

## Evaluation the Using of Nano Materials as Self Cleaning Agents of Different Kinds of Stained Archeological Textiles

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NANO-SIZED TiO<sub>2</sub> and ZnO have demonstrated efficiency in many application fields due to their photocatalytic features that provide self cleaning properties to the materials with simple and non-expensive procedures. Recently, nano TiO<sub>2</sub> and nano ZnO started to be embedded in the archeological field of stones and wood, while there is a lack of information about using in ancient textile artifacts. So this work aimed to investigate the effectiveness of both TiO<sub>2</sub> and ZnO as potential self cleaning agents for three different types of stains (pomegranate extract, linseed oil and pencilium fungi stains) applied on linen fabric samples. Two groups of the satins, *i.e.* old s and new occurring stains were applied on the fabric samples and studied under the effect of either nano TiO<sub>2</sub> or nano ZnO. The prepared stained samples were characterized using FTIR-ATR, static contact angle calculation and photocatalytic activity. The photocatalytic behavior of the treated samples was investigated by measuring the color parameters (L, a & b) according to CIELAB. Photocatalytic performance was judged by assessing the color difference of the tested samples after each treatment. The results revealed that the best behavior in terms of hydrophobicity and self-cleaning properties were shown by the nano ZnO treated stained samples.

**Keywords:** Nano metal oxides, Photocatalytic behavior, Contact angle, Linseed oil, pomegranate extract, Fungi, archeological textiles,

### Introduction

The collection, preservation, exhibition and interpretation of objects of historical significance are the primary missions of most of the history museums. Many factors affect the deterioration of the historical artifacts such as environmental conditions, handling and natural decay. It is vital that museums practice proper preservation measures in order to maintain the objects. A significant number of years can be added to the life of the objects just by knowing how to handle, display and store the artifacts in the museum's collection.

Cleaning artifacts is important but could be dangerous and time-consuming task in every archaeological project and it is important to take care when dealing with the cleaning chemicals. Regular cleaning will prevent dust build-up from causing long-term damage to artifacts. It will also present a positive, clean image to the

visitor. Commercial cleaners are too harsh to use on historic surfaces. If something has to be cleaned more than just dusting it, a professional specialized conservator must be consulted [1].

Self-cleaning surfaces use light to clean their surface, as a consequence, less detergents and manual labor are required; this in turn leads to decrease in subjecting the historical object to more damage. The research interest for the use of self cleaning property of the nanomaterials in the textile industry has increased rapidly in the recent years [2], among the nanomaterials are TiO<sub>2</sub> and ZnO. In fact, both nano TiO<sub>2</sub> and nano ZnO are non toxic and chemically stable under exposure to high temperature and are capable of photocatalytic oxidation due to the large surface area to volume ratio when compared to bulk materials [3,4].

TiO<sub>2</sub> exists in both amorphous and crystalline forms. The amorphous form is photocatalytically

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DOI :10.21608/ejchem.2017.1462.1096

inactive. There are three natural crystalline forms of  $\text{TiO}_2$ : anatase, rutile and brookite. Anatase and rutile are photocatalytically active, while brookite has never been tested for photocatalytic activity. However, it is interesting that the coupling of different crystalline phases of nano  $\text{TiO}_2$  results in the increase in photocatalytic activity [5-7].

On the other hand, ZnO is also a photocatalyst, and the photocatalysis mechanism is similar to that of titanium dioxide; the only difference between them is the band gap, i.e. in case of ZnO= 3.37eV, while in case of  $\text{TiO}_2$ = 3.2 eV. Once Nano ZnO is illuminated by light, it provides effective photocatalytic properties and so it is employed to impart anti-bacterial properties to textiles[8].

The wettability is the force that drives the penetration by liquid and it depends on the surface energy and roughness of the material [9]. The wettability of surfaces by fluids, in particular by water, has been the subject of great interest for many years since it affects a large number of fields ranging from medicine to electronics. Among the natural surfaces having very interesting water-repellent properties are lotus and rice leaves. Many experiments have been made to mimic the behavior of these surfaces on the basis of the origin of the observed contact angles [10]. Based on the contact angle (CA), surfaces are conventionally classified as either hydrophobic ( $\text{CA} > 90^\circ$ ) or hydrophilic ( $\text{CA} < 90^\circ$ ). A surface is said to switch wettability if, by a change in an external parameter such as surface morphology and temperature the wetting of the surface changes from complete wetting (superhydrophilic) to complete non-wetting (superhydrophobic). Therefore, an additional feature of interest is the reversible wettability of these surfaces leading to self-cleaning. Self-cleaning surfaces have drawn considerable interest from perspectives of both fundamental research and applications[11]. The synergy of photocatalysis and super-hydrophilicity is the basis of sustaining self cleaning ability of metal oxides. Photocatalytic activity degrades organic and inorganic contaminants under UV light. In contrast photo induced hydrophilicity reduces the water contact angle and thus removes the contaminant from the surface by water[12].

Since the archeological objects are too sensitive, precious and need expert sensitive care to deal with, so the main goal of this research work was to study the potential effect of using

either nano  $\text{TiO}_2$  or nano ZnO as self cleaning agents to protect the archeological artifacts from further deterioration due to accumulation of stains whether these stains are as old as the artifact itself, or newly occurred on the artifact due to handling.

## **Experimental**

### *Materials and chemicals*

- Raw unbleached linen fabric of weight 234.9 g/m<sup>2</sup> was purchased from Eglyan Co., Egypt.
- Nano anatase  $\text{TiO}_2$  and nano ZnO (3-18 nm in diameter ) were purchased from HBRC, Egypt.
- The following chemicals used as were: Acrylic binder, ethanol and glacial acetic acid.

### *Samples Preparation*

- The tested linen fabric samples were cut dimensions 4 x16 cm.
- Three different stains were applied on the tested fabric strips individually, namely; pomegranate extract, linseed oil and penciliun fungi stains.
- 2 ml of each of pomegranate extract and linseed oil were applied on the fabric strips to make a stain spot of 5 cm diameter. While, fungi stain was used by oculation of the strips with the penciliun fungi and incubation for 4 weeks at 30 °C and 80% humidity. Dark spots were visually detected after 21 days of incubation.
- 1% solution of nano  $\text{TiO}_2$  was prepared by soaking 1g of  $\text{TiO}_2$  alongside with 2 g of acrylic binder and 10 ml of ethanol. Complete the volume to 100 ml using distilled water with continuous stirring for two hours using magnetic stirrer [13].
- 1% of nano ZnO was prepared by adding 1 g of nano ZnO with 1 ml of glacial acetic acid and 1 ml of acrylic binder, 10ml of ethanol was added to this mixture gradually. Finally complete the mixture volume to 100 ml with distilled water, and continuous stirring for two hours until we obtain a clear solution of nano ZnO [14].

### Staining the samples

Mimic samples of ancient fabrics were prepared to simulate those ancient stained samples where the stain is as ancient as the artificial artifact itself. Moreover, another group of samples was prepared to mimic those samples which were stained recently or during handling in the museums. So, two groups of different kinds of the tested samples were used through this research work to investigate the self cleaning effect of nano metal oxides on stained, artificially aged linen fabrics. As follows:

- i) Group 1: the simulated old stained samples: where the fabric strips were stained with pomegranate extract, linseed oil or pencilium fungi then artificially aged using Tera Light fastness Tester[15] for 100 hours at temperature of  $25 \pm 2^\circ\text{C}$  and relative humidity of  $65 \pm 5\%$ . After exposure, adequate volume of each of the prepared nano metal solutions individually was sprayed on the stained aged fabric strips as protective layer from further staining using fixed distance and spraying speed to ensure the spraying homogeneity. Moreover, another light aging for 100 hours was done for each treated sample to assess the performance of the applied protective layer.
- ii) Group 2: The simulated newly occurring stained samples: where the fabric sample strips were firstly artificially light aged for 100 hours then stained using each of the three above mentioned stains individually. After staining, the samples were cleaned using the traditionally used cleaners [16] then applying each of the prepared nano metal oxide solutions as a protective layer. Furthermore, second light aging for 100 hours was done for each treated sample to assess the performance of the applied protective layer.

### Testing and analysis

*Fourier Transform Infra-Red Spectroscopy with Attenuation Total Reflection (FTIR-ATR):*

FTIR-ATR spectra of both the untreated and treated samples were recorded by means of Nicolet 380 Spectrometer using a zinc selenide crystal, in the wavelength range  $650\text{-}4000\text{ cm}^{-1}$ . To ensure reproducible contact between the crystal face and the fabric, a pressure of about 18 kPa was applied to the crystal holder. The FTIR absorbance frequencies for the treated samples were recorded with an average of 128 scans using a resolution of  $4\text{ cm}^{-1}$ .

### Color measurements

To assess the color variation of the stained samples induced by the protective nano metal oxides layer on the fabric surface, the color changes of fabric surfaces were measured by using Color Eye 3100 Spectrophotometer SDL, England. Such tests were carried out both before and after each treatment. The mean value of three measurements is recorded for each sample through the determination of L, a, and b coordinates of the CIELAB space, where brightness (L: 100 = white 0 = black), chroma (a: red +, green -; b: yellow +, blue -) and the global chromatic variation expressed as  $\Delta E$  [17]. The color differences ( $\Delta E$ ) between the samples before and after each treatment were measured taken the difference between each treated sample and the blank (untreated) as reference, according to the following relation[18] :

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

### The contact angle

The surface wettability was evaluated from the value of the contact angle measured with a drop of distilled water on the surface of the tested samples. Drops shape and the contact angle measurements were carried out using video microscope (CVM) SDL- UK, with horizontal plate camera and the angle between the substrate surface and the tangent from the edge to the contour of the drop provided the contact angle measurement. The volume of the drops was maintained as  $250\text{ }\mu\text{L}$  (ASTM 724-99 and ASTM 596-96). The reported angle is an average of 5 measurements on different areas of each sample.

## Results and Discussion

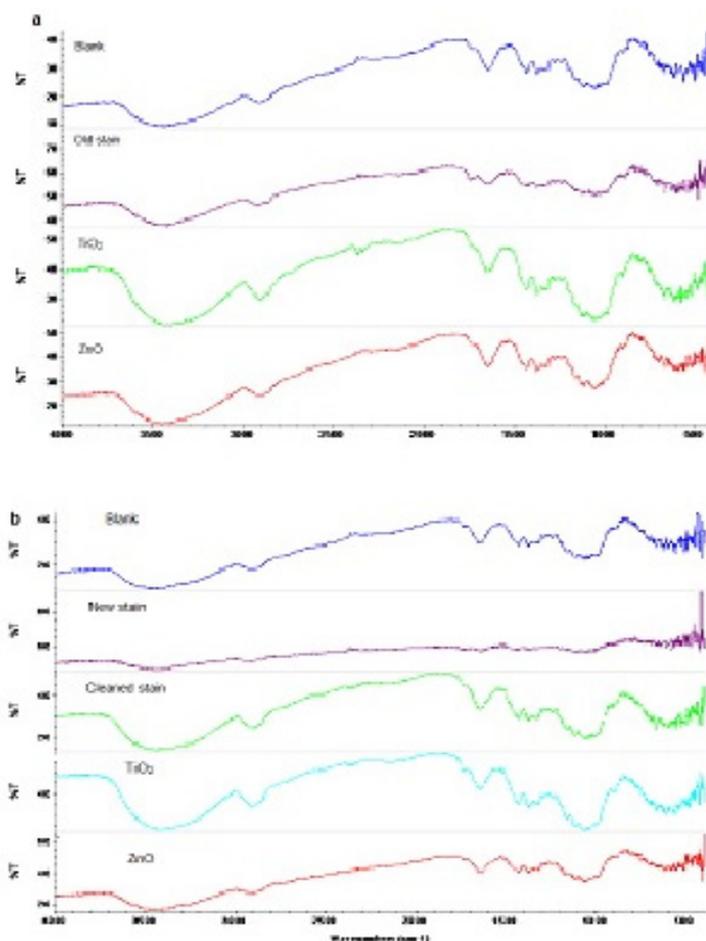
### FTIR

FTIR-ATR has been employed to study the behavior of all tested samples, *i.e.* simulated old stained or new occurring stained samples, under the effect of either nano  $\text{TiO}_2$  or nano  $\text{ZnO}$  on prolonged artificial daylight aging for 100 hours, the IR spectra are shown in Fig. 1-3. On comparing the blank and the old pomegranate stained samples spectra represented in Fig. 1 a, it is clear that, some peaks are common between the untreated and treated spectra[19], *i.e.* broad peak at around  $3436\text{ cm}^{-1}$  assigned to O-H stretching vibration,  $\nu \approx 2910\text{ cm}^{-1}$  assigned to C-H stretching vibration mode, sharp peak at  $\nu \approx 1643\text{ cm}^{-1}$  related to O-H bending, in-plane bending vibrations of H-C-H

group at  $\nu \approx 1429 \text{ cm}^{-1}$ , in-plane C-H bending at  $\nu \approx 1368 \text{ cm}^{-1}$ , C-O-C asymmetric stretching at  $\nu \approx 1115 \text{ cm}^{-1}$ . There are two new peaks after staining and ageing appeared as a small shoulder at  $\nu \approx 2847 \text{ cm}^{-1}$  and a sharp one at  $\nu \approx 1740 \text{ cm}^{-1}$  assigned to stretching vibration of carbonyl group. Those two peaks disappeared after treatment using either  $\text{TiO}_2$  or  $\text{ZnO}$ . Moreover, almost all the peaks after staining are intensified and sharpened more than their correspondings in the untreated spectrum. This may be due to the fact that, light ageing increased the aggregated particles of the dye and stain leading to increasing the crystallinity to amorphousity ratio, so the peaks sharpened and intensified [20,21]. Also, it could

be due to the depolymerisation that was caused by the heat and moisture during the process of aging.

Regarding the new occurring pomegranate stained samples represented in Fig. 1 b, it is noticed that, the above mentioned peaks appeared after staining with more broadness compared to the old stained samples, meaning, less crystallinity to amorphousity regions. Moreover, the peak at  $\nu \approx 2847 \text{ cm}^{-1}$  related to the pomegranate disappeared after treatment with either  $\text{TiO}_2$  or  $\text{ZnO}$ . This is attributed to the formation of O-Ti or O-Zn covalent bonds between  $\text{TiO}_2$  or  $\text{ZnO}$  with the linen fibers. Thus, it may be deduced that  $\text{TiO}_2$  and  $\text{ZnO}$  nano particles react with the linen fibers [22,23].



**Fig.1.** FTIR spectra of the pomegranate extract stain on the linen fabric samples where a : old satin and b : the spectra of the newly occurred stain.

Figure 2 (a –c) represent the old and new oil stained samples respectively. The spectra are dominated by the presence of vibration modes around  $3440\text{ cm}^{-1}$  caused by C-H stretching in the fatty acids found in the oil structure, a peak at  $\nu \approx 2921\text{ cm}^{-1}$  related to C-H stretching with a

shoulder at  $\nu \approx 2847\text{ cm}^{-1}$  attributed to deformation vibrations of C-H groups in methyl and methylene groups. All the peaks in Fig. 1 a (old stain) are shifted compared to their new stain corresponding spectra (Fig. 2 b).

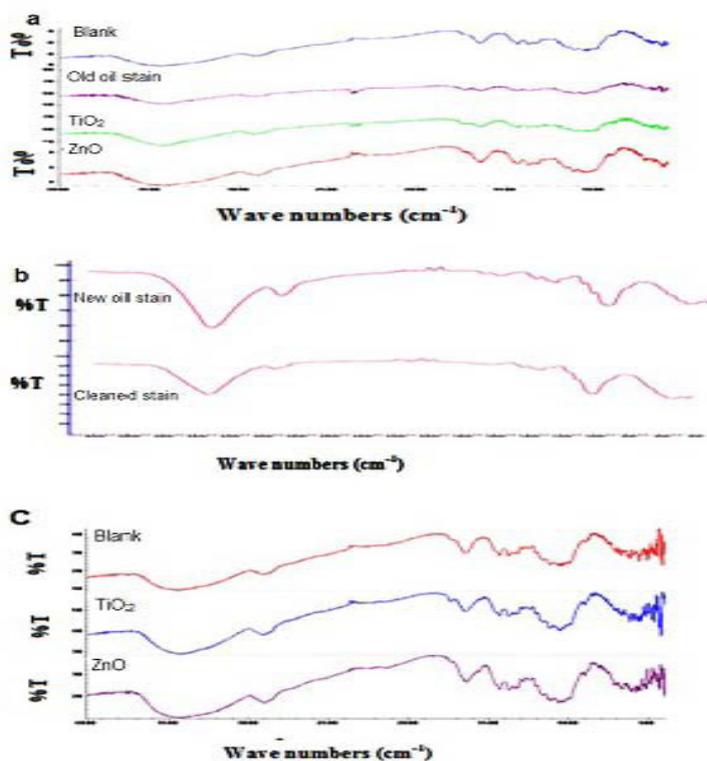
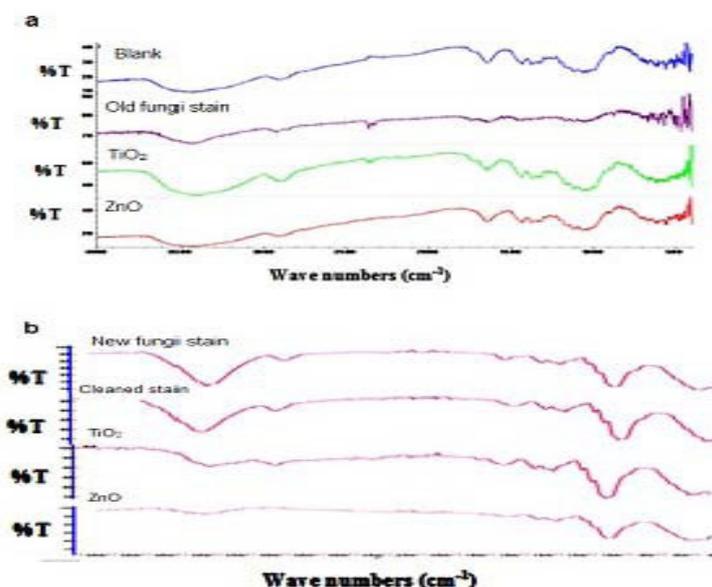


Fig.2. FTIR spectra of the linseed oil stain on the linen fabric samples where a : old stain and b : the spectra of the newly occurred stain.

In considering the spectra of the fungi stained samples represented in Fig. 3 a & b, it is clarified that, the peaks belonging to the new occurring fungi stain are more sharper and having higher intensity than those of the old stained samples. The major part of amine groups in the fungi structure are bound in amide linkages which is proved by the strong absorption at  $\nu \approx 1653\text{ cm}^{-1}$  assigned to C=O, amide I and the band at  $\nu \approx 1554\text{ cm}^{-1}$  assigned to  $\delta$  N-H, amide II. Furthermore, the peaks near  $3436\text{ cm}^{-1}$  and  $2917\text{ cm}^{-1}$  were assigned to O-H stretching. The band at  $1625\text{ cm}^{-1}$  corresponds to amide I due to carbonyl stretch in proteins. The peak at around  $1049\text{ cm}^{-1}$  corresponds to C-N stretching vibration of amine [25].

The most evident sign of the deterioration caused by the fungi was the carbonyl band in the region  $\nu \approx 1744\text{ cm}^{-1}$ , which appears in the old fungi stain spectrum and arises mainly as a consequence of depolymerisation. A sign of decreased crystallinity in the analyzed samples was seen as a shift of the  $1450\text{ cm}^{-1}$  band (CH<sub>2</sub> and intramolecular H bonds) which appears in the old fungi stain spectrum to lower wave numbers at  $\approx 1425\text{ cm}^{-1}$  in all other analyzed samples[26]. The band at  $\nu \approx 2895\text{ cm}^{-1}$  appeared in the new fungi stained spectra (Fig. 3 b), split into two peaks at  $\approx 2917\text{ cm}^{-1}$  and  $\approx 2843\text{ cm}^{-1}$  in the old stain spectrum (Fig. 3 a).



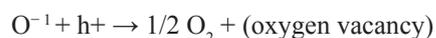
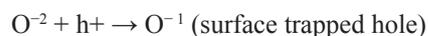
**Fig.3.** FTIR spectra of the pencilium fungi stain on the linen fabric samples where a : old satin and b : the spectra of the newly occurred stain.

#### Photocatalytic Measurements

The data listed in Table 1 represent the color parameters (L, a & b) of all tested samples, either the simulated old stains or the new occurring stains. Photocatalytic activity was assessed in terms of color variation of a stain caused by the effect of both nano TiO<sub>2</sub> and ZnO particles applied on linen fabric samples, taken the untreated (blank) fabric's photocatalytic efficiency as reference. It is observed that, in case of simulated old stained samples represented in Fig. 4, ΔE values of the nano metal treated samples are higher than ΔE of the blank ones due to light fading of the samples, yet, in case of stained samples treated with nano ZnO, ΔE values are lower than those samples treated with nano TiO<sub>2</sub>. This is very clear in the lightness L values, where L values of nano ZnO treated samples are lower than their corresponding treated with nano TiO<sub>2</sub>. Moreover, all the color parameters (a & b) are also decreased. This may be explained by that; when the ZnO surface is illuminated by light it became energetically unstable, as it is a photocatalyst. TiO<sub>2</sub> is also considered as photocatalyst but the only difference between them is the band gap, where in case of ZnO = 3.3eV and in case of TiO<sub>2</sub> = 3.2eV. A larger band gap means that, more energy is required to excite an electron from the

valance band to the conduction band and hence light of a higher frequency and lower wavelength would be absorbed, *i.e.* narrow band gap means higher photocatalytic activity [27].

So, the nano ZnO treated samples need more energy to act as self cleaning agent, subsequently the ΔE values after illumination are lower than that of nano TiO<sub>2</sub>. The typical mechanism of photocatalysis in ZnO can be represented as follows [28,29]:



Regarding the new occurring stained samples, where those samples were firstly cleaned using the traditional well known methods for cleaning ancient fabrics [16], then protected with a layer of either nano ZnO or TiO<sub>2</sub>. The efficiency of this protective layer was assessed though measuring the color difference (ΔE). From the results listed in Table 1 and represented in Fig. 5, it is obvious that, ΔE values after cleaning-either the pomegranate extract stain or the fungi stain-

TABLE 1. Photocatalytic parameters of untreated and treated fabric samples using three different stains under the effect of nano TiO<sub>2</sub> and nano ZnO.

Satin Type	Color parameters	Blank sample (untreated)	Treated samples						
			Aged fabric with new staining	Aged fabric with new staining & cleaning	Aged stained fabric	TiO <sub>2</sub> layer	ZnO layer		
Pomegranate extract	Old stain	ΔE	-----	-----	-----	1.60	5.49	3.47	
		L	61.96	-----	-----	63.15	67.09	64.88	
		a	2.59	-----	-----	3.07	2.95	2.25	
	New stain	ΔE	-----	2.93	3.85	-----	8.31	3.96	
		L	61.96	64.73	65.68	-----	69.98	66.79	
		a	2.59	3.44	1.83	-----	1.37	1.40	
	Linseed oil	Old stain	ΔE	-----	-----	-----	6.61	7.09	7.02
			L	61.96	-----	-----	58.37	61.40	60.00
			a	2.59	-----	-----	4.01	4.39	4.03
New stain		ΔE	-----	6.87	2.82	-----	4.26	2.48	
		L	61.96	60.59	64.27	-----	65.15	63.76	
		a	2.59	4.02	2.76	-----	2.76	1.73	
Fungi stain		Old stain	ΔE	-----	-----	-----	1.58	3.86	2.55
			L	61.96	-----	-----	60.80	65.64	60.19
			a	2.59	-----	-----	2.48	2.48	1.78
	New stain	ΔE	-----	6.23	12.94	-----	14.27	12.55	
		L	61.96	55.93	74.58	-----	75.93	73.76	
		a	2.59	2.91	1.39	-----	1.98	1.35	
			b	12.26	13.80	14.84	-----	16.36	15.10

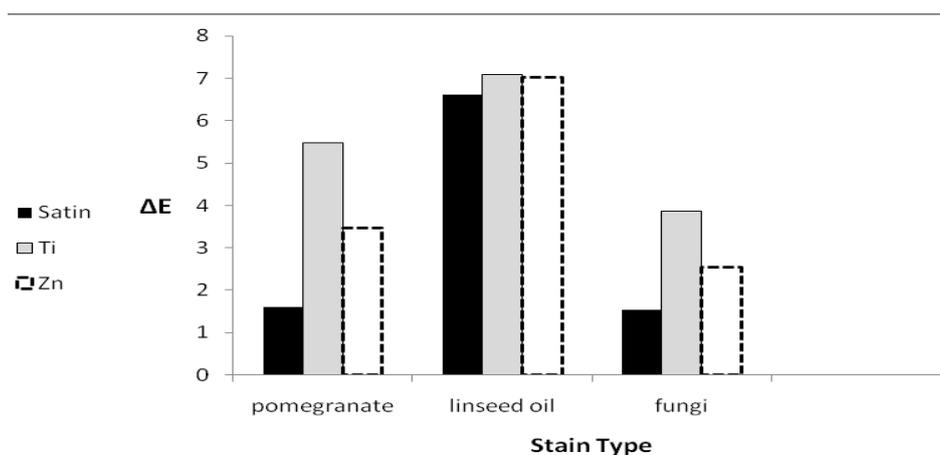


Fig. 4. Color difference (ΔE) of different types of old stained simulated samples .



are brought together. The degree of wetting (wettability) is determined by a force balance between adhesive and cohesive forces. Adhesive forces between a liquid and solid cause a liquid drop to spread across the surface. Cohesive forces within the liquid cause the drop to ball up and avoid contact with the surface [35]. Depending upon this force balance, the interface can be classified as wetting or dewetting.

The contact angle ( $\theta$ ) which is the angle where the liquid–vapor interface meets the solid–liquid interface is determined by the result between adhesive and cohesive forces. As the tendency of a drop to spread out over a solid surface increases, the contact angle decreases. Thus, the contact angle provides an inverse measure of wettability[36].

The data listed in Table 2 represent the behavior of the contact angle ( $\theta^\circ$ ) of both old simulated stains and new occurring simulated stains under the effect of the nano  $\text{TiO}_2$  and nano ZnO compared to the contact angle of the untreated sample (blank). The obtained results revealed that, a significant increase of the contact angle was found for all treated samples (up to  $140^\circ$ ) compared to the untreated one ( $110^\circ$ ). This means that, treating linen fabric with either nano Ti or nano Zn lead to decreasing the adhesive force between the treated sample and water and so increasing the cohesive force, leading to increasing the contact angle. Also the results clarified that, the contact angle of the different new occurring stains are larger than the contact

angle of the old simulated stains. This means that, the old stains are more hydrophilic than the new stains due to light fading and temperature which could decompose the stains particles leading to more hydrophilicity and so less contact angle and less adhesive force between the new simulated stained samples and the drop of water.

In comparing between the use of nano  $\text{TiO}_2$  and nano ZnO as self cleaning agents for all the tested samples, it is clear that, the contact angle of the nano Ti treated samples are higher than that of nano treated Zn samples due to the higher photocatalytic effect of nano  $\text{TiO}_2$  as explained above 27-28 and because of the lower adhesive force between the nano  $\text{TiO}_2$  treated samples and drop of water. Since, these samples are simulated archeological ones, so the effect of ZnO is preferable to be used than the use of nano  $\text{TiO}_2$  as self cleaning to maintain the integrity of the ancient artifact.

### Conclusion

Self-cleaning concept in the archeological field has massive effect in the riskiness decreases of the hazardous cleaning chemicals used on the object for both the environment and the artifact itself. This could add several years to the artifacts life by saving them from deterioration.

This study assessed the efficiency of both nano  $\text{TiO}_2$  and nano ZnO as self cleaning agents for three different types of stains; pomegranate extract, linseed oil and pencilium fungi, on linen

**TABLE 2. Contact angle values of the different old and new simulated stained samples under the effect of nano  $\text{TiO}_2$  and nano ZnO.**

	Tested sample	Contact angle of different stain types ( $\theta^\circ$ )		
		Pomegranate extract	Linseed oil	Fungi
Old simulated stain	Blank (Untreated)	110		
	Stain	125	125	110
	Stained treated with $\text{TiO}_2$	140	130	140
	Stain Treated with ZnO	130	125	125
New occurring simulated stain	Stain	135	130	135
	Cleaned stain	135	110	140
	Cleaned stain treated with $\text{TiO}_2$	125	125	135
	Cleaned stain treated with ZnO	125	120	125

fabric samples. To mimic the original ancient artifacts the stained samples were classified into two groups; simulated old stains and new occurring stained samples. Then the tested samples were treated with either nano TiO<sub>2</sub> or nano ZnO individually. The obtained samples were characterized using FTIR-ATR before and after each treatment. The results revealed the various function groups of all the tested samples.

The efficiency of both nano TiO<sub>2</sub> and nano ZnO as self cleaning agents based on their photocatalytic activity for the three types of used stains (old or new stains) were assessed through measuring the color parameters (L, a and b). The color difference ( $\Delta E$ ) between the untreated (blank) and the treated samples were calculated and compared. It was obvious that, samples treated with nano TiO<sub>2</sub> showed higher L and higher  $\Delta E$  values compared to that of ZnO, meaning more fading of the stains due to the higher photocatalytic activity of nano TiO<sub>2</sub>.

Moreover, the contact angle between drop of water and all tested samples' surfaces was measured and interpreted. It was found that, the samples treated using nano TiO<sub>2</sub> having higher contact angle compared to that of treated samples with nano ZnO revealing the increase in the cohesive force of the water particles and decreasing the adhesive force between the nano TiO<sub>2</sub> treated samples and the drop of water, *i.e.* nano TiO<sub>2</sub> treated samples are more hydrophobic than nano ZnO treated ones. This means that the self cleaning effect of nano TiO<sub>2</sub> is higher than that of nano ZnO and could affect the sensitive archeological artifact. So, It is better to use the nano ZnO as potential self cleaning agent for the ancient fabrics.

Based on all the above obtained tests and results, it is clear that, using nano ZnO as potential self cleaning agent for the ancient objects is more favorable and safer than using nano TiO<sub>2</sub> as it need more energy than nano TiO<sub>2</sub> to react with the stain and remove it safely. So, it is more tender or subtle when used with archeological stained fabrics.

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(Received 10/8/2017;  
accepted 7/9/2017)

## تقييم استخدام اكاسيد معادن نانوية كعوامل تنظيف ذاتي محتملة لعدة أنواع مختلفة من المنسوجات الأثرية المبقعة

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نظرا لاهمية المنسوجات الاثرية وضرورة الحفاظ عليها وحمايتها من عوامل التلف التي قد تتعرض لها على مر السنين، وكذلك لقلة الابحاث الخاصة باستبدال مواد التنظيف التقليدية باخرى حديثة مثل اكاسيد المعادن النانوية. فقد تم في هذا البحث دراسة امكانية استخدام كل من نانو اكسيد التيتانيوم و نانو اكسيد الزنك كعوامل تنظيف ذاتي للبقع القديمة وكطريقة حماية من الاتساخ في حالة البقع الحديثة. حيث تم اختيار ثلاثة انواع من البقع الشائعة على المنسوجات الاثرية (عصير الرمان، زيت بذر الكتان، فطر البنسليوم) وتطبيقها على نسيج الكتان. ثم تقسيم العينات الى مجموعتين لكي تحاكي احدهما البقع القديمة الموجودة على الاثر منذ القدم وتحاكي المجموعة الاخرى البقع الحديثة على نسيج الكتان المتقدم ضوئيا التي قد يتعرض لها الاثر نتيجة التعرض او التداول. وقد تم عمل توصيف للعينات المختبرة باستخدام الاشعة تحت الحمراء. كذلك فقد تم تقييم فعالية اكاسيد المواد النانوية المستخدمة من خلال قياس معاملات اللون لكل عينة مختبرة (L, a, b) طبقا لنظام ال CIELAB ثم حساب الفروق اللونية  $\Delta E$  بين العينات المختبرة والعينة الغير معالجة. واخيرا فقد تم تقييم العينات المختبرة عن طريق قياس زاوية التماس بين قطرة المياه وبين سطح العينات المختبرة ومقارنتها بالعينة الغير معالجة blank والتي تعتبر مؤشر لفعالية التنظيف الذاتي.

وقد اتضح من خلال نتائج البحث والتحليل التي تم الحصول عليها ان استخدام مادة اكسيد الزنك النانوى كعامل تنظيف ذاتي او كمادة حماية من الاتساخات ضد البقع المختلفة على عينات نسيج الكتان المتقدمة (الاثرية) افضل وأمن tender & subtle في استخدامه من مادة اكسيد التيتانيوم النانوى  $TiO_2$ .