MTLA 33 (2024) 102030

Contents lists available at ScienceDirect

Materialia

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Full Length Article

Environmentally friendly surface treatments used to avoid algal colonization on mortars

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ARTICLE INFO

Keywords:
Mortar
Biofilms
Biodeterioration
Thymol
Surface treatments

ABSTRACT

Biodeterioration is a major problem with construction materials. Presence of biofilm, biofouling, or biopatina, causes decomposition processes of the material both on its surface manifesting as undesirable aesthetic alterations as well as within the material. In this study, two environmentally friendly treatments were evaluated in an attempt to prevent the growth of phototrophic biofilms on mortar surfaces. Those surfaces were treated using a water-based solution with surfactants with and without thymol 1 %. The algaecide effect was evaluated, leaving a set of samples without treatment as a control of algae growth. The inoculum used in the tests was an algae community isolated from the mausoleum studied. Samples were inoculated with this community and they were incubated under controlled photoperiod and temperature conditions for 30, 60 and 120 days. For surfaces treatments stability assay, other mortars samples were inoculated 30, 60 and 90 days after surface treatments were applied. For surfaces studies were used stereoscopic microscopy, Environmental Scanning Electron Microscopy and epifluorescence microscopy, also surface contact angle and colour and bright were measured. Both treatments inhibited algal growth in mortar surfaces. We propose that these surface treatments would be potentially useful for cleaning and preventing phototrophic formation of biofilms on historic buildings.

1. Introduction

When considering the construction materials used since antiquity, one of those that appears as a cementitious composition material is mortar. Its use is known 2000 years ago by the analysis of the remains of this material left by ancient civilizations. This mixture of cement, sand and water is actually mainly used for finishing façades, sealing, joints, etc. All these applications will depend on the water-cement ratio of the mixture that is made [1]. Like all materials, mortar ages depending on the environment in which it was placed, and is concerned that all construction materials are able to be colonized by microorganisms [2]. The biological influence on its surface alteration and/or deterioration has been studied because material-microorganism interactions have aesthetic changes, impacting its durability; this process was defined as biodeterioration [3]. Another concept related with this process is bioreceptivity which is defined as the capability of material to favour microorganism emplace and development [4,5]. For mortars, it depends on environmental factors, such as surface pH compatibility, presence of necessary water and nutrients and atmospheric phenomena exposition [6]. Materials roughness promotes attachment, retention, and hence proliferation of microorganisms. In order to investigate the role of mortar roughness and porosity, the same research experiments were performed [7].

Some research studies consider that cyanobacteria and green algae are pioneer microorganisms that inhabit outdoor surfaces [8]. The major impact of algal biofilm colonization is caused by pigments produced by biofilm itself; this action promotes substrate chromatic changes which can alter the aesthetic appearance of façades surfaces and due to the biofilm absorbing atmospheric pollutants, they able to accumulate and to alter the surface too. It is also reported that biofilm drying-wetting cycles contribute to produced mechanical stresses on the material structure that trigger fragmentation and lost material by micro-decohesion (e.g., cracking, pits generation) [9]. Biodeterioration process on mortars by algal activity causes material damage that is

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https://doi.org/10.1016/j.mtla.2024.102030
Received 12 October 2023; Accepted 31 January 2024
Available online 1 February 2024

Table 1
Contact angle measurements of control and treated mortar surfaces.

Sample	Contact angle	Hydrophobicity
C-M4	0.0 ± 0.0	superhydrophilic
C-M6	0.0 ± 0.0	superhydrophilic
P-M4	40.6 ± 0.9	hydrophilic
P-M6	45.0 ± 0.8	hydrophilic
PT-M4	51.0 ± 0.8	hydrophilic
PT-M6	36.3 ± 0.9	hydrophilic

classified as chemical when its effects are due to enzymes and/or secondary metabolites which are produced by biofilm [8]. Taken together, these impacts compromise materials durability properties, including their mechanical resistance. Approximately 30 % of visible alteration on building materials is due to biodeterioration [10] and the cost in infrastructure maintenance and repair has been estimated at almost billions of dollars a year [11].

The applicability of treatments to prevent biofilm algal development and to conserve and restore materials construction requires extensive analysis of the effectiveness and effects on the materials of these treatments. The goal of this research was to determine both their application and effectiveness of treatment without compromising the original aesthetic appearance of the material. One common product to clean material construction surfaces, like monuments, heritage pieces and artefacts, artworks, etc., is an aqueous-base formulation commercialized as Papetta AB57, developed by the Istituto Superiore per la Conservazione ed il Restauro (ISCR) [12]. The use of natural substances applied as antiseptics has been known for a long time, among these are essential oils or those derived from plants, which have a natural conservation power for food. This property makes them used in the field of treatment and prevention of biodeterioration, since the concentration for its application is safer compared to traditional chemical biocides [13]. Currently there is a tendency to use natural and those eco-friendly products obtained from plants as biocides incorporated on paints or coatings to avoid the formation of biofilms on the materials and thus biodeterioration [14]. One of the components of these plant-derived essential oils is thymol, which is naturally part of citrus fruits and herbs used as condiments, and is also found among the compounds included as food additives for human consumption [15,16]. Thymol, carvacrol and eugenol are compounds that show biocidal activity on microorganisms [17,18]. Fidanza and G. Caneva 2019, describes that among the bioactive components of essential oils derived from plants the most effective is thymol [13].

The study of materials biodeterioration is an interaction between different disciplines that may include ecology, microbiology, materials engineering and architecture, among others. The techniques that can be applied include measurements of physical properties of materials (e.g., porosity, density, brightness, colour and hydrophobicity) and microscopy and microorganism culture techniques. One of the most relevant issues is related to the products used to control the harmful effects caused by biodeterioration. According to these concepts this work has an initial stage that was obtaining a material similar to that constitutes the façade of a mausoleum, also its present biofilm affection. The microorganisms that form the biofilm that affects the façade material were isolated from the surface of the mausoleum. Once the material that simulates the façade was obtained (mortar), laboratory experiments were conducted to determine the effectiveness of two surface treatments (one of them commonly used for cleaning heritage materials) on mortars with different porosities in order to avoid the algal colonization. We also observe if the applied treatments do not affect the aesthetic characteristics of the material and if that they have a long-term effect. Then, the biofilm was inoculated on the mortar surfaces and it was observed if treatments prevented its development. This efficacy was tested at the beginning of the treatment and after different periods of its application.

2. Material and methods

2.1. Algal community identification

Algal samples were taken from the façades of Yalour Mausoleum (Fig. 1 Supplementary material) located in the La Plata City Cemetery (Buenos Aires, Argentina) by scraping with a sterile scalpel. The taxonomic identification of the algae was carried out by optical microscopy and according to bibliography [19,20], and maintained by culturing in BG11 broth. This algal community was used as an inoculum of phototrophic biofilms on the concrete mortar surface assays.

2.2. Mortars preparation and characterization

Mortars of 35 mm diameter and 5 mm thickness were prepared in two proportions of water/cement ratio 0.4 (M4) and 0.6 (M6) to carry out the tests; they were left to cure 14 days and were moistened every 12 h. An energy-dispersive spectroscopy (EDS) analyser coupled to a Scanning Electron Microscope environmental mode (ESEM, Quanta 200, Thermo Fisher, USA, SeMFi-LIMF, UNLP) was used to screen, in detail, elemental chemical composition of mortar surfaces.

Gaosuo digital microscope and software were used to determine surface contact angle, and measures were carried out in triplicate. The hydrophobicity of the surfaces was determined from established standard values of the contact angle [21].

Characterization of M4 and M6 mortars was carried out by measurements of dry density, saturated density and percent of absorption and porosity. The porosity was calculated by applying an expression found in the ASTM C642 standard on concrete [22]. For comparison of means, Student's tests with a 95 % confidence (α =0.05), two-tailed distribution were applied.

Measurements of brightness and colour were taken on the mortars at the beginning of the treatments applied (T_0) and after 90 days of application (T_{90}). These parameters were taken with BYK Gardner equipment, using the illuminant D65, diffuse illumination geometry d8°/spin, standard observer 10° and specular brightness at 60°. The CIELAB system was used to represent colour differences and colour change. The total colour difference between the beginning of applied treatments and after 90 days of treatments application (ΔE) were

Table 2
Colour and brightness measurements. Average values ($n = 3$) of the colour parameters: luminosity (L^*), a coordinate (a^*), b coordinate (b^*) and brightness of control (C-M4 and C-M6) and surfaces treated mortars (P-M4, P-M6, PT-M4 and PT-M6), at two different time courses: at the beginning and 90 days post surfaces treatment applied.

	Inicial (T_0)				90 days post surfaces treatment (T_{90})			
Sample:	L^*	a^*	b^*	*Brightness*	L^*	a^*	b^*	*Brightness*
C-M4	56.06	2.52	8.75	0.7				
C-M6	59.27	2.63	9.14	0.63				
P-M4	55.06	2.8	10.43	0.8	56.40	2.78	9.22	0.7
P-M6	59.62	3.04	11.25	0.8	60.55	2.60	9.53	0.8
PT-M4	55.39	2.63	10.14	0.76	51.48	3.23	11.50	0.6
PT-M6	59.95	2.82	10.72	0.86	57.78	3.30	12.34	0.6

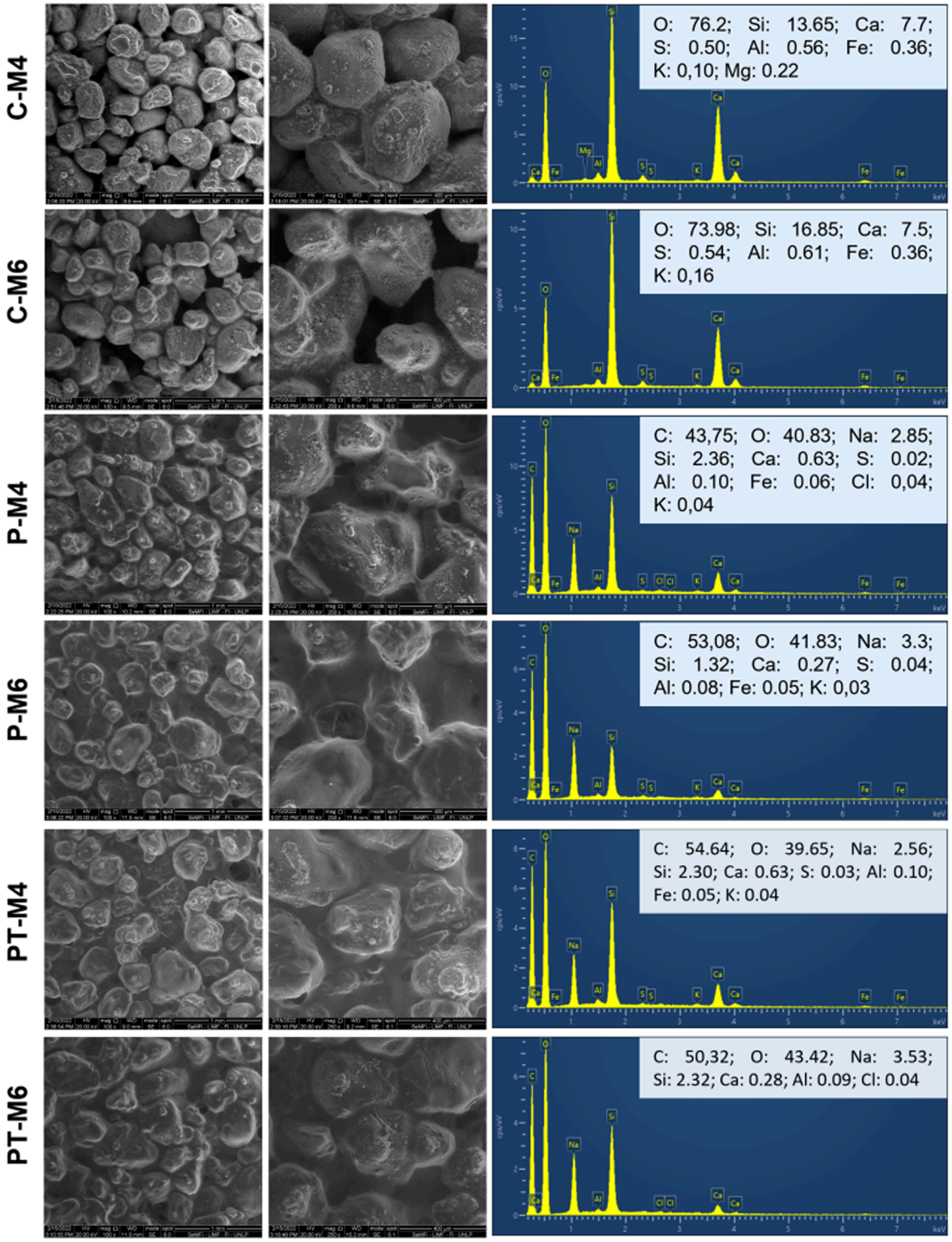

Fig. 1. ESEM image and EDS analysis of control (C) and treated (P and PT) surface mortars.

estimated by $\Delta E^*_{76} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ [23,24].

2.3. Material surface treatments and algal inoculations

Two surface treatments were used. One of them, "P", composed of 0.38 M ammonium-bicarbonate; 0.6 M sodium-bicarbonate; 0.085 M EDTA-disodium salt; 20-polyoxyethylene sorbitan monolaurate polysorbate, 1 % and 6 % carboxymethylcellulose dissolved in distilled water. This formulation from ISCR, arose as an alternative to the use of strong acids and bases or exclusively mechanical methods for cleaning surfaces [25]. The other surface treatment, "PT", consists of the same formulation with Thymol (Sigma-Aldrich) at 1 % w/w. Thymol is a plant-derived compound with biocidal activity due to its phenolic chemical structure [17,18,26].

Mortar surface treatments were applied with brush in three layers. To corroborate the presence of the treatment on the surface, a FTIR spectrum by diffuse reflectance technique (DRIFTS) was obtained using a control mortar as background (Spectrum ONE spectrometer, Perkin Elmer, USA). Algae community culture was inoculated on each mortar's surface as spray in a concentration of approximately 4×10^6 algae.ml^{-1}.

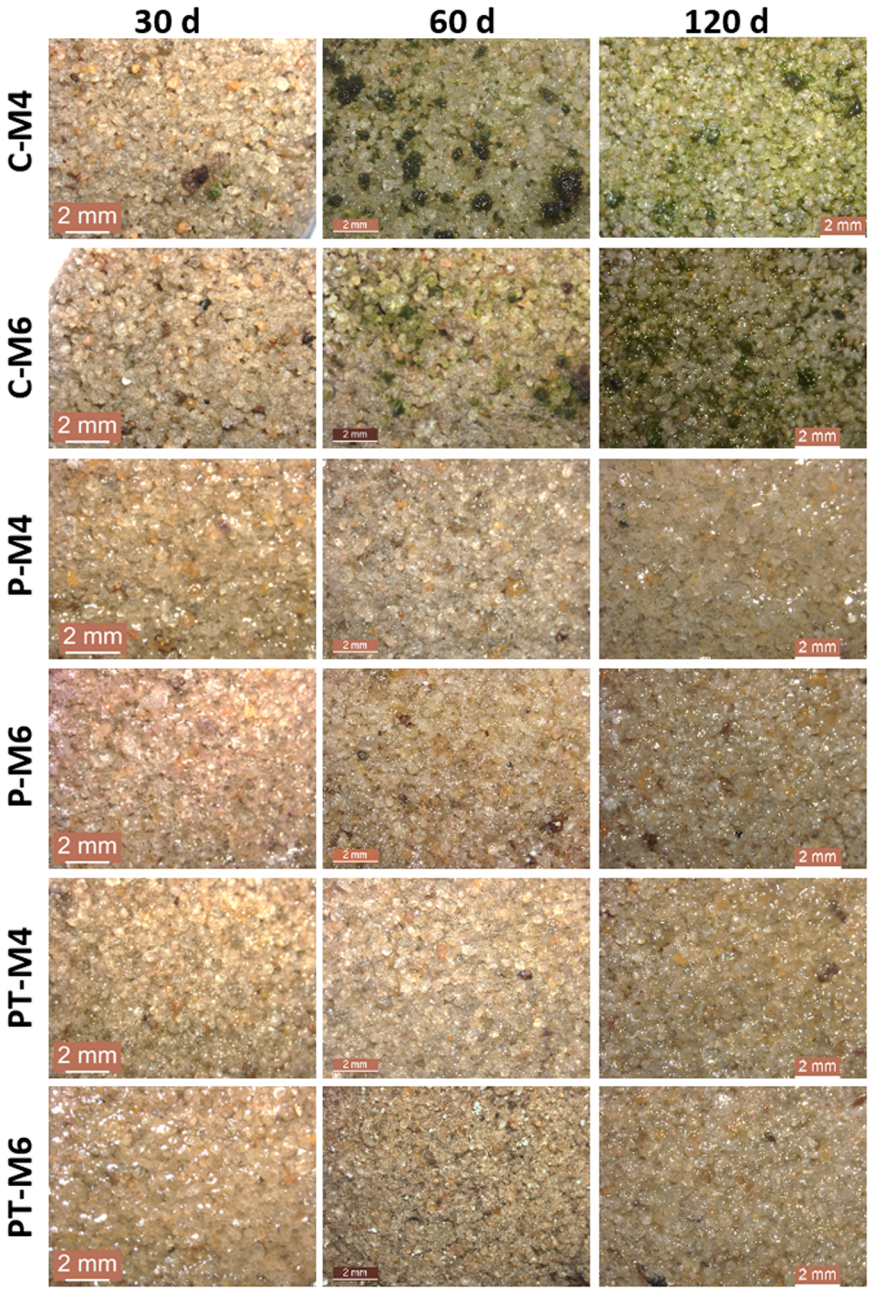

Fig. 2. Stereoscopic microscope photographs of mortars M4 and M6 after 30, 60 and 120 days of inoculum incubation, of control surface *C*, surface treated with P and surface treated with PT. Scale bar: 2 mm.

Subsequently, mortars were placed in triplicate in Petri dishes with BG11 agar (Fig. 2 Supplementary material) and incubated under controlled photoperiod cycling conditions (8–16 h, darkness-light) and 25ºC for 30, 60 and 120 days. As a control "C", a set of mortars without surface treatment were inoculated and they were cultured at the same periods as mortars treated surfaces. Algal growth on mortars surfaces for each treatment and period were observed under a stereoscopic microscope (Leica S8APO) with digital camera (Leica, MC 170 HD magnifying glass), epifluorescence microscope (Olympus BX51, Olympus Japan), ESEM and EDS analyser coupled to ESEM.

In order to corroborate the antimicrobial activity of treatments over time, a set of treated mortars were left in the laboratory environment for 30, 60 and 90 days. Then, they were inoculated in spray form with the same algal culture and incubated with the same conditions and periods as previously described.

3. Results

3.1. Taxonomic identification of algal community

A variety of taxa was found in the algal community from the mausoleum scraped surface (Fig. 3 supplementary material). Cyanobacteria of the genera *Gloeocapsopsis* sp., *Gloeocapsa* sp. and *Scytonema* sp. were identified and a homogeneous population of a unicellular green alga belonging to the genus *Chlorococcum*.

3.2. Mortars characterization

Contact angle values of mortar surface with and without treatments are shown in Table 1. Control mortar surfaces (C-M4 and C-M6), were qualified as superhydrophilic, while treated mortar surfaces with P (P-M4 and P-M6) and with PT (PT-M4 and PT-M6) were qualified as

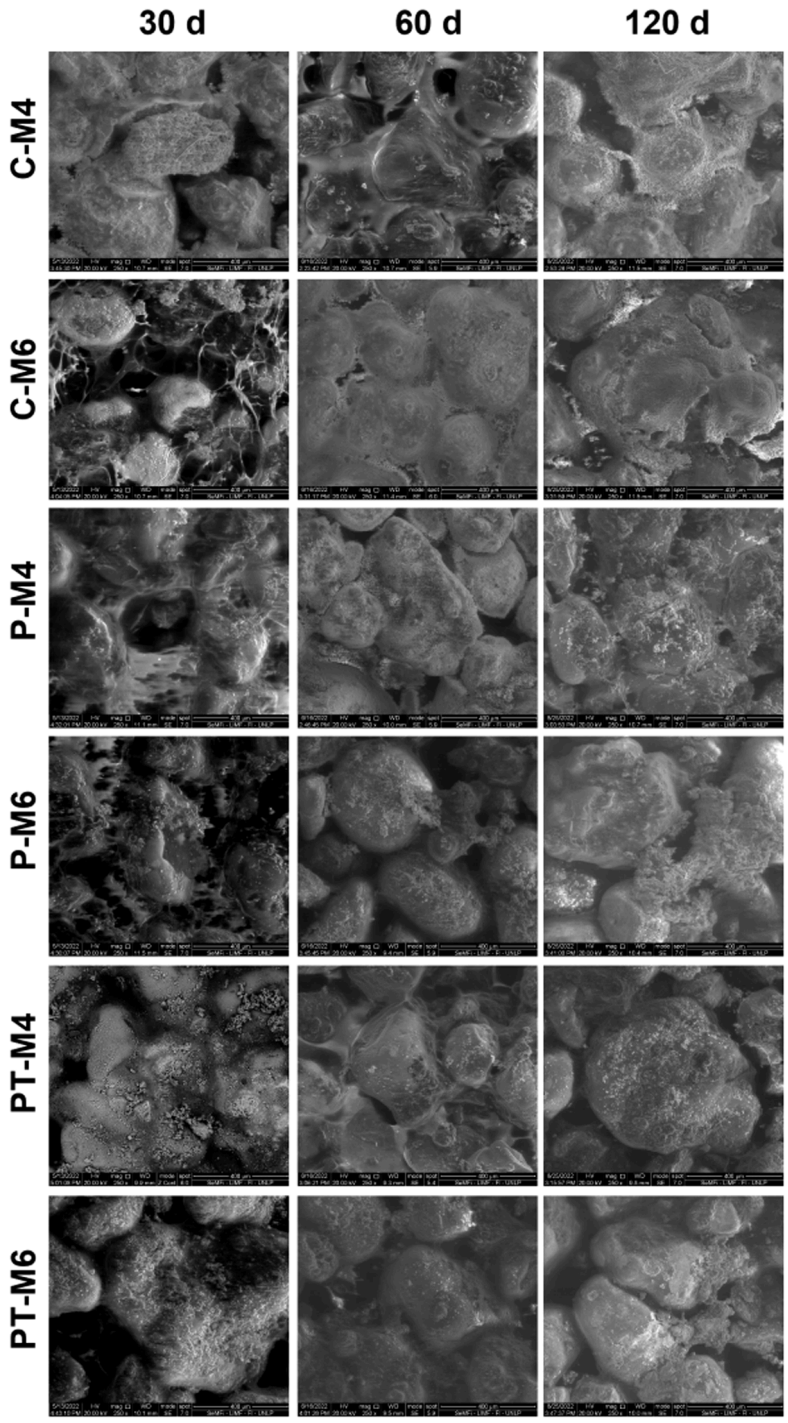

Fig. 3. ESEM images of mortars M4 and M6 after 30, 60 and 120 days of inoculum incubation, control surface *C*, surface treated with P and surface treated with PT. Scale bar: 400 μm.

hydrophilic.

Measurement results obtained of dry density (dd), saturated density (sd) (in g.cm^{-3}) and percentage of absorption (ab) and porosity (po) in both M4 and M6 mortars are shown in Fig. 4 Supplementary material. Statistical analysis (Student's test comparison of means, 95 % confidence, α=0.5) indicates that there are no significant differences for these characteristics (p_{dd}= 0.66; p_{sd}= 0.52; p_{ab}= 0.16; p_{po}= 0.16) between the values obtained for the two water/cement ratio (M4 and M6) mortars assayed.

Intervention on material surfaces should not produce inappropriate changes on them. The possibility of colour changes produced on the surface are important to take into account, especially when these treatments will be applied to pieces, buildings or constructions of patrimonial and/or cultural importance, Average values for brightness and colour parameters at the beginning (T_0) and 90 days post surface treatment application (T_{90}) were summarised in Table 2.

Colour changes of treated respect to untreated surfaces at the beginning (T_0) are shown in Fig. 5 Supplementary material. Although statistically significant differences were not observed for dry density, saturated density, percentage of absorption and porosity between both mortar ratios (M4 and M6), the application of treatments produced differential changes on these mortar surfaces.

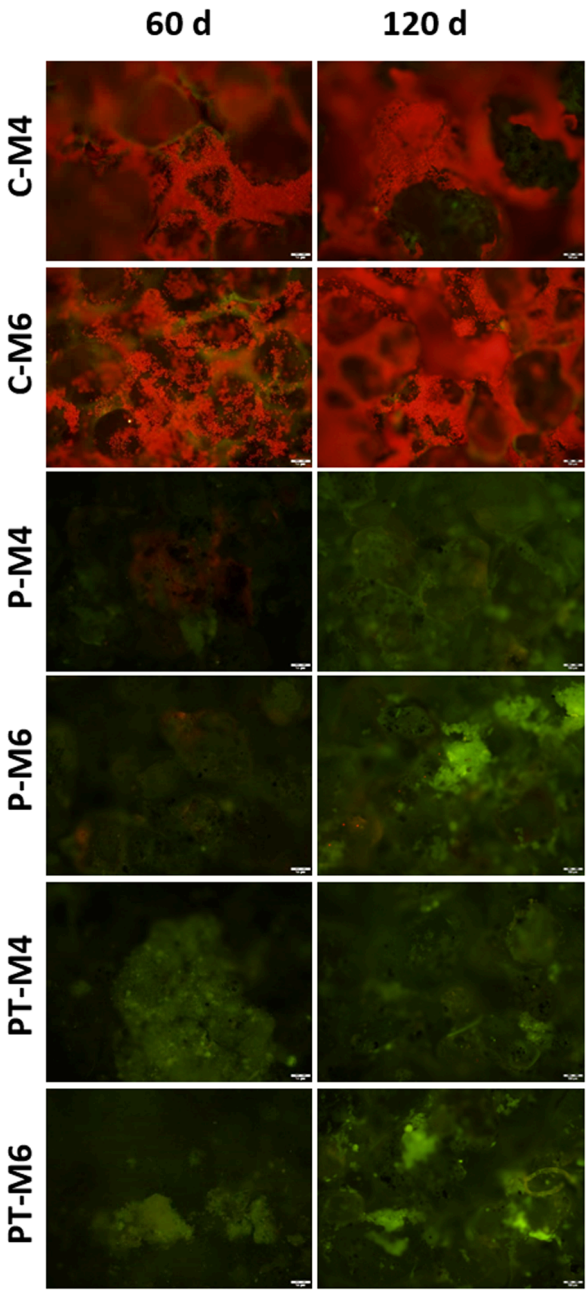

Fig. 4. Epifluorescence microscope photographs of inoculated mortars M4 and M6 after 60 and 120 days of incubation. Can be noted the high autofluorescence of chlorophyll (red) in control surface (C), and very low autofluorescence on surfaces treated with P or with PT. Scale bar: 100 μm.

The results obtained for the colour difference at 90 days post surface treatment application ($\Delta E_{T90\text{-}T0}$) were: $\Delta E_{T90\text{-}T0}$ P-M4 = 1.805; $\Delta E_{T90\text{-}T0}$ P-M6 = 2.008; $\Delta E_{T90\text{-}T0}$ PT-M4 = 4.186 and $\Delta E_{T90\text{-}T0}$ PT-M6 = 2.754. Respecting the brightness measure, a slight decrease can be observed over time (T_{90}) (Fig. 6 Supplementary material).

To assess material spatial distribution and elementary components, mortar appearance surfaces were analysed by ESEM and EDS. Control surfaces (C-M4 and C-M6) show similar material grain distribution and elementary components such as Si, Al, Mg, K, Fe, S and Ca, all of them were expected for cementitious materials realized with sand, Portland cement and water (Fig. 1). The mortar's surface treated, P-M4, P-M6, PT-M4 and PT-M6 (Fig. 1) shows similar material grain distribution respect to C-M4 and C-M6. For mortar treated surfaces (P and PT) it can be detected a greater proportion of carbon and sodium, due to carboxymethylcellulose present in treatment formulation.

As can be seen through the DRIFTS analysis, it was possible to detect the presence of the organic coating on the treated mortars (Fig. 7, Supplementary material). A greater reflectance of the treated mortars can be observed compared to the control, but this difference is due to the greater brightness of the samples when they are treated, and not to their absorbance. This result is consistent with the data obtained when analyzing the brightness at the beginning (T_0) of the tests.

3.3. *Biofilms development on treated and untreated mortar surfaces*

Development of biofilms on mortars surfaces was observed by stereoscopic microscopy, ESEM and epifluorescence microscopy, at 30, 60 and 120 days after inoculated mortars surfaces. The results obtained using stereoscopic microscopy are shown in Fig. 2. For C-M4 and C-M6 after 30 days showed a low surface coverage of the biofilm that incremented according to the incubation time 30 < 60 < 120 days (Fig. 2, rows C-M4 and C-M6). Treated mortars surfaces with P or PT for 30, 60 and 120 incubation days, exhibit a reduced biofilm algae development (Fig. 2, rows P-M4, P-M6, PT-M4 and PT-M6) with respect to C-M4 and C-M6 coverage surfaces.

The growth of the inoculated algal community was observed in control and treated mortars are shown in Fig. 3. Control surfaces at 30 days of incubation show low coverage (Fig. 3, rows C-M4 and C-M6). After 60 and 120 days of incubation these mortars showed an extended coverage in all surfaces (Fig. 3, rows C-M4 and C-M6 at 60 and 120 days). Mortar treated surfaces (Fig. 3, rows P-M4, P-M6, PT-M4 and PT-M6) presented low surface coverage with respect to control conditions. Those results were similar at all times tested (Fig. 3, columns 30, 60 and 120 days for all surface treatments).

The development and coverage of the mortar surfaces observed by epifluorescence microscopy to analyze the viability of the biofilm is presented in Fig. 4. Chlorophyll fluorescence is commonly used to determine the effects of biocides on photosynthetic organisms, and allows the photosynthesis process to be analysed [27]. When the chlorophyll fluorescence signal is positive, autofluorescence of chlorophyll in chloroplast is red, indicating a development of a living biofilm. This positive signal was observed by epifluorescence on C-M4 and C-M6 mortar surfaces incubated at 60 and 120 days (Fig. 4).

To assess efficacy in time-course of post applied surfaces treatments, surfaces treated mortars were inoculated after 30, 60 and 90 days after treatment application. Once the respective period has passed, mortars were inoculated and incubated for 90 days and analysed using the same microscopy techniques applied before; results are shown in Fig. 5.

4. Discussion

For this work in the first place, we taxonomically identified the algal community from a sample site (Fig. 3 Supplementary material). The species reported in our study are comparable to those found in earlier studies, [8,28]. Gaylarde and Gaylarde (2005), reported Chlorophyceae and Cyanophyceae are the most prevalent algal microorganisms when growth depends on moisture and porosity of the material, and Cyanophyceae was mostly present on concrete walls exposed to wet and dry periods [29]. Taxa observed on the mausoleum do not always suggest high bioreceptivity of that substratum, since several other environmental conditions (climate, solar radiation, rain, temperature, etc.) have a vital effect in successful colonisation. Additionally, Chroococcales and Scytonemataceae provide a gelatinous coating that functions as a supply of water that is held by strong molecular forces, allowing these cyanobacteria to colonise stone even in dry environments [2]. Ariño and Saiz-Jimenez (1996) demonstrate that when cyanobacteria and algae colonize the surfaces are capable of forming small cavities, they suggest that the process occurs because this microbial community has a contributing factor in calcium carbonate dissolution, influencing strongly on the chemical mortar alteration [30].

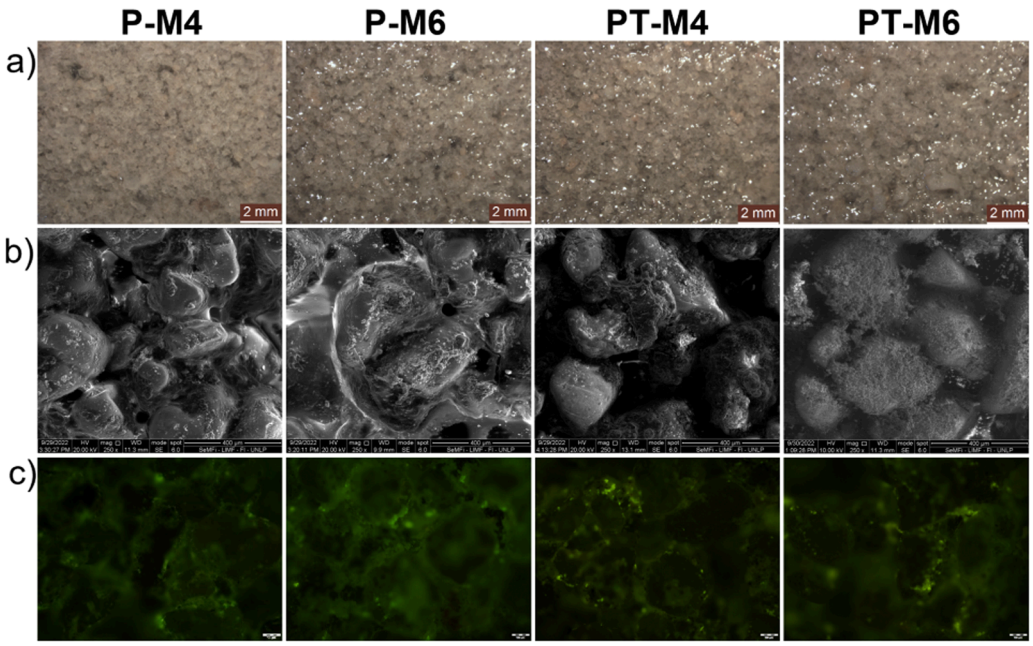

Fig. 5. Stereoscopic microscope, ESEM and epifluorescence microscope images of algal biofilms development on mortars (M4 and M6) inoculated after 90 days of applied surface treatments (P and PT). Scale bars: (a) 2 mm, (b) 400 μm, (c) 100 μm.

For the physico-chemical and morphological characterization of the control and treated mortars, measurements of the contact angle, density, percentage of porosity, brightness and colour and elemental chemical analysis were carried out. The angle contact values indicate that surface treatments reduce material hydrophilicity. Although the treated surfaces maintain a high wettability, favourable for the biofilm development, treatments application decreases the hydrophilicity ($36^o < \theta < 51^o$) respect to the control mortars surface ($\theta = 0^o$). The main mineral composition of cementitious materials is aluminium (Al), calcium (Ca), iron (Fe), oxygen (O), silicon (Si) and sulphur (S). Calcite and silica play an important role in bioreceptivity as they can favour colonization by providing a source of nutrients [31]. On the other hand, these cement-based materials are very porous and absorb a significant amount of water and possess an important primary bioreceptivity. Values of porosity in cementitious materials from about 14 %, lead to a deeper penetration of moisture [32]. However, in agreement with our results, Morin et al. (2018) consider that a permeable surface from 30 % porosity is a condition to be a bioreceptive surface [33].

The analysis of the colour measures shows that the values of a^* as those of b^* were positive, indicating a tendency towards red and yellow, respectively. The low values obtained for a^* demonstrate a low purity of this colour. This characteristic is maintained both for the control mortars (C) and for those treated (P and PT) at T_0, observing a very slight increase at T_{90}. It can be seen that the difference in a^* and b^* coordinates are slightly greater in the M6 proportion of the treated mortars compared to the controls (Fig. 5, a, b, Supplementary material) likewise, the difference in luminosity (L^*) generates a darkening in M4 ($\Delta L^* < 0$) and a clearance in M6 ($\Delta L^* > 0$) (Fig. 5. c, Supplementary material). The difference of total colour at the beginning (ΔE^*_{76} at T_0) between control and treated mortars reveals a "notable difference" (1.54–2.17) according to the scale indicated in the used EN 12,878 standard, however these changes are not visually detectable, being the perceptibility threshold ($\Delta E<3$) [19,29,30]. The results obtained to corroborate if the used treatment cause colour changes after 90 days post its application ($\Delta E_{T90\text{-}T0}$) shows notable changes for P-M4, P-M6 and PT-M6 and very notable for PT-M4 although, as mentioned, values of $\Delta E<3$ are not visually detectable [34,35]. Regarding the surface brightness, it can be said that both control and treated mortars have a matte appearance, being brighter treated mortars at the beginning (T_0), a slight decrease can be observed over time in treated surfaces (T_{90}). Due to one of the most important issues in the conservation of materials is that the intervention on them does not cause negative changes in their characteristics, taken together, these results allow us to propose these surface treatments for mortar.

Cement based materials are porous, and hence have a significant primary bioreceptivity, this contributes to the microorganism adherence and biofilm development [28]. Regarding the treatments of the mortars analyzed by ESEM and EDS it was highlighted that both treatments surrounded and were introduced between the grains of the material. The fact that those treatments can introduce inside of interstitial spaces of mortars, generates surfaces less bioreceptive for algal biofilm colonization and development. Our results indicate that both surface treatments P and PT have similar antimicrobial activity. P formulation can act by destabilizing and interrupting intracellular transport. PT has added thymol, which its biocidal activity, is mainly attributed to the action of its phenolic structure. This compound action of its phenolic structure is responsible. These chemical effects on the cytoplasmic membrane, causing structural disorganisation and cell permeability failure [36]. Our findings with respect to the characteristics for positive material bioreceptivity can explain surface colonization and biofilm development on control mortars C-M4 and C-M6. In contrast, with those facts, treated surfaces P-M4, P-M6, PT-M4 and PT- M6 could not be colonized or not be able to develop biofilm.

The viability of the biofilm developed on the mortar surface (positive red signal) observed by epifluorescence microscopy indicates that the algal biofilm was able to develop only on control mortar surfaces. Contrary to control conditions, chlorophyll fluorescence signals were very low on P-M4 and P-M6 and negative on PT-M4 and PT-M6 (Fig. 4), verifying the mortality of the algal community. This indicates that the presence of algal structures observed by ESEM (Fig. 3) for treated surfaces may be due to the initial algae inoculum metabolically inactive or dead. Photographs of 30 days of incubation are not presented due to very low or no algal development (absent chlorophyll signal).

In this work we also explore the effectiveness over time of treatments applied to surfaces. All the periods evaluated, 30, 60 and 90 days after applying the treatment, show that the treated surfaces can prevent the development of algae biofilms (Fig. 5). The efficacy of surface treatments was demonstrated by analysing the fluorescence of the

chlorophyll signal in mortars, which was negative on all treated surfaces, both for M4 and M6 mortars. This is because the algae inoculum is metabolically inactive or dead.

5. Conclusions

In this work we performed at laboratory scale two formulations for mortar with the aim to reproduce buildings facades characteristics. On those materials we confirmed the effectiveness of two treatments (P ant PT) to prevent the development of algae biofilms, over time. These strategies were aimed towards bioreceptivity decrease.

We must clarify that the treatment used (P) is only used in the general cleaning of heritage materials, including buildings. In this work we tested it in order to avoid the formation of algae biofilms, giving good results. The addition of 1 % thymol did not improve the effectiveness of the treatment.

Can be considered that these treatments would be potentially effective in the control and prevention of algae biofilms formation on monuments and buildings being able applied also in cultural heritage monuments because they accomplish the mandatory condition for heritage intervention: they are easily removable which makes so the intervention on the material become minimal and does not promote undesirable changes.

Reducing the impact of the activity of microorganisms is part of the conservation strategies and prevention of biodeterioration of materials. The progress in the development of environmentally friendly solutions has become a priority effort to achieve more sustainable practices that prevent materials from biodeterioration, minimising the use of invasive methods and accelerating deterioration processes. Likewise, these products present compatibility with the constituent materials of the constructions. Materials technology, together with appropriate construction techniques, could contribute to minimising the biodeterioration of cementitious materials, obtaining smoother and less porous surfaces to avoid any type of attack.

More research is required to explore if the products used in this work can be leached by atmospheric action and what is its surface treatments durability in real environmental conditions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported under grants Res.1517/20 and Res. 389/21 from Comisión de Investigaciones Científicas de la Prov. de Buenos Aires and National University of La Plata 11/I238. The authors thank Dr. Erasmo Gamez Espinosa (from CIDEPINT) for the contact angle measurements and to Concrete Technology Area staff from L.E.M.I.T.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mtla.2024.102030.

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