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Different Cleaning Techniques for Removal of Iron stain from Archaeological Bone Artifacts: A Review

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Abstract

Archaeological bone artifacts are found in different locations in Egypt, and they represent multiple values that should be preserved from different deterioration factors. Iron contamination is considered one of the most aspects of deterioration for bones extracted from excavation areas. This study aims to make an integrated study for the first time on the formation of iron rust stain on archaeological bones, explain the aspects and mechanism of its deterioration, explain traditional and advanced techniques of cleaning used for stain removal, and presents the analysis and investigations used to explain the deterioration mechanism or evaluate the materials and methods used in this process. The nature and formation of iron stain and its effect on archaeological bone components were explained. The cleaning techniques (mechanical, chemical, laser, and plasma) for removing it were discussed. Some analyses and investigations [such as different types of microscopes, X-ray fluorescence, Atomic absorption, fourier transform infrared (FTIR) spectroscopy, etc.] that can be used in this process were mentioned. The results confirmed that iron is present within sediments can lead to the breakdown of collagen. It can cause an increase in the porosity of bone artifacts. Hydroxyapatite can undergo alterations such as ionic exchange, cationic exchange, and substitution of phosphate with carbonate. All cleaning techniques have many advantages and some disadvantages. The choice of method for cleaning of iron rust stain depends on the condition and size of the bone piece, and on the thickness and nature of the iron stain.

Keywords: Archaeological bone artifacts, Iron stain, deterioration, color change, cleaning techniques, analytical techniques.

1. Introduction

Bone is a composite material consists of both organic and inorganic components, and water [1-4]. The mineral consists of nano apatite crystals, which is about 60 wt % in fresh bone and 70 wt % in dry bone [5]. Hydroxyapatite $(Ca_{10}(PO_4)_6(OH)_2)$ is the basis of the inorganic component of bone, but it is not stoichiometric concerning hydroxyapatite, the apatite therefore, requires additionally to the Ca^{2+}, PO_4^{3-} and OH^- ions, substantial amounts of carbonate ions, lesser amounts of pyrophosphate, Mg^{2+}, Na^+ and K^+ [6]. The organic portion of bone consists largely of Type I collagen ,Which represents about 90% of the organic fraction of bone, the rest being composed of non-collagenous proteins – including bone sialoproteins and osteocalcin - various lipoproteins, and mucopolysaccharide [1]. Water exists in bone in cells, collagen, fluid, and bone mineral-apatite crystals. Water interaction with mineral and collagen. It's critical to the

mechanical behavior of fresh bone. There are many kinds of water that are existing in bone, such as free water, the structural water forming hydrogen bonds within the triple helix of collagen molecules, and crystal water bonding to apatite surface or within the crystal lattice, etc. [5].

The deterioration of archaeological bones has been discussed. Kyle [7] said that changes in bone begin to occur after death and burial, which are the results of several factors like biological, physical, and cultural processes. The changes in the physical properties are contemporary with chemical changes which occur within the organic and inorganic bone constituents.The deterioration of bones depending on the surrounding environmental conditions. There are several characteristics of soil that will affect the preservation of bone. Pokines [8] referred to various common taphonomic changes that may be caused by direct contact with soil. Bradfield [9] reported that

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the solution of the soil, unique chemistry and pH, all parts lead to deterioration and color change in the outer layers of bone. Manganese and iron in the soil can lead to dark stains on the bone and other porous osseous materials.

Some author discussed the contamination of bone with iron stain. Dupras and Schltz [10] informed that the color of the stain depends on the composition of the soil, which can include various minerals and organic matter. Soil coloration can be due to sodium salts, carbonates, and silt-sized or smaller quartz grains without pigmenting coatings. Dark soils with a black or brown coloration are the results of organic matter (humus) as well as magnetite (Fe_3O_4). Black or bluish-black colorations are the result of reduced manganese (Mn^{2+}). Bright red and brown colorations are associates with well-drained soils and oxidizing conditions (iron-bearing). It's necessary to be familiar with the natural color of unstained bone, to understand how bone changes color and to describe staining found on bones.

The natural fresh bones freed from the meat have been described as being a whitish to yellowish brown color due to the retention of fats and other fluids [10]. Schultz [11] reported that when the bone is in direct contact with the corroded iron body or near the corrosion products in the soil, staining of the bones can occur. Archaeological bones are light in weight, When dealing with archaeological material, the overall quality of the bone surface may be eroded rather than smooth, and the bones generally show a uniform staining ranging from tan to chocolate brown from tannins in a soil solution or iron oxides in the soils. Thorgirsdottir [12] explained that Iron is an unstable metal and when it's raw, it is usually covered by a thin oxide film. For iron to corrode, the corrosion requires access to water, oxygen and an electrolyte, and even the pH matters. All of these factors are present in the soil and can cause corrosion on the surface of the metal so that the volume changes and the corrosion moves inward to the metal core and encasing the surrounding sand and other particles in the burial environment. Pokines [8] wrote this was due to the closeness to corroding mineral sources Bones from cemetery cases can suffer from localized patches of staining. These can consist of green stains possibly due to corroding copper alloys, reddish stains possibly due to corroding iron alloys, and dark metallic stains possibly due to mercury. The sources of metal will be from coffin hardware or personal items left in the coffin or, in the case of mercury, from dental amalgam restorations. Such metallic staining can also occur among terrestrial surface-deposited remains, however, including military airplane crashes that often produce large amounts of iron- and copper-based alloy objects in nearness to human bones.

Turner-Walker[13] defined cleaning as the removal of decomposition products and soiling from the surface of an object .The soiling is damaging to the preservation of cultural objects in the form of soil from burial, dust from storage and adhering mud, and grease, dirt, oil, sweat or blood acquired from use. López-Polín [14] also defined Cleaning as removing any matter that prevents the surface of bones from being clearly viewed or that entails a risk to maintaining their integrity, for example, roots, water-sensitive sediments exposed to volumetric changes, etc. Casaletto et al. [15] referred to the choice of the cleaning procedure as critical, because it is an irreversible process and it could induce irrecoverable damage. The conservator needs to be aware of the chemical nature and structure of the contaminations to be removed. Cronyn [16] said that the physical, chemical, and structural nature of the material to be removed, the choice of method for cleaning should be controlled.Coladonato et al. [17] referred to different devices, from brushes and small metallic tools (scalpels, needles, etc.) to stronger tools, whether manual (like chisels) or automatic (ultrasonic scalers, pneumatic air scribes, grinding rotary tools, sandblasting) can be used in mechanical cleaning of bones.

López-Polín[14] wrote that mechanical cleaning is a common practice. It has the advantage of being residue-free and non-toxic. One disadvantage of mechanical methods is that blows or vibrations can cause fragments to be detached or even give rise to serious fractures on the samples. It is useful when liquids cannot be safely introduced onto the samples. Casaletto et al[15] defined Chemical cleaning as a process usually consists of the use of chemical solutions or the application of poultics saturated by cleaning chemical or biological solutions or enzymatic systems. Turner-Walker[13] reported that Chemical cleaning is a chemical reaction between the applied solution and the contamination to be removed. Chemical materials such as oxalic acid or ethylene diaminetetraacetic acid (EDTA), will isolate Fe3+ ions and are used in removing rust or iron staining from the surface. López-Polín [14] referred to the depth washing and rinsing process is required after the acid treatment, to ensure the removal of all traces of acid or salts produced during the treatment through a chemical reaction. Di Francia et al. [18] said that laser-based techniques are widely used as advanced tools for cleaning artefacts surfaces, reduce or avoid both mechanical and chemical disruption of historic surfaces, and in particular circumstances, be able to remove contaminating dirt or coatings selectively. Initially, laser beams have been utilized for cleaning of stone sculptures and paintings, but subsequently, other classes of artworks have been treated, as metals, fossils, bones, wood, leather, paper, etc. Tino et al.[19] reported that Plasma cleaning

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is a new technique. It's used for removing invisible oil films, dust, microscopic rust, or other dirt that usually accumulate on surfaces as a result of exposure, handling, or cleaning processes, plasma cleaning can be used also in the cleaning of objects of cultural heritage.

Bone analysis is vital to reconstruct and interpret associated taphonomic events, bone staining, body movement, identification of associated artefacts, and possible perimortem events. Color change may provide vital clues about the burial or depositional environment and about associated burial artifacts. Determining the cause of bone staining may be very helpful with the interpretation of taphonomic events, but it is important to recognize that different causative factors can create similar coloration or staining on bone [10].

This study aims to:

- Explain the formation, aspects and deterioration mechanism of iron rust stain on archaeological bones;
- Explain different cleaning materials and techniques used for stain removal;
- Presents the analytical techniques used to explain the deterioration mechanism or evaluate the cleaning process.

2. Natural of iron stain

According to Cole and Waldron[20], Archaeological bone rarely matches the normal color of natural human bone. Such matches occur only in rare circumstances of excellent preservation, such as undisturbed burial in graves directly cut into chalk. Thorgeirsdottir [12] mentioned to the existence of metallic grave goods in close to bone may cause staining on the surface of the bones in addition to composite artefacts are commonly consist of a combination of organic and inorganic materials, for example, iron knifes, cutlery, or tools, with handles made of wood, or bone may also exposed to staining. Pokines et al. [21] wrote that skeletal remains from coffin burials also may exhibit localized staining because of contact with metals reacting with other compounds. The metals include copper (Cu), iron (Fe), and mercury (Hg), which can result in red, green, or dark metallic staining areas. Cronyn[16] referred to artefacts may be glued together, joined by bone pins, or riveted with iron or copper alloy rivets. Kendall et al.[1] said that the color of excavated bones provides clues to the evolution of the burial environment. Bones from anoxic layers tend to be stained brown or black from manganese and iron oxides adsorbed onto the pore structure or fixed within the tissues, and hence availability to enter the pore structure of buried remains and interact with either the collagen or mineral, are dependent upon both pH and Eh.

Pokines& Higgs [22] reported that mineral and other dark staining may appear on buried bones especially those in contact with oxidizing metal, including all-over color changes or more isolated and variable patches of staining. According to Schweitzer [23]Corrosion is known as deterioration of material due to its reaction with the surroundings. It takes place because most of the metals naturally tend to return to their original state on which they are found in nature. For instance, iron turns to iron oxide, which is considered its natural state, when it is exposed to moist air. DuprasandSchltz [10] wrote that rust, a brown, crumbly corrosion product composed of hydrated iron oxide (Fig. 1), is formed when iron and its alloys are exposed to a moist, oxygenated environment. Jegdić et al. [24] explained that during corrosion of iron, buried in a wet ground when dissolved oxygen is present, the external layer of iron gradually turns into a corroded, rusty layer with corrosion products that resemble small rocks, sand, clay and soil minerals on its outer surface. These products, which are often combined in layers with compounds that are well-known for their lower oxidation state, directly appear on metal surfaces, while compounds with higher oxidation are formed in the outer layer.

Fig. 1: Iron mineralization on the surface of bone [25]

Einarsdóttir [26] defined Corrosion is an electrochemical process and like all electrochemical processes requires an anode, a cathode and an electrolyte. When iron corrodes in the ground the surface is the anode, and at the beginning of the corrosion process, the other partition of the surface is the cathode. As layers of corrosion products build up, there is a higher chance that the cathode will be an area of magnetite, Fe_3O_4, which is an electrically conducting corrosion product (Fig. 2) .The electrolyte in this
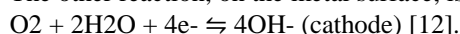
process, is the soil water, which contains chloride from dissolved salts. Selwyn et al. [27] explained that a very thin air-formed oxide film usually form the cover of pure iron. As iron is buried and predisposed to aqueous electrolytes, it is no more protected by this thin film, then, the corrosion process of iron takes place. Iron undergoes oxidation process at the anode site and it turns into iron (II) (ferrous, Fe2+) ions which dissolve:
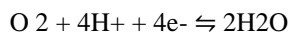
Fe ⇆ Fe2+ 2e-

Iron (II) ions can be further oxidized to iron (III) (ferric, Fe3+) ions:

Fe2+ ⇆ Fe3+ + 1e-

Being an electrochemical process, electrons lost in corrosion must be counterbalanced by a corresponding reduction reaction, where electrons are gained. The other reaction, on the metal surface, is:
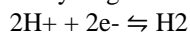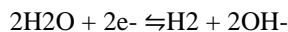
O2 + 2H2O + 4e- ⇆ 4OH- (cathode) [12].

Or

O 2 + 4H+ + 4e- ⇆ 2H2O

(When the oxygen level is high and the local pH is less than 6).

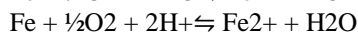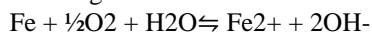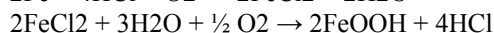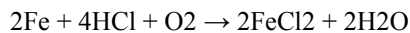Or hydrogen evolution:

2H+ + 2e- ⇆ H2

Or

2H2O + 2e- ⇆ H2 + 2OH-

(When the oxygen level is low and the local pH is less than 4) [10, 25].

Thorgeirsdottir[12] argued that Hydrogen evolution usually occurs at a pH of 4 or below. Oxygen reduction, not hydrogen evolution, is the main cathodic reaction balancing the oxidation of iron during burial, resulting in a net reaction:

Fe + ½O2 + H2O ⇆ Fe2+ + 2OH-

Fe + ½O2 + 2H+ ⇆ Fe2+ + H2O

Fe2+ ions can react directly with hydroxyl ions (OH- ions) to form solid Fe (OH)2 and passivation can occur, since both the anodic and cathodic reactions take place on the metal surface in a direct manner. Over time, Fe (OH)2 can turn into goethite by losing moisture, and over longer periods the corrosion will turn into stable magnetite. Magnetite formation occurs in presence of less oxygen than goethite. This corrosion process eventually slows down as the iron becomes covered with insoluble corrosion and soil particles that prevent further oxidation of the metal surface. The water in the soil, with its dissolved ions, works as the electrolyte in the process and contains dissolved salts like chloride ions (Cl-). Chloride ions tend to pile at the surface (the anode) on the metal. Acidic iron (II) chloride solution tends to fill the openings, cracks and pores that are present within the corrosion layer on archaeological iron. The present Cl- ions will accelerate corrosion after the object has been excavated [12]. Jegdic et al.[28] have proposed a cycle of corrosion which illustrates how chloride ions accelerate iron corrosion:

2Fe + 4HCl + O2 → 2FeCl2 + 2H2O
2FeCl2 + 3H2O + ½ O2 → 2FeOOH + 4HCl

According to Jegdić et al. [29]β-FeOOH (akaganéite) may be formed if the surrounding environment that the artefact was buried in contains sufficient amounts of chloride ions, another iron oxyhydroxide. Akaganéite formation is an indication of active iron corrosion under layers of corrosion products. Chloride ions may be implanted into the tunnels of the crystal lattice of akaganéite, stabilizing its structure. Jegdić et al. [24] said that corrosion products layer typically contains: an internal layer of black magnetite, Fe3O4, that conducts electricity and an external layer of iron oxy-hydroxide, goethite, α-FeO(OH) and lepidocrocite, γ- FeO(OH) with corrosion steel products that are orange, red or brown in color. Schultz[11] reported that bone staining can take place when an item that is closely associated with the corroding iron object or is placed in soil near the corrosion products. Close association of bone with oxidizing coffin nails or different artifacts composed of iron can cause a localized orange.

Cronyn[16] states that rust that is green in color is also probable as a result of iron (II) and iron (III) hydrated oxidation. Even though this rust was sometimes detected on marine cast and wrought iron, it has also been found on wrought iron brought from land. This green color that is found on bones is from copper and copper alloys, and it is usually a stain that is not adherent green corrosion product. Although this example is rarely found, it probably does not have to be taken into consideration as copper-derived during interpretation of green staining.

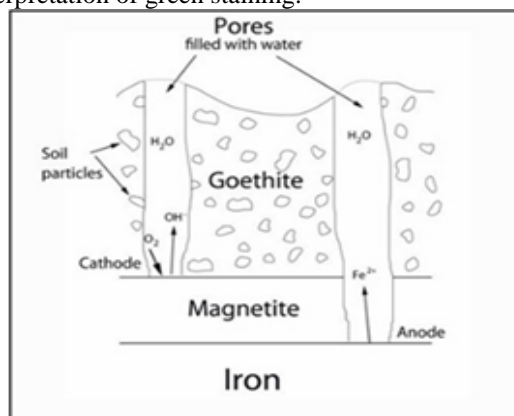**Fig. 2: A schematic showing the iron corrosion process and the stratigraphy of the corrosion layers of an iron artifact [26]**

According to Jegdic et al. [28], protective layers of yellow-brown siderite (FeCO3) or vivianite [Fe3(PO4)2 8H2O] may be formed When the carbonates or phosphates coexist in the soil in addition to more reductive conditions than necessary for the formation of magnetite. Although the pure vivianite

is white, the color of artefacts is usually dark-blue, because a certain amount of Fe^{2+} ions oxidized to Fe^{3+}, so that the blue color results from the transfer of charges between Fe^{2+} and Fe^{3+}. The source of phosphate ions may come from the burial of bones, skeletons of fish, garbage dumps or in recent time of phosphate fertilize. Dupras and Schltz[10] explained that it is rarer to see a bright blue to blue-black and these colors may appear on bone because of vivianite deposits (iron phosphate). In the form of iron (II) phosphate [$Fe_3\ PO_4)_2\ \cdot 8H_2O$], vivianite exhibits a whitish-gray coloration in its unoxidized condition when first excavated, but with air exposure, the mineral changes color to a brilliant blue. When referring to paleontological bones, this mineral staining occurs on buried organic remains that are high in phosphates and low in iron and that are buried in damp soils rich in iron and low in phosphates .With the combination of a phosphate and iron source, there must be a reducing and acidic. Kendall et al. [1] reported that the deposition of iron sulphides within pore structure of bone caused rapid deterioration.

3. The effect of iron on bone components

Ba [30] had discussed with more detail in accordance with Rapp and Hill [31]; Breuning-Madsen and Holst [32]; Konhauser [33]; Florian [34]; and Godfrey [35] the role of iron in burial environments in the deterioration of bones and related materials (such as antler and ivory) components. Ba [30] reported that "iron is most commonly present in soils in different forms such as goethite, which is hydrous iron oxide and a major iron ore. This is one of the commonest and most widespread of mineral deposits often forming iron pan capping oxidized sulfate deposits. Iron may be precipitated if the Eh [plotting the boundaries of water oxidation and reduction (redox processes) in waterlogged environment]/pH balance becomes oxidised in higher Eh environments. This reaction is a good indicator of environmental status between moderately reduced and oxidised environments. Redox processes can lead to the concentration or removal of iron in certain soil horizons. Redox processes occur primarily in waterlogged soils where biological activity can cause the soil to become anaerobic reducing ferric iron. The more soluble ferric iron can then re-precipitate in other areas where oxygen is more plentiful. Iron species are reduced and generally mobile in low Eh environments. In free draining soil iron is usually present in the form of ferric hydroxides and ferric oxyhydroxides which give the soils a reddish colour. Some of the iron minerals responsible for these colors in freely drained soils are goethite [$FeOOH$], haematite [Fe_2O_3], lepidocrocite [$FeOOH$], ferrihydrite [Fe_2O_3] and limonite [$FeOH(OH).nH_2O$]. Waterlogged gleyed soils tend to have iron present in its reduced state with minerals such as iron sulfide [FeS] and pyrite [FeS_2], which color the soils

grey/black or olive green. These iron oxides can change in response to Eh variations for example if the environment becomes increasingly reduced soluble ion species become reduced from Fe3+ to Fe2+ and conversely if the environment becomes increasingly oxidised the soluble iron species are oxidised from Fe2+ to Fe3+ . Where soluble iron is present within sediments ionic exchange occurs which can lead to the breakdown of collagen resulting in changes to the crystal structure of the mineral component of antler, ivory or bone. This causes an increase in the porosity of the materials resulting in ion exchange and the subsequent deposition of the iron minerals. As a consequence waterlogged bone and related materials (such as antler and ivory) are often heavily stained by surrounding sediments. The presence of iron can disrupt disulfide bonds in proteins because of its high affinity and attraction for sulfur. Hydroxyapatite, the major mineral component of bone, ivory and antler, is known to undergo alterations such as ionic exchange, cationic exchange and substitution of phosphate with carbonate. Under aerobic conditions iron acts as a catalyst to cause oxidation of sulphur dioxide which forms sulphuric acid. This sulphuric acid then causes solubilisation of collagen by hydrolysis. In reduced conditions there are a number of organisms which use ferric iron as an electron acceptor. Many of these organisms also reduce nitrate and as they are facultative anaerobes they can also utilise oxygen. Organisms which are capable of catalyzing the reaction belong to *Micrococcus, Bacillus,* or *Desulfovibrio*".

4. Cleaning techniques of bone artifacts

Cleaning is a basic procedure in conservation. It stands for the process of removing the matrix or matters that prevent clear visualization of bones[36]. According to Abdel-Maksoud and El-Amin [37], cleaning is a removing of foreign material which may be abrasive, acidic, hygroscopic, or degrading.

Casaletto et al [15] explained that cleaning is a very critical process, because of its irreversibility, it can result in irreversible damage to the bones if not done correctly. Every conservator must be deeply knowledgeable regarding the chemical composition of the enclosing materials that will be removed. These encrustations may be formed of insoluble salts, like calcareous concretions, sulphated encrustations, alumino-silicate crusts and can also contain soluble salts (e.g., chlorides, phosphates and nitrates) in addition to a variety of inorganic species (e.g., iron, manganese, copper and black sulphides) or organic stains. Moreover, remains of preceding treatments that aimed for restoring the bone (e.g., glue, wax and acrylic resin) and bio-deteriogens (e.g., bacteria, algae, lichens, fungi, lower plants and weeds) may also be found.

Different cleaning procedures are available based on the chemical, physical and structural characteris-

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tics of the material to be removed [17]. The extent to which any bone-cleaning technique will be successful is determined by the time taken, the resources required, and the final outcomes in relation to the intended purpose for which cleaning has been performed [38].

4.1. Mechanical cleaning

Mechanical cleaning is a term which is utilized to describe physical removal of foreign matters or corrosions enclosing an object by using external force [13]. Mechanical cleaning treatments are accomplished carefully using scalpels, scrapers, micro-drills and micro-sandblasting Physically removing deposit includes using pressure (e.g., cleaning by pressurized water and abrasion using compressed gases) and/or radiation (e.g., ultrasonic generators and laser ablation [15]. This type of cleaning is often done under a magnifying glass or a microscope [12]. Mechanical cleaning is a widespread practice. It is a common practice that is safely used if introducing liquids onto the specimens cannot be done safely, it is also a non-toxic and residue-free process which counts as another advantage. One disadvantage of mechanical cleaning it can contain blowing or vibrating which may lead to detachment of fragments or even lead to serious fractures on the specimens [36]. Thorgeirsdottir [12] reported that mechanical cleaning of corroded iron may be done using different tools like a scalpel, dental tools and micro air abrasion depending on how thick and hard the corrosion layer is and on the robustness of the artefact. The shape of the artefact may be found underneath the outer corrosion layer, in the denser layer of magnetite. Controlled mechanical cleaning is utilized to expose this layer and thereby the artefact's shape. The aim of mechanical cleaning is not removal of all the corrosion layers but to reveal the original surface of artefacts. This process cannot be undone, so great care should be taken when cleaning the artefact.

Vest [39] stated that the choice of surface cleaning depends on the structure of the surface of the material. She also informed that dry cleaning methods are usually excluded if the material is in an advanced state of deterioration.

4.2. Chemical cleaning

As mentioned by Abdel-Maksoud and El-Amin[37], one of the cornerstones of conservation is reversibility: any process that is performed for preserving a piece must be able to be undone with as minimal damage as possible to the piece itself. Chemical cleaning is irreversible, this is why it must be the last choice that is only used when absolutely necessary. Chemical nature of the object, degree of deterioration, type of materials to be removed and the type of cleaner used should be taken into account. Before chemical cleaning, the ideal treatment should be determined for particular combination of objects and soils, and to make sure if the object is able to be cleaned, or if the object will be suspected to damage throughout the process.

Susan [40] wrote that water is one of the acceptable solvents to use in cleaning of stable bone while making sure small amounts are being used and the bone is not soaked. Soaking or immersing the bone in water forces the expansion and contraction of the bone, causing stress and cracking. Water, if used correctly, is not harmful to bone, and it is inexpensive, readily available, and not hazardous to people. Distilled water is preferable to tap water because it contains fewer impurities.

López-Polín[36] refered to solvents (e.g., acetone, alcohol, etc.) and referred to their usage for a variety of purposes, including removing consolidants or other organic materials like grease from the objects. Some of them, (e.g., ethanol, often substitute for water to soften some matter, like clay or sand. In addition, solvents may be utilized with water to obtain a more volatile mixture than pure water).

Hamilton[41] confirmed that always make sure that the material is thoroughly wetted with water before any chemical is applied , This ensures that chemicals used for the treatment remain on top of the artifact and is not absorbed..

Mairs et al. [38] reported that Enzymatic maceration is regarded as the most convenient method, with trypsin, pepsin, or papain being commonly employed. For optimum activity, specific conditions are required. If these conditions are maintained, enzymes will completely digest the soft tissue from samples within 24 to 48 hours.

Turner-Walker [13] referred that EDTA and oxalic acid can both cause sequestration of Fe^{3+} ions and are utilized in removal of rust or iron staining from some organic and inorganic materials such as paper, ceramics, wood and leather, and wrought iron.

Hamilton[41] informed that 5-10% oxalic acid has been utilized in removal of iron stains from bones. For resistant stains, 5% ammonium citrate can be utilized alone or followed by 5% oxalic acid. Both were reported as effective treatments. He also informed that 5-10% hydrogen peroxide can be utilized for removal of sulfide stains. Stained bone may be soaked in a hydrosulfite solution then in a dilute hydrogen peroxide for removal of any remanent stains. Cukrowska et al [42] confirmed that Hydrogen peroxide offer a satisfactory means for removing manganese dioxide–iron oxide coatings from fossilized bones, which can greatly increase the level of information obtainable from studies of bone.

Locally applying the solution with a brush or swab can be used in treating unsound bones. In case

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of submerging unsound bone, CaCO3 will decompose and will result in carbon dioxide evolution which will subsequently break up the specimen. Very fragile bone may need local application of acid to stubborn spots, scraped, and blotted; repeat all steps until fully cleaning the area.

López-Polín [36] said that protecting the bones from excessive exposure to acid is always recommended by first coating them with consolidating products. moreover, after the acid treatment, an in-depth washing/rinsing process is required to ensure removing all traces of acid or salts produced during the treatment by means of chemical reactions.

According to Thorgeirsdottir[12], aqueous sodium hydroxide is a very common treatment solutions for cleaning iron corrosion from iron artifact or composite materials. It is relatively inexpensive, readily available, and has a high pH. The common concentrations used are 0.1M to 0.5M with pH 13-14.

Einarsdóttir [26]discussed that one reason why sodium hydroxide is such a successful method is its high pH. High pH passivates the iron and reduces the corrosion rate, as an adherent layer of insoluble corrosion products forms on the iron. When iron corrodes in an alkaline solution, Fe2+ ions precipitate as Fe $(OH)^2$ which is then easily oxidized and hydrolyzed to an insoluble film of Fe $(OH)_3$. If this corrosion film is formed touching iron surface, it can prevent Fe^{2+} ions from being transferred from the iron metal to the solution, preventing further corrosion.

Matero and Tagle [43] reported that for the removal of iron stains, sodium citrate, citric acid, and oxalic acid has been used in chemical cleaning. They also said that chelating agents such as EDTA (ethylenediaminetetraacetic acid) have been used for rust reduction and iron stain removal from the bone. The use of ammonium citrate for conservation treatments has been tested and reported to clean rust from metallic artifacts, especially when the presence of chlorides must be avoided. .

4.3. Laser cleaning

Laser ablation is one of the most important irreversible irradiation effects [44]. over the last 20 years optical methods and particularly laser processing of materials and related techniques were increasingly applied to the preservation, cleaning and characterization of objects of cultural value [45]. Developing novel high-repetition-rate and high-power lasers enables laser application on wide areas in order to clean and depaint large surfaces. In case of industrial depainting, there are countless advantages for using laser compared to chemical or mechanical processes. Laser provides a dry process and leads to reduction in waste volume and it can also be automated [46]..

The laser cleaning by ablation is a combination of evaporation and sublimation of the components by means of photothermal and photochemical processes [47]. The interaction of various material surfaces with laser beam depends on both the composition surface and the type of laser, when the beam is focused on the surface, it cleans deposits like the corrosions patina that accumulate as a result of outdoor or indoor weathering especially in high concentration of hazard gases, aged preservation coatings, dirt deposits, traces of paint, rust or lime.

Several experiments have been performed to test laser cleaning techniques, specifically to determine whether or not bone surfaces have been damaged as a result of treatment. Laser cleaning was compared to scalpel cleaning, and it was found that both can cause surface damage. Comparing laser cleaning with scalpel cleaning, it was proven that the two can result in surface damage. Laser beam can result in burn or detachment of the bone surface. While scalpels can cause scratches or cuts, this depends on how the instruments are being used, the state of bone preservation, the nature of the sediments and the degree of its adherence to the bone [48].

According to Al Sekhaneh et al. [47] Q-Switched Nd:YAG laser was capable of removing archaeologically grown corrosion from copper and relatively thin corrosion products from bronze and thin layers of calcaeous patina on bone, and the result were found satisfactory.

According to Yandrisevits et al. [49], and Abdel-Maksoud et al. [48] Q switched Nd:YAG laser at two different wavelengths: 1064 nm (infrared) and 532 nm (green) have been considered successful tool in cleaning iron corrosion..

Yandrisevits et al. [49]used An Nd:YAG Q-switched laser at 1064 nm and 532 nm outputs with a pulse duration of 8 ms with a repetition rate of 2 Hz to removing iron rust from composite artifact consists of tiny, flat iron alloy rectangular plates that are riveted to sides of a textile strips and then sewn in overlapping horizontal rows across a bib-shaped textile support with textile back straps and bone collar buttons. Koh[50] said that the possibility of using pulsed near infrared and green Nd: YAG-lasers for cleaning bright and oxidized metallic surfaces seems to be limited by risks of surface melting and blackening due to thermo- and photochemical changes and dehydration effects.

Abdel-Maksoud et al. [48] said that there are some advantages for the application of laser cleaning on cultural heritage materials, these advantages are:
1. Selectivity, so the restorer can determine the cleaning procedures time.
2. It has low environmental impact, versatility and reliability, localized action, the laser cleans only where directed.

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3. Contactless tools, which offered no mechanical scratches or harmful stress of the fibres.
4. Chemical free, no chemicals used in cleaning stains which may have district reaction with the chemical structure.

Abdel-Maksoud et al. [48] also said that there are some disadvantages for the application of laser cleaning on cultural heritage materials, these disadvantages are:

1. Laser cleaning technique has thermal effect, so it can damage fibre structure of parchment manuscript.
2. Laser cleaning may lead to discoloration and degradation induced by photothermal reactions for very fine and very sensitive materials.

4.4. Plasma cleaning

Plasma is the fourth state of matter and exists in thermal and non-thermal forms. It is a quasineutral gas composed of ions, electrons, and a variety of neutral species such as free radicals and stable molecules in ground and excited states [51].For its properties, it is found suitable for many applications. Plasma technology is a novel group of processes for modifying the surface of materials and is well-known for being environment-friendly. In the area of cultural heritage safeguard, plasma treatments might be recommended to clean and protect various types of artefacts from paper to metallic works of art since they are non-destructive technologies and conducted under low pressure and in atmospheric conditions [52]. Generally, plasma is classified as hot/thermal and cold/nonthermal according to the plasma zone temperature [53]. Plasma cleaning is an easy, inexpensive method requiring simple installations. It is safe and excellent cleaning results and can be obtained within a few hours of receiving the necessary equipment. Plasma cleaning is proper for the removal of very thin films, particularly hydro-carbonates and oxides, which is usually remaining after traditional cleaning. Plasma cleaning is performed by the interaction between the plasma components (i.e., electrons, ions, photons and radicals) and the first layers of contaminations. This interaction causes mainly three basic processes that lead to surface cleaning: heating, sputtering, and etching. Heating by Plasma is mainly performed by electron and ion bombardment and by plasma radiation. Heating to moderate temperatures can remove only the physiosorbed or lightly bonded contaminants. Sputtering is the most universally applied cleaning process. It is non-selective and not always a sufficiently effective cleaning process. Sputtering yield strongly depends on the nature of the surface and the type of contaminants. Despite that, plasma cleaning by sputtering is widely carried out in various technological processes, where plasma etching and heating alone cannot pro-

vide the desired cleanness. In plasma cleaning by etching, atoms or radicals from the plasma chemically react with the surface. The choice of the plasma chemistry, that is the gas mixture used for etching, is determined by the volatility and stability of the etch products. Various halogen-, hydride-, and methyl-compounds can be used depending on their volatility. Plasma cleaning is significantly enhanced, when all or some of these three main processes are combined [54].

It is vital to select the proper plasma gas, as gases react and work in various mechanisms to remove contaminants. Oxygen removes contaminants by oxidation and reduction [55].

Plasma cleaning, however, removes contaminants from surfaces by using energetic plasma which results from gaseous species. For example, a contaminant layer on a metal strip can be thicker than 1 $\Box$m (10-6m) [54]. Gases such as argon, oxygen, nitrogen and hydrogen, and mixtures of air and hydrogen/nitrogen, are utilized [56]. Plasma cleaner exposes the surface to a gas plasma discharge, it scrubs the surface in gentle manner and is capable of removing invisible oil films, microscopic rust, dust, or other contaminating agents that accumulate on surfaces due to handling, exposure or previous manufacturing or cleaning processes; in addition, plasma cleaning leaves no residue on the surface [19].

Plasma cleaning can be very important step in the restoration of archaeological artifacts. Tino et al [19] said that, the majority of corrosion products contain oxygen and/or chlorine-containing compounds. These corrosion products layers can be effectively treated and cleaned from ancient artifact objects using low-pressure hydrogen-based plasmas operating in flowing regime where the reaction products are continuously pumped out of the system. The radiofrequency discharge, typically with electrodes from a glass-made cylindrical reactor can also be used. In the case of planar metallic samples, volume dielectric barrier discharge can also be applied using hydrogen or a hydrogen-argon gaseous mixture. The advantage of such discharge is possible operation at atmospheric pressure. The pilot experiments in the surface treatment of metallic objects have also been carried out using cascading arc plasma source. Probably the last currently tested technique is the application of plasma jets operating at atmospheric pressure. They can be supplied by high frequency, radiofrequency, or microwave sources.

Řádková et al. [57] showed that, the plasma chemical reduction of corrosion layers has been broadly applied mainly for iron artifacts. They treated several types of corrosion layers of some metals by low-pressure and low-temperature hydrogen RF plasma. During the plasma chemical reduction, hydrogen ions, radicals and excited molecules react

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with oxygen and chlorine that are the main elements of the corrosion layers and OH radicals and HCl molecules are formed by these reactions. This method can be very important step in the restoration of archaeological artifacts in future. According to Schmidt-Ott and Boissonnas[58], Low-pressure hydrogen gas plasma reduction has become an integral part of the conservation procedures for archaeological iron. In order to avoid alterations in the metallurgical structures of quenched iron artifacts, the treatment has been performed at low temperatures. Low treatment temperatures (around 120^0C) do not remove substantial amounts of chlorides, but the reduction process introduces micro-fissures into the corrosion products of the treated artifacts that facilitate subsequent mechanical cleaning and the removal of chlorides during an alkaline sulphite treatment. Hydrogen plasma reduction has proved to be effective and successful in conjunction with other stabilization methods. El-Gohary and Metawa[59]used the radio frequency (RF) hydrogen plasma (H_2) for removing some metallic stains which affected the historical brick surfaces. Investigation results show that, both iron and copper aged samples had been cleaned, where the stains thicknesses' were removed perfectly through. Therefore it can be concluded that *RF* plasma is an effective cleaning technique, particularly in the removal inorganic surfaces contaminants. Levitin et al. [60]..mentioned a number of advantages of Low-pressure plasmas that meet specific needs for metal conservation. They showed that, the plasma reduction was performed in several cycles; each cycle included exposure to a hydrogen plasma followed by mechanical removal of the remaining corrosion layer. H_2 plasmas reduce hematite to magnetite to ensure long-term stability of iron-based artifacts. Atomic hydrogen produced by hydrogen plasma at elevated temperatures (573–673 K) reduces corrosion layers (Fe3O4 and F2O3) to metallic iron and removes chlorides, which mitigates corrosion processes.

5. Analysis and investigations

Analysis and investigations are vital in the conservation field. They can use for the determination of the state of preservation or deterioration of archaeological materials. They gave more details about the state of the object in order to make a very good plan for the conservation treatment or preventive conservation. They are also used for the evaluation of conservation materials and methods. Concerning the iron contamination, the analysis and conservation are very important for the identification of iron compounds or other materials, and to make a very good plan for removing of these contaminations. The following techniques of analysis and investigations can be used for these purposes:

5.1. Visual examination

A visual examination is very important for the primary identification of stains and give some idea of the nature and extent of bone deterioration. Abdel-Maksoud and Abdel-Hady [61] discoloration of bone can be noticed by the critical eye of a conservator. The cause of discoloration can arise from different surrounding deposits, and a dark brown stain was observed on crocodile bone from Hawara Excavation, Fayoum, Egypt (Fig. 3). It is also utilized for evaluating the effeciency of the cleaning process for removing iron stain. It can be added that lenses and digital microscopes can also be used in this process in order to give more details about the iron stain contamination. It is also important to detect the most effectiveness properties that should be investigated either or iron stain or for the purposal of cleaning materials and methods.
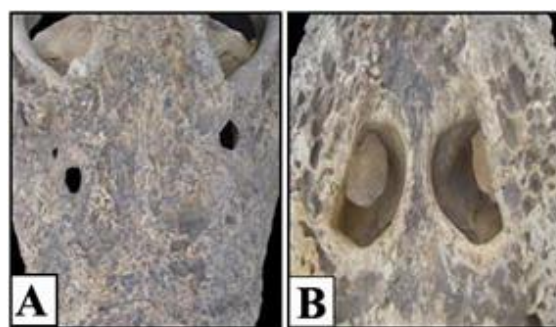

Fig. 3. Brown stain on some parts (A and B) of crocodile bone from Hawara excavation, Fayoum, Egypt [61]

5.2. Scanning electron microscopy with energy disper- sive X-ray microanalysis (SEM- EDX)

A scanning electron microscope has been utilized for observing the surface morphology [37, 62, 63] and evalute the cleaning materials and methods. It is used for identifying how stains are composed, from a chemical perspective (by the identification of elements), and explain the aspects of deterioration found on the surface of bone artifacts. It is also help for the choose of the effectivness cleaning methods and materials used for stains removal [48]. Is is also used for the evaluation of the conservation materials and methods in the experimental studies. Cukrowska et al. [42] have used the SEM to evaluate the chemical cleaning for a manganese coating using hydrogen peroxide (Fig. 4), which gave a good result.
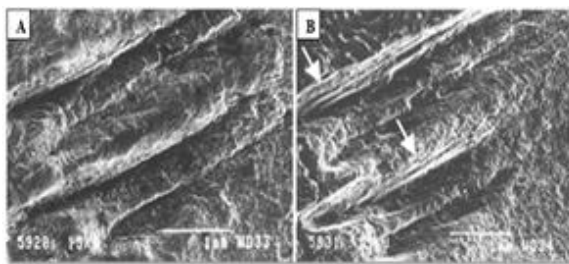
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Fig. 4. SEM micrographs of cleaned manganese contamination on the surface bone: (A) Bone before cleaning, (B) Bone after cleaning [42]

5.3. Transmission electron microscope (TEM)

TEM is a microscopy method in which an electrons beam is passed through an ultrathin specimen, and it interacts with it, as it travels through the fiber structure of bone. Transmission electron microscope (TEM) have been used for studying osseous tissues. It is an ultrasensitive technique for evaluating and analyzing the morphology of bones [64]. It can be used for detecting how deep the stain is through the fibre. It can also be used for the evaluation of the effectiveness of different cleaning methods and materials used for removal of stains[48].

5.4. Energy dispersive X-ray fluores- cence (EDXRF)

Energy Dispersive X-ray Fluorescence (EDXRF) technique is a common fully matured instrumental analytical method. it provide non-destructive multi-elemental analysis, for all the elements with atomic number higher than 13 (or even less in vacuum), in a wide range of concentrations [64]. This technique is used for detecting the element on the surface of stained bones and to detect remains of elements detected after the cleaning process.

5.5. Fourier transform infrared (FTIR) spectroscopy

FTIR became vital in the conservation field.it can be used for deferent purposes (deterioration detectionand evaluation of the conservation materials and methods,especially in the experimentalstudies [66-72] according to Shahack-Grosset al. [73], Fourier transform infra-red (FTIR) spectroscopy used to analyse the stains and distingusied between different stains. It can also be used for the identifiction of the effect of stains on bone components, especially for collagen.

It was also used to detect the deterioration process in archaeological bones. Abdel-Maksoud and El-Amin [37] proved that FTIR (Fig. 5) gave a good result to explain the deterioration process of an archaeological bone sample taken from Gazelle mummy preserved in the Agricultural Museum, Giza, Egypt. The study proved that there was degradation

in the collagen of the archaeological sample compared to the modern sample, since the loss of amides was noticed in the archaeological sample.

5.6. Colorimetry

Colorimetric analysis is an objective technique to measure colour values within the visible light spectrum and quantify these colors in numbers. It is a safe and non-destructive method to be used on archaeological materials. A spectrophotometer provides a measurement of colours by illumination of a sample and analysis of the light that is reflected in a diffused manner. To calculate the unique spectral characteristics, the resulting colour spectrum is compared to a reference standard (usually a pure white background) and the differences in the three colour values (i.e., a*, b* and L*) are calculated and added together to get the ΔE value, which is a measure of the total color difference of known values. The L* value indicates the extent to which a sample is relatively light/dark while the a* value indicates the extent to which hues are green/red and the b* value indicates hues that are yellow/blue in color [74]. This methods can be used before and after cleaning to evalute the cleaning materials and methods .
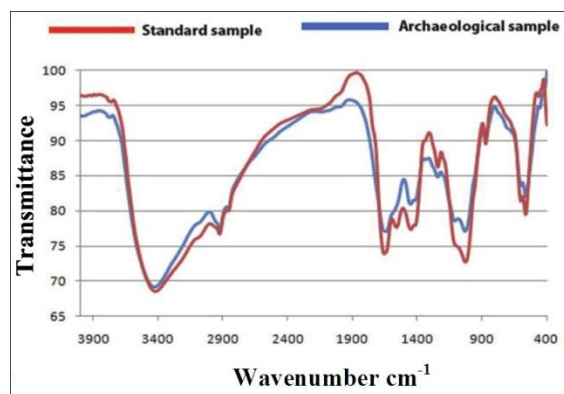

Fig. 5. FTIR spectra of the modern and archaeological bone samples [37]

5.7. Atomic force microscope(AFM)

Atomic-force microscopy (AFM) is a potential method which is capable of iamging almost any kind of surfaces, such as polymers, ceramics, composites, glass, and biological samples. Atomic Force Microscope (AFM) is a device that is utilized in the nanotechnology field to study the topography of surfaces with Nano-particles. AFM provides several advantages over conventional microscopy techniques, AFM explores the sample and makes measurements in three different dimensions X, Y, Z, allowing 3D image[75]. AFM test measures the surface roughness of the treated and untreated samples. AFM test is

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used for detecting the effect of the cleaning methods and materials on the surface morpholog.

5.8. X-ray diffraction

The authors conform that this technique used to characterize the various compounds attched to the surface of the bone [76] and used for analysing the compositions of corrosion products[24]. This method is very important to select the the cleaning materials and methods for iron stains removal.

5.9. pH value measurement

The pH meter was used to measure the pH of sample after calibration with known standards. It determines the effect of the stain to decrease or increase the pH value of bone artifacts,especially when using the cleaning materials on the surface of bones[61].

5.10. Porosity

human bone is porous in nature, containing three essential anatomic cavities: Haversian/Volkmann's canals, osteocytic lacunae, and canaliculi. in healthy bone, Haversian/Volkmann's canals have diameters on an order of 50 pm but are much larger for osteoporotic bone [77]. Bone porosity plays an important role in the taphonomic changes in the bone to understand the changes that occur at a microscopic scale. Bone porosity is also a critical factor in determining the proportion of mineral recrystallization or dissolution and bone survival [78]. This method can be used to determine whether or not bone porosity changes after cleaning methods.

Porosity was measured according to the following equation:

$$porosity = \frac{w2-w1}{v} \times 100 = …. \%$$

Where, W1 is the mass of the sample before immersion, W2 is the mass of the sample after immersion in water for 24 h and V is sample volume.

5.11. Density

Bone mineral density measurement (BMD) plays an important role in determining levels of osteoporosis in a sample of archaeological bones. It is defined as the physical density of the minerals that make up bone. BMD calculations are important in working out changes with age, disease, Taphonomic problems [79]. This method is very important to determine an effect of cleaning materials and methods on the density of bones.

5.12. Contact angle

It is very important to understand how different treatment and environmental conditions affect surface properties. The contact angle is the angle at the interface where water, air, and steel meet, and its value is a measure of how likely the surface is to wetting by water. Lower contact angle values show the tendency of water to diffuse and stick to the surface, while higher contact angle values show the tendency of the surface to repel water. Contact angle, as a representative measure of surface wettability, is one of the properties of a surface that is controlled by chemical composition and surface roughness[80]. This method can be a method for determining the effect of iron stains, or cleaning materials and methods on the bone surface of bone artifacts.

5.13. Amino acid analysis

Amino acid analysis is particularly useful to characterize The changes induced in these proteins as a result of decomposition [6]. It can be said that this method can determine the effect of different stains on the collagen in bone artifacts.

Abdel-Maksoud and El-Amin [37] have used the amino acid analysis for modern and archaeological bone sample taken from the gazelle mummy (from the Agricultural Museum, Giza, Egypt) to determine the state of its preservation. The amino acid analysis (Fig. 6) showed decreasing levels of lysine, arginine and histidine in the archaeological sample, which indicated oxidation breakdown. The high value of NH4+ and decrease in the aspartic acid of the archaeological sample indicated the presence of hydrolysis breakdown.
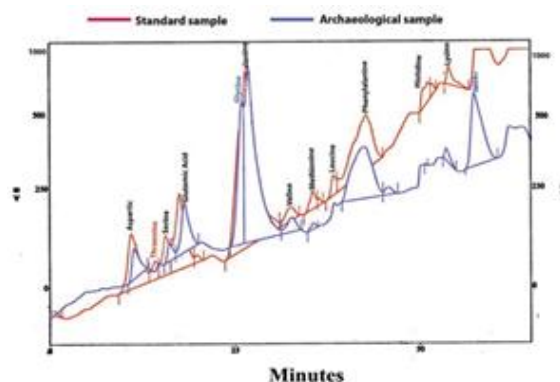

Fig. 6. Amino acid analysis of the modern and archaeological bone samples [37]

6. Conclusions

The iron stain is considered one of the most important aspects of deterioration of bone artifacts, especially bones extracted from burial environment in excavation area. The color of natural fresh bones ranged from whitish to yellowish brown color, but when the bone is in direct contact with corroded iron body or neat from corrosion products in the soil, the color of the bone became tan to chocolate brown color from iron oxides in the soil. Redox processes and

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other factors such as pH, water, temperature, micro-organisms and other factors play an important role for the conversion of color and thickness of bone in the soil. All cleaning techniques have many advantages, and some disadvantages. The selection of the effective cleaning technique for iron stain depends on the condition and size of the bone piece, and on the thickness and nature of the iron stain. The analysis and investigation techniques are very important for the Identification of iron stain, determination of its composition and describe its morphology. They are also important for the evaluation of the cleaning materials and methods, especially in experimental laboratories studies.

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