper according to the TAPPI method (TAPPI T 509 om-11) (TAPPI, 2002); the pH values were measured directly, with the help of a drop of water on samples (Strlič et al., 2005) by using (Adwa AD 1030 pH/mV & Temperature Meter) with a flat surface glass electrode, made in Romania, between pH 4.01 and 7.01 at 20 □C.

Color change due to the hydrogel treatment was measure using Ultra Scan PRO Hunter Lab D65, 10 A by comparing the color after stain treatment with stained paper as a standard sample. The circle of 8 mm diameter was drawn on the stains to identify the location of analysis.

Change of color was measured using CIE L*a*b*; L* scale measures lightness and varies from 0 (black) to 100 (perfect white), a* scale measures red-green; +a* means more red, -a* measures green; b* scale measures yellow-blue; +b* means more yellow, -b* bluer (Schanda, 2007). The total color difference(ΔE^*) is calculated according to the following equation:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

3.Results and Discussions

3.1. Hydrogel preparation

Tylose and Funori are polysaccharide materials have a large number of OH groups and consequent hydrogen bonding formation and can be used as an adhesive and plaster additive due to their viscosity (Gattuso et al., 2021). Due to their biocompatibility, biodegradable, and non-toxicity, Tylose and Funori used to prepare ecofriendly hydrogels. Calcium acetate can inter the hydrogel pores and joins its chains together to form hydrogel consequently it can be used as a cross linker (Dacrory et al., 2018). In addition, ethylene diamine tetra acetic acid (EDTA), sodium dithionite, and nano calcium carbonate can remove tidelines, rust, and foxing stains so, they loaded to the prepared hydrogels to provide their cleaning efficiencies.

3.2. Hydrogels characterization

Swelling Test

One of the most critical properties of hydrogels is the swelling rate. Taking free-absorbency capacity measurements at regular intervals makes it possible to determine the swelling capacity versus time (Fig. 1). From Fig. 1, it is shown that the swelling of TH and FH reached an equilibrium state after 3 h due to their highly porous structure. Generally, the swelling capacities of THM and FHM were significantly decreased compared to those of TH and FH. This phenomenon can be explained based on their porous occupation with multifunction agents (Dacrory, Kamal, et al., 2021). It is evident through the swelling test that THM and FHM started to become soluble in water after 3 h and utterly soluble after approximately 6 h, which means they are environmentally friendly and can be disposed of by dissolving them in water, and that the loading of multifunction agents onto hydrogels accelerated the time of the hydrogels to fade.

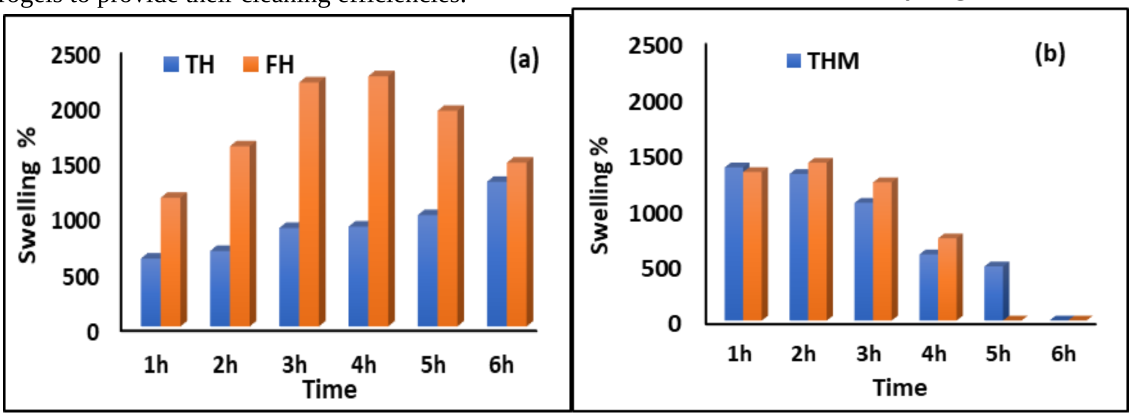

Fig. 1. Swilling of; (a) TH and FH, and (b) THM and FHM.

Attenuated total reflectance (ATR)

The chemical structure of polymer materials and the presence or absence of specific functional groups can be determined using Fourier transform infrared spectroscopy - attenuated total reflectance (FTIR-ATR). Changes in the absorption bands' relative band strengths and frequency point to alterations in the sample's chemical composition or surroundings. Therefore, FTIR-ATR spectroscopy can be utilized to analyze the surface chemistry, particularly after generating chemical or physical alterations. The ATR spectra of Tylose (T), Funori (F), and their hydrogels are depicted in (Fig. 2). It is shown that the spectra are quite different; all samples have peaked around 3400 - 3200, 2900 – 2800, and 1600 - 1645 cm-1 which attributed to hydroxyl groups (-OH), hydrocarbon groups (-CH), and H-O-H absorbed for water, respectively (Catenazzi, 2017). Other peaks at 1400 – 1200, 1300 – 1000, 1450 – 1370, and 900 - 700 cm-1 are related to O-H bending, C-H stretching, C-H bending, and C-H, respectively (Swider & Smith, 2005). It is also clear that the intensities of peaks of -OH groups increased with the formation of hydrogels and after loading of cleaning agents; this is attributed to the adsorbed water and hydroxyl content of cleaning agents.

XRD Analysis

XRD is an advantageous technique for characterizing materials' crystalline and amorphous regions. XRD diffractograms of TH, FH, THM, and FHM hydrogels are shown in (Fig. 3.a). The prominent diffraction peaks of TH and THM were observed at $2\theta = 10°$ and $20°$, representing the crystalline polymorph. Also, by loading multifunction agents, the intensities of these peaks were decreased. In contrast, for the Funori, the pattern of FH is near to being smooth, with a crystalline peak around $2\theta = 20°$, and the intensity of the amorphous peak was increased by loading the multi-function agents (Hashem, Hasanin, Kamel, & Dacrory, 2022)

Thermogravimetric analysis (TGA)

TGA determined the thermal degradation of TH, FH, THM, and FHM hydrogels regarding weight loss (Fig. 3.b). TGA curves of THM and FHM showed a similar pattern to that of the corresponding hydrogel (TH and FH). The decomposition behavior of the hydrogels can be divided into three stages; the first stage occurs at 100 °C to remove the moisture content of hydrogels. The second step occurred at 100-200 °C. Funori was more stable in this step than Tylose with weight residue 50 and 25 mg, respectively. The third step occurred from 200-400 °C, where the almost weight due to removing sulphur, hydrogen, and carbon with weight residue 35 and 5 mg, for Funori and Tylose, respectively with high stability at temperature 400-700 °C. Multifunction hydrogel, THM and FHM showed characteristic stability that increased due to the presence of inorganic multifunction compounds with weight residue 35 and 15 mg for FHM and THM, respectively (Dei et al., 2023).

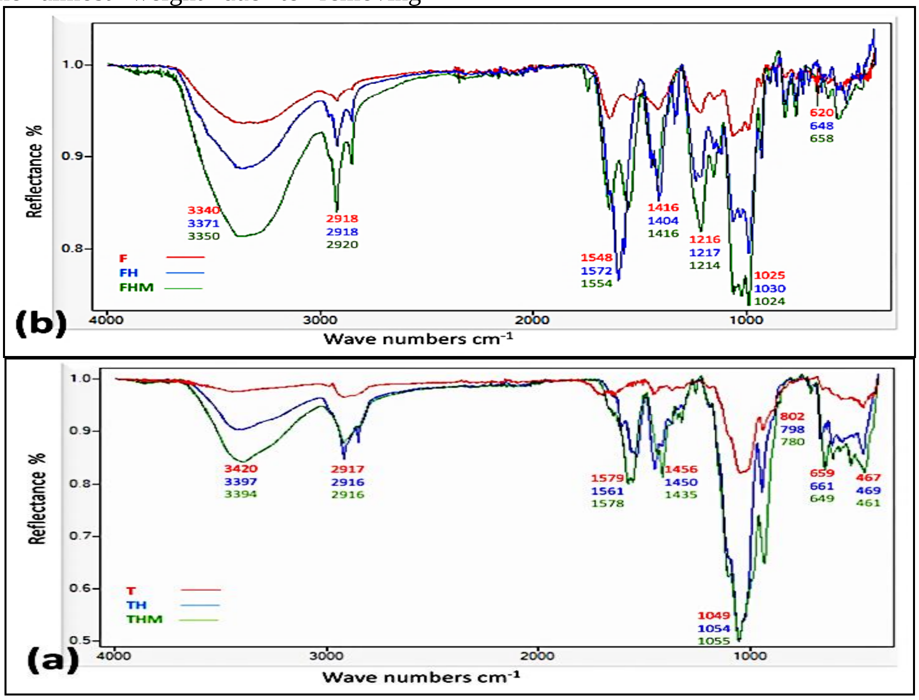

Fig. 2. ATR spectra of; (a) T, TH, THM, and (b) F, FH, FHM hydrogels.

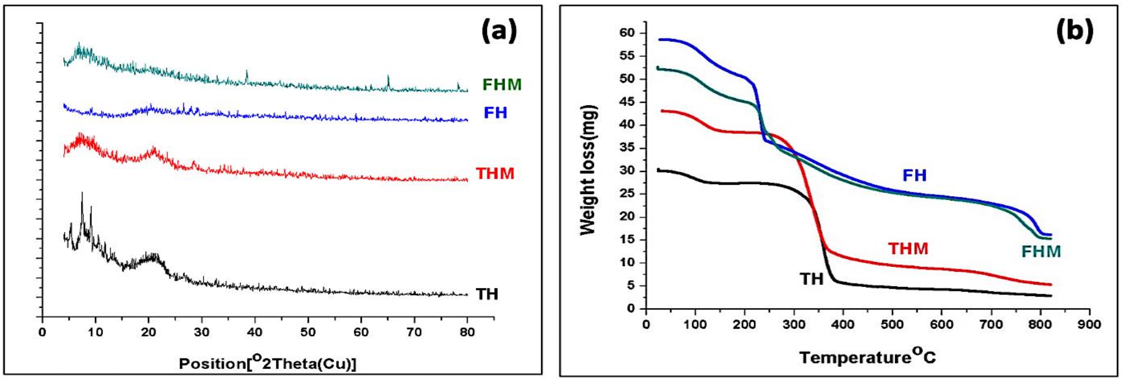

Fig. 3. a) XRD analysis of; TH, FH, THM, and FHM hydrogels. b) TGA analysis of; TH, FH, THM, and FHM hydrogel

Morphological study and EDX analysis

The morphology of the TH, FH, THM, and FHM hydrogels was observed by SEM, as shown in (Fig. 4.) Through SEM investigation, the Tylose hydrogel (TH) appears as a pore-widened sponge capable of absorbing substances. Still, in introducing the multifunction agents, they occupied the pores and appeared as impurities. As for the Funori hydrogel (FH), the pore sizes decreased and occurred as closed, and the multifunction agents occupied the pores FHM. On the other hand, the hydrogel consists of natural materials represented by the two elements Carbon (C) and Oxygen (O) with the addition of Calcium (Ca) as a cross-linker, so it is clear from EDX analysis that the TH and FH hydrogels are mainly C and O with Ca while Sodium (Na) and Sulfur (S) peaks have appeared in the EDX analysis of THM and FHM hydrogels which confirmed the loading of multifunction agents (Gattuso et al., 2021).

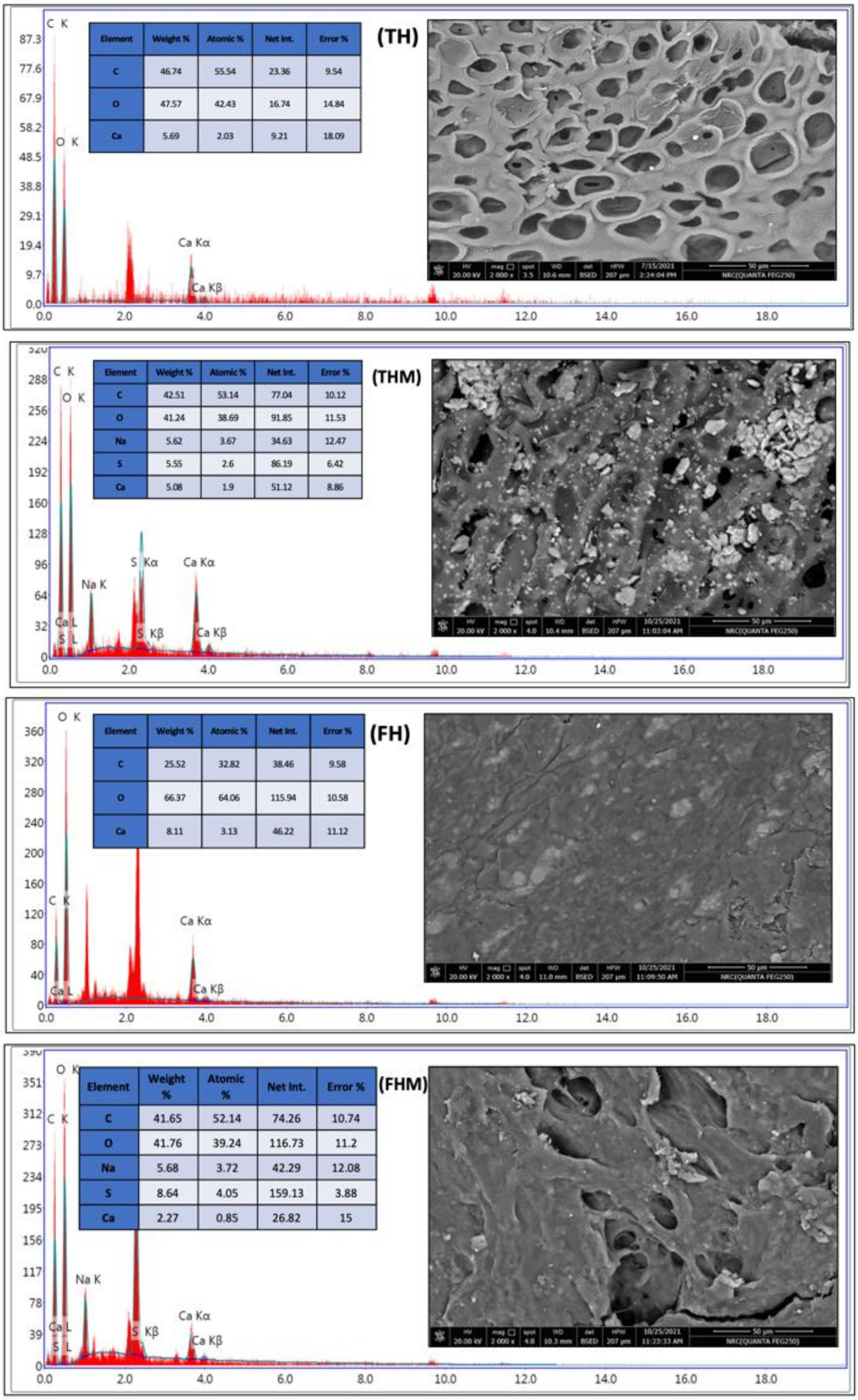

Fig. 4. SEM and EDX analysis of; TH, FH, THM, and FHM hydrogels.

3.3. Paper samples characterization

Photography and digital microscope investigations

Photo snapshots were taken for paper stains before and after treatment to know the effect of different types of hydrogels and multifunction hydrogels on the appearance of the paper samples; the snapshots are shown in (Fig. 5.a). To confirm the results of the visual investigations, a digital microscope was used to examine the extent of change in the surface of the treated paper, affected by removing and cleaning the stains, and to monitor the leaving of any traces of hydrogel residue on the surface after treatment (Fig. 5.b). It was revealed through photographic and morphological surface investigations with a digital microscope of the paper samples all types of hydrogels showed relative cleanness of the stains applied to the paper samples. However, multi-function hydrogels were distinguished from hydrogels. This was demonstrated by the photos of the paper samples used with multi-function Funori hydrogels, especially with rust and tideline stains. Residual traces were observed on the surface of paper samples treated with Tylose.

Mechanical studies

The results of tensile strength and elongation ratio of the paper samples treated with the prepared hydrogels before and after accelerated wet thermal aging are shown in (Fig. 6). Through these results, it was clear that there was an improvement in tensile strength and elongation ratio for paper samples treated with all hydrogels. TH recorded an increase in elongation by about 15 mm, followed by FH by 5 mm. The improvement in mechanical properties appeared more clearly with papers treated with THM and FHM, where the paper treated with THM had the highest elongation 36 mm, followed by that treated with FHM 5 mm. This improvement in the mechanical properties of the treated papers may be due to the effect of the hydrogels on the paper samples as a cleaning agent and also as a multifunction hydrogel that reduces the acidity of the paper, and this has the greatest effect in improving the mechanical properties according to the improvement of the chemical properties of the paper. The superiority of Tylose hydrogel is due to its texture being affected by the surrounding atmosphere and thinned due to its high hygroscopicity as the sizing material (Tylose) penetrated the paper fibers, which led to the improvement of mechanical properties represented in the bonding of the cellulosic fibers to each other. On the other hand, there is no significant difference in the behavior of paper mechanical properties after conducting accelerated wet thermal aging.

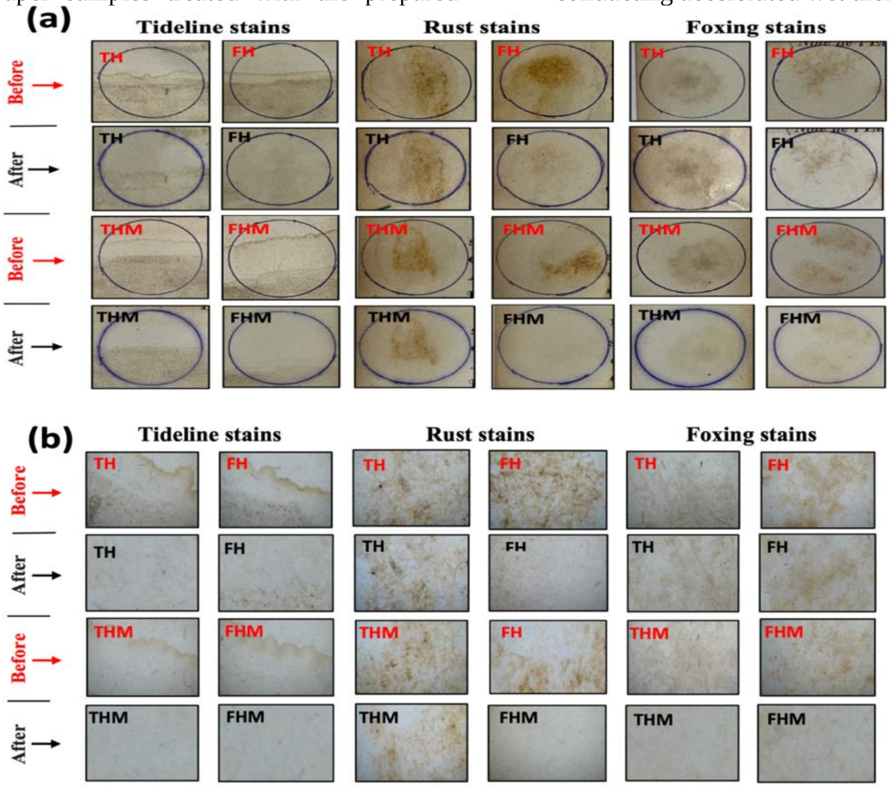

Fig. 5. a) Photography images of paper samples before and after treatment by TH, FH, THM, and FHM hydrogels, against Tideline, Rust, and Foxing stains. **b)** Digital microscope images (40X) of paper samples before and after treatment by TH, FH, THM, and FHM hydrogels, against Tideline, Rust, and Foxing stain

pH Measurements

The pH values during the cleaning process measure the acidity or alkalinity of the paper surface after the cleaning Table 1. During the paper cleaning process, the hydrogel's ability to adsorb the contaminants must be rationalized regarding the interactions between the adsorbate, i.e., the paper stains and the hydrogel. The pH of the aqueous solution within the hydrogel is one of the most critical parameters because both adsorbent and adsorbate may have functional groups that can be protonated or deprotonated to produce different surface charges. Consequently, the process can be rationalized as electrostatic interactions between charged adsorbate molecules and adsorbents (Barrulas, Nunes, Sequeira, Casimiro, & Corvo, 2020). Table 1 shows the surface pH of untreated and treated papers by TH, FH, THM, and FHM hydrogels. Treated papers by all hydrogels showed an increase in pH value after cleaning; this means there is stability in scaling cleaning degrees and affinity between different gels.

Color change measurements

A colorimetric test was used to investigate the color changes induced by hydrogels during the cleaning process, and the total color change ΔE values were calculated for papers after cleaning Table 2. 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 (Baldevbhai & Anand, 2012; Mirjalili, Luo, Cui, & Morovic, 2019). Table 2 shows that the loading of cleaning agents increased the ΔE values, and the FHM hydrogel was more highly affected than other hydrogels in removing stains

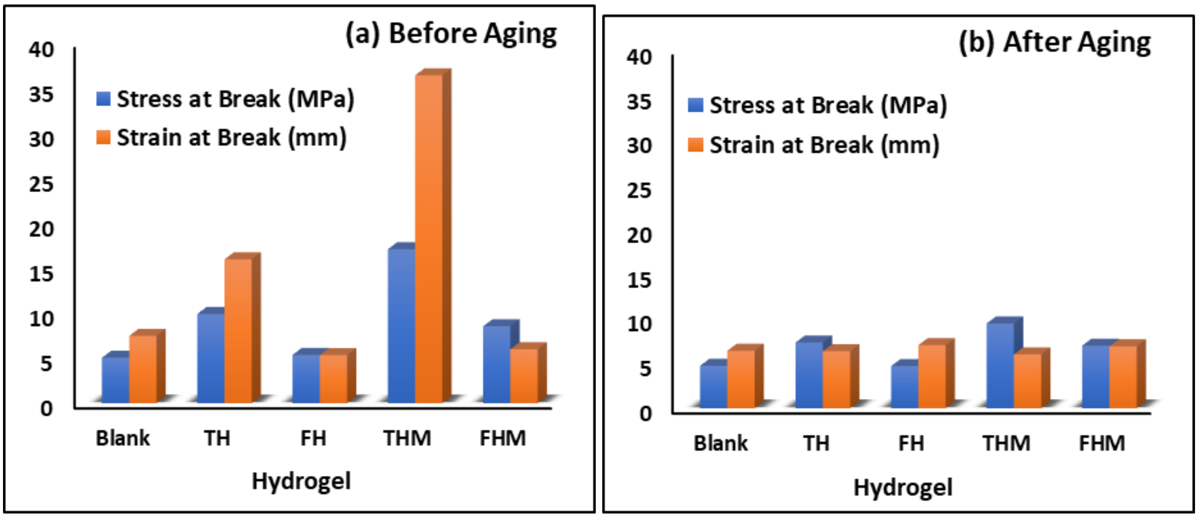

Fig. 6. Mechanical properties of untreated and treated paper samples by TH, FH, THM, and FHM hydrogels, **(a)** before and **(b)** after aging.

Table 1. pH of untreated and treated paper samples by TH, FH, THM, and FHM hydrogels.

Hydrogels	**Blank**	**TH**	**FH**	**THM**	**FHM**
Before Aging					
Tideline	5.23±2	6.75±2	6.50±2	6.82±2	6.77±2
Rust	5.34±2	6.45±2	6.38±2	7.03±2	6.67±2
Foxing	5.20±2	6.25±2	6.69±2	6.57±2	6.90±2
After Aging					
Tideline	5.21±2	6.51±2	6.28±2	6.68±2	6.63±2
Rust	5.25±2	6.38±2	6.29±2	6.42±2	6.41±2
Foxing	5.04±2	6.07±2	6.40±2	6.16±2	6.72±2

Table 2. The effect of color changes on paper stains before and after treatment by hydrogels.

	L	**a**	**b**	**ΔL**	**Δa**	**Δb**	**ΔE**
Standard	79.99	-31.78	2.79	----	----	----	----
Tideline stain	73.99	-32.17	3.61	----	----	----	----
TH	77.99	-27.36	4.84	4.00	4.81	1.23	4.6
FH	79.04	-26.34	5.00	5.05	5.83	1.40	5.7
THM	80.89	-27.93	5.19	6.90	4.23	1.58	7.2
FHM	82.62	-27.31	4.02	8.63	4.86	0.41	8.9
Rust stain	65.31	-6.77	12.72	----	----	----	----
TH	71.51	-16.13	9.02	6.20	-9.36	-3.70	10.1
FH	80.92	-22.53	5.40	15.61	-15.76	-7.32	20.6
THM	77.74	-13.21	8.20	12.44	-6.44	-4.52	14.0
FHM	83.05	-23.06	5.86	17.74	-16.29	-6.85	22.3
Foxing stain	72.38	-17.18	6.94	----	----	----	----
TH	76.49	`-19.35	4.41	4.11	-2.17	-2.53	4.8
FH	81.33	-25.57	2.21	8.95	-8.38	-4.81	11.0
THM	80.85	-18.85	5.55	8.47	-1.67	-1.39	8.6
FHM	83.42	-20.40	5.71	11.04	-3.22	-1.23	11.3

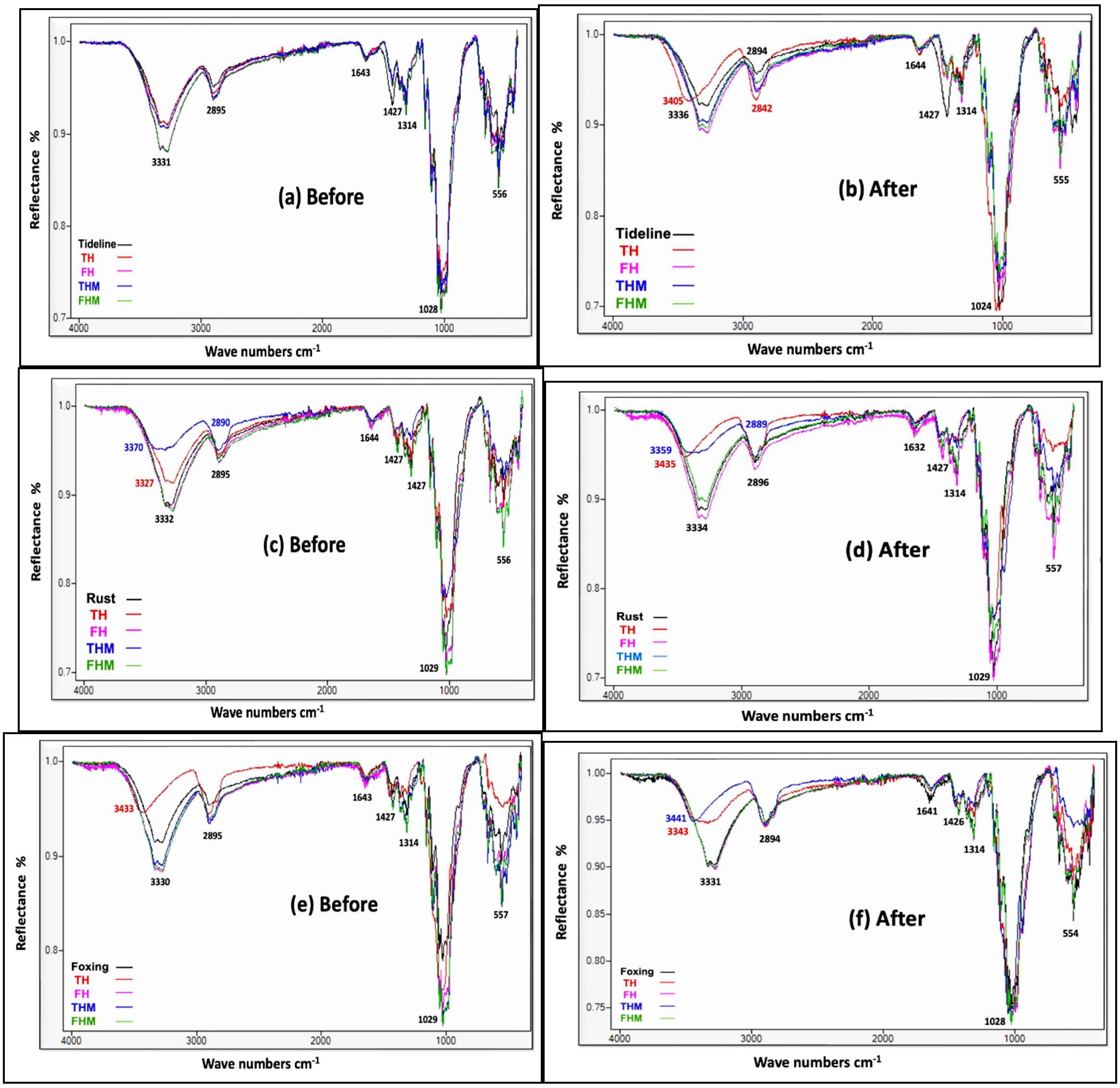

Fig. 7. ATR analysis of stains and treated papers by TH, FH, THM, and FHM hydrogels, **a, b)** Tideline stains which treated before and after aging, **c, d)** Rust stains which treated before and after aging, **e, f)** Foxing stains which treated before and after aging

FTIR–ATR analysis

FTIR-ATR analysis was performed to evaluate the change in chemical properties of paper samples after the cleaning processes, before and after aging (Fig. 7). FTIR-ATR spectra show the typical pattern of cellulose characterized by absorption bands in the region 1500–950 cm^{-1}, for instance, to C-O and C-C stretching, C-CH and O-CH deformation, and C-OH and H-C-H bending (Di Vito et al., 2018). All the spectra were collected, and slight differences are present in the spectra; we can summarize as follows:

The bands around 3400 – 3300 cm^{-1} refer to the O-H stretching of hydrogen-bonded. The spectra for primary and secondary amides contain a strong carbonyl absorption band in the region of 1650 cm^{-1}, called the amide I band. Secondary amides display an additional band near 1550 cm^{-1}, called the amide II band that combines C-N and N-H vibrations. A C-H bending vibration occurring near 1450 cm^{-1} has sometimes been called the amide III band. The relative intensities of the amide I, II, and III bands in polyamides occur in a stair-step pattern. The asymmetrical and symmetrical N-H stretching vibrations occur near 3350 and 3180 cm^{-1}, respectively. Hydrogen bonding may broaden the bands, giving the appearance of one band, although they are usually sharper than O-H bands. Often a stronger O-H band overlaps this region, and the N-H stretches appear as shoulders or peaks on the broader O-H band (Calvini & Gorassini, 2002; Derrick, Stulik, & Landry, 1999; Ion et al., 2008). The dissociation of the hydrogen bonds with the hydroxyl group O-H at 3400 cm^{-1} and the ether C-O at 1028 cm^{-1} may be due to photochemical degradation, which is responsible for the yellowing phenomenon (Leal-Ayala, Allwood, Schmidt, & Alexeev, 2012), which is a strong and sharp curved spectrum. Also, the absorption peaks at frequencies 1430 and 897 cm^{-1} are sensitive to the crystal structure of cellulose in cellulosic materials. The most interesting peaks were observed at frequencies CH_2 in cellulose 1425 and 1316 cm^{-1} and two smaller peaks at 1335 and 1370 cm^{-1}; these peaks are very sensitive to the paper aging process.

In general, there is a decrease in wave numbers, intensity, and broadening of the OH and CH groups for paper treated by Funori hydrogels. This behavior may result from rearranging the hydrogen bonds during the treatment and cleaning of the paper. For samples treated with Tylose hydrogels, an increase in wave numbers and intensity with the same functional groups was observed, perhaps due to leaving traces of the hydrogels on the surface of the treated paper.

4. Conclusion

In this work, one of the modern methods was used in the treatment and cleaning of archaeological paper by making a comparison between Tylose and Funori hydrogels; the results showed the following:

- The multifunction materials loaded on the hydrogel improved its properties and increased its cleaning efficiency.
- By comparing the Tylose and Funori efficiencies, the Funori hydrogel was superior.
- Gel treatment and cleaning improved the paper's optical, chemical, and mechanical properties, which cleaned the stains, raised the pH, and strengthened the treated part.
- This study has proven that Tylose and Funori hydrogels are safe for use with archaeological paper and humans and are environmentally friendly.

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