XRD and SEM analyses of newly modified Bentonite poultices in desalination of ancient Egyptian limestone monuments

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Abstract

Salt-induced decay is deleterious threat for ancient stones and monuments, further salt decay is considered as a problematic in more recent buildings, as well causing repeated pulverizing, crumbling and peeling also it increased hygroscopic moisture content. Here, the desalination process of experimental limestone model-blocks salinated with NaCl and Na2SO4 solution by application of treated bentonite poultice for 7 days and repeated for three cycles, has been proposed with successful results. This modified poultice mainly consisted of bentonite, sand, and potassium ferrocyanide as crystallization inhibitor. The efficiency of the modified bentonite poultice depends on the ratio of crystallization inhibitor, amount of sand and volume of water content. This efficacy was determined using total dissolved Solids (TDS) and electric conductivity (EC) of extracted salts. EC values were 5.73 and 38.3 mmohs/cm for traditional and modified bentonite poultice respectively.

The most effective poultices were poultices of Bentonite: Sand: potassium ferrocyanide as crystallization inhibitor ratio was 3: 0.5: 1, and the poultice of Bentonite: Sand: Crystallization inhibitor ratio was 3: 1: 0.05 with TDS of 19262.3 and 27497.3 ppm, and EC of 25.5 and 38.3 mmohs/cm, respectively.

On the other hand, it has been found that concentrations of potassium ferrocyanide ranged from 2.30×10^{-4} up to 2.70×10^{-3}M proving significant crystallization inhibitory effects.

The other advantage of modified poultice is that potassium ferrocyanide acts as disinfectant against a wide range of bacteria and fungi commonly isolated from limestone surfaces. These isolates were identified morphologically and biochemically; bacterial isolates were belonging to (*Bacillus subtilis*; *Streptococcus* sp.; *Pseudomonas aeruginosa*) and fungi were of (*Fusarium* sp., *Geotrichum* spp., *Penicillium* sp.) phyla. Finally, this modified poultice of Bentonite: Sand: potassium ferrocyanide as crystallization inhibitor was applied on limestone statue heavily salinated with NaCl.

Keywords: Salt inhibitor, Bentonite, Desalination, Potassium ferrocyanide.

1. INTRODUCTION

Architectural heritages (building materials and sculptures among others) and other movable cultural heritage objects are continuously deteriorated by soluble salts, in particular chlorides such as sodium and potassium chloride, which are considered as the main responsible agents for heritages deterioration [1-15].

The sources of soluble salts may be natural impurities in the composition of stone, pollution, and sea ions [16-41], or may be derived from fertilizers used in the surrounding cultivated lands or from the soil upon which the building is constructed or wherein the object is buried [29].

The most common deleterious salt encountered in the field of archaeology is sodium chloride (NaCl) [42-47]. The soil is its main source, and NaCl ions reached 4160 ppm in the investigated soil samples collected from different places in Delta as well as its being as impurities in the natural composition of limestone occurrences [48-60]. The seriousness of halite could be ascribed to its high solubility and hygroscopic nature, so it could inwards in stone walls by capillary action from the soil in contact [4].

The second deleterious soluble salt is potassium chloride (KCl); its main source is the surrounding cultivated lands where nitrogen fertilizers were utilized [47]. The third common salt deteriorating heritage objects and building is sodium sulphate, which may be encountered in the form of Mirabilite ($Na_2SO_4.10H_2O$) or Thenardite (Na_2SO_4) originated from external sources such as pollution [19].

These soluble salts are involved significantly in deteriorating the architectural heritage and movable objects through the immense crystallization and hydration pressures exerted on pore walls [4,39] that erupts the binding medium and cause collapsed structure of stone [29]. This phenomenon was well-documented in different cases such as mural paintings of Amenhotep III (18^{th} dynasty), where salts are interlocked with paint layer; inscription of the King Thutmose III, limestone, New Kingdom, 18^{th} dynasty, Tell Heboua, Egyptian Museum, Cairo whereas soluble salts cause flaking of paintings and reliefs [26]; Clay limestone statue within the Egyptian Museum, Cairo, by pressure exerted by salts and sodium chloride (NaCl) is the most present (**Fig**. 1).

Due to hygroscopic character of soluble salts, in particular halite that causes continuous hydration of building materials reduced the compressive strength of lime stone from 87.72 kg/cm^2 to 16.32 kg/cm^2 for both dry and wet limestone samples respectively [46]. These repeated drying and wetting cycles caused the collapse of the inner structure of limestone turning the salted objects into powdery form [35, 36, 41], and losing paintings and reliefs [6].

This volumetric expansion should depend on different determinates such as high diurnal range of temperature interfered with other agents with the most important being wind [59], and the crystallization pressure P exerted by the salt in a confined space such as pores of stone could be calculated from the Correns' s equation [12], as following: $P=\frac{RT}{Vm}\ln\frac{C}{C0}$ where R is gas constant, T is temperature, Vm is the molar volume of the solid phase, C/C_0 is super saturation, and if this pressure exceeds the strength of the porous material, mechanical failure occurs causing flaking and disintegration of stone surfaces [30].

Physical properties (e.g., porosity, pore size, and permeability) are essential in salt deterioration mechanisms; it has been referenced that the damage rate by salt crystallization should depend on the stone's pore system, evaporation conditions, and the nature of the saline solution [9]. In addition to the mechanical deterioration of salts, these salts are involved in the chromatic alteration of azurite blue ($Cu^{2+}3(CO_3)_2(OH)_2$ and formation of paratacamite ($Cu_2Cl(OH)_3$) with green color in mural paintings and fiance causing what is termed bronze disease, giving a false impression on the nature of the original pigment [49].

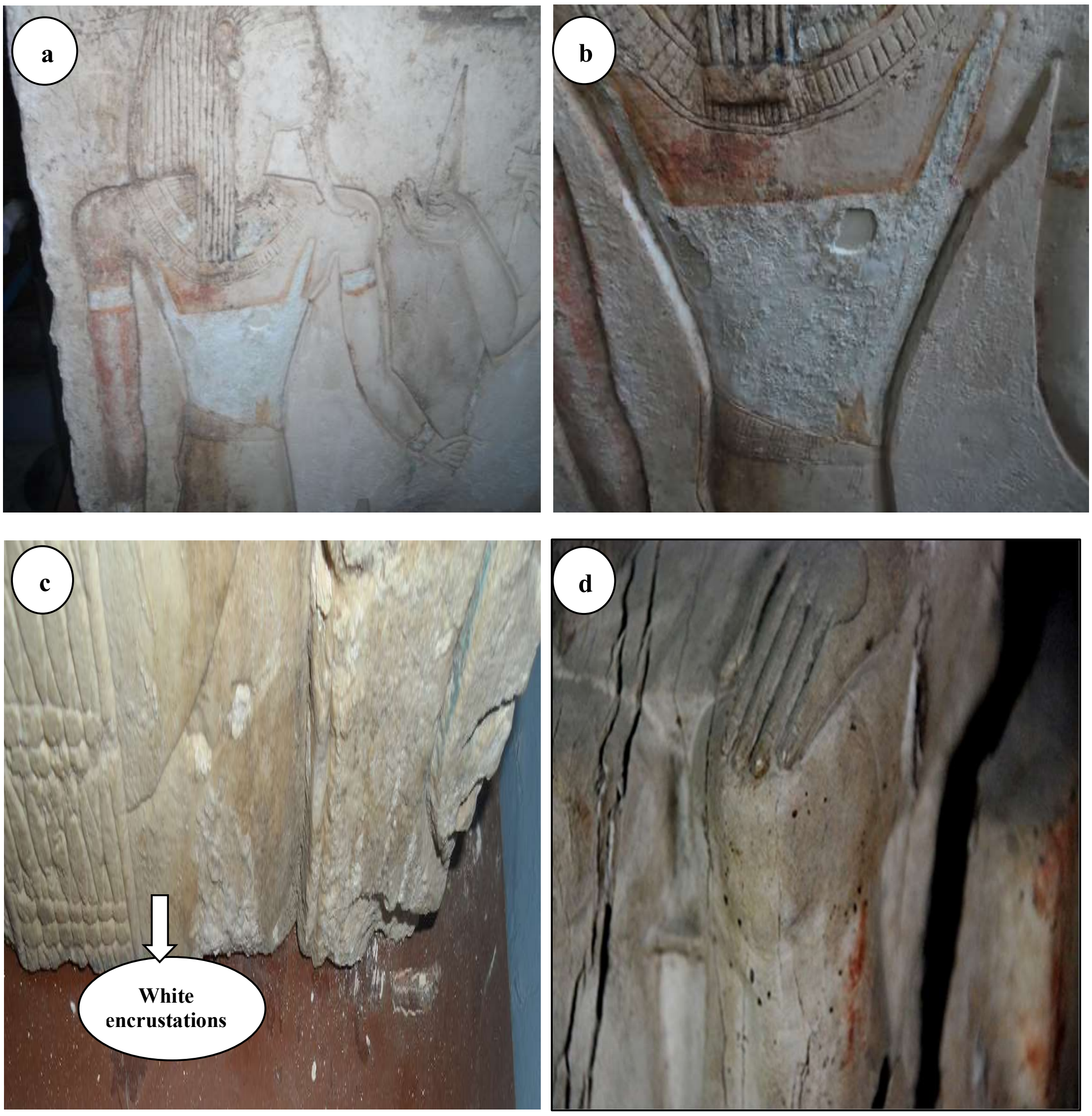

Fig.1. Deleterious effect of salts on stone monuments: (**a**) salts crystals on the mural paintings of Amenhotep III, (18th dynasty), Egyptian Museum, Cairo. (**b**) Close up of Fig. a; (**c**) Inscription of the King Thutomse III, limestone, New Kingdom, 18th dynasty, Tell Heboua, Registration no.924, Egyptian Museum, Cairo. (**d**) Cracking of clay limestone statue within Egyptian Museum, Cairo by pressure exerted by salts.

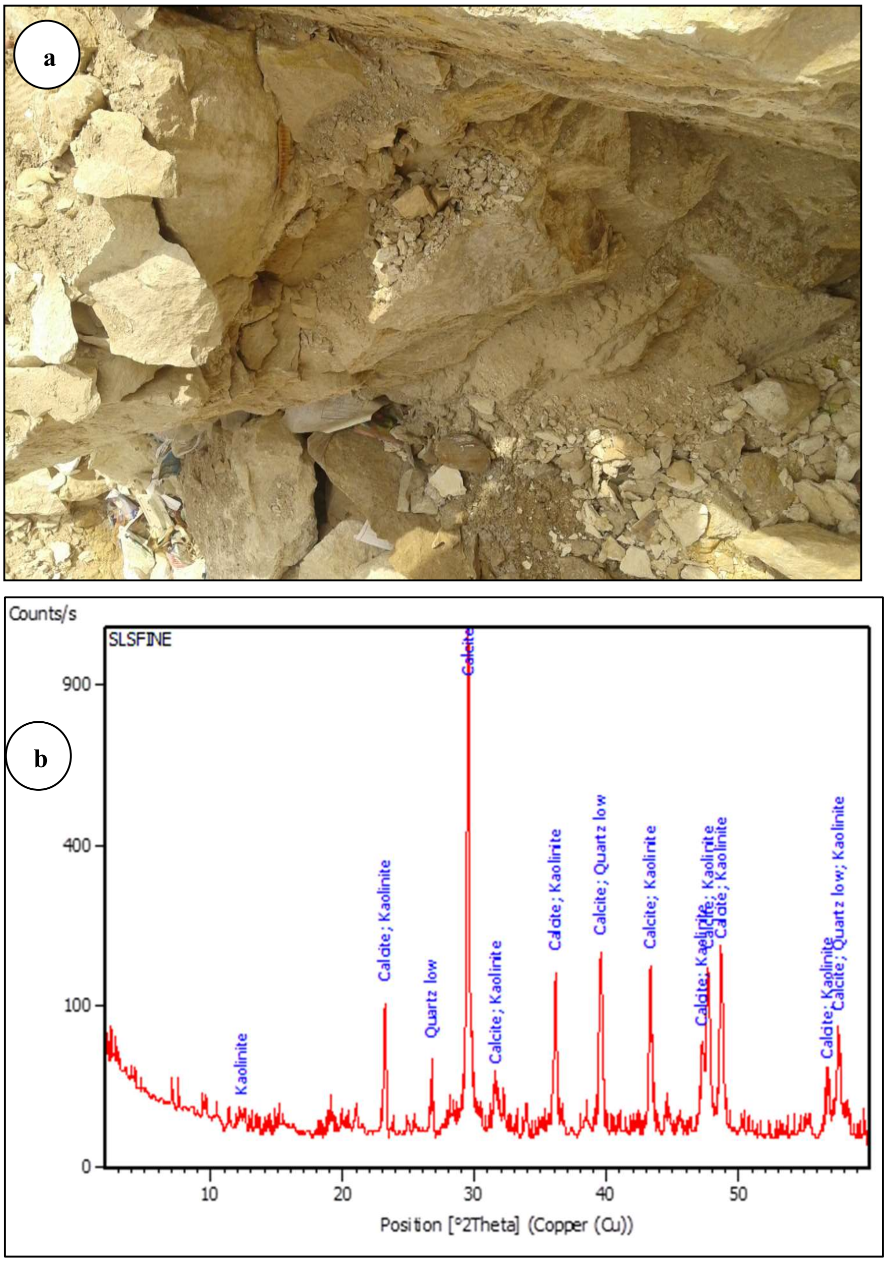

Fig. 2. (a) Sampling location of limestone blocks. (b) XRD pattern presenting mineralogical composition of treated limestone.

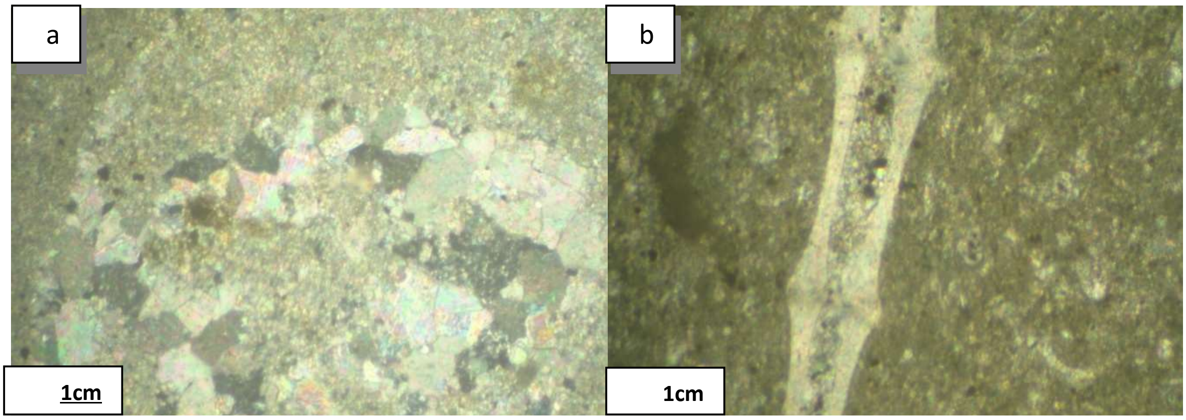

Fig.3. Thin sections photomicrograph. **a**) Indicating shell fragment has recrystallized with replacement of quartz grains. **b**) Indicating shell fragments with biomicrite composition to biomicrospar (XPL).

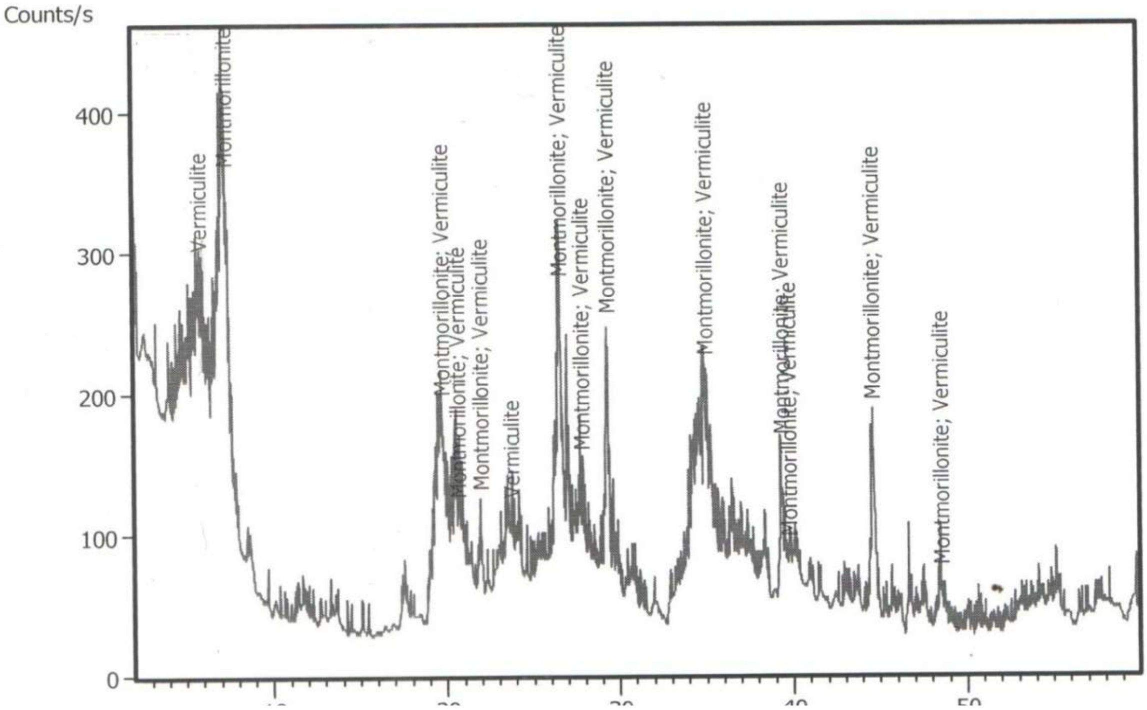

Fig. 4. XRD pattern pointing out the mineralogical composition of used bentonite

Fig.5. Illustrates efflorescence of salts over blocks in the presence of water

Fig.6. Illustrates the application of different wet bintonite poultices

The other deterioration aspect caused by salts is enhancing biopigment production by colonizing microorganisms as a defense mechanism against the adverse environmental conditions such as hypersalinity, radiation, and biocides that stain the colonized surfaces with different colors (red, black, brown etc.) that resist chemical and physical disintegration reducing the esthetical value of the salted objects [2,47].

This is because of the deleterious effects of these salts and difficulty of its extraction due to the complexity and seriousness of these salts, and less efficacy of traditional desalination methods such as poultices of moist paper pulp, tissue paper [33], and carboxy methyl cellulose (CMC), agar, clay and Bentonite poultice [32]. Bentonite poultice has many characteristics qualifying it to be a promising method in desalination of stone surfaces; it is commercially available and its chemical characteristics enhance ion exchange, inert, no harmful residues are resulted, but this poultice is less efficient in extracting these deleterious salts [17]. To overcome this shortage, bentonite poultice was modified by adding potassium ferrocyanide as crystallization inhibitor in the extraction of salts deteriorating cultural heritage objects [3, 51, 55,56], and the efficacy of this modified poultice could be ascribed to the main role of crystallization inhibitors in modifying crystal habit or delay nucleation of salts [42].

Selecting potassium ferrocyanide ($K_4Fe(CN)_6$) as crystallization inhibitor to modify bentonite poultice is because it is a very powerful nucleation suppressor through inhibiting NaCl nucleation in the stone pores by enhancing capillary passage within porous limestone further away of stone pores [50]. Besides, both sodium and potassium ferrocyanide have been in use for many years for anticaking in salt for human consumption and animal feeds according to the scientific committee on animal nutrition in the European Commission 2001.

The efficacy of bentonite poultice should depend on several factors such as sand, it has been well established that fine particle size sand could be added to reduce the shrinkage rate of this modified poultice on one hand; On the other hand, adding fine sand would enhance adhesion of the poultice to stone surface and continuity of the poultice [20]. This efficacy was evaluated via determining Total Dissolved Solid (TDS) that is a measurement of inorganic salts, organic matter in water, and Electrical Conductivity (EC) that is faster than measurement of TDS and more effective than other laboratory measurements [58]. The relationship between TDS and EC is a function of the type and nature of the dissolved cations and anions in the water [53], and could be calculated from the following formula: TDS = k_eEC where TDS is expressed in mg/L and EC is estimated in microsiemens per centimeter at 25 °C., *ke* is a correlation factor with a value that varies between 0.55 and 0.8 [5].

The mechanism of extracting soluble salts from stone buildings is based on ions exchange, the total number of exchangeable cations is expressed in the total sorption capacity which give the number of milli-equivalents of cations per 100 g of dry clay [16]. The other advantage of this modified bentonite poultice is disinfection of colonized surfaces; however, it has been reported that potassium ferrocyanide acts as a disinfectant against halotolerant microorganisms colonizing stone surfaces, in particular multi-resistant bacteria such as *E. coli*, and fungi thus reducing the conservation interventions [27].

The purpose of the current study is twofold; a) develop a modified bentonite poultice to enhance the desalination process from cultural heritage objects, supplemented with different concentrations of potassium ferrocyanide (as the crystallization inhibitor) to reduce the times of poulticing to remove these salts and reducing the humidity in these stone buildings, and b) to evaluate efficacy of this new poultice using total dissolved solids (TDS) and electric conductivity (EC) of extracted salts.

2. MATERIALS AND METHODS

2.1. Limestone sampling

Limestone samples were collected from Al-Fustat area near historical buildings (Religion Complex) at old Cairo, belonging to the Middle-Eocene Mokattam formation.

2.2. XRD investigations

To estimate the efficacy of modified poultice, XRD investigation was used through determination the mineralogical composition of limestone cubes (5×5×5 cm) after application modified poultice for desalination, X-ray diffraction analysis was carried out with a Philips PW-1710 diffractometer, automatic slit using Cu*K*ά radiation (National Research Center, Cairo) according to Stuart (2007).

2.3. Limestone blocks preparation

To investigate the efficacy of crystallization inhibitors, firstly limestone cubics were treated with the most common salts in the field of archaeology according to [38], as illustrate in Tables 1-2. These blocks 5×5×5cm were vertically immersed in sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) and mixture of both of them (0.55 Mole) with purity 99.8%, provided by Sigma Co., Cairo, Egypt (**Fig**. 5). Immersion of these blocks was for 4 days to a height 2 cm above the base of the limestone blocks promoted solution capillary flow through the stone pore system forming white margin (**Fig**. 6). These processes were repeated for six cycles under laboratory condition at 35 °C, and at the end of the six cycles, the treated limestone samples were investigated using SEM.

2.4. Determination of porosity

Porosity of cubics of limestone was measured by immersion under vacuum [28], in Materials Labs., Faculty of Engineering, Zagazig University.

2.5. Characterization of bentonite

Bentonite is commercial clay provided by Al Andalus Company, Cairo, Egypt. To point out mineralogical composition of bentonite, small sample was investigated using XRD (Philips PW-1710 diffractometer, automatic slit, using Cu *K*ά radiation (National Research Center, Cairo) according to Stuart (2007).

2.6. Poultices mixture preparation

After preparing limestone cubics, the bentonite poultices with different ingredients was performed in dry condition. To compare the efficacy of control and poultice supplemented with crystallization inhibitor, five poultices were used as follows:

(1) Bentonite with distilled water only;

(2) Bentonite: Sand: Crystallization inhibitor $(K_4Fe(CN)_6)^{-4}$ with concentrations (1.30×10^{-4} M) ratio was 3: 0.5:1;
(3) Bentonite: Crystallization inhibitor (1.7×10^{-4} M) ratio was 3: 0.05;
(4) Bentonite: Sand: Crystallization inhibitor (2×10^{-3}M) ratio was 1:1:1;
(5) Bentonite: Sand: Crystallization inhibitor (2.70×10^{-3}M) ratio was 3: 1: 0.05.

The four poultices were prepared by mixing dry materials of bentonite and fine sand with grain size between 0.64 and 1.0 mm with three volumes of water (70, 110 & 134 ml), as illustrated in Table 3, in flask for about 30 min with magnetic stirrer until being homogenous mixture like mortar.

The fifth poultice was modified by adding potassium ferrocyanide ($K_4Fe(CN)_6$) with purity 99% as crystallization inhibitor with different concentrations (1.30×10^{-4} M up to 2.7×10^{-4} M). These poultices were applied on the prepared limestone cubes with approximately thickness 3 cm in homogenous layer without pre wetting of substrate and covered with polyethylene film to avoid rapid evaporation [57]. After 7 days, these poultices were removed to desalinate these cubics by absorption. The applications of these poultices were repeated for three cycles for all limestone cubics at 35°C.

2.7. Hydrochemical analysis

After three cycles of poultice application, each cycle was 7 days; the efficacy of different poultice types was evaluated using hydrochemical analysis. In this analysis, samples of these poultices were collected to determine TDS in ppm and EC in millimoh/cm of the extracted salts [38].

To confirm these results, samples of bentonite poultices, either control or modified ones, were placed in a plastic tube with 5 ml of distilled water, centrifuged for 20 mins at 5000 rpm/min to get rid of traces of sand and bentonite. One ml clear solution was tested using latex (USA), every number on the latex indicates to the ratio of removed salt in the poultice[46].

2.8. SEM-EDX investigation

To confirm the efficacy of modified bentonite poultice (P5), samples of this poultice after the three cycles applications were investigated using Scanning Electron Microscope supplemented with EDX unit (SEM, QUANTA FEG 250, National Research Centre, Dokky, Giza, Cairo) according to procedures provided by Berzioli [8] where poultice samples were dried at 40°C for 2 days and SEM-EDX investigations were carried out.

2.9. Morphological and biochemical Identification of bacterial and fungal isolates

To culture and purify bacterial isolates, 0.1 ml of saline was prepared on nutrient medium (5g peptone, 3g beef extract, 5 g NaCl, 20 g agar in L distilled water, pH 7–7.1) incubated at 37°C for 24 hs, so that the bacteria obtained single colonies. The isolates were confirmed on the basis of Gram staining and morphology. In addition, all bacterial isolates were identified based on culture dependent methods, biochemical, microscopic examinations, and other properties such as the color of colonies.

2.10. Antimicrrobial activity of potassium ferrocyanide

To test the antimicrobial activity of potassium ferrocyanide on the identified fungi and bacteria, 1 ml of saline was cultured on Dox-Czapks plates (g/l) (30 g sucrose, 1 g K_2HPO_4, 3 g $NaNO_3$, 0.5 g $MgSO_4\cdot7H_2O$, 0.5g KCl, 0.01 g $FeSO_4\cdot5H_2O$, 20 g agar in 1000 ml distiled water) and incubated at 28 ± 2 °C for (7 days), so single colonies appeared. Filter paper discs were saturated with potassium ferrocyanide different concentrations of potassium ferrocyanide (2.30×10^{-4} up to 2.70×10^{-3}M) used in modification of the poultice were tested against some of the most common bacteria deteriorating cultural heritage objects (*Bacillus subtilis*; *Streptococcus* sp.; *Pseudomonas aeruginosa*) and fungi (*Fusarium* sp., *Geotrichum* spp., *Penicillium* sp.) using filter paper disc method, and at the end of incubation period, inhibition zone was determine in mm. At the end of incubation period, the inhibition zone is determined in mm.

2.11. Applied study

After the experimental evaluation of poultice P5 (Bentonite: Sand: Crystallization inhibitor (2.70×10^{-3} M) with ratio 3: 1: 0.05), this poultice was applied onto a limestone statue its measurements 52 cm length × 27 cm high; this statue was installed in aquatic niche in fountain where microbial pigmentation and saline of white efflorescences in particular NaCl could be observed. This poultice was repeated four times, its efficacy was evaluated in using total dissolved solids (TDS) in ppm and electric conductivity (EC) in millimho/cm.

3. RESULTS AND DISCUSSION

3.1 Petrographic investigation

Used limestone samples were extracted from Middle-Eocene Mokattam formation from which most monuments in ancient Egypt were built, that homogeneous and buff colored stone [1,44]. Moreover, the XRD pattern of limestone showed that the major elements were calcite (96%), with secondary elements of quartz (1%), and kaolinite (less than 0.5%) (**Fig**. 2); this is in agreement with results obtained by [22].

This type of limestone is more susceptible to deterioration by underground water and soluble salts evidenced by continuous delaminating of the surface and turning the stone surface into cuneiform shape [21, 43].

Polarizing micrographs revealed that shell fragment has recrystallized with replacement of quartz grains, and shell fragments with biomicrite composition to biomicrospar (XPL) (**Fig**. 3), with some shell fragments have recrystallized wall side with mono subrounded wavy extinction quartz grains thought to be of detrital origin, parts of the matrix is also recrystallized into sparry calcite that is one of the main characteristics of Gebel Mokattom formation that was subjected to different types of digenesis processes as re-crystallization and widely used in construction of buildings and monuments in most of the south Egypt [1].

Our finding revealed that total porosity of limestone samples yielded values of 3.34 ± 1.40%, it has been referenced that there is an increasing relation between porosity and water absorption as the samples that exhibited highest values of porosity also showed high water absorption capillarity coefficients [6, 25,51].

3.2 Characterization mineralogical composition of bentonite

Data derived from XRD pattern of standard sample bentonite indicated that its mineralogical composition being mainly montmorillonite (89%) and vermiculite (11%), and no salts were detected (**Fig**. 4). This result was supported by literature reported that bentonite clay consists mainly of motmorillonite and vermiculite [20], which are the most active clays owing to their high ion exchange capacity [56].

3.3 Ingredients of poultices mixture and their efficacy

Current results pointed out that the amount of salts extracted using different poultices (P1, P2, P3, P4 & P5) is varied according to the type of the poultice, it was found that poultice P5 was the most effective with total extracted Cl^- ions was 10472.5 (Table 3). Poultice (P5) is mainly composed of bentonite, sand and crystallization inhibitor, and adding fine size sand stand wet for a long period, and contained amount of salts more than P3 which has the same ratio of bentonite and inhibitor but without sand. This result was confirmed by [16], who reported that efficacy of bentonite poultice should depend on its ingredients, and adding sand to the poultice reduced shrinkage rate specially if these poultices are applied in dry conditions.

From data presented within Table 4, the bentonite poultice types could be arranged according to their efficacy expressed by captured cations and ions as following: P5 >P2 >P4 >P3 >P1. The other determinant of efficacy of bentonite poultice is water content; it has been observed that although the concentration of inhibitor in poultices No. P4, P2 & P5 was 50, 33.33 and 7.5 g, respectively, the poultice P5 is the most effective. This effect could be ascribed to the matter of fact that water content is responsible for transporting salts into the stone blocks with 70, 110, and 134 ml for poultices No. P2, P4, and P5, respectively. This is in parallel with [35] who delineated that the solubility of salts is a function with high relative humidity and temperature where the poultice is applied, and it was found that covering the poultice with polyethylene sheets reduces evaporation rate of water that prolonged its action, it was well established that the poultice should have a lower critical moisture content (CMC) than the substrate in order to improve the transport of the salt solution from substrate to poultice [61].

Also, it has been observed that supplementing bentonite poultice with potassium ferrocyanide in different concentrations (P5) enhanced the extraction of soluble salts from limestone cubic more than 10 times in comparison with bentonite poultice free potassium ferrocyanide (P1). This may be attributed to the matter of fact that potassium ferrocyanide is able to be invaded into the salted stone blocks to modify crystal habit or delay nucleation of salts. So, salts migrate in the form of solution through the complex capillary system of the stone towards the surface, and being absorbed by the bentonite poultice [30]. Also, it has been reported that the synergetic effect of bentonite and the crystallization inhibitor prevents or delay nucleation of salts, inducing salts to flow out forming efflorescence instead of subefflorescence [50].

In principle, adding potassium ferrocyanide ($K[Fe(CN)_6]^{-4}$) to the poultice enhanced its efficacy, but its concentration is another determinant of this efficacy. Our findings indicated that concentrations ranging from 2.30×10^{-4} up to 2.70×10^{-3}M enhanced the efficacy of poultice that could be ascribed to the matter of fact that increased the solution critical supersaturation (up to 8%) could inhibit crystallization of NaCl to great extent, so efflorescence go further to stone surface. This in agreement with [42] who reported that concentrations of $K[Fe(CN)6]^{-4}$ ranging from 2.48×10^{-4} up to 2.85×10^{-3}M have the same crystallization inhibitory effect.

On the other hand, the XRD pattern of limestone blocks treated with NaCl and Na_2SO_4 after application of the modified poultice mainly composed of bentonite, sand and crystallization inhibitor indicated that its mineralogical composition is mainly being of calcite (96%), quartz (3%), and minor portion of halite (**Fig**. 6) as an indicator to the efficacy of modified poultice in removal of halite from the salted limestone blocks.

This result was confirmed by SEM-EDX micrographs of modified bentonite poultice in **Fig**.7c illustrated higher percentage of halite extracted from the treated limestone cubics expressing the efficacy of bentonite poultice [32]. The form of extracted halite varied according/ to crystallization conditions, it has a semi cubic form normal poultice (**Fig**.7a) but in amorphous form with modified poultice (**Fig**.7b), this is in parallel with results obtained [19].

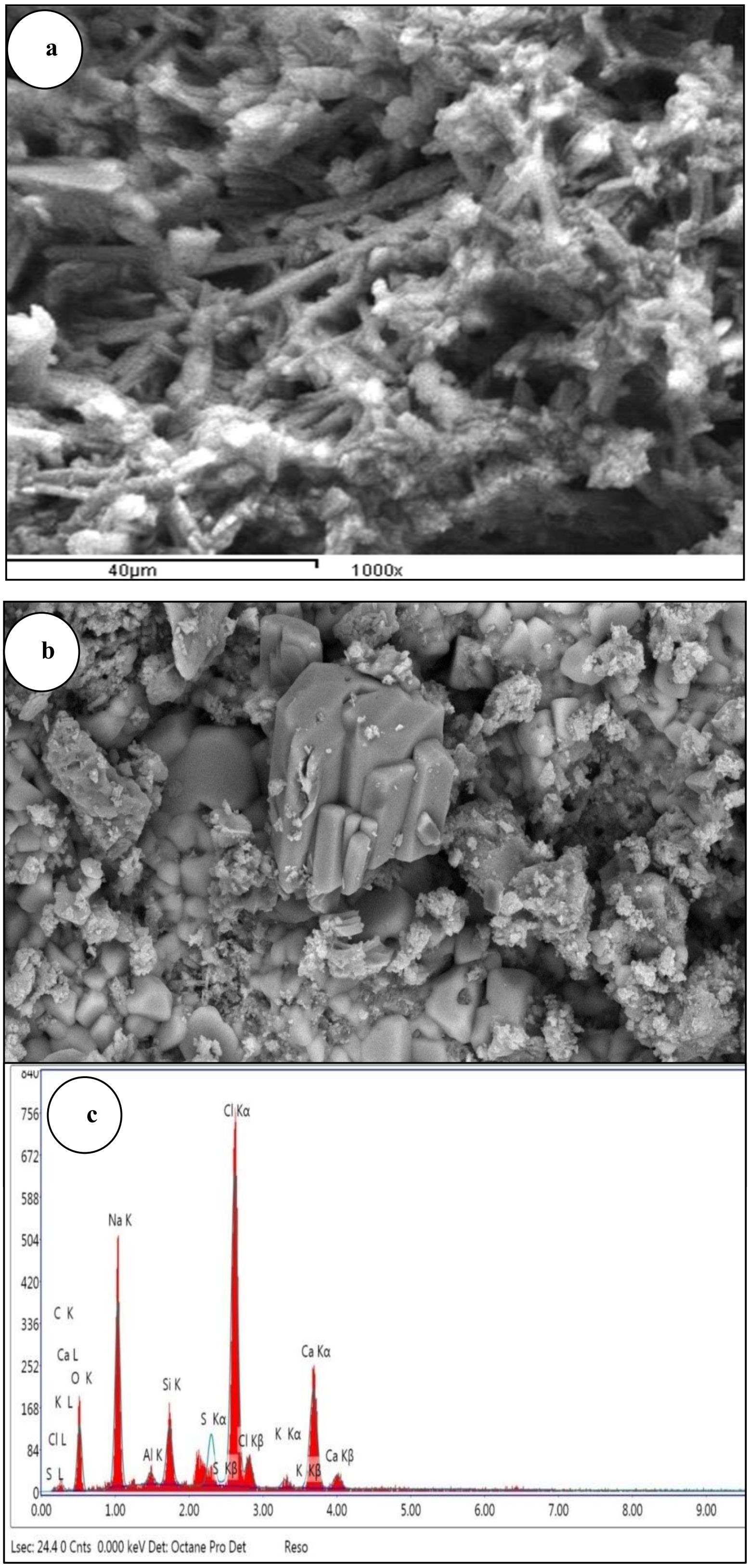

Fig. 7. SEM of halite: (**a**) in amorphous form with modified poultice with adding ($K_4Fe(CN)_6$ in concentration 2.70×10^{-3}M, (**b**) SEM micrograph of halite in semi cubic form with normal poultice without $K_4Fe(CN)_6$, (**c**) SEM-EDX pattern of modified bentonite poultice showing a high percentage of halite and small portion of sand and calcite.

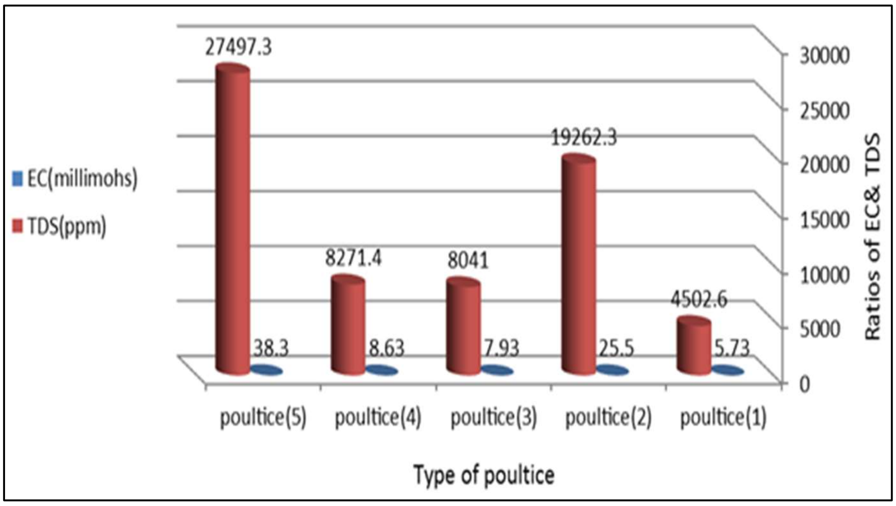

Fig. 8. Illustrates the relation between TDS and EC for the poultices under investigation.

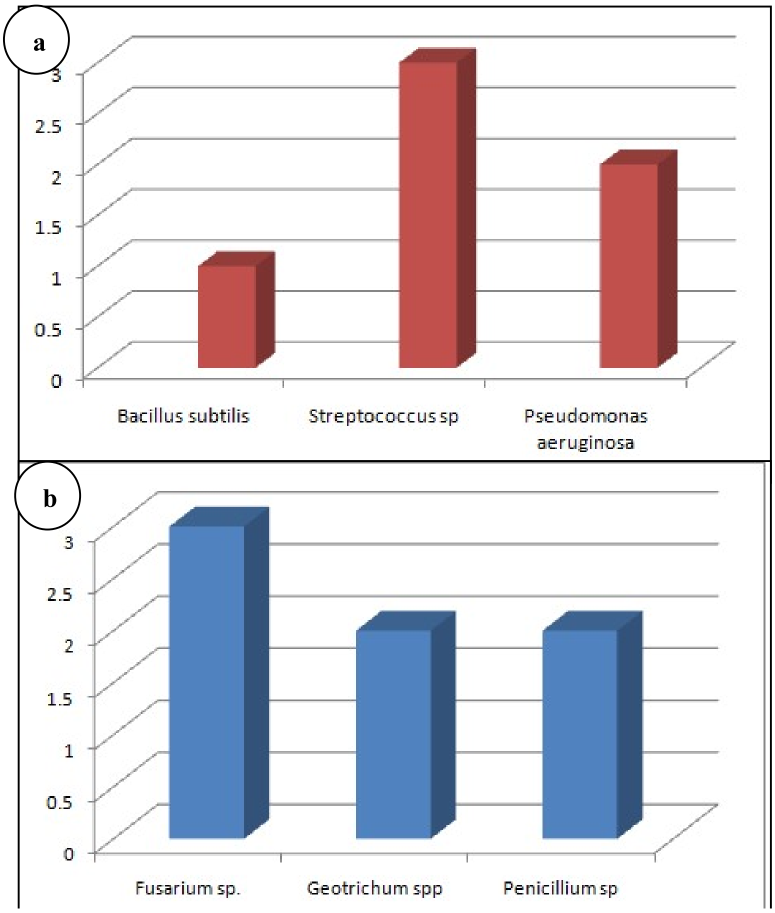

Fig. 9. (a) Sensitivity of bacteria (b) fungi to potassium ferrocyanide with concentration (2.70× 10^{-3}M)

Table. 1 Illustrates ratios of ions for natural salts from original environment of limestone.

Type of ions	Cations (ppm)				Anions (ppm)			
	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	Cl^{-}	SO_4^{--}	CO_3^{--}	HCO_3^{-}
Ratios of ions	240	170.2	85.1	30	1136	19.2	3	30.5

* ppm(part per million).

Table. 2. Percentage of hypothetical dissolved salts

Type of salts	KCl	NaCl	$CaCl_2$	$MgCl_2$	$MgSO_4$	$MgCO_3$	$Mg(HCO3)_2$
Ratios of salts	2.6	12.1	39.3	43	1.2	0.3	1.5

Table. 3. Illustrates the ratios of poultice ingredients

Ratio of mixture / Poultice mixture type	Ratio of dry powder in weight	Amount of water (ml)	Weight of dry materials(g)
(P1) Ben	100	134	150
(P2) Ben: S: Inhibitor	3: 0.5:1	110	149.99
(P3) Ben: Inhibitor	3: 0.05	134	157.5
(P4) Ben: S: Inhibitor	1:1:1	70	150
(P5) Ben: S: Inhibitor	3:1: 0.05	134	207.5

Table. 4 Hydrochemical results of extraction solutions of poultices

Poultice No.	EC (mmohs/cm)	TDS (ppm)	Cations (ppm)				Anions (ppm)			
			Ca^{++}	Mg^{++}	Na^{+}	K^{+}	Cl^{-}	SO_4^{--}	CO_3^{--}	HCO_3^{-}
poultice(1)	5.73	4502.6	601.2	608	276	156.3	1065	576	0.0	1220
poultice(2)	25.5	19262.3	4208.4	1824	1035	977.4	5857.5	480	0.0	4880
poultice(3)	7.93	8041	1402.8	486.4	345	1954.8	1420	480	0.0	1952
poultice(4)	8.63	8271.4	1683.3	778.24	161	1563.8	1775	480	0.0	1830
poultice(5)	38.3	27497.3	3406.8	2553.6	2875	2541.2	10472.5	768	0.0	4880

* ppm(part per million),TDS(total dissolved salts), EC (electric conductivity).

3.4 Hydro chemical analysis

Current results pointed out that poultices P2 and P5 have TDS of 19262.3 and 27497.3 respectively and EC of 25.5 and 38.3 respectively; so, the efficacy of these poultices could be established (Table 5). This action may be assigned to the ability of potassium ferrocyanide to prevent crystallization so the soluble salts being extracted easier using this bentonite poultice [50]. In addition, data obtained from Table 5 pointed out that Cl^- ions and Na^+ cations were the most abundant in TDS. This could be attributed to high solubility and hygroscopic nature of halite diffused in bentonite poultice with assistance of potassium ferrocyanide that delayed crystallization of halite [50]. Moreover, the TDS of the modified poultice is similar to the ratio obtained from hydrothermal analysis and modified poultice gave a significant difference (**Fig**. 8). Hence, in the light of literature, TDS could be used as an accredited criterion of efficacy of poultice [5].

3.5 Microbial disinfection of modified poultice

Potassium ferrocyanide with concentration of 2.70×10^{-3}M showed high antimicrobial activity against identified bacteria (*B. subtilis*; *Streptococcus* sp.; *P. aeruginosa*) and fungi (*Fusarium* sp., *Geotrichum* spp., *Penicillium* sp.); the most common bacteria and fungi isolated from the limestone, with inhibition zone ranged from 8-13 mm (**Fig**. 9). It was found that tested fungi varied in their resistance profile to different concentrations of potassium ferrocyanide, and this lethal action should depend on the type of microorganisms and concentrations of potassium ferrocyanide [23]. The lethal effect of potassium ferrocyanide against a wide spectrum of microorganisms could be attributed to blocking protein synthesis and dysfunction the microbial cell [27].

Moreover, current results revealed that bacteria were the most sensitive to different concentrations of potassium ferrocyanide added to bentonite poultice as a crystallization inhibitor. These results could be explained by thick fungal cell membrane or biofilm of extracellular polymeric substances (EPS) that retarded the penetration of biocides and other toxic substances into the fungal cell as a defense mechanism against adverse environmental onditions [18]. Finally, this modified poultice of Bentonite: Sand: Crystallization inhibitor ratio of 3: 1: 0.05 was applied on limestone object heavily salinated with NaCl to extract this salt effectively where TDS value was 22345 and EC value was 35 mmoh/cm.

CONCLUSIONS

Soluble salts cause serious deterioration due to hydration and crystallization pressures on walls of stone pores. This deleterious effect was proved under laboratory conditions using NaCl and Na_2SO_4; the most common in the field of archaeology. To overcome this problem, a poultice of bentonite and sand modified with potassium ferrocyanide as crystallization inhibitor was used in extracting the soluble salts. Efficacy of this modified poultice in extraction of salts was proved through determining TDS for both poultices No. 1 and 5, and it has been found that rations of anions in poultice 5 (P5) containing potassium ferrocyanide as crystallization inhibitor were 10472.5, 768, 4880 ppm of Cl^-, SO_4^- and HCO_3^- respectively, but values of these anions in poultice 1 (P1), bentonite free inhibitor, were 1065, 576. 1220 ppm of Cl^-, SO_4^- and HCO_3^- respectively. Furthermore, it has been found that EC values for traditional (P1) and modified poultice (P5) were 5.73 and 38.3 mmohs/cm respectively. Potassium ferrocyanide acts as a disinfectant for halo identified bacteria and fungi colonized salined stone surfaces reducing conservation interventions. Finally, P5 provide efficacy in desalination of NaCl from the statue.

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Conflict of Interest
The authors declare that they have no conflict of interest

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