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COMPARATIVE STUDY OF BIOLOGICAL CLEANING AND LASER TECHNIQUES FOR CONSERVATION OF WEATHERED STONE IN FAILAKA ISLAND, KUWAIT

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ABSTRACT

The present research showed two types of cleaning methodology based on: a) biological self-cleaning technique, and, b) laser technique, were used to clean the weathered stones from black encrustation layers. This paper aim was to compare the efficacy of using biotechnology and lase methodology for cleaning the deteriorated surface layer of the limestone by sulphation which is called black crust. Nd: YAG laser and a Sulfate-reducing bacteria *Desulfovibrio desulfuricans* were carried out on fragments stone from three columns in Failaka Island in Kuwait.

Both two techniques succeeded in removing the black encrustation, the laser procedure was fast and well controlled, but it doesn't save the noble patina of the stone. The biological technology was risk-free, high-quality performance, simple to apply, cost effective, and it protects the noble patina of the surface stone.

KEYWORDS: Laser cleaning- Desulfovibrio desulfuricans- Black encrustation- Biological cleaning- Failaka Island.

1. INTRODUCTION

Recent developments in technology and their use were attracted considerable attention in the field of cultural heritage, the experiments were started a few years ago, by using the field of laser technology and biotechnology treatments in cleaning the archaeological stone with surficial deterioration products.

The interactions between carbonaceous materials and the sulfuric acid resulted from Sulphur dioxide in the polluted air dissolved in moisture led to the transformation of dissoluble calcium carbonate to soluble gypsum by moisture, which was embedded in mineral pores causing solid black hard crust. (Khallaf, 2011; Christodoulakis et al, 2017).

The traditional methods, mechanical or chemical, were uncontrolled. They had many disadvantages such as color change, took a long time application, the uncontrolled interaction between the substrate of the stone and the synthetic materials, etc.. (Matteini *et al*, 2003).

The Conservators used laser technology in the removal of the deteriorated layers, because of its fast and easy operation. Laser involved no chemicals and its clean and safe step for the restorators. (Mazzinghi & Margheri, 2003). An additional advantage of laser cleaning technique was it automatically stops after cleaning and could be used in both out and indoor areas. (Copper et.al, 1992; D'Urbano et al., 1994).

Salimbeni *et al.*, 2000 mentioned that John Asmus in 1970 in the 20th century used Ruby LASER to remove solid crusts precipitated on the stone surfaces by a high-purity laser (Nd: YAG). He produced one wavelength in a very narrow beam and is more selective (Frantzikinaki et al., 2007; Fotakis, 2007) .

The other Laser technique (Robert, 2000; Sekhaneh et al., 2015) combined energy through a lens that has achieved power and density to provide the energy needed to remove the distresses from the archaeological surface which gave satisfying results.

Later, (El- Naggar, 2010) stated that unwanted substances could be withdrawn by laser cleaning based on a study of morphology surface before and after cleaning by different examination and analysis devices.

Chemical and Physical characterization of the surface stone before and after cleaning was evaluated to assess the effectiveness of the two methodologies by XRD, FTIR, SEM- EDX.

The biocleaning method was depended on using a living cell of microorganisms mainly bacteria. This cleaning method has been used in the last ten years. (Troiano et al., 2013).

The first right application of the anaerobic sulfate-reducing bacteria *Desulfovibrio desulfuricans* reported by Atlas et al., (1988) and Gauri & Chowdhury (1988).

The *Desulfovibrio desulfuricans* was utilized for the cleaning of a marble deteriorated by gypsum crust which was the first time for using Sulfate Reducing Bacteria (SRB) for cleaning carbonaceous stones. (Gauri et al., 1992).

(Ranalli et.al,1997) Used both *D. desulfuricans and D. vulgaris* for cleaning two marble objects. They used inorganic material sepiolite as a delivery system for these bacteria, But this method has many disadvantages. It was taken about two weeks for the bacteria colonization, and the sulfide hydrogen may react with the iron ions presenting in media which will result in precipitation iron sulfide.

Sulfate-reducing bacteria can be able to convert gypsum into Ca^{+2}, and SO_4^{+2}. Because bacteria are capable of reducing the SO_4^{+2}, whereas the Ca^{+2} reacts with CO_2 to form new calcium carbonate crystals according to the following chemical formulae (Gauri& et al., 1999):

$$6CaSO_4+4H_2O+6CO_2 \longrightarrow 6CaCO_3+4H_2S+2S+11O_2$$

In the present study, *Desulfovibrio desulfuricans* used self-cleaning methods. The deteriorated black crust of the surface stone. *D. desulfuricans* can convert gypsum (calcium sulfate into H_2S and the free calcium Ca^{+2} which released after anaerobic reaction reacts with Carbon dioxide to forms calcium carbonate $CaCO_3$, This kind of methodology can be used both for cleaning and consolidation.

The hydrobiogel-97 is a polymer created by an acrylic resin hydrogel, that was used as a delivery system for this study (Cappitelli et al, 2006; Giacomucci et al, 2012). The hydrobiogel-97 is the perfect delivery system for the stone and frescos, because of no chromatic changes, with no physical or chemical modifications of the composition of the archaeological stone (Ranalli et al., 2000).

2. MATERIALS AND METHODS

2.1. *Laser description*

The laser used was a Q-switched Nd: YAG (Diode) Conium – sure lite 2 pumped laser at 1064 nm pulse duration eight ns, energy 2-12 MJ adjustable, repetition rate 5-200 HZ adjustable, average power 2.1 W, fiber transmitted handheld device beam size 6 mm.

2.2 *Culture and bacterium media*

The strain *Desulfovibrio desulfuricans* ATCC 27774 D-5 used in this study, maintained in ATCC1279 medium ($MgSO_4$:2g, Sodium Citrate: 5g, $CaSO_4.2H_2O$: 1g, NH_4Cl: 1g, K_2HPO_4:0.5g, Sodium Lactate 3.5 g, Yeast extract 1g, DI water 1000ml) (Ghazy et al., 2011).

For easy application, hydrobiogel-97 was used as a delivery system which was prepared in a chemistry lab in AUC, Egypt. Before starting the bio-cleaning proses suspension of bacteria in water solution, the hydrobiogel-97 was added and applied as a poultice over Japanese paper surface for 48h which can remove poultice more quickly.

2.3 Stereo Microscope

Fragment samples observed by Wild Makroskop M420 stereo-microscope (Heerbrugg, Switzerland), equipped with an Olympus OM1 camera (Chicago, USA).

2.4 (XRD) X-Ray Diffraction Analysis

The Analysis of Failaka Stone determined by XRD analysis The purified crystals examined by X-ray diffraction (XRD powder diagrams) with Philips PW 1140 and Rigaku- Miniflex Ca 2005 diffractometers equipped with a Ni Filter and a Cu-Kα radiation source, and identified according to JCPDS and ASTM, 1974, 1981 criteria. The diffraction peak corresponding to planes 104 (d_0.3 nm) was used to determine approximate Mg Content of calcite (Goldsmith, 1961).

2.5 (SEM) Scanning Electron microscope

The Examination and Analysis of Failaka Stones carried by SEM microscope the micrographs obtained by Jeol JSM (5600 LV), Philips XL 30; the EDX Unit attached to the SEM, 30 K.V., magnification started from (10x to 400.000x), the resolution for W is 3.5nm.

3. RESULTS

3.1. X-Ray Diffraction Analysis (XRD)

The XRD spectrum shows that Failaka stone is a Dolomitic limestone deteriorated with Gypsum and Halite. The data presents that the sample contains Calcite ($CaCO_3$) 40%, Dolomite $CaMg(CO_3)_2$ 31%, Gypsum $CaSO_4.2H_2O$ 15%, Halite NaCl 14%, as shown in Fig. 1.

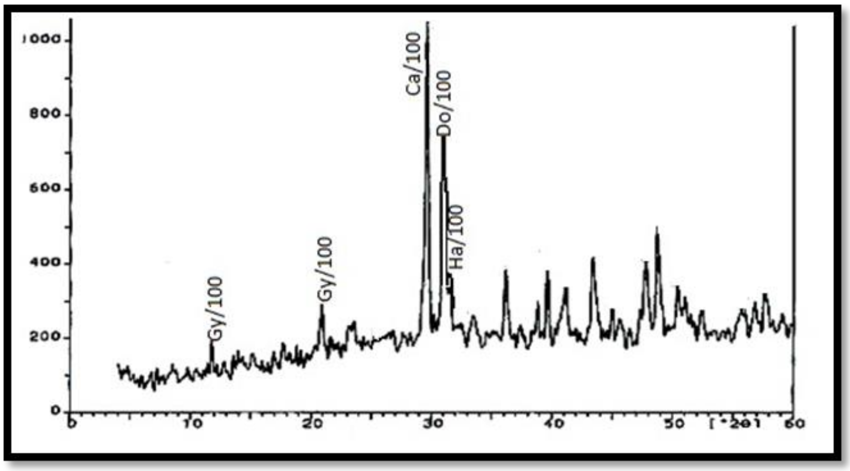

Figure 1. The mineral composition of Failaka stone.

3.2. Scanning Electron microscope (SEM) and the EDX

The data indicate that Failaka Island stone is an organic limestone, Some Fossils present in the matrix of the stone as shown in Fig. 2.

The analysis data of black crust surface presents: (a) Before treatment the limestone is consist of Calcite, Gypsum as a deteriorated layer and Halite. (b) the same layer after treatment by Bacteria. (c) the layer after treatment by Laser as shown in Fig. 3.

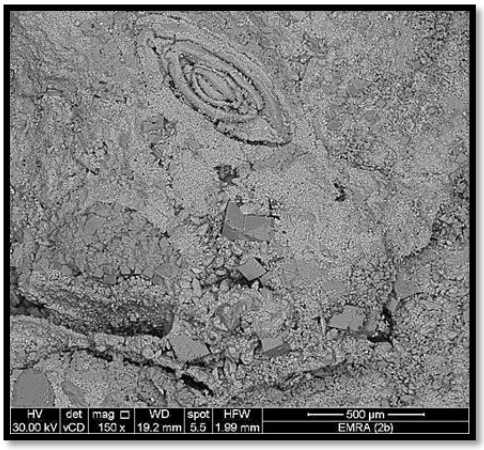

Figure 2. The Fossils in the limestone structure

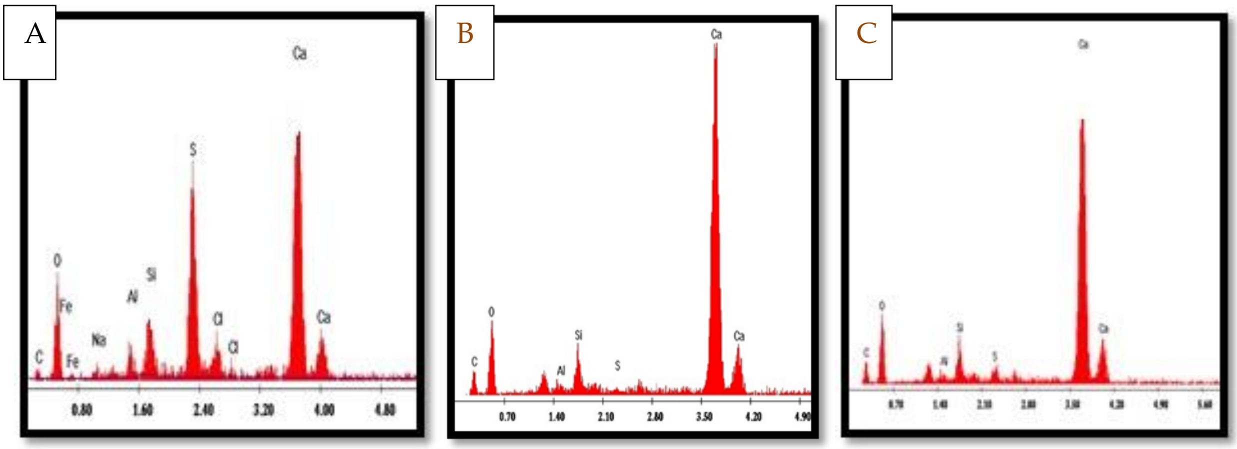

Figure 3. A: the untreated layer, B: Biological cleaning layer, C: Laser cleaning layer.

3.3. Laser methodology

Different cleaning methods were carried out on the black crust to find the best parameter in succeeding to remove the deteriorated layer. The data shows that the best methodology is a wet sample and using 100w, 100MJ, for the only 3min, as shown in the Table 1, and Fig.4.

Table 1 The cleaning parameters of black crust spots on the surface of the limestone

No.	Time of Pulse	Energy MJ	Power W	Frequency HZ	Cleaning Method	Notes
A1	10 M	50	0.5	10	Dry	It did not show any difference
A2	10 M	50	0.5	10	wet	a few result
A3	4.5 M	75	0.75	10	Dry	Reducing the thickness of the spot
A4	3 M	75	0.75	10	wet	Much higher than the third one
A5	4.5 M	100	100	10	Dry	Fast clean but cause effect
A6	3 M	100	100	10	wet	Quick cleaning without effects

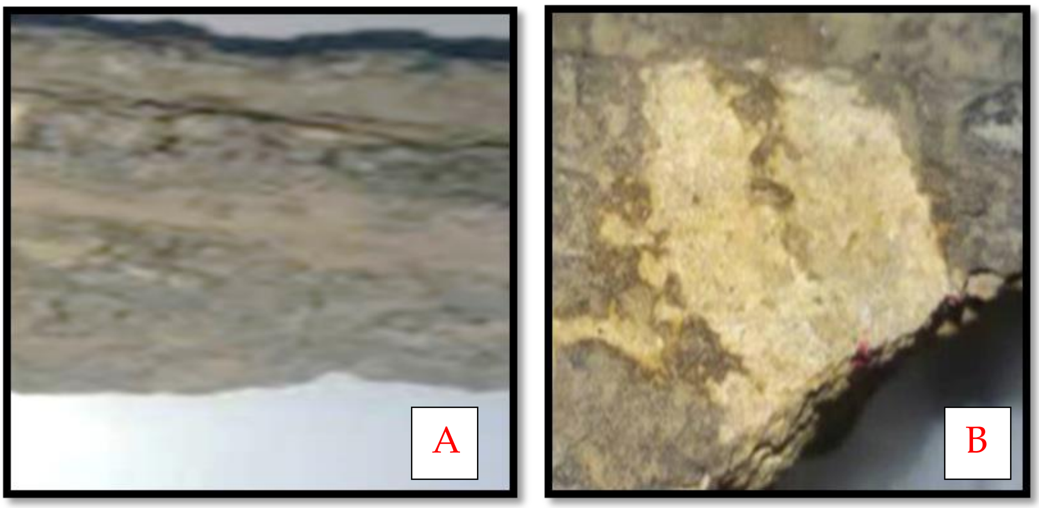

Figure 4. (A) the sample before treatment, (B) the sample after cleaning for 3 min in wet with energy 100MJ, and power 100w.

3.4. Biological Cleaning methodology

The bio-cleaning procedure applied on samples of stone deteriorated with black gypsum. A hydrobiogel-97 mixed with *Desulfovibrio desulfuricans* was used on a tissue paper (Japanese Paper) and covered by polyethylene for 24h three times. The data show that using *Desulfovibrio desulfuricans* with hydrobiogel-97 as a delivery system for 72h at room temperature (25-27°c) can remove the black crust without causing any damage to the stone as shown in fig (5). New calcite precipitation over the sample after treatment process as the SEM present in Fig.6.

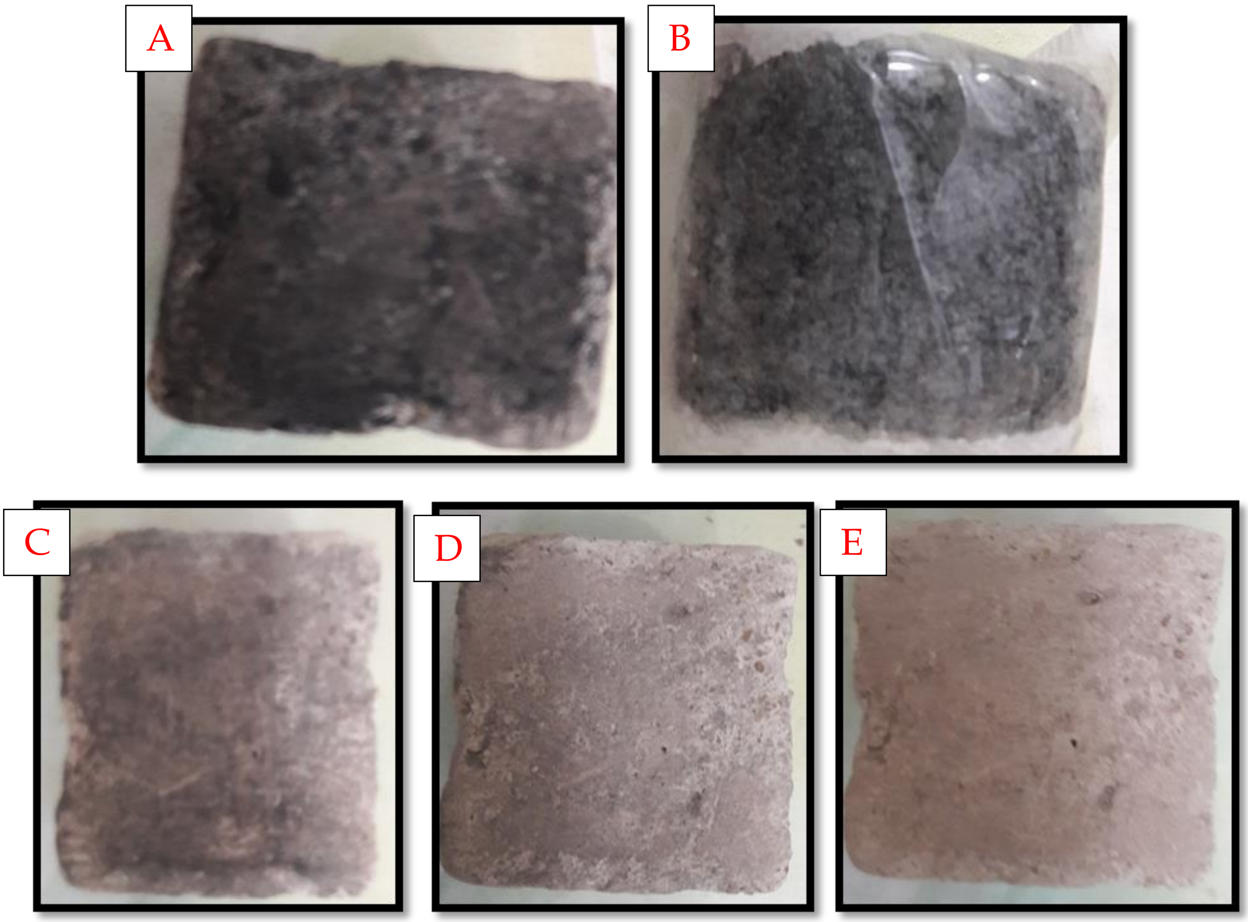

Figure 5. The steps of the bio- cleaning process, (A) Sample before treatment, (B) the Application of bacteria on tissue paper, (C) first applied after 24h, (D) second used after 48h, (E) final applied after 72h.

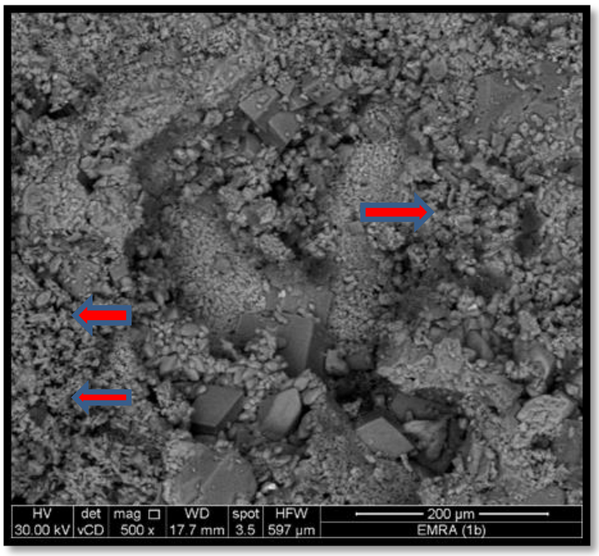

Figure 6. The new calcite precipitation after biological treatment

3.5. *Stereo Microscope*

Failaka stone examined under stereomicroscope before and after treatment. The photos show that both cleaning methods can remove the black crust, but only biological cleaning remove it entirely while saving the patina of the stone as shown in Fig.6.

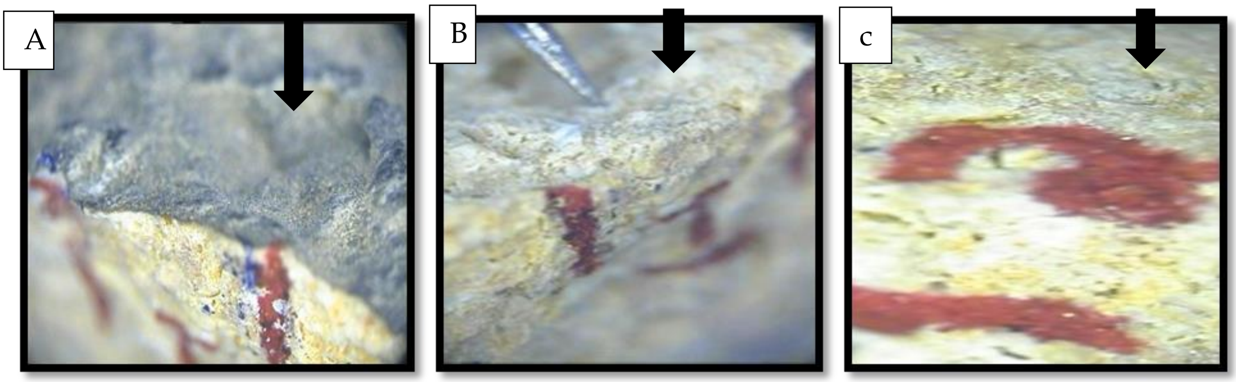

Figure 6. (A) the sample before treatment, (B) Laser cleaning, (C) Biological cleaning.

4. DISCUSSION

The X-ray diffraction analysis and the EDX confirmed that the black crust of Failaka stone consisted of Gypsum as reported elsewhere (Heselmeyer 1991; Moropoulou 1998; Esbert 2001).

The XRD presents that the Failaka stone is a Dolomitic limestone. The observation by SEM demonstrates that the limestone is an organic limestone depending on the fossils appeared in the structure of the stone.

The removable of the undesirable materials by laser determinants many experiments carried out, such as the use of YAG laser in England to clean marble and limestone without any chemical composition changes. (Cooper,1992, Barakat, 1992, & Pollard, 2008)

In this study, three parameters of energy (50, 75, 100 MJ) carried out according to (Abd EL- Hakim, 2016) with frequency 10 HZ. The cleaning method was dry and wet for each of the experiment. The findings showed 100 MJ with wet (water: Alcohol 1:1) was the best condition, quick cleaning without effects on the noble patina.

Biological Cleaning as new biotechnology for cultural heritage treatment applied from years ago by using living microorganisms cell or enzymes. Living cells of *Desulfovibrio desulfuricans* used successfully in removing sulfates from marble and stones (Castanier 2000; Ranalli 2005; Cappitelli 2006, 2007; Alfano 2011; Bosch- Roig 2012). *Desulfovibrio desulfuricans* is a sulfate-reducing bacteria that can convert black gypsum to calcite as a step for cleaning and consolidation at the same time.

The SEM-EDX analysis for the treated stone shows that the percentage of the sulfate ions (a central component of gypsum) was decreased after cleaning by biological treatment and laser treatment. The same analyses showed that the calcium ions (a central element of calcite) increased due to the new formation of calcite after biological treatment. (Gauri & Chowdhury, 1988). The calcium ions released by gypsum dissolution react with CO_3^{-2} from bacterially produced CO_2 and from calcite.

5. CONCLUSION

Air pollution caused by petroleum refining made a deteriorated layer over Failaka stones which appeared as a black crust over the archaeological stone surface.

The biological cleaning methodology used sulfate-reducing bacteria *Desulfovibrio desulfuricans* and showed a highly efficient process in removing the black layer after 72h by using a hydrobiogel-97 as a delivery system. This technology was cost-effective. Also, was safe for both conservators and stones. It was easy to use and protected the patina of stone.

The laser cleaning methodology can remove the black crust in only 10 min; this technique is risk-free, easy to use, but it is costly, and it can't save the patina of the stone.

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