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A New Plasma Electrolysis Technique in Archaeological Glass Cleaning

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Abstract

Archaeological glass pieces covered with soot, gypsum and black corrosion crust was cleaned for the first time by using novel plasma technique. Plasma electrolysis was done by gas discharging between a cathodic metallic pin and anodic water electrode. The glass pieces completely immersed inside the water and discharge take place over the surface of the water in open air. Different kinds of active species formed over and inside the water surface including OH, O, O_3, atomic oxygen and hydrogen, H_2, H_2O_2 and UV radiation. The cleaning mechanism will be discussed at discharge current 0.268 A with exposure time range from 10: 15 min., applied at frequency (10 kHz) and sustaining voltage (500v). This current successfully removed 95.46% from soot and totally removed gypsum from the glass surfaces. Cleaning results for black corrosion were amazing. It could be concluded that, 0.268 A is considered the safest and successful current to be used in cleaning the archaeological glass samples despite the relatively long time of exposure to plasma. From the previous, it was clear that plasma electrolysis can be used successfully as a novel method in cleaning different types of small archaeological and historical glass. This method hasn't been used yet with fragile, large-scale and outdoor archaeological and historical glass, so it needs future experimental work to be made.

Keywords: Archaeological-Glass; Cleaning; Soot; Gypsum; Corrosion; Plasma-chemistry.

1. Introduction

Despite that the archaeological glass is considered inert and stable material. Some types from it are subjected to corrosion/deterioration because of many factors such as: methods of manufacture, chemical composition, and chemical bonds inside glass matrix[1–4].For chemical composition reason; glass was made mainly from silica, modifier, and stabilizer[5,6]. Previous studies said that silica must be above 66 mol% and below of that may prone the glass to corrosion. For stabilizer; the ideal percentage for it 6-10 mol% and above 15 mol% leaching out will be occurred for glass network. For modifier the optimum percentage is 12 wt% for sodium and 9 wt% for potassium, but sodium makes the glass more stable[7,8]. It is certainly that glass doesn't corrode alone; also surrounding environment make it corrodes especially in the existence of water. This type of corrosion is called as chemical deterioration/ corrosion, which formed by a yield for 3 main processes (Ion exchange, hydration and hydrolysis). Corrosion started by ion-exchange when modifier ions started to leach out in the existence of water and H_3O ions formed, which is strongly coupled with glass corrosion and formed firstly gel layer or hydrated glass, then water reacted with this layer to start the next process (hydration), to produce OH ions inside glass matrix which is known as (hydrolysis) which increased the glass corrosion and transformed the glass to corroded one, which can be called as "Disease of glass"[6,9–12]. But not only chemical corrosion by water causing deterioration for glass, but also there are many exterior aspects which causing superficial deterioration for glass, such as dirt, soot, and grime, these aspects resulted from pollution or smoke, for example, the formation of soot on the surface of lamps inside mosques and churches due to the burning of candles inside these lamps. Also, soot may be existed on the surface of glass because that glass was subjected to fire. The risk of fires can range from soot formation to artifact destruction, All the previous make glass needs for conservation process [13–16]. In case of archaeological materials, the most important objective is to increase the chemical stability, and cleaning is considered from the most important stages that increase artifact stability[17,18]. Cleaning is the removal of deposits which have loose contact with artifact such as hard crusts, adherent crusts, and any foreigner material from the surface of the artifact [19,20]. Glass has a special philosophy in cleaning process which is; the removal of only encrustations or dust without the removal of the surface weathered layer (iridescence layer), because the removal of this layer meaning the removal of glass original surface, reducing the glass thickness and reveal the glass core, hence causing destruction for glass [21,22]. Iridescence layer is an aesthetic part that gives value to the glass. These layers are formed as an initial layer for

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corrosion process and sometimes may be strongly stick with glass surface and sometimes be so fragile easily separate. In all case these layers must be kept on the glass surface to keep the authenticity of glass [23,24]. Glass was cleaned by traditional methods such as mechanical and chemical methods. For mechanical cleaning, it is controllable, simple, and selective, but it can cause scratches on glass surface, couldn't reach to narrow places and in some cases it can destroy the glass [18,25–27]. For chemical cleaning; despite its superior effect in cleaning, it is uncontrollable, and may cause further deterioration for glass [25,28,29]. For these reasons many researches recommended the usage of plasma for culture heritage materials cleaning [30]. Cleaning by plasma is the removal of contaminants from the materials surfaces using plasma species generated from gaseous species, such as free electrons and ions, active species like OH, O, O_3, atomic oxygen and electromagnetic waves such as ultra-violate radiation. Gases such as argon and oxygen, as well as mixtures such as air and hydrogen or nitrogen, are used. The plasma is created by using high voltage power supplies, DC or medium frequency (typically 1 kHz to 30 kHz) or high frequency (1MHz-1GHz)) to ionize the gas at low pressure (typically around 1/1000 atmospheric pressure). Low cost atmospheric pressure plasmas (APP) are now regarded as emerging technique that can use instead of low pressure plasma [30–32] .The usage of plasma in culture heritage materials started at the beginning of 1980s [33]. Non-thermal APP was used successfully with archaeological materials, it can treat sensitive materials, eco-friendly, cheap, and easy operation [34,35]. Plasmas formed inside liquids or at the surface of liquids (called plasma electrolysis) have become of increasing interest in the last few years, mainly due to their practical applications in many areas[36–39] including synthetic chemistry, waste water treatment, degradation of polymers, electrosurgical tools, surface engineering, nanoparticle fabrication, machining and micro-machining, hydrogen production with very encouraging results [40,41]. Discharges inside and in contact with water generates intense UV radiation and active species (OH, atomic oxygen, hydrogen peroxide, etc.) generated through the interaction of energetic particles of the plasma with species in gas/liquid contact area. All the generated active species are effective in surface cleaning against different contaminants[31,42]. The first cleaning process for archaeological glass based on discharge under water was described by Krčma et al. in 2014, they used it to avoid the excess temperature of plasma either APP in dry conditions or LPP [27]. They tried firstly to use low-pressure plasma (LPP) , which was useful for metals but not for glass , they said that LPP wasn't acceptable for glass because it produces heat stress on the glass causing break in glass, so, they suggested the usage of underwater Plasma technique" which was used in biomedical field, they considered the founders of this technique in archaeological field to avoid the excess heating of plasma on glass surface, the effectiveness of this technique depending on some factors such as: salt concentration and the distance between electrode and sample, salt in this technique increase the conductivity of the liquid. They used 0.9% NaCl water solution (13 Ms.cm-1 conductivity), and distance between electrode and sample was 1 mm and applied power 5w, this method appeared perfect results in the removing of organic contaminations from glass surface (Figure 1) [27].

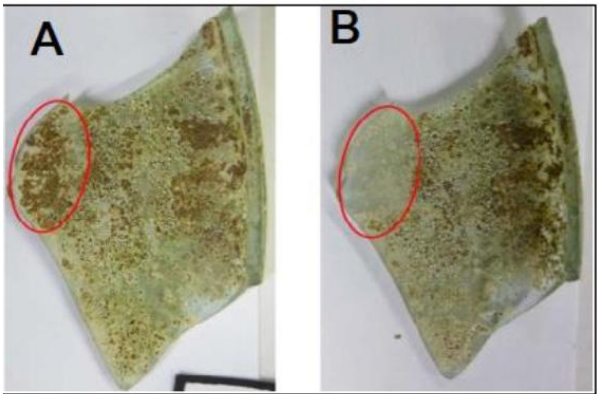

Figure 1:Glass cleaning results by using plasma inside water. (A) before and (B)after

Then in 2019, they used atmospheric plasma named remote dielectric barrier discharge (RDBD), plasma was generation by 15 kw AC power source, 40 KHz and 15 kV. Nitrogen and compressed air were injected in the plasma reactor, that this method clean the glass from organic and inorganic contaminations, but it increased the sample temperature approximately to 55oc and that made the glass susceptible for breaking danger. Another disadvantage of this technique was the high power used for generating the plasma and that made the glass susceptible for breaking danger[43]. Then in 2021, Tiňo et al.[30] described the mechanism of cleaning strategy for discharge under water; they concluded that the under-water discharge **creates** many active species such as OH, O, H, O_3, H_2O_2, which have both reduction and oxidation reactions, that makes this method effectively in cleaning glass. They also mentioned the advantages of this method that it reduces thermal stress, contaminations will dissolve in water without precipitation on the glass surface; it can be used with big-sized objects, also can be used in outdoor conditions. They mentioned that discharge in liquid systems not necessary to be used under/ inside liquid, but also can be used on the surface of liquids with or without external gas source [30]. In this technique fluoride or chloride salts were recommended to increase the conductivity of water, but both of those salts have a corrosive effect on glass surface, so, they use K_2CO_3 as an alternative salt to increase conductivity and they also mentioned that this salt was used anciently in glass production process, so, it considered the most safe salt that can be used in such a process. They applied the discharge under water system already on archaeological glass with conductivity (400-900 mS/cm), fixed frequency (16,780 ± 30) HZ, 23± 1.5 w for 10 min to clean glass , actually, the results was impressive and observed by necked eye easily (Figure 2)[30].

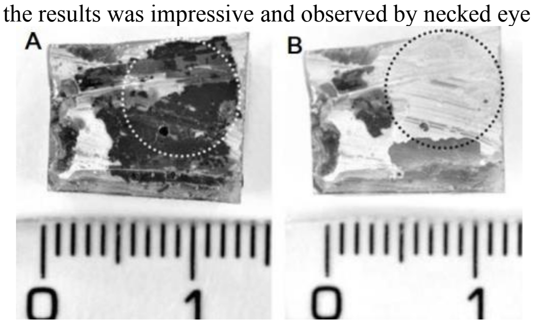

Figure 2: Cleaning results by using plasma electrolysis technique. (A) before and (B) after

Aim of study: This research is showing the effect of cleaning different archaeological glass pieces by using “plasma electrolysis on the surface of water”. The optimum conditions for cleaning glass without destruction were studied. According to the results obtained from this study, it can be recommended the use of plasma electrolysis technique in archaeological glass cleaning.

2. Materials and methods

2.1. Materials

2.1.1. Glass pieces

Four glass pieces were chosen from Rashid excavation site store. These pieces are dedicated to research purposes.

2.1.2. Plasma device (Experimental setup)

Atmospheric pressure plasma electrolysis discharge technique was designed for cleaning glass samples. Schematic diagram and **photo of the discharge system** are shown in (Figure3)

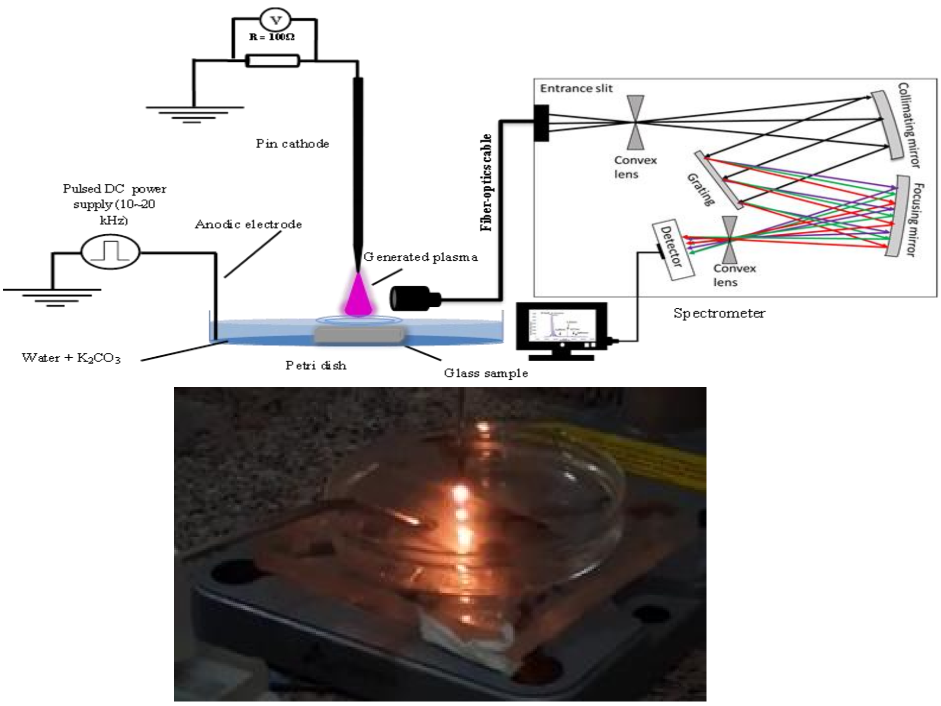

Figure 3: Schematic diagram of discharge cell with real cell

A high voltage pulsed DC signal (1-5kV, 1A, 5-20 kHz) was applied between stainless-steel grounded electrode (pin electrode) with a tip radius of curvature of approximately 0.75mm was placed 2 mm above a 50 ml salty water loaded in a Petri dish (Distilled water with dissolved 0.5 gram of potassium carbonate which was used to adjust the conductivity of the solution. Stainless anode inserted inside the salty water, regarded as anode electrode. The water was continuously refreshed after each sample treatment. When the applied voltage reaches the breakdown voltage, discharge takes place in the shortest gap between the electrode and water surface. A stable discharge voltage was obtained after switching on the plasma. A high voltage high frequency switch mode pulse generators has been designed and developed for atmospheric pressure plasma applications including pin to liquid discharge.

Cleaning process for glass samples was done at current 0.268A at exposure time 10: 15 min, at constant pulse frequency, 10 kHz. The discharge current was measured by detecting the applied voltage dropped over 100-ohm resistor connected between the pin electrode and ground. A digital oscilloscope (model: RIGOL DS1102E, 100MHz, 1Gsa/s) was used to measure the voltage dropped upon the resistor. The discharge current was calculated by dividing the voltage recorded by the oscilloscope by the resistor value (100 ohm). Figure 4 shows the current waveform at 0.268 A, sustaining voltage at 500v and 10 kHz frequency.

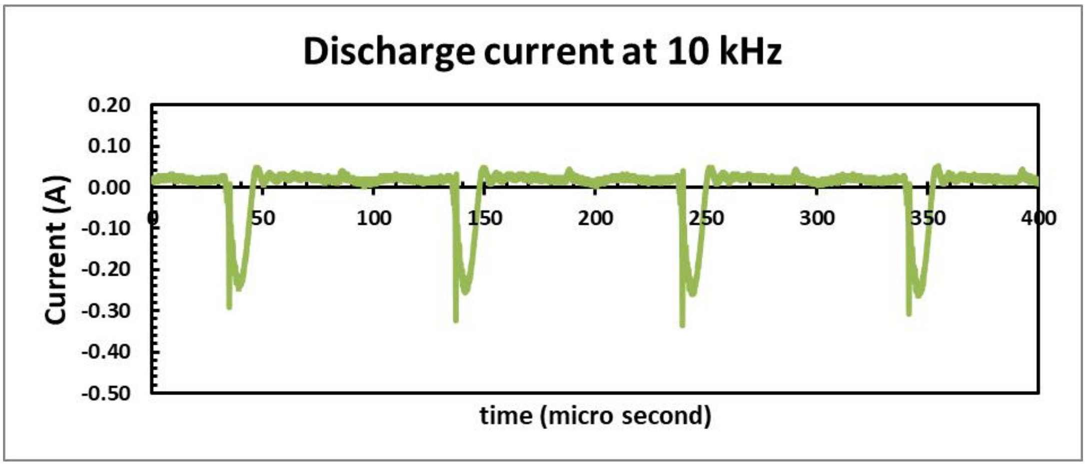

Figure 4: The discharge current shows the pulsed mode of the discharge at 0.268 A sustaining voltage at 500v and 10kHz frequency.

2.2. Methods

2.2.1. Visual Assessment

Visual assessment was done to illustrate the difference between before and after cleaning process.

2.2.2. Digital microscope

VHX-900F series digital microscope with CMOS image sensor; up to 30 FPS frame rate and focus range 15mm-40mm with magnification 1600×; was used to investigate the surface of glass understudy.

2.2.3. Surface X-Ray Diffraction (XRD)

It was carried out in Desert Research Center, Egypt with Bruker D2 phaser 2nd gen X-ray diffraction using Cu-Kα radiation at 30KV and 10 mA over a 2θ range 5–80° with a step size of 0.02°and 0.2 second per step.

2.2.4. Scanning electron microscope coupled with EDX (SEM-EDX)

FEI Quanta 3D 200i scanning electron microscope equipped with thermo-fisher pathfinder EDX, operated under conditions of low vacuum, with acceleration voltage 20.0~ 30.0 kV using large field detector with working distance 15~ 17mm, and that was done in Grand Egyptian Museum to illustrate the cleaning effect.

3. Result and discussion

3.1. Cleaning mechanism by plasma

Soot (carbon), gypsum and black corrosion were removed from the surface of glass pieces without causing destruction either for glass or iridescence layer was a great challenge.

Plasma could remove soot, gypsum and black corrosion successfully from the surface of glass.

The cleaning process by plasma was done according to certain mechanism, which was described and divided into 2 main reactions (reactions in anode and reactions in cathode)[44]. As mentioned before that plasma in liquid system produced many active species such as H_2O_2, O_3, OH, O, and H radicles.

I. <u>Cathodic pin reactions</u>

Electrons in this process will react with liquid vapor and produce species such as $H^{\bullet}$, $OH^{\bullet}$, H_2O, H_2O_2, HO_2 and UV radiation, which may react with liquid or absorbed in it. These active species are formed from the water vapor interaction with gas electrons according to the following reactions modeled and studied by Hickling et al and Bruggeman, et al.:[37,45].

$$H_2O\,(g) + e^- \longrightarrow H^{\bullet} + OH^{\bullet} + e^- \qquad (R1)$$
$$OH^{\cdot} + OH^{\cdot} \rightarrow O + H_2O \qquad (R2)$$
$$H_2O\,(g) + e^- \longrightarrow O + H_2 + e^- \qquad (R3)$$
$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \qquad (R4)$$

Reactions occurred inside the liquid

Almost all applications in plasma electrolysis depend on chemical reactions which are initiated in the liquid phase by reactive species generated in both gas interface and inside liquid. In these reactions hydrated electrons (they are the electrons which formed due to the ionization of water as the principal reactive chemical species[46,47]), produced through the contact of a non-thermal atmospheric-pressure plasma with an aqueous solution, became very reactive and all reactions are done inside liquid. In plasma-liquid cell, the hydrated electrons directly react with water to produce hydroxyl radicals (OH) and hydrogen molecules (R5 & R6)[44,48–51].

II. At the anode, the corresponding charge transfer reactions should be identical to a standard electrochemical cell which lead to molecular O_2 and hydrogen so that electrical continuity can be maintained and charge neutrality in solution is preserved (R7) [44].

Cascaded chemistry, defined as coupled and multistep reactions involving different species, will result from the proposed reactions induced at the plasma–liquid interface. The formation of H_2O_2 is a clear example of cascaded chemistry and can involve several different reaction paths. One of the more likely reaction paths is (R8) [44,52]:

$$H_2O(l) + e_{aq} \rightarrow OH^- + H^{\cdot} \qquad (R5)$$
$$2H^{\cdot} \rightarrow H_2 \qquad (R6)$$
$$2H_2O(l) \rightarrow 2O_2(g) + 4H^+ + 4e \qquad (R7)$$
$$2OH^{\cdot} \rightarrow H_2O_2 \quad (In\ liquid) \qquad (R8)$$

In contrast to traditional techniques, plasmas enable exceptionally large fluxes of electrons, which lead to a high concentration of electrons in a near plasma–liquid interfacial region. These conditions enable unique chemical transformations that may not be available with traditional techniques[53]. And that made these active species (O, H, OH, and H_2O_2) can easily remove carbon, gypsum and corrosion without any destruction [54]. As mentioned, oxygen and hydroxyl ions have their influence on oxidation reactions. And hydrogen ions have an influence on reduction reactions. So, in combination with all species all the contaminations or pollutions can be removed effectively [30].

3.2. Visual examination

Visual examination shows great results in cleaning process by using plasma for glass pieces 1,2 &3. The glass piece 4 was subjected to plasma for 15 min for each face, which caused cracks in the black crust and facilitated its mechanical removal by scalpel (Figure 5). Visual Assessment doesn't determine to which extend plasma can clean different dirt (Figure 6).

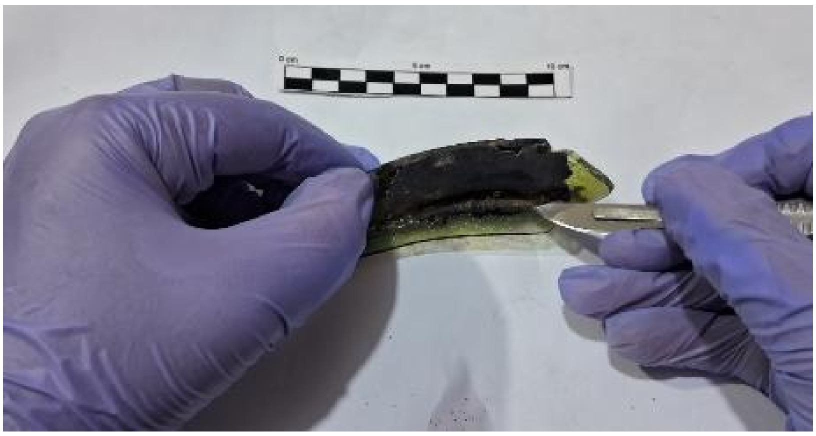

Figure 5: During removing black corrosion crust with scalpel

3.3. Digital microscope

Digital microscope was used to illustrate to which extend the glass can be cleaned. Also to estimate if the cleaning method destructive or not. Almost all the glass was cleaned (Figure 7). But the percentage of dirt removal has not been precisely determined by digital microscope.

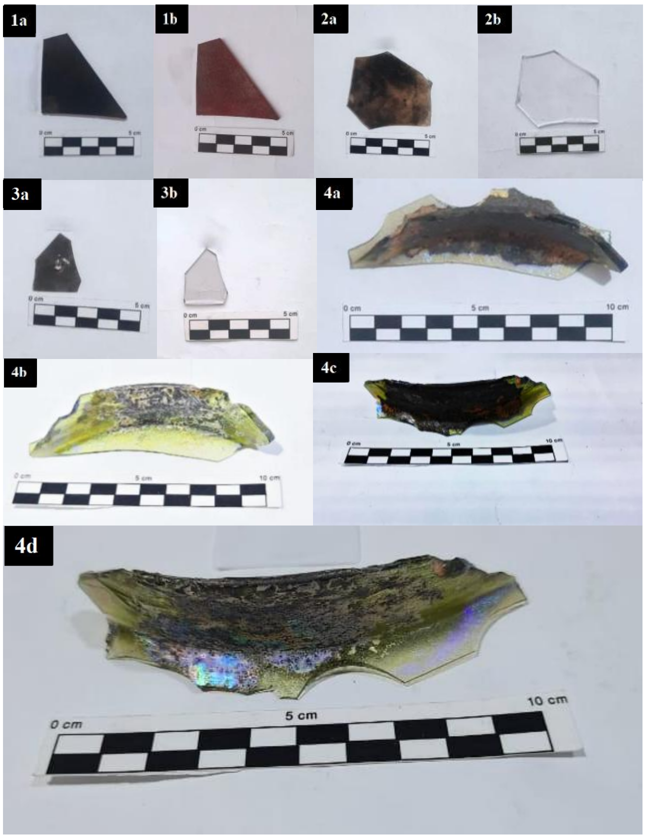

Figure 6: Visual assessment images show the effect of using App in removing dirt; (1a) piece 1 before cleaning; (1b) piece 1 after cleaning; (2a) piece 2 before cleaning; (2b) piece 2 after cleaning; (3a) piece 3 before cleaning;(3b) piece 3 after cleaning; (4a) face of piece 4 before cleaning; (4b) face of piece 4 after cleaning; (4c) back of piece 4 before cleaning; (4d) back of piece 4 after cleaning.

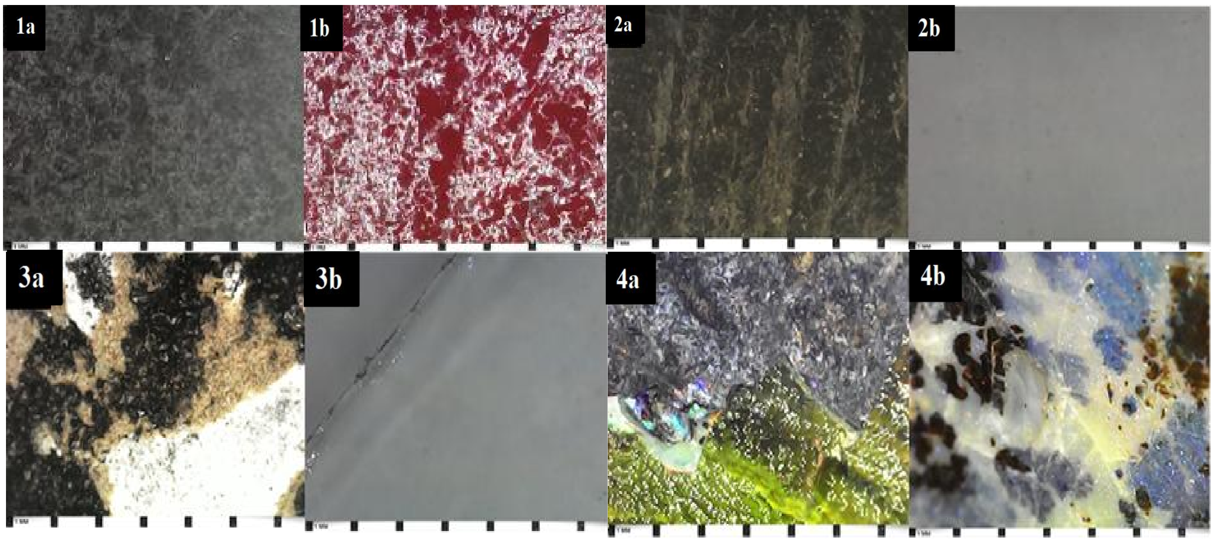

Figure 7: Digital microscope images show the effect of using App in removing dirt; (1a) piece 1 before cleaning; (1b) piece 1 after cleaning; (2a) piece 2 before cleaning; (2b) piece 2 after cleaning; (3a) piece 3 before cleaning;(3b) piece 3after cleaning; (4a) piece 4 before cleaning; (4b) piece 4 after cleaning.

3.4. Surface XRD

This chemical analysis was carried out to determine the corrosion or dirt compounds which exist on the surface of glass pieces. XRD technique is only used to analyze crystalline materials. As known that glass is an amorphous material, which make XRD can't determine any components from glass matrix [55]. XRD results obtained from charts (Figure8). It can be concluded that piece 1, 2 &3 are suffered from carbon (soot) as a deterioration aspect. The existence of soot on the surface of glass may because that these pieces were subjected to fire. The risk of fires can range from soot formation to artifact destruction [13,16]. Also soot may be formed on glass surface as a result of anciently using glass as lamps for lighting process [14].

In case of piece 3, XRD chart also showed the existence of calcium sulphate ($CaSO_4$) with soot on the surface of glass. That may refer to that this fragment may be a part of window. Anciently, glass was used in gypsum windows (Stucco windows) in mosques or any other building especially in Islamic period [56]. As known that gypsum is composed of ($CaSO_4.2H_2O$). $CaSO_4$ is Anhydrite, which resulted from the transformation of gypsum in process known as dehydration by losing water molecules as result of high temperature (90^{o}c) [57,58]. That explain the existence of gypsum stuck to glass surface.

For piece 4, XRD showed that glass surface is composed of black crust layer from Iron platinum, iron manganese and aluminium iron manganese. Iron and manganese compounds are formed on the surface of glass in a form of corrosion layer when glass was buried in wet environment, especially on the surface of non-transparent glass. This corrosion layer was formed after the formation of iridescence layer (rainbow like layer), which is considered the first step for corrosion [24,59].

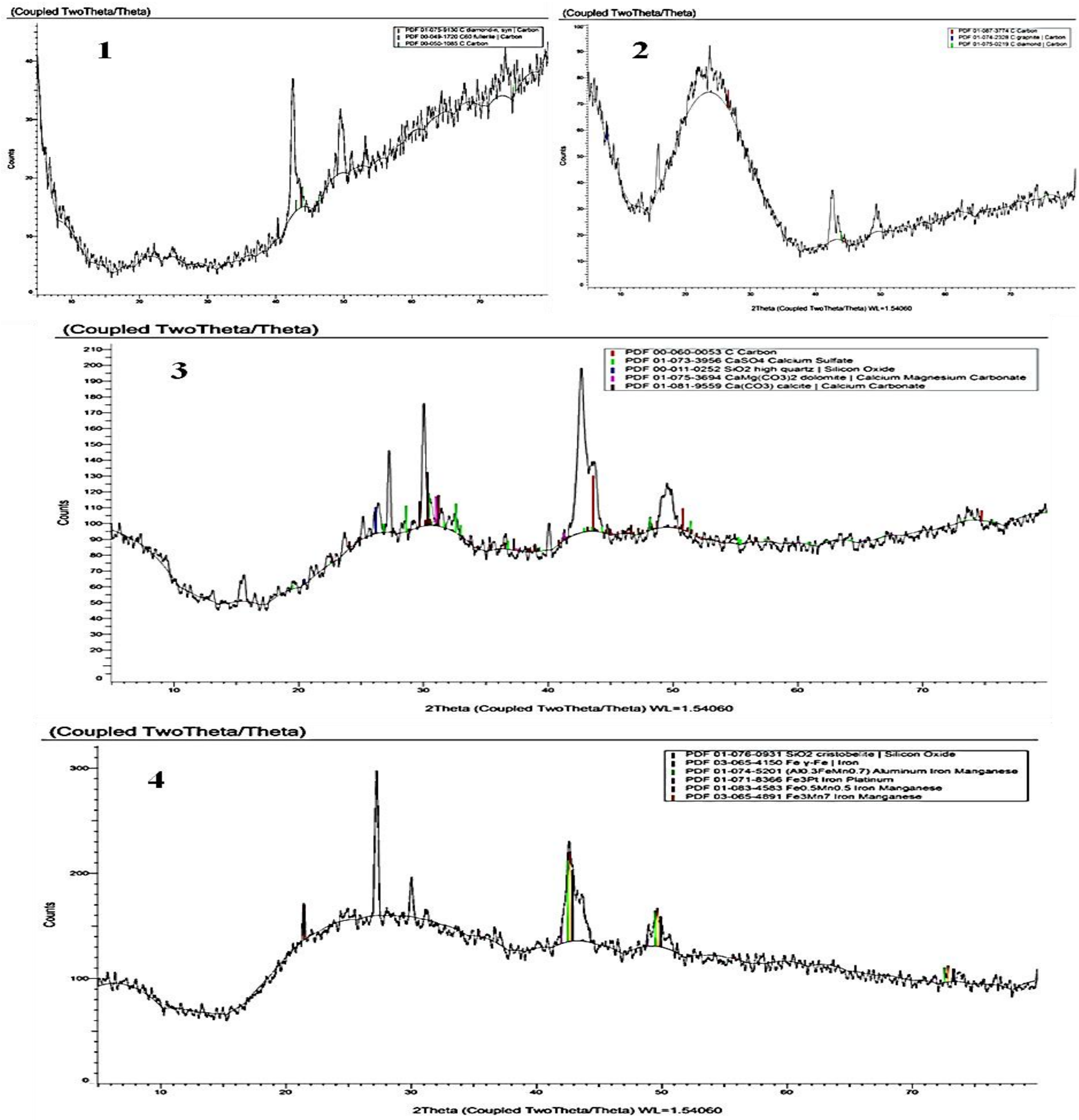

Figure 8: XRD chart for 1,2,3 &4 pieces

3.5. SEM-EDX

From data obtained from SEM images (Figure 9), it can be concluded that the cleaning process by using plasma is very effective in removing different types of dirt especially in 1,2 &3 archaeological glass pieces. Plasma could remove transformed gypsum (anhydrite) from piece 3. For corrosion layer which exist on the surface of piece 4, plasma was able to remove it with the aid of mechanical tools without removing the iridescence layer. EDX is a chemical analysis that carried out to estimate cleaning process. EDX results showed 17 elements in all glass samples; (C, Na, O, Al, Si, P, S, Cl, K, Ca, Fe, Zn, Mg, Ti, N, Mn & Sb), these elements may represent glass former, stabilizer, modifier, colorant, decolorant, opacifier, impurities or even dirt or corrosion [60,61]. According to EDX results, it was clear that all glass pieces are from the type of soda-lime glass. Except piece 4, it is soda-potash glass. Soda-potash glass was produced from 11th century BC by using mixture from ashes which rich in soda or potash or both of them according to the composition of ashes [62,63]. The minor elements percentage which exists in (Table1) may represent impurities. For elements which disappeared or decreased after cleaning process, they represent dirt or corrosion. Zn element (Zinc) appeared in piece 1 with high percentage (20.819 %) after cleaning. This percentage can't be Considered as impurities. Zn may exist in a form of ZnO, ZnO is known as Zincite. Zincite is a rare zinc oxide red crystal which was used as a colorant material to produce the red color of glass [64,65]. According to [66,67] that the high content of ZnO can give indication that ZnO was used as glass modifier. But most likely in this case that ZnO was used as a colorant material. For "N" element (Nitrogen) which exist in piece 4. The existence of this element explained by [68,69] as a gaseous problem, that nitrogen was entrapped in the glass molten during manufacturing process and doesn't came out from the glass. EDX results also showed that there is a new element appeared in piece 4 after cleaning. This element is Antimony (Sb). Antimony appeared with percentage (8.891%). Sb was used anciently in Roman period as opecifier material, decolorant or as a fining material to remove bubbles during glass manufacturing process [70]. The minor percentages from (Ti) may be existed as impurities. Also, it may be existed in a form of titanium dioxide, which added as a colorant material to produce a smoky white color [71,72]. It most properly in this case that titanium is an impurity which is migrated during corrosion process (especially during the formation of iridescence layer) to the surface of glass [73]. For Fe, Mg and Mn, due to burial environment where glass existed for a long time. There are 2 processes (hydration and ion exchange) which had occurred with the aid of alkali earth elements and water to form a black corrosion layer which is formed from these elements, this black layer is formed above iridescence layer [74]. EDX results illustrate that plasma can effectively clean carbon (soot) from pieces 1, 2&3 with average (95.46%), and all the elements of glass percentage increased. Also, gypsum was removed from the glass surface (piece 3). For piece 4, the elements of iridescence layer appeared, glass elements percentage increased in general and carbon percentage decreased by 32.83%.

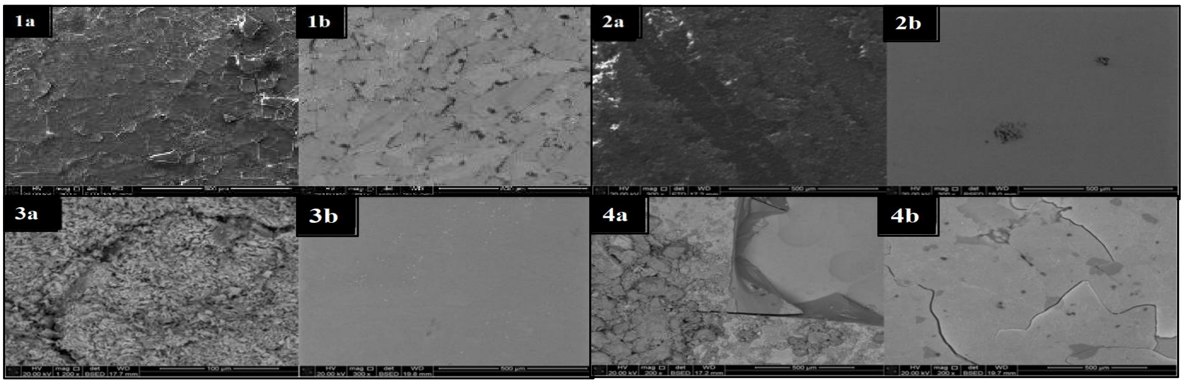

Figure 9: SEM images show the effect of using App in removing dirt; (1a) piece 1 before cleaning; (1b) piece 1 after cleaning; (2a) piece 2 before cleaning; (2b) piece 2 after cleaning; (3a) piece 3 before cleaning;(3b) piece 3 after cleaning; (4a) piece 4 before cleaning; (4b) piece 4 after cleaning

Table 1:EDX results for glass samples ; (1) piece 1 before cleaning; (2) piece 1 after cleaning; (3) piece 2 before cleaning; (4) piece 2 after cleaning; (5) piece 3 before cleaning;(6) piece 3 after cleaning; (7) piece 4 before cleaning; (8) piece 4 after cleaning.

Samples	Spot no.	Elements (%)																
		C	Na	O	Al	Si	P	S	Cl	k	Ca	Fe	Zn	Mg	Ti	N	Mn	Sb
1	1	50.196	-	-	0.595	30.679	0.942	0.299	-	2.400	1.440	-	8.131	0.245	-	-	-	-
	2	2.799	3.313	2.650	1.292	60.308	0.595	-	1.811	3.728	2.686	-	20.819	-	-	-	-	-
2	3	43.159	1.803	3.145	0.114	23.454	-	0.374	-	1.216	18.782	6.170	-	-	-	-	-	-
	4	2.600	5.633	9.880	1.058	60.700	-	-	-	1.329	18.801	-	-	-	-	-	-	-
3	5	33.251	2.092	1.689	0.890	2.905	-	38.607	-	1.435	19.131	-	-	-	-	-	-	-
	6	1.593	4.852	2.296	7.607	67.885	-	-	-	4.917	10.85	-	-	-	-	-	-	-
4	7	11.377	2.677	3.970	2.693	46.976	-	2.669	2.830	1.253	6.888	4.454	-	1.158	0.730	7.360	4.965	-
	8	7.642	2.564	4.345	4.094	58.932	-	-	3.493	-	-	1.676	-	0.352	3.913	4.098	-	8.891

Conclusions

Plasma-electrolysis on the surface of water technique which used in 0.268A, 500v as a sustaining voltage, 10kHz could successfully cleaning soot (Carbon), which indicated as a deterioration aspect on the surface of glass by surface-XRD, from archaeological glass pieces (1, 2 &3) by percentage 95.46% and totally cleaned gypsum from the surface of glass, that was proved by using SEM-EDX analysis technique. For piece 4, plasma could make cracks in the black crust corrosion layer and ease its removal with scalpel without removing the iridescent layer. That was proved with SEM-EDX by showed that all the glass elements increased, and corrosion products decreased. So, from the previous, it can be concluded that plasma-electrolysis on the water surface technique in 0.268A, 500v as a sustaining voltage, and 10kHz can be used safely in the cleaning of only small archaeological glass pieces. Recently, we are trying to develop the device to be used in a large-scale objects cleaning. Also, this method didn't used yet with fragile and outdoor archaeological glass, so it needs a future experimental work to be made. But in general, our manuscript a novel atmospheric pressure plasma technique was used to remove not only organic contaminations but also inorganic contaminations. The technique could be regarded as indirect treatment technique since the glass samples were under water and the plasma generated over water surface. The glass samples were exposed only to active species which have no harmful effect on the glass surface. The currently used technique is flexible and can be extended to be applied to large scale heritages with low power consumption and no heating effect.

Abbreviations: APP; Atmospheric Pressure Plasma**,** LPP; low pressure plasma

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