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CLEANING OF ARCHITECTURAL BRICKS USING RF PLASMA. I. METALLIC STAINS

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Abstract

RF Plasma is a glow discharge typically generated through using oxygen and hydrogen as the input working gas. In the current study the radio frequency (RF) hydrogen plasma (H2) is used for removing some metallic stains (iron and copper) which affected the historical brick surfaces in Prince Yousef Kamal place. Untreated and treated surfaces were evaluated by OLS, EDX-SEM & FTIR. Investigation results show that both iron and copper aged samples had been cleaned, where the stains thicknesses' were removed perfectly through. Analytical results of the accumulated particles demonstrate that they are decreased after cleaning process. In addition, morphological investigations proved the clearness of positive effects in the reducing of the samples surfaces' darkening and thickness' accumulations in all cleaned samples.

Keywords: *Dielectric barrier discharge; Capacitive coupled plasma; Artificial ageing; SEM-EDX, FTIR*

Introduction

The *Radio Frequency* (*RF*) capacitive gas discharge is widely used in various technological surface processes such as thin film deposition, plasma etching and surface cleaning [1-5]. Plasma cleaning involves the removal of impurities and contaminants from surfaces through using different types of energetic plasma such as RF plasma, DC glow discharge and *Dielectric Barrier Discharge* (*DBD*). It was created from gaseous species (ions, excited atoms, electrons and positive ions), as well as other mixtures (air and hydrogen/nitrogen) [6]. *Plasma cleaning*, that can be produced by active gas oxygen, hydrogen or argon usually refers to the removal of some contamination layers from the material surface due to the reaction between the discharged components (i.e., ion, electrons excited atoms) with the impurities at the surface [7, 8]. In the current study *RF plasma* has been formulated to clean some brick surfaces collected from *Prince Yousef Kamal Palace in Nag Hammadi* (Fig. 1). It has suffered from severe contamination symptoms created by different organic and inorganic effects. Among these symptoms, there are some stains and rested spots created by iron and copper as inorganic sources, as well as soot as an organic source.

Cleaning of monumental buildings is an essential operation that has a wide range of techniques ranging from large facades to some small findings [9-12]. Moreover, it ranges from regular dusting and damp-mopping of objects to removing dirt, accumulations or stains [13]. Though care must be taken to retain dirt that is part of the history of an object, such as soot on

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an ancient cooking spot [14, 15]. This process, which is a positive action, means protection against harmful materials accumulated on the surface such as crusts, weathering products or different salt crystals [16]. It prevents adverse reactions between the object and its environment [17]. It is often one of the first steps to be undertaken for removing all accumulated dirt to enhance the better seen of the underlying stone conditions, thus judging what further conservation may be necessary [18, 19]. However, it is one of the most difficult operations in building conservation and restoration [9, 20]. In this regard, the ideal cleaning should lead to the removal of as much of the fouling and as little of the material as possible by a combination of physical and chemical techniques [21].

Fig. 1. Prince Yousef Kamal place in *Nag Hammadi*

According to I. Bristow [9, 22-25] these techniques may have negative effects if they are done without sufficient investigations. They vary from mechanical, abrasive, chemical (wet & dry), poultices, enzymes, laser and plasma cleaning techniques. RF plasmas are more efficient in converting the power from the supply into the plasma and more importantly in etching [26-30]. RF plasmas are a glow discharge typically generated by an RF source**.** RF discharge may be divided into two types according to the form of electromagnetic field interaction; *Inductively Coupled Plasma* (*ICP*) or *Electrode Less Discharge* (*ELD*) and *Capacitive Coupled Plasma* (*CCP*). It is a discharge that has been produced between two parallel plates (electrodes), where, the area of the two electrodes and the gap space between them affected the discharge condition. Also, it is widely used in various technological processes such as thin films deposition, treatment and surface cleaning [29, 30]. In the current study, *CCP* has been used to clean some historical brick surfaces through using two regions within the discharge. They are **sheath region* at the electrodes and **bulk region* at the center [31-33]. The ions accelerated within sheath region play the important role in the cleaning and modification processes on the solid material surfaces through using active species produced by plasma treatment. This mechanism that may be achieved by adding or removing adsorbed monolayers involves chemical reactions with the surface; adds or removes surface charge; changes physical or chemical state of the superficial monolayers of a material [34]. According to some specialists [35-39] the main principle of the plasma cleaning is that the ionized excited molecules and radicals, created by the electrical field, bombards and reacts with the surface of the sample. These activated molecules may etch, sputter, some layer from the substrate surface. These mechanisms lead to changes to the surface properties of substrates. When introducing molecular gases into plasma, chemically, active species are formed, such as molecules in excited states, radicals and ions. Layer corrosion is removed from the substrate through seven steps [40]. These steps are: **a)** Formation of the reactive particle, **b)** Arrival of the reactive particle at the surface to be etched, **c)** Adsorption of this particle at the surface, **d)** Forming chemical reaction "the reactive particle" at the surface, i.e. a chemical bond is formed, **e)** Formation of the product molecule, **f)** Adsorption of the product molecule, **g)** Removal of the product molecule from the reactor.

The surface may be cleaned by plasma etching if a volatile chemical compound is formed by the bombardment [41]. These species can react with each other, neutral molecules or with the surface of the sample. Within the same context, it could be claimed that the reaction of the plasma has two forms: reduction and oxidation reactions based on the nature of the molecules and the process conditions. On one hand, plasma reduction or hydrogen plasma allows the reaction of chlorinated products, oxides as well as corrosion products from the historical bricks through a reduction process based on the presence of atomic hydrogen [42].

Experimental

The experimental apparatus used in this study is a capacitively coupled parallel plate reactor with an asymmetric electrodes configuration. It consists of a stainless steel vacuum chamber and a powered electrode connected to an RF power supply (10MHz). Some residual brick units were collected from Prince Yousef Kamal Palace (built in *Nag Hammadi* 1925) on the west bank of the Nile. They were investigated and analyzed to estimate the quantitative and qualitative proportions of their surface's accumulations using some scientific techniques. These processes were achieved by *EDX* attached to *SEM* & *DBM*. Furthermore, some cubes samples' (4×4×1cm.) of historical bricks were laboratory prepared from the original blocks to be a target for experimental tests.

Stains simulation (Artificial ageing)

The brick samples collected from the site under the study were prepared in a square shape (4×4×1 cm.). They were submitted to the aging processes by using some metallic rusting stains. These stains lead to creating some artificial deposits or stains matched with the original ones. These accumulated stains were divided into two types according to the following criteria:

- Iron corrosion layers; they were laboratory prepared by putting some fragments of corroded iron on the samples of brick surface and spraying some water drizzle, then heating in 70-80ºC. This step results in forming an orange color on the samples surfaces. This demonstrates that rusting of iron and creating of manifested stains was composed of ferric oxides according to the following formulas. These oxides are mostly *goethite*, *limonite* or *hematite* through a complex electrochemical process that begins with the transfer of electrons from iron to oxygen [43].

$$Fe^{2+} + 2H_2O \rightleftharpoons Fe(OH)_2 + 2H^+$$

$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$$

As do the following dehydration equilibria:

$$Fe(OH)_2 \rightleftharpoons FeO + H_2O$$

$$Fe(OH)_3 \rightleftharpoons FeO(OH) + H_2O$$

$$2FeO(OH) \rightleftharpoons Fe_2O_3 + H_2O$$

- When light is being shed on the *copper stains* sample; through the preparing of a simulation study (different stains on the surface of brick) the copper stain has been prepared by mixing the sulfuric acid with the copper sheets on the brick surfaces according to the following formulas. Then, copper sulfates are composed, which is called *brochantite* $Cu_4SO_4(OH)_6$, and much rarely *antlerite* $Cu_3SO_4(OH)_4$ [44], see following formulas:

$$Cu + H_2SO_4 \rightleftharpoons CuSO_4 + 2H+ + 2e- \text{ or}$$

$$2Cu + 2H_2SO_4 \rightleftharpoons Cu_2SO_4 + 2H_2O + SO_2$$

Cleaning procedures

The contaminated samples have been put between two electrodes in the plasma chamber that can be evacuated down to 50 mtorr (Fig. 2). Then the gas has interred the cell with 70-mtorr pressure, the discharge can be generated with different timing. The cleaning time varies from 1 to 3 hours; the RF power works for 15 min. every time.

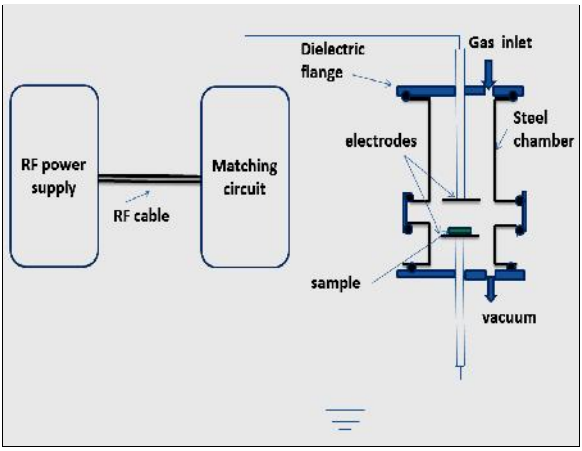

Fig. 2. Schematic diagram of the CCP cleaning experiment arrangement

Evaluation processes

In the conservation field, different techniques based on different scientific referential have been used for evaluating the quantitative and qualitative dirties accumulated on the archaeological surfaces. Some of these techniques are based on physical methods [45-47] and others are based on chemical ones [48-50]. In the current study, *Bausch & Lomb* attached to computerized *Jenalux 20 stereo-microscope* has been used to investigate the external features of the sample surfaces.. As well as *JSM 5300* scanning electron microscope coupled with energy dispersive x-ray spectroscopy (*SEM-EDX*) had been used for assessing chemical proportions and surface morphology of the samples before and after cleaning processes. *FTIR* is one of the widest and useful applications used in the diagnosis of the historical object and treated surface after cleaning [51]. These applications include the identification of molecular compounds created at the artwork surface, studies of the composition of painting layers and investigations of epoxy resins [52]. According to some specialists [53-54], *FTIR* investigations have been carried out with *Alpha Bruker Optics Middle, and Fourier transformation* in 3500 to 400 cm^{-1} frequency region. They are used to study the vibrational bands that provide information about the chemical functional groups of collected powder samples (before & after the cleaning process by RF Plasma).

Results

OLS investigations results

The stereomicroscope captures of aged and cleaned samples were completely different due to ageing processes. On one hand, the aged samples are characterized by the presence of some severe inorganic stains on the brick surfaces simulated with those present on walls. The colors of these samples surfaces are **orange** in the state of iron corrosion layers (A), and **blue** with heavy particles of copper chloride (B). In addition, there is an increase of brightness and roughness of iron corroded samples; all of these features are shown in figure 3a. On the other hand, the results of cleaned samples show that both the iron aged samples (A) and cupper-aged samples (B) had been cleaned where the stains thickness were removed perfectly through treating by hydrogen (H_2) plasma, figure 3b.

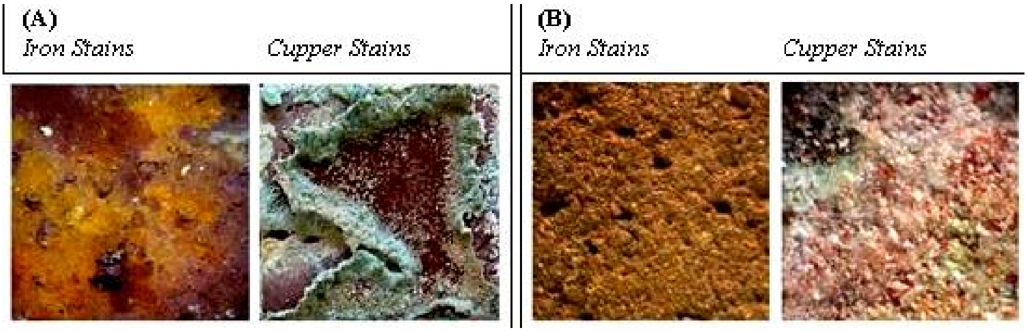

Fig. 3. OLS photos of brick samples **a**. iron corrosion layers & copper stains before cleaning, **b**. the same samples after plasma cleaning

EDX coupled with SEM results

EDX analytical results of the particles accumulated on brick surfaces demonstrate that they vary according to the stain types. On the other hand, the same analytical results after plasma cleaning attest that there are some differences between up and down in samples (A) and (B). These results are listed in table 1. SEM obtained results prove that there are heavy, entangled, dense and harsh layers of iron rust (A) and copper stains (B) accumulated on the brick surfaces, figure 4a. SEM-EDX investigations that were used to check the efficiency of cleaning processes proved the next points:

a. the clearness of positive effects in the reducing of darkening of samples surfaces;
b. the reduction of stain and accumulations thickness in all cleaned samples (A) and (B);
c. the increase of the samples porosity both in samples (A) and (B), in addition to the observation of clear porosity indexes and brightness and micro damaging in some zones of brick surfaces, compared to the same samples before cleaning (Fig. 4b).

FTIR results

The FTIR spectrum analysis results of ***iron corrosion layers*** before and after cleaning by RF plasma prove that both quartz and hematite are the main minerals occurring in different concentrations in the samples surface layers. The absorption bands in the region (800-1200cm^{-1}) are attributed to Si−O stretching vibrations, and the region (700-1000cm^{-1}) is attributed to the hydrated iron oxides FeO(OH). In addition, there is a presence of iron oxides in the region (400-700cm^{-1}), and a presence of AlO_6 at the vibrational bands (575cm^{-1}) and $Al(OH)_3$ at (691cm^{-1}), both before and after cleaning processes. On the other hand, it could be noticed that there are some differences (both qualitatively and quantitatively) in FTIR results due to the effect of RF plasma (table 2). Regarding the investigation results of ***copper stains*** by FTIR, it could be noted that there are 11 vibrational bands before the cleaning process and 13 bands after. Sulphur (S−O) group are registered 11 times; 6 before plasma cleaning at the vibrational bands (451-781cm^{-1}), then they are decreased to 5 after the cleaning process (542-793cm^{-1}). On the other hand, the silicate (Si−O) group are present at 2 vibrational bands (791 and 1067cm^{-1}) before cleaning that were increased after cleaning to 6 bands, which made their appearance at the regions between (459, 777, 1067, 1436, 2053 and 2977cm^{-1}). Finally, it could be noted that hydroxyl (OH) group is registered 3 times before cleaning at (1648, 1665, 3097cm^{-1}) vibrational bands and decreased into 2 vibrational bands after cleaning (1632 and 1659cm^{-1}) (table 3).

Table 1. Percentages of stain types before and after cleaning processes

Stain Types	Elemental Ratios								
	C	***Al***	***Si***	***S***	***Cl***	***Ca***	***Fe***	***Cu***	***Total***
Before cleaning									
Iron (A)	79.10	3.00	7.40	-	0.277	1.85	8.37	-	99.997
Copper (B)	-	6.52	2.23	20.14	2.16	1.04	-	67.91	100.00
After cleaning									
Iron (A)	37.4	32.4	18.6	-	2.85	2.5	6.254	-	100.00
Copper (B)	-	8.11	4.77	19.99	4.96	4.27	-	57.9	100.00

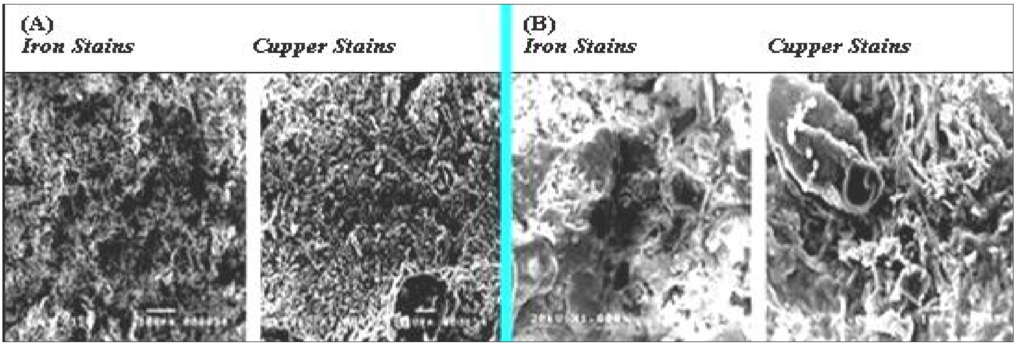

Fig. (4) SEM photomicrographs of brick samples **a** iron corrosion layers & copper stains before cleaning, **b** the same samples after plasma cleaning

Table 2. FTIR analytical results of iron corrosion layers before and after cleaning

Peaks Identifications Bands (cm^{-1})			
Compounds	***Before Cleaning***	***Compounds***	***After Cleaning***
		FeO	430
Si–O / FeO	461	Si–O / FeO	461
FeO	536	FeO	534
AlO6 / FeO	575	AlO6 / FeO	575
FeO	630	FeO	626
FeO	675	FeO	677
Al(OH)3 / FeO	691	Al(OH)3 / FeO	691
Si–O	734	Si–O	732
Si–O	777	Si–O	777
Si–O	793	O–H	940
Si–O	1010	Si–O	1004
Si–O	1036	Si–O / FeO	1020
Si–O / FeO	1053	Si–O / FeO	1053
Si–O	1075	Si–O	1079

Table 3. FTIR analytical results of cupper stains before and after cleaning

Peaks Identifications Bands (cm^{-1})			
Compounds	***Before Cleaning***	***Compounds***	***After Cleaning***
S−O	451	Si−O	459
S−O	542	S−O	542
S−O	593	S−O	591
S−O	610	S−O	612
S−O	675	S−O	673
S−O	781	Si−O	777
Si−O	791	S−O	793
Si−O	1067	Si−O	1067
OH	1648	Si−O	1436
OH	1665	OH	1632
OH	3097	OH	1659
		Si−O	2053
		Si−O	2977

Discussion

Through explaining the previous data, it could be said that the dirt and dust accumulated on the archaeological surfaces gathered over the years both represent a threat and great problem during the conservation of these surfaces [55]. Furthermore, these accumulations are not only capable of retaining moisture on the buildings' surfaces, which in turn help in the growth of fungal spores, but also attract the fungal spores in question [56]. From an aesthetic~~al~~ perpsective, this problem has increased in urban areas [57, 58] where the impact of the dirt makes ~~the~~ cleaning a relevant task within the conservation activities, and also very expensive, due to the frequency that would be required [20]. Therefore, the cleaning of archaeological surfaces requires multidisciplinary approaches, in order to develop new strategies for the conservation and protection of their units from the severe effects of accumulations. These strategies should be matched with an international code of ethics and practices [59-63]. Moreover, these strategies should be achieved through enhancing new techniques, such as low-pressure plasmas (*cold plasma*). It is considered one of the new techniques used in the archaeological field due to its major aforementioned advantages. Within the same context, the effectiveness of cleaning should be advisably evaluated from the variation of several parameters. These parameters include surface colors by *OLS*, quantities of stains accumulations by *EDX* and the minor damages existent on the cleaned surfaces by *SEM*.

The results of the RF plasma cleaning, (Figure 3-b) prove that there are noticeable changes in the samples' external surfaces (A), iron-aged samples and (B) copper-aged samples. These changes are mainly due to two factors: the suing of H_2 plasma in the cleaning processes of (A) and (B) samples, and also the decreasing of accumulated impurities, both in their depth profiling and in their concentration. In addition, OLS photos attest that sample (A) is completely cleaned and sample (B) is only partially cleaned. Moreover, the distortion on surface (B) is decreased and is smoother when compared to the sample before treatment. On the other hand, the removal of chlorine (B) depends on the sample temperature, whereas the subsequent data proves that chlorine removal is better carried out in hydrogen-containing plasma than in other types of plasmas, as previously attested [64-66].

The analytical results of EDX (Table 1) demonstrate that the components of these accumulations decrease and vary according to the stain types. In the case of iron-aged samples (A), the percentages of (Fe) indicate that its concentration was decreased by (25.28 %) after plasma treatment. Regarding sample (B), the percentage of Cu was decreased accurately and became (14.75 %) after plasma treatment. Additionally, it may be noted that there is a noticeable increase concerning the main components of the brick surface that contain (Al, Si and Ca) in all sample types. This increase (437%) is recorded in sample (A) and also (179 %) in sample (B). From this perspective, it may be argued that the results prove that RF hydrogen plasma is extremely useful, in terms of maintaining optimum cleanliness after the samples' preparation. In addition, it is a useful technique for the cleaning of the corrosion products and elimination of chlorides responsible for deterioration, due to its significant ability to reduce the thickness of the corrosion layers [64, 65, 67-69].

In *SEM*, imaging was performed in order to evaluate the changes in the surface's morphology and the efficiency of the samples' morphology induced by plasma treatment. Through evaluating heavy, entangled, dense and harsh layers of iron rust (A) and copper stains (B) observed by SEM in untreated brick samples Figure 4a, it could be said that these accumulations are essentially owed to the effects of aging processes mentioned in the experimental section. Furthermore, the changes in surface morphology show significant differences after cleaning processes by plasma reduction, where, a clear separation of the outer corrosion layers from the original surface was observed [70, 71]. The changes in surface morphology were noted in Figure 4b after cleaning processes; the basic structure of the brick surface appeared and the dirty layer was etched by plasma. Regarding micro damaging in some zones of brick surfaces, it could be claimed that these symptoms resulted essentially from the effects of plasma processing on silicon lattice as a main component of the brick structure [72-73].

Through explaining FTIR spectrum analyses before cleaning (Table 2), it could be observed that peaks at (461, 734, 777, 793, 1010, 1036, 1053 and 1075cm^{-1}) correspond to the stretching vibration of Si−O. This indicates that those peaks deal with the presence of silicates either in its amorphous or crystalline phases (one of the brick components such as quartz and kaolin) [74, 75]. Furthermore, it could be noted that iron oxides are observed in the spectral region of 400-700 cm^{-1}, as previously attested by *Sathya*, *et al* [76]. In those cases where the obtained peaks at (461, 536, 575, 630, 675, 691 and 1053cm^{-1}) correspond to the vibrational bands of iron, peak (536cm^{-1}) in particular indicates the presence of Ferric oxide [77]. The presence of magnetite and hematite provides interesting information about the weathering products [78], and could also offer further information regarding the provenance of the clay used for the mixture [79]. Finally, the presence of AlO_6 at the vibrational bands (575cm^{-1}) and $Al(OH)_3$ at (691cm^{-1}) indicate the presence of (aluminum oxide) and (bayerite), which are considered two of the essentials of brick components [80]. Regarding the FTIR data of the same samples after cleaning, it could be noted that the peaks' transmittance increases and the position of the peaks has been shifted towards the upper wave number. Moreover, the gradual concentration decrease has been observed in cleaning processes by RF plasma, where there are some bands of Si−O are contained (461, 575, 777 and 1053cm^{-1}). In addition, the appearance of another 5 peaks at (732, 1004, 1020 and 1079cm^{-1}), after cleaning could be owed to the effects of plasma cleaning procedures [81]. Within the same context, it could be noticed that the vibrational bands of FeO appear 7 times (461, 536, 575, 630, 675, 691 and 1053cm^{-1}) before cleaning and then increase after cleaning (430, 461 534, 626, 677, 575, 691, 1020 and 1053cm^{-1}). This may be due to the occurring of α-FeOOH (goethite) at (461cm^{-1}) and γ-FeOOH (Lepidocrocite) at (1020cm^{-1}) [82, 83]. In addition, O-H deformation vibrational mode is separated into (940cm^{-1}) [84]. The FTIR spectrum analyses the results of cupper stains before and after cleaning showed in Table 3.

It is therefore proven that the copper sulfates before the cleaning process are present in three forms; Brochantite $Cu_4SO_4(OH)_6$, Antlerite $Cu_3SO_4(OH)_4$, and Posnjakite $Cu_4SO_4(OH)_6{\cdot}6H_2O$. This is proved by displaying the characteristic stretching bands of S−O vibration in SO_4 groups at the region between (400-800cm^{-l}) [74]. Where, it appears at medium bands (451, 593, 610 cm^{-l}) and weak bands (542, 675, and 781cm^{-l}) [85]. On the other hand, Si−O group registered at the absorption of the strong band (1067 cm^{-l}) and weak band (791cm^{-l}). Within the same context, stretching bands of O−H groups are located at the region (1648-3097cm^{-l}) [44], where, it was recorded at a broad band (3097cm^{-l}) and narrow bands at (1648 & 1665 cm^{-l}). After the cleaning process, all FTIR bands shift beyond (542 and 1067cm^{-l}) and the quantity of bands increases up to 13 instead of 11 bands before cleaning. The bands attributed to brick components (Si−O) increase from 2 to 6 bands at the regions (459, 777, 1067, 1436, 2053 and 2977cm-l) as noted before by many scientists [76, 86, 87]. While the numbers of the bands attributed to copper sulfate (S−O) are decreasing from 6 into 5 bands, the bands attributed to hydroxyls groups are decreasing after cleaning to 2 instead of 3 before cleaning. Furthermore, through explaining the deconvolution diagram of FTIR of brick surface contaminated by the copper stain; it could be said that there is an increase in the height of some peaks after cleaning. This increase, which is essentially due to the increase of these peaks' transmittance, cause a decrease of both these peaks' width and their total area, as previously established by certain specialists in their case studies [88, 89]. These results are confirmed through the deconvolusion of FTIR curves before and after plasma treatment (Figure 5a, b, c and d).

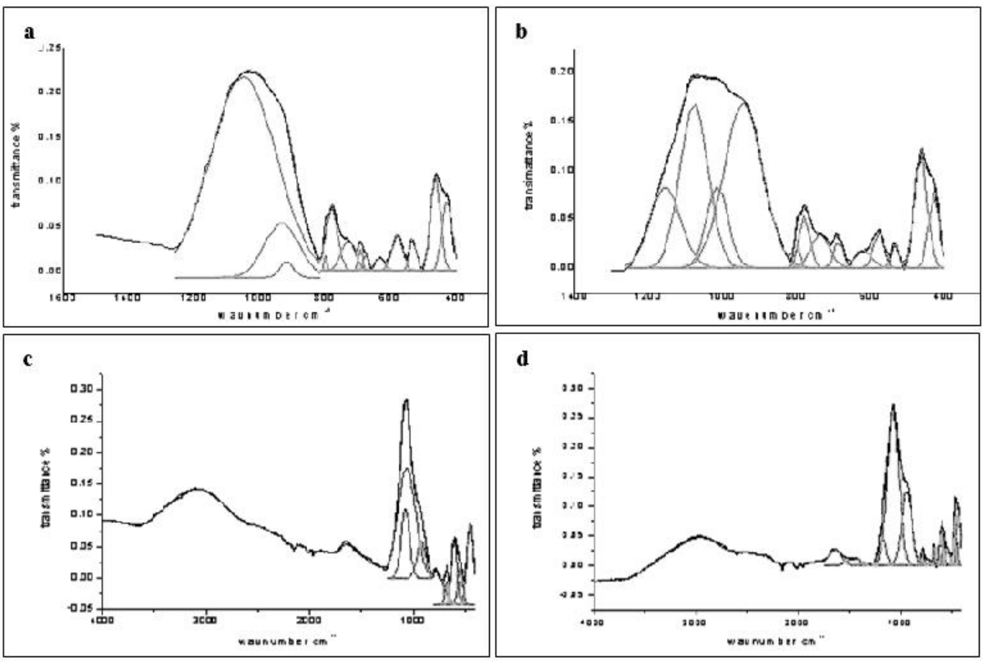

Fig. 5. FTIR spectrum of brick surface **a** with iron corrosion layers, **b** after plasma cleaning c with copper stains, d after plasma cleaning

Conclusions

The main objective of this paper is to present the effectiveness of plasma as *NDT* in the cleaning processes of historic buildings. From our diagnostic studies that were performed on the architectural surfaces of Prince Yousef Kamal Place, it could be claimed that it was affected by different types of stains. Iron and copper represent the vast majority of these stains as inorganic matters. *RF* plasma was performed for cleaning many samples collected from the palace's surfaces; our assessment processes provide significant information after RF plasma treatment.

These information indicate that the (Fe) concentration was decreased about (25.28%) and (Cu) was decreased accurately and became (14.75%) after plasma treatment. In addition, increasing the main components of a brick surface that contain (Al, Si and Ca) recorded (437%) in sample contaminated by (Fe) and (179%) in the sample contaminated by (Cu). Therefore it can be concluded that *RF* plasma is an effective cleaning technique, particularly in the removal inorganic surfaces contaminants. To sum up, it could be claimed that RF plasma is an important cleaning technique used for the removal surfaces contaminants. In addition, other experiments should be carried out, using several different types of gases and contaminations, particularly of an organic nature. This target shall be achieved in the 2nd part of the research, which is entitled Cleaning of architectural bricks using RF plasma: "None Metallic Stains", in order to evaluate the validity of this technique as a pioneer and non-destructive cleaning technique for both inorganic and organic materials.

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