ROMA TRE UNIVERSITÀ DEGLI STUDI

LiquidsGroup

Nano 2020 Innovation Conference & Exhibition

An innovative multifunctional coating with controlled antifouling properties based on the encapsulation of two different biocides

M. Zuena, L. Ruggiero, G. Della Ventura, M.A. Ricci, A. Sodo

INTRODUCTION: THE WEATHERING PROCESS

Stone materials used in artistic-architectural field

WEATHERING

ATMOSFERIC POLLUTION

WATER

SOLUBLE SALTS

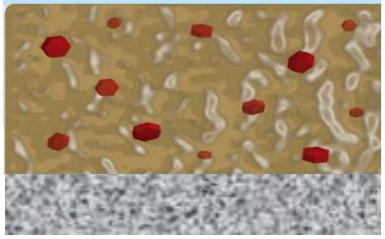
BIOLOGICAL COLONIZATION

INTRODUCTION: THE BIODETERIORATION

COMMON APPROACH

DIRECT APPLICATION

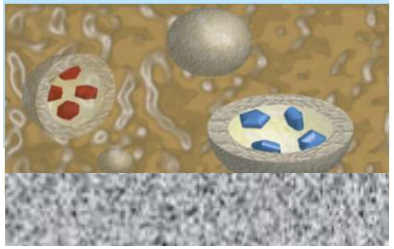
COATINGS



- **Biocides degradation**
- **Low control of release rate**
- **Immediate action of the biocide**

INNOVATIVE APPROACH

ENCAPSULATION



- **Control of the release**

AIM OF THE PROJECT

A MULTIFUNCTIONAL COATING

SELF-CLEANING

TiO_2 nanoparticles

ANTIFOULING

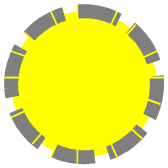
Encapsulated biocides

AIM OF THE PROJECT

A MULTIFUNCTIONAL COATING

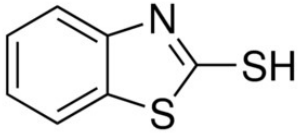
ANTIFOULING

Encapsulated biocides

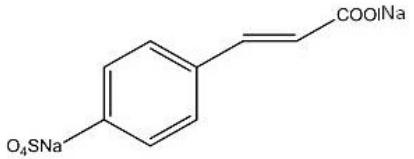


Silica nanocapsules (SiNC)

Mesoporous silica nanoparticles (SiMNP)



2-mercaptobenzothiazole (MBT)



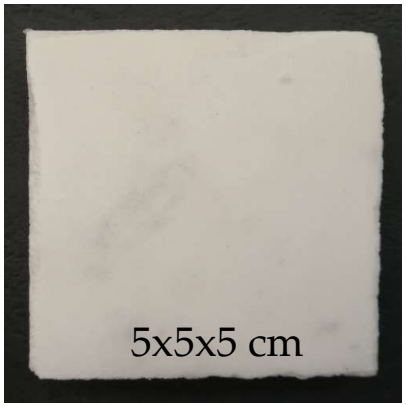
Sodium zosterate (ZS)

4 COATING FORMULATIONS

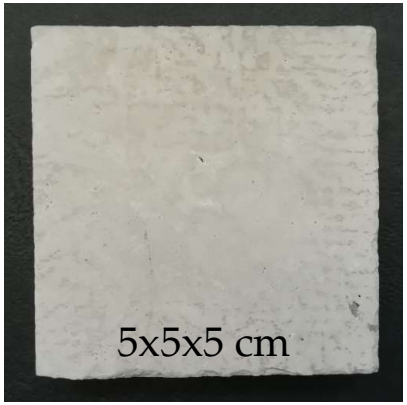
AIM OF THE PROJECT

APPLICATION OF 4 COATINGS

Carrara marble

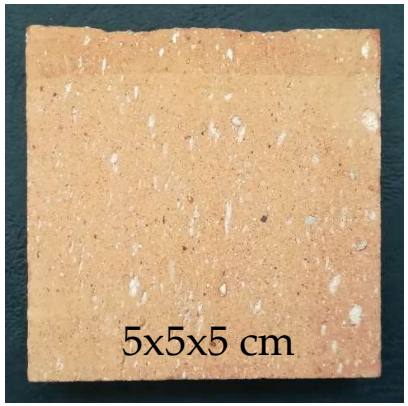


Travertine



Mortar

Brick



LABORATORY TESTS → **COMPATIBILITY AND EFFECTIVNESS**

ENCAPSULATION METHODS

Nanoconteiners	Morphology	Diameter	Loading capability
MBT	Spherical	140 nm ± 20	10%
ZS	Spherical	170 nm ± 2	2.1%
MBT	Spherical	39 nm ± 4	8.2%
ZS	Rods	-	7.8%

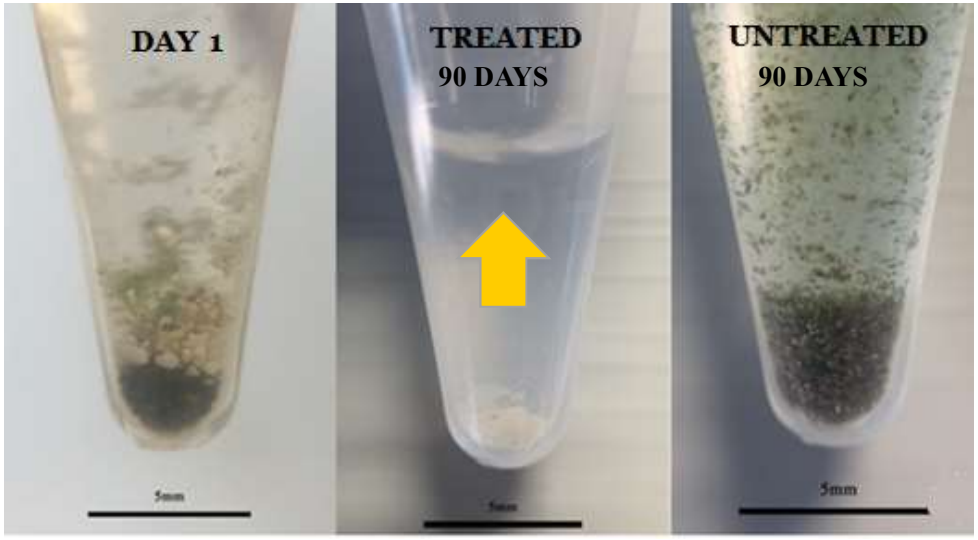
[1] L. Ruggiero et al., Journal of Alloys and Compounds, 2019, 798, 144-148.
[2] L. Ruggiero et al., Applied Surface Science 2020, 514, 145908.

ANTIFOULING EFFICACY

4 NANOCONTAINERS

VS

Common biodeteriogens



ALL nanocontainers are effective against photosynthetic microrganisms

COATING FORMULATION

1	TEOS, ETHANOL	Matrix
2	N-OCTYLAMINA: non-ionic surfactant	IMPROVE interaction
3	PDMS-OH: Poly(dimethylsiloxane) hydroxy terminated	MODIFY of the elastic properties of the gel
4	Si-NANOCONTAINERS (0.05% w/w)	Biocide effect
5	TiO_2 nanoparticles (0.05% w/w)	Photocatalitic effect

Xu F. et al. Progress in Organic Coatings, 75 (2012), 429-434

EVALUATION OF THE PERFORMANCE

STONE SUPPORTS

BRICK (BR)
MORTAR (MR)
CARRARA MARBLE (CM)
TRAVERTINE (TR)

→ Thermal ageing
2 cycles of heating at 600 °C and stored in water overnight [1]

APPLICATION

BY BRUSH TILL SATURATION

→ **BRICK - 16**
MORTAR -16
CARRARA MARBLE - 6
TRAVERTINE - 4

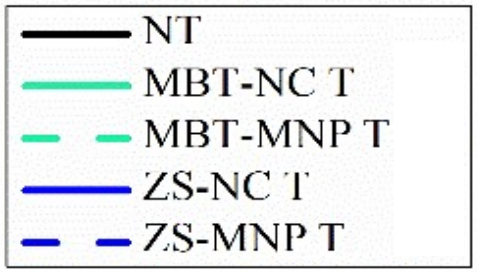
TESTS

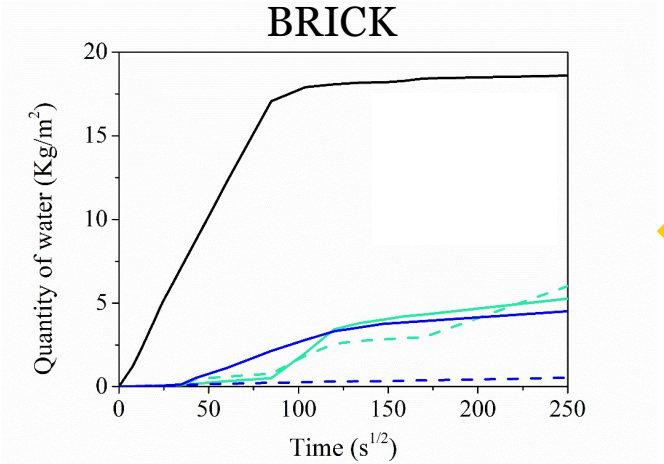
- ✓ **WATER ABSORPTION BY CAPILLARITY**
- ✓ **WATER VAPOUR PERMEABILITY**
- ✓ **STATIC CONTACT ANGLE**
- ✓ **OPTICAL SURFACE ROUGHNESS (OSR)**
- ✓ **SCANNING ELECTRON MICROSCOPE (SEM)**
- ✓ **COLORIMETRIC MEASUREMENTS**

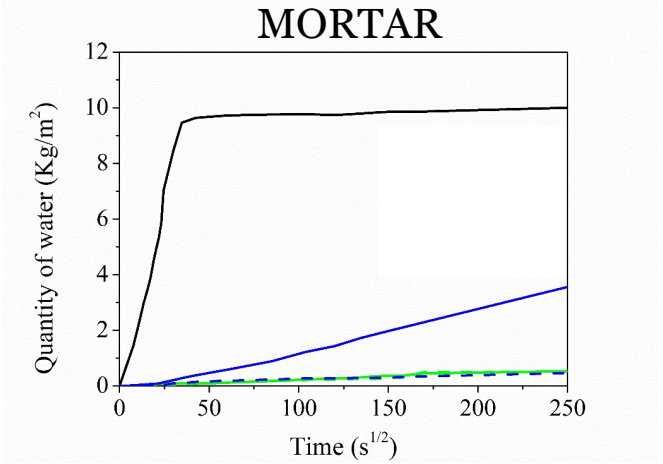
[1] Haake S. et al., Proceedings of the 10th International Congress on Deterioration and Conservation of Stone, Stockholm, June 27th -July 2nd, 2004 p.423-430

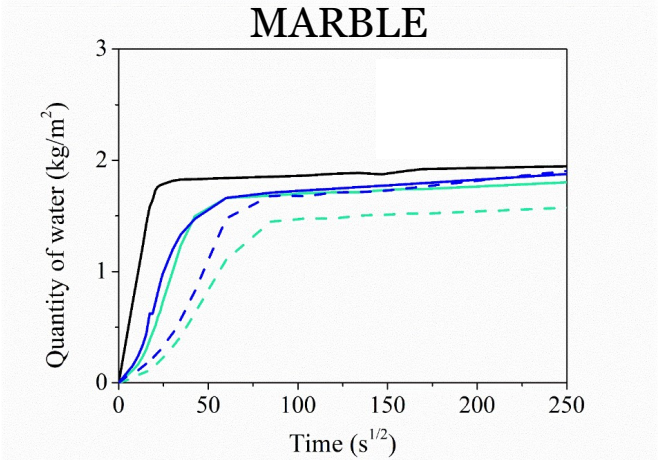
WATER ABSORPTION (capillarity) - UNI EN 15801:2010

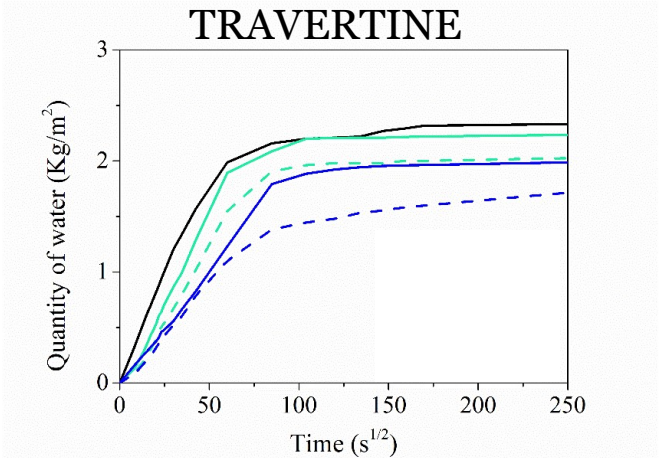
The water transport inside the stone by capillary process



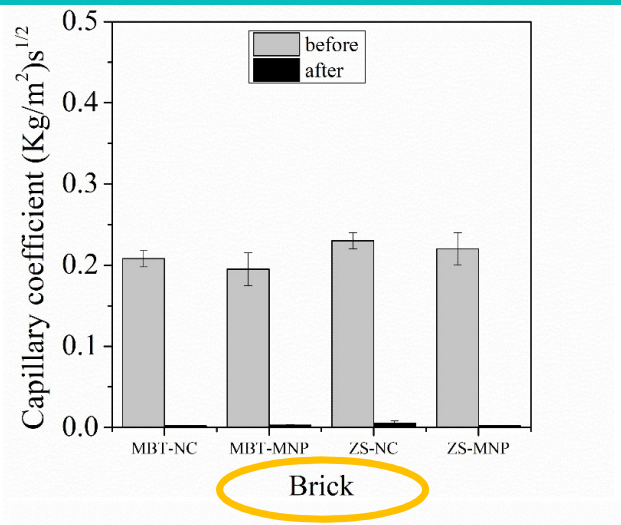


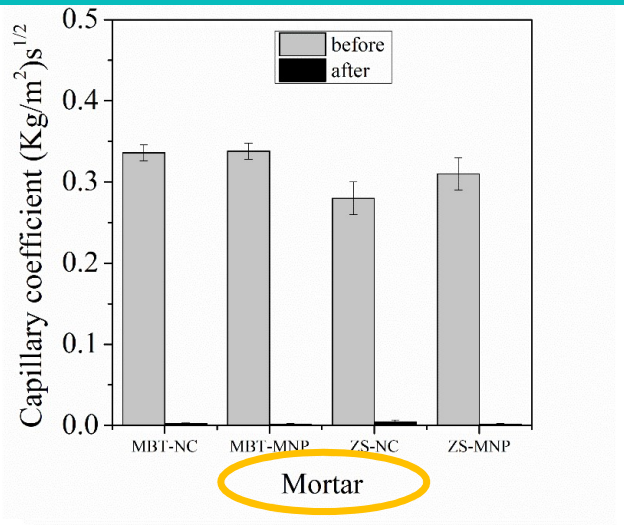


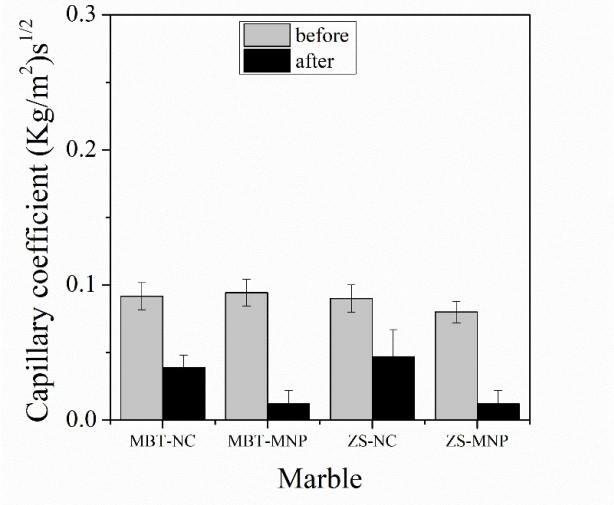


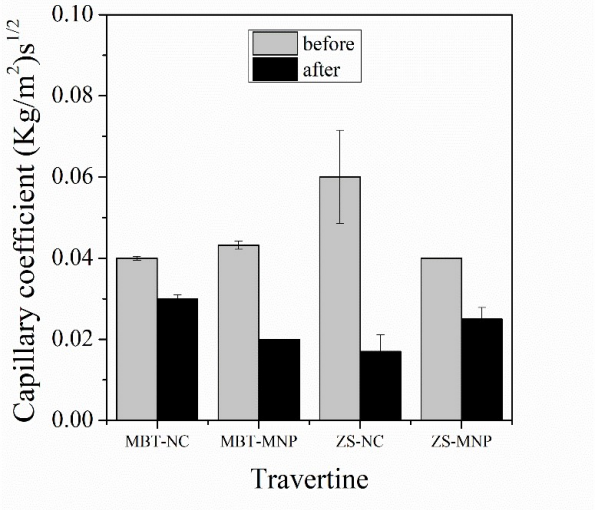


WATER ABSORPTION (capillarity) - UNI EN 15801:2010





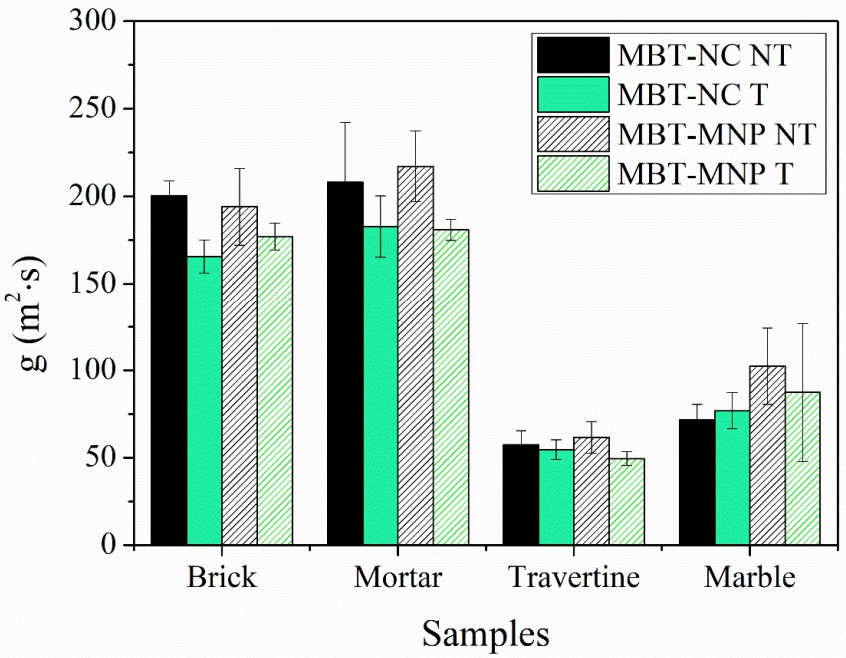




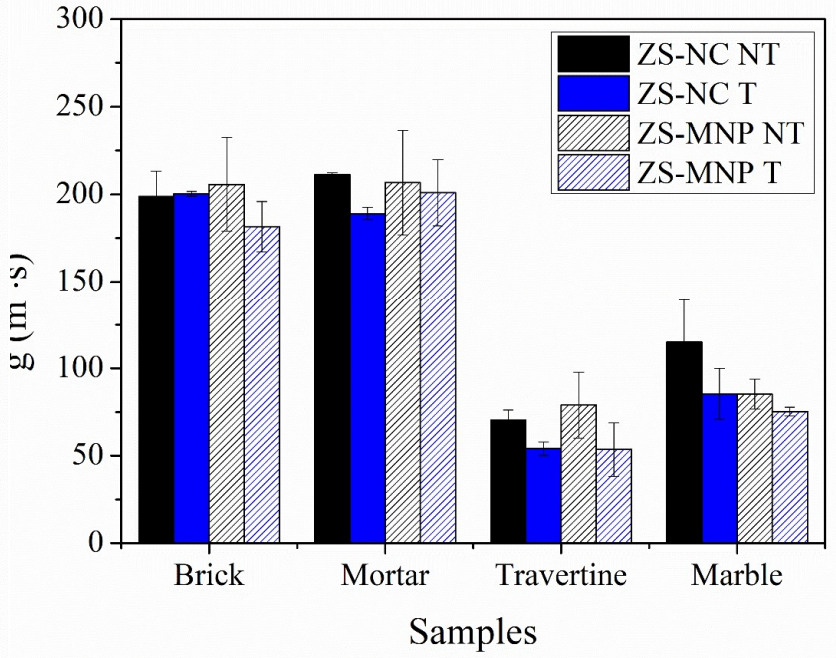
PERMEABILITY TEST - DIN 52 615

The behaviour of a material at humidity passage

BIOCIDE: MBT



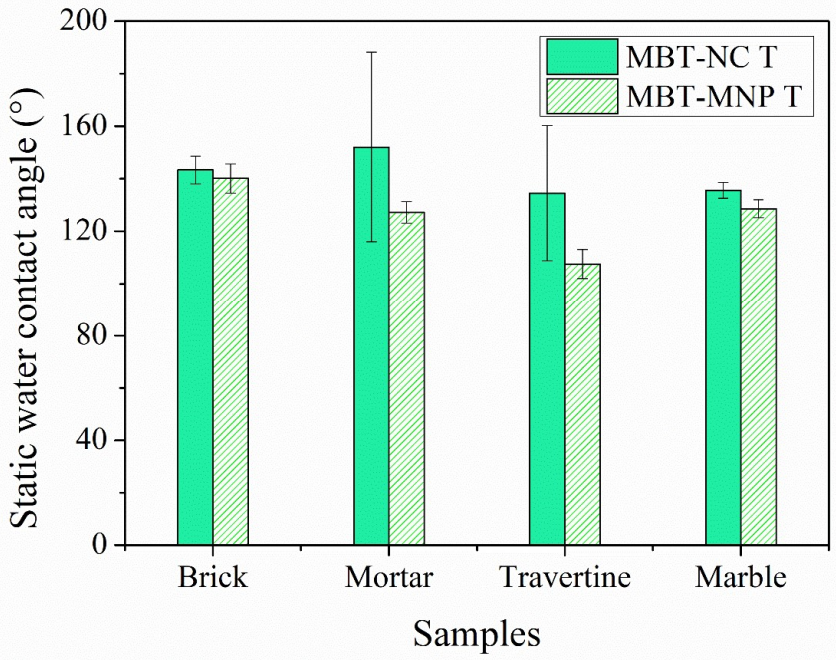
BIOCIDE: ZS



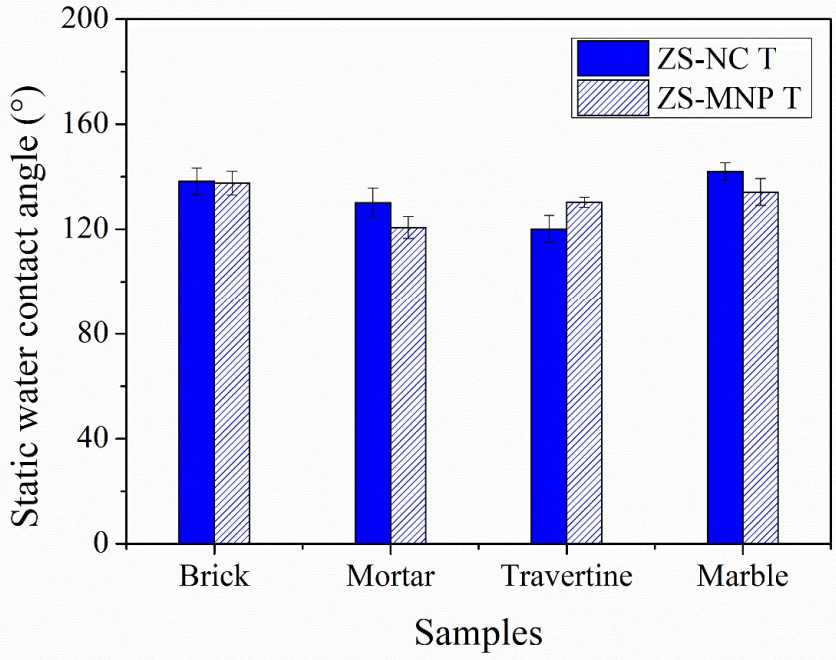
STATIC WATER CONTACT ANGLE (SCA)

The efficiency as waterproofing agents

BIOCIDE: MBT



BIOCIDE: ZS

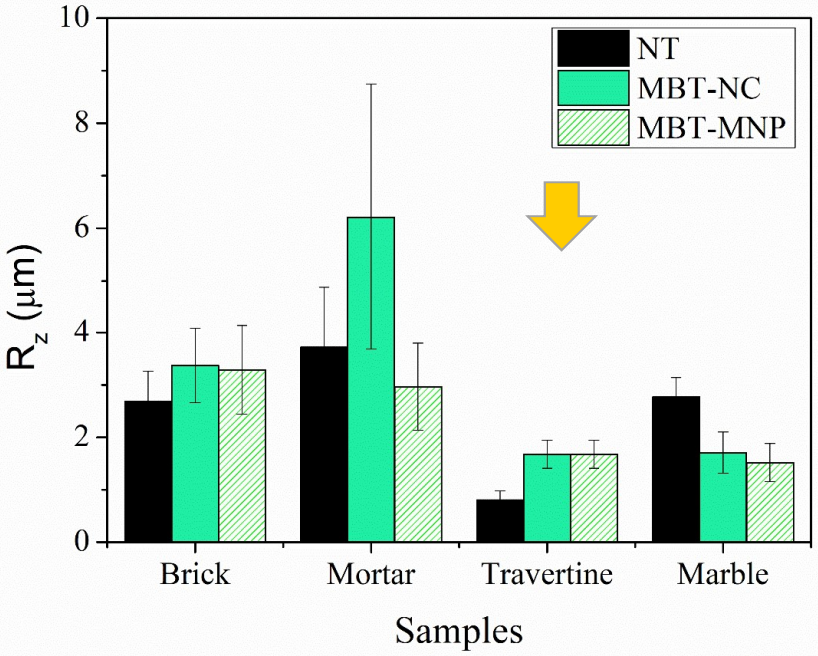


INCREASE of SCA for all treatments and stones. Usually, Si-NC is more waterproofing

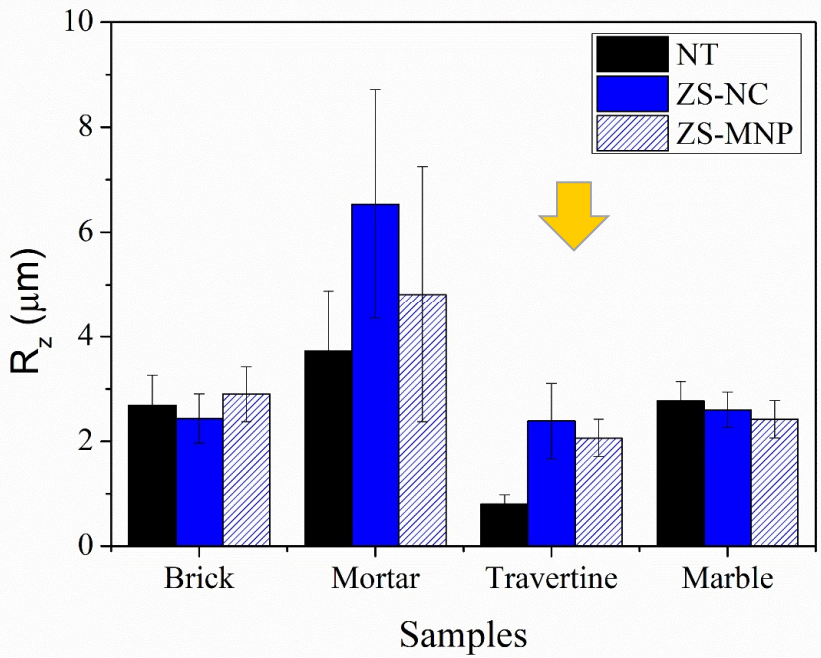
OPTICAL SURFACE ROUGHNESS (OSR)

The physical and morphological changes of the treated surface

BIOCIDE: MBT



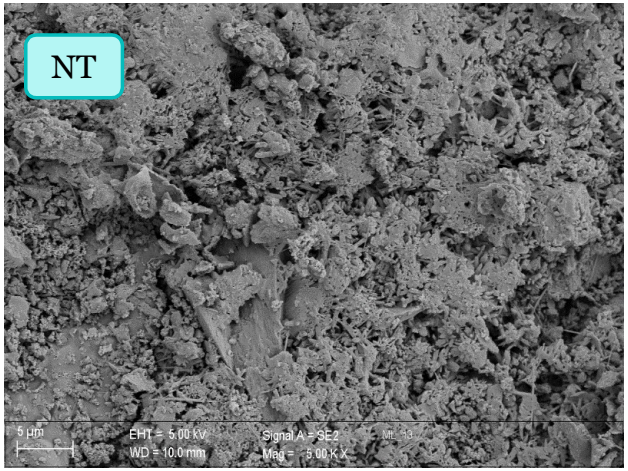
BIOCIDE: ZS

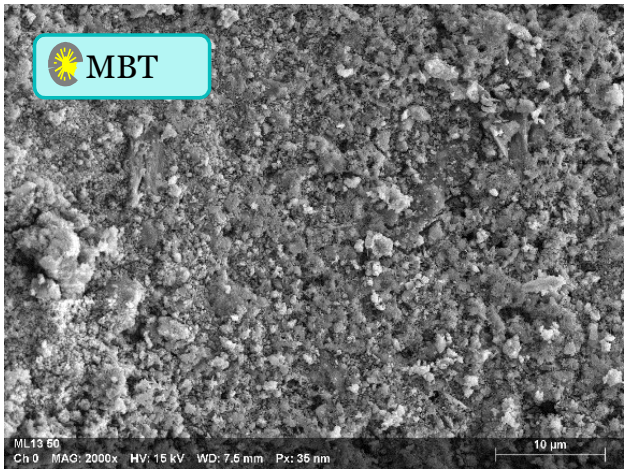


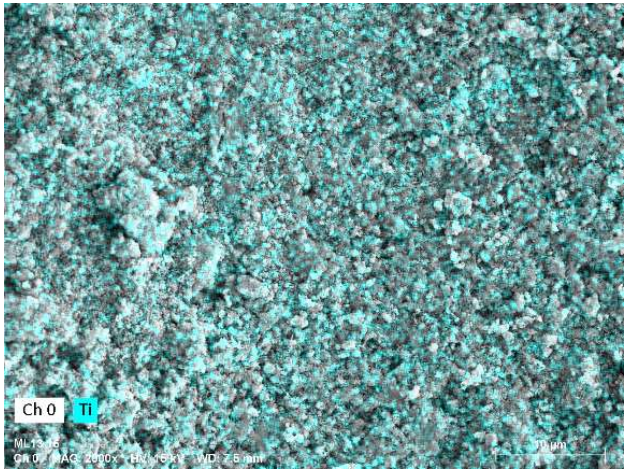
NO particular trend in the roughness value with the 4 coatings, except for travertine

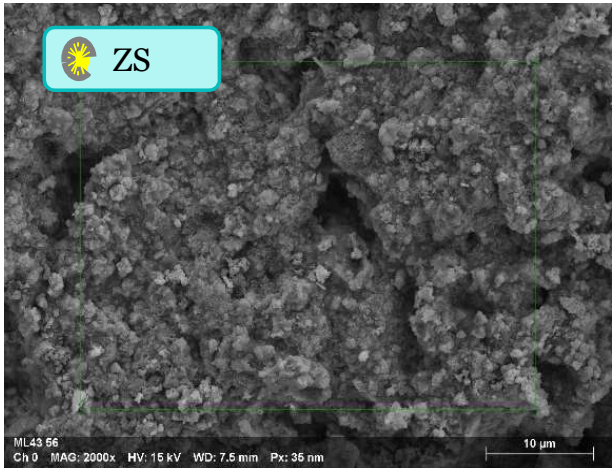
SEM ANALYSIS - SURFACE

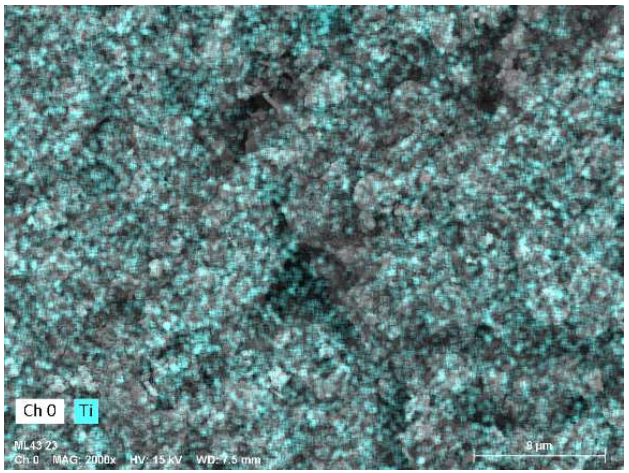
MORTAR



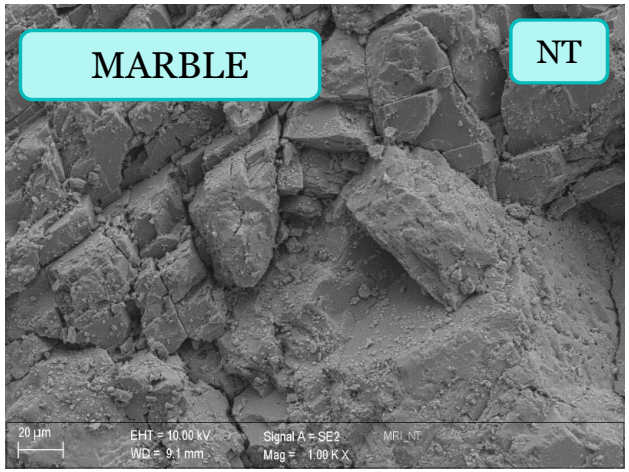


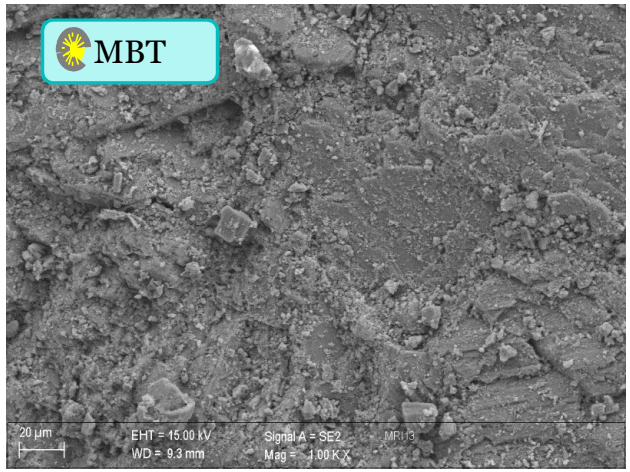


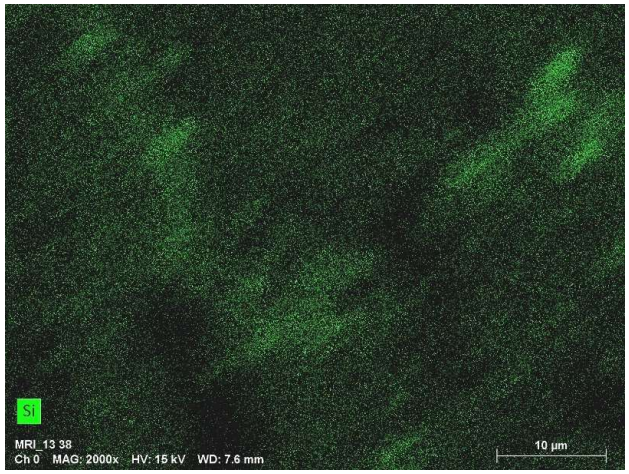


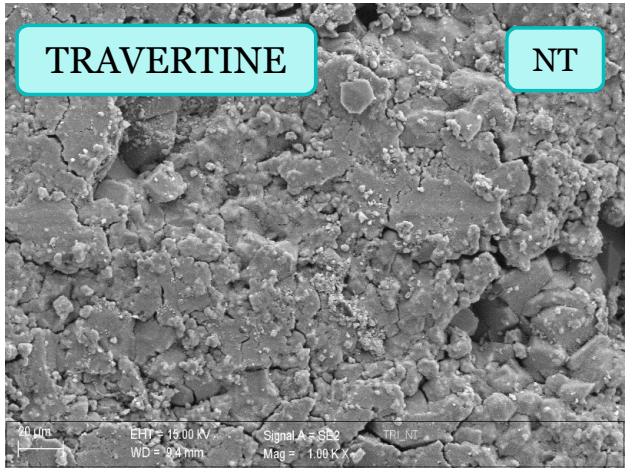


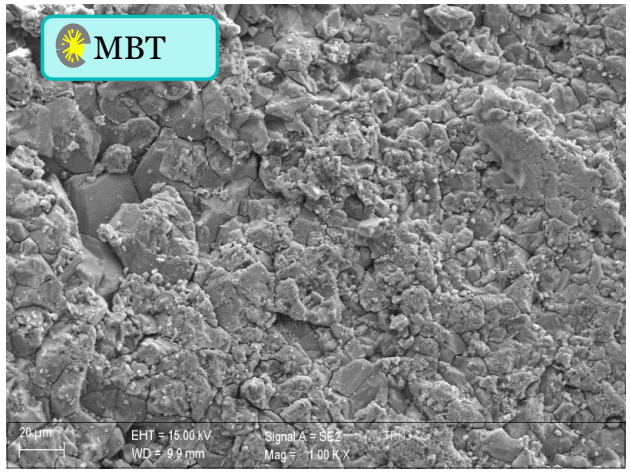
SEM ANALYSIS - SURFACE

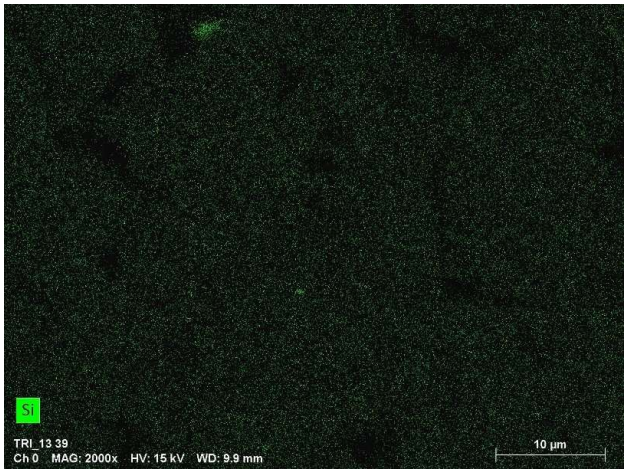






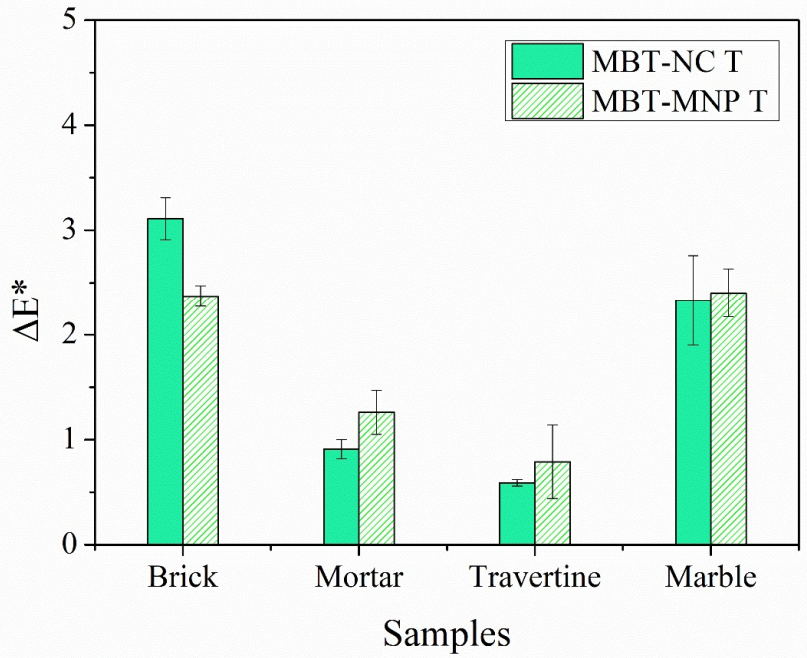




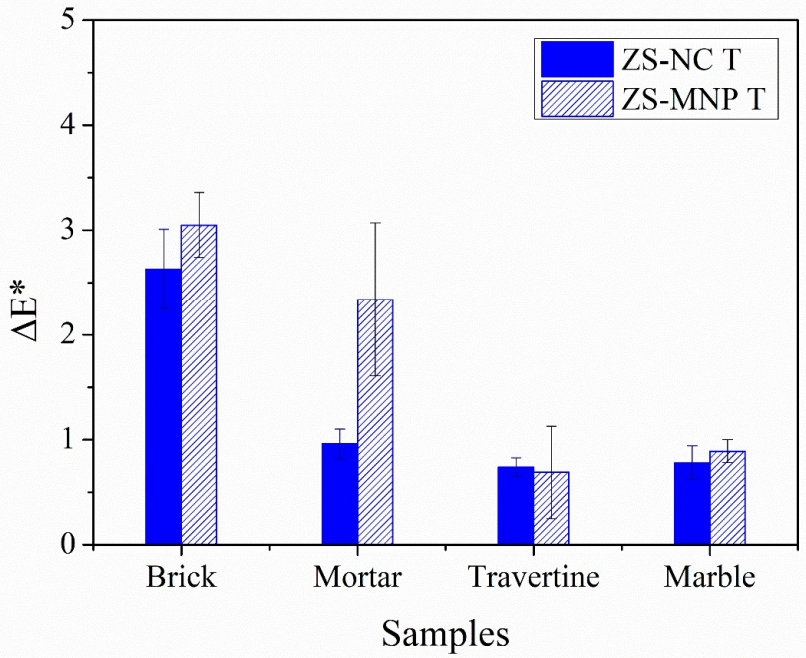


COLORIMETRIC MEASUREMENTS

BIOCIDE: MBT



BIOCIDE: ZS



ΔE*< 5

FINAL REMARKS

CONCLUSIONS

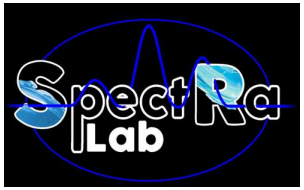
- Antifouling efficacy for all nanocontainers and biocides
- All 4 coatings impart waterproofing properties to the stone surfaces by reducing the CWAC, higher for MR and BR
- The treatments maintain a diffusion of water vapour similar to untreated stone
- An homogeneous distribution of the treatments on the stone
- No visible chromatic variations after one month from the application

FUTURE PERSPECTIVES

- Photocatalytic activity due to TiO_2 nanoparticles on outdoor environment
- Antifouling efficacy in situ

ACKNOWLEDGMENTS

SCIENZE
Dipartimento di Eccellenza



ACKNOWLEDGMENTS

PUBLICATIONS

- L. Ruggiero et al., *Synthesis and characterization of TEOS coating added with innovative antifouling silica nanocontainers and TiO_2 nanoparticles,* Frontiers, Vol. 7, article 185, 2020.

- L. Ruggiero et al., *Encapsulation of environmentally-friendly biocides in silica nanosystems for multifunctional coatings*, Applied Surface Science 514, 145908, 2019.

- L. Ruggiero et al, *Raman and ATR FT-IR investigations of innovative silica nanocontaniers loaded with biocide for stone conservation treatments,* Microchemical Journal, 155, 104766, 2019.

- L. Ruggiero et al, *Silica nanosystems for active antifouling protection: nanocapsules and mesoporous nanoparticles in controlled release applications*, Journal of Alloys and Compounds, 798, 144-148, 2019.

- L. Ruggiero et al, *Incorporation of the zosteric sodium salt in silica nanocapsules: synthesis and characterization of new fillers for antifouling coatings,* Applied Surface Science, 439, 705–711, 2018.