



**An-Najah National University**  
**Department of Materials Science and Engineering**

**Graduation Project 2**  
**Contribution of Materials Science & Engineering to the Conservation of**  
**Materials Heritage in Palestine**

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**Dec 2018**

## **ABSTRACT**

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The physical remains of the arts of past ages in the form of objects and artifacts in Palestine are quite precious. Very little has survived out of the vast quantity of material from days long ago. It's crucial- therefore- to ensure that those are protected and conserved because they are an indicator of a man's cultural heritage. Conservation and restoration aim to preserve the artifacts as long as possible. This can be achieved by consulting several scientific techniques and approaches that restore the aesthetic properties of the artifacts. In this report, cupreous and silver coins were selected to undergo chemical and mechanical treatments. Chemical treatment, which involves using acids and bases, was used to remove corrosion products with further mechanical treatment. These processes not only aimed for restoring the original look of the artifact, but also prepares for protection of those cleaned metal objects to prevent the recurrence of corrosion. The coins were cleaned by the previously mentioned treatments, and different results were observed.

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# CHAPTER 1

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## INTRODUCTION

There are different stages prior to conservation. In the first place, the object or artefact needs to be characterized and defined to get to know more about the methods for their production, and their composition. This facilitates the whole conservation process, and has led to utilizing the most efficient techniques for this concern by having a wide knowledge of material science and technology. By understanding the properties of a material, greater insight will be gained as to how the material will perform in different conditions, or how it may be altered to suit a particular use, or how it may be preserved. The application of scientific analysis in studying ancient materials has brought new light into archaeology. Nowadays, material science is an integral part of the archaeological work.

In the early days, harsh methods were used for conservation. Nowadays, more delicate techniques have been developed to retain the original look of objects. There is a variety of techniques used for this purpose. The most common procedure in conservation and restoration of metals is the cleaning process. This process can vary between mechanical, chemical, electrochemical, ultrasonic, plasma and laser cleaning. Chemical treatment includes acids, bases, electrolysis, electrochemical reduction, ultrasonic, and other processes. Mechanical treatment includes frozen water cleaning, cleaning with toothpicks/brushes, soaking before cleaning and other processes. The application of low-pressure hydrogen plasma for the restoration and conservation of iron artifacts has been developed. This method of treatment at temperatures below 400°C is relatively fast and efficiently removes chlorides. Laser cleaning also represents the most important contribution of physics to the conservation of cultural heritage.

## CHAPTER 2

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### METHODOLOGY

There are different processes used in conserving coins from the Islamic era.

#### A. Formic Acid (HCOOH)

50 ml Formic acid (98M)

25 ml Acetic acid (98.85 M)

50 mL graduated cylinder

250 mL beaker

80 mL beaker

#### Procedure

1. Formic acid is the main chemical throughout this experiment. 50 ml was added to the beaker. Then, acetic acid was poured to HCOOH, and the beaker was gently swirled. By using a clamp, the coin was immersed into the beaker.
2. The solution was then heated for ten minutes. At first, the solution was colorless. After heating, the color slightly turned to light turquoise.
3. 10 mL of the solution was poured to a smaller beaker to insert another coin. Again, the smaller beaker was boiled releasing hydrogen gas.
4. The two coins were left for three days. After three days, the coins were removed and rinsed with tap water.

#### B. Alkaline Glycerol

##### Materials

100 mL D.I water

10 mL Glycerol

30 gms NaOH

250 mL beaker

## Procedure

This is an alkaline sequestering agent. This process characteristically removes cupric compounds. All cupric compounds are green to blue in color.

1. 30 gms of NaOH were added to a 250 mL beaker. 12 mL of glycerol was measured using a graduated cylinder. The two mL were added to account the loss of glycerol in the cylinder as it's highly viscous.
2. After pouring 100 mL D.I water, the solution was stirred with a spatula and the coin was immersed. Initially, the solution was colorless. After 35 min of heating, it turned to blue.
3. This treatment (Alkaline glycerol) was followed by immersing the coin in hydrogen peroxide for 3 days.
4. After three days, the coin surface was still reacting with hydrogen peroxide. It was removed and rinsed with tap water and dried.

## C. Sequestering Agent (EDTA)

Ethylenediaminetetraacetic acid (EDTA), tetra-sodium was selected for the experiment.

### Materials

20 gms of EDTA

50 mL D.I water

80 mL beaker

### Procedure

1. 20 gms of EDTA were measured and added to the beaker. Then, D.I water was poured and stirred with a spatula. Then, the coin was immersed.
2. The solution was heated for 35 min. After heating for five minutes, the solution turned yellow. After 20 min of heating, it turned green. After 35 min of heating, it turned dark turquoise.
3. In another beaker, 20 mL of the heated EDTA solution was poured, 20 mL of acetic acid, and 20 mL of hydrogen peroxide were added respectively.
4. The coin was rinsed with tap water, dried, and then submerged again in the new solution for hours.

#### **D. Hydrogen Peroxide**

250 mL beaker

Hydrogen peroxide

##### **Procedure**

1. Two coins were immersed in 50 mL hydrogen peroxide.
2. The coins were left in hydrogen peroxide for three days.

#### **E. Acetic acid (5% solution) & EDTA**

- 1- The coin was treated with acetic acid for 2 hrs. Stainless steel scourer was then used to remove the corrosion products.
- 2- After immersing the coin in 10% solution of the EDTA, the solution was heated to speed up the reaction for an hour, and then it was kept at room temperature for 24 hrs.

#### **F. Electrochemical process**

##### **Procedure:**

In this experiment, a small electrolytic cell was constructed.

A power supply of 5V and 2A was used.

Electrolyte: Aqueous solution (Sodium carbonate)

Anode: A piece of iron metal.

Cathode: Silver coin

- 1- An aqueous solution was prepared (150 ml of sodium carbonate dissolved in deionized water), then the electrolytic set-up was placed in a 250ml beaker.
- 2- An iron piece was attached with a clip to the negative terminal acting as an anode, and the silver coin attached to the positive terminal acting as a cathode.
- 3- The plug was inserted in the socket (source of electricity), with a converter of 5V and 2A.
- 4- The electrolytic cell was left 90 minutes for the reaction to complete. After seven minutes of setting up the cell, the coin was detached from the clip and cleaned with a toothpick.



The toothpick was used to clean the location of the engraving (lettering) on the coin. Again, the coin was attached to the clip and immersed in the solution.

- 5- The reaction took 90 minutes to clean the coin completely forming a thin black layer on the surface of the silver coin.
- 6- The coin was detached from the clips and rinsed with water. After that, it was cleaned with a pad to remove the thin black layer that formed during the reaction.
- 7- Again, rinsing with water to remove any stuck material. It was then dried.

### **G. Oxidation- Reduction reaction (REDOX)**

An aluminium plate

Hot water

Sodium carbonate

#### **Procedure**

- 1-  $\text{Na}_2\text{CO}_3$  was put in an aluminium concave dish.
- 2- Hot water was poured to speed up the reaction, and then the silver coin was set in the plate.

### **H. Alkaline Dithionite**

#### **Procedure**

- 1- 20 grams of  $\text{Na}_2\text{S}_2\text{O}_4$  were added to a 250 ml beaker, then stirred until dissolved by a spatula.
- 2- The silver coin was immersed in the solution, and the beaker was tightly sealed to avoid the upcoming gas ( $\text{H}_2\text{S}$ ).

This is a chemical reducing agent, so that after weighing the intended amount of  $\text{Na}_2\text{S}_2\text{O}_4$ , the can should be tightly sealed to avoid oxidation of sodium dithionite.

## **I. Olive oil and lemon juice**

### **Procedure**

- 1- 100 ml of olive oil was poured to a 250 ml beaker.
- 2- 20 ml of lemon juice was added.
- 3- The silver coin was then immersed and then heated for 15 minutes.
- 4- The coin was removed and rinsed with tap water and then dried.

## **J. Citric acid**

### **Procedure**

- 1- A lemon was cut into halves.
- 2- The silver coin was then soaked in one half of the lemon, and left for an hour.
- 3- The coin was then removed and rinsed with water.
- 4- It was cleaned by a toothpick and by hand to remove corrosion products.
- 5- Rinsed again with water and then dried.

## CHAPTER 3

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### RESULTS AND DISCUSSION

In the **Formic acid** experiment, it was evident that the smaller beaker showed a dark turquoise color.

\*Sample 1: is the coin present in the 250 mL beaker

\*Sample 2: is the coin present in the 80 mL beaker

Sample 1

Sample 2



*Figure 1: Two copper coins immersed in formic acid*

At first, it was explicated that because the small beaker was heated until it started boiling, the color became dark. But when the large beaker was further heated for five minutes, it was obvious that it didn't undergo any change in color. That meant the elevated temperature wasn't the reason for color change. This led to the second possibility: that the two coins were made of different materials.

(Sample 1)



*Figure 2: A copper coin and its other side before treatment*

(Sample 1)



*Figure 3: A copper coin and from both sides after treatment*

The coin in the large beaker had a chalk-like material covering it while the coin in the small beaker - the obverse that had a direct contact with the bottom of the beaker - was covered with a thin blue layer. When the coin was rinsed with tap water, the layer vanished.

(Sample 2)



*Figure 4: A copper coin before treatment (obverse and its opposite)*

(Sample 2)



*Figure 5: A copper coin after treatment (obverse and its opposite)*

It is clear that this experiment should be followed with mechanical treatment. The engraved locations on the coin were attacked by Formic acid leaving the top surface exposed to corrosion.

## Alkaline Glycerol

It was observed that the corrosion products floated at the top of the solution. However, the coin needed further mechanical treatment although the strong alkalinity of this chemical.



*Figure 6: A copper coin in an alkaline solution*

In tests (obtained from the internet), tin bronzes were etched fairly rapidly using this treatment. The etching was accelerated in the presence of corrosion products.

On leaded tin bronzes, there was very little etching when corrosion products were not present. When corrosion products were present; the degree of etching was considerably enhanced.



*Figure 7: A copper coin before treatment (obverse and its opposite)*

The usual cause of darkening of copper alloys is the development of a thin protective tarnish of red-brown copper(I) oxide.



*Figure 8: A copper coin after treatment (obverse and its opposite)*

It is obvious that this process needs further mechanical treatment to remove the residual corrosion products.

### **Sequestering Agent (EDTA)**

In (Figure 9), heating the solution speeds up the reaction. The color of the solution changed over time as the outer layer of corroded copper dissolved. This chemical solution removes cupric compounds as do the alkaline sequestering agents, such as Alkaline glycerol. However, it continues to remove them with only slightly less rapidly, as was observed in the alkaline glycerol-part. Using this process was useless. And this led to using a new approach; combination of EDTA, acetic acid and hydrogen peroxide.



*Figure 9: Colour change of the solution as a function of time ( only EDTA )*



*Figure 10: A copper coin before EDTA treatment (obverse and its opposite)*





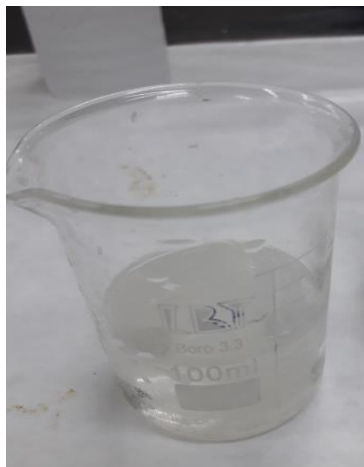
*Figure 11: A copper coin after EDTA, acetic acid and hydrogen peroxide treatment; the material is entirely corroded*

When the reaction was left for long, the result was catastrophic as the coin was highly corroded (Pitting corrosion occurred). The solution turned to dark blue, and small pieces of the coin were precipitated.

Leaving the solution for long was a mistake. Moreover, adding hydrogen peroxide oxidizes any cuprous compounds to a cupric state, thus allowing EDTA to continue its attack on the cupric compounds.

### **Hydrogen Peroxide**

Hydrogen peroxide was still reacting after left for three days as shown in Figure (12). Bubbles can be observed as an evidence for the reaction continuity.



*Figure 12: A copper coin in hydrogen peroxide.*

When the coins were removed and rinsed with water then dried, there was no enhancement observed for using this method.



*Figure 13: Two different copper coins before treatment with hydrogen peroxide*



*Figure 14: Two different copper coins after treatment with hydrogen peroxide*

### **Electrochemical process**

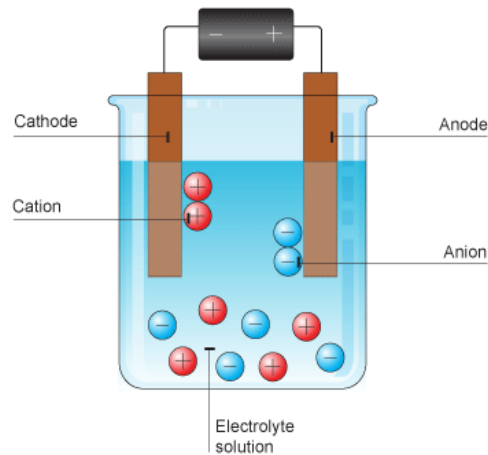
Another method used for conservation of coins is electrolysis. Electrolysis is the process of inducing a chemical reaction which does not occur naturally or spontaneously with the help of Direct Current or electricity.

The principle of electrolysis:

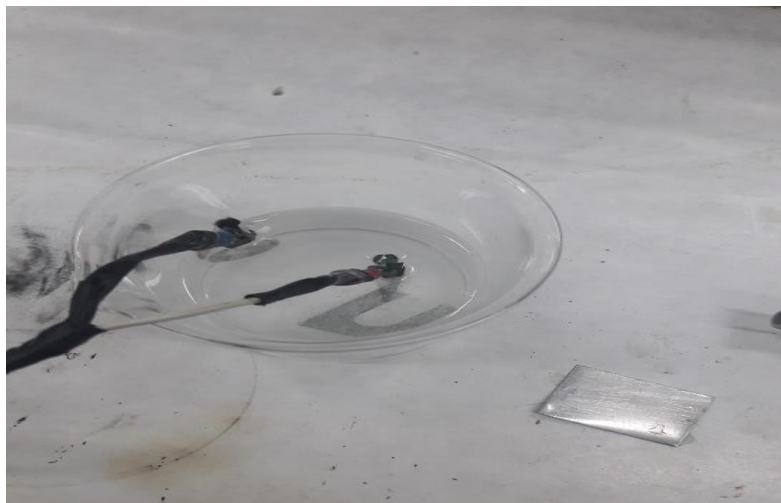
When an electrolyte is dissolved into a solution forming an electrolytic solution and the electrodes from an external energy or current source are immersed into the electrolytic solution. Then the

Cations of the electrolyte gets attracted to the cathode and anions to the anode. Then the anions lose their electrons to the anode and cations get the deficient electron from the cathode thus creating a flow of electrons through the external energy source thus exchanging the atoms and charges by utilizing the energy from the external energy source.

When this method was implemented, there was an enhanced result as the silver coin was cleaned efficiently.



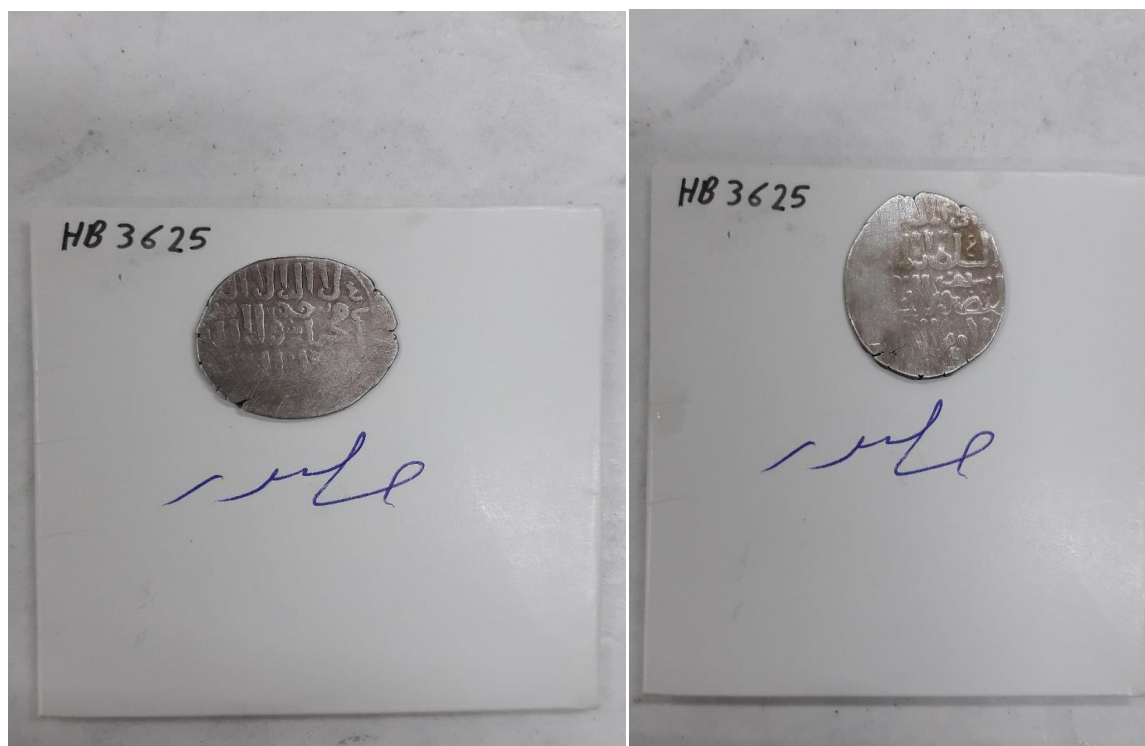
*Figure 15: A scheme of an electrolytic cell*



*Figure 16: An electrolytic cell constructed at the university's lab*



*Figure 17: The silver coin before treatment*



*Figure 18: The silver coin after treatment (obverse and its opposite)*

As can be seen in (Figure 19), the coin shows scratches on its surface as a result of using further mechanical treatment. The coin was cleaned with a pad to remove the thin black layer that formed after electrolysis. There are two possible explanations for the formation of the thin black layer on

the surface of the coin: silver might precipitate on the obverse after being reduced(nano-sized), or because it is in the nano scale, it oxidizes forming silver oxide on the top surface of the silver coin.



*Figure 19: The silver coin after electrolysis (before mechanical treatment); The upper half is treated*

#### **Acetic acid (5% solution) & EDTA**

The coin was treated with acetic acid for 2 hrs. Stainless steel scourer was then used to remove the corrosion products.



*Figure 20: A Roman copper coin before treatment*



*Figure 21: The copper coin after treatment*



*Figure 22: The copper coin after further treatment with EDTA*

## **Oxidation reduction**

Any chemical reaction in which the oxidation numbers (oxidation states) of the atoms are changed is an oxidation-reduction reaction. Such reactions are also known as redox reactions, which is shorthand for reduction-oxidation reactions.

Oxidation involves an increase in oxidation number, while reduction involves a decrease in oxidation number. Usually, the change in the oxidation number is associated with a gain or loss of electrons.

Aluminum is very reactive, and when present in water it produces hydrogen in the form of gas bubbles. Sodium carbonate is a strong base enough to activate aluminum. It dissolves the

aluminum oxide layer after it forms instantly allowing the reaction to go on until the aluminum is completely converted to aluminum hydroxide.

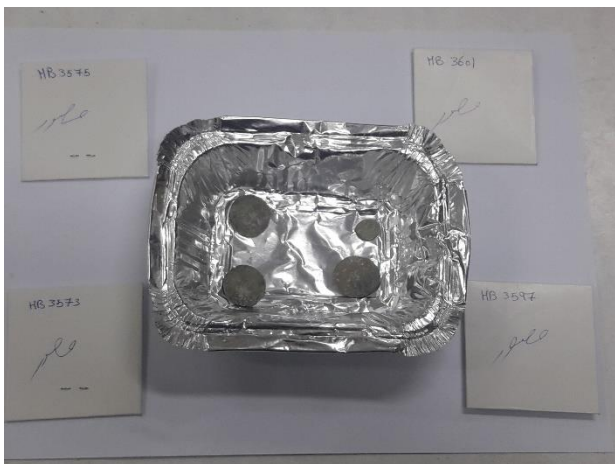


Figure 23: A silver coin before REDOX reaction

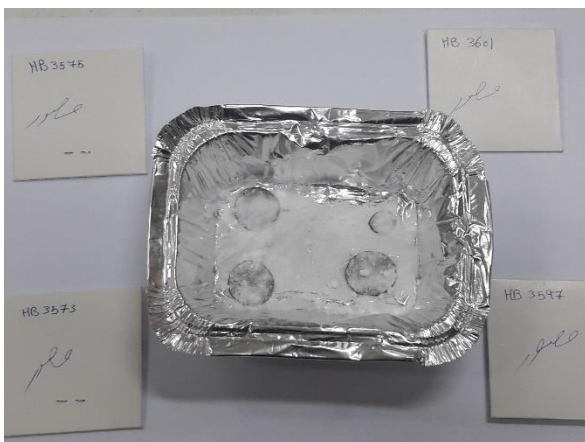
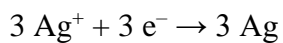
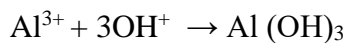
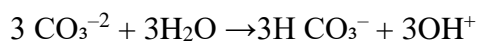
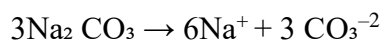
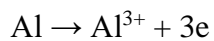
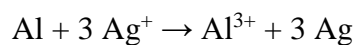


Figure 24: The silver coin during REDOX reaction

Aluminium is oxidized and silver is reduced according to the following equations:



Combining these two half equations gives us the full redox equation for the reaction:




Aluminum also reacts with water forming hydrogen gas observed as bubbles in the following reaction:



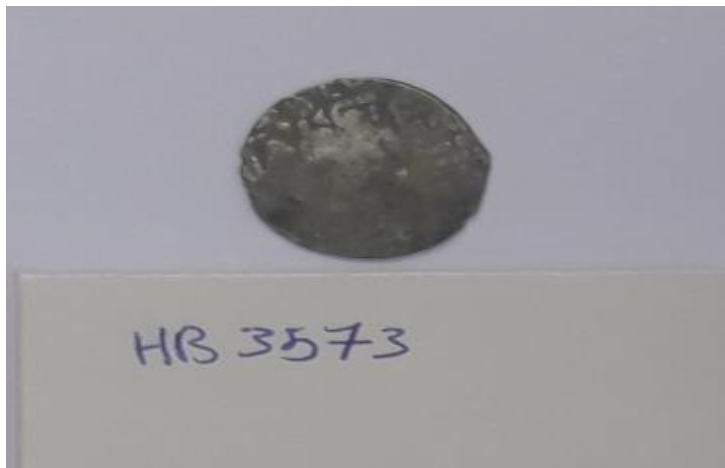
.Aluminum was selected to be oxidized because it is more reactive than silver

Figure 25: Reactivity Chart

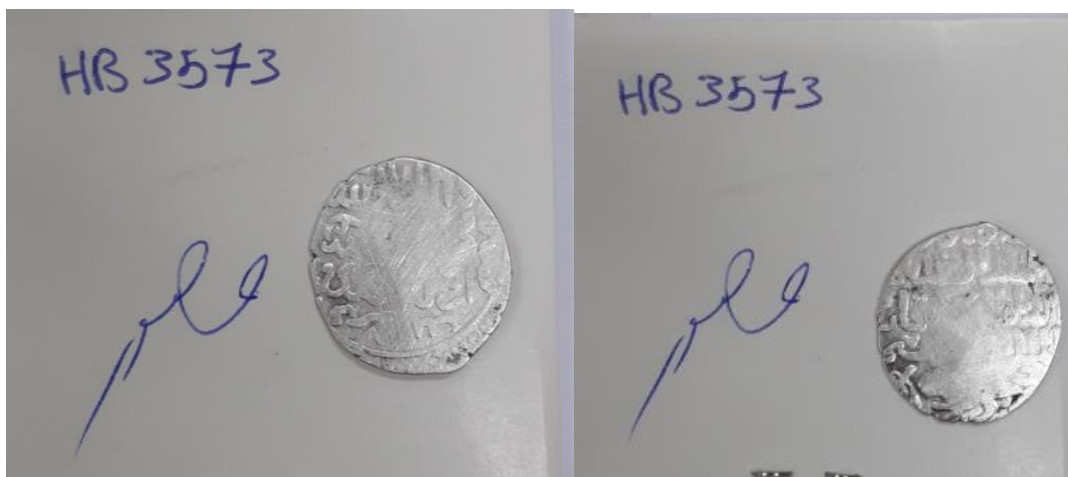
<i>Elements</i>	<i>Symbol</i>	
Potassium	K	<div>Most Reactive</div>  <div>Least Reactive</div>
Sodium	Na	
Calcium	Ca	
Magnesium	Mg	
Aluminium	Al	
Zinc	Zn	
Iron	Fe	
Nickel	Ni	
Tin	Sn	
Lead	Pb	
Hydrogen	H	
Copper	Cu	
Mercury	Hg	
Silver	Ag	
Platinum	Pt	
Gold	Au	



*Figure 26: The silver coin before treatment*



*Figure 27: An Islamic silver coin after treatment (obverse and its opposite)*



Using the pad led to the formation of scratches on the top surface of the silver coin.

### **Alkaline Dithionite**

Using this treatment destroys the patina as seen in (Figure28), but it removes the corrosion product effectively in a short period of time.



*Figure 28: A Silver coin before treatment with alkaline dithionite*



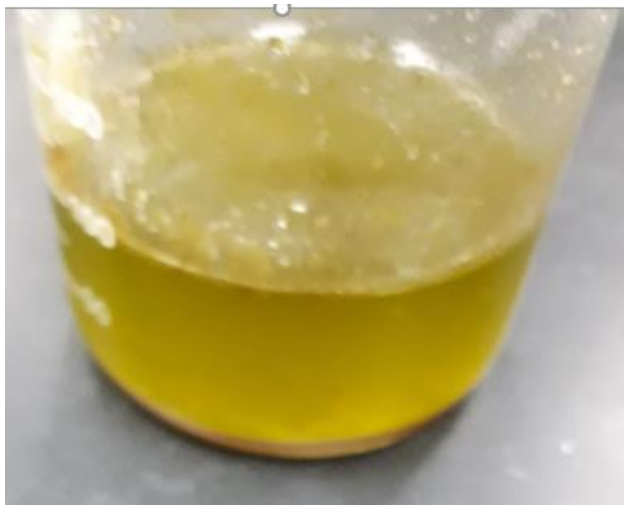
*Figure 29: After treatment*

Because the coin was left in the aqueous solution for 30 minutes, it needs further mechanical treatment. Or the coin could be left for an extra time so that the coin could be totally cleaned. This is one of the efficient methods for cleaning coins without the need of further mechanical treatment

if left for sufficient time in the solution. This method could also be used for cleaning copper as it is effective on cupreous objects.

### **Olive oil and citric acid**

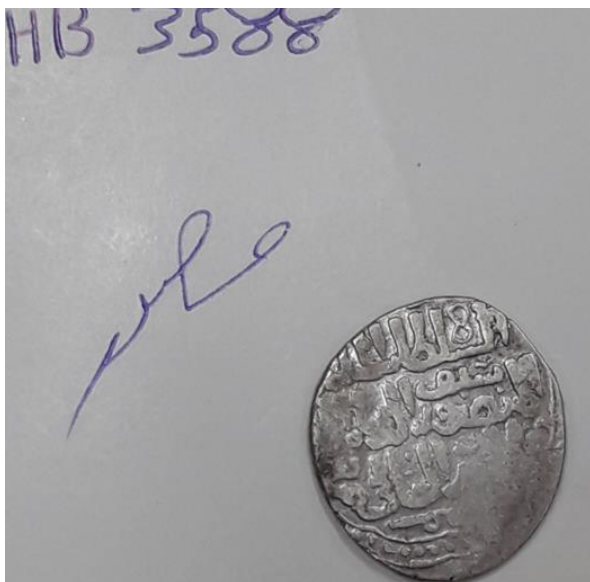
This is an effective method for cleaning silver and copper coins without the need for further mechanical treatment. It is an easy method, and only requires a short period of time to clean the object.



*Figure 30: Olive oil and lemon juice during heating*



*Figure 31: Before treatment*



*Figure 32: After treatment*

### **Citric acid**

This is also an easy and effective method for cleaning silver coins. It needs further mechanical treatment to remove the extra residual corrosion products. Citric acid is useful for removing corrosion products. It has a problem that it is not volatile and if not thoroughly rinsed from the object, it can continue attacking and etching the metal.



*Figure 33: A silver coin soaked into a half of a lemon*



*Figure 34: Before treatment*



*Figure 35: After treatment*

## FINISHING

Lacquering protects all coinage metals against the usual effects of air, water and soil. Lacquering can be used only for coins in collections that are touched infrequently, because with even slight abrasion, the lacquer loses its luster and the details of the coin are no longer clearly visible.

The following two methods are used for lacquering coins:

Zapon Lacquer: This lacquer is most frequently used and obtainable in every paint store. However, brush application is not recommended because the brush marks are often visible, and pores result from the air occlusions in the brush.

Nail Polish: If only one or a few coins are to be lacquered, nail polish can be used.

For preservation of coins, some other methods can be used:

- A. Beeswax: On coins that have had problems, like pitting, wear, broken, or too light, a good finishing treatment is beeswax applied during the final heat treatment. This soaks into the porous metal and seals it somewhat, also smoothing out discriminations in the surface a little. It can be lightly polished with paper towel once it is dried and hardened, and it will still keep its color. Beeswax is perfectly safe to use. The only drawback to wax is that once it is used it is very hard to remove, and it is not a perfect seal on porous metal, and may allow further oxidation, corrosion, in the future.
- B. Vaseline: It is a particular characteristic of Vaseline that they are insoluble in water and are not attacked by acids, but is not suitable for preserving the objects for a long period of time. That is because when applied, it forms a porous film that permits entry of air and moisture.

To conclude, the previously mentioned methods can be used for preservation of coins but not for long, and that's because they form a porous film that allows further corrosion from the surrounding environment.

## CHAPTER 4

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### CONCLUSIONS

Conservation can be seen as a practice within Archaeology and Materials Science. Until fairly recently, Materials Science has been supplementing new methods of conservation. Several techniques are being developed in this broad aspect.

Of all of the ancient artifacts that have been passed down to us, coins are the most numerous. The most crucial part to be considered in conservation, is the inscription on the coins. Those engravings reveal our heritage, and history can be unfolded when knowing what is written on those coins such as the coins presented in this report. Most of the coins show us Islamic inscriptions from the Islamic Empire, and others show us Roman coins.

## BIBLIOGRAPHY

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- 1- Goffer, Zvi., 1980. Archaeological Chemistry: A Sourcebook on the Applications of Chemistry to Archaeology. Canada: Wiley-InterScience, 222-226
- 2- Cronyn, J.M., 1990. The Elements of Archaeological Conservation. Cornwall: TJ Press, 43-63
- 3- Leute, Ulrich., 1987. Archaeometry. NewYork: VCH Publishers, 127-143



