A SIMPLE METHOD FOR MEASURING THE STATIC WATER CONTACT ANGLE FOR EVALUATION THE HYDROPHOBICITY OF THE CONSOLIDATING AND PROTECTIVE MATERIALS

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Abstract

Many scientists and researchers, have confirmed that water in any physical state, is considered the major deterioration factor of stones. It has not only a direct role in the damage of the stones, but also it works as a catalyst in their chemical and microbiological deterioration processes, which result in diverse deterioration aspects. From this standpoint, the materials which are used in the consolidation and protection of stones, must have the property of hydrophobicity in order to protect them from the harmful effects of water.
This paper presents a simple method for measurement the static water contact angle, which is considered the most important method for evaluation the hydrophobicity of the consolidants and protective materials.
Silicon-based polymers; Wacker OH 100, Dow Corning MTMOS, Mega Protec 1, Mega Protec 2 were used to consolidate and protect sandstone samples. The hydrophobicity of the treated sandstone samples, were evaluated comparatively by using a simple and low cost method for measuring the static water contact angle and total immersion water absorption. Morphological aspects were determined by scanning electron microscope (SEM).

Keywords: static water contact angle; hydrophobicity; consolidation; protection; hydrophobic; sandstones.

1. Introduction

There is no doubt that the ancient Egyptian civilization, is considered one of the oldest and the greatest civilizations over the world. Many historians, believe that the experience of ancient Egyptian about the extraction of stone from quarries, and using it in the fields of the construction and sculpture, played a substantial role in the preservation of Egyptian civilization features.
Sandstone is considered one of the most important types of stones, which was used in the fields of arts and architecture in ancient Egypt. In particular, they were used in the construction of numerous ancient Egyptian temples in Upper Egypt, such as Luxor and Karnak temples. they were also used in the sculpting of the finest statues, as well as many other important sculptures such as obelisks, columns, coffins, and Stelae.

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Unfortunately, due to the high porosity of the sandstones, they are easily affected by water from its different resources such as rain, relative humidity, and groundwater [Abd El-Hady M. M. 2000, Amoroso, G., Fassina, V. 1983, Fitzner, B., et al. 2003, Saleh, S. A. et al.1992].

Water, in any physical state, is considered the major deterioration factor, due to its ability to dissolve the salts and the other soluble substances in the stone, in addition to cause cracking in freeze-thaw and wet-dry cycles, as well as its roles as a catalyst in the chemical and microbiological deterioration processes of the stone, which result in diverse deterioration aspects such as granular disintegration, exfoliation, detachment, erosion, as well as cracking, deformation, efflorescence, discoloration, different microbiological colonization, and finally loss of the monuments which were carved or constructed from those stones [Hosono, T., et al. 2006, Jain, A., et al. 2009, Petuskey, W. T., et al. 1995, Turkington, A.V., et al. 2003, Warscheid, Th., Braams, J. 2000, Weaver, M. E. 1991].

In order to prevent the damage processes of the stone, there is necessity to treat it with a material has the ability to consolidate its internal structure, as well as protect it from the harmful effects of water, by means of hydrophobic materials [D'arienzo, L., et al. 2008, Price, C. A., Doehne, E. 1996, Tsakalof, A., et al. 2007].

Hydrophobicity of materials mainly depend on their chemical composition and structure. The hydrophobic material has water contact angle larger than 90º , due to its low surface energy. By contract, the hydrophilic material has water contact angle smaller than 90º , due to its high surface energy [Wu, J., et al. 2011, Yuan, Y., Lee, T. R. 2013].

This paper presents a simple method for measurement the static water contact angle, which is considered the most important method for evaluation the hydrophobicity of the consolidants and protective materials .

Silicon-based polymers; Wacker OH 100, Dow Corning MTMOS, Mega Protec 1, Mega Protec 2 were used to consolidate and protect sandstone samples. The hydrophobicity of the treated sandstone samples, were evaluated comparatively by using a simple and low cost method for measuring the static water contact angle and determine the total immersion water absorption. Morphological aspects were also evaluated by scanning electron microscope (SEM).

2. Materials and Methods

2.1. Materials

The sandstone blocks were collected from the quarry of Gebel Ahmar, one of the most important quarries of sandstone in Egypt. The mineralogical composition was determined by X-ray diffraction analysis, which was performed using Philips Analytical X- Ray Diffractometer. The operating conditions were:
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.
Four types of silicon-based materials were applied in the consolidation and protection of sandstone samples by brushing: (1) Wacker OH 100 (Wacker Chemie, Germany) ethyl silicate based product; (2) Dow Corning (Sigma-Aldrich, Germany) methyltrimethoxysilane based product; (3) Mega Protec 1 (Intrade chemicals, Egypt) silane and siloxane – water based product; (4) Mega Protec 2 (Intrade chemicals, Egypt) silane and siloxane – solvent based product.

2.2. Methods
2.2.1. Application of silicon polymers

The sandstone blocks were cut into cubic samples $2.5 \times 2.5 \times 2.5\ cm^3$. The cubic samples were washed by distilled water, and dried in an oven at 105 $^{\circ}C$ for at least 24 hours to reach constant weight, and left to cool at room temperature and controlled RH 50%, then weighed again. The polymers were applied onto samples by brush (three applications). 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.

2.3. Evaluation tests

2.3.1. Appearance

The effect of polymers on the appearance of the treated samples was evaluated by the visual appraisal of the color difference between the treated and untreated sandstone samples.

2.3.2. Static water contact angle

Static water contact angle measurement is the common method for determination the hydrophobicity of different materials. by studying and analyzing the techniques and machines which have been used in the measuring of static water contact angle, it was found that their scientific basis depends on obtaining an image of water droplet on the material surface, and then the contact angle is measured from the image using either manual or automatic goniometer [ASTM C813-90. 1994, ASTM D724-99. 2003, ASTM D5725-99. 2008, Duncan, P., et al. 2005, Erbil, H. Y. 2006].

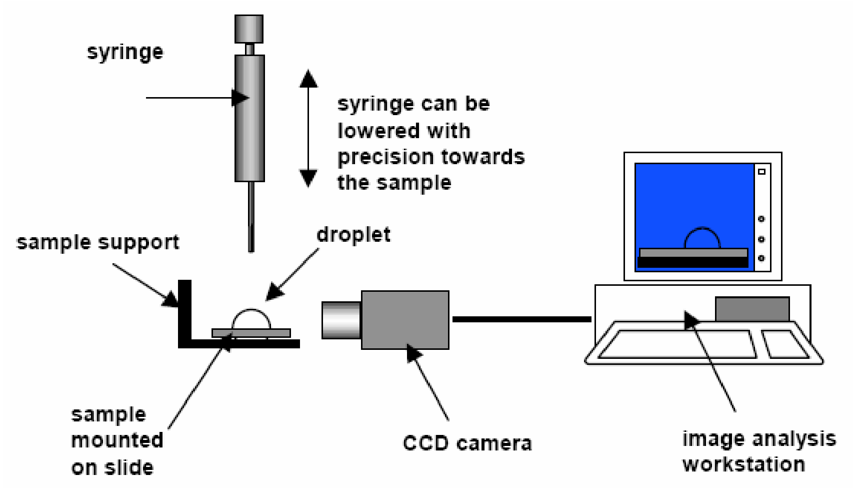


Fig.1. Components of the machines of static contact angle measurement. (After: Duncan, P., et al., 2005)

There is no doubt that these methods are effective, but the process is complex, very expensive, and not available. In the present study we measure static water contact angle of the materials used in the consolidation and protection of sandstones by using a simple method consisting of the following components:-

2.3.2.1. Support

A wooden support was designed, in which the camera and the sample stage were positioned. The main purpose of this support to obtain a system with stable parameters such as (1) the camera position and its stability, (2) sample stage, (3) the distance between the camera and the sample.

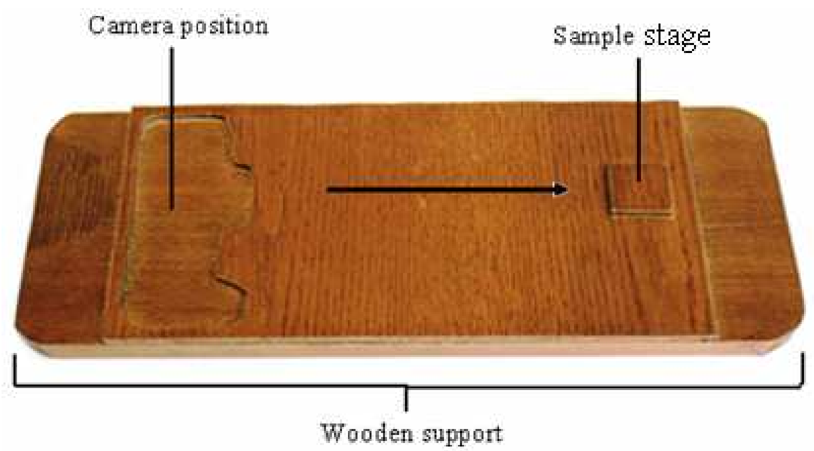


Fig.2. The wooden support .

2.3.2.2. Liquid Delivery System

A syringe was used to apply or stroke de-ionized water droplets onto the sample surface. The length of this stroke was been as short as possible in order to minimize the force exerted to the droplet.

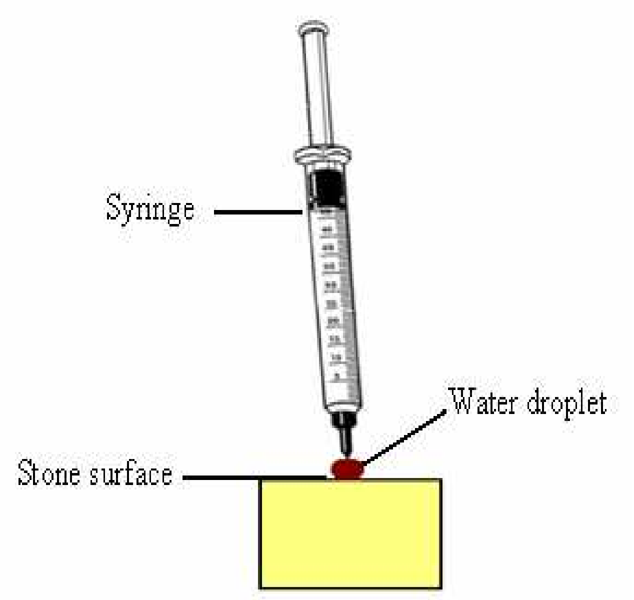


Fig.3. Method of stroking water droplet on the stone surface.

2.3.2.3. Camera

High resolution Canon camera is equipped with a lens 18-55 was used to capture the images of water droplets on the surface of sandstone samples.

Fig.4. The method of capturing the images of static contact angle.

2.3.2.4. Computer

After capturing the images of water droplets on the stone samples, the images were loaded to the computer, and the contact angles were measured with the help of software program (such as AutoCAD).

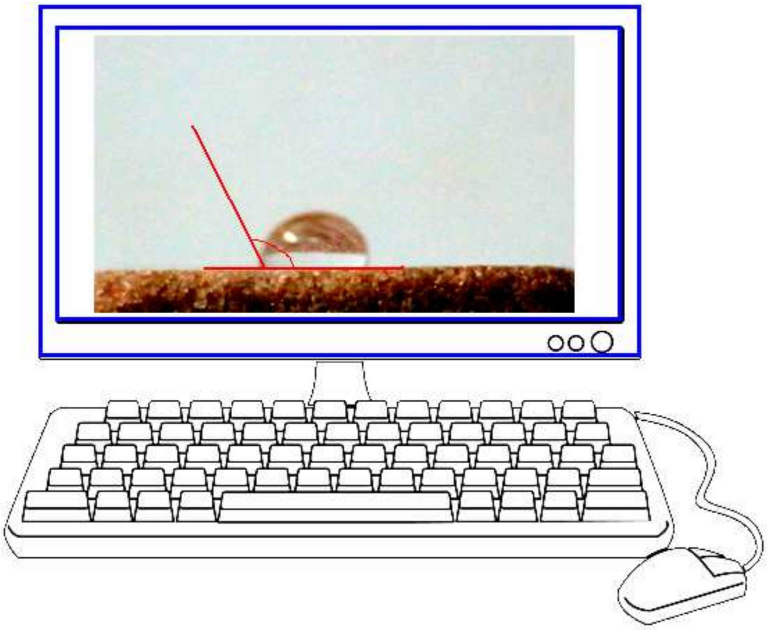


Fig.5. Automatic calculation of the static contact angle by using computer software program.

The contact angle can also be measured by printing the images, and determination of the droplet edges, and finally the angle of a line tangent with the drop at the stone surface can be measured.

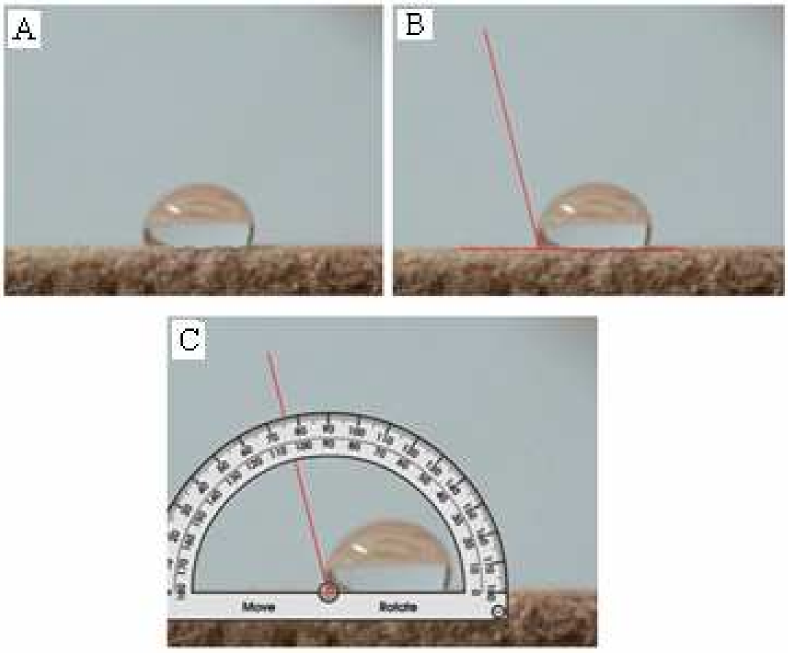


Fig.6. Manual calculation of the static contact angle by using a protractor.

2.3.3. Water absorption

The amount of the absorbed water was calculated using the following equation:-

$$\text{Water absorption} = \frac{(W_2 - W_1)}{W_1} \times 100 = \cdots\cdots \%$$

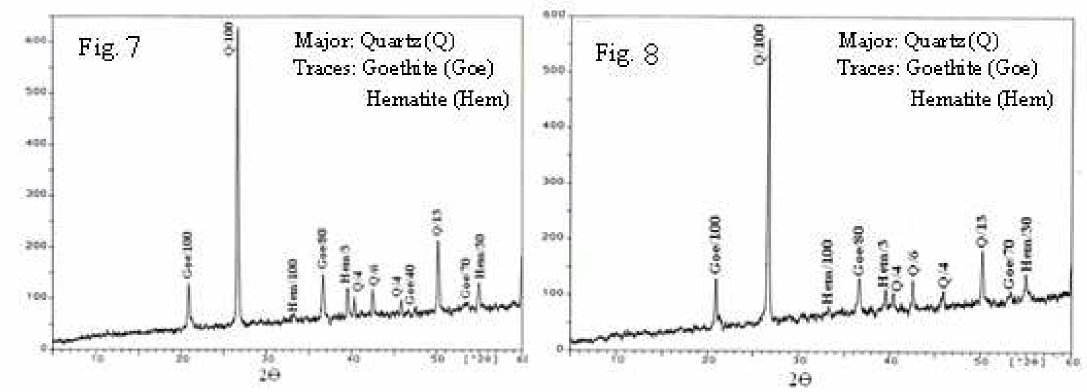
Where (W_2) is the mass of the sample after immersion in water for 24 hours, and (W_1) is the mass of the sample before immersion.

2.3.4. Scanning electron microscope

INSPECT S scanning electron microscope was used to examine the morphological aspects of the consolidants and protective materials, which were used in this study.

3. Results and Discussion

X- Ray diffraction patterns (Figs. 7, 8) showed that the sandstone samples consists mainly of Quartz [SiO_2] as a major mineralogical constituent, with trace amounts of Goethite [FeO (OH)] and Hematite [Fe_2O_3]. The results are summarized in Table 1.



Figs. 7, 8. X-ray diffraction patterns of two sandstone samples.

Table 1
Mineralogical composition of the sandstone samples

Composition %	Quartz	Goethite	Hematite
Sample 1	80	12	8
Sample 2	78.5	13.5	8

By comparing the values of polymer uptake (Table 2), it was observed that Wacker OH 100 achieved the highest value of polymer uptake. This result can be attributed to the low viscosity of Wacker OH 100, which allows to high penetration inside the sandstone pores.

Table 2
The values of polymer uptake by treated sandstone samples.

Polymer	Symbol	Polymer Uptake (%)
Wacker OH 100	A	4.4
MTMOS	B	1.5
Mega (1)	C	1.3
Mega (2)	D	3.3

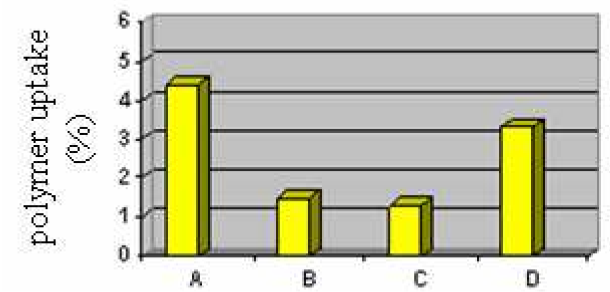


Fig.9. The values of polymer uptake by treated sandstone samples.

The effect of the used materials on the appearance of the treated samples was evaluated by the visual appraisal of the color difference between the treated and untreated sandstone samples. It was found that Wacker OH 100 and MTMOS didn't have a noticeable effect on the color of the samples. Mega (1) led to a slight change in the color of the treated sample. Mega (2) failed in this test, as it led to a significant change in the color. Therefore it was excluded from the rest of the tests.

Fig .10. General appearance of the treated samples.

The hydrophobicity of the samples was evaluated by measuring of static contact angle of water droplets placed on three different positions of the surfaces of the sandstone samples, and the average values were taken.
The static water contact angle (SCA) of the untreated sandstone sample was zero^{o}, as the water droplet not only spreads on the stone surface, but also it penetrates inside the pores. The consolidants and protective materials increases the static contact angle of the sandstone samples. MTMOS achieved the highest

static water contact angle, this is attributed to its hydrophobic character, resulting in the presence of non polar methyl group connecting to the silicon atoms (the backbone in this polymer). However, Mega (1) had the ability to water repellency, it was found to be less hydrophobic than MTMOS. Since Wacker OH 100 loses the organic radical (Ethyl groups) when it reacts with water (Hydrolysis process),it had a little effect on water repelling, and achieved the lowest contact angle.

Table 3
Results of static water contact angle of the treated sandstone samples.

Polymer	Symbol	Static contact angle
Wacker OH 100	A	37º
MTMOS	B	104º
Mega (1)	C	71º

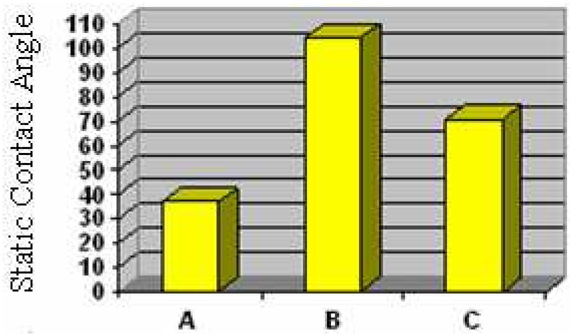


Fig .11. Results of static water contact angle of the treated sandstone samples.

The results of hydrophobicity were confirmed by measuring of water absorption, which demonstrated that the hydrophobic properties of the consolidants and protective materials, have an important role in decreasing the rates of water absorption of the treated sandstone samples.

Table 4
Results of water absorption of the treated sandstone samples.

Polymer	Symbol	Water absorption %	Rate of decrease in Water absorption %
Untreated sample	U	9.3	--------
Wacker OH 100	A	4.9	47.3
MTMOS	B	1.1	88.1
Mega (1)	C	3.6	61.2

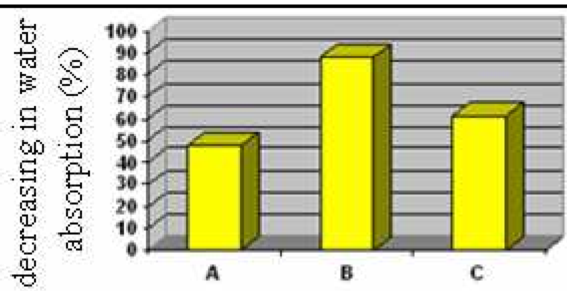


Fig.12. Rates of decreasing in water absorption (%) of the treated samples.

The morphological aspects were evaluated by scanning electron microscope. SEM micrographs showed that the treatment of the sandstone by different materials resulted in better connection between the grains, and partially filling of the big pores. These results confirmed that the hydrophobic properties mainly depend on the chemical composition of the materials.

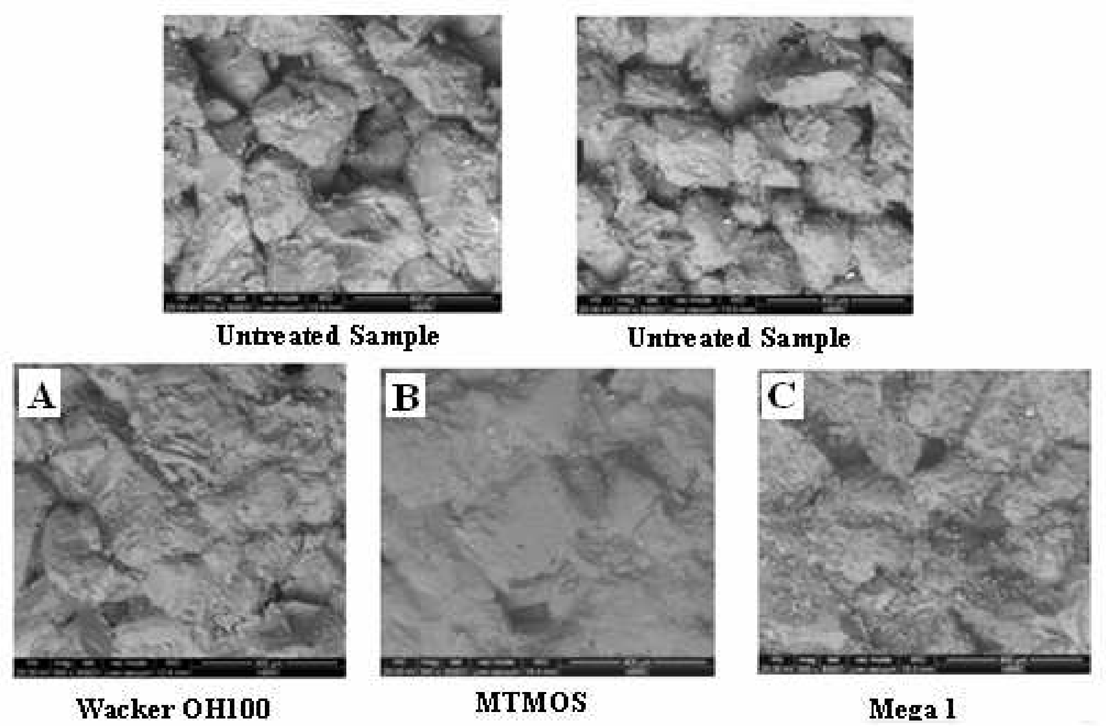


Fig.13. SEM micrographs of the treated and untreated sandstone samples.

4. Conclusions

In this study, we present a simple, low cost, and effective method for measurement the static water contact angle, which is considered the most important way for evaluation the hydrophobicity of the materials used in the consolidation and protection of archaeological stones.

This method was applied in determination the hydrophobicity of 3 different silicon-based materials, which were used in the consolidation and protection of sandstone samples. The results showed that methyltrimethoxysilane (MTMOS) was the best hydrophobic material in this study, as it achieved the highest contact angle (104º), in addition to its ability to decrease the rates of water absorption of the sandstone samples.

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