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Different low-cost materials to prevent the alteration induced by formic acid on unstable glasses

Rodrigo Arévalo¹, Jadra Mosa², Mario Aparicio² and Teresa Palomar^{2*} 

Abstract

The most frequent cause of glass degradation is environmental moisture, which is adsorbed on its surface forming a hydration layer that induces the rupture of the glass network. This pathology is accelerated by the accumulation of volatile organic compounds (VOCs), like formic acid. Although there is extensive knowledge about their impact, concentrations inside display cases are difficult to reduce efficiently. This study presents the assessment of different materials to reduce the concentration of formic acid to mitigate the degradation produced in unstable glasses. With this objective, copper threads, steel wool, silica gel, and activated carbon were chosen as low-cost materials with good adsorption or reactivity to the VOCs, exposing them in desiccators to an environment of 100% RH and 10 ppm of formic acid. Given that silica gel obtained the best results, its optimization as a sorbent material was evaluated by maintaining, regenerating, or renewing it when exposed next to the same glass. The tests carried out concluded that the hygroscopic capacity of the glasses exposed with silica gel decreased and, therefore, a lower degradation is observed on its surface. In addition, regenerating and renewing weekly the silica gel improved the results.

Keywords: Glass, Alteration, Museum, Showcases, VOCs, Formic acid

Introduction

Works of art exhibited in museums are affected by environmental factors such as light, temperature, humidity, and pollutants. Pollution in museums comes from two sources. On the one hand, the air from outside, which usually brings dust and inorganic particles [1]. On the other hand, the internal sources, which correspond to the materials used in the showcases such as wood, sealants, textiles, and varnishes that emanate organic compounds. These compounds are the main source of organic acid contamination, being the most common the acetic and formic acids [1–3]. For this reason, currently there is interest in monitoring and preventing the pollution in

showcases and museum galleries, and in analyzing the effects of pollutants on cultural objects.

The concentration of organic acids in museum galleries is usually low presenting little risk of damaging objects. Room ventilation volumes and rates are usually sufficient to dilute the acid concentration to low levels [4]. However, the situation is very different within the display cases used to protect objects. The volume/surface emissive ratio and the ventilation rate in display cabinets are much lower than in the rooms. This tightness favors the accumulation of the volatile organic compounds (VOCs) released, which leads to the accumulation of these species in higher concentrations inside the cabinets than in rooms [4–6]. Although the amounts of VOCs released by these materials are low, closed spaces can reach relatively high concentrations [2]. Additionally, the ventilation of rooms maintains a low concentration of VOCs in comparison with sealed showcases. Some of the most common VOCs are acetic and formic acids. Natural reference

*Correspondence: t.palomar@csic.es

² Instituto de Cerámica y Vidrio (ICV-CSIC), c/ Kelsen 5, Campus de Cantoblanco, 28049 Madrid, Spain

Full list of author information is available at the end of the article

values for formic acid in urban areas are between 0.1 and 32 $\mu\text{g}/\text{m}^3$. However, inside the showcases they are usually between 10 and 38 $\mu\text{g}/\text{m}^3$, being considered high to be between 38 and 230 $\mu\text{g}/\text{m}^3$ and extremely high between 290 and 860 $\mu\text{g}/\text{m}^3$ [7]. Similarly, acetic acid normal values in urban areas are between 0.3–40 $\mu\text{g}/\text{m}^3$; while inside the showcases it is between 100–697 $\mu\text{g}/\text{m}^3$, being considered high in 498–1195 and extremely high in 1494–2490 $\mu\text{g}/\text{m}^3$ [7]. The concentration values of hundreds of $\mu\text{g}/\text{m}^3$ of formic acid and acetic acid are frequent, reaching concentrations of $> 1000 \mu\text{g}/\text{m}^3$ inside the display cases in extraordinary situations [2, 4].

There are multiple factors that can act as source of indoor pollution such as the ventilation, the heating and air conditioning systems, the exchange of indoor/outdoor air, the impact of visitors and, above all, the indoor pollutants of the materials used in the lining or construction of the showcases [4, 6, 8]. The movement of air masses favors the decrease of VOCs' concentration inside the museum. Nevertheless, it must be considered that heritage objects themselves can be also an internal source of VOCs [9, 10].

Several studies identify wooden furniture or derivatives as the main source of acetic and formic acids [1, 5, 8]. Wood components degrade under the influence of light, humidity, oxygen or high temperatures creating volatile compounds such as aldehydes (formaldehyde) and organic acids (acetic acid and formic acid) [1]. However, these high emissions can also be detected in modern and new enclosures, which are mainly constructed from low-emission materials such as metal and glass [5]. This is due to the fact that acetic and formic acids can also be emitted by lacquers, varnishes, paints, adhesives, sealants (polyurethane foams), and derivatives of the degradation of cellulose acetate [1, 8]. Likewise, these VOCs can be adsorbed by other materials from the boxes and be released slowly in time. In this way, they continue their action on the exhibited objects, even though they have eliminated the source of contamination [1]. On the other hand, historical furniture can be an integral part of a museum, being also a source of VOCs [5].

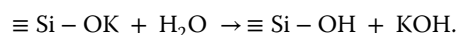
There are many pollutants that can affect museum objects, but there are also many methods and techniques to control the presence and concentration of harmful particles and gases [1]. Some display cabinets may be equipped with technical devices for active air circulation or for purging with inert gas. However, due to financial reasons, most enclosures are passive systems, as the costs of current solutions can be a problem [5]. These facts confirm that, although there is extensive knowledge about the impact of pollutants on the cultural property, concentrations within display cases have been difficult to reduce efficiently so far. For this reason, despite the importance of a correct choice of construction materials,

it is necessary to treat the interior environment with sorbent materials capable of reducing the concentrations of the pollutants emitted and, in this way, avoiding the degradation of the exhibited objects.

Currently, a wide range of different adsorbents is commercially available, ranging from activated carbons and zeolites to molecular sieves [2, 11, 12]. The use of these sorbent materials can represent a cost-effective approach to minimize the damage caused by air pollutants in museum display cabinets. To identify VOCs and determine their concentrations, different devices based on active or passive sampling can be used. Active sampling uses the absorption of contaminated air in a tube, with the help of a pump. The gases accumulate in a sorbent material to later desorb and analyze them. In passive mode, a layer of sorbent is simply placed near the materials to be protected. This diffusive sampling works by allowing gas or vapor molecules to diffuse through a defined volume of still air until they reach a sorbent bed [13]. Examples of adsorbents are silica gel or activated carbon. Another way to remove contaminants from an environment is using sacrificial materials. Gases react with them forming solid stable compounds on the material surface. The periodical substitution of these materials induces the decrease of the contaminant concentration. In this group appears metals or salts such as carbonates.

As previously mentioned, different cultural materials can be affected by VOCs, including glasses. Its degradation is mainly affected by its chemical composition and by the environment in which it is exposed [14, 15]. Damage can appear immediately after obtaining the glass, due to its exposure to adverse conditions, or as a consequence of the passage of the centuries. Among them, it is worth highlighting crizzling, which is a degradation pathology that causes a network of fissures on the surface, resulting in a loss of transparency.

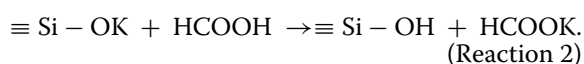
The most frequent cause of glass degradation in the atmospheric environment is environmental humidity, which is adsorbed on the surface forming a thin film of water [6, 14, 16]. Water induces the ion exchange of alkaline cations (Reaction 1), which are easy to extract due to their strong lattice distortion. This exchange results in their migration from the internal network to the surface, generating an increasingly basic solution due to the accumulation of OH^- groups [3, 14, 17, 18].



(Reaction 1)

The degradation rate in glass objects generated by environmental humidity is increased when they are also exposed to environments contaminated with organic acids [15]. Wooden objects used for storage in display cabinets are considered the main source of VOCs

in museums, emitting aldehydes (formaldehyde) and organic acids (acetic acid and formic acid) [1]. The production of formic acid is linked to the division of pyruvic acid during the metabolic processes of wood [2, 3]. The corrosion process begins with dissolution of formic acid in the gas phase on the surface aqueous film. This is followed by the dissociation of formic acid, which increases the concentration of protons, thus accelerating the ion exchange process and, consequently, the leaching of metal ions from the glass (Reaction 2) [15, 19]. Therefore, the alteration of glass exposed to a humid and acidic atmosphere is faster than in an uncontaminated humid atmosphere [3, 4, 14, 15, 18]. The Cannizzaro reaction can also form formate species on the glass surface as result of the reaction of formaldehyde in the alkaline surface films on glass [20, 21].



Previous studies of air pollutants in museums showed a clear positive correlation between temperature and relative humidity and the presence of acetic and formic acid [10, 17, 18]. At higher temperatures, the emission rate of VOCs increases [9]. Regarding relative humidity, the emission of acetic acid vapors increased by a factor of 2 to 3 as the humidity of the environment increased from 54 to 100% [3]. Therefore, controlling the factors that increase the emission of acids allows to reduce the damage they generate [4].

In the presence of acidic organic contaminants, anhydrous sodium formate is the predominant precipitate found on the glass surface. Likewise, it must be considered that the alkaline hydroxide film generated on the surface can be carbonated by the action of carbon dioxide in the atmosphere. In the same way, calcium hydroxide is also generated, which also evolves towards its carbonate form [16]. In addition, other air pollutants such as SO_2 and NO_x , which would give rise to sulphates and nitrates, must be considered. The deposits formed accumulate, giving rise to opaque crusts [17, 18, 22].

The main objective of this work is to evaluate how the properties of sorbent materials allow to reduce the concentration of formic acid and mitigate the degradation produced in heritage objects, specifically in unstable glasses. Formic acid was chosen because previous studies have detected high contents of formic acid in museographic collections and point to the formic acid as a relevant alteration agent for glasses [1–3, 6]. Additionally, in previous experiments, it has been probed that the formic acid increases more the degradation rate in unstable glasses in comparison to the acetic acid or formaldehyde [23]. To control the acid environment, low-cost materials susceptible of reaction or adsorption of formic acid were

selected. For that purpose, passive catchment tests and the subsequent characterization of the materials used will be carried out. Then, the performance of the material with the best capture capacity will be evaluated by studying the degradation produced in a soda glass. With this study, we aim to initiate further research to finally obtain feasible solutions and real application in museums.

Materials and methods

This work is divided into two studies. The first one is focused on the selection of the most adequate low-cost material to remove formic acid. The second study was the assessment of the protective capacity of the sorbent with an unstable soda glass.

Selection of sorbents

Four low-cost materials were selected to evaluate the reduction of the concentration of atmospheric formic acid. The materials tested were activated carbon, silica gel, copper, and steel. Two of them (carbon and silica) are general sorbents; however, metals are materials that react specifically with the formic acid.

Activated carbon

Activated carbon is the most common sorbent due to its availability, low cost, and good efficiency. Previous studies consider it the most effective material to reduce air pollution generated outdoors and organic acids in showcases [4, 10, 12, 13]. Grosjean et al. studied how in all the tests in a passive way, 20 g of activated carbon removed pollutants from the air by passive diffusion at a rate that exceeded by a factor of 10 the loss of pollutants on the walls of the showcase [24]. On the other hand, Schieweck observed that both under active and passive conditions, pure and impregnated activated carbons showed good adsorption efficiency for formaldehyde, formic acid, and acetic acid [5].

Activated carbon corresponds to porous carbon in which microporosity has been enhanced through activation, usually through steam oxidation [13]. The carbon is injected into a stream of hot air to create activated carbon [5]. The stream of hot air creates a large number of small pores that increase the surface area [12]. It is characterized by having a fine porous structure, a high specific surface area between 300 and 2000 m^2/g and a density between 200 and 600 kg/m^3 [4, 5]. In addition, its adsorption capacity varies depending on the diameter of its pores, distinguishing between micropores (< 1 nm), mesopores (1–25 nm) and macropores (> 25 nm) [4]. This material is capable of reducing polluting gases by physical adsorption on the inner surface. This mechanism is generally based on relatively weak intermolecular forces, such as van der Waals interactions. Organic compounds

with a molecular weight greater than 45 g/mol are considered good adsorbates on activated carbon [5]. The water capacity of the coals in this region is close to 30% of their dry mass. This water can displace adsorbed organic molecules [13].

Nutshell carbons are particularly useful for this purpose, as they have a very suitable original porosity for activation [13]. However, a drawback of using plant materials is the existence of residual content of inorganic ash [13]. Activated carbon is available in powder, granule, foam, or fabric form. From a practical point of view, activated carbon fabric is better to install than foam, which is better to install than granulate [4]. Carbon foams are easy to cut to size; however, they tend to lose some of the carbon, leaving numerous black spots [4].

Silica gel

Silica gel is used primarily for two functions, to maintain a stable relative humidity or as a desiccant to dehumidify the air [12]. Since this material absorbs moisture from indoor air, the impact on relative humidity should be considered when using it as passive adsorbent for organic acids. Previous studies consider that silica gel does not eliminate some air pollutants generated outside but that it can be a good option to control humidity while it is used in combination with another specific sorbent [5, 12]. Another possibility to consider is that since silica gel strongly adsorbs water vapor, previously adsorbed organic molecules can be displaced [13].

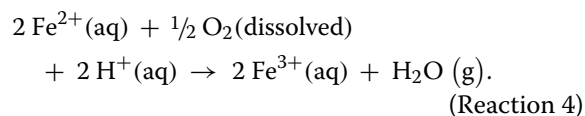
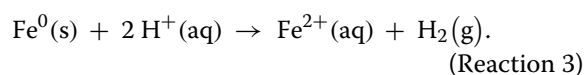
Metals

Metal objects are also susceptible to organic acid attack just like glass. Corrosion caused by the vapors of these acids on different metals and alloys has been studied for years [25–28]. Taking this into account, metals could be used as sorbents when acting as sacrificial material. Lead is the most cited metal in terms of degradation; however, it is not chosen due to its toxicity since the sorbent materials studied are intended to have real applicability in museums. Bronze, iron, and copper are other materials that can be used as possible sorbents, due to the degradation they present when exposed to organic acids [3].

There are numerous studies on the degradation of copper due to its exposure to organic acids, since they are able to cause metal corrosion even at very low concentrations of acid vapor [28, 29]. López-Delgado et al. studied the corrosion it presents when exposed to both formic and acetic acid and a relative humidity of 100% [29]. Tetreault et al. also studied the formation of copper corrosion products in the presence of formic acid, obtaining that at levels above 4 ppm copper increases in weight at both 54% and 75% RH [28]. An increase in the concentration of formic acid results in

a strong effect on copper corrosion. At 8 ppm of formic acid, the copper samples are covered by a thin layer of an opaque green to gray matte film [28]. At a concentration of 10 ppm, the components of the patina are mainly cuprite (Cu_2O), hydroxide of copper ($\text{Cu}(\text{OH})_2$), and copper formate ($\text{Cu}(\text{HCOO})_2$), although the latter appears as a small signal [25, 28]. Above 14 ppm, copper samples show whitish surface colors. The corrosion compounds found at 14 and 140 ppm were identified respectively as copper formate and copper formate dihydrate [28]. It is important to note that the higher the concentration of formic acid to which it is exposed, the more corrosion appears at lower relative humidity.

The other metal option that arises to study it as a sorbent material is steel wool [26, 27]. This material is composed of iron, which can react with organic acids to which it is exposed in the environment. Steel wool is made up of fibers that are often used for cleaning and polishing metal or wood surfaces. Steel wool is easily solubilized when reacting with dilute acid, forming ferrous ions when reacting with protons (Reaction 3). Furthermore, ferrous ions can be oxidized to ferric ions by dissolved oxygen (Reaction 4) [27]. Similarly, adsorption of formate ions on the iron surface may occur [26].



Preparation of sorbent materials

The copper was a 2491X tempered wires from the *RS* brand, used as an electrical material, with a cross-sectional area of 0.75 mm^2 and a filament of 0.2 mm. The 24 copper wires were separated to increase the specific surface area. The cables weighted 4.63 g. The steel wool used from the *Dexter* company corresponds to category 00, which has a very fine fiber size ($8.89\text{--}12.7 \mu\text{m}$) within the market range. To prepare it, the fibers were separated, as in the case of copper, and 4.64 g were weighed. Activated carbon, from the *Scharlau* brand (CAS: 7440-44-0), is used in powder with a heavy mass of 4.66 g and of “very pure” quality. Finally, the silica gel is from the *Labkem* brand (Ref: SGE0-002-1K0) and is granulated with a diameter size of 2–5 mm. To prepare it, it remained in the oven at 70°C for three days, just until the moment of introduction into the desiccator, obtaining a weight of 4.61 g. During the test, the Petri dish with renewed or regenerated silica gel was

maintained at 70 °C for 90 min in an oven before their substitution in the desiccator.

Glass preparation

The composition of the soda glass prepared is based on real nineteenth century soda glasses [14] but simplified to be more susceptible to the environment. The minor components were not considered to avoid interferences, and their percentage was added to the alkaline content. The fusion was made at 1600 °C for two hours in an alumina crucible in a Termolab electric furnace, followed by an annealing at 500 °C in a Carbolite furnace.

The glass obtained was later adapted for the accelerated aging tests. Slices and small glass blocks were cut and dried in an oven at 70 °C for 30 min to remove the water used in the process to lubricate the cutting disc. Subsequently, the slices were polished with the *Buehler* brand *MetaServ 3000* polisher. Polishing was carried out progressively with P320, P600 and P1200 sandpaper according to FEPA standards, which correspond to a grain size of 46.2, 25.8 and 15.3 µm respectively, using ethanol or ethanol-based lubricant to lubricate the sandpaper. Finally, it was finished with a diamond paste polishing with 3 µm and 1 µm particles. On the other hand, the small glass blocks were ground and sieved following the standard UNE 400322:1999 [30]. For this, two mortars and sieves with different sizes were used, thus obtaining fractions between 0–300 µm, 300–500 µm and greater than 500 µm, which were stored in Eppendorf tubes.

Accelerated aging tests and experimental set-up

The humid and acidic environment was recreated in different desiccators. The prepared environments had 100% RH and 10 ppm of formic acid. These values were chosen in order to increase the hygroscopicity of glass and, therefore, the alteration rate [15].

To generate the acidic atmospheres, 0.549 mL of formic acid was added to 600 mL of distilled water to obtain 10 ppm following the description of Bastidas et al. [31]. The different sorbents and materials were exposed during a period of 21 days, time in which the sorbents, sacrificial materials or glasses were reacted.

For the first test, the materials were deposited in Petri dishes inside the desiccators (Additional file 1: Fig. S1). In turn, the Petri dishes were supported on lower base supports to allow the formic acid and water vapors to rise more easily from the bottom of the desiccator.

For the second test, ~5.00 g of silica gel, a slice of the prepared glass embedded in resin, a porcelain weight boat with approximately 0.50 g of the glass fraction smaller than 300 µm and a thermohygrometer were introduced into each desiccator (Additional file 1: Fig. S1).

Characterization of the environment

The environments were monitored using thermohygrometers, and the adsorption capacity of the materials by ion exchange chromatography (IC).

The thermohygrometers, model *BL-1D* from the *Rotronic* company, were kept in the desiccators during the entire period of preparation and exposure to the environment. The thermohygrometers, with an accuracy of ±3.0% HR and ±0.3 °C, were programmed to record data every five minutes, obtaining the corresponding values for relative humidity and temperature.

The adsorption capacity for formic acid of the materials was evaluated by an indirect method by ion exchange chromatography. Samples of the solution from each desiccator (<2 mL) were taken on days 0, 3, 7, 10, 14, and 21. All chromatographic analyzes were performed at room temperature using the Metrohm Advanced Compac ion chromatographic instrument (861 IC) with conductivity detector (IC-819), liquid Handling Pump Unit (IC Pump 833), sample degasser (IC-837) and an 800 Dosino Dosing Device. Data acquisition, calibration curve construction and peak integration were carried out with a *Metrohm 761* data acquisition system interconnected to a computer running *MagIC Net 3.3* software. The identification and quantification of formate was carried out in a *Metrosep Organic Acids* column (250 × 4 mm, Ø 5 µm). The mobile phase is 0.5 mM sulfuric acid and 15% acetone, with a flow rate of 0.5 mL/min. The injection volume was 20 µL and the analysis time 30 min. The standard used was Supelco's Formate Standard for IC. The calibration curve was done between 15 and 500 µl with a correlation of 0.99.

The calculation of the decrease in formic acid was carried out using the Eq. (1).

$$\Delta \text{Concentration}(\%) = \frac{[\text{Formate Day } X] - [\text{Formate Day } 0]}{[\text{Formate Day } 0]} \times 100. \quad (1)$$

Characterization of materials

Sorbents and glass samples were characterized by X-ray fluorescence (XRF), surface area analysis, gravimetry, Fourier Transformed Infrared Spectroscopy in Attenuated Total Reflectance mode

(FTIR-ATR), Scanning Electron Microscopy with X-ray Energy Dispersive Spectroscopy (SEM-EDS), μ -Raman spectroscopy, and Optical Microscopy.

The exact composition of the glass was analyzed with a PANalytical MagicX (PW-2424) wavelength dispersed X-ray spectrometer equipped with a rhodium tube (SUPER SHARP) of 2.4 kW. The results were treated with the quantitative silicate analysis curve after analyzing the samples as pearl (fusion of 0.3000 g sample and 5.5 g of $\text{Li}_2\text{B}_4\text{O}_7$). The specific surface area was evaluated by the *Monosorb Surface Area Analyzer MS-13* equipment from the *Quantachrome* company. The samples are degassed for 2 h in a 70:30 He:N_2 gas stream at 150 °C. The measurement takes place by nitrogen adsorption at 77 K by the one-point Brunauer–Emmett–Teller (BET) method. The BET equation considers the van der Waals forces to be solely responsible for the adsorption process. From this method, the area of a solid can be determined by knowing the amount of adsorbed gas that is necessary for a monolayer to form and the area that an adsorbed molecule occupies. The specific surface area of each material is evaluated three times, obtaining the average result.

The hygroscopic capacity of each glass was determined by gravimetry in 0.5000 g of the glass fractions with $\varnothing < 300 \mu\text{m}$ using three porcelain weight boats for each glass. Before starting the test, the empty weight boats were stored for three days in their corresponding desiccator to ensure that they are hydrated. Every week, the weight boats were weighed. Likewise, a slice of each glass was inserted into the desiccators leaving the polished face exposed. After the period of exposure to the different environments (21 days), all the weight boats and slices were stored in a desiccator with silica gel ($\varnothing = 2\text{--}5 \text{ mm}$). The percentage of the increase in weight of the glass due to hydration with respect to the initial value was calculated using Eq. (2).

$$\Delta\text{weight}(\%) = \frac{\text{Weighing boat day } X - \text{Weighing boat day } 0}{\text{Weighing glass day } 0} \times 100. \quad (2)$$

In order to observe the changes on silica gel and glasses, Fourier transform infrared spectroscopy (FTIR-ATR) was performed. In each spectrum, eight scans were made with a sweep from 4000 to 400 cm^{-1} . The equipment used was the *PerkinElmer* brand *Spectrum 100 FT-IR Spectrometer*, together with a *PIKE Technologies* brand *GladiATR* Attenuated Total Reflectance accessory. This technique allows characterization through reflection or

absorption spectra in the infrared range of the electromagnetic spectrum. From the frequencies of the functional groups, the compounds that compose it can be identified. In addition, it is necessary to consider the advantage that it can be used for both inorganic and organic substances in solid, liquid or gaseous state.

The surface of copper, steel, and silica gel samples was observed and analyzed by scanning electron microscopy with X-ray energy dispersive spectroscopy (SEM-EDS), using the *Hitachi S-4700* equipment. This technique allows morphological and microanalytical characterization through electronic images and energy dispersion X-ray microanalysis. The interaction of the electron beam on the sample generates X-rays that reach the detector and allow obtaining microanalytical information, qualitative in this case. Prior to measurement, the samples were made conductive by sputtering with carbon. Likewise, the alteration products formed on copper and silica gel were characterized by Raman spectroscopy before and after the test. Raman spectra were recorded using a confocal Raman microscope integrated with atomic force microscopy (AFM) on an *ALPHA 300AR* microscope from *WITec*. This equipment allows combining the potential of an AFM microscope, being able to obtain images of up to 3 nm of lateral resolution, with the structural and compositional characterization of the materials at a submicron scale of confocal Raman spectroscopy. The microscope is equipped with a Nd:YAG laser. The spectra obtained were analyzed with the *WITec Control Plus* software. The acquisition time was 3.6 s for one single spectrum and the Raman image consists of 3000 spectra with a laser excitation of 532 nm and the incident laser power of 1 mW, using a tested area of $10 \mu\text{m} \times 10 \mu\text{m}$. The colors in the spectra correspond to different areas in the Raman image using a filter for $172\text{--}260 \text{ cm}^{-1}$.

The surface of the glass samples was observed by optical microscopy in a *Zeta Systems* brand optical profilometer model.

Table 1 Specific surface area results

Material	Specific surface area (m^2/g)
Copper	0.1
Steel	0.5
Silica gel	63.1
Activated carbon	788.8

Results and discussion

Selection of the best sorbent for formic acid

The first study was focused on the evaluation of the materials and their characterization to identify the best low-cost formic-acid sink.

Specific surface area

The specific surface area results showed the low values of metals (Table 1). Of all the materials, copper presented the smallest value with a specific surface area of $0.1 \text{ m}^2/\text{g}$, followed by steel with $0.5 \text{ m}^2/\text{g}$. On the other hand, the silica gel obtained a significantly higher value with $63.1 \text{ m}^2/\text{g}$. Finally, activated carbon presented the highest result, as expected, with $788.8 \text{ m}^2/\text{g}$ of specific surface area.

The best materials for the adsorption of formic acid and water from the environment would be silica gel and activated carbon. However, this does not mean that copper and steel were useless; rather other factors must be taken into consideration. For example, they have a minimum specific surface area but these materials acted as a

sacrifice material, degrading it before the exposed historical glass.

Environmental conditions

The environments were monitored with the thermohygrometers in order to identify how stable they are and how they evolve after the desiccator opening (Fig. 1a–e). The evolution of the humidity in each desiccator should be similar to the behaviour of the concentration of gaseous formic acid.

Figure 1 shows that in the case of steel, the relative humidity remained stable at 99.9% throughout the test, except for the second day. The temperature undergoes oscillations associated with changes between the day and night periods, in addition to those associated with the weather of each day. The representation associated with temperature coincides in all the figures, as expected. In the case of copper (Fig. 1b), the relative humidity does not remain stable. However, these oscillations do not exceed 2%, so it is not a significant variation. The minimums in

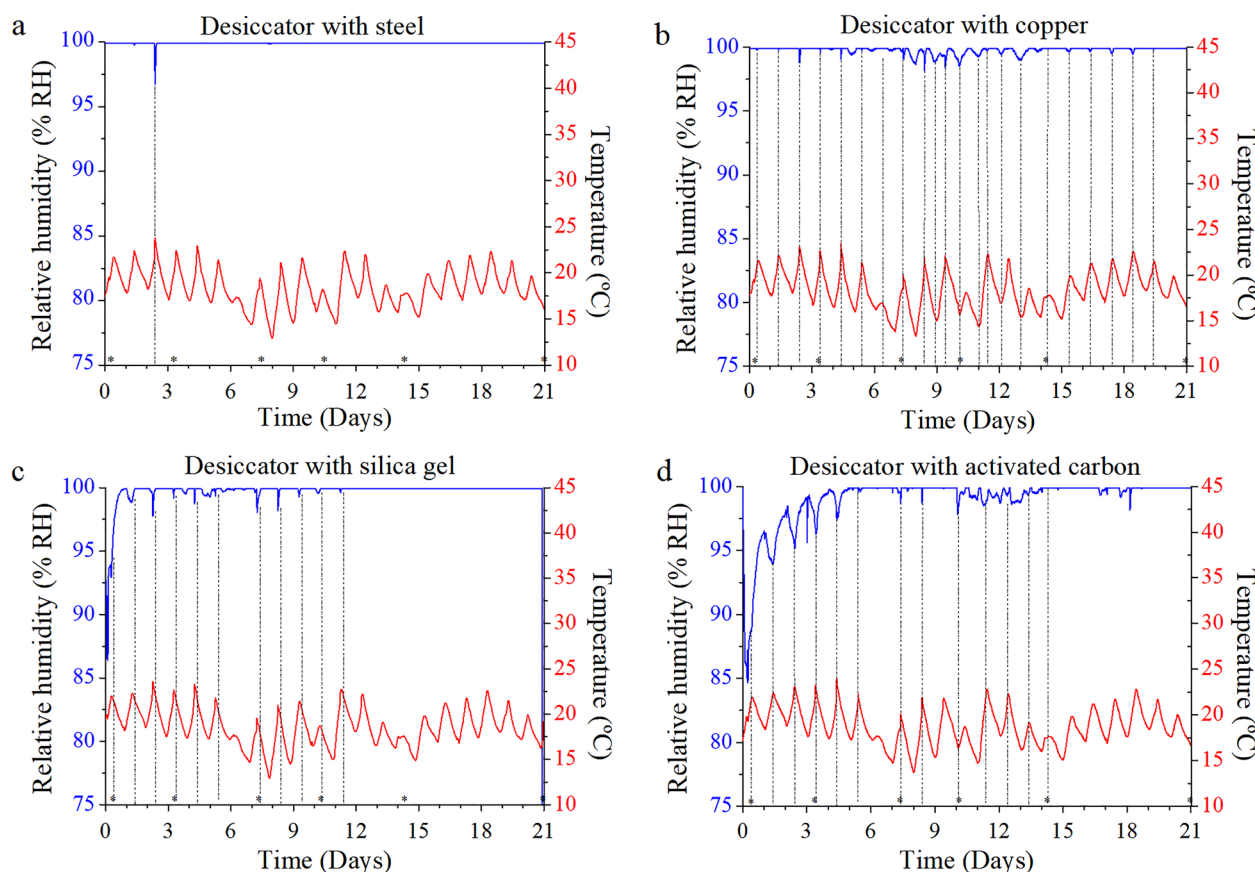


Fig. 1 Evolution of the environmental conditions inside the desiccators as a function of time for (a) steel, (b) copper, (c) silica gel and (d) activated carbon. The asterisks on the abscissa axes mark the moments when the desiccator was opened

relative humidity are mostly associated with temperature maximums. This is because the relative humidity is inversely proportional to temperature, as defined by the saturation pressure of water vapor.

Figure 1c, d, corresponding to silica gel and activated carbon, show relative stability during the test. The lowest values were detected in the first days of the test because the materials were sensible to the formic acid but also to the environmental humidity. From that moment on, the

activated carbon does not exceed 5% in its oscillations and silica gel does not even 2.5%.

None of the materials have been found to reduce relative humidity in a stable manner. Steel, copper, silica gel and activated carbon manage to keep the fluctuations in relative humidity within acceptable ranges.

Material's alteration

Scanning electron microscopy made it possible to observe the changes that occurred in the surface of copper wires, steel wool, and silica gel. As result of degradation, the copper wires were covered with degradation products (Fig. 2a, b). The Raman analyses of the degraded copper show the peaks at 151, 221 and 649 cm^{-1} (Fig. 2c) that corresponds to the active Raman bands of the copper oxide and low intensity bands of copper hydroxides that overlap with some of the formate ions. [32–34]. These results agree with the bibliography, according to which at a concentration of 10 ppm of formic acid the components of the patina are mainly cuprite (Cu_2O), copper

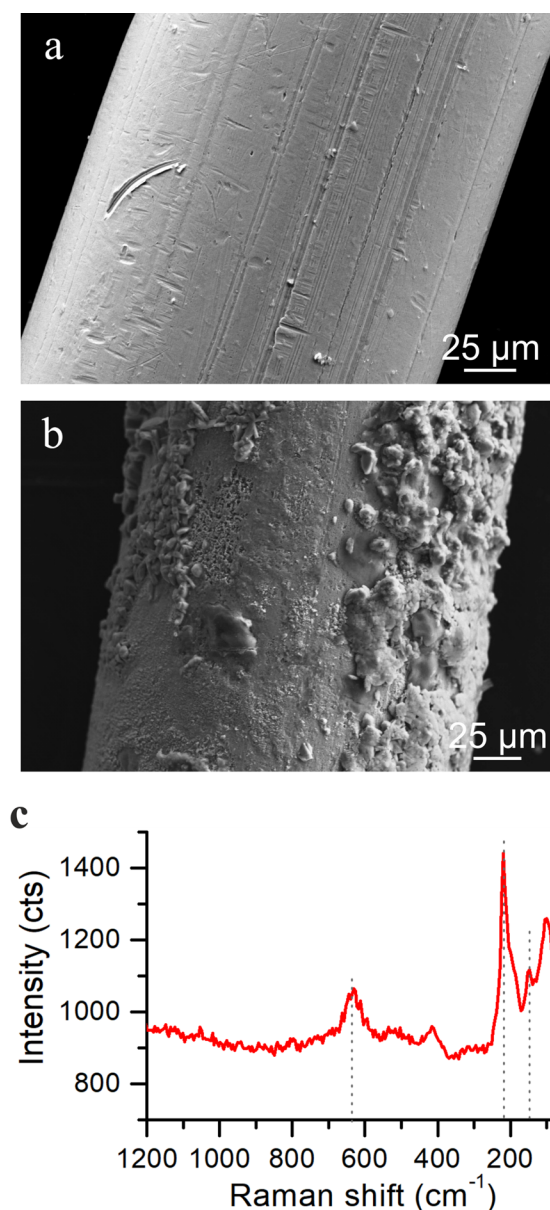


Fig. 2 SEM image of copper wire (a) without degradation and (b) degraded and (c) Raman analysis of the deposits

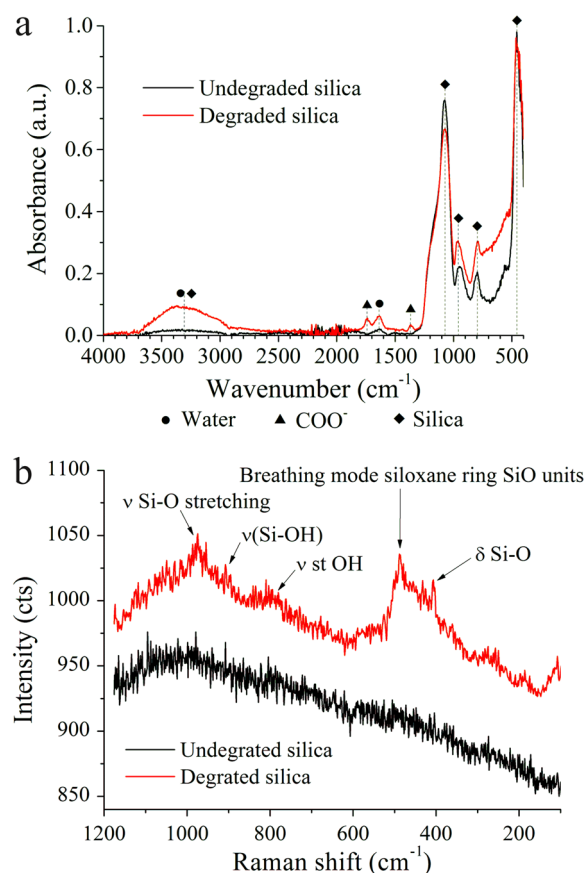


Fig. 3 a FTIR-ATR spectra and b Raman spectra of undegraded and degraded silica gel. The FTIR-ATR peaks identification is resumed in Additional file 1: Table S1

hydroxide ($\text{Cu}(\text{OH})_2$), and copper formate ($\text{Cu}(\text{HCOO})_2$), although the latter appears as a small signal [25, 28].

Regarding silica gel, the surface of the sphere is homogeneous except for some craters and cracks in which small deposits were observed (Additional file 1: Fig. S2). The silica gel was analyzed before and after the test by FTIR-ATR and Raman spectroscopy. Figure 3 a shows the FTIR-ATR spectra obtained. The degraded silica gel clearly presents the bands associated with water at 1640 and 3300 cm^{-1} , corresponding to the scissors bending of H–O–H and the stretching of O–H (Additional file 1: Table 1), respectively. Likewise, a signal associated with formate ions stands out at 1739 cm^{-1} , due to the asymmetric stretching of COO^- . Furthermore, the signal at 3300 cm^{-1} associated with the O–H stretching may be due to the formation of Si–OH groups. Similar results were observed by Raman spectroscopy on crushed spheres (Fig. 3b). Unaltered silica gel showed fluorescence but on degraded ones, new Raman bands assigned to the silica and the hydroxyls appeared [35–37].

Finally, there were no significant changes in steel and activated carbon before and after exposure to the acidic and humid environment. No formation of deposits or changes of color were detected on their surface (Additional file 1: Fig. S3).

Removal efficiency

The capacity to remove the environmental formic acid by the material is directly related to the concentration of ion formate in the solution. The acid in the vapor phase tends to dilute in the water adsorbed or to react with the metals, so the equilibrium is recovered with the dilution found in the desiccator. Thus, more acid is adsorbed in

the vapor phase, lower is the formate concentration in the dilution.

Analyzing Fig. 4, which represents the decrease in the formate concentration in the dilutions considering each material; it is observed that the best material is silica gel, which is the one that gives rise to a greater decrease in the concentration of formate ions. It is even worth noting its higher performance than activated carbon, which is an outstanding sorbent material. Until the 14th day of the test, the steel shows a behavior on a par with copper. However, at the end of the test, it shows a greater decrease in the formate concentration, separating from the trend that followed with respect to copper. This latter material could have already reached saturation, while steel had not. It is expected that the behavior of each material was maintained after more than 21 days of the test until their saturation.

Optimization of silica gel and impact on glass

According to the results of Sect. 3.1, silica gel is the most suitable material for the adsorption of formic acid. It was, therefore, the material selected for the following tests to evaluate the procedure to reduce the acidic environment and its impact on the glass surface.

Three different procedures for the silica gel were assessed: maintaining the same silica during the test, renewing the silica each week, or regenerating the same silica each week. One environment was monitored without silica as reference.

The impact of the removal of formic acid in the glass was assessed by the exposure of glass slices and glass powder. Table 2 gathers the chemical composition of the soda glass.

Environmental conditions

Figure 5a–d correspond to the monitoring of the environmental conditions recorded by the thermohygrometers in the desiccators. They showed differences based on the different use of the silica.

Figure 5a shows that maintaining the silica during the test, the relative humidity was stable at 99.9% throughout the process. On the other hand, the temperature

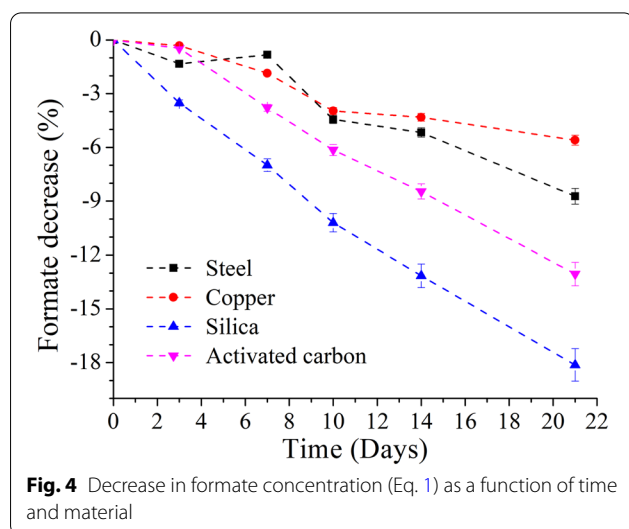
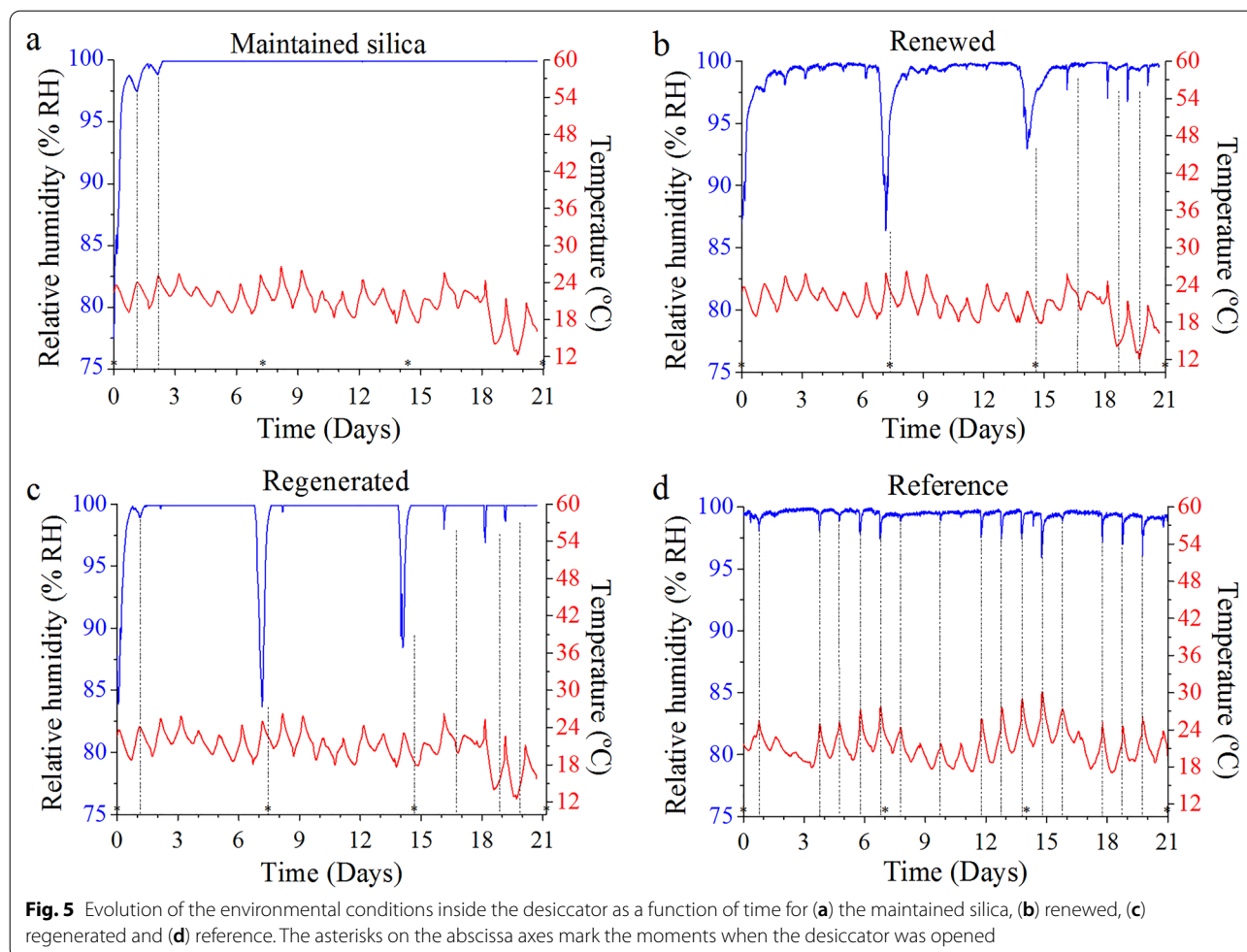


Fig. 4 Decrease in formate concentration (Eq. 1) as a function of time and material

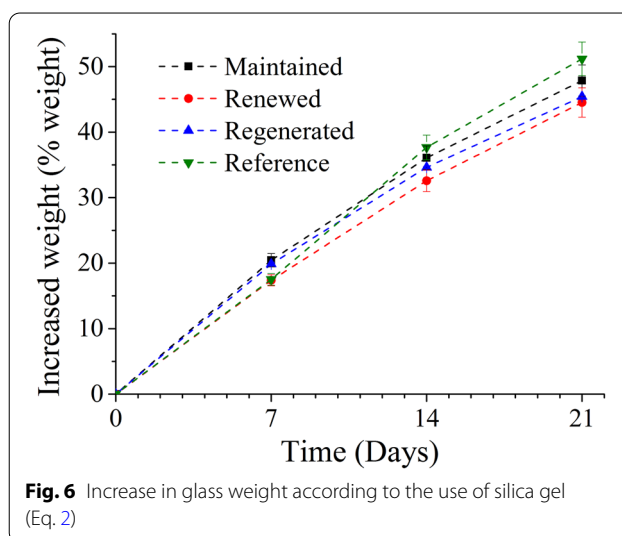
Table 2 Chemical analysis of the prepared glass analyzed by XRF

	Chemical composition XRF	
	wt %	mol %
SiO_2	74.9	75.9
Na_2O	19.9	19.5
CaO	3.06	3.32
Al_2O_3	2.10	1.25
Total	100.0	100.0



undergoes fluctuations due to changes between the day and night periods. Figure 5b, c, corresponding to the renewed and regenerated silica gel, show very similar values. Relative humidity remained without significant variations since it was close to 99.9% and the oscillations did not exceed 5%. It is only worth highlighting the moments on days 7 and 14, where the decrease is greater than the maximum 10% allowed by preventive conservation standards in museums [38]. However, these falls coincide with the moments when the desiccators were opened and the dry silica was put inside. Finally, Fig. 5d corresponds to the desiccator used as a reference, where silica gel was not used. Its behavior in relative humidity also remained within the allowed values, its oscillations not exceeding 5%, being the minimums of relative humidity mostly coincide with the maximums of temperature.

All desiccators maintain stable relative humidity values, achieving the environmental conditions set during the study.



Gravimetry

The evolution in weight, according to Eq. (2), depending on the use of the silica gel is reflected in Fig. 6.

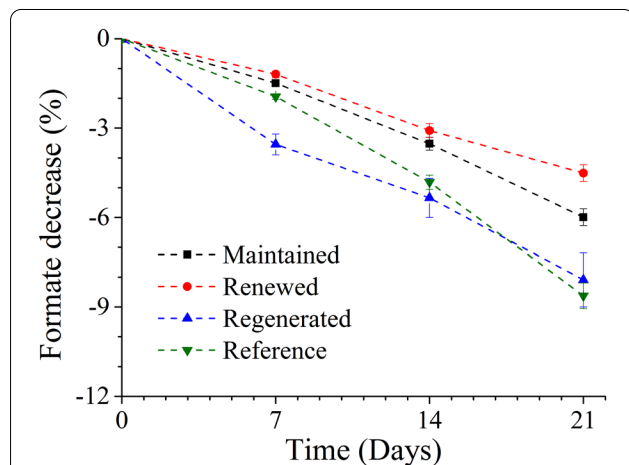
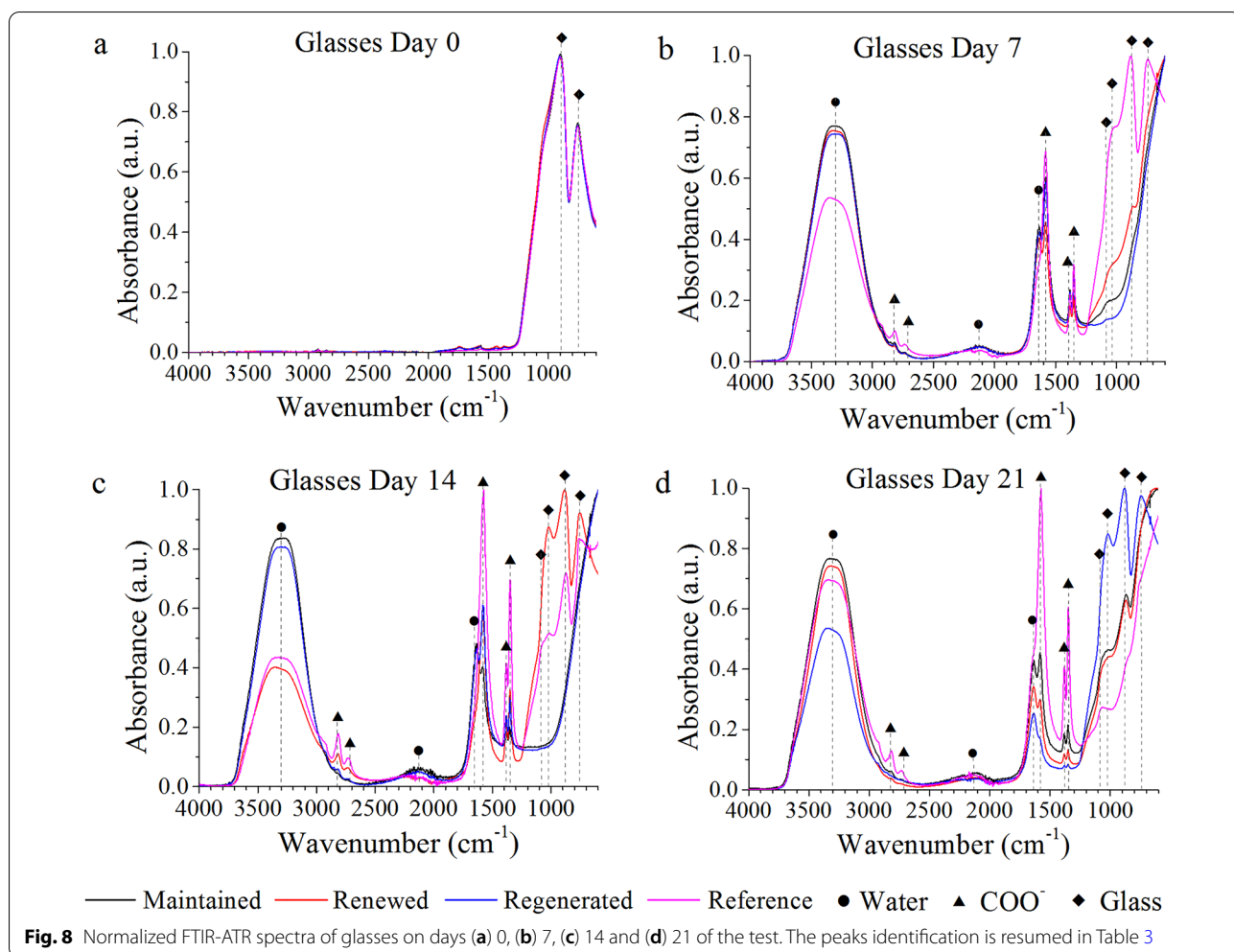


Fig. 7 Decrease in formate ions concentration (Eq. 1) according to the use of silica gel

The boat with glass powder exposed to the humid and acidic environment without silica gel experienced the greatest increase in weight as opposed to the other environments. The absence of a sorbent material favors a higher hydration of the glass fraction. Regarding the weight increases of the glasses that had silica gel in their desiccators, when the same sorbent material is maintained during the 21 days, a greater increase is observed compared to the other two protocols. In this case, the silica gel becomes saturated and its capacity as sorbent decreases, which leads to a greater hydration of the glass. On the other hand, the lower weight increase is observed if the silica gel is regenerated or renewed. These weekly regeneration or renewal processes allow the sorbent material not to become saturated. The lowest increase was observed in the test in which the silica gel was renewed.

Ion chromatography

Figure 7 represents the evolution of the concentration of formate ions of the original solution as a function of the



silica used. Higher is the decrease of the formate ions in the desiccator solution, higher is the materials' adsorption (non-stable glass and/or silica) of these ions.

The greatest decrease in formate ions corresponds to the reference desiccator. The acid atmosphere increased the hygroscopic capacity of the glass, as observed in Fig. 6, being the formate ions concentrated in the glass surface.

On the other hand, when the desiccators have silica gel, the sorbent adsorbs the formate ions and, therefore, higher is the decrease of the formate ions in the desiccator solution, higher can be the protection of the glass. In Fig. 7, it is observed that the greatest decrease in formate ions is obtained when the silica gel is regenerated every week, followed by the maintained silica gel and, finally, when the silica gel is renewed. This does not match with the observed in Fig. 6; however, there is a competition between the sorbent and the glass surface, mainly when the sorbent is saturated.

Infrared spectroscopy (FTIR-ATR)

The analysis through infrared spectroscopy (FTIR-ATR) allows to observe the evolution of the glass surface in humid and acidic environments. The degradation of glass slices is mainly related to hydration, which depends on the test duration or the way in which the silica gel is used (Fig. 8). Table 3 shows the assignment of the bands that appear in the different spectra represented.

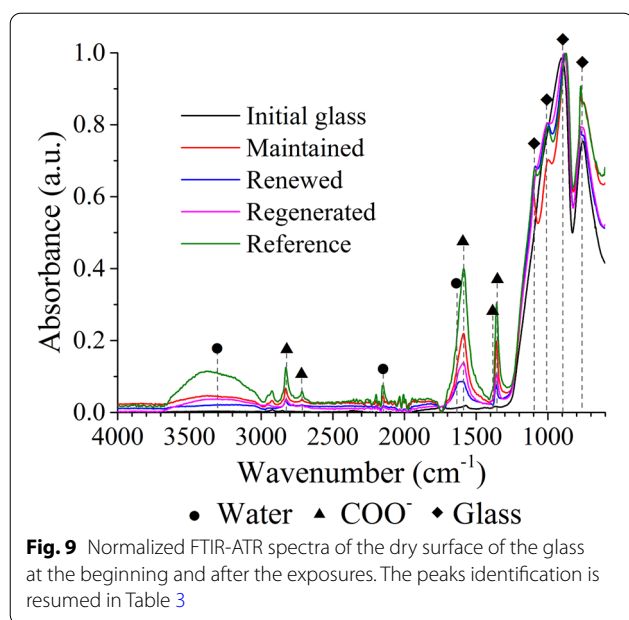
Figure 8a–d show the evolution of the spectra of the surfaces of the glass slices as a function of the mode of use of the silica gel, within each day of measurement. Initially, all surfaces show the same spectrum (Fig. 8a). These signals correspond to the structure of the glass, with the band associated with the symmetric stretching

of Si–O–Si at 750 cm^{-1} and the stretching of the silanol groups at 890 cm^{-1} . Figure 8b–d show the appearance of new signals and a change in their intensities. The bands associated with the symmetric stretching of Si–O–Si (750 cm^{-1}) decrease due to the hydrolytic attack of the glass network, while those corresponding to the stretching of the SiOH groups (900 cm^{-1}) increase due to the formation of silanol groups. In addition, new bands associated with water appear at 1630, 2160 and 3300 cm^{-1} , corresponding to scissors bending H–O–H, bend + libration H–O–H and stretching OH respectively, due to hygroscopic attack. Likewise, due to exposure to the acidic environment, the appearance of new bands associated with formate groups is observed due to the dissociation of formic acid in solution and interaction with the metal ions of the glass. These bands correspond to the bending of COO^- (750 cm^{-1}), symmetric stretching of COO^- with Na (1350 cm^{-1}), rocking of COO^- (1080 and 1380 cm^{-1}), asymmetric stretching of COO^- with Na (1580 cm^{-1}), bending vibration of CH (2730 cm^{-1}) and stretching of CH (2820 cm^{-1}). In none of the spectra obtained are the bands corresponding to the stretching of C=O of HCOOH, neither as monomer nor as dimer, located in the interval between 1731 – 1743 cm^{-1} for the monomeric form and between 1685 – 1712 cm^{-1} for dimeric [19]. This is because the dilution of formic acid in the adsorbed water has fully interacted with the metal ions on the surface of the glass.

The appearance of these bands associated with water and formic acid and the decrease of those corresponding to the initial structure of the glass is related to the advance in the hydration of the glass surface due to the atmosphere with 100% relative humidity and 10 ppm of formic acid.

Table 3 Allocation of glass FTIR-ATR bands identified in Fig. 8

Wavenumber (cm^{-1})	Assignment	References
3300	ν (OH) stretching (water and silanol)	[39–41]
2820	ν (CH) stretching (formate)	[39, 42]
2730	δ (CH) bending vibration (formate)	[42]
2160	δ (H–O–H) bend + libration (water)	[43]
1630	δ (H–O–H) scissors bending (water)	[44]
1580	ν (COO^-) of Na stretching asymmetric (formate)	[39, 42, 45]
1380	ρ (COO^-) rocking (formate)	[39, 45]
1350	ν (COO^-) of Na stretching symmetric (formate)	[39, 42, 45]
1100	ν (Si–O–Si) stretching asymmetric (glass)	[46, 47]
1080	ρ (COO^-) rocking (formate)	[39, 48]
1020	ν (Si–O–Na) stretching (glass)	[47, 49]
890	ν (Si–OH) stretching (glass)	[46, 47]
750	δ (COO^-) bending (formate)	[42, 44, 45, 48]
750	ν (Si–O–Si) stretching asymmetric (glass)	[47, 49]



The intensities of the bands in infrared spectra are highly dependent on the specific area of the surface being analyzed. To know the real effect of the degradation on the glass slices, the infrared spectroscopy analysis was carried out again two weeks after the degradation test ends, once the samples were dry (Fig. 9). In this way, the humidity of the glass surface does not interfere. Analyzing the Fig. 9, it is observed that in the glass exposed in the reference desiccator (without sorbent material), the bands associated with water at 1630, 2160 and 3300 cm^{-1} present a higher intensity than in the other glasses. Likewise, this glass has the most intense bands at 1380, 2730 and 2820 cm^{-1} , corresponding to the formate ions. This glass together with the slice exposed to the maintained silica gel were the glasses in which the bands related to glass degradation were more intense, such as the low increase in the band of the asymmetric stretching of the Si–O–Si (750 cm^{-1}), related to the formation of the silica gel layer on the surface [18, 22]. Higher is the intensity in these bands of water and formate ions, more advance is the degradation [18, 22]. Finally, the bands of water and formate ions from the glasses exposed with regenerated and renewed silica gel continued, following the descending order of intensity. These results coincide with those obtained in the gravimetry test.

Optical microscopy

The surface of the glass slices was observed by optical microscopy at the end of the alteration test. Figure 10a–d correspond to the glasses treated with the

maintained, renewed, regenerated silica gel and in the absence of sorbent material, respectively. Clearly, the difference is observed between the surfaces of the glasses that had sorbent material in their desiccator (Fig. 10a–c) versus the glass that did not have silica gel (Fig. 10d). Likewise, the alteration is in a lower degree when the silica gel was renewed (Fig. 10b) or regenerated (Fig. 10c), than in the case of maintaining the same silica during the 21 days of the test (Fig. 10a).

Conclusions

A set of four low-cost materials (copper wires, steel wool, activated carbon, and silica gel) have been evaluated as formic acid sinks. The highest value of specific surface area corresponds to activated carbon, followed by silica gel. The low values of steel wool, and copper wires do not mean that they cannot act as sorbent materials, since they were used as sacrificial material.

The FTIR-ATR analyses showed the bands of water and formate ions in silica gel after their exposure showing that both materials acted as sorbents. SEM-EDS and μ -Raman spectroscopy identified the large deposits on degraded copper wires were associated with Cu_2O , $\text{Cu}(\text{HCOO})_2$ and, probably, $\text{Cu}(\text{OH})_2$, and hydroxyls bands in degraded silica.

Regarding the capacity to remove the atmospheric formic ions, silica gel was the material that produced the greatest decrease, followed by active carbon. Furthermore, the relative humidity inside the silica gel desiccator was kept close to 100%, without significant variations. Therefore, it was concluded that the silica gel was the best material for the adsorption of formic acid in the evaluated conditions.

The second part of the study analyzed the degradation produced in a soda glass and evaluated its applicability in museum showcases. For that, four different procedures were evaluated: without the sorbent material and maintaining the silica gel, renewing and regenerating it during the test.

In the desiccator without silica gel, the glass showed the highest increase in weight, in contrast with those with sorbent material. The order from highest to lowest increase in weight was the maintained, regenerated and renewed silica. The ion chromatography analysis showed that the highest decrease in formate ions in dilution occurred in the desiccator without silica gel. This is justified by the higher hygroscopic capacity of glass, previously studied by gravimetry. For their part, the three desiccators with sorbent material can be compared with each other, obtaining that the silica regenerated each week achieved the best result. The

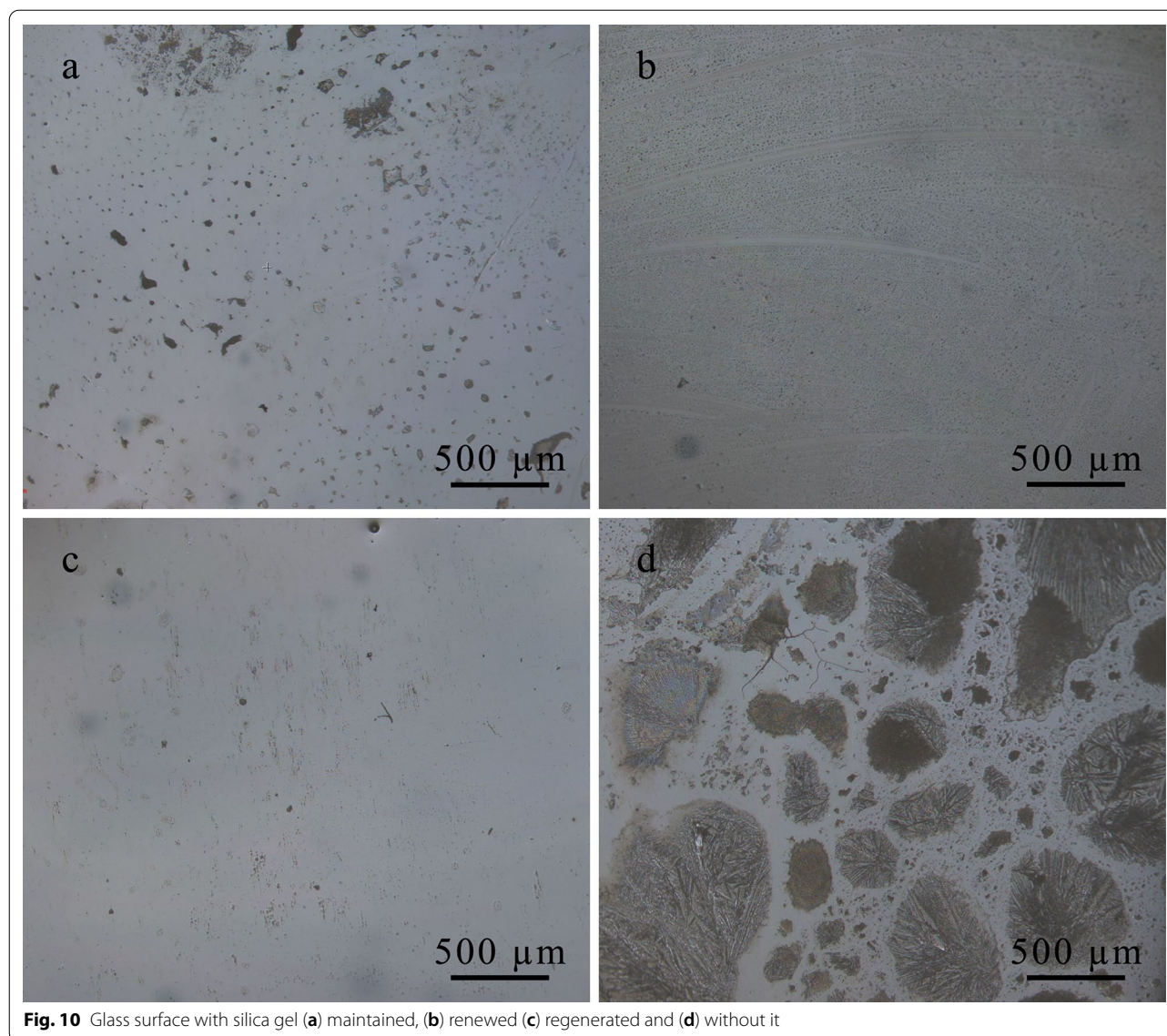


Fig. 10 Glass surface with silica gel (a) maintained, (b) renewed (c) regenerated and (d) without it

characterization of the surface of the glass slices by FTIR-ATR clearly showed bands assigned to water and formate ions in all environments and throughout the exposure period. The comparison of the glass surface after the test showed that in the glass without sorbent material the signals of water and formate ions had a higher intensity than in the other glasses as result of its alteration. The alteration of the glasses with silica gel depended on the method used, being the renewed one as the best option. These results also agree with the observed by optical microscopy.

In summary, the presence of formic acid sinks always favors the removal of the acid environment improving the conservation of cultural objects. In the

condition tested, silica gel turned out to be the best option. This material had the best efficiency to reduce the concentration of formic acid and mitigate the degradation produced in heritage objects exposed to a humid and acidic environment. One of the limitations of this procedure is that the material has to be regularly renewed to avoid their saturation. In addition, the evaluation of the material after studying the degradation produced in a soda glass showed the optimization of its use by regenerating it or renewing it weekly. These results should be complemented with more studies with other relevant pollutants and at lower humidity, e.g., to check if silica gel behaves superior to activated carbon also at 55% RH.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-021-00617-x>.

Additional file 1: Fig. S1. Distribution inside each desiccator during the (a) First test: selection of the best formic sink, (b) Second test: Optimization of silica gel. **Fig. 2.** SEM image of (a) the silica gel surface and (b) the deposits formed. **Fig. 3.** SEM image of the steel (a) before the test and (b) after the test. **Table 1.** Assignment of FTIR-ATR bands for silica gel.

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Authors' contributions

TP designed the study; RA carried out the tests and analyses; MA analyzed the samples by SEM; JM analyzed the samples by μ -Raman spectroscopy; RA and TP prepared the original draft. All authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analyzed during this study are included in this published article. Raw data (including spectra) are available upon request from the authors.

Declarations

Competing interests

The authors declare that they have no competing interests.

Author details

¹Dpto. Ciencias. Univ. Autónoma de Madrid. Campus de Cantoblanco. Avda. Tomás y Valiente, 7, 28049 Madrid, Spain. ²Instituto de Cerámica y Vidrio (ICV-CSIC), c/ Kelsen 5, Campus de Cantoblanco, 28049 Madrid, Spain.

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