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Increasing the effectiveness of a liquid biocide component used in antifungal waterborne paints by its encapsulation in mesoporous silicas

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ABSTRACT

SBA-15 and MCF mesoporous silicas were used as solid porous adsorbent for supporting a liquid commercial biocide, and the biocidal activity of the so-obtained loaded solids was checked after being incorporated in a waterborne paint. Starting from an acrylic latex free of biocidal agent, three series of paint formulations were obtained: two series were prepared by adding increasing amounts of the different biocide compounds (one series using SBA-15 and the second using MCF supported biocide) and a third series where the nonsupported, liquid biocide was added instead. Afterwards, the biocidal activity against *Alternaria alternata* of the different coatings prepared was measured by means of the current standard procedures used for dry coating sample evaluation. An increase in the inhibitory activity and a lower development of the fungal mycelium were generally observed when the concentration of the encapsulated biocide was increased. The film samples, corresponding to the two coatings formulated using a 2 wt.% of biocide loaded in MCF silica, showed a total inhibition of fungus growth after 1 month, in spite of the clear deterioration observed when the liquid biocide at 2 wt.% was incorporated. These two paints were selected for being tested under more severe deterioration conditions in the presence of *Aspergillus fumigatus*, *Alternaria alternata* and *Chaetomium globosum* spores. The paint films incorporating MCF loaded silica exhibited optimal efficiency, presenting a null development of the inoculated strains after 9 months. This behavior could be associated with the shape and pore size of the MCF particles, which favor biocide intraparticle diffusion, and also with the low density of this disordered material, which promotes its location close to the top surface of the dry paint.

1. Introduction

Absorbent substrates such as wood, masonry, plaster, etc., are usually attacked by microorganisms. As a consequence, their physico-mechanical properties can be significantly modified. Coatings are often used to avoid or minimize this deterioration. It is known that some drawbacks are associated with the fact that the biodegradable components included in paint formulations could act as nutrients for the vital functions of the microorganisms [1,2]. As a consequence, depending on their quality and elapsed time, the paints commonly suffer deterioration in both the storage state (loss of viscosity, pH reduction, odor changes due to putrefaction, elimination of gases, etc.) and the dry film state (esthetic changes and poor film adhesion by formation of dark spots) generating a negative economic impact [3]. Particularly, waterborne paints are especially vulnerable to microbial growth because of the great amounts of water and organic materials usually involved in their formulations [4].

On the other hand, the filamentous fungus species commonly found as part of biofilms in indoor environments are eventually exposed to high relative humidity such as those prevailing in bathrooms and kitchens [5]. Fungi are heterotrophic organisms that usually colonize building materials to degrade them through organic acids and enzymes [6]. Particularly, *Chaetomium globosum* strains are known to degrade cellulose and its derivatives, which are used as thickener in paint formulations [6]. Moreover, indoor fungal biofilms can affect people´s health [7]. Particularly, the development of allergies to *Alternaria* and *Aspergillus* species has been studied in the past decade. The airborne spores of these fungi are generally considered to be important causes of both immediate and delayed-type asthma in individuals already sensitized to these organisms [6,7]. Spores are released into the environment and their size allows them to penetrate deep into the lower respiratory tract and cause a wide range of diseases [8,9]. It is clear that human

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exposure to these kinds of fungi must be avoided, and the employment of antimicrobial paints in buildings may contribute to create healthier environments.

It is well known that biocide compounds present in paint formulations are the components responsible for microbial growth inhibition, and the consequent coating and substrate preservation. Nevertheless, the extensive use of biocides can cause environmental problems and human health risks. Also, many biocides have high solubility in water that makes them prone to leach under humid conditions, losing the inhibitory effect on the dry paint film.

Isothiazolinone-based biocides are very commonly used in the coating industry for growth inhibition of bacteria, fungi and yeast [10,11]. A typical commercial waterborne paint formulation used in the coating industry consists of an aqueous mixture of different ingredients, where both 5-chloro-2-methyl-4-isothiazolin-3-one (CMIT) and 2-methyl-4-isothiazolin-3-one (MIT) are present in a CMIT/MIT = 3 wt ratio [12]. Nevertheless, the expected increase in restrictions on the use of toxic biocides, coupled with the increased public awareness of air pollution, will reduce their consumption [13].

To avoid the mentioned drawbacks, a promising solution could be found in the use of different solid porous matrices that can encapsulate and stabilize the biocide molecules inside their open structures prior to the biocide incorporation in the coating formulation. This methodology could increase the biocide performance, as encapsulation prevents biocide degradation or leakage and also provides controlled biocide exposure to the environment, enhancing the biocide/biocidal properties of the coating [14–17].

For these purposes, mesoporous silica-based structures have recently been envisaged as promising solids in terms of offering the mentioned beneficial increase in biocide/biocidal activity [18–22].

As in previous work we demonstrated that CMIT/MIT mixture could be successfully loaded and stabilized on mesoporous silica [23,24], in this work we study the antifungal activity presented by paint formulations where the biocidal efficacy was provided by an encapsulated CMIT/MIT mixture.

2. Experimental

2.1. Chemicals

The chemicals used in this study include triblock copolymer poly (ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (Pluronic P123, MW: 5800, Aldrich), tetraethyl orthosilicate (TEOS, 98%, Aldrich), hydrochloric acid (HCl, 37%, Anedra), mesitylene (MES, 98%, Aldrich) and a commercial aqueous biocide for latex preservation composed of a mixture of 5-chloro-2-methyl-2H-isothiazol-3-one and 2-methyl-2H-isothiazol-3-one (Rohm and Haas). An acrylic paint free of biocide compounds was prepared in our laboratory using the same ingredients and following the procedure described in [25], and a commercial latex (Borgolatex acrylic latex) was used as reference for biocidal activity tests. The strains used for the bioassays were: *Aspergillus fumigatus* (KU936230), *Alternaria alternata* (KU936229) and *Chaetomium globosum* (KU936228) isolated from biodeteriorated acrylic coatings studied in a previous work [26].

2.2. Synthesis of materials

Following the procedure described by Zhao [27], the ordered mesoporous silica was synthesized using the amphiphilic block copolymers Pluronic P123. The structure-directing polymer was dissolved in 2 M HCl aqueous solution, under stirring at 35 °C. After homogeneity, TEOS was added to the mixture, and the stirring was maintained for 20 h. Then, the reacting mixture was transferred to a hermetic flask and maintained at 80 °C for 24 h. The molar composition used was 1TEOS:5HCl:0.018PEO:184H_2O. After the reaction time, the solid phase obtained was separated and washed with water, dried at 120 °C, and calcined for 6 h at 540 °C. The sample was named SBA-15. A similar methodology to that previously described was employed for the non-ordered silica synthesis, differing in the mesitylene incorporation to the synthesis mixture [28,29]. The molar composition of the gel was 1TEOS:0.724MES:3.1HCl:0.0111PEO:111,4H2O. The product obtained was named MCF.

2.3. Characterization of silica matrices

Siliceous materials were characterized by scanning electron microscopy using a Philips 505 microscope. Transmission electron microscopy (TEM) was performed with a JEOL 100CX microscope operated at 100 kV.

Fourier transform infrared (FT-IR) spectra were collected in an FT-IR Spectrometer Shimadzu IRAffinity-1 using pellets in KBr in the frequency range of 400–4000 cm^{-1}.

2.4. Biocide loading

Two methods were used to incorporate the biocide onto the siliceous materials: batch adsorption and incipient wetness.

2.4.1. Batch adsorption

SBA-15 and MCF samples were added to an aqueous solution of the biocide (concentration 200 mg/mL). The resulting suspensions (10 mg solid/mL liquid) were mechanically stirred in a water bath shaker (SHZ-88) at 25 °C until equilibrium was achieved. The mesoporous materials with the adsorbed biocide were separated from the remnant solution by filtration and dried at room temperature. The samples were named SBA15/bio and MCF/bio. The equilibrium concentration of each solution was determined by UV–vis spectroscopy at 274 nm (Perkin Elmer lambda 35 equipment).

2.4.2. Impregnation by incipient wetness

The biocide was added dropwise to the sample until total wetting of the solid. The impregnated sample was dried at room temperature. The resulting solids were named SBAimpreg and MCFimpreg.

2.5. Coating sample preparation

To investigate the antifungal effectiveness of the adsorbed biocide, three series of acrylic coating samples differing in the type and amount of biocide (SBA-15bio, MCFbio or liquid commercial biocide mixture) were prepared. Table 1 shows the compositional percentages corresponding to the three sets of the prepared coatings.

In order to get thin coating films of the different latex formulations, glass and gypsum surfaces were painted. For the A, B, C and D series, the prepared coatings were applied on one side of a glass surface (19 cm^2) using a film applicator (film thickness: 150 μm) and dried at 30 °C for 7 days. For D series, the commercial latex was used. The film thickness homogeneity throughout the coated area was achieved by using standardized film extenders. For obtaining the samples required for the long-term testing in controlled environmental conditions (B3-L, B6-L and control-L series), the film samples were prepared in the same way but using gypsum surfaces of 77 cm^2 as support.

2.6. Antifungal activity

To evaluate the bio-resistance of elaborated paints, the ASTM D5590 standard procedure based on a four-week assay was followed [30]. This test allows a rapid assessment of the formulation resistance to fungal growth. The glass-painted substrates were placed in Petri dishes containing malt extract agar culture medium (MEA) and then inoculated with the same volume of a spore suspension (10^5 spores / mL). The inoculum concentration used was adjusted by means of a Neubauer chamber, and the plates were incubated for four weeks at

Table 1
Coating classification according to the amount and type of biocide incorporated.

Coating	Aggregate	Percentage (w/w) of biocide in paint
A0	SBA-15	0
A1	SBA/bio	0.4
A2	SBA/bio	1.1
A3	SBA/bio	2
A4	SBAimpreg	2
B0	MCF	0
B1	MCF/bio	0.4
B2	MCF/bio	1.1
B3	MCF/bio	2
B4	MCFimpreg	1.3
B5	MCFimpreg	1.5
B6	MCFimpreg	2
C	Biocide-free	0
C1	Pure biocide	0.4
C2	Pure biocide	1.1
C3	Pure biocide	2
C4	Pure biocide	1.3
C5	Pure biocide	1.5
D	Pure biocide (commercial paint)	2

28 °C. The fungus employed was *Alternaria alternata*. The qualification according to the standard was done using a reference scale that considers the superficial growth (in terms of covered surface/total surface) as: 0 null (0%), 1 scarce (< 10%), 2 mild (10%–30%), 3 moderate (30%–60%) and 4 abundant (60%–100%).

In a next stage, paints with a null development of the inoculated strains were selected to perform a long-term test. Gypsum substrates were placed in an environmental chamber with controlled relative humidity for 9 months, following a methodology similar to the BS 3900 standard [31]. Relative humidity and temperature were regulated inside the chamber at 99% and 21 ± 1 °C, respectively. The painted plates were inoculated with the same volume of a spore suspension (10^4/mL) of the selected strains: *Aspergillus fumigatus, Alternaria alternata and Chaetomium globosum*. At the end of the test, observations were made directly, using a magnifying glass, and photographic images were taken.

3. Results and discussion

3.1. Characterization of the siliceous solids

SEM images of the original mesoporous silicas are shown in Fig. 1. From the image of SBA-15 (Fig. 1.a), it can be seen that the ordered silica consists of many rope-like domains with relatively uniform sizes, 1 μm in diameter and 14–16 μm in length, conforming small cylinders that are aggregated into wheat-like macrostructures. On the contrary, in the starting MCF sample the analysis reveals a distinct geometry consisting of spherical particles about 4–6 μm in size (Fig. 1.b).

TEM images confirmed the typical structure of both materials. For the SBA-15, one-dimensional ordered channels and two-dimensional hexagonal structure (p6mm) are observed (Fig. 1.c). In contrast, the MCF image shows oval-shaped cells, characteristic of this disordered structure (Fig. 1.d).

3.2. Biocide loading

3.2.1. Batch adsorption

In this case, from the remnant adsorbate concentration in the liquid phase (determined by UV), the percentage of adsorbed biocide onto the materials was calculated, resulting in 18 wt.% for the SBA-15 and 27 wt.% for the MCF (taking the biocide amount present in the initial solution as 100 wt.%). The samples were analyzed by FTIR before and after biocide adsorption (Fig. 2.a for the SBA/bio and Fig. 2.b for the MCF/bio). It can be seen that the characteristic bands of

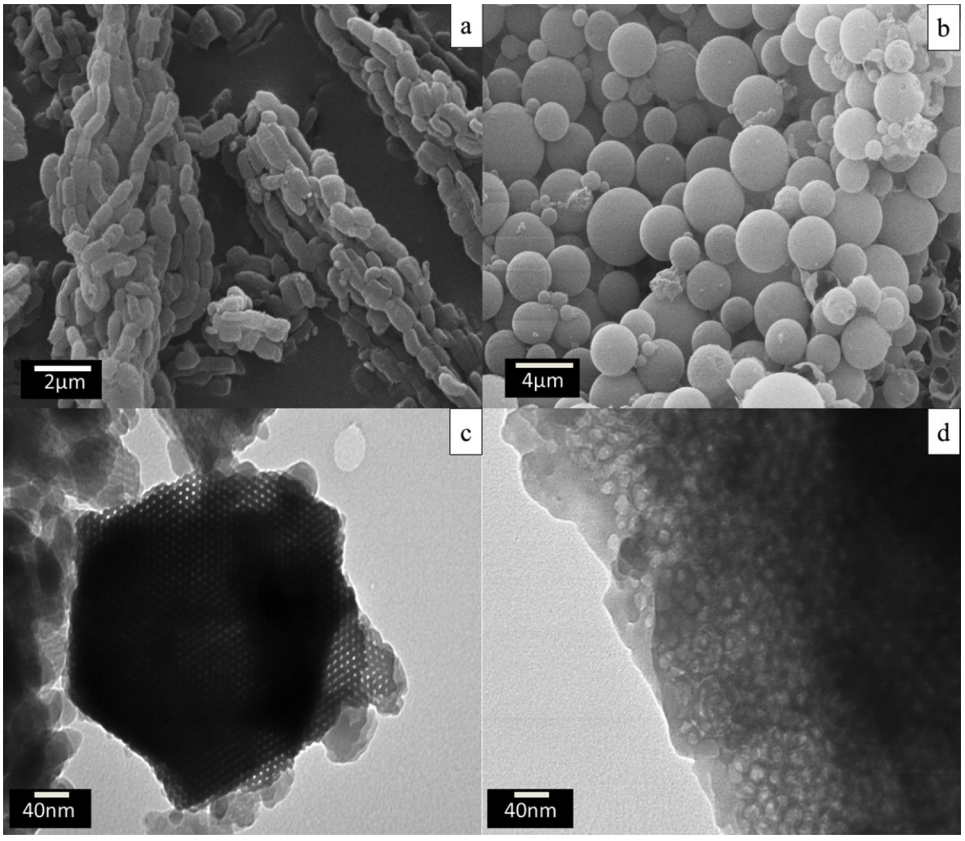


Fig. 1. SEM images of the original silicas SBA-15 (a) and MCF (b). TEM images of SBA-15 (c) and MCF (d).

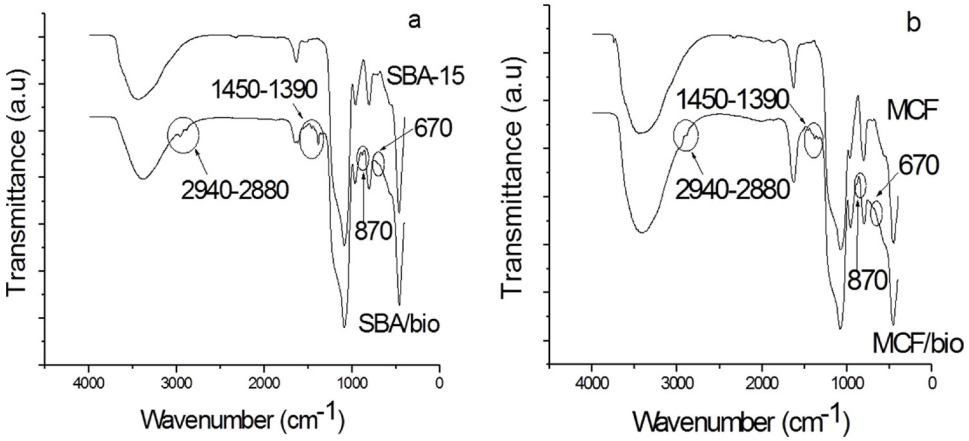


Fig. 2. FTIR spectra of SBA-15 (a) and MCF (b) before and after biocide adsorption.

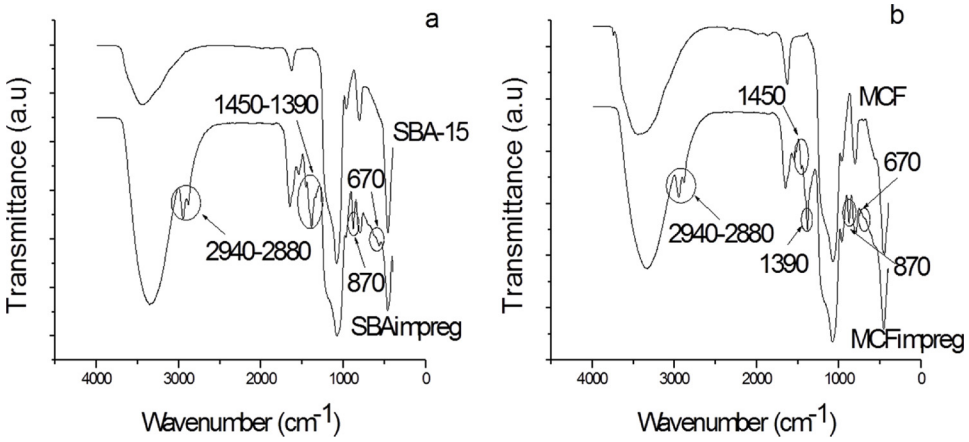
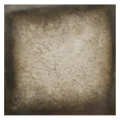
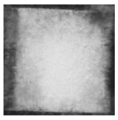
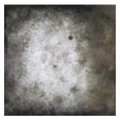


Fig. 3. FTIR spectra of SBA-15 (a) and MCF (b) before and after biocide impregnation.

Table 2
Paint bio-resistance assay against *A. alternate* (first part).

A0 Paint + SBA-15  Qualification: 4	A1 Paint + SBA/ bio (0.4% w/w)  Qualification: 3	A2 Paint + SBA /bio (1.1% w/w)  Qualification: 3	A3 Paint + SBA /bio (2% w/w)  Qualification: 3
B0 Paint + MCF  Qualification: 4	B1 Paint + MCF/bio (0.4% w/w)  Qualification: 3	B2 Paint + MCF/bio (1.1% w/w)  Qualification: 3	B3 Paint + MCF/bio (2% w/w)  Qualification: 0
C0 Paint free of biocide  Qualification: 4	C1 Paint + biocide (0.4% w/w)  Qualification: 4	C2 Paint + biocide (1.1% w/w)  Qualification: 4	C3 Paint + biocide (2% w/w)  Qualification: 3

isothiazolinones are present in the loaded materials, i.e., the biocide retains its chemical integrity after being adsorbed (bands appearing at 2940, 2890 and 886 cm^{-1} assigned to the C—H stretch vibration, bands in the range of 1450 − 1390 cm^{-1} attributable to the C—H flexion and the band corresponding to the stretching of C—Cl at 600 cm^{-1} [32].

3.2.2. Impregnation loading

By using this methodology, the material pores were completely

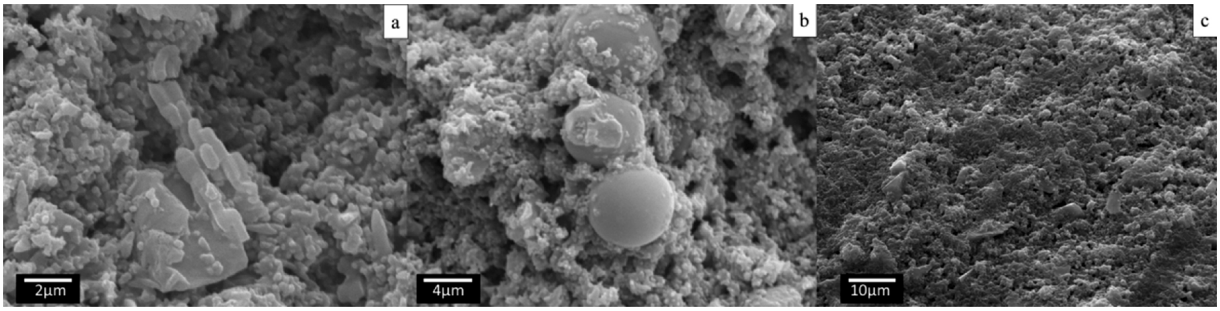
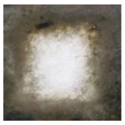
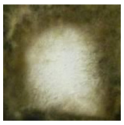


Fig. 4. SEM images of selected paint films: (a) sample A1 (containing SBA-15), (b) sample B1 (containing MCF), and (c) sample C (biocide-free).

Table 3
Paint bio-resistance assay against *A. alternate* (second part).

A4 Paint + SBAimpreg (2% w/w)	B4 Paint + MCFimpreg (1.3% w/w)	B5 Paint + MCFimpreg (1.5% w/w)	B6 Paint + MCFimpreg (2% w/w)
			
Qualification: 4	Qualification: 3	Qualification: 3	Qualification: 0
C Paint free of biocide	C4 Paint + biocide (1.3% w/w)	C5 Paint + biocide (1.5% w/w)	D Commercial paint
			
Qualification: 4	Qualification: 3	Qualification: 3	Qualification:4

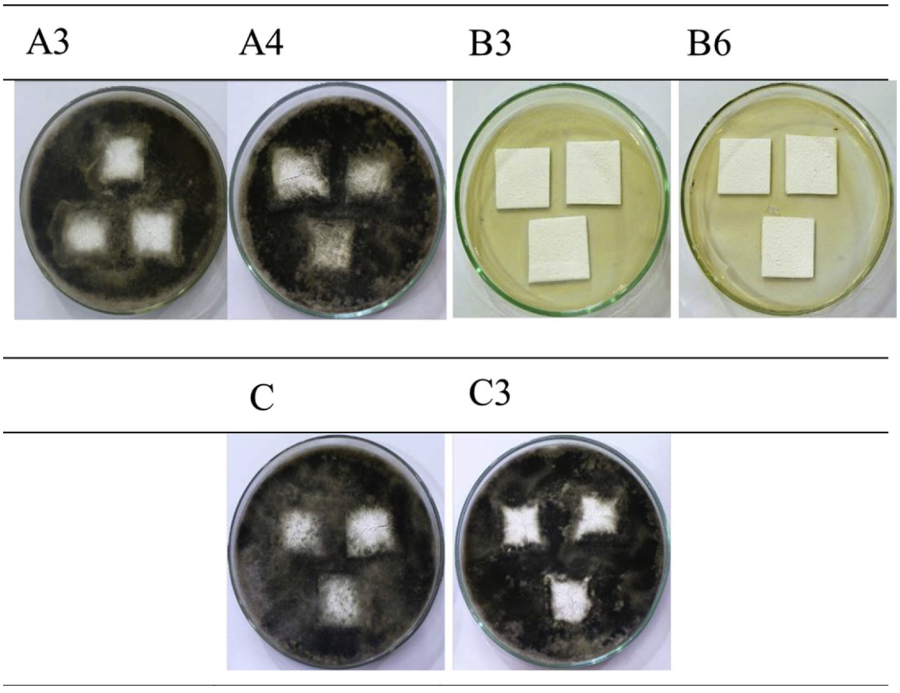


Fig. 5. Plates with samples of paints inoculated with *A. alternata*.

filled with a known biocide amount. After the impregnation process, the materials contained 2.8 g of biocide/g of solid and 3.6 g of biocide/g of solid for SBA-15 and MCF respectively. The impregnated amount of CMIT/MIT in the MCF was greater than in the SBA-15, due to the larger size and pore volume of MCF samples compared to SBA-15. When the impregnated solids were characterized by FTIR and the spectra obtained were compared with those corresponding to the non-impregnated materials, the characteristic bands of isothiazolinones appeared in the loaded samples (Fig. 3), as was detailed before for the batch adsorption sample analysis.

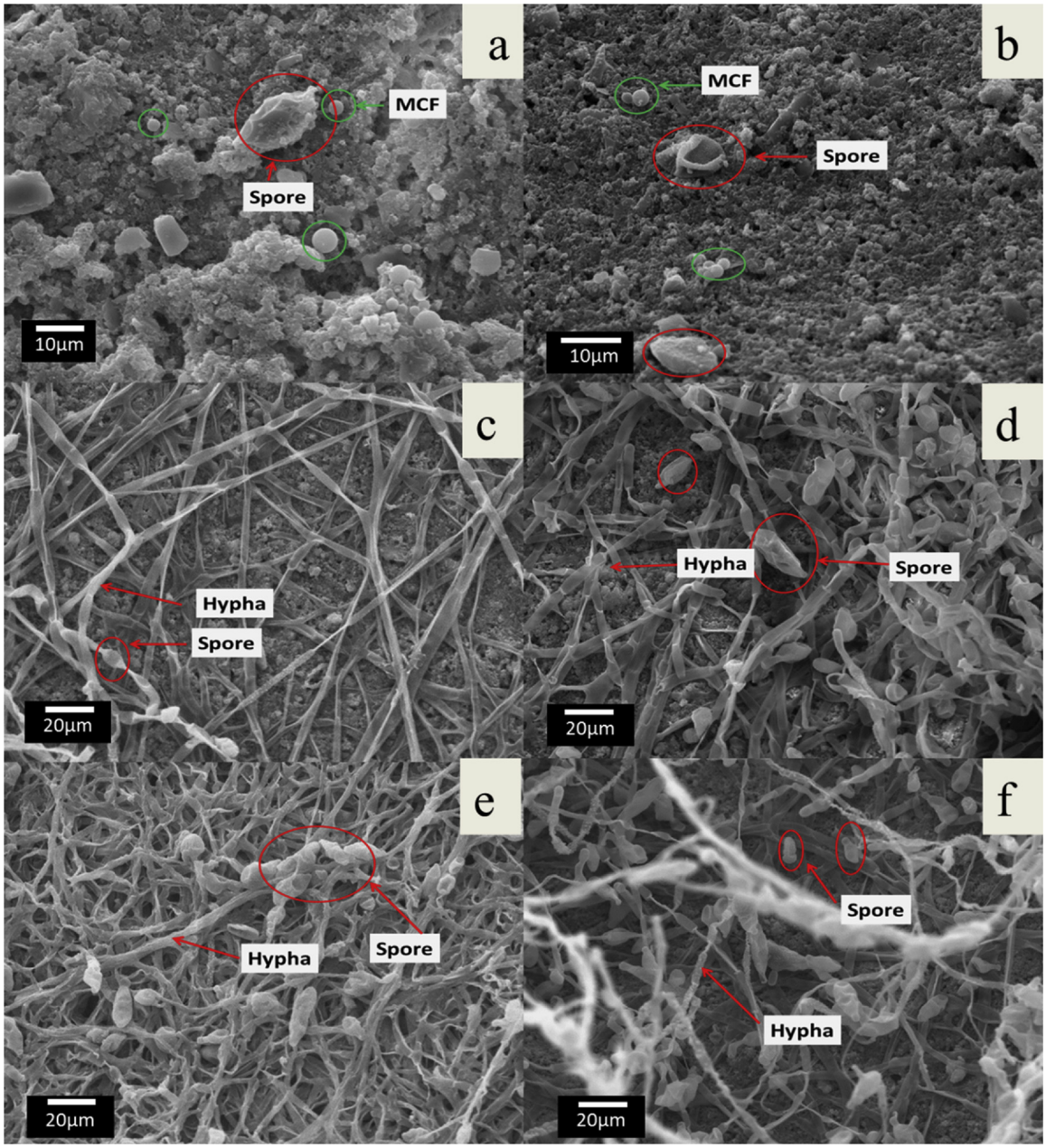


Fig. 6. Paint images taken after ASTM D5590 standard evaluation. B3 (a), B6 (b), A3 (c), A4 (d), C3 (e), C (f).

3.3. SEM analysis of the dry films

The dry paint films obtained using the different coating formulations described in Table 2 were characterized by SEM. Fig. 4 shows the SEM images of film samples prepared from three paint formulations selected from Table 1. Fig. 4.a shows the amorphous material that constitutes the film surface obtained from the coating A1, free of biocide. In Fig. 4.b, corresponding to the coating B1, it is possible to identify the MCF spherical particles spread onto the surface, and in Fig. 4.c, the rod-like particles characteristic of the SBA-15 contained in the film coating C. It should be noted that abundant MCF particles were clearly observed on the film surface of B1 sample, while SBA-15 particles were hardly detected in A1 sample. The lower density of the MCF compared to that corresponding to the SBA-15 would cause this difference in particle location, resulting in a more superficial biocide concentration when the dry paint film was prepared by adding MCF loaded particles.

3.4. Biocidal activity

According to ASTM D5590 standard [30], the antifungal activity qualification corresponding to the studied paints is presented in Tables 2 and 3. From these results, it can be observed that the paints formulated with SBA-15 and MCF free of biocide allowed a fungal growth qualified as abundant. The same result was obtained for the control paint without biocide, confirming that the silica matrices and the prepared paint do not have inhibitory properties themselves (Table 2, 1st column, samples A_0, B_0, C_0). As expected, by increasing the concentration of the pure and encapsulated biocide in the different samples, an increase in the inhibitory activity and a decrease in the growth of fungal mycelium were generally observed in all the paint films (Tables 2 and 3).

Fig. 5 shows photographic images of the Petri dishes used in the biocidal evaluation of paints A3, A4, B3, B6 and the control. These Petri dish images were taken at the end of the test, before removing the

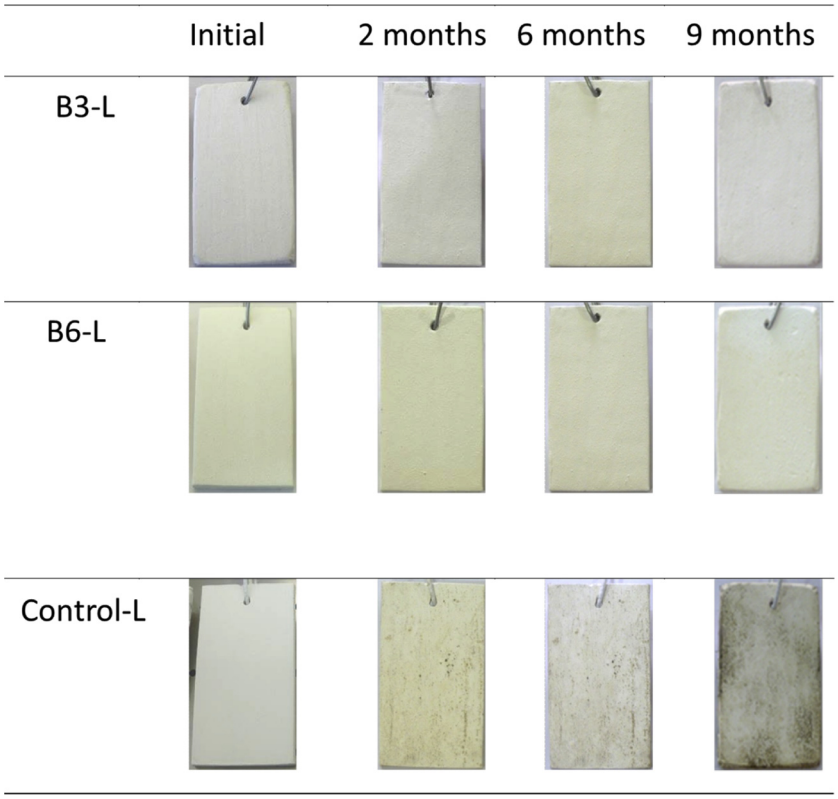


Fig. 7. Samples submitted to the deterioration paint test carried out in the environmental chamber.

coated samples. It can be observed, in agreement with the results detailed in Tables 2 and 3, that formulations B3 and B6 showed the best results without fungal growth. It is important to note that in these samples growth inhibition was not limited to the surface of the painted substrate, being extended to the entire surface of the Petri dish. On the other hand, an abundant fungal growth on Petri dish surface corresponding to the other formulations could be observed. The SEM images of the paints containing 2 wt.% of biocide and the paint without biocide after antifungal activity test are shown in Fig. 6. In Fig. 6.a and b, no germinated spores (there are no hyphae) can be seen in the paints containing MCF/bio and MCFimpreg, respectively [8,9,33,34], indicating total fungus inhibition. Additionally, the MCF spheres can be clearly detected. Fig. 6.c and d show the SEM images corresponding to films A3 and A4, with SBA/bio and SBAimpreg, respectively. In both images, spores and incipient fungal mycelium are present, spreading their hyphae almost on the entire paint surface. On the other hand, the paint with liquid biocide (Fig. 6.e) and the paint without biocide (Fig. 6.f) show a greater and abundant fungal development than the paints with SBA-15.

It can be noted that B3 and B6 were the most efficient formulations for Aa inhibition, regardless of the method used for the incorporation of the biocide. On this basis, paints B3 and B6 were selected to perform the long-term test in a regulated, humidity-controlled environmental chamber.

Fig. 7 shows the panels exposed in the environmental chamber at different times. Paints B3 and B6 presented an optimum efficiency, with a null development of the inoculated strains, showing total growth inhibition. On the other hand, the control paint without the inclusion of biocide in its formulation showed abundant fungus development from the second month. These results reveal the ability of the MCF with encapsulated biocide (MCF/bio and MCFimpreg) to protect the dry film of paint in the extreme conditions of ˜100% relative humidity. This behavior can be due to the shape and pore size characteristic of the MCF. Compared to SBA-15, the textural properties of MCF make this material the best matrix for getting the maximum biocide amount released in a controlled way. Additionally, as was mentioned earlier, the low density of the MCF promotes a silica particle location closer to the dry paint surface, favoring the presence of biocide molecules on the top surface, enhancing the biocide molecule exposure and consequently, the biocidal activity. The biocidal activity measured showed that the MCF structure could help to maintain the biocide minimum inhibitory concentration over time and under the wet conditions imposed in the long-term test.

4. Conclusions

Different paint formulations where the biocidal action was exerted by a liquid biocide supported on MCF and SBA-15 mesoporous silicas were prepared. The two silica structures employed as supports showed a clear biocidal activity against all the microorganisms used. For the two supported biocide types prepared, the testing of the formulated paints against *Alternaria alternate* indicates an increase of the inhibitory activity in the paint films and a delayed development of the fungal mycelium as the encapsulated biocide concentration increased. Regarding the inhibitory action, paints containing MCF encapsulated biocide showed the best inhibitory properties, indicating that the disordered MCF matrix possesses a suitable release capacity for the inhibition of *Alternaria alternata*.

In the long-term environmentally controlled test, the paint formulation containing 2 wt.% of biocide supported in MCF showed optimum efficiency. Null development of the different inoculated strains was observed, showing total growth inhibition and no film deterioration after 9 months of exposure. The control paint without the inclusion of biocide in its formulation showed abundant growth from the second month, thus revealing the ability of the MCF matrix to elongate the commercial liquid biocide action by releasing it in a controlled manner. Consequently, the useful life of the consolidated paint film was also lengthened and the environmental human risks were reduced by

improving the quality of the products.

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