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Natural and Synthetic Polymer Hydrogels for Conserving Paper Manuscripts: Bridging Polymer Science and Archaeology

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Abstract

Paper manuscripts in museums, stores, and libraries often exhibit various stains contributing to their degradation. Cleaning these stains is crucial for the preservation of these valuable artifacts. Unfortunately, cleaning these stains frequently affects the manuscript, whereas traditional cleaning methods can harm the delicate fibers of the paper. As a result, art conservators are constantly seeking innovative cleaning techniques to address this challenge. Recently, hydrogels have appeared as a promising substitute to traditional methods, offering effective stain removal while minimizing damage to paper. This review article provides a comprehensive overview of common stains found on archaeological paper manuscripts, their deterioration mechanisms, and the importance of proper cleaning techniques. It also explores the structure, classification, and characterization of hydrogels, essential tools in art conservation. Codependency: Different hydrogels, such as those based on polysaccharide hydrogels and synthetic polymers, are examined in detail, highlighting their suitability and unique properties for specific conservation applications. Moreover, this review also notices and discusses these materials' physicochemical properties and practical aspects, offering a range of innovative formulations to address the limitations of conventional solvent thickeners. Integrating knowledge of stain removal techniques and gel properties provides valuable insights to the conservation community and enhances the preservation of paper manuscripts for future generations.

Keywords: Paper manuscript, stain cleaning, hydrogels, polysaccharide hydrogel, synthetic hydrogel.

1. Introduction

Paper is one of the most commonly used materials in historical objects, and several paper-based items have been identified in libraries, archives, and museums. Manuscripts were the main preoccupation of those interested in human heritage and history during human civilization. However, paper manuscripts are vulnerable to mechanical, chemical, and biodegradation damage, generally when not stored under controlled environmental conditions [1]. Paper manuscripts can be exposed to various conditions that can impact their chemical stability, causing deterioration and discoloration. While aging can naturally cause deterioration, poor storage conditions, such as humidity or chemical effects, may accelerate the degradation process. One sign of deterioration is discoloration or staining on the surface. Paper manuscripts are often contaminated by soiling and damaging elements, such as ancient adhesives or natural polymeric coatings from previous restoration efforts, which may affect the appearance and readability of manuscripts [2, 3]. In paper manuscripts, there are various sorts of stains, including water stains; stains by ink, blood, and adhesive; rust and metal stains; soot; wax; dust and finger marks; and oily stains. Most of these stains can be found on paper manuscripts and appear in the text area or margin on the white background. In addition, inadequate storage and interaction with water, soil, and dust made different stains appear on the paper's surface [4, 5]. Due to the previous, stains on manuscripts must be removed. The cleaning process is one of the most vital processes for the treatment of paper manuscripts. Cleaning can be divided into two main types of chemical and mechanical approaches. Lasers, vibrating tools, ultra-high-pressure water, etc., are placed in mechanical approaches, while using chemical compounds such as acids, bases, and solvents belongs to the chemical approach [6].

Organic solvents in cleaning processes are one of the most important steps during paper artwork restoration, allowing for the removal of pollution materials, degradation byproducts, and chromophores so as to obtain an improvement of their optical properties and a slowing down of paper aging. However, it is also a very delicate step: if performed in the wrong way, it may lead to irreversible damage, such as alteration of colorants, pigments, and inks; stain formation; modification of paper dimensions; and cellulose crystallinity. To this aim, the use of gelled systems has emerged as a valid cleaning protocol, since they can confine the solvent in the gel matrix, thereby ensuring a more controlled solvent release than simple washing by liquid solvents [7, 8, 9].

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Recently, innovative cleaning methods have been proposed based on applying suitable hydrogels. Because of viscosity and the high retention power of gels, the penetration of the solvent and liquids into the paper sheets is significantly reduced, thus minimizing damage [10-11].

Hydrogels are capable of regulating water released into paper during cleaning processing and absorbing decomposition products and dust adhering to the paper surface (Figure 1). Hydrogels can address the limitations of traditional cleaning methods, making them increasingly popular in the preservation of paper [12-14]. Recent developments in soft matter and colloid science have led to the creation of materials with tunable properties that can adapt to several conservation needs. High viscoelasticity is key for easy handling and removal of the gels, ideally in one step (e.g., peeling), without rinsing [12, 15].

Hydrogels are mainly defined as three-dimensional cross-linked networks of polymers. They are capable of absorbing large amounts of water through the swelling process. During the swelling process, the polar groups in the polymer chain swiftly draw the first water molecules into the hydrogel network (bound water), and the hydrogel network absorbs more water molecules as a result of the osmotic pressure of the interstitial water and free water [16, 17]. Hydrogels may be composed of natural polysaccharides or synthetic polymers, and their rheological properties can vary widely [18, 19]. Some of them are stimulus-responsive ones, such as physical stimuli like light, pressure, temperature, magnetic field, and electricity, as well as chemical stimuli such as ionic strength, solvent composition, pH, and molecular species [20, 21]. Polymers can be formed as hydrogels, cryogens, aerogels, nanogels, xerogels, films, microgels, or composite materials incorporating micro- and nanoparticles [22]. Hydrogels are classified into different groups depending on their structure, origin, crosslinking mechanism, preparation method, physical aspect, charge, responsive nature, and degradation [23, 24].

There have been a lot of hydrogels used in cleaning paper manuscripts. Rigid aqueous gellan gels, for instance, were utilized in the removal of auxiliary supports, substances left on the surface, and adhesives [25, 26]. The combination of agar-agar and semi-IPN p(HEMA)/PVP hydrogel has been tested on paper with a sensitive ink. Poly(vinyl alcohol)/poly(N-(2-hydroxyethyl) acrylamide) (PVA/PHEAA) hydrogels were utilized in cleaning dust stains from paper [14]. Mazzuca et al. [11] used polyvinyl alcohol (PVA) hydrogel in cleaning stains from paper artwork.

Hydrogels can be manufactured into thin films or formed into any shape, length, size, or different architecture, depending on the requirement [22]. The osmosis cleaning system in hydrogel operates based on Fick's first law. It states that water will move from the gel to the paper, and decomposition products will move from the paper to the gel as a consequence of a concentration gradient. Hydrogel contains water or a solvent, which works on surface dirt, oil, and degradation products. The water molecules are drawn from hydrogel to the contaminated surface because the contaminants have a higher concentration of dissolved materials. The solvent is pushed to areas with higher solute concentrations by osmotic pressure, dissolving and pulling out the contaminants. This process does not significantly alter the original look of the paper and prevents bleed-through of dyes, inks, and pigments. Furthermore, with this method, conservators can manipulate even poisonous solvents safely. [9, 26, 27].

The pore size and the diffusional properties of gels allow the absorption into the gels of the products removed from the paper during the cleaning process. Porosity allows the hydrogel to release a sufficient amount of water (enzyme or solution) that acts as a cleaning agent at the interface between paper and gel; the characteristics (hydrophobicity and porosity) render them able to absorb degradation products (cellulose degradation products or hydrolyzed glue or starch) from the interface [6, 28, 29].

Using hydrogels in cleaning has several advantages. Advanced composite hydrogels can control the evaporation rate of organic solvents and the flow of the solution to other areas and layers on a surface. This control reduces human exposure to toxic organic solvents and allows for precise cleaning times. The porous structure of gels also allows them to trap contaminants. A more porous gel has a greater capacity to hold unwanted materials. [30-33].

However, some disadvantages arise when using hydrogels to clean painted surfaces, as residual stains may remain, which may negatively affect the artwork. This may occur when using a specific type of gel, such as solvent gels containing carbopol and other thickeners. Therefore, in the field of cultural heritage preservation, chemical gels are considered more effective than conventional solvent thickeners due to their specific properties, such as controlled solvent release, selective cleaning, and leaving less residue (either polymer residue or solvent residue) compared to physical gels [6]. This article aims to provide a comprehensive analysis of hydrogels in cleaning paper. It begins by explaining the most common types of stains found on ancient paper manuscripts and their deterioration mechanisms. Then, it explores the basic properties, structure, and classification of hydrogels in cleaning processes, highlighting their advantages and disadvantages as essential tools in the field of conservation.

1. The most common stains on paper manuscripts

Worldwide, paper has long been the most utilized medium in documentation/registration of achievements in cultural fields for centuries. Paper is mainly composed of cellulose together with trace amounts of organic and inorganic components [34, 35, 5].

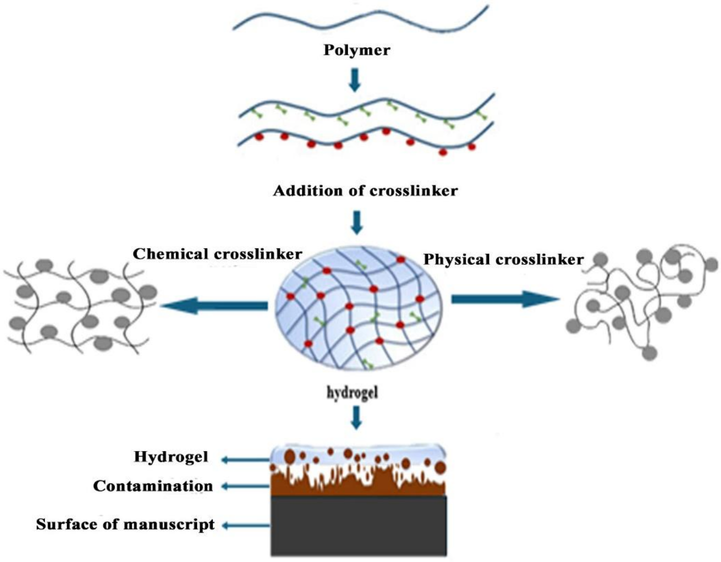

Fig. 1. Suggested mechanisms of hydrogel cleaning, namely the entrapment of impurities in The gel's porous structure.

Preservation and conservation of paper documents are essential operations aimed at extending the lifespan of artifacts by decreasing physical and chemical deterioration to avoid and reverse further decay [36, 37]. The study of mechanisms and causes of deterioration is the basis for the formation of measures and improving storage conditions. Paper manuscripts present in museums, libraries, and stores become contaminated with dirt and are affected by acidity and therefore require deacidification and cleaning [4, 7]. The degradation can be caused by environmental factors (temperature, pollutants, light, and relative humidity), natural or artificial disasters and climate changes, and microorganisms and inadequate previous restoration efforts using materials incompatible with the original artifacts' components [18, 38]. Paper-based archives, prints, and books often exhibit dirt and various stains due to high acidity or aging byproducts, leading to cellulose paper support deterioration. Techniques of printing may also cause an increase in the acid decomposition and degradation that leads to yellowing, staining, and increasing acidity levels in paper-based artworks and printed products [39, 40]. Stains are frequently observed in archaeological papers, resulting in surface deformation and color changes. Stains are commonly observed in archaeological papers, resulting in surface deformation and color changes. The danger of the stains lies not only in the appearance of the distorted surface but also in the formation of different damaged aspects, such as high acidity due to rust spots, as well as biological stains [41]. Bukovský et al. [41] pointed out that the reason for staining in historical artifacts depends on the usage of materials and storage environment. A wide range of stains can be observed on paper-based materials (Figure 2), including water, pigment, ink, adhesive, rust, blood, metal, dust, dust, soot, wax, fingerprint, and oil stains. These stains may affect multiple consecutive pages and can appear on the text, margins, or other areas of a manuscript. They include poor storage, water, dust, and spoilage, and the stains normally develop on paper when in use. The whole point is to know what kinds of stains are often seen on the papers and what reagents can be found in the stains, as well as to develop non-destructive methods of cleaning papers gently [42].

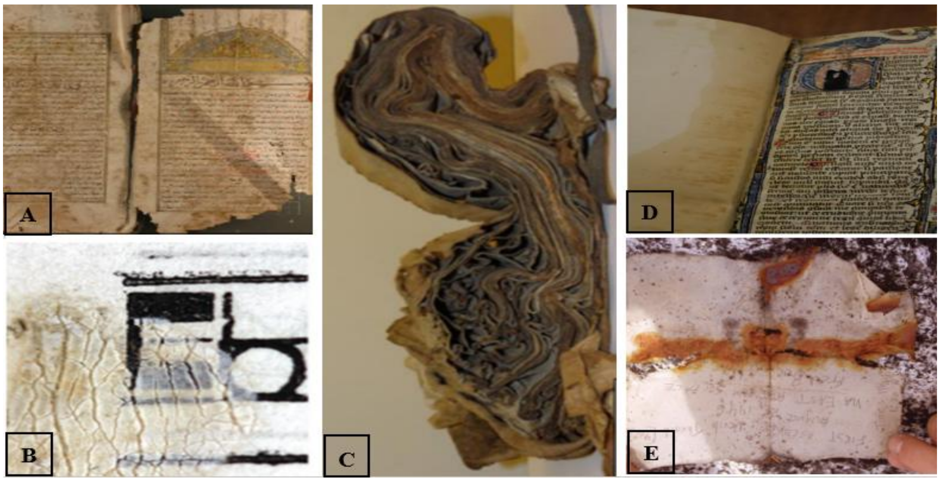

Fig. 2. The most common stains on archaeological paper manuscripts: (A) dust attained, (B) wax stains, (C) soot stains, (D) oil stains, and (E) rust stains on paper, with parts of the paper replaced by thick grains of rust [43, 44].

1.1. Dust and dirt stain.

Dust is dry, fine particles that are spotted in the air and include soil, metal particles, tar, and fungus spores. When dust is left on paper surfaces, especially in high humidity conditions, the dust will become dirty; hence, it is difficult to clean the paper [44, 45]. This dirt is typically abrasive and may cause harm to manuscripts on paper (**Figure 2A**). In addition, the paper may also turn acidic by exposing the paper to other pollutants in the atmosphere, such as sulfur dioxide, which could hurt the mechanical properties of the paper [7, 46]. Therefore, it was necessary to clean manuscripts of dust and other sorts of stains. Hassan [5] stated that dust stains on paper manuscripts can be removed mechanically with soft or firm brushes. However, mechanical cleaning has its drawbacks. Incorrect mechanical cleaning may lift or damage fibers and cells, especially if the deposits firmly adhere to the paper surface. Furthermore, using numerous tools in mechanical cleaning may produce minor scratches on the paper surface. Some traditional cleaning methods, like chemical whitening and solvents, are used for removing stains that may damage the fibers of the cleaned paper. Most organic solvents, such as toluene, used in cleaning paper manuscripts, can cause the degradation of the treated paper. These solvents can trigger hydrolysis and accelerate paper oxidation [47].

Chelazzi et al. [12] stated that water-loaded gels effectively remove dust. Gel use is a crucial cleaning process for paper manuscripts due to its controlled and easy application. Zidan et al. [36] utilized cellulose nanocrystal gel and hydrogellan gum to remove surface soils and dust, resulting in improved mechanical properties of paper samples. Therefore, it can be safely used in conservation treatments of cellulosic supports. However, water treatment is recommended for uncolored paper to prevent the bleeding of dyes or pigments.

1.2. Wax stain

Wax is a hydrophobic organic compound composed of long alkyl chains. They consist of lipids and higher alkanes that are soluble in organic, nonpolar solvents but insoluble in water. Waxes are classified based on their origin: natural waxes are derived from animals and plants, while synthetic waxes are long-chain hydrocarbons (paraffin or alkanes) without substituted functional groups [48-49]. Wax has been used temporarily to protect from fugitive pigments on paper during aqueous treatments. In addition to conservation treatments involving waxy compounds, historical paper documents may have wax present due to the mishandling of candles during events like "reading by candlelight." On formal occasions, candles were placed around collections, leading to the possibility of hot wax dripping onto paper documents (**Figure** 2B). The existence of wax in paper artifacts can accelerate the degradation of paper by releasing fatty and oily compounds into cellulose fibers, causing mechanical stresses such as brittleness and cracking, as well as staining and transparency of the substrate. Wax coatings or stains can obscure surface details and attract dirt and dust [4]. Wax is challenging to remove from objects, limiting their repeatability. Traditional cleaning methods often involve using room-temperature solvents, which may not completely dissolve the wax [50, 51]. Restorers commonly use dry cleaning to quickly remove waxy layers from paper surfaces. However, it can be aggressive and uncontrolled, especially when using traditional tools like cotton swabs, brushes, scalpels, and hot tools. Mixes such as kerosene, odorless mineral spirits, petroleum ether, and white spirits have low efficacy in removing wax stains and can harm health [23].

In recent years, advancements in substance science, soft matter, and colloids have provided safer solutions for removing wax. New methodologies for wet cleaning artworks include nanostructured cleaning fluids like microemulsions, swollen micelles, surfactants, and chemical and physical gels. These methods work on various physicochemical mechanisms to selectively eliminate undesirable layers sustainably and cost-effectively [10]. Chelazzi et al. [12] stated that organogels of poly (methyl methacrylate), laden with average polarity solvents, aid the fast removal of wax from solvent-sensitive inked manuscripts. Polymethyl methacrylate-methyl ethyl ketone organogels were used on a 19th-century printed missal book to eliminate paraffin wax stains [10].

1.3. Soot stain

Soot is carbon dust formed by the gas-phase decomposition of hydrocarbons during a fire. It comprises carbon particles and an oily matrix [52, 53]. Soot comprises ultrafine particles (~2.5 microns), smaller than most pigments (2.5 to 10 microns). Fine soot particles can penetrate interstices and become embedded in surfaces [54, 55]. Particulate matter, such as ash particles and soot from manufacturing activities, is plentiful outside and can enter archives or libraries through heating and cooling ducts, doors, and windows. These particulates, which may be abrasive, greasy, and biologically or chemically active, settle on manuscripts (**Figure 2C**) [56]. Nanoparticle sizes of soot can be challenging to remove from porous surfaces, particularly when deeply embedded. Organic materials like paper are particularly susceptible to this issue. The primary goal in such cases is to eliminate soot for enhanced stability and readability [57]. Many reagents have been used for removing soot particles from the surfaces of artifacts, including solvents, salts, and surfactants. Solvents such as ammonia, ethanol, white spirit, acetone, trichloroethylene, and ethyl acetate are among the most commonly used. Some, like ethanol, are sometimes used instead of water to soften soot. Solvents can also be used with water to produce a mixture that is more volatile than pure water. [51]. Due to the limitations of traditional chemical and mechanical cleaning techniques, gel cleaning has been suggested as an alternative method for testing soot removal from surfaces when addressing soot on manuscripts. Since the 1980s, the conservators have known that gel-based aqueous cleaning methods, which include organic solvent gels, offer many advantages over pure organic and mixture solvents [58]. Abdel-Hamied et al. (2024) used hybrid nanogels composed of carbopol and nanoparticles (NPs) of zinc oxide (ZnO) and titanium dioxide to remove soot stains from the surface of paper manuscripts [59].

1.4. Oil stain

An oil stain is a common issue found on paper manuscripts (**Figure 2D**). It can be transmitted to paper through spills, handling, and contact with oily objects or media. The stained area on the paper becomes discolored, more transparent, and less absorbent as oil molecules fill the gaps between cellulose fibers [60]. Bookbinders use "oiling" or "dressing" to describe the procedure for adding waxes, fats, oils, and other things to bindings of animal skin. These oils can be absorbed into leather bindings and migrate onto pastedowns, gutters, end sheets, and text blocks [61]. Over time, the discoloration caused by oil oxidation can affect legibility, and gradual disintegration of the stained paper may compromise the entire volume at risk [62]. In traditional methods, a solvent mixture of alkali, such as ammonia, is often applied to break down the network of oil into smaller components. However, this method can be harmful and sometimes inefficient [61]. Organic solvents like white spirits, ethers, or chlorinated hydrocarbons can remove fat and oil stains from paper manuscripts [61]. However, these solvents may lead to issues like softening, degradation, and bleeding in oil-based printing inks. Therefore, it is crucial to choose a method that is effective in stain removal without causing harm to the inks [62]. Blüher et al. [63] stated that removing oil stains from paper, particularly drying oils like linseed oil, poses a challenge for conservators. Lipase enzymes can degrade oils and fats with triacyl glyceride structures. In paper conservation, lipases remove stains by breaking down aged oil films. This method is safer than alkaline mixtures or very polar organic solvents and has a certain action that minimizes damage to the artwork. Lipases are a type of hydrolase that targets carboxylic ester bonds. Their physiological function is to break down triglycerides into fatty acids, diglycerides, glycerol, and monoglycerides. Enzyme activity can be disrupted by physical, chemical, or thermal methods that alter the protein's tertiary structure [60].

Campbell [61] recommended using non-aqueous solvents before aqueous ones, as they cause less disruption to the paper surface.

Morlotti et al. [64] and Campbell [61] confirmed that poulticing with lipase and trypsin in an agarose gel effectively reduces oil stains on paper manuscripts.

1.5. Foxing stains

Foxing stains are roundish, tiny spots of reddish-brown or yellowish color that appear on paper manuscripts. This fuzzy definition occasionally makes it difficult to identify foxing [22]. Possible causes of foxing include metal contamination, moisture condensation, microorganisms (bacteria and fungi), and localized capillary evaporation processes at the wet-dry interface. Metal and microorganism impurities may come from paper-making or airborne dust. Airborne dust may contain up to 15% iron as an inorganic constituent. Another source of metal stain may include contact with metal objects or iron gall inks [65, 67]. Sarantopoulou et al. [68] stated that foxing is a critical issue because the stains could transfer to subsequent pages and cause irreparable damage to the paper. It was long thought that foxing was caused by rust from small iron fragments worn off paper-making machinery. However, it is now understood that the initial cause of foxing was a group of conidia deposited on the paper surface that germinated in situ [69, 70]. Irwin [71] stated that rust could cover most of a paper artifact or be as minor as a residual stain left by rusty paper clips or staples. The accumulation of rust stains in the paper may cause parts of the paper to be replaced by thick deposits of rust (Figure 2E).

Ciofini et al. [65] mentioned that in research on the corrosion of ink, most iron gall inks contain an excess of iron that is not bound to the complex-forming component in the ink and can migrate a short distance to the surrounding areas. In summary, transition metal ions, including copper(I) and iron (II), can act as catalysts for free radical oxidation of cellulose, resulting in the degradation of cellulose chains and discoloration of cellulose-containing paper. Furthermore, carboxyl groups and carbonyl groups formed from the oxidation of cellulose may enter an amino carbonyl reaction with nitrogen-containing compounds inherent in paper (fungal amino acids, gelatin sizing) or pollution (starch grains, spores, dust). The amino carbonyl reaction, often known as the Maillard reaction, produces melanoidin-like brown chemicals known as age pigments. In fox stains, paper products are more acidic, brittle, and weaker than uncolored ones, although they are not severely harmed structurally [72, 73].

Fungi can grow by establishing vegetative colonies and producing new spores under ideal conditions. Paper can absorb water by capillary condensation in a moist environment. Particularly in the heterogeneous parts of the cellulose chains, resulting in a biological attack that compromises the structural stability of cellulose fibers. This distinguishes foxing from typical mildew or mold damage. Bioremediation considerably impacts the mechanical characteristics of paper and media during enzymatic activity. Breaking down fats, proteins, and carbohydrates into amino acids, simple sugars, and fatty acids. Traditional methods to remove foxing stains, such as solvents, mechanical cleaning, and chemical solvents, can damage paper fibers [69, 72].

Foxing stains on paper have continuously posed a challenge for conservators due to iron in a ferric state, which is not easily soluble in water. This makes it difficult to clean rust stains using solvents or pure water washing alone. The most applicable treatment for removing rust stains from paper involves two steps. The first step is to reduce the ferric iron to its ferrous state using a reducing agent. In the ferrous state, iron becomes soluble in water and can be washed out of the paper [74, 75].

Foxing stains are usually removed by washing the paper with demineralized water or detergent solutions, or by removing the color with solutions of hydrogen peroxide, acetic acid, oxalic acid, ammonia, potassium perborate, or sodium and calcium hypochlorite, depending on the type of stain. Chemical reactions involving acid formation are among the most damaging biological degradation processes for paper, as they can severely damage the cellulose structure [29].

According to Campanella et al. [76], agar gels supplemented with citrate or EDTA have been utilized to remove iron stains from surfaces. De Filpo et al. (2016) [29] studied the ability of gellan gum hydrogels in cleaning foxing stains from paper, as well as the capacity of deacidifying calcium compounds and titanium dioxide in decoloring paper. The study confirmed that hybrid gellan gum hydrogels incorporating titanium dioxide nanoparticles can be considered an effective tool to improve the conservation, protection, and usability of library and archive materials. The use of these hybrid hydrogels is easy and inexpensive and allows for the single-step cleaning and decoloring of paper artworks.**Hydrogel**

De Filpo et al. (2016) [29] studied the ability of gellan gum hydrogels in cleaning foxing stains from paper, as well as the capacity of deacidifying calcium compounds and titanium dioxide in decoloring paper. The study confirmed that hybrid gellan gum hydrogels incorporating titanium dioxide nanoparticles can be considered an effective tool to improve the conservation, protection Hydrogels are viscoelastic, solid-like materials. They consist of a flexible cross-linked network and a solvent as the main component. The hydrogel's solid appearance is due to liquid entrapment within a three-dimensional matrix formed by cross-linking polymeric strands. This cross-linking can occur through chemical or physical interactions [13, 16, 78].

A crosslinking agent is used in the synthesis of hydrogel to form a three-dimensional network of hydrogels by physical linkage, hydrogen, and ionic bonding. Chemical crosslinking refers to the formation of chemical links between molecules. Hydrogels created by strong chemical bonding are thermally irreversible (e.g., polyester, polyvinyl alcohol, polyethylene, polyamide), but hydrogels formed by weak noncovalent contacts are reversible (e.g., polyacrylate, polymethacrylate) [16, 79, 80].

1.6. Hydrogel structure

Hydrogels comprise a structural framework comprising three-dimensional networks of randomly cross-linked polymeric chains categorized into three distinct phases. The initial phase comprises a solid polymer network matrix, while the subsequent phase comprises interstitial water or biological fluid. The hydrogel's solid component consists of a network of cross-linked polymer chains arranged in a three-dimensional mesh structure, with fluid occupying the interstitial spaces. The network meshes maintain the fluid's position and exert a viscoelastic force that resists expansion or contraction of the hydrogels, thus ensuring dimensional stability. The water content is a significant characteristic of the hydrogel. Water can interact with any hydrogel structure in four distinct ways, as illustrated in **Figure 3**. Regarding the ionic phase of the hydrogels, generally it is composed of ionizable groups bound onto the polymer chains and several mobile ions, which include counter ions and co-ions, due to the presence of electrolytic solvent that surrounds the hydrogels [81]. Nowadays, hydrogel-based cleaning protocols are recognized as well-grounded and effective methodologies, thanks to their high retention and interesting rheological properties that allow a precise and selective treatment confined to the outermost layer [52, 53].

Rheological testing is used to study the viscoelastic properties of hydrogels. A thorough knowledge of the rheological properties of hydrogels used for cleaning is crucial to avoid unwanted damage to artwork. A rotational rheometer can monitor the gelation process either isothermally or during a temperature ramp experiment. A frequency sweep test is commonly used to study the mechanical properties of formed hydrogels.

To prevent slippage during the test, it's recommended to use cross-sectional geometry. Proper control of the normal force on the hydrogel sample is also essential during measurement. If the sample must be tested under submerged conditions, a Peltier immersion cell can be utilized [5, 81].

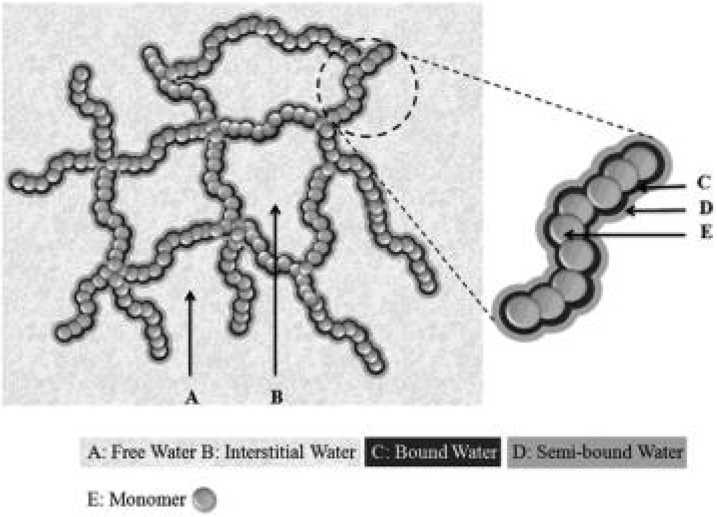

Fig. 3. A schematic structure of hydrogel at the molecular level and different types of water present in hydrogel [81].

1.7. The classification of hydrogels

Hydrogels can be categorized in several ways, including by their origin, monomer type, cross-linking, charge, and preparation procedures [6]. In this context, Zhao and Nasution et al. [16] reported that hydrogels have been categorized into two types based on their sources: natural polymer-based hydrogels and synthetic polymer-based hydrogels. Previous research has identified two types of synthetic hydrogels: those made of polyacrylamide (PAAm) and those made from polyvinyl alcohol (PVA). Synthetic hydrogels are artificial polymers. Synthetic hydrogels outperform natural hydrogels regarding water retention capacity, shelf life, and modification ease.

Natural hydrogels can be classified based on the origin of their components, which may be derived from plants, animals, or microorganisms. For instance, starch and cellulose are plant-based polysaccharides, while glycogen is derived from animals and chitin from arthropods such as insects, spiders, crustaceans, and fungi [85].

Hydrogels are cross-linked three-dimensional polymeric networks that can absorb great amounts of water, swelling up to more than a thousand times their weight. This water-absorbing property is attributed to the presence of hydrophilic groups such as OH^- , $-CONH_2$, $-SO_3H$, $-CONH^-$, -COOH, etc., within the hydrogel network [81, 82].

According to Park & Nho [83], hydrogels can be categorized into different types: copolymer hydrogels, interpenetrating polymeric hydrogels, homopolymer hydrogels, and multipolymer hydrogels. Homopolymer hydrogels are formed through the cross-linking of chains of one hydrophilic monomer unit. Copolymer hydrogels are prepared by cross-linking two comonomer units, with at least one being hydrophilic. Interpenetrating polymeric hydrogels are formed by swelling a network in a monomer and then forming a second interconnected network system. Multipolymer hydrogels contain more than three monomers and their cross-linked networks. Copolymer and multipolymer hydrogels are interesting materials for medical uses because they can possess a wide variety of chemical and physical characteristics depending on the monomers incorporated into the hydrogels.

Giraud et al. [17] and Singhal & Gupta [81] classified gels into two types based on their bonds: physical and chemical. According to Nasution et al. [16], physical gels are categorized into two types:The first includes strong physical gels, formed by specific biopolymers with double-helix structures, which create semi-rigid yet peelable films. Examples include agarose gels, gellan gum, and gelatin. The second subtype encompasses weaker physical gels, which rely on non-covalent interactions such as hydrogen bonding and result in viscous pastes. Examples of these polysaccharides are cellulose ethers, xanthan gum, and polyacrylics such as Carbopol® or Pemulen® [17]. One of the disadvantages of physical gel is that it remains as a layer on the applied surface after application. It can also collect dirt over time and make the cleaned section develop a different color from the rest of the surface. This problem should be solved by washing the treated area with organic solvents to remove the gel residue [84]. Chemical gels have polymer chains linked by covalent bonds, providing strong chemical and mechanical stability. These chemically cross-linked gels, also called irreversible gels, are exemplified by the Nanorestore Gel® developed by CSGI. Nanorestore Gel® is a transparent chemical hydrogel made from a pHEMA/PVP semi-interpenetrated network that retains liquid effectively [4, 6, 84]. Chemical gels are distinguished by the presence of covalent bonds, which give them an exact shape determined during synthesis. They exhibit strong gel cohesion, and no gel residue is expected after treatment with chemical gels [10]. According to Weiss & Terech [85], the best-used gels are chemical ones, where cross-linked covalent bonds maintain a three-dimensional network. These covalent cross-links make these gels robust and resistant to physical deformation. Gels can be classified based on the solution embedded in them. Organogels contain an organic solvent, while hydrogels contain water [32]. Du et al. [14] said that the gels used in conservation methods were divided into two types based on their macroscopic mechanical behavior: soft gels (SGs) and rigid gels (RGs). (**Figure 4**) SGs have a low modulus and are sticky, like Silly Putty. The main advantage of SGs is their good adhesion to textured surfaces. However, this adhesion can sometimes damage fragile artwork or result in gel residues sticking to the art. On the other hand, RGs maintain a stable shape and have a high modulus, leaving no gel residue after cleaning. While significant progress has been made, cleaning paper requires controlling water release and considering protective cleaning to prevent damage to cellulose fibers caused by adhesion between paper and hydrogel, a factor often overlooked. Rigid gels contain chemical semi-interpenetrated (semi-IPN) poly (2-hydroxyethyl methacrylate)/poly(vinylpyrrolidone) hydrogels and physical polysaccharide-based hydrogels, like agarose and gellan gum [86].

Fig 4. Gels used in cleaning: (A) a rigid gel (gellan gum); (B) a soft gel (Klucel™) [82].

Theodoridis & Kraemer [87] stated that hydrogels can also be classified according to the size of hydrogel particles: bulk gels, macrogels, microgels, and nanogels. The typical size range of microgels is from 10 to 1000 nm, while the size of nanogels is less than 100 nm [4]. The size of materials is a crucial factor that determines their properties. Small gels provide much quicker and more efficient performance. If the particles are too small, then they can cause problems; this makes microgels, in some cases, preferable to nanogels [87]. This property makes microgels ideal for the selective cleaning of artifacts without damaging the underlying layers. Microgels are colloidal-scale particles made of cross-linked polymer networks, usually suspended in water. Microgels have a stable structure, with their polymer network held together by covalent bonds or strong physical forces. However, similar to other colloidal dispersions, microgel particles have the potential to aggregate through flocculation or coagulation processes [26, 6]. Microgels have been used for a variety of applications, and their size and shape make them particularly desirable [88].

Microgels have a long tradition for the cleaning of several kinds of artworks, including paper cleaning. Indeed, thanks to their retentive properties, they offer substantial advantages with respect to the traditional wet cleaning method, which involves contact with free water [26]. Microgels could offer several advantages when compared to hydrogels: first, their reduced size may be suitable to achieve better penetration in the porous structure of paper, where they could absorb pollution materials and degradation byproducts in a shorter amount of time; second, the softness of the microgel suspensions could be tuned to make them easily adapt to the irregular surfaces of artifacts without inducing alteration of the latter. This would possibly extend their use also for materials with very delicate surfaces.

Franco et al. [18] utilized microgels composed of gellan gum and demonstrated their effectiveness as a cleaning agent for paper. Their results indicated that microgels outperform both water and traditional hydrogels in the removal of carboxylic compounds. Additionally, they suggested a cleaning method that utilizes water-based microgel solutions derived from gellan gum polymer modified with methacrylate groups (GGMA). This approach is beneficial in terms of health and time efficiency due to the chemical composition and unique properties of microgels.

1.7.1. Polysaccharide-based hydrogel

The macromolecular polymers known as polysaccharides are widely distributed and come from renewable sources, including algae, plants, and microorganisms such as fungi [89]. Hydrogels based on natural polymers like agarose, xanthan gum, gellan gum, and chitosan have been utilized as cleaning tools by conservators due to their hydrophilic properties, ability to hold water-based cleaning systems, non-toxicity, biodegradability, biological compatibility, and easy availability [31]. Gellan gum and agarose rigid polysaccharide gels have become popular among paper conservators [84]. Montreal & Sullivan [90], Bertasa et al. [91], Kwan [92], and Mastrangelo et al. [93] explained the cleaning mechanisms of hydrogel, reporting how hydrogel methods improve the cleaning process by successively removing contamination layers through various mechanisms. Hydrogels utilize various mechanisms in the removal of stains from surfaces, which can be broadly classified as solvent-mediated removal and chemical breakdown and interaction. The prevailing mechanism depends on the nature of the stain and the properties of the hydrogel used. Hydrogels, being aqueous, can act as a source of moisture that can dissolve or mobilize water-based stains from the surface. Hydrogels can also be used to deliver organic solvents to hydrophobic layers, i.e., aged varnish and adhesives, which are characteristic of works of art. The porous nature of the hydrogel allows these cleaning solutions to diffuse to the interface of the hydrogel-stained surface, thereby enhancing the removal process. For certain types of stains, hydrogels can facilitate their removal through chemical mechanisms. For example, hydrogels can be impregnated with chelating agents such as ethylenediaminetetraacetic acid (EDTA) or tri-ammonium citrate (TAC), which can then bind to metal ions present in corrosion products, literally removing these stains from surfaces. Gels are generally safe and effective methods of cleaning artwork surfaces in terms of satisfactory cleaning procedures [93].

1.7.1.1. Agarose

Agarose is a linear polysaccharide that can be extracted from agar (also known as agar-agar), which is extracted from cultivated red sea algae. Agar consists of agarose, a linear polysaccharide with strong coagulating properties, and agaropectin, a non-coagulating sulfated polysaccharide [4, 93]. In the conservation literature, agarose has garnered substantial interest as a poultice material. It has been employed alone to remove moisture-sensitive adhesives from paper and is frequently used with enzymes. In addition, using agarose in conjunction with bleaching compounds was suggested for the local bleaching of paper [94].

Agarose linear chains form double helix structures that combine to create "suprafibers" containing up to 104 helices. Agarose gels show a unique reversible property: they soften when heated and solidify upon cooling. This process can be repeated indefinitely without the presence of competitive substances. To create agarose gel, 1-5% agarose is mixed in an aqueous solution and heated to 85°C, forming a random coil structure that gels as it cools below 40°C [6, 10, 95].

Over the last ten years, studies have shown a growing interest in agarose for targeted cleaning among paper conservators. This increased interest is due to the numerous benefits of treatment with stiff polysaccharide gels [90].

Ali [96] also recognized that applying agarose is effective for water-sensitive surfaces, as it is quite rigid and can both prevent the formation of biofilm and confine soiling removed within a gelled matrix. Besides, agarose offers resolution of surface features, and it provides a lens-like capability that enables the conservators to see features that cannot be seen naked.

Gels are applied mainly as cleaning agents since they can be easily wiped off. It also reduces mechanical contact of the tools with the artwork and generates negligible deposition of contaminants that can be easily eliminated using a cotton swab or other tools. This makes gels suitable for cleaning surfaces of artworks and fulfilling the basic principles of cleaning. It is important to note that gel efficiency can be increased by altering concentration, casting thickness, increasing contact with light pressure, changing the aqueous solutions to prepare gels, and adding organic solvents [82].

Khaksar-Baghan et al. [6] referred to the advantages of using agarose gels as the cleaning medium, including controlled release of solvent, effective soil cleaning, accessibility, minimal impact on historical materials, and environmentally friendly properties. Wahba et al. [24] said that agarose is used for removing moisture-sensitive adhesives on paper artifacts, and it achieves the best results. Additionally, Ali [96] successfully used agarose gels loaded with solvents to treat paper to remove soil stains. Kwan [92] also said that agarose is particularly appealing for cleaning stains, as it absorbs solubilized degradation products into the gel network via capillary action, so that no mechanical action is required. Collectively, agarose hydrogels are a safe, effective, and residue-free method for cleaning and preserving sensitive paper-based cultural heritage.

2.2.1.2. Gellan gum

Gellan gum is a high molecular weight polysaccharide synthesized through the fermentation of the microorganism Sphenodons elodea, previously known as Pseudomonas elodea [9]. It is formed by the repetition unit of (1,3)-β-D-glucose, (1,4) β-D-glucuronic acid, (1,4) β-D-glucose, and (1,4) α-L-rhamnose [26]. When cooled, the molecules adopt an ordered double-helical shape and associate with each other through weak interactions such as hydrogen bonds and van der Waals forces [32]. Gellan gum has two forms: high acyl (HA) and low acyl (LA) [97], which produce soft and hard gels in return. This material is capable of retaining water and then gradually releasing it and, in return, absorbing the undesired contaminations within itself. So, it can be a useful choice in the conservation of paperwork [6].

The basic principle of paper cleaning by gellan gum hydrogels is the controlled release of water from gel to paper and the ability of gellan gum to absorb the surface deposits and contaminants responsible for the acidic degradation of paper. The cleaning by gellan gum hydrogels is based on the trapping and removal of the contaminating organic material (including hyphae and spores) by the gel's three-dimensional network. They are stable in a wide pH range and can be prepared with different degrees of viscosity (soft and rigid gels) [21].

Khaksar-Baghan et al. [6] said that gellan gum gel is typically clear, homogeneous, and stable in response to pH variations. This property reduces its thermo-reversibility. The pH stability of gelatin gum renders it appropriate for application on paper samples exhibiting diverse acidity or alkalinity levels. Gellan gum, like agar gel, creates a firm gel that can absorb acidic and basic solutions after preparation. It is most effective when applied warm. The gel formation is affected by factors like temperature, concentration, thickness of the layer, pH, and the presence of cations [17].

Chelazzi et al. [12] noted that agar and gellan are commonly prepared as rigid sheets, exhibiting strong gel network properties. These gels can be removed from surfaces with minimal or no polymer residues. Compared to agar, gellan gum is slightly heat reversible, and thus conservators cannot reuse the film or any excess gel that has been prepared [9].

Surface dirt and dust can be effectively washed off samples using hydrogel gellan gum, according to research by Zidan et al. [36]. Additionally, they observed an improvement in the mechanical properties of the paper. Therefore, it can be safely utilized in conservation procedures for cellulosic support.

Micheli et al. [98] stated that the application and removal of gellan gum and calcium acetate are simple, allowing for a localized cleaning operation (**Figure 5**). Due to its stiff and non-sticky nature, it can be peeled from residues in one piece, minimizing leftover residues.

Severini et al. [97] chemically modified the natural polysaccharide gellan gum by adding methacrylic groups to create methacrylate gellan gum (GGMA). The GGMA hydrogel effectively removed naturally aged linseed oil derived from Whatman paper and aged rubber-based pressure-sensitive adhesive tape sourced from contemporary notebook paper.

Casoli et al. [25] compared washing by immersion in free deionized water and using the Gellan gum application for removing organic acids, metals, and harmful degradation products from paper, and he showed that the application of Gellan gum seems to be more respectful of the original 'status' of the handmade paper, limiting gelatine removal and so allowing a less invasive cleaning treatment compared to traditional methods based on the use of free liquid water.

De Filpo et al. [29] also used pure gellan gum hydrogels on paper samples contaminated by Aspergillus. In particular, the results showed that the treatment with pure gellan gum hydrogels ensures the cleaning of paper supports due to the 'gelled water content' of these materials.

So that we can say that gellan hydrogels are useful in cultural heritage conservation, cleaning, and diagnostics since there is no possibility of harming an artwork with liquid treatment. They are easy to prepare, and in addition to that, they can be designed to target certain compounds, which makes this kind of biosensor suitable for cleaning monitoring. Thus, more research needs to be done to improve the effectiveness of using paper artwork restoration techniques and get the best outcome [36]

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Fig. 5. Application of Gellan gel on paper artwork [98].

2.2.1.3. Xanthan gum

Xanthan gum is a heteropolysaccharide produced by strains of Xanthomonas spp. [87, 99]. Xanthan gels produced by dissolution at ambient temperature exhibit significant viscosity. The double helix structure is preserved at neutral pH levels. Xanthan gels demonstrate significant viscosity across a broad pH spectrum (between 4 and 10) [32].

Xanthan gum produces highly viscous solutions even at low concentrations because of its high molecular weight and structural configuration. Xanthan gum has two conformations: an ordered conformation (helix) and a disordered one (random coil). This double conformation does not allow for a peelable gel, like agar or gellan gum gels, to be obtained, but only a viscous gel: a weak physical gel. The properties of xanthan gum vary with its concentration, pH, and temperature. However, it is possible to form a viscous gel in a wide range of pH at room temperature [17].

Xanthan gum gels are commonly used to remove corrosion products, but they tend to leave a significant amount of residue on the surface. Viscous gels, like xanthan gum, adhere well to the object's surface and can be used with various active agents [32]. Kanth et al. [100] suggested that xanthan gels must be optimized for cleaning delicate surfaces.

2.2.1.4. Alginate

Alginate is a linear polysaccharide derived from brown algae. The structure comprises copolymers formed from β-D-mannuronic acid and α-L-guluronic acid units, interconnected through 1,4 glycosidic bonds. Alginates containing univalent metals are highly water soluble. Upon dissolving in water, alginates yield a viscous and adhesive solution. Water-soluble complete alginate comprises various cations, like magnesium, sodium, potassium, and ammonium ions. Calcium alginate exhibits insolubility in water, whereas sodium alginate (Na Alg) demonstrates solubility [82, 99, 101, 102]. It has been used in cell cultures due to its flexible gelation rate, low toxicity, biocompatibility, and affordability [82, 103].

Polysaccharides like gellan gum, agarose, and alginate form an ice-like structure in water due to hydrogen bonding between polymer and water molecules, even at concentrations of 0.1% - 1.0% (W/V) at room temperature, leading to gelation [93]. Lee et al. [104] studied alginate, a natural polysaccharide crosslinked with differe[illegible] agents and laden with a biodegradable surfactant for optimal cleaning conditions. Calcium alginate (CA) showed high solvent retention and surface contact, effectively cleaning various surfaces. CA gel is biocompatible and can retain solvent within its network, preventing excessive spreading and offering a cost-effective solution for cultural heritage conservation. Sodium alginate has been used to clean and consolidate archaeological materials like wood, textiles, bone, and leather. Abdel-Maksoud et al. [103] used sodium alginate to consolidate bone artifacts. Meanwhile, Lee et al. [104] applied sodium alginate hydrogel on wood surfaces to remove soil and sweat, demonstrating its efficiency in artifact cleaning.

2.2.1.5. Konjac glucomannan

Konjac glucomannan (KGM) is a water-soluble neutral polysaccharide obtained from konjac tubers [105]. KGM consists of β-1,4-linked α-mannose and α-glucose arranged randomly. It features a low degree of acetyl groups and a significant number of hydroxyl functional groups along the molecular chain. These structural characteristics give it excellent gelling properties. [106-107]. The acetyl group contributes to the water solubility of glucomannan, whereas unsubstituted β-1,4-linked glucomannan remains insoluble in water. KGM is deacetylated using an alkali treatment to obtain an aqueous KGM gel, which is thermally stable. KGM can produce combined hydrogels with other polysaccharides, including κ-carrageenan, xanthan gum, and gellan gum [107]. KGM is a natural product that forms hydrogels that exhibit excellent features of film-forming, gelling, and thickening properties [108].

The formation of KGM gels occurs when heating a solution of KGM in the presence of alkaline chemicals or a high concentration of a neutral salt. The alteration in the molecular constitution is due to the action of the acidic constituents of KGB with the alkalis to produce gelation. This also allows the chains of the KGM to enter hydrogen bonds and hydrophobic interactions and form a network gel structure [109]. Lee et al. [31] said that KGM was a soft gel with a high level of solvent and could be useful for cleaning rough and irregular surfaces. The gel can maintain the solvent in its structure, thus limiting excessive spread on the substrates. This makes it a cost-effective and practical way of undertaking cultural heritage conservation.

In the experiment conducted by Lee et al. [104], KGM hydrogel was utilized to clean the surface of dispersed soil to understand its efficiency in artifact cleaning.

2.2.2. Synthetic Polymer-Based Hydrogels for cleaning paper manuscripts

Synthetic polymers, known as human-made polymers, are made through several approaches, including crystallization, grafted copolymerization, ionic interaction, amphiphilic block protein interaction, and hydrogen bonding. Synthetic polymer gels are used in several areas of materials science and engineering due to their tunable nature of degradation and mechanical characteristics. Some of the most common synthetic gels are polyacrylamide gels, poly (vinyl alcohol), poly (ethylene glycol), poly (methyl methacrylate), poly (hydroxyethyl methacrylate), poly (amino acids), polyurethanes, and poly (vinyl pyrrolidone). These are artificial gels made to mimic natural biopolymers, and the synthetic gels serve specific purposes for intended uses [6, 110]. One of the benefits of hydrogels produced from synthetic polymers is the ability to regulate their chemical content and the mechanical characteristics of the material [16]. The blending of the synthetic polymers leads to the synthesis of hybrid hydrogels that are functionalized polymers with specific properties that enable harnessing the advantages of both types of polymers, like biodegradability, precise control of rigidity and viscosity, and high strength [111].

2.2.2.4. Polyacrylamide

A polyacrylamide is an artificial product formed from an acrylamide monomer. When it is a cross-linked network, it has high water absorptive capacity, forming a soft, gel-like structure. Frequently, polyacrylamide hydrogels are synthesized via the polymerization of acrylamide with another multifunctional cross-linking agent, often N, N'-methylene-diacylamine [101, 112, 113]. Casini et al. [10] noted that many compounds have been tried for art cleaning using the synthetic polymer hydrogel networks that include hydrogels of p(HEMA), PVP, polyacrylamide, and PVA. Polyacrylamide nanogel was used by Sennakesavan et al. [111] for cleaning artworks, and the authors opined that due to the heterogeneity between the structure of polyacrylamide and water, microemulsion easily penetrates through the gel. At its basic level, the microemulsion droplets dissolve the substance that has to be removed. Liang et al. [33] stated that if exfoliated sodium montmorillonite is added to the polyacrylamide hydrogels, it enhances the strength of the hydrogels because of strong bonding interaction. In addition, reducing graphene oxide and incorporating it into hydrogel could enhance the hydrogel's electrical conductivity. For hydrogels applied in the electrochemical cleaning of paper artwork, large mechanical strength and electrical conductivity are required to avoid leaving residues on the surface of paper and to enhance electron transfer at the electrode for effective electrochemical reactions.

2.2.2.5. Polyvinyl alcohol

Polyvinyl alcohol PVA is a water-soluble, biocompatible, and biodegradable polymer. PVA can form physical or chemical gels by a combination of different cross-linkers by hydrogen bonding to hydroxyl groups. For aqueous PVA solutions, ions of boron form viscous and thermoreversible systems due to cross-linking between and in PVA chains and ions [9, 113]. PVA hydrogels have been used in cleaning and are especially ideal for cleaning paper since they are biocompatible. These gels are not dangerous to restorers, which is why they're used in biomedicine [11].

Casini et al. [10] highlighted PVA as a promising candidate for gel networks, since it was affordable, toxicity-free, and water-soluble. Physical gel networks of desired structure can be made directly without cross-linkers and additives by freeze-thawing PVA water solutions.

Meng et al. [113] demonstrated cross-linking these transparent, biocompatible, and stable chemical hydrogels using novel PVA. These hydrogels effectively remove degradation by-products that cause paper yellowing, leaving no residue upon removal. They maintain the paper's flexibility and fiber integrity. However, only hydrogels with appropriate rigidity ensure complete removal without leaving residues.

Salim et al. [114] used PVA gel to clean wax stains from ancient paper. When loaded with polar solvents or water, PVA can be loaded with water or polar solvents, applied to artworks (e.g., to remove yellow varnishes), and removed from the surface in a single step. Films of PVA can be cast from polymer dispersions (for instance, loaded with chelators) directly on the surface of metallic artifacts; then, the films are peeled off the surface, selectively removing corrosion patinas. Organogels. The films can then be scraped away from the surface for selective elimination of corrosion patinas [32].

Ortega Saez et al. [56] utilized PVAc-borax gels to remove soot stains from prints made with silver gelatine baryta. PVAc-borate, or poly (vinyl alcohol)-borax (xPVOH-borax), is a polymeric gel system where polymer chains and borate ions, such as poly (vinyl alcohol) (PVOH) or poly (vinyl acetate), form reversible chemical crosslinks [115].

2.2.2.6. Poly (hydroxyethyl methyl acrylate)

Poly (2-hydroxyethyl methacrylate), or pHEMA, is a biocompatible, hydrophilic, optically transparent, and non-degradable polymer. Its significant load-bearing capacity is attributable to its resistance to crack propagation [116, 117].

Chelazzi et al. [12] noted that pHEMA hydrogels were initially developed and characterized for biological applications by Wichterle and Lim. These hydrogels have a high-water content, a rubbery and soft consistency, and little interfacial tension, making them like living tissue in terms of physical properties. As a result, they have been utilized for use as biomaterials in synthetic prostheses, contact lenses, corneal replacements, artificial skin, and drug delivery systems.

A lot of comonomers can be loaded into the pHEMA network to improve their physical, chemical, and mechanical properties. For example, modifying the levels of N-vinyl-1-pyrrolidone can raise the water content, modify porosity, and improve optical transparency [10]. Chemical hydrogels utilizing semi-interpenetrating networks of PVP and pHEMA have been suggested for artifact-cleaning applications. These hydrogels integrate the hydrophilic properties of PVP with the mechanical strength of pHEMA. Aqueous formulations and certain polar solvents, including methanol, benzyl alcohol, and ethanol, are primarily used for loading. The pHEMA/PVP gels have been effectively utilized in various case studies to remove soil, adhesives, aged varnishes, and overpainting, such as vandalism, from the surfaces of sensitive artifacts [80, 116].

Casini et al. [10] said that pHEMA/PVP hydrogels consist of a pHEMA network that imparts an interpenetrated polymer and mechanical strength and PVP, which improves porosity and hydrophilicity. The researchers showed that these hydrogels were more mechanically robust, more retentive, and safer than gellan gel when used on paper artworks. Also, enzymes have been loaded into hydrogels to facilitate the removal of cellulose degradation products and adhesives.

Mazzuca et al. [26] focused on the importance of hydrogels, especially semi-IPN p(HEMA)PVP hydrogels, as effective tools for cleaning paper manuscripts. These hydrogels have high absorbency and clean deteriorated and fragile paper manuscripts with high efficiency. They also have a stiff-like behavior, can be easily bent to ensure uniform contact with the paper, and don't leave any residue during cleaning. In addition, they are reusable and release less water onto the paper surface than gellan, making them suitable for water-sensitive and damaged artwork. Du et al. [14] used a robust poly (vinyl alcohol)/poly(N-(2-hydroxyethyl) acrylamide) PVA/PHEAA hydrogel to clean paper in their study. This hydrogel was synthesized using a simple method, as shown in **Figure 6.** During photo-crystallization and self-assembly, HEAA monomer self-crosslinking occurs without the use of chemical crosslinking agents in the presence of large PVA molecules. The overall analysis indicated that PVA/PHEAA hydrogels contain a denser network with a lesser amount of water released and lesser adhesion on paper. These hydrogels also have a favorable elastic modulus, which enables the hydrogels to embrace the uneven surface of the paper to clean it properly.

Dominguez et al. [118] observed that semi-IPN p(HEMA)/PVP hydrogels are transparent and smooth for the conservation of artifacts. Due to its transparency, it is easy to monitor the material during the cleaning process, while the smoothness of the material allows it to adhere well to various surfaces. Also, these hydrogels can support such other loads as other aqueous systems and even pure solvents and remain transparent.

Fig. 6. Schematic illustration of the main synthesis procedure of the PVA/PHEAA gel [14].

2.2.2.7. Poly(methacrylate)

Polymethyl methacrylate (PMMA) is a highly resistant polymer and is used in different technologies such as aesthetics and medical applications. Organogels from PMMA can be synthesized in organic solvents through the copolymerization of diacrylate monomers with methyl methacrylate (MMA). Its hydrophobicity makes it effective in water-repellent activities [12]. Polymeric organogel derived from PMMA networks has been successful in eliminating unwanted chemicals from paper manuscripts [116]. Casini et al. [10] revealed that PMMA gels loaded with methyl ethyl ketone have improved retention properties when applied on the surface of the paper. A gel was used for removing wax stains from 19th-century manuscripts while preserving the sensitive parts. The controlled evacuation of solvents avoided damage to the artifact. The PMMA-MEK approach allowed for a safer and more progressive solvent release, removing wax contamination and slow swelling. After cleaning, the gel removed stains without leaving any residue [2].

In the early twentieth century, Baglioni et al. [84] applied a PMMA gel infused with ethyl acetate to a canvas. After five minutes, the gel was removed, leaving a softened and swollen layer of varnish that could easily be wiped off with a cotton swab. The varnish also partially dissolved and was absorbed into the gel, causing the gel to turn yellow. This method allows for the precise swelling and softening of various natural and synthetic coatings. The coatings either dissolve and migrate into the gel or become swollen and softened, after which they are gently removed through light mechanical action.

Conclusions

Stains commonly appear on paper manuscripts and affect the paper by making it discolored and distorted. They also cause damage, such as high acidity from rust and biological stains. Therefore, in the process of cleaning methods that will inhibit the destruction of paper, it is essential to obtain more information on the stains and chemical properties. Efforts to conserve paper artwork should focus on identifying the right restoration methods, as this helps avoid liquid treatments that could damage the artwork and allows for better monitoring of the cleaning process. Hydrogels have advantages like control of the rate at which solvents and solutions flow, reduced exposure to toxic substances, and their popularity with art restorers. Strong hydrogels are more suitable for preventive and effective cleaning of paper artwork compared to soft hydrogels because of their denser network structure and suitable elastic modulus. We must avoid the hot application of peelable gels on paper manuscripts, as they can cause significant surface loss during removal. Gel residue and its long-term effects on artifact surfaces should be evaluated. In some cases, integrated gels and nanofluids may be necessary for effective conservation. These tools offer advantages such as minimal residue and nano-mesh size of gels, providing a new generation of cleaning tools to address the limitations of traditional cleaning techniques.

Therefore, the future of this research is to expand the application of these hydrogel-based systems in cleaning a wide range of stains on ancient paper manuscripts. Additionally, the long-term effects of these hydrogels on the surfaces of the artifacts should be investigated if complete elimination is not possible. Integrating hydrogels with nanotechnology or materials science has the potential to lead to more efficient and targeted cleaning and conservation methods. Moreover, the discovery of new synthetic and natural polymers can broaden the range of hydrogels available for use in the field. The objective is to capitalize on the unique properties of nanohydrogels—such as solvent release control, selective cleaning, and reducing conservators' exposure to harmful solvents—to offer a safe and efficient cleaning solution for various types of stains and impurities.

Further research should focus on improving hydrogel formulations while ensuring their compatibility with different surfaces.

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