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Original article

Iron(III) based Metal-Organic Frameworks in cellulose acetate film preservation: Fundamental aspects and first application

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ABSTRACT

Low-temperature storage to slow down degradation is accepted by the film conservation community. Still, this solution prohibits public access, is price-sensitive, has high energy costs, and there are concerns about their effects on the physical stability and material lifetime. In this research, a smart solution is developed based on the selective capture of acetic acid produced by the cellulose acetate polymer. This innovative approach is based on Metal-Organic Frameworks (MOFs) for acetic acid adsorption, specifically a highly selective porous iron(III) based MOF, MIL-100(Fe), which was synthesized using a green approach. The stability of MIL-100(Fe), under acetic acid exposure, was demonstrated by accelerated aging experiments, with no noticeable changes in crystallinity and/or porosity as deduced from powder X-ray diffraction analysis, infrared spectroscopy, thermogravimetric analysis, nitrogen porosimetry, and electron microscopy. Compatibility tests with the artefacts were performed to prove the safety of the MIL-100(Fe) to the artefacts. A field application in a demonstration prototype (*smart box*) was performed at Institut Valencià de Cultura. A recently developed hybrid model provided recommendations on the quantity of adsorbents to use in the *smart box*. Good agreement was observed between the model predictions and the in-field experimental results, which validated the model application. The model predicted that the new adsorbent (5% of the film's weight, replaced every 10 years, at 16°C or 22°C) extends the film's lifetime equivalently to cold storage (5°C). Finally, environmental impact assessment and life cycle analysis were performed to compare the two preservation approaches. The new approach based on this Fe-MOF yielded an average reduction of carbon footprint related to movie film preservation of about 50% considering the current European Union (EU) energy mix and about 40% considering the 2030 EU energy mix (where a transition towards renewable energy is expected). The proposed innovative technology represents a robust solution towards efficient and more sustainable film preservation while significantly contributing to moving toward climate transition objectives in the culture heritage sector.

Introduction

The "vinegar syndrome" appeared shortly after the cellulose acetate polymer was introduced and replaced the inflammable

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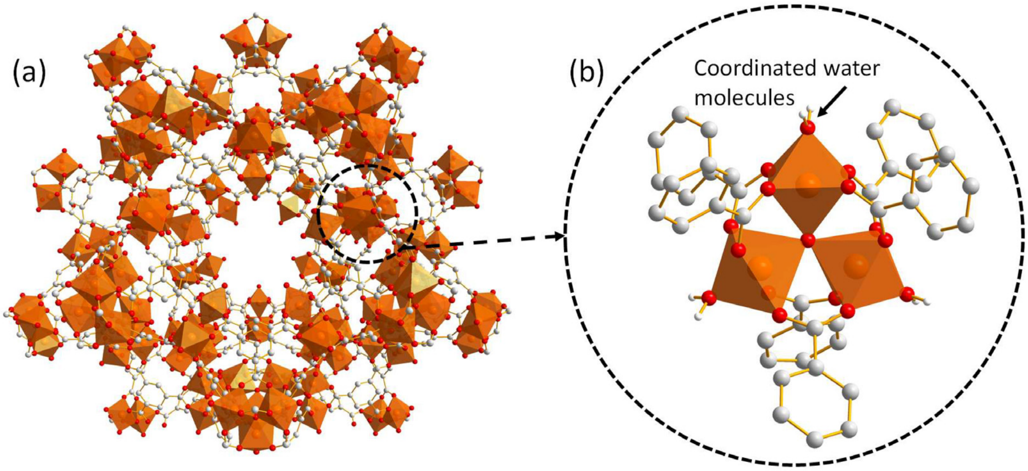

Fig. 1. MIL-100(Fe) structure with (a) a view of the large cage, (b) A close-up of the structure which is made up of iron trimers with open metal sites. Acetic acid adsorbs to MIL-100(Fe) in the presence of moisture due to its ability to displace coordinated water molecules [16]. Iron polyhedra, oxygen and carbon atoms are in orange, red and grey, respectively; hydrogen atoms have been omitted for the sake of clarity.

cellulose nitrate in the movie film industry in 1950s. It became evident that the presence of the acetic acid catalyzed the degradation of the films [1–5]. Recent quantum chemical calculations showed that the acid-catalyzed channel yielded about 10^8 times faster kinetics than the non-catalyzed water hydrolysis [6] (details are given in the SI - section 1). Since the degradation kinetics depends exponentially on temperature, the two main key parameters affecting the degradation kinetics are the temperature and the concentration of acetic acid. To conserve the artefacts, the approach practiced so far, the one that meets the International Organization for Standardization (ISO) recommendations for acetate films, is storing at cold temperatures, typically below 4 C° [7]. Nevertheless, this solution comes with high energy consumption and costs, and additionally, not all materials held in archives and collections can withstand freezing, due to their chemical composition (e.g. binders in magnetic tapes [8]). Searching for alternatives, clearing the atmosphere from acetic acid was considered before. A few studies investigated the commercial adsorbents such as activated carbons, zeolites and silica gel as a general preservation strategy to remove acetic acid [9–11]. Nevertheless, these adsorbents, were deemed ineffective [11], as they fell short in responding to the sophisticated requisites of the field of preservation, particularly in films preservation. The activated carbons' low selectivity made them inefficient in capturing trace amounts of acetic acid to meet the conservation objectives while the cationic zeolites, even if moderately selective toward vapors [12,13], were too hydrophilic (high affinity to water) which prevented their practical use. Hydrophobic Metal-Organic Frameworks (MOFs) recently made their advent to the field of conservation [14], nevertheless such MOFs are in most cases highly expensive, with scale-up feasibility and optimization still to be considered. In a search of an effective alternative solution to improve the traditional storage, the NEMOSINE European project, put together a multidisciplinary consortium with powerful synergies composed of academic research scientists, industrial partners, preservation practitioners and end-users, all sharing the main goal of making energy savings compatible with preservation lifetime extension [15]. Working on this objective, a significant number of MOFs was developed and tested for the acetic acid capture in the presence of moisture. It revealed that MIL-100(Fe), a benchmark mesoporous iron(III) trimesate prepared at large scale and via a green scalable route [16], exhibited an exceptional ability to clear the atmosphere from acetic acid and other noxious vapors like formic acid and propionic acid. This was ascribed to its very high concentration of open metal sites (or coordinatively unsaturated sites) resulting in a high affinity for acetic acid even at trace concentrations in the presence of moisture. The structure of MIL-100(Fe) is presented in Fig. 1. Noteworthy, it was shown through an extensive experimental and computational study, that in the presence of air moisture these sites are occupied by coordinated water molecules, yet the acetic acid could easily replace these water moieties due to their much higher affinity to the site [16,17]. Another very well performant MOF was developed within NEMOSINE, MIL-53(Al)-CF_3, constructed from a perfuorinated ligand, where its high selectivity for VOCs was the result of strong hydrophobicity as well as optimal host-guest interactions [18]. The two MOFs, MIL-100(Fe) and MIL-53(Al)-CF_3, were recommended for acetic acid adsorption, nevertheless, we moved forward with the former due to its exceptional performance, scalability and availability (from the pilot scale synthesis at the lab) at the kg scale that was necessary for the validation tests.

Despite the premises, prior to being considered in the field of preservation, several aspects still needed to be studied such as the stability and the compatibility of the MOF with the cultural artifacts. Important is to note that, as it was not possible to perform the compatibility tests with MIL-100(Fe) in powder state, a cellulose composite paper membrane loaded with 75wt% MIL-100(Fe) was tested instead. The formulation, fabrication and performance of this membrane are described elsewhere in a very recent publication [19] and have been filed in a patent [20]. For the in-field validation tests, 100 g of MIL-100(Fe) powder was packed inside a prototype (demonstration package) and tested with around 2 kg of film reels in Filmoteca Valenciana, Institut Valencià de Cultura (IVC). The acetic acid concentration reduction measured in-field agreed well with the predictions made using a recently developed hybrid model [21]. This model was applied in the current work to establish the conditions in which the MIL-100(Fe) should be used to achieve the same life extension as that of cold storage (5°C). A life cycle assessment analysis was finally made to compare the carbon footprint of the new proposed solution based on the prototypes, in comparison of that of cold storage, upon keeping the same lifetime extension.

Research aim

The aim of the current work is to validate an innovative approach based on the use of highly performant iron-based MOF and compare it to the classical conservation by cold storage (5°C). To validate such an innovative conservation approach, several aspects

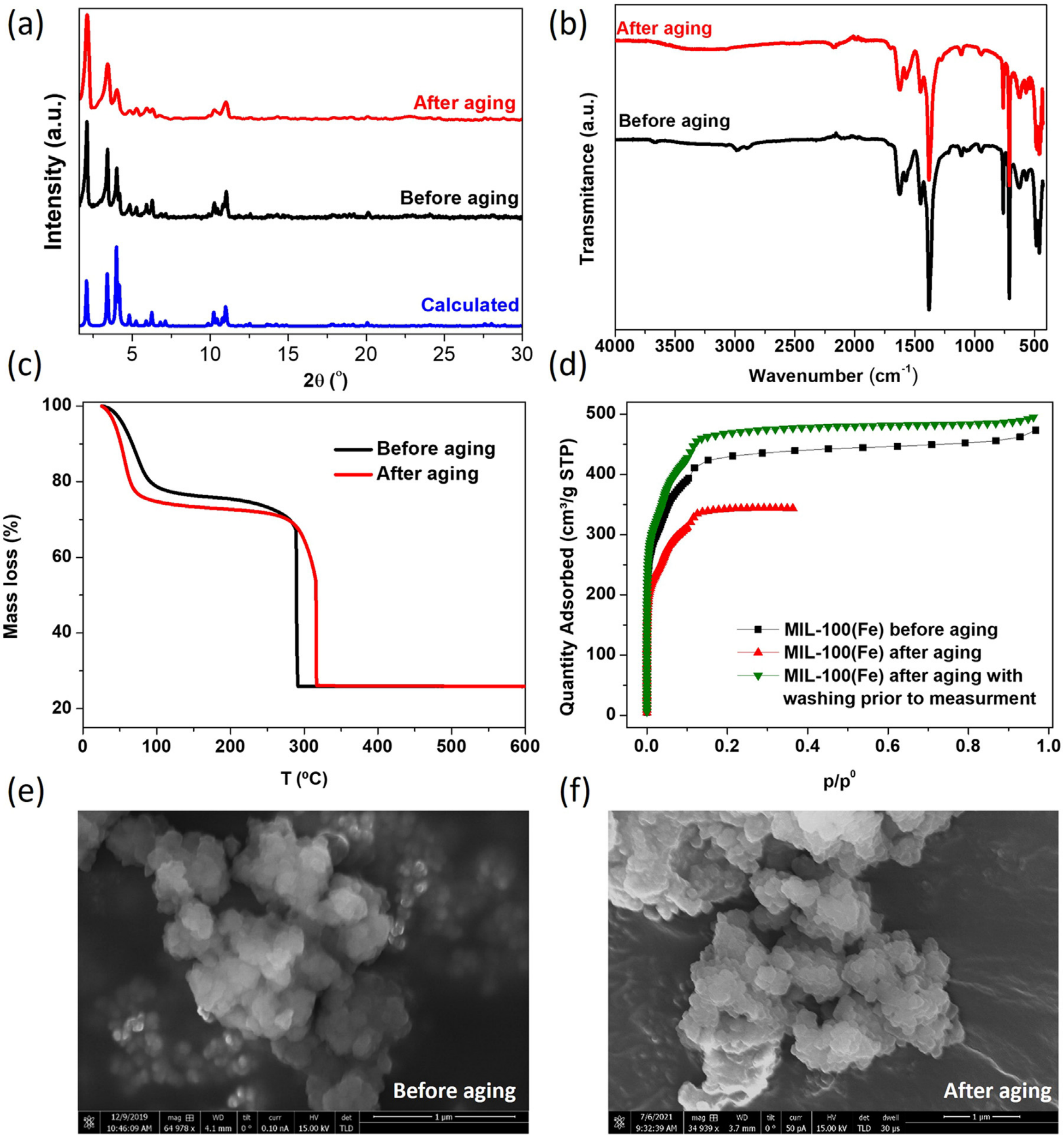

Fig. 2. (a) PXRD patterns of the original MIL-100(Fe) in 2Θ range 1.6–30° before and after aging compared with the calculated pattern from the literature (CuKα radiation, λ = 1.5418 Å) [22] (b) FTIR spectra of MIL-100(Fe) before and after aging in the region 4000 cm^{-1} and 435 cm^{-1} (c) Thermogravimetric analysis (air atmosphere, 3°C/min heating rate) of MIL-100(Fe) before and after aging (5°C per min under O_2). (d) Nitrogen adsorption isotherm, at −196°C, for the MIL-100(Fe) before and after aging. (e) and (f) SEM images for the MIL-100(Fe) before and after aging respectively.

such as compatibility, stability, preservation forecasts and quantity recommendations along with an in-field application were studied and understood while, in order to evaluate the carbon footprint of preservation, a life cycle assessment of the new solution was analyzed and compared to the classical way.

Materials and methods

Synthesis and characterization of the MOF samples

MIL-100(Fe) was synthesized using a recently reported protocol [16]. The structure was confirmed by powder X-ray diffraction (Fig. 2(a)) which fits well with the calculated pattern [22]. The absence of free linker was verified by Fourier-transform infrared spectroscopy (Fig. 2(b)). Thermogravimetric analysis, Fig. 2(c), confirmed the expected decomposition of the material. The surface area was confirmed by nitrogen porosimetry (Fig. 2(d)), where the results were in good agreement with the previously reported data [16]. To perform the compatibility tests, an adequate shaping protocol that is simple, cheap and doesn't hamper the MOF's adsorption properties was required; we selected a flexible high MOF loading cellulose based composite paper membrane, containing up to 75% in mass of MOF, prepared according to a recent in house protocol [20].

Thermal aging under acidic conditions

The MIL-100(Fe) samples were placed in a desiccator with an 18.57 mL solution of 2% V/V acetic acid in water, following the procedure proposed by Cruz.et al. [10]. The desiccator was then placed inside an oven at 70°C. The prepared solutions correspond to a molar fraction of 0.0064 in the liquid phase which gives a concentration of 1.7899×10^{-5} mmol/cm^3 in the gas phase. More details on the concentration calculation are given in a recent study [6]. The acetic acid solution was replaced each week, and the acidic aging chamber was cleaned to maintain constant conditions. A total aging of 17 weeks was performed within the framework of this study.

Compatibility tests

Two artificial aging procedures were performed with MIL-100(Fe) powder in order to: (1) evaluate possible airborne cross contamination that could damage cellulose-based artefacts, and (2) verify the innocuousness towards photographic materials. The chemical compatibility between the MOF and cellulose-based artefacts was assessed using ISO 23404:2020 standard method [23], and adapting it to the specific characteristics of the MOF material under test. This standard method allows to evaluate through capillary viscosity measurements if volatile compounds formed and emitted by a given material - to be used for the preservation and storage of cellulose based items – have an impact on paper stability. In order to perform the tests, the MOF was shaped in a paper-based membrane [19] at *ca* 75 wt% loading. All experimental details are available in the Supplementary Information (SI - Section 2).

Theoretical methods: predictive model

A hybrid model to provide accurate prediction of the long lifetime behavior of the cellulose acetate-based movie films was developed within the NEMOSINE project and reported recently [21]. The problem was addressed by coupling data-based models to a first-principles model. That latter described the degradation kinetics of the pure cellulose diacetate polymer [6]. Brief description of the hybrid model along with all the input parameters are presented in Section 3 of the SI.

Validation tests procedure

150 g of the synthesized MIL-100(Fe) were used to fill a pouch made from Tyvek^{TM} (Fig. S6). These bags were inserted into the demonstration propylene NEMOSINE package container lid, the lid was then sealed in Marvelseal^{TM} enclosures (Fig. S6) and sent for further testing under real conditions.

Life cycle assessment

Life cycle assessment (LCA) is a technique to assess the environmental aspects and potential impacts associated with a product, process or service through all stages of its life cycle. The life cycle embraces all the activities from raw material extraction, through manufacturing, distribution, use, as well as final disposal or recycling. Energy, material and water resources are used in creating, packaging, transporting and using a product whilst the associated process generates emissions to air, land and water, causing strong environmental impacts. More details on this analysis is found in Section 5 of the SI.

Results and discussion

MOF aging

MIL-100(Fe) was exposed to acetic acid at a vapor concentration of 1.7899×10^{-5} mmol/cm^3, i.e. an order of magnitude higher than the highest archival acetic acid concentrations [24]. Visually no color change was observed in the MOF sample (Fig. S7 (a)). Different characterization techniques were used to understand the possible evolution in the MOF structure after aging. The MIL-100(Fe) maintained its crystallinity as shown in Fig. 2(a), where the PXRD patterns of the original sample and that of the thermally aged under acidic conditions are comparable. A slight peak widening is observed which very likely to be caused by the presence of the acetic acid captured during the aging procedure. Important to note that the crystallinity is sensitive to the pore content particularly in the case of mesoporous MOFs such as MIL-100(Fe). FTIR spectra of the aged MIL-100(Fe) along with the non-aged sample are shown in Fig. 2(b) (Fig. S7 (b) shows the FTIR spectra with emphasis on wavenumbers from 400 to 2000 cm^{-1}), indicating no clear sign of potential deterioration; only a tiny increase in the 1700 cm^{-1} peak was observed possibly indicating the presence of traces of free linker or AA, thus ruling out the release of carboxylic acids into the environment. An increase of the OH band (3000–3500 cm^{-1}) was, as expected, observed due to the capture of the acetic acid in agreement with a slight increase of the band at 1690 cm^{-1} which corresponds to the acetic acid bounded to the Lewis acid sites through the oxygen lone-pair electrons of the carbonyl group [16]. Some variations in the region between 1300 and 1200 cm^{-1} are also observed which could be a result of the acetic acid physisorption as well. The thermogravimetric analysis is shown in Fig. 2(c), with a first weight loss between 25 and 100°C being attributed to the departure of the adsorbed water molecules inside the pores or on the surface of MOFs. The second weight loss between 100 and 300°C is attributed to the loss of water molecules coordinated to the Fe(III) trimers. For the aged sample, the second step also involves the desorption of the adsorbed acetic acid molecules (2–3%). This latter occurs at temperatures around 200°C, as shown in previous temperature programmed desorption studies [16]. The last and third weight loss at 300°C is due to the collapse of the structure, with the loss of linker, followed by the decomposition of the material into Fe_2O_3, and the same mass was obtained for both samples as expected. Important to note that the weight loss related to linker is similar to the theoretical weight loss expected before and after MOF aging. Nitrogen porosimetry measurements are shown in Fig. 2(d), a decrease in nitrogen uptake was measured for the aged sample. Nevertheless, after washing the aged sample and removing all the adsorbed acetic acid the performance was fully recovered with a slight increase that may be attributed to some minor amounts of defects or eventually a more thorough washing compared to the starting material. SEM images are shown before aging (Fig. 2(e)) and after aging (Fig. 2(f)), the particle shape and size seem to be maintained. As a preliminary conclusion, based on the performed tests, MIL-100(Fe) proved to be stable enough under the used conditions of accelerated aging. This casts out a major risk of contamination of the artefacts due to organic molecules being released as a result of the adsorbents degradation. In the future, further tests will be carried out to assess its safety fully.

Compatibility tests

For MIL-100(Fe) to be used as a preventive preservation material in cultural heritage institutions, it was important to ensure that it could be safely placed in the vicinity or in contact with the artefacts. Among possible adverse effects, materials can emit volatile compounds (such as acids, sulfur or nitrogen containing compounds, etc.) that can enhance the depolymerization of cellulose-based historic artefacts and artwork, and therefore shorten their lifetime [25,26]. One compatibility evaluation test consisted of measuring the airborne cross-contamination impact that volatile compounds emitted by the material under test has on cotton linters filter paper (Whatman no.1) placed in its vicinity.

This is done by comparing the *DP* of cellulose of Whatman no.1 after artificial aging in the same vial as the material in question, to that of a reference paper exposed only to pure cellulose paper in the same T/RH artificial aging conditions.

The DP_v results are shown in Fig. S8. From the initial value of about 2706±49, the DP_v of cellulose dropped after 21 days of aging to 2079±10 in the Control vials and to 2100±17 in the test vials, meaning that the presence of MIL-100(Fe) paper membrane did not impact the kinetics of degradation of cellulose. This result allows to conclude that MIL-100(Fe) did not emit volatile compounds during aging that could be detrimental to cellulose based materials.

The Photographic Activity Test (PAT) aims to assess the compatibility of materials used for preservation with photographic material. However, the PAT is often used to evaluate many other types of materials used in cultural institutions for storage and display of non-photographic media and inks. After the aging, the colloidal silver detector in contact with the Whatman no.1 paper (control sample) was evaluated by subtracting the mean value of its blue diffuse transmission density before and after the aging (Fig. S9). For the test with MIL-100(Fe) composite paper to pass, any density change must fall within +/- 20% observed on the detectors in the control stack, i.e. in this case between 0.86 and 1.29. The density change observed due to MOF paper sheet being 1.08, a value well within the limits, indicates that it passed the test. The performance of the stain detector in contact with the Whatman no.1 paper control was also assessed by subtracting the blue reflection density before and after aging. Any staining caused by the tested material must be below the stain limit determined as: blue reflection density of control sample + 0.08. The density change of MIL-100(Fe) was 0.18, while the stain limit was 0.19, indicating that the test passed. These compatibility tests demonstrate that the MIL-100(Fe) composite paper membrane appears as a suitable candidate to be used for the preventive preservation of cellulosic and photographic materials.

Model predictions and recommendations

The current section is providing answers based on the hybrid model predictions [21] upon including the effect of the MIL-100(Fe). Nevertheless, there is no single answer as there are a number of parameters like the initial film degradation state, the type of available storage (22°C, 16°C, 5°C), the type and quantity of the adsorbent that is used as well as the adsorbent replacement time in addition to the film type. The film type contributes to accelerated kinetics, the acceleration coefficient is considered constant in the current work for simplicity. Relative humidity (RH) is set to 40%, the periodic MOF replacement time (pmrt) of 10 years, the mass of the film 2 kg (film reels) and the considered life span is 100 years. These values are reported in table S1.

Model predictions

We discuss the effect of temperature and the MIL-100(Fe) adsorbent presence for the two extreme cases of a fresh film and a severely degraded one, since the current state of the film affects its future behavior. The degradation state of the film is represented in the model by either no initial AA concentration in the atmosphere (fresh film) or 19 ppm initial AA concentration (severely degraded film). These values were meant to represent the AD-strip value of 0 and 2.5 respectively [27]. Important to note that, when possible, the concentration of AA can be measured accurately using highly sensitive sensors [28]. Fig. 3(a) shows the cellulose acetate-based film stored under controlled room temperature of 22°C, where for a fresh film (0 ppm – AD-strip 0) an eventual decay happens in 20 years if no actions are taken, i.e. accumulation of acetic acid inside the films' storage containers. Lowering the temperature would extend the film's lifetime to at least 100 years. Interestingly, introducing 100 g (5% of film's weight) of MIL-100(Fe), along with a replacement of the MOF every 10 years, at 22°C would lead to the same preservation extension as that storing at 5°C without any MOF. Important to note that, the MOF can be supported inside the film package by a Tyvek bag (like in the validation tests) or any other support, like paper membrane [19], that doesn't impede or the deteriorate the performance of the MOF (NB: it doesn't impact the Henry's constant of the MOF – initial slope of the acetic acid adsorption isotherm). For the severely degraded film with significant acetic acid concentrations (19 ppm – AD strip 2.5), the presence of 200 g (10% of film's weight) of MIL-100 (Fe), at 22°C, shows to do an equivalent effect to storing at cold temperature of 5°C.

Table 1
Storage recommendations of MIL-100(Fe) amounts to be added to a film storage container to achieve a shelf life equivalent to storage at 5°C. Values are given for a 2 kg film, at 40% RH with the adsorbent renewal every 10 years stored at $T = 22°C$ and $T = 16°C$.

$T = 22°C$		$T = 16°C$	
Film condition: degraded?	MIL-100 (Fe) amount (g)	Film condition: degraded?	MIL-100 (Fe) amount (g)
No	100 g (5%)	No	50 g (2.5%)
Yes	200 g (10%)	Yes	100 g (5%)

Fig. 3(b) shows the degradation kinetics upon using a storage temperature of 16°C, where with no adsorbent, for a fresh film (AD=0), an eventual decay would take off in 75 years. Storing this film at 5°C temperature would not allow any degradation, at least within 100 years. Interestingly placing 50 g (2.5%) of MIL-100(Fe), along with a replacement time of 10 years, would lead to the same effect, not allow any degradation at least within 100 years, at a temperature of 16°C. As a comparative scenario, for a film with 19 ppm initial acetic acid in the atmosphere, the degradation kinetics are so fast at 16°C that the film would last less than 20 years. Lowering the temperature to 5°C would slow down the degradation and extend the lifetime of this film. Nevertheless having 100 g (5%) of MIL-100(Fe), with 10 years replacement time, at 16°C would attain better preservation than that at $T = 5°C$. It is important to note that for the cases where the degradation started and/or there is acetic acid in the atmosphere, coupling controlled temperatures at 16°C and tackling the AA concentration accumulation by the presence of adsorbent proves to be the most efficient strategy in extending the films lifetime. Special attention must be given to the truncated scale of 96% non-degraded, in Figs. 4a) and b) since we are focusing on the early onset of degradation.

Fig. 3(c) and (d) show the AA concentration in the atmosphere as function of time at storage temperature of 22°C and 16°C respectively, where one could easily correlate the effect of AA accumulation on the acceleration of degradation kinetics. It is noticed that lowering down the temperature to 5°C retain the AA production, while the use of MIL-100(Fe) limits the AA accumulation. In other words, MIL-100(Fe) is predicted to be highly efficient in keeping the AA concentration to a very low limit and doesn't allow the acceleration of degradation to happen.

Model recommendations

Recommendations on the usage of MIL-100(Fe) adsorbent are given in Table 1 based on the model predictions provided in the section above. It is important to note that intermediate degradation cases of AD-strip values of 1, 1.5 and 2 were studied upon considering the respective equivalent initial concentrations of 1.5, 4 and 7 ppm. The amount of MIL-100(Fe) to be present is similar to that of AD-strip value of 2.5. In other words, the recommendations are given based on a binary condition of fresh film or degraded

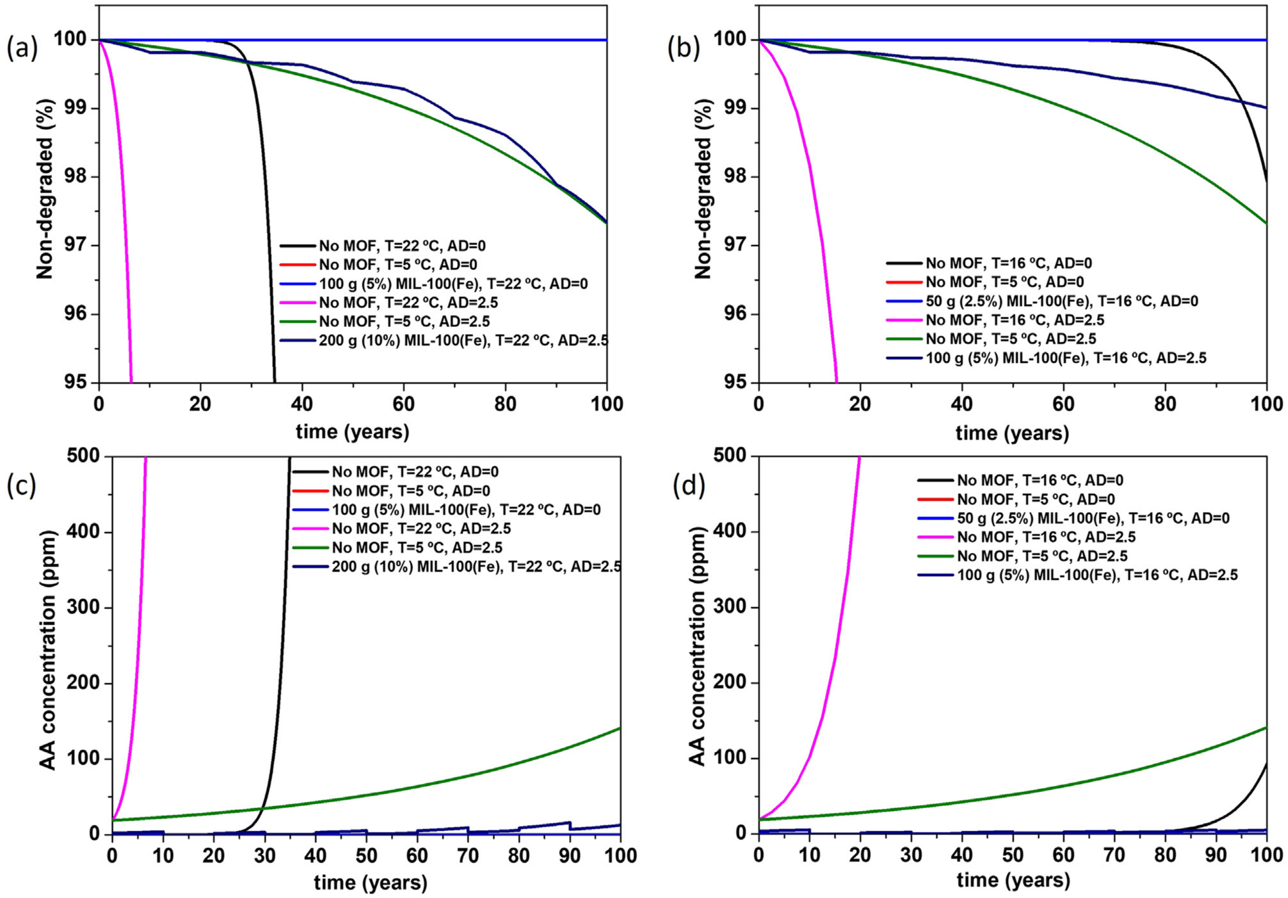

Fig. 3. Effect of temperature and MOF presence on a fresh film (AD=0, or initial acetic acid =0) as well as severely degraded film (AD=2.5, or initial acetic acid = 19 ppm). The degradation kinetics are reported where the film is stored at (a) $T = 22$°C, (b) $T = 16$°C. The acetic acid concentration in the atmosphere is reported for (c) $T = 22$°C, (d) $T = 16$°C.

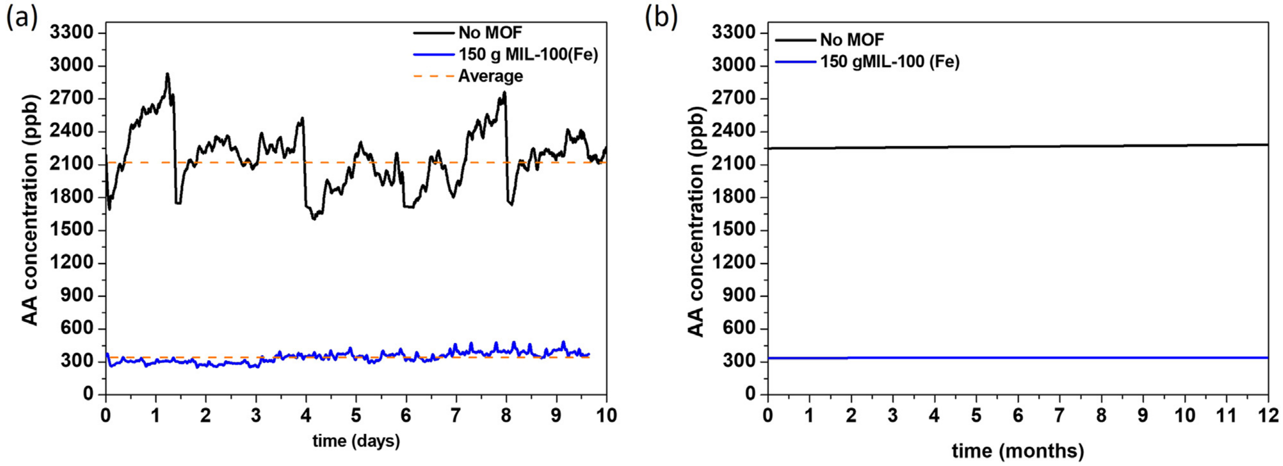

Fig. 4. Validation test at IVC (a) without MOF and with MOF (MIL-100(Fe)). (b) Model predictions with IVC storage conditions as input with and without MOF.

film. The recommended amount is given to lead to either equivalent or better results than cold storage ($T = 5$°C). The best scenario is when a combination between lowering down the temperature and having MIL-100(Fe) powder are used to tackle the two main drivers of the degradation kinetics (temperature and acetic acid concentration). Thus, in these conditions, the autocatalytic point or accelerated kinetics does not happen in at least 100 years. The mass of the adsorbent is indicated in grams as well as percentage of the movie weight.

Validation tests

Validation tests were conducted to verify the MIL-100(Fe) performance under real conditions. For this, 150 g of MIL-100(Fe) were placed inside the prototype using a Tyvek pouch as shown in Fig. S6. The acetic acid gas concentration was detected by an acetic acid selective sensor developed by BIOSENSOR [29]. The IVC validation test storage conditions were fed to the predictive model as shown in Table 2.

Table 2
Institut Valencià de Cultura validation test storage conditions (same conditions were used as input to the hybrid model).

Condition	Value
Free box volume	2000 cm^3
Mass of the film	1.956 kg
Storage temperature	5°C [4 – 6°C]
Relative Humidity	40% [38 – 42%]

Fig. 4(a) presents the acetic acid concentration recorded before and after the introduction of the MOF. An average of 2120 ppb is recorded. Remarkably, the acetic acid concentration dropped to an average value of about 340 ppb after the introduction of 150 g of MIL-100(Fe). Note that this concentration was maintained over the period of the trial, which was 10 days. To obtain the model predictions of the effect of MOF, the IVC storage conditions as well as the measured acetic acid concentration of the film prior to the MOF introduction were implemented as input in the model (Table 1). Fig. 4(b) presents the outgas predictions over a period of one year with and without the MOF. The model predicts a decrease from 2250 ppb to 337 ppb. The decrease recorded by the IVC archive from an initial average value around 2250 ppb to an average value around 300 ppb that agrees very well with the expected reduction to be induced by the Fe-MOF in the powder form validating the model predictions. Note that during an initial period of time ventilation along with the adsorbent presence was tested and a later period only the adsorbent presence was tested with no ventilation (Fig. 4(a)). No significant difference was measured, demonstrating that the presence of the adsorbent established the gas phase equilibrium between the gas phase and the adsorbed phase of acetic acid.

Life cycle assessment

As a first step of the LCA study, the scope of the study was defined as the assessment of the carbon footprint of the proposed innovative solution in respect with the state-of-the-art with a cradle to grave approach, to guide the further development and use of MOF in movie film preservation. The functional unit was defined as 1 package unit stored for 100 years, and the 5 scenarios described in Table 3 were analyzed, upon considering the MOF replacement time of 10 years (for the case of fresh film, scenario 1, 100 g of MIL-100(Fe) is needed, this amount needs to be replaced every 10 years this yields a total of 100×10 g of MOF). The as-synthesized adsorbent come in powder shape and a supporting matrix is usually needed for better handling. Different support matrixes types were studied and reported [19,30]. In the NEMOSINE prototype the MIL-100(Fe) powder was supported in a Tyvek bag pouch, which was protected in an inner cavity; for more details see the NEMOSINE video [31]. The mass of the used Tyvek bag was 11 g. In Table 3, in addition to the MOF, 110 g of Tyvek bag was considered as the bag is to be changed with the MOF every 10 years.

After defining the scope, the second step regarded the collection of data about the processes to be compared. The environmental impacts of the state-of-the-art preservation processes are mainly related to the electricity consumption for the refrigeration of the rooms at 5°C. To calculate the annual energy consumption, several locations were considered having different climate conditions (Athens, Valencia, Marseille, Milan, Paris, Prague and Birmingham). On the other side, for the 4 scenarios using MOF, besides the energy consumption for refrigeration at 16 and 22°C respectively, calculated for all the locations indicated above, the study considered the impacts of MOF preparation, from raw materials to manufacturing and end-of-life: data regarding the materials used and energy consumption as well as final disposal of MOF were collected.

Based on the defined Life Cycle Inventory, the environmental impacts of the state-of-the-art as well as of the new proposed solution using MOF were calculated. The impacts of raw materials, waste and emissions associated with the preparation and disposal of MOF were taken from recognized databases, such as Ecoinvent. As for the emissions associated with the electricity consumption, we considered the carbon footprint of current EU energy mix as well as the carbon footprint of the expected EU energy mix in 2030 [32] that, thanks to the higher use of renewable energy sources, will have reduced CO_2 emissions.

Finally, the impacts of the 5 analyzed processes were compared. The results are reported in Fig. 5, that shows how the use of MOF enables an average, very significant, reduction of carbon footprint

Table 3
The scenarios considered in the LCA to obtain an equivalent lifetime extension.

Scenarios				
Scenario 0	Scenario 1 (fresh film)	Scenario 2 (degraded film)	Scenario 3 (fresh film)	Scenario 4 (degraded film)
No MOF $T = 5°C$	1 kg MIL-100(Fe) $T = 22°C$	2 kg MIL-100(Fe) $T = 22°C$	0.5 kg MIL-100(Fe) $T = 16°C$	1 kg MIL-100(Fe) $T = 16°C$

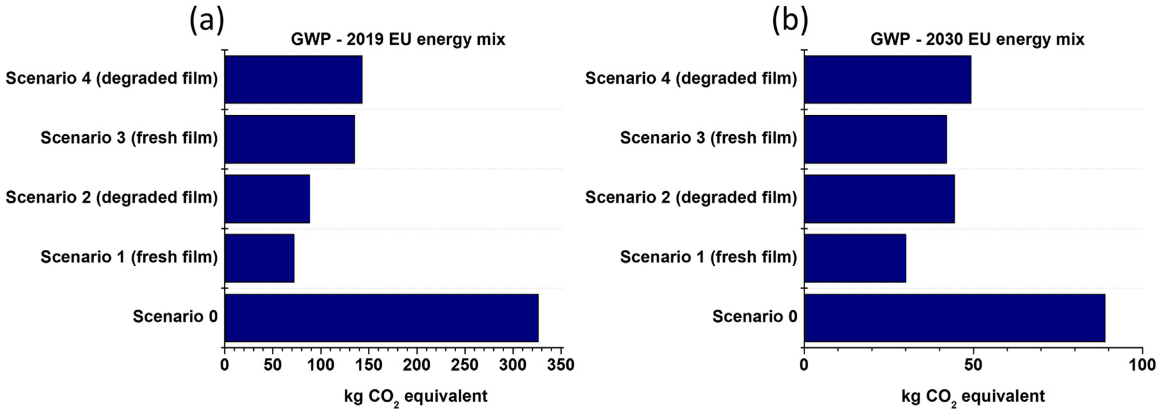

Fig. 5. Carbon footprint predictions of the five considered scenarios, for (a) current and (b) 2030 EU energy mix respectively.

related to movie film preservation of about 50% considering the current EU energy mix and about 40% considering the 2030 EU energy mix.

Conclusion

The stability of a promising benchmark MOF material (MIL-100(Fe)) for preservation cinematographic and photographic films based on cellulose acetate was demonstrated. The safe use of the new adsorbent with the artefacts was evaluated and proved to be compatible with a variety of culture heritage items, since this Fe-based MOF was shown to be stable under accelerated aging. The performance of the MIL-100(Fe) to capture acetic acid in the presence of moisture was estimated to significantly extend the life of the of movie films based on cellulose acetate by considerably slowing down their degradation kinetics. The recommendation to use 5 to 10% of this MOF (by weight in comparison to the movie film weight) for a fresh film and severely degraded one respectively, was given so that a life-extension at room temperature (22°C) is equivalent to cold storage (5°C). A real demonstration of the new material performance was carried out proving that the material was effective in purifying the air from acetic acid, with a decrease in the acetic acid concentration from around 2120 ppb to 340 ppb, in perfect agreement with the model predictions. The acetic acid concentration was maintained at low levels during the demonstration test of two weeks. It was also shown that using a ventilation strategy does not reduce further the acetic acid concentration. In other words, the reduction of the concentration is dictated by the adsorbent rather than the ventilation process. Cradle to grave life cycle assessment was finally performed upon considering an extension of the lifetime for the movie films to 100 years as the functional unit, obtained either by cold storage or by the presence of MIL-100(Fe). Remarkably, the use of this MOF enables an average reduction of the carbon footprint related to movie films preservation of about 50% considering the current EU energy mix and about 40% considering the 2030 EU energy mix, where a transition towards renewable energy is expected.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2023.11.013.

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