

Antifungal and Photocatalytic Activity of Smart Paint Containing Porous Microspheres of TiO₂

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In this study, porous microspheres of TiO₂ (μ TiO₂) were synthesized, characterized and incorporated into an acrylic paint formulation to obtain a photocatalytically active paint. In a novel approach, the antifungal properties of the μ TiO₂ paint were evaluated using *Monascus ruber* as the representative microorganism and compared to those of a photocatalyst-free paint. The photocatalytic activity of paint films was determined by methylene blue (MB) degradation under real conditions of application. High photocatalytic and antifungal activity was observed, with the microorganism culture showing the formation of growth inhibition halos, typical of materials that produce biocides that diffuse into the culture medium.

Keywords: Active paint, fungicide, photoactivity, titanium dioxide, *Monascus ruber*.

1. Introduction

Photocatalytic paints are self-cleaning, since undesirable substances on the surface are removed through the simple incidence of light¹. This photocatalytic activity, however, is not selective and in addition to pollutants the polymer paint matrix can be degraded^{1,2}. Most research has been focused on photocatalytic paints formulated with anatase nanoparticles, due to their high photocatalytic activity³⁻⁸. However, nanoparticles, which have a high surface area, when homogeneously distributed in the film and under a light source, tend to rapidly degrade the paint film around them, causing photochalking^{1,9}.

Therefore, the stability and the photocatalytic activity of paint films are two important aspects to consider in the development of an effective photocatalytic paint. It is necessary to achieve a balance between these two aspects, so that the paint is efficient without accelerating the autodegradation.

Different strategies have been proposed to improve the stability of acrylic photocatalytic paints^{10,11}. One way to control the photocatalytic effect of titanium dioxide is to modify the particle morphology and size¹²⁻¹⁶. Among the various TiO₂ morphologies reported, the mesoporous TiO₂ spheres are notable for their high surface area and they allow a greater absorption of light due to a high crystallinity^{17,18}. Recently, porous TiO₂ microspheres with high specific surface area have been synthesized and applied in photovoltaic^{19,20} and photocatalytic^{21,22} technologies.

Hierarchical structures in the form of mesoporous TiO₂ microspheres have been added to acrylic paint formulations to obtain paints with photocatalytic properties and greater

stability in relation to photocatalytic paint containing commercial TiO₂ nanoparticles¹. The advantage of using a photocatalyst with high surface area, but with a diameter in the micrometric order, is the much lower contact of the active area with the paint surface, which reduces the degradation of the binder by photocatalysis^{1,23}. Only tests to determine the photocatalytic activity and stability under severe aging conditions have been reported for the use of mesoporous TiO₂ microspheres in paint formulations¹. However, it is also important to ascertain the behavior of smart paints under the conditions of the environments in which they will be applied.

Most previous studies evaluated the TiO₂ antimicrobial performance with bacteria such as *Escherichia coli*, commonly applied as the test microbe. The photocatalytic sensitivity of fungi was shown to be much weaker than bacteria due to their structural differences, particularly in the complexity and thickness of the cell envelope²⁴. Nevertheless, there are still no concentrated studies focusing on the photocatalytic disinfection of fungi.

Fungi are generally considered the principal microflora on painted surfaces and they can enhance the paint degradation^{25,26}. Moreover, they can live on the surface dirt or utilize the underlying substrate, causing allergies, respiratory symptoms, asthma, and serious health effects in people with suppressed immune systems²⁷. Although several authors have evaluated the antifungal character of photocatalytic paints using *Aspergillus niger* as an environmental model, along with non-pathogen molds^{8,28,29}, these fungal species were not found on deteriorated paint surfaces and, therefore, they are not considered as paint degraders²⁵. A list of fungi and phototrophs detected on paint films was reported by Allsopp et al.³⁰, and *Monascus* was one of the genera found.

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The main objective of this study was to evaluate the antifungal and photocatalytic properties of acrylic paints containing novel porous microspheres of TiO_2 . To the best of our knowledge, this is the first report of the antifungal properties of paint containing mesoporous microspheres of TiO_2 evaluated using *Monascus ruber* as the representative microorganism. It is also the first time that results for the photocatalytic activity of paint containing μTiO_2 have been obtained under real conditions of application in external (sunlight) and internal (UV light) environments. These important results demonstrate the applicability of photocatalytic paint containing μTiO_2 and therefore represent a significant advance in the development of paints with photocatalytic and antifungal properties.

2. Material and Methods

The methylene blue dye (MB) was purchased from Lafan (Brazil). The formulated commercial acrylic-water base was supplied by a paint company (Anjo Tintas, Brazil) and contained water (42 wt.%), extenders (15 wt.%), binder slurry (38 wt.%) and additive slurry (5 wt.%).

2.1 Synthesis of TiO_2 microspheres

The titanium dioxide microspheres (μTiO_2) were prepared using the methodology which combines a sol-gel method, a solvothermal treatment and a calcination process¹. In brief, 3.9 g of hexadecylamine (HDA, 90.0%, Sigma-Aldrich) were mixed in 400 mL of ethanol absolute (99.8%, Neon) and 1.6 mL of 0.1 M KCl (A.R., Nuclear) solution. Then, 9.0 mL of titanium (IV) isopropoxide (TIP, 97.0%, Sigma-Aldrich) was added dropwise under intense stirring, and the obtained suspension was allowed to stand for 24 h. In sequence, the precipitate was filtered and washed with ethanol, thereby obtaining the amorphous TiO_2 microspheres. The solvothermal treatment was carried out at 130 °C for 16 h in a Teflon-lined autoclave (110 mL) by adding 3.2 g of amorphous TiO_2 microspheres to a mixture of 20 mL of distilled water and 40 mL of ethanol. The obtained precipitate was filtered, washed with ethanol absolute and dried at room temperature. Lastly, the TiO_2 microspheres (μTiO_2) were calcined at 500 °C for 2 h under air atmosphere.

2.2 Preparation of paint films

The formulation of the photocatalytic paint was obtained by adding 10 wt.% μTiO_2 to an acrylic/water-based paint. The photocatalyst was added to the paint using a high-speed disperser with a high shear impeller (1700 rpm) for 1 h.

Cement samples of approximately 4 cm² were prepared. The surfaces were previously sanded and covered with two layers of paint. The drying time between each layer was 1 h and the final drying time was 24 h.

2.3 Characterization

The morphology of μTiO_2 was determined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) using a JEOL JSM-6390LV and JEOL JEM-1011 TEM microscope, respectively. For the SEM analysis, the powder samples were adhered to a metallic support with carbon tape and covered with gold. Prior to the TEM analysis, the samples were ultrasonically dispersed in ethanol as a solvent and then dried over a carbon grid.

The particle size distribution was obtained through dynamic light scattering (DLS) analysis using a particle size analyzer Nano-Flex S3000/S3500 Series Microtrac®. The samples were ultrasonically dispersed in distilled water (10 g L⁻¹) for 1 h. The refractive index used to detect the TiO_2 particles in the analysis was 2.5³¹.

The morphology of the paint film surface was also determined by SEM analysis using the same equipment and, simultaneously, a semi-quantitative elemental chemical analysis was performed by energy-dispersive X-ray spectroscopy (EDX). As previously described, the paint films were also adhered to a metallic support with carbon tape and covered with gold.

Finally, the dry solids content of the paint films with and without μTiO_2 was determined gravimetrically after the evaporation of all volatile material in an oven at 60 °C for 24 h.

2.4 Antifungal test

The cement samples were placed in contact with the microorganisms *Monascus ruber*, since this fungal species is frequently found on degraded paint surfaces²⁵. The inoculation was performed by the pour plate method in petri dishes using the appropriate growth medium (potato dextrose agar - PDA)³². After inoculation, the cement sample coated with photocatalytic paint and the cement sample containing a paint film without photocatalyst were placed in different petri dishes. Samples were incubated at 30 °C for 24 h and subsequently exposed to visible light for 48 h. Control experiments under dark conditions were also performed and no antifungal effect was observed.

2.5 Photocatalytic tests

The cement samples coated with paint films received two layers of aqueous MB solution (1 g L⁻¹). They were then dried and exposed to UVC light (8 W) or sunlight (geographic coordinates: 27°35.8' S; 48°32.95' W), from 10:00 to 16:00 (December 12th, 2017 to January 31st, 2018). At regular intervals, samples were photographed to assess the change in the dye coloration.

3. Results and Discussion

3.1 Antifungal test

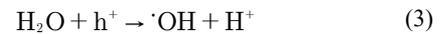
The antifungal activity of titanium dioxide has been studied extensively³³⁻³⁶. However, most previous studies carried out with immobilized photocatalysts involve surfaces coated with TiO₂ films³⁷⁻⁴⁰ and only a few authors report the antifungal activity of photocatalytic paint^{8,26,41,42}. To the best of our knowledge, this is the first report of the antifungal properties of paint containing mesoporous microspheres of TiO₂ evaluated using *Monascus ruber* as the representative microorganism.

According to Figure 1(a) and 1(c), an inhibition halo was clearly formed in the case of the samples coated with the photocatalytic paint and placed under visible light. This result could be attributed to the formation of oxidizing radicals, such as •OH or peroxides, capable of migrating to the culture medium and preventing the growth of the microorganisms, not only on the sample but also around it. In contrast, in the case of the paint without the photocatalyst, Figure 1(b), the inhibition of fungal growth was apparent only on top of the sample. Although the paint containing TiO₂ P25 has shown a more evident inhibition halo, the presence of these nanoparticles provokes a fast degradation of the paint film around them^{1,9}.

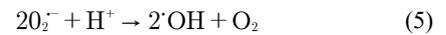
The mechanisms for the primary events occurring at the catalyst surface have been well described⁴³. The irradiation of TiO₂ with photons of energy equal or greater than its band-gap (Eg ~ 3.2 eV) result in the promotion of electrons (e⁻) from the valence band to produce holes (h⁺) at the conduction band of the particle (Eq 1):



At the TiO₂ particle surface, the holes (h⁺) react with surface hydroxyl groups (OH⁻) and adsorb H₂O, to form •OH radicals (Eq 2 and 3).



In the absence of electron acceptors, the electron-hole recombination is possible. The presence of oxygen prevents this recombination by trapping electrons through the formation of superoxide ions (Eq. 4). The final product of the reduction may also be a radical (Eq. 5).



The reactive oxygen species (ROS), such as hydroxyl radical, superoxide anions and hydrogen peroxide, generated on the surface, are considered responsible for the inactivation of the microorganism (Eq. 6)



According to our studies, the mechanism of cell death or inhibition of microorganism growth was still not elucidated. The most accepted mechanism for microorganism inactivation by ROS indicates that the •OH radicals or peroxides would initially promote the oxidation of the out membrane leading to a disorder in the cell permeability, even decomposition of the cell walls, and further oxidation of intracellular components that inhibit the cell respiration. The loss of the cell integrity could finally lead to the cell death. Another suggestion is that the •OH radicals are not the only species responsible for the biocide effect, i.e., the co-operative action can also promote peroxidation of phospholipid components of the lipid membrane, responsible for essential functions as respiratory activity and cell death.^{24,44}

It is important to note that the acrylic paint used in this study contains a small percentage of fungicide (around 0.2%) in its formulation. However, fungicidal activity in the culture medium was not observed for the non-photocatalytic paint sample and occurred only with the paint containing the μTiO₂. This is due to the formation of oxidant species on the photocatalyst surface, activated by light.

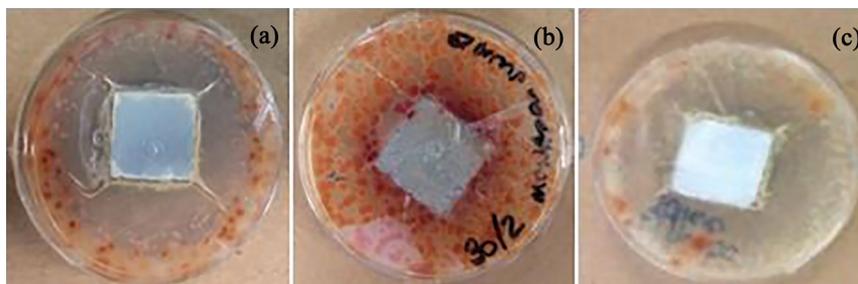


Figure 1. Paint films: (a) with 10% μTiO₂; (b) without TiO₂ and (c) with 5% TiO₂ P25, after the fungal test (*Monascus ruber*) under visible light.

Thus, the photoactivity is related to the inhibition of the growth of the microorganisms by the action of radicals generated by the TiO_2 microspheres under light irradiation.

3.2 Photocatalytic tests

The results for the methylene blue dye decolorization tests using the cement samples coated with photocatalytic paint (μTiO_2) under UVC light and sunlight are shown in Figure 2. It can be seen from Figure 2(a) that the MB decolorization under UVC light is fast, as expected.

After the initial color change, in which the characteristic blue color of the dye is removed, there are still components of the dye molecule adhered to the paint surface, giving a yellowish coloration, as also observed by Galenda et al.⁴⁵ for commercial photocatalytic paints. According to Figure 2(b), the MB decolorization also occurs under sunlight. However, it is apparently slower than the process observed under UVC light, since the μTiO_2 is more active under UVC light. Some authors have reported the degradation of dyes in photocatalytic paints containing nanoparticles and observed the removal of color over time^{9,46}.

On the other hand, in addition to the degradation of the dye present on the paint surface, interaction between the

mesoporous microspheres and the polymer matrix of the paint may occur. A scheme of the degradation of the acrylic paint film containing the mesoporous TiO_2 microspheres produced in this study is shown in Figure 3. This mechanism consists of two stages of degradation after constant irradiation of the intact film by a light source: the initial photodegradation of the paint film and subsequently the exposure of the μTiO_2 . When the microspheres are exposed, pollutants and the irradiation can access the surface of the pores present within the particles, allowing the photocatalytic activity to be maintained or increased during the light exposure.

Particle size and surface area clearly play an important role in the dispersion and polymer-titanium dioxide interactions⁴⁷. This is due to the fact that nanoparticles, such as TiO_2 P25 (~25 nm), have a large outer surface area ($52.7 \text{ m}^2 \text{ g}^{-1}$), being generally characterized as non-porous^{1,48}. Thus, the μTiO_2 in this study, due to the micrometric dimensions and mesoporosity, has a smaller outer surface area, most of the surface area of this photocatalyst being located inside the mesopores. Therefore, the area effectively in contact with the polymer matrix of the paint is reduced, increasing the stability of the photocatalytic paint obtained with this photocatalyst (μTiO_2), as verified by Amorim et al.¹.

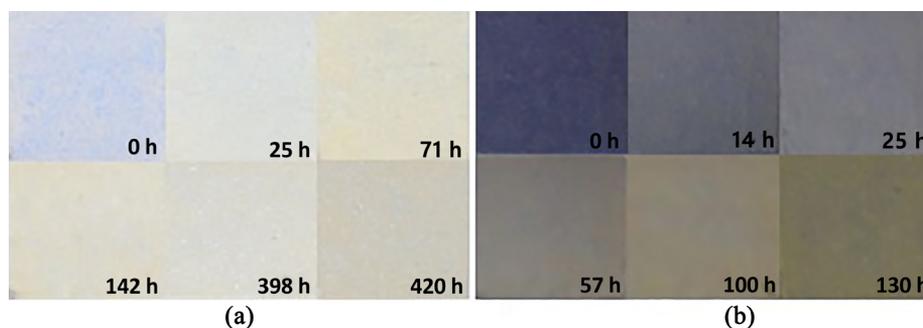


Figure 2. Decolorization of MB using photocatalytic paint (10% μTiO_2) under (a) UVC and (b) sunlight.

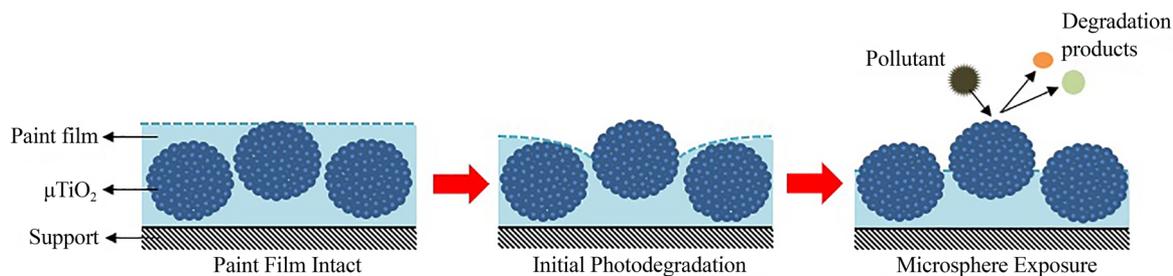


Figure 3. Scheme proposed for interactions in a paint film containing mesoporous TiO_2 microspheres.

3.3 Characterization

SEM and TEM analyses (Figure 4(a) and (b)) were performed to obtain high resolution images of the particle morphology of the μTiO_2 . The particles show a spherical shape and micrometric size. Also, the particles surface is rough and irregular (Figure 4(b)). This porous structure is formed due to the elimination of hexadecylamine (driving agent with boiling point of 330 °C) in the calcination step at 500 °C, causing the rupture of the microspheres ^{1,19}.

According to the porous structure analysis, the average pore size of the μTiO_2 was 13 nm ¹, which is typical for mesoporous materials (2-50 nm) according to IUPAC ²⁴. The N_2 adsorption-desorption isotherm at 77 K is classified as a type IV isotherm with a hysteresis H2 loop ¹, and according to IUPAC classification this is characteristic of mesoporous materials ⁴⁹.

The particle size distribution curve for the μTiO_2 is shown in Figure 5. Titanium microspheres have a uniform particle size distribution in the range of 600 to 1300 nm

with a maximum peak at 945 nm (which is the effective diameter). This result confirms the micrometric dimensions observed in the SEM and TEM images (Figs. 5(a) and (b)).

In order to evaluate the morphology and to identify differences related to the addition of μTiO_2 in the paint formulation, the surfaces of the paint films were analyzed by scanning electron microscopy and the images are presented in Figure 6. At the base of the paint film, Figure 6(a), large insoluble particles can be seen and these are attributed to other components, such as extenders or additives ^{1,50}. The paint film with μTiO_2 , Figure 6(b), shows the presence of the microspheres on the paint surface (some highlighted by circles, which is not observed in Figure 6(a)). The μTiO_2 particles are partly exposed on the surface and some are agglomerated. The importance of good dispersion is characterized by the need to minimize contact between the microspheres and the polymer matrix of the paint and consequently reduce the degradation, according to the mechanism proposed in Figure 3.

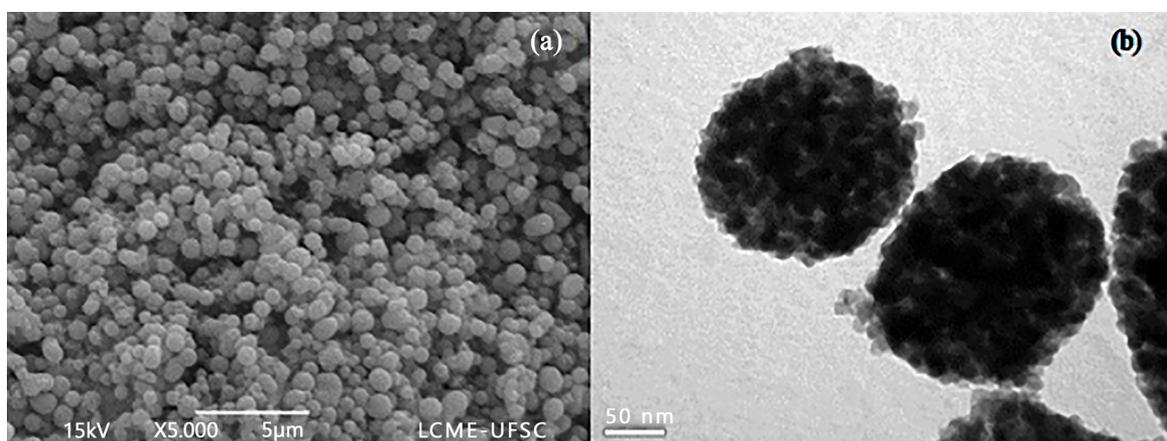


Figure 4. (a) SEM and (b) TEM images of the μTiO_2 .

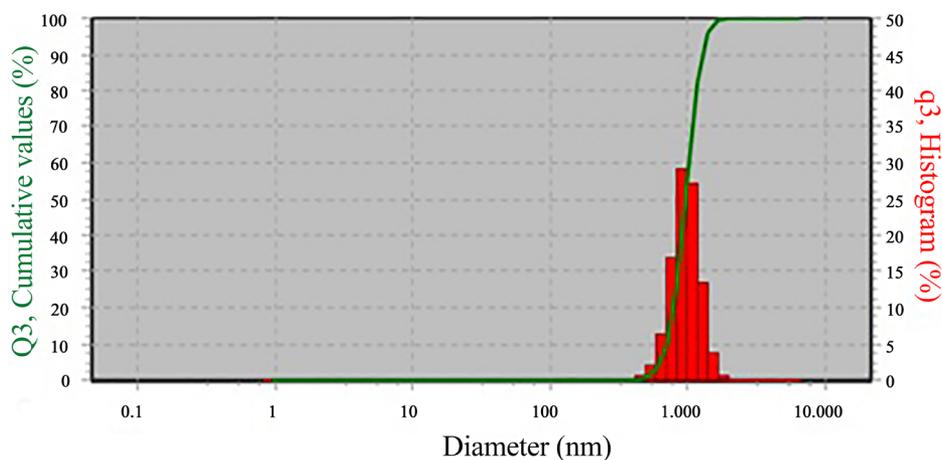


Figure 5. Particle size distribution of μTiO_2 .

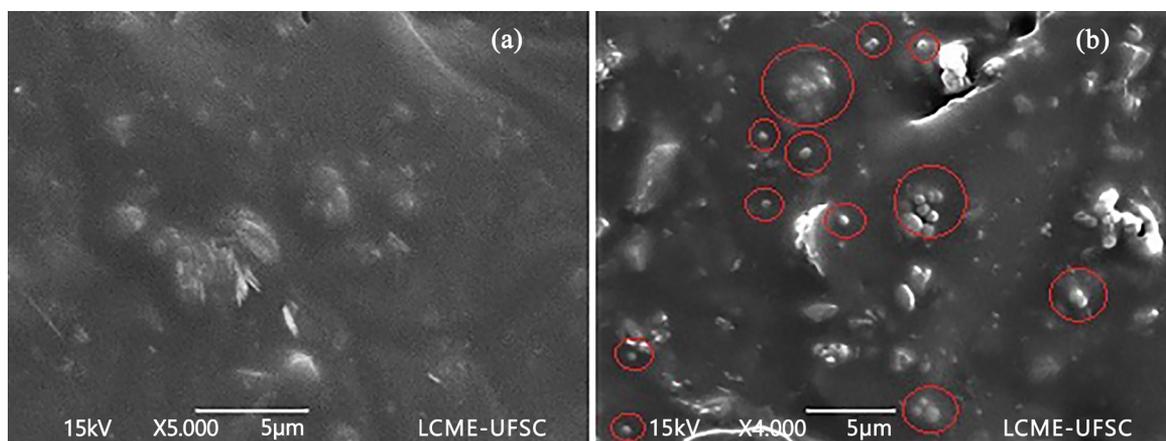


Figure 6. SEM images of the paint (a) without and (b) with μTiO_2 .

Table 1. Semi-quantitative results for the chemical elements and values for the total dry solids content in paint samples with and without μTiO_2 .

	Dry solids (wt.%)	Elements (wt. %)						
		C	O	Mg	Al	Si	Ca	Ti
Paint base	36.34	73.29	18.02	0.28	2.17	2.06	4.18	-
Paint (+ μTiO_2)	44.21	66.40	20.34	0.27	1.66	2.47	4.40	4.46

The solids content of each paint was determined and the results are reported in Table 1. The final dry film is composed of the resin, extenders and additives present in the paint formulations. The percentage of dry solids in the paint (+ μTiO_2) increased by around 8 wt.%, which corresponds to the 10 wt.% of titanium dioxide microspheres initially added.

To confirm the presence of the titanium dioxide microspheres in the photocatalytic paint, semi-quantitative EDX analysis was performed and the results for the elemental composition are shown in Table 1. The paint containing μTiO_2 presented titanium as an additional element in its composition, in contrast to the paint base, which confirms the presence of the titanium dioxide in the formulation. However, the percentage was below the nominal value of 10 wt.%, indicating a non-uniform distribution of the TiO_2 microspheres in the film, as observed in the SEM image, Figure 6(b).

The durability of acrylic paint containing μTiO_2 , with photocatalytic properties, has been demonstrated in a previous study¹. Paint prepared with μTiO_2 was found to be more stable than paint containing TiO_2 P25 nanoparticles and exhibited degradation similar to that of a commercial paint containing TiO_2 rutile (non-catalytic pigment) under the same extreme conditions applied in the cyclic analysis¹. The use of TiO_2 with micrometric dimensions and a porous structure (Figure 5) can greatly reduce the contact area between the photocatalyst and the organic binder, leading to its enhanced durability. In addition, important results presented herein show, for the first time, the possibility of applying this smart paint containing mesoporous TiO_2 microspheres under real aging conditions to combat the accumulation of microorganisms and pollutants on surfaces.

4. Conclusions

This paper reports a study on the antifungal and photocatalytic activity of an acrylic paint containing synthesized TiO_2 microspheres. The fungicidal activity of the paint was verified through the production and release of oxidizing species in the culture medium. These species are responsible for preventing the growth of microorganisms (*Monascus ruber*) and consequently a characteristic inhibition halo is formed around the sample containing μTiO_2 . In addition to the fungicidal activity, the photocatalytic activity of the paint with μTiO_2 , under UVC and solar light, was evidenced from MB dye degradation over time.

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