Photocatalysts and essential oils: could they ever be friends?

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Significance and Relevance

The combination of photocatalysts and essential oils, both encapsulated on mesoporous silica, was tested as the main component of a protective coating for stone and cementitious surfaces. The promising synergic results showed that this system could be of interest for inhibiting and preventing microbiological growth on such surfaces, while also avoiding visible aesthetic impacts or color changes, being non-toxic for the environment or the operator, and increasing the duration of the antimicrobial effect, thus preventing future colonization by threatening microorganisms.

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Introduction and Motivations

Even though stone and cementitious surfaces might seem made of very resistant materials, they still undergo several degradation phenomena, which are strictly related to the environment they are exposed to. These phenomena can derive from different sources: chemical, physical-mechanical, or biological. In the latter case, it is referred to as biodeterioration. To avoid such degradation phenomenon, preventive actions must be considered, such as the application of antimicrobial protective coatings.[1]

This work presents a green nanostructured system aimed at developing a protective coating for stone and cementitious surfaces exposed outdoors. Currently, most antimicrobial products used to contrast microbiological growth are highly toxic not only for the target organisms but also for the operators and the environment. For this reason, attention must be given to employing sustainable alternatives. In this regard, the use of essential oils (EOs) has emerged. EOs have a high antimicrobial power; however, their action is often time-limited and regulated by the evaporation time of the active molecules. To increase the duration of the antimicrobial effect, we have investigated the possibility of adding a photocatalyst to the coatings, in which EOs-impregnated silica had already been incorporated. The presence of a photocatalyst in the mixture would not only prolong the biocide effect, but also ensure air pollutants abatement and a self-cleaning effect on the stone surface. However, the question raised: photocatalysts and EOs would act in conflict or cooperate in a synergistic action?

Materials and Methods

The silica mesoporous material MCM-41 was synthesized and employed as a nanocontainer to host and subsequently release antimicrobial products such as EOs (i.e., *Origanum Compactum* and *Thymus Vulgaris*).[2] Furthermore, the system was enriched by adding different titanium dioxide photocatalysts (Degussa P25, Mirkat 211, and Kronos VLP), varying in size and crystalline phase. These enriched nano capsules were incorporated into a hydrogel for the formulation of the coating. A hybrid hydrogel was chosen, employing chitosan bio-polymer as organic component and silica precursors methyltriethoxysilane (MTES) and tetraethylorthosilicate (TEOS) as inorganic components. To evaluate photocatalytic activity, tests on different mock-ups (e.g. Carrara and Serpentine marbles, plaster, Serena stone, …) were carried out, simulating organic deposition using Methylene Blue as a model stain compound. *In vitro* microbiological tests were conducted on two Fungi (*Aspergillus niger* and *Penicillium rubens*), taken as model microorganisms from real-case scenarios.

Results and Discussion

First, two EOs (namely *Origanum Compactum* or *Thymus Vulgaris*) were encapsulated in MCM-41. This ensures that the antimicrobial features of EOs are maintained for a longer duration, reducing the evaporation rate and diminishing the quantity required: the amount necessary to achieve the minimum inhibitory concentration (MIC) and the minimum fungicidal concentration (MFC) was halved. Moreover, since the silica can host a higher quantity of products than is necessary to exert the antimicrobial effect, the duration of activity is prolonged, releasing the EOs over time. This combination of mesoporous silica and EOs was tested as the principal component of a protective coating for stone surfaces. The promising synergic results show that this system could be of interest for inhibiting and preventing microbiological growth on stone surfaces, while also avoiding visible aesthetic impacts or color changes, being non-toxic for the environment or the operator, and preventing the EOs from evaporating holding them for gradual release.

Furthermore, the system was enriched by adding titanium dioxide (TiO_2) photocatalysts (Degussa P25, Mirkat 211, or Kronos VLP) to increase the duration of the antimicrobial effect, thus preventing future colonization by threatening microorganisms. In addition, the presence of a photocatalyst in the mixture would ensure air pollutants abatement, such as NOx and VOCs, and a correlated self-cleaning effect on the surface. For the development of the protective coating, a two-step impregnation process was used. First, MCM-41 was impregnated with EO to ensure its penetration to the silica pores. Titania was added afterwards to ensure it remained on the surface, providing sites for its photocatalytic activity. The latter was tested in the degradation of methylene blue, used as a model stain compound. The essential oil-impregnated silica particles enriched with titania proved to be effective. The best results were obtained with the material containing Degussa P25. This result was correlated to the appropriate band gap and to the combination of rutile and anatase crystalline phases of the sample.

Finally, this multifunctional material was incorporated into a hydrogel for the formulation of the coating. The formulation was then applied to stone and cementitious mock-ups to evaluate its hydrophobic and colorimetric properties. The newly formulated coating proved to be highly effective, as it did not alter the morphology or color of the substrate. Additionally, it significantly improved the hydrophobic properties of the mock-ups.

The antimicrobial activity of the coating was tested using two Fungi (*Aspergillus niger* and *Penicillium rubens*), taken as model microorganisms from real-case scenarios. The results highlight the potential of mesoporous MCM-41 silica encapsulating both vegetal extracts and photocatalysts as a sustainable and effective solution for inhibiting microbiological growth on stone and cementitious surfaces. The promising synergic results showed that this system could be of interest not only for inhibiting and preventing microbiological growth on stone surfaces, but also for avoiding visible aesthetic impacts or color changes, being non-toxic for the environment or the operator, and increasing the duration of the antimicrobial effect, thus preventing future colonization by threatening microorganisms.

Future studies will focus on evaluating the shelf life of the product, since understanding how long the coating remains effective under various storage conditions is crucial.

References

1. F. Bartoli, *et al.*, *Coatings* **2024**, *14 (2)*, 163.
2. A. Campostrini, *et al.*, *Next Materials* **2025**, *7*.

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