



DOI: 10.5281/zenodo.48820

# NANOCOMPOSITES FOR THE PROTECTION OF GRANITIC OBELISKS AT TANIS, EGYPT

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Received: 15/03/2016

Accepted: 05/04/2016

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## ABSTRACT

Granite has widely been used in the fields of architecture and sculpture in Egypt, especially in the carving of obelisks, which were one of the most important features of ancient Egyptian civilization. Many granitic obelisks of Ramses II, were found in the ancient city Tanis (San el-Hagar), Nile Delta, Egypt, that has been considered one of the most important ancient Egyptian cities.

Unfortunately, the granitic obelisks at Tanis have been subjected to many deterioration factors, which resulted in numerous deterioration aspects, such as granular disintegration, scaling or spalling, cracking, efflorescence, soiling, microbiological colonization.

From this standpoint, the materials which are used in the protection of those granitic obelisks must have the property of hydrophobicity in order to protect them from the harmful effects of water. In the last decade, polymer-nanoparticle composites have attracted great interest in the field of culture heritage conservation due to their unique multifunctional properties, resulting from the high surface area and chemical activity of the nanoparticles dispersed in the polymers.

In this paper, three types of nanocomposites (PF 4, Fluotanium, Fluozinc) were used for the protection of granitic samples collected from Tanis. The petrographical, mineralogical, and chemical study of the granitic samples were determined by means of polarizing microscope, X-ray diffraction, and X-ray fluorescence, respectively. The properties of the treated samples were estimated by visual examination, colorimetric measurements, static water contact angle, total immersion water absorption, abrasion resistance, scanning electron microscope, and self-cleaning test. The durability of the nanocomposites used in this study was evaluated by repeating the measurement of static water contact angle for the treated granitic samples after exposure to ultraviolet irradiation.

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**KEYWORDS:** nanocomposites; granite; protection; obelisks; hydrophobicity; water contact angle; superhydrophobic; self-cleaning; Tanis.

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## 1. INTRODUCTION

Tanis (San el-Hagar) is considered one of the most important ancient Egyptian cities, as it was the capital of Egypt during the 21st Dynasty (1069-945 B.C.), and it was also the nome capital in the Late and Ptolemaic periods.

Tanis lies in the eastern portion of the Nile Delta in Egypt (30° 59' N, 31° 53' E), about 130 kilometers northeast of Cairo, and about 20 kilometers south of Lake Manzala (Fig. 1). (Pillet, 1931; Montet, 1933; Montet, 1942; Bard, 2007).



Fig.1. The site of Tanis in the Delta, Egypt. (After: Google Earth)

The monumental remains of Tanis were first investigated by the scholars accompanying Napoleon's expedition to Egypt, as the drawings and descriptions of the site appeared in the book of "Description de l'Égypte" (Bard, 2007). The first archaeological exploration of the city was undertaken by Auguste Mariette in 1860. Flinders Petrie excavated at the site and published some results of his work in 1884. A systematic investigation of the site was undertaken by Pierre Montet (1928–56), and has been continued, first under the direction of Jean Yoyotte (1965–86) and later by Philippe Brissaud (from 1987 onward). (Brissaud, 1992; Bard, 2007). About twenty-six obelisks, all but one of Ramesses II, were found among the monumental remains of Tanis in the temple of Amen, which was the main temple in the city (Petrie, 1885). Most of those obelisks were sculpted from granite, the stone which was commonly used in the sculpting of obelisks in ancient Egypt. (see Fig. 2).

Unfortunately, most of those granitic obelisks are broken, and suffer from several decay features related

to the damage factors that affect the minerals of granitic stones of those obelisks. Deterioration of granitic stones is a combined process caused by physical, chemical and microbiological factors (Honeyborne, 2006; Young, 2006; Kwon and Oh, 2011; Giménez et al, 2013).

Water, from any of its different resources (such as rain, relative humidity, and groundwater) is considered the major deterioration factor of granitic obelisks of Tanis. It plays a major role in the mineralogical alteration of granite. Moreover, it works as a catalyst in its chemical and microbiological deterioration processes. Finally it will cause diverse deterioration aspects, such as granular disintegration, scaling, cracking, efflorescence, soiling, microbiological colonization (La Iglesia, 1994; Fitzner et al., 2000; Wongfun et al., 2010; Gour et al., 2014).

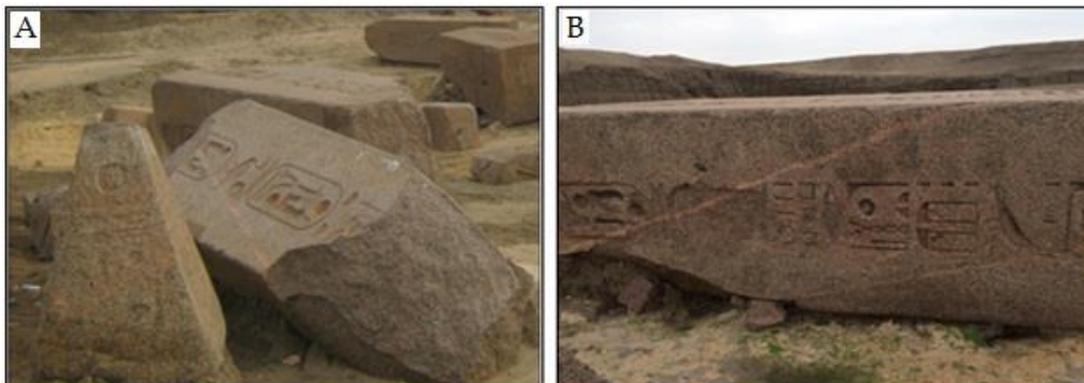


Fig. 2 (A and B) Some granitic obelisks at Tanis.

From this view of point, the materials which are used in the protection of those granitic obelisks must have the property of hydrophobicity in order to protect them from the harmful effects of water (Price and Doehne, 1996; Ballester and Gonzalez, 2001; Torraca, 2009). In the last decade, polymer nanocomposites have attracted great interest in the field of culture heritage conservation due to their unique properties, such as superhydrophobicity, self-cleaning (Manoudis et al., 2008; Mosquera et al., 2008; Manoudis et al., 2009; De Ferri et al., 2011; Baglioni et al., 2012; Kapridaki and Maravelaki-Kalaitzaki, 2012).

A superhydrophobic surface is a surface on which the water droplets form almost perfect spheres with contact angle larger than  $150^\circ$ , and even a very slight tilting is sufficient to cause the droplets to roll off (Latthe et al., 2012). These surfaces are of special interest as they also have the property of self cleaning, resulting from the rolling action of the water, which can carry the dirt away (Zhou et al., 2009). The self-cleaning process can also take place by using photocatalytic nanoparticles that can chemically break down the dirt when exposed to sun light (Bergamonti, et al., 2013).

In the present study, three types of nanocomposites were used in the treatment of granitic samples collected from Tanis. The first nanocomposite is a ready for use product, based on titanium dioxide nanoparticles in alkoxy silane polymer, while the other two nanocomposites were prepared by adding titanium dioxide and zinc oxide nanoparticles to a fluorocarbon commercial polymer.

This research aims to determine the efficiency of the used nanocomposites in order to select the best of them for the protection of granitic obelisks at Tanis.

The properties of the treated granitic samples, were comparatively investigated by visual appraisal, colorimetric measurements, static water contact angle, total immersion water absorption, abrasion resistance, scanning electron microscope, and photo-degradation test.

## 2. MATERIALS AND METHODS

### 2.1. Materials

#### 2.1.1. Granite samples

Granitic fragments were collected from a site near the archaeological city Tanis, and then were cut into cubic samples  $3 \text{ cm}^3$ .

#### 2.1.2. Nanocomposites

The first nanocomposite used in this study is PF4 (Aqueous dispersion of alkyl alkoxy silane modified titanium dioxide nanoparticles), which was supplied by Chem Spec Company, Italy.

The other two nanocomposites were prepared by adding 0.5% w/v of Titanium dioxide, and Zinc oxide nanoparticles to the commercial polymer PK 50 AE (Fluorocarbon based polymer in organic solvent), which was supplied by La Nuova Chimica Ossolana, Italy. The nanoparticles of  $\text{TiO}_2$  and  $\text{ZnO}$  were purchased from Sigma Aldrich chemical company, Germany. The selection of the nanoparticles concentration was suggested by several preliminary tests, which were carried out to select a suitable concentration of nanoparticles in the polymer PK 50 AE, in order to obtain a homogenous dispersion.

### 2.2. Methods

#### 2.2.1. Transmission electron microscope

$\text{TiO}_2$  and  $\text{ZnO}$  nanoparticles were examined using Jeol JEM-2100 transmission electron microscope. TEM micrographs declared that the grain size of Titanium dioxide nanoparticles are less than 25 nm, where the grain size of Zinc oxide nanoparticles are less than 50 nm, as shown in Fig. 3.

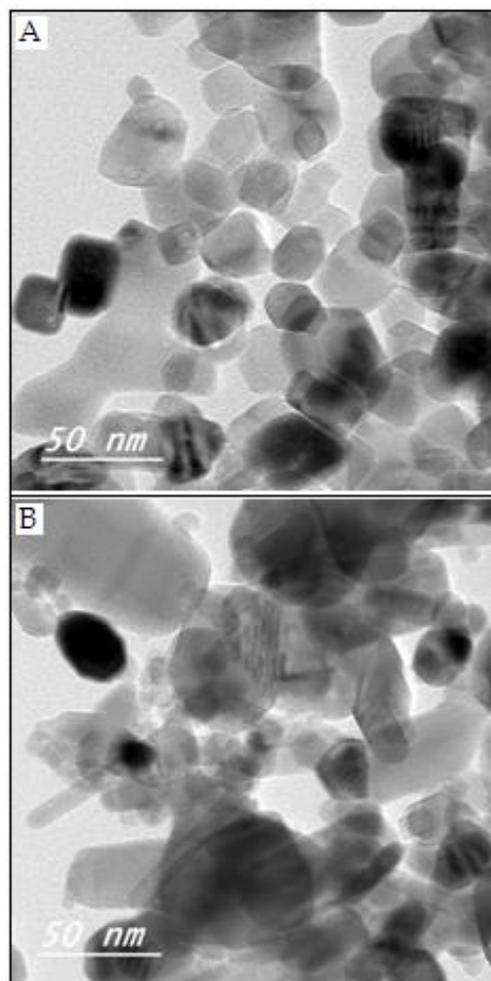


Fig. 3 TEM micrographs of A)  $\text{TiO}_2$ , B)  $\text{ZnO}$  NPs.

### 2.2.2. Polarizing microscope

The petrographic study of the granitic samples was performed using Nikon eclipse LV100POL polarizing microscope.

### 2.2.3. X-Ray diffraction analysis

The mineralogical composition was determined by means of X-ray diffraction analysis, which was performed using Philips Analytical X-Ray Diffractometer, with the following operating conditions:- Diffractometer Type : PW1840, Tube anode : Cu, Generator tension (KV) : 40, Generator Current (mA) : 25, Wavelength Alpha1(Å) : 1.54056, Wavelength Alpha2(Å) : 1.54439, Intensity ratio (Alpha2 / Alpha1) : 0.500, Receiving slit: 0.2, Monochromator used : NO.

### 2.2.4. X-Ray fluorescence analysis

The chemical analysis was carried out using X-ray fluorescence (Axios spectrometer, PANalytical Company, Netherlands).

### 2.2.5. Color alteration

The effect of nanocomposites on the general appearance of the treated samples was evaluated by visual appraisal and colorimetric analysis. The colorimetric measurements were carried out on the treated and untreated granitic samples, on homogenous spots, by means of Optimatch 3100, based on the L\*, a\* and b\* coordinates of the CIELAB color space (Schanda, 2007).

### 2.2.6. Hydrophobicity

The hydrophobicity of the treated samples was evaluated by measuring the static water contact angle using Drop master DM-701, fully automated contact angle meter.

### 2.2.7. Water absorption

Total immersion water absorption measurements were carried out using the gravimetric method. The granitic samples were completely immersed in distilled water at room temperature. After 24 hours, the samples were taken out, wiped with tissue paper carefully and weighed immediately. The amount of the absorbed water was calculated using the following equation:-

$$\text{water absorption} = \frac{W_2 - W_1}{W_1} \times 100 = \dots\dots \%$$

Where (W<sub>2</sub>) is the mass of the sample after immersion in water for 24 hours, and (W<sub>1</sub>) is the mass of the sample before immersion.

### 2.2.8. Abrasion resistance

Mechanical properties were determined by testing the abrasion resistance of the treated and untreated samples using Bohme abrasion wheel 1006.

### 2.2.9. Scanning electron microscope

Quanta 250 scanning electron microscope was used to examine and evaluate the ability of the nanocomposites to protect the granitic samples.

### 2.2.10. Photo-degradation test

The effectiveness of nanocomposites under study as self-cleaning materials was estimated by the test of photo-degradation. The treated and untreated granitic samples were stained with Methylene-blue dye. Next, the treated and untreated samples were irradiated with ultraviolet light working at 350 nm, 500 W. Colorimetric variations were determined using the same procedure described above.

### 2.2.11. Procedures of protection

The cubic samples were washed by distilled water, and dried in an oven at 105 °C for at least 24 hours to reach constant weight, and left to cool at room temperature and controlled RH 50%, then weighed again. To simulate the treatment as it happens in the archaeological field, the nanocomposites were applied onto the granitic samples by brushing until visible refusal (Persia, et al., 2012).

Treated samples were left for 1 month at room temperature and controlled RH 50% to allow the polymerization process to take place. The samples were weighted again, and the polymer uptake was calculated (Table 1).

Table 1: The values of polymer uptake in treated granitic samples.

Nanocomposite	Polymer uptake (%)
PF4	0.05
Fluotanium (PK 50 AE+TiO <sub>2</sub> )	0.04
Fluozinc (PK 50 AE+ZnO)	0.04

## 3. RESULTS AND DISCUSSION

### 3.1. Stone characterization

The petrographic study revealed that the granitic samples contained very fragile and fine cracked grains. Feldspars and quartz are the minerals with the highest presence in the samples. Partial altera-

tion of biotite and potash feldspar into sericite was also observed. (see Fig. 4).

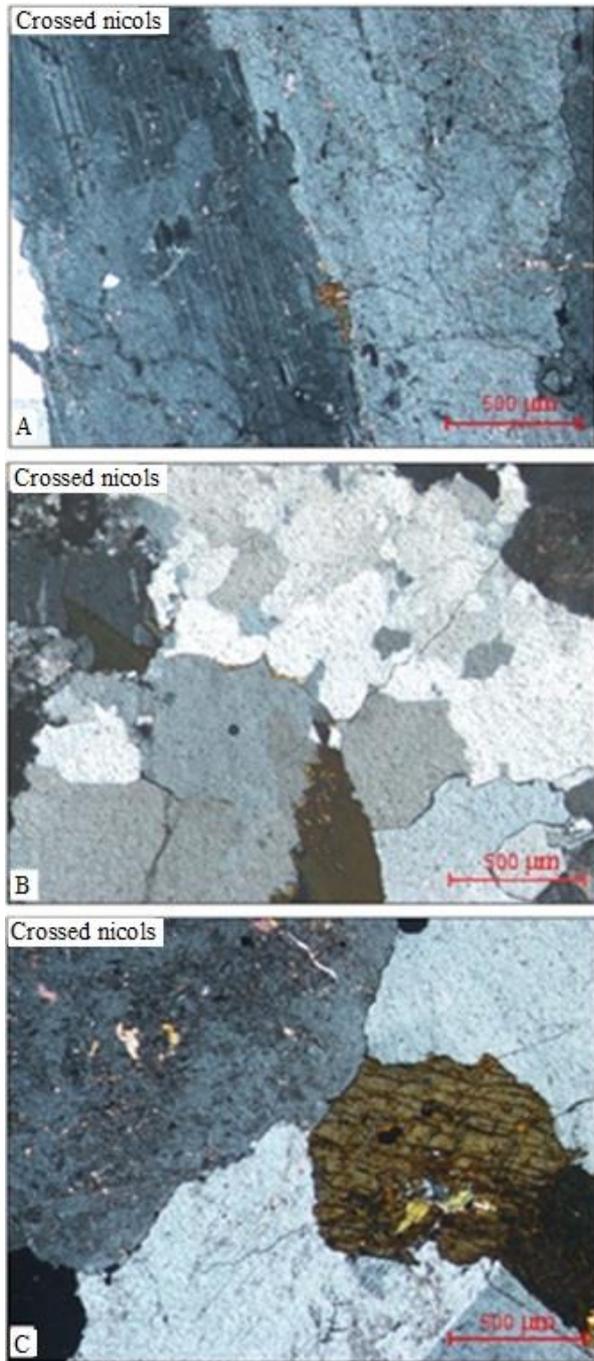


Fig.4. A) Partial alteration of plagioclase Feldspar, B) Cracked grains of quartz, C) Alteration of potash feldspar and biotite into sericite.

The mineralogical composition of the granitic samples collected from Tanis was determined by means of X ray diffractometer. This analysis showed that the samples are composed of quartz, microcline, albite, and biotite in addition to sericite, and halite as weathering products. The results are reported in Table. 2.

The chemical analysis was performed by using X-ray fluorescence, and the results are summarized in Table. 3.

Table 2: Mineralogical composition of the granitic samples.

Minerals	Approx. percentages	
	Sample 1	Sample 2
Quartz	44.66 %	40.06 %
Microcline	18.17 %	18.06 %
Albite	29.20 %	34.45 %
Biotite	02.85 %	04.56 %
Sericite	02.59 %	02.84 %
Halite	02.50 %	00.00 %

Table 3: Chemical composition of the granitic samples.

Main constituents	Concentration (wt%)
SiO <sub>2</sub>	67.27
Al <sub>2</sub> O <sub>3</sub>	13.27
K <sub>2</sub> O	7.06
Fe <sub>2</sub> O <sub>3</sub>	4.39
Na <sub>2</sub> O	2.99
CaO	1.84
MgO	0.70
TiO <sub>2</sub>	0.61
BaO	0.16
MnO	0.06
P <sub>2</sub> O <sub>5</sub>	0.21
Cl	0.07
SO <sub>3</sub>	0.06
ZnO	0.01
SrO	0.03
Co <sub>3</sub> O <sub>4</sub>	0.01
ZrO <sub>2</sub>	0.30
L.O.I	0.81

As a result of petrographical, mineralogical, and chemical characterization, the granitic obelisks at Tanis are subjected to hard physiochemical weathering, which resulted in partial alteration of both biotite and potash feldspar into sericite. This is due to leaching of iron from the crystal structure of biotite, oxidation of ferrous ions to ferric ones forming iron oxide stains on microfracture cleavages, as shown in fig. 4. On the other hand, addition of wa-

ter molecules in the crystal structure of potash feldspar.

Also there is a disintegration due to differential expansion during physical weathering process by splitting on basal cleavage (Helmi, 1985).

The presence of Halite (NaCl) was also detected in the granitic samples. It is suggested that the soil of Tanis is the main source of NaCl salt which rises with the subsoil water through the surfaces of granitic obelisks (Baptista-Neto et al., 2005). Also sodium is slowly removed from plagioclase feldspar (albite) as an alternative source (Helmi, 1985).

### 3.2. Aesthetical properties

Visual appraisal and colorimetric measurements were carried out to evaluate the aesthetic alteration of the treated granitic samples. By the test of visual appraisal, it was demonstrated that all the used nanocomposites don't have a noticeable effect on the color of the treated samples.

The chromatic changes  $\Delta E^*_{ab}$  were also carried out by means of Optimatch 3100, in order to calculate and determine the variation of the aesthetical properties induced by the treatments, according to the following equation:-

$$\Delta E^*_{ab} = \sqrt{[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]}$$

where  $\Delta L^*$ ,  $\Delta a^*$  and  $\Delta b^*$  are the differences in the,  $L^*$ ,  $a^*$  and  $b^*$  coordinates (according to CIELAB color space) of the treated and untreated granitic samples.

The  $\Delta E^*_{ab}$  values obtained from the chromatic measurements of the treated granitic samples (Table. 4), confirmed the results of the visual appraisal.

Table 4: The chromatic measurements of the treated samples.

Nanocomposite	$\Delta E^*_{ab}$
PF4	2.01
Fluotanium	3.55
Fluozinc	3.84

### 3.3. Static water contact angle

There is no doubt that water repellency is the most important property of the protective materials, as water is considered to be the main deterioration factor for stones and stone-based monuments (Helmi and Hefni, 2014). The water repellency of the treated granitic samples was determined by measuring the static contact angle (sessile-drop method) of water droplets placed on different positions on the samples, and the average values were taken. The untreated and treated samples with PK 50 AE were included in this test for comparison.

The results showed that all nanocomposites used in this study enhanced the property of water repellency of the granitic samples. PK 50 AE achieved high degrees of contact angle.

This is attributed to the presence of fluorine atoms that significantly reduces the surface energy of the polymer (Constancio et al., 2010).

The data declare that the addition of  $TiO_2$  and ZnO nanoparticles to the polymer of PK 50 AE resulted in superhydrophobic nanocomposites, due to the surface roughness resulting from nanoparticles, that lead to trapping of air between water droplets and the rough surface, which is illustrated in the Cassie-Baxter scenario (Cassie and Baxter, 1944). PF4 achieved static contact angle degree less than Fluozinc, and Fluotanium. Table. 5, and Fig. 5 illustrate the results of static water contact angle measurement.

Table 5: Static water contact angle of treated and untreated granitic samples.

Product	SCA (°)
Untreated sample	20.4 °
PK 50 AE	108 °
PF4	135.4 °
Fluotanium	150.2 °
Fluozinc	156.3 °

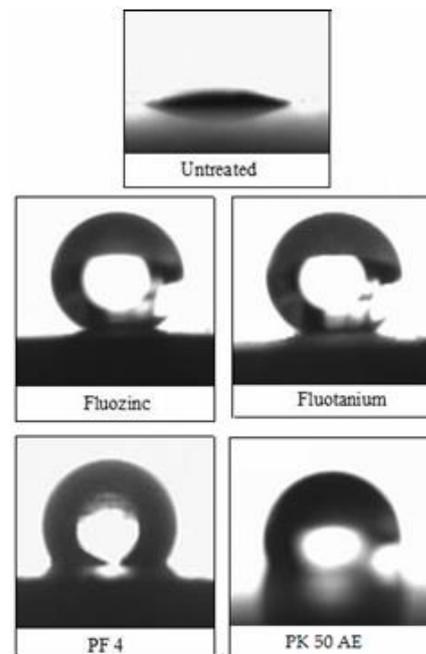


Fig.5. Photographs of water droplets on the treated and untreated granitic samples.

### 3.4. Water absorption

All the nanocomposites used in this study, led to reducing the amount of water absorbed by the gra-

nitic samples. The results of water absorption are reported in Table 6.

The nanocomposites of PK 50 AE (Fluotanium and Fluozinc) achieve almost the same values of water absorption, so it can be suggested that the water absorption rates of the nanocomposites substantially depends on the chemical composition of the polymers used in their fabrication (Tsakalof et al., 2007).

Table 6: Rates of decrease in water absorption of the treated granitic samples.

Nanocomposites	Rate of decrease in Water absorption %
PF4	87.96
Fluotanium	93.51
Fluozinc	93.51

### 3.5. Abrasion resistance

Mechanical properties were determined by testing the abrasion resistance of the treated and untreated samples by means of Bohme abrasion wheel 1006. The abrasion resistance was determined by calculating the percentage of the loss in weight for the granitic samples. The results are reported in Table. 7.

As expected, all products used in this study achieved slight improvements in abrasion resistance, this can be attributed to the low amount of polymer uptakes resulting from the low porosity of the granitic samples. PF4 realized the best result in abrasion resistance, this can be attributed to the high mechanical properties associated to alkoxy silane, the main component of this nanocomposite. (Charola, 1995).

Table 7: Rates of the loss in weight for treated and untreated granitic samples.

Nanocomposite	loss in weight (%)
Untreated sample	1.95
PF4	1.08
Fluotanium	1.34
Fluozinc	1.29

### 3.6. Scanning electron microscope

Textural and morphological characterization was performed by using scanning electron microscope in order to examine and evaluate the ability of the nanocomposites used in this study to consolidate and protect the surfaces of the granitic samples.

According to SEM micrographs of the treated and untreated granitic samples (Fig. 6), it can be concluded the following points:-

- The untreated samples appeared to be very fragile, and had many fine cracks (Fig. 6a).

- The nanocomposites of Fluozinc and Fluotanium succeeded in covering the grains of the granitic samples with rough nanostructural polymeric networks, containing a lot of tiny protruded aggregates (Fig. 6b, 6c).

• These rough nanostructures explain the reason of the superhydrophobicity, which were achieved by these nanocomposites (Manoudis et al., 2008). However, Fluozinc and Fluotanium led to the formation of rough nanostructure, the granitic samples treated with Fluozinc achieve water contact angles higher than the samples treated with Fluotanium. This may be attributed to the hydrophilic character of titanium dioxide nanoparticles. (Pinho and Mosquera, 2013).

- The nanocomposite of PF4 covered the samples with almost homogenous polymeric coat, containing tiny individual nano aggregates (Fig. 6d).

### 3.7. Self-cleaning properties

The effectiveness of the nanocomposites used in this study was investigated by the test of photo-degradation, in which the treated and untreated granitic samples were previously stained with methylene-blue, and irradiated with Ultraviolet.

By measuring the total color variations (Table. 8) of the samples after staining with methylene-blue and irradiation with Ultraviolet, we can conclude the followings:-

The untreated samples achieved the high values of total color variation ( $\Delta E^*_{ab} = 28.13$ ), as it hadn't the ability to catalyze the photo-degradation of methylene-blue.

- The nanocomposites used in this study, show good self-cleaning properties, as the samples were treated by them had a good ability to reduce and remove the stains of methylene-blue.

• High photo-degradation action of methylene-blue was occurred in the first few hours of exposure to Ultraviolet.

- The nanocomposites based on titanium dioxide nanoparticles achieve better results than the nanocomposite of zinc oxide NPs, regarding to the highest photocatalytic activity of TiO<sub>2</sub>.

Table 8: Total color variations (for methylene-blue stains) on treated and untreated samples.

Nanocomposite	$\Delta E^*_{ab}$
Untreated sample	28.13
PF4	7.17
Fluotanium	7.75
Fluozinc	9.52

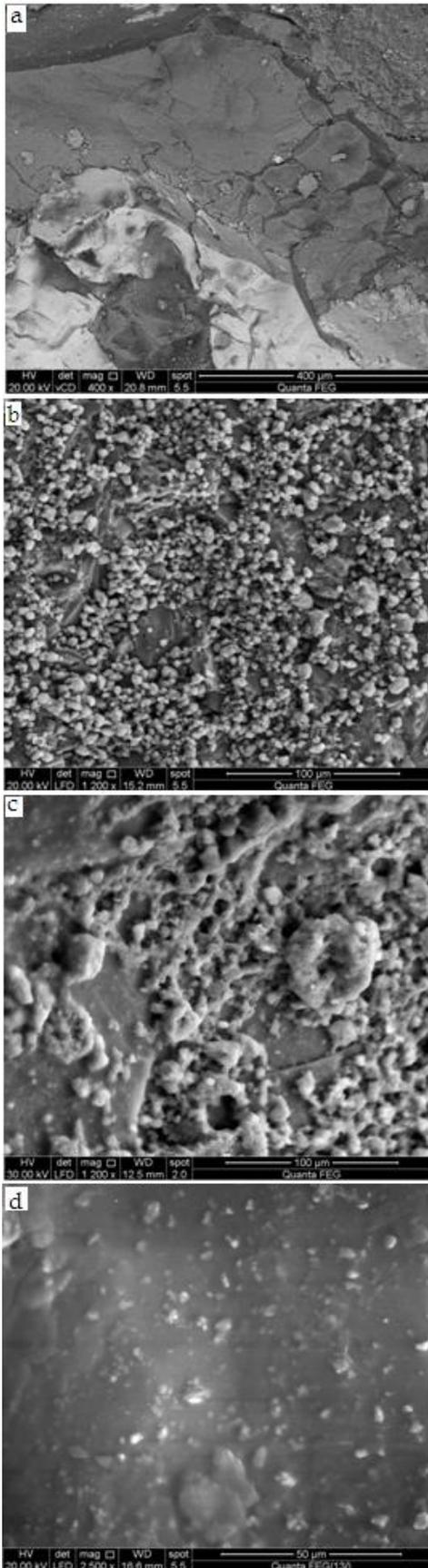


Fig.6. SEM micrographs of a) untreated granitic sample, and the samples treated with b) Fluotanium; c) Fluozinc; d) PF4.

### 3.8. Durability of nanocomposites

The durability of the nanocomposites is very important requirement, especially for the architectural and archaeological surfaces that are exposed to natural weathering in outdoor environments.

To evaluate the durability of the nanocomposites used in this study, the treated samples were exposed to ultraviolet irradiation, and then the static water contact angle measurement was repeated.

For all nanocomposites, the values of static water contact angle clearly reduced after exposure to ultraviolet irradiation, as shown in Fig. 7. This can be attributed to the photo-oxidative effect of ultraviolet, which is considered to be one of the most deterioration factors of polymers. It was also observed that the nanocomposite of Fluozinc is more resistance than the nanocomposites of Fluotanium and PF4 (Both contain  $\text{TiO}_2$ ), this may be regarded to the highest photocatalytic activity of  $\text{TiO}_2$ , that can play important role in the photo-degradation of the polymers during exposure to ultraviolet radiation.

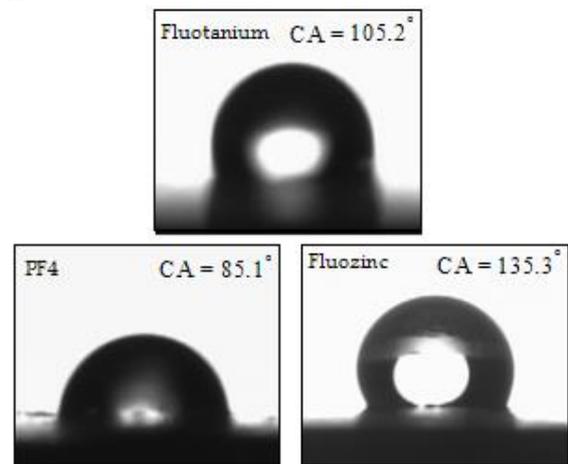


Fig.7. Photographs of water droplets on the treated granitic samples after exposure to ultraviolet radiation.

## 4. CONCLUSIONS

In the present study, the efficiency of the three nanocomposites (PF 4, Fluotanium, Fluozinc) was comparatively evaluated in order to select the best one for the protection of granitic obelisks at Tanis. The colorimetric measurements before and after treatment demonstrated that the three nanocomposites didn't have a noticeable effect on the general appearance of the treated granitic samples.

The results showed that the nanocomposite Fluozinc is the most suitable polymer for the protection of the granitic samples, as it achieved the highest values of static water contact angle without causing total closure of the pores as observed from SEM micrographs.

It will inhibit the chemical weathering effect of water, which is the main source of deterioration in granite. Moreover it showed good self-cleaning properties, and high ability to resist the physical weathering induced by ultraviolet irradiation.

The achieved results in this study will be useful for the protection and preservation of granitic obelisks and monuments at Tanis.

## ACKNOWLEDGEMENTS

The authors are very grateful to all the members of the archaeological site "Tanis", for their assistance during collecting the archaeological information of the site, and also for their permission to study the granitic obelisks at Tanis.

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