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Chemical, Electrochemical and Corrosive Wear Behavior of Nickel-plated Steel and Brass-plated Steel Based Coins from Egypt in Artificial Sweat

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The corrosion behavior of two types of Egyptian coins were investigated. Coins are available as 25 piaster (25P); (nickel-plated steel) and 50 piaster (50P); (brass-plated steel) Egyptian coins. These coins were studied in Artificial Sweat Solution (ASS) by using weight-loss and electrochemical techniques. The ASS was analyzed during weight-loss by Atomic Absorption Spectroscopy during the immersion of these coins for up to seven days. Electrochemical techniques showed that the corrosion rates of 25P were faster than 50P Egyptian coins, while the polarization resistance of 50P (brass plated layer) in the ASS was higher than that of 25P coin (nickel-plated layer). Wear behavior was studied before and after corrosion measurements using the weight-loss method. The optical microscopy was used for the investigation of the surface morphology of these Egyptian coins after immersion in ASS before and after wear. The weight-loss results confirmed that the corrosion rates of 25P were faster than that of 50P Egyptian coins after immersion for seven days in ASS. Atomic Absorption Spectroscopy results showed that Ni ions released to unacceptable safety limit. On the other hand, the Cu and Zn ions released in ASS did not present any hazard to the human. The specific wear rate of the plating layer of the two Egyptian coins increased by increasing the immersion time in ASS, and the specific wear rate of the 50P Egyptian coins was about three times greater than that of the 25P Egyptian coins.

Keywords: Corrosion behavior; Electrochemical behavior; Wear; Coins; Artificial sweat solution

1. INTRODUCTION

During coins' circulation, depending on coin materials and time of circulation, coins lose their original appearance, color, and clear pits may be formed on the surface. This behavior mainly caused by human sweat that destroys the surface of coins gradually [1]. Coins are made of metals/alloys that have standard designs [2, 3]. Recently, most of the alloys used in manufacturing of coins are Ni and Cu alloys [4, 5], as their prices are lower compared to other precious metals and for its decorative appearance. Ni resistance is unequally by any other metal or alloy except precious metals [6]. However, Ni is classified as one of the most hazard metal that causes skin sensitivity (may cause an allergy to skin), affecting about 10–20% of the general population [7-10].When Ni ions reached a 0.5 μg/cm^2/week after prolonged contact, it is considered as a restricted limit that cause skin allergy [9-13]. Potential applications of alloys and metal of Ni included production and processes, transport, and jewelries [6, 12, 14, 15]. Cu alloys, especially brass possesses strong wear resistance and processing properties, hence it has a wide range of applications, such as daily hardware, manufacturing of outdoor/indoor machines. The attractive golden color acquired by brass is of special interest to different applications. However, different colors are often reported [16-18].

The ASS is more aggressive than that of water on the surface of the coins [13, 19]. This may affect the corrosion behavior particularly in coins. For example, Euro coin in ASS was investigated and found that the Ni-released percentage was in the ranges between 23.2–65.1 μg/cm^2/week. The Ni ions released was rapid in the first days of immersion then it started to slowdown. The Ni ions release from Euro coin can be precipitated onto the skin. This was investigated after Euro coin immersion for 1 h in artificial sweat, where the amount of Ni released from Ni-plated coins was 7.5 μg/cm^2 [11].

The risk of allergy during handling Ni-plated alloy coins are more in comparison to the risk of handling brass-plated alloy coins. The corrosion behavior for mild steel, galvanized steel and SS316L in ASS were studied according to ISO 3160-2 [20]. The interaction of corrosion and wear properties is important in many engineering applications such as the components of marine structures, chemical pumps, piston rings, cylinder walls and mechanical seals [21]. The literatures dealing with the corrosive wear behavior for engineering applications were intensively investigated [21], but corrosive wear research is limited for coins. The aim of this work is investigating the corrosive wear behavior of the minted coins (25P and 50P Egyptian coins) in ASS for up to seven days. The electrochemical investigation included the study of the corresponding blanked coins. The surface morphology of the immersed coins were investigated by optical microscopy, Atomic Absorption Spectroscopy was used to follow the ions release during immersion of coins during seven days. The wear behavior of the coins before and after immersion in ASS were investigated as well during this period.

2. EXPERIMENTAL WORK

2.1 Materials

Blanked Egyptian coins (25P Egyptian coin and 50P Egyptian coin) specification were given by the importer (British Mint Authority) and illustrated in Table 1. Table 2 shows plated layer thickness and composition of these coins. Table 3 lists the chemical composition of steel. The chemical composition of the ASS, according to ISO 3160/2 [22], is given in Table 4. The pH of the ASS electrolytic solution is adjusted to a value of 4.7 using a pH meter (HI 9021 Micro Processor) by adding few drops of NaOH.

Table 1. Dimensional specification of 25P and 50P blanked Egyptian coins

Blanked coins	Diameter-Cut (mm)	Diameter-Rimmed (mm)	Edge thickness-Rim (mm)	Diameter-Plated (mm)	Weight (g)
50P	22.74 ± 0.05	22.54 ± 0.03	2.21 ± 0.10	22.6 ± 0.05	6.5 ± 0.2
25P	20.67 ± 0.05	20.47 ± 0.03	1.87 ± 0.10	20.66 ± 0.05	4.5 ± 0.17

Table 2. Plated layer composition of blanked Egyptian coins

Blanked coins	Composition of element in the plate (wt.%)			Thickness, µm
	Ni	Cu	Zn	
25P	100	-	-	7.5
50P	-	69.86	30.14	25

Table 3. Chemical composition of steel in wt.%

Elements	Fe	Mn	C	P	Cr	Other impurities
%	99.40	0.15	0.08	0.03	0.02	0.32

Table 4. Chemical composition of ASS [22]

Compound	Sodium chloride	Ammonium chloride	Lactic acid	Acetic acid	Urea
(g/L)	20	17.5	15	5	2.5

2.2 Corrosion behavior

Two different Egyptian coins (25P and 50P) were investigated using weight-loss method. First, the sample was cleaned by distillate water, dried air and then the weight of each sample was measured before and after immersion in ASS using three samples in each test and taking the average. For weight-loss test, immersion in ASS for 1 h, one day, three days, five days and seven days. The corrosion rate were calculated according to Eq. 1 [23-25]:

$$\text{Corrosion rate (mm/year)} = \frac{87.6\times W}{D\times A\times T} \qquad (1)$$

Where w is weight loss (g), D is density (g/cm^3), A is surface area (cm^2), T is immersion time (h).

The Atomic Absorption Spectroscopy (model Agilent-technologies 200 series AA) was used to measure the concentrations of ions in ASS after immersion of samples for up to seven days. A digital camera was used for taking images for the coins before and after the corrosion for up to seven days. Optical microscopy was used using Olympus BX41M-LED for the investigation of the surfaces of coins after immersion in ASS for 1 h, one day, three days, five days and seven days.

Electrochemical techniques were utilized in studying the corrosion rates after 1 h and seven days. The open circuit potential (OCP) was performed at 25 ± 1ºC, using a conventional two-electrode cell, working electrode (specimen) and Ag/AgCl as reference electrode. The electrochemical cell connected to Workstation Autolab PGSTAT302N for 1 h and seven days. Potentiodynamic polarization was carried out by workstation Autolab PGSTAT302N- High- Performance potentiostat/galvanostat instrument. Three-electrode cell used where the sample served as a working electrode, a platinum as a counter electrode, and Ag/AgCl as reference electrode while ASS was used as electrolytic solution at room temperature. The samples were measured from steady state potential ± 250 mV at a scan rate of 1 mVs^{-1}. The Stern–Geary method [26] was used for the determination of the corrosion current (I_{corr}). The corrosion current was gained by extrapolation of anodic and cathodic Tafel lines and the corresponding corrosion potential ($E_{corr.}$) for samples. Corrosion rate was calculated from Eq. 2 where the I_{corr} estimated from polarization curves [27]:

$$CR = \frac{3.27 \times 10^{-3} \times I_{corr} \times EW}{D} \qquad (2)$$

Where CR is the corrosion rate (mm/year), D the density (g/cm^3), EW the equivalent weight of specimen in grams and i_{corr} (plated) and i_{corr} are the corrosion current densities (μA/cm^2) values with and without plating, respectively.

OCP results were obtained in aerated ASS as a function of time showed a varied behavior. The samples used in this test were 25P coin “Ni-plated steel”, and 50P coin “brass-plated steel”.

2.3 Wear test

The wear test before and after immersion time of 25P and 50P Egyptian coins in ASS was performed according to ASTM G99-04 [28], during different immersion time in ASS of 1 h, one day, three days, five days and seven days. Wear tests were conducted under dry sliding at room temperature 23±2°C using a ball-on-disk wear tester with a 5 mm diameter Al_2O_3 ball rigidly hold by a holder employed as the ball and the coins as the disk with the flat plane oriented horizontally. The test was carried out at a normal load of 7 N at a 100 mm/s sliding speed. The total sliding distance was set to 100 m. The coefficient of friction (COF) was calculated from Eqs. 3 and 4:

$$\Delta V\ (mm^3) = \frac{Weight\ loss\ (g)}{Density\ \left(\frac{g}{cm^3}\right)} \times 1000 \qquad (3)$$

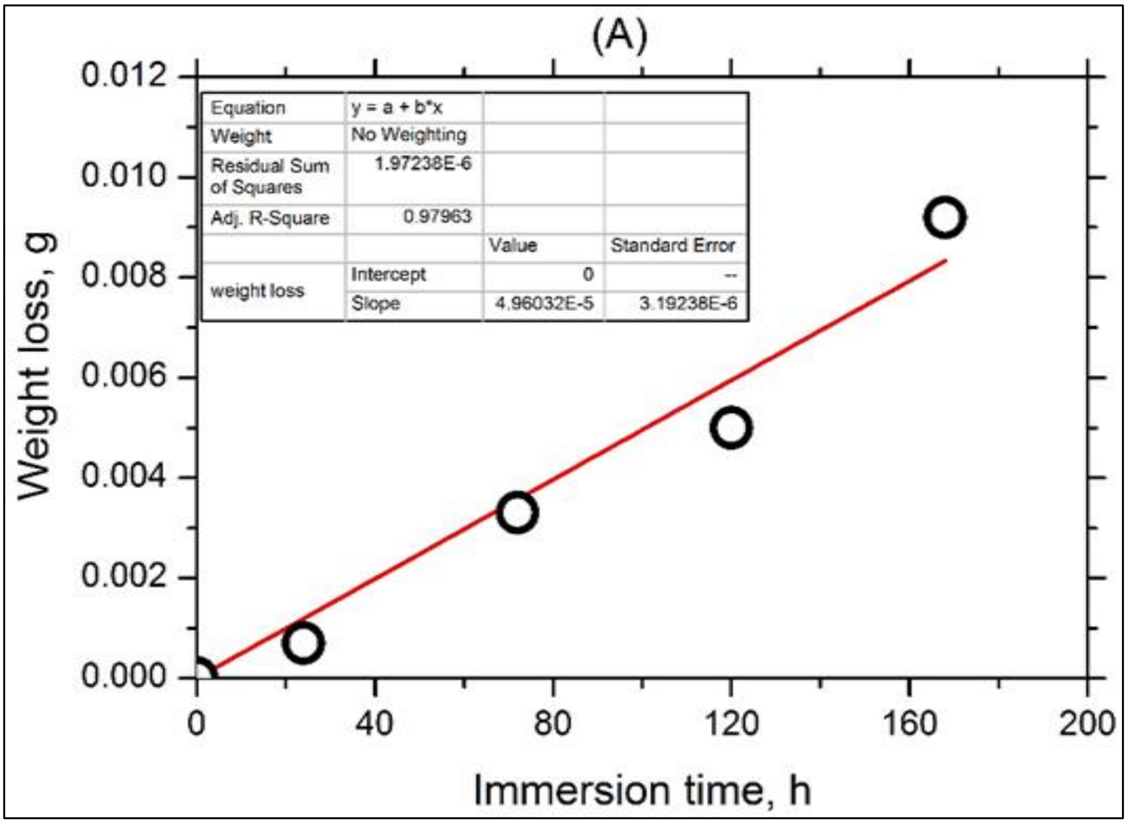
$$W\ (mm^3/N.m) = \frac{\Delta V}{SL} \qquad (4)$$

Where ΔV is the volume of coating removal during the test, W is the specific wear rate, S is the sliding distance (in meter), L is the normal load applied (in Newton).

3. RESULTS AND DISCUSSION

3.1 Weight-loss

Fig. 1 depicted the weight-loss of the minted coins. The corrosion rate was extracted from Fig. 1 by substituting the slope value into Eq. 1. Fig. 1(a) the experimental results (hollow circles) were fitted linearly (solid line) and the linear slope has a value 4.96×10^{-5}, consequently; the corrosion rate of 25P coins after immersion in ASS for seven days is equal to $6.89\text{x}10^{-5}$ mm/yr.



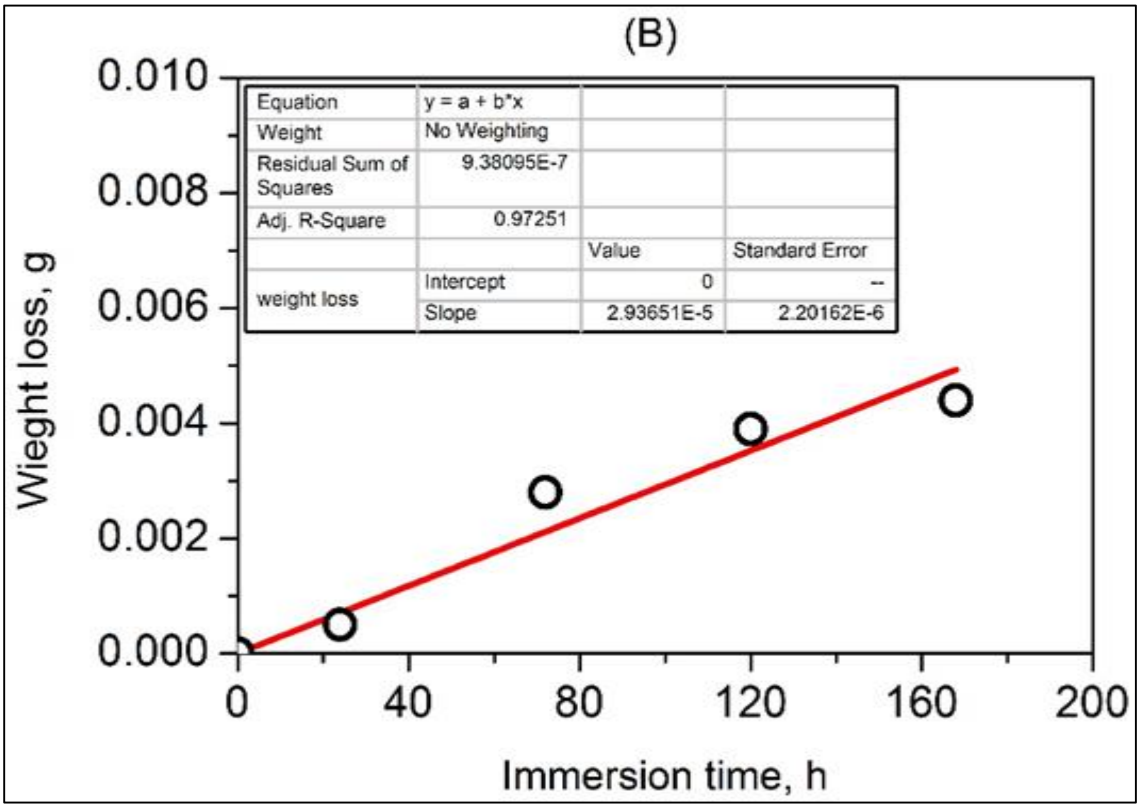


Figure 1. Weight-loss versus immersion time for up to seven days for (A) 25P minted coins, and (B) 50P minted coins immersion in ASS at room temperature.

From Fig. 1(b), the slope of line value (a) has a value 2.94×10^{-5}, density of 50P Egyptian coin (ρ) equal to 7.9 g/cm^3, and exposed area for corrosive environment (A) equal to 9.66 cm^2. Thus, the corrosion rate of 50 P coins after immersion in ASS for seven days is equal to $3.37\text{x}10^{-5}$ mm/yr**.** Weight-loss method confirmed that the corrosion rate in the ASS for Ni-ply coat is the higher than that 50P coins. It might be due to the immersion of Ni-plated steel immersed in AAS has the highest level of nickel in a short time which confirmed that the people handled Ni-alloy in a short time and constantly, more susceptible to injury [11].

3.2 Atomic Absorption Spectroscopy

The Atomic Absorption Spectroscopy for the 25P and 50P minted coins immersed in ASS for seven days were investigated. When Ni-plated steel immersed in ASS, it could suffer from oxidation to form Ni^{2+} which has a more noble potential than that of Ni metal. The rate of Ni ions released form 25P minted coins are higher than the safe limit of Ni released (0.5 μg/cm^2/week). It was indicated that the study of Ni deposition in ASS for seven days is not enough time to compute the circulation risk of items with high Ni content that come into people handled Ni alloys in short time [11].

$$Ni \longrightarrow Ni^{2+} + 2e^- \tag{5}$$

$$2O^+ + 2e^- \longrightarrow O_2 \tag{6}$$

On the other hand, for 50P Egyptian coins showed that Cu started to react with the chloride from the ASS as shown in Eqs. 7-10 [19].

$$Cu + Cl^- \rightarrow CuCl_{ads} + e^- \quad (7)$$
$$CuCl_{ads} + Cl^- \rightarrow CuCl_2^- \quad (8)$$
$$Cu + 2Cl^- \rightarrow 2CuCl_2^- + e^- \quad (9)$$
$$2CuCl_2^- + H_2O \rightarrow Cu_2O + 2H^+ + 4Cl^- \quad (10)$$

Cupric oxi-chloride ($Cu_2(OH_2)Cl_2$) produced from passivation of Cu as a result of the presence of chlorides, ($Cu_2(OH_2)Cl_2$) or due to the formation of cuprous and cupric oxide on the top of the brass-plated steel. Chloride ion in ASS accelerates the anodic active dissolution of brass, which is the main reason of corrosion. Lactic acid and ammonia water also promote the anode reaction. The presence of urea has little influence on the corrosion process [29].The corrosion product formed on brass surface contains cupric chloride hydroxide, cuprous oxide, urea complex formed with copper (II), and low content of lactic acid or lactic acid radical ions (or both) [29].

The ions released from 25P minted coin after seven days immersed in ASS are 54.51 mg/L Fe and 134.02 mg/L Ni. The ions released from 50P minted coin for seven days immersed in ASS are 510.89 mg/L Fe, 43.58 mg/L Cu and 80.19 mg/L when the ions reached the Fe substrate, the Fe corrodes and its corrosion was faster than the plated Ni or plated brass due to the formation of stable iron oxide (e.g. Fe_2O_3). It is important that coin composition minimizes allergenic ion release [30].The Fe ions released from 50P Egyptian coins is larger than that Fe ions released from 25P Egyptian coins. This confirmed that the dezincification process produce pit corrosion on the surface of 50P coins which make the solution react easily with iron [19].

3.3 Open circuit potential (OCP)

The variations of OCP of the two blanked coins samples in the presence of ASS for 1 h are presented in Fig. 2(A). After 1 h of immersion, brass-plated steel sample showed a slight shift towards more negative potential during the first few seconds of immersion. The potential then shifted toward a steady state value of -380 mV after around 120 min of immersion. This behavior may be due to the formation of Cu(I), Cu(II) chloride or oxides as shown in Eqs. 7-10. For the Ni-plated steel sample, the OCP curve showed a slight shift of potential to more negative after 200 s of immersion as shown in Fig. 2(A). After 1h of immersion, the steady state potential for the two coin samples may be arranged according to active potential as Ni-plated steel > brass-plated steel. After seven days of immersion, Fig. 2(B), brass-plated steel sample showed a slight shift from -600 mV to -610 mV during the first few minutes of immersion. The curve shifted to less negative direction after passing 500 s after seven days in ASS (604800 s), and then reached a steady state value of -607 mV. A slight increase in the negative direction from -587 mV to -594 mV was observed for Ni-plated steel sample after immersing in ASS for seven days.

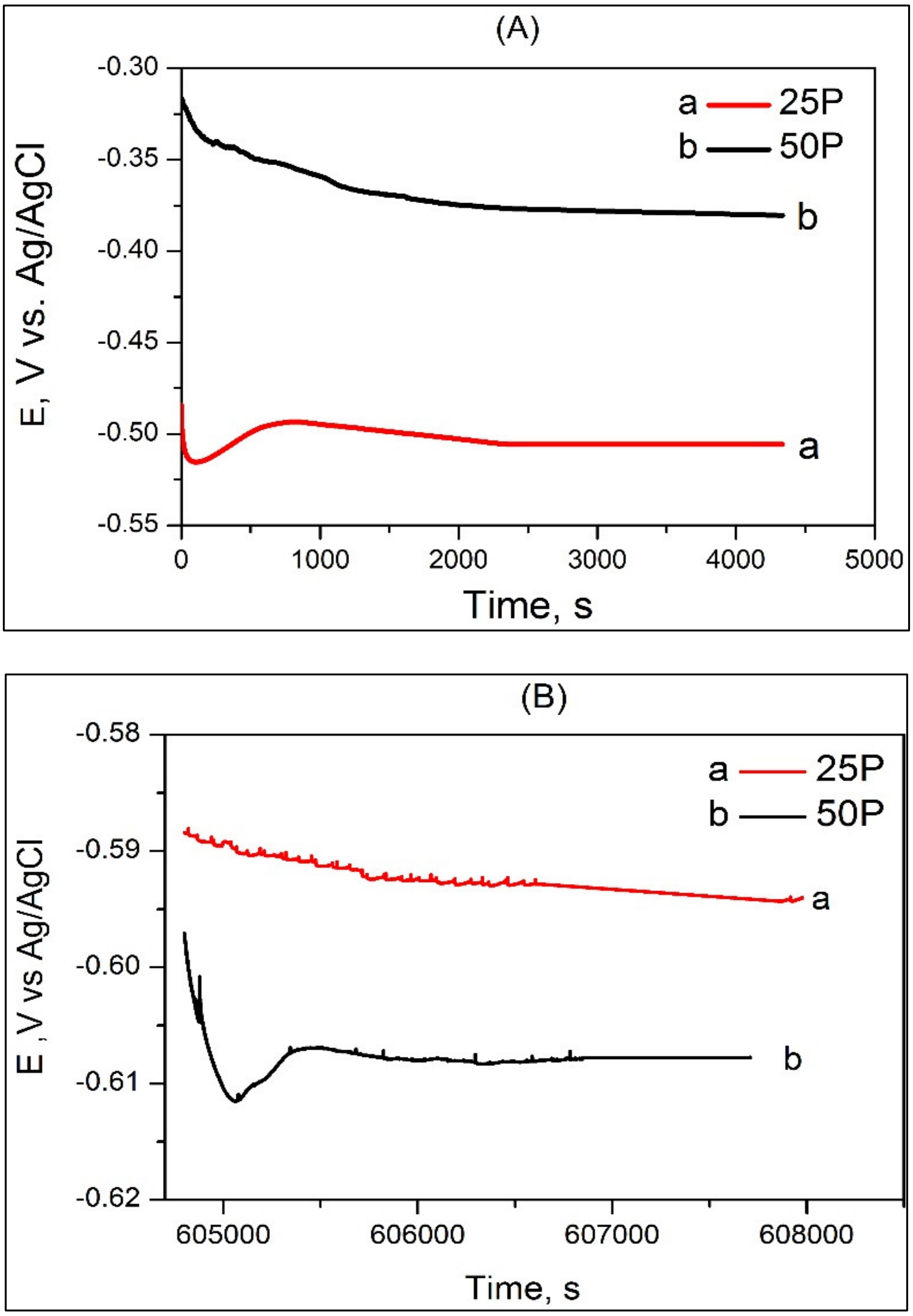


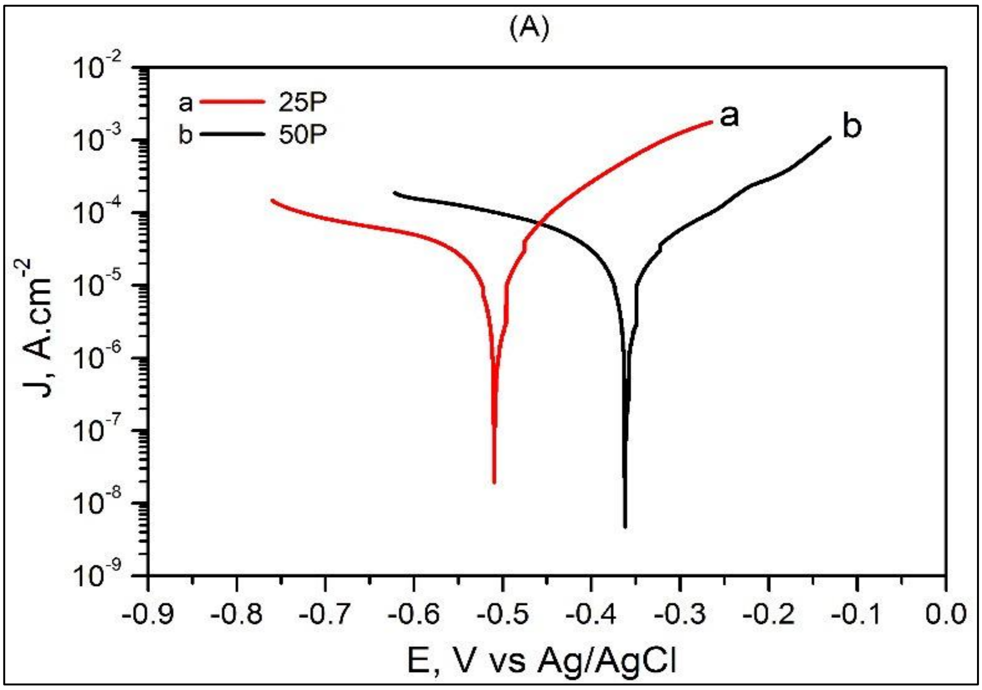
Figure 2. OCP curves of 25P Egyptian coins (Ni-plated steel) and 50P Egyptian coins (brass-plated steel) for (A) 1 h and (B) seven days of immersion in ASS at room temperature.

For all time of immersion, ranged from 1 h to seven days in ASS, the brass-plated steel and Ni-plated steel showed different behavior. It was attributed to the formation of oxide on the surface on the brass-plated steel and Ni-plated steel. The OCP alone could not confirm this behavior but in general, Ni-plated steel showed that the potential shifted to less negative direction (speculating the oxide film formation at this point). On the other hand, for brass-plated steel, noise in the potential with time was observed which indicated a more complex behavior, this behavior may be due to the formation of oxide on the Cu and to dezincification on the same time [19, 29]. The brass-plated steel potentials went to more negative potentials while Ni plated steel went to less negative potential. This could be attributed to dezincification in the brass-plated steel while oxide film was deposited on Ni-plated steel.

3.4 Potentiodynamic polarization

The potentiodynamic polarization results of Ni-plated steel, and brass-plated steel immersed in ASS were depicted in Fig. 3. Corrosion parameters, namely corrosion potential (E_{corr}), polarization resistance (R_p), corrosion current density ($I_{corr.}$), and corrosion rate (mm/year) are presented in Table 5. When samples were immersed in ASS for 1 h, different corrosion processes started which included either dissolution or deposition of some species. If the value of E_{corr} shifted towards a negative value, then this will indicate a dissolution process (or oxidation process). On the other hand, if the E_{corr} shifted towards positive potential this may indicate the oxide film formation formed on the surface that are inert (reduction process), matching with the results of OCP shown in the previous section. It is clear that the free corrosion potential for 25P Egyptian coin (Ni-plated steel) was -509 mV while it was -366 mV for 50P Egyptian coin (brass-plated steel). is I_{corr} obtained for 25P Egyptian coin (Ni-plated steel) was around 1.90×10^{-7}A/cm^2 while it was 1.52×10^{-7} A/cm^2 for 50P Egyptian coin (brass-plated). . After 1 h, the polarization resistance of Ni-plated steel polarization resistance reached 5.4 k.Ω while it reached 8.3 k.Ω. for brass-plated steel.

For 50P Egyptian coin (brass-plated steel), E_{corr} behavior showed a noble potential after 1 h immersion time in ASS compared to seven days of immersion of immersion where the E_{corr} shifted towards more negative value.



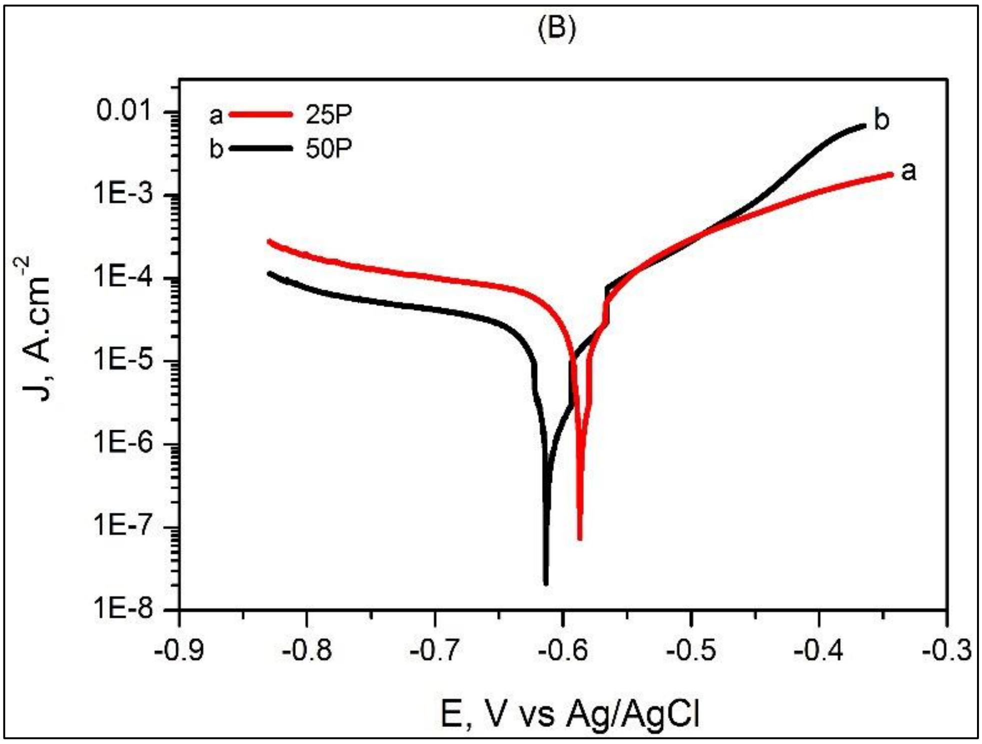


Figure 3. Potentiodynamic polarization curves of 25P (Ni-plated steel) and 50P (brass-plated steel) Egyptian coins after (A) 1 h, and (B) seven days of immersion in ASS at room temperature and a scan rate of 1 mVs^{-1}.

For the 25P Egyptian coin, after seven days of immersion the E_{corr} was slightly shifted towards more negative value. It was believed that the Ni-plated steel layer was oxidized to form NiO_2 on the surface according to Eqs. 5 and 6. Ni-plated steel when immersed in ASS which then could be suffered from oxidation to form Ni^{2+} which has a more noble potential than that of Ni metal. As anticipated, the formation of Ni^{2+} was gradually increased then reached a maximum value on the seventh day of immersion as in Eqs. 5 and 6. From literature, Ni is classified in active region in ASS which mean the $Ecorr < E_P$ [31]. It was noticed from Table that the value of E_{corr} of 25P more negative than E_P of Ni/Ni^{2+} which equal (-0.23V).

Table 5. Electrochemical parameters obtained from potentiodynamic polarization measurements of 25P and 50P Egyptian coins in ASS after 1 h and seven days of immersion at room temperature.

Time	Coin	$-E_{corr.}$ (mV)	$I_{corr.}$ (A/cm²)	CR (mm/year)	Polarization resistance (k.Ω)
1 h	25P	509	1.90 x10^{-7}	2.0x10^{-3}	5.45
	50P	362	1.52 x10^{-7}	1.8x10^{-3}	8.34
seven days	25P	587	3.67 x10^{-7}	3.9x10^{-3}	2.52
	50P	613	2.47 x10^{-7}	3.2x10^{-3}	6.22

3.5 Wear test

The specific wear rate value was used to indicate wear performance. Lower specific wear rate represents a higher wear resistance. The specific wear rate value of 50P Egyptian minted coins in air (before immersion in ASS) is around four times larger than the 25P minted Egyptian coins as shown in Fig. 4. The Ni-plated layer is higher wear resistance than brass-plated layer. After three days of immersion in ASS, the specific wear rate of 50P minted coins is rapidly increased until the seventh day of immersion in ASS. The 25P minted coins have a wear resistance in air (before immersion in ASS), this wear resistance decreased after immersion in ASS as shown in Fig. 4. This behavior indicated that the Ni-plated layer affect with ASS in short period [11]. The coefficient of friction of the two minted coins provided in Fig. 5. The figure indicated that Ni-plated layer is higher surface strength against friction but the surface strength decrease with increase of immersion time in ASS. The coefficient of friction values of Ni-plated layer were higher than brass-plated layer. From literature review, the electroless nickel coating in the as-deposited state exhibits high rates of wear which related to adhesive wear, and the susceptibility to abrasive wear [32]. However, the coated of mild steel is improves the wear resistance [33].

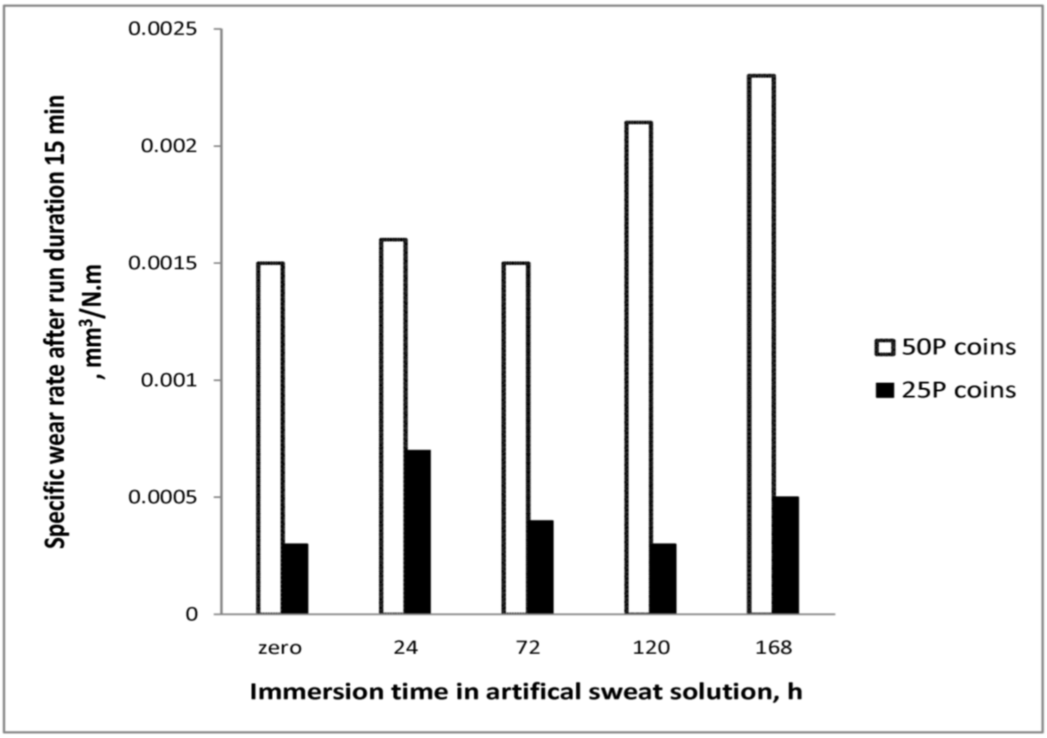


Figure 4. The specific wear rate vs immersion time of minted 25P and 50P Egyptian coins in ASS after run duration 15 min

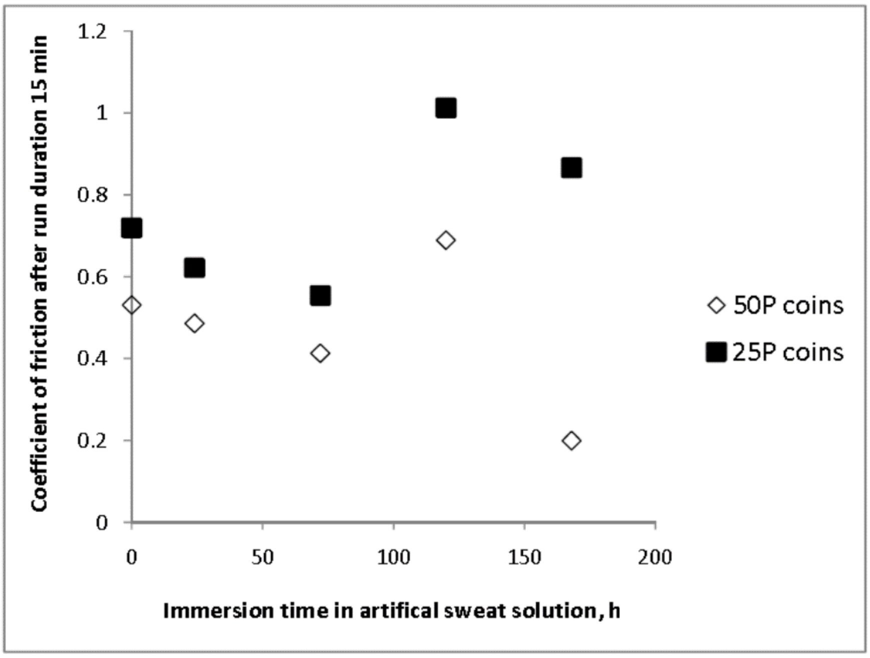


Figure 5. The coefficient of friction vs. immersion time of minted 25P and 50P Egyptian coins in ASS after run duration 15 min

3.6 Surface Morphology of the corroded coins

(a) **(b)** **(c)** **(d)**

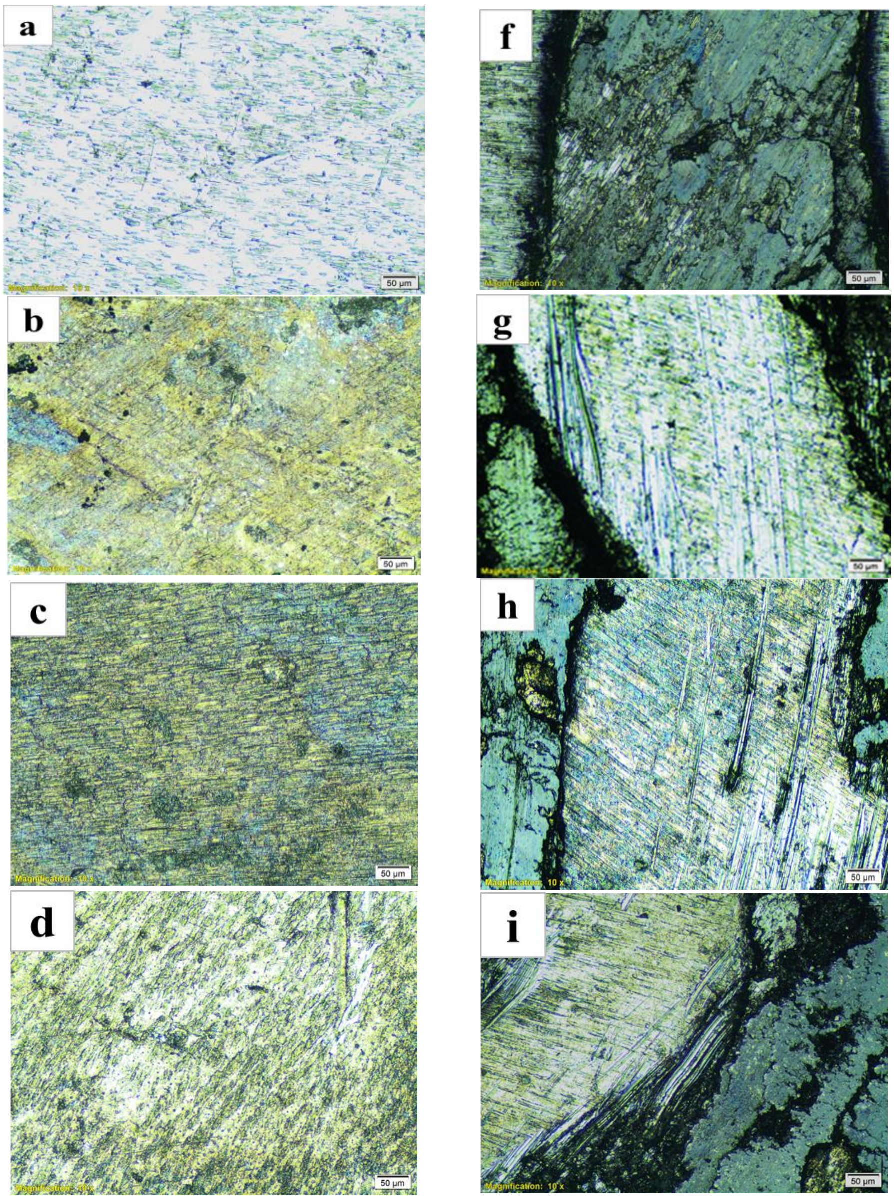
Figure 6. The Images for (a) The minted 25P Egyptian coins, (b) after wear in air, (c) after corrosion for seven days in ASS, and (d) after corrosion for seven days in ASS followed by wear test.

(a) **(b)** **(c)** **(d)**

Figure 7. The Images for (a) The minted 25P Egyptian coins, (b) after wear in air, (c) after corrosion for seven days in ASS, and (d) after corrosion for seven days in ASS followed by wear test.

Figs. 6 and 7 show digital camera images for the minted 25P and 50P Egyptian coins, respectively before (in air) and after (during immersion in ASS) running wear test. Fig. 7 shows that the 50P Egyptian coins surfaces have a brownish yellow corrosion product.

The optical images of wear of minted 25P Egyptian coins at zero (before immersion in ASS) and seven days (after immersion in ASS) are given in Fig. 8. While for minted 50P Egyptian coins were illustrated in Fig. 9. Figs. 8 and 9, optical images revealed almost a uniform structure with some patches of deposits at the beginning of immersion. The corrosion mechanism involves the weakening and the partial removal of the protective oxides layer that spontaneously forms at the alloy surface. This removal of this layer allows the starting of pitting corrosion that eventually leads to the coating failure. Therefore, the key point to improve the corrosion performances is to increase the stability of these oxides layers [34]. In addition, the dezincification of the brass is the main localized corrosion type beside the pitting corrosion [29]. Thus, the pitting corrosion appear in 50P Egyptian coins as shown from Fig. 9.



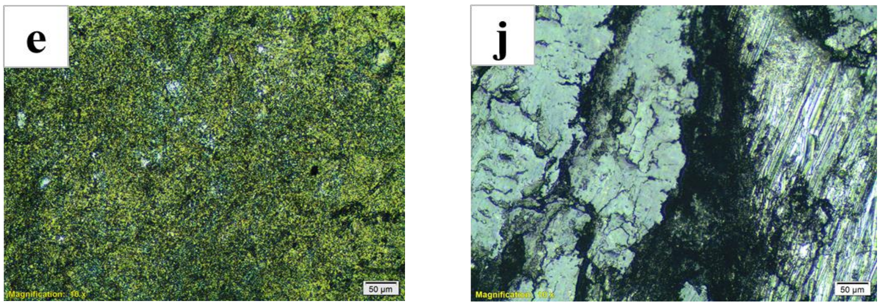
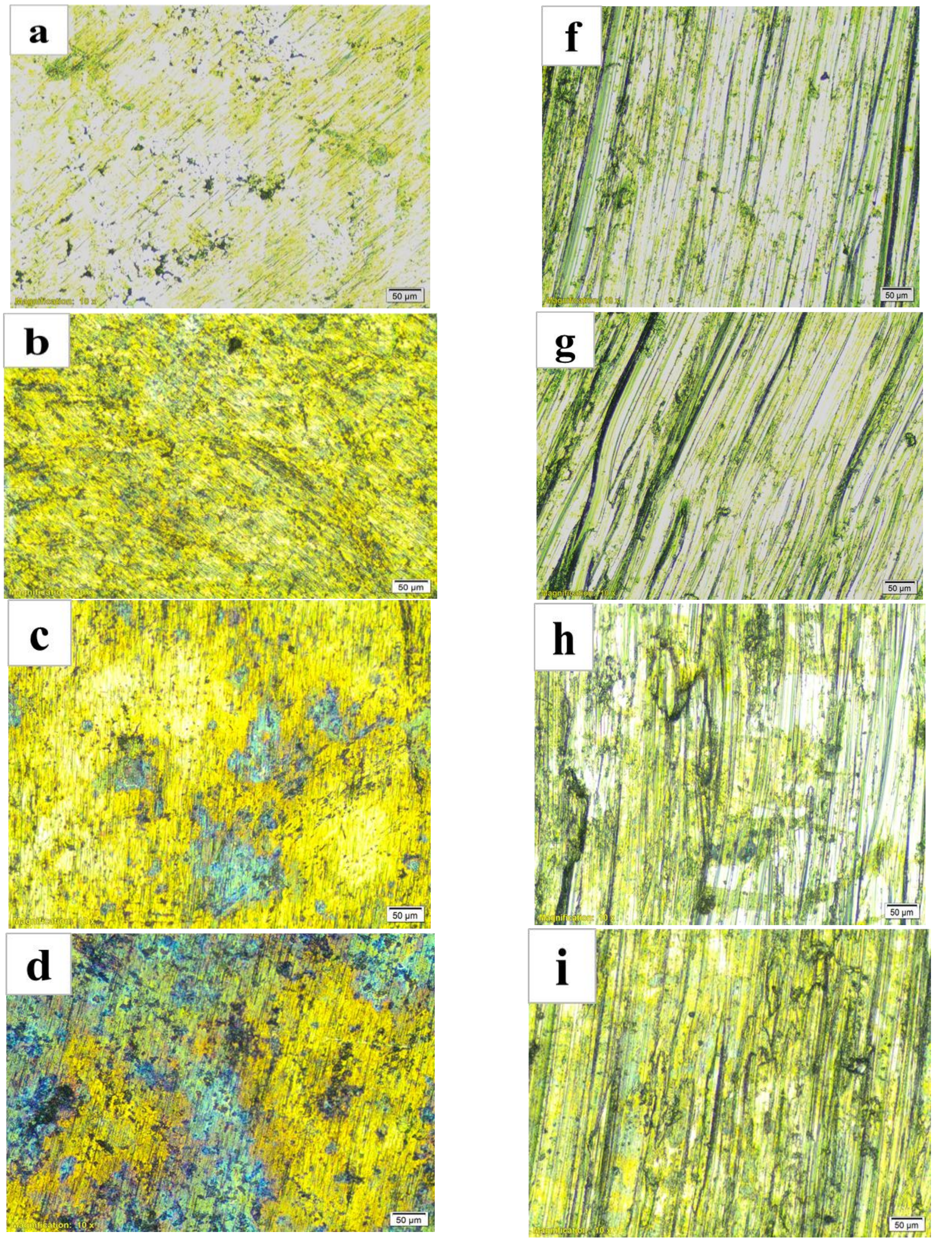


Figure 8. Optical images of minted 25P Egyptian coins after immersion in ASS for (a) 1 h, (b) one day, (c) three days, (d) five days and (e) seven days, and after immersion in ASS followed by wear for (f) 1 h, (g) one day, (h) three days, (i) five days, and (j) seven days



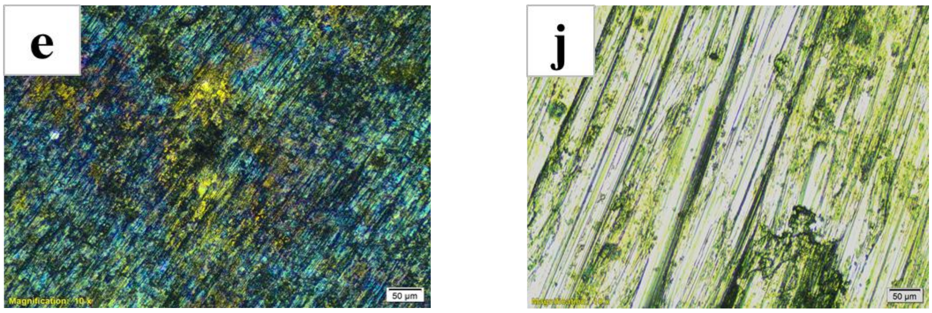


Figure 9. Optical images of minted 50P Egyptian coins after immersion in ASS for (a) 1 h, (b) one day, (c) three days, (d) five days and (e) seven days, and after immersion in ASS followed by wear for (f) 1 h, (g) one day, (h) three days, (i) five days, and (j) seven days,

4. CONCLUSION

The Egyptian coins alloys were studied in ASS by weight-loss and electrochemical (open circuit and potentiodynamic polarization) techniques up to seven days. Commercially, these coins were available as 25P Egyptian coins (nickel-plated steel) and 50P Egyptian coins (brass-plated steel). Weight-loss of the minted coins after seven days cleared that the 25P Egyptian coins were rapidly corroded in comparison to 50P Egyptian coins. The results were confirmed by Atomic Absorption Spectroscopy of immersed minted coins in the ASS. Atomic Absorption Spectroscopy after seven days for minted coins showed that the concentration of Ni-ions released by minted 25P Egyptian coins exceed the safe limit of Ni release. OCP indicated clearly a possibility of oxide film formation on the surface of 25P and 50P coins. From OCP, 25P coins are more active than 50P coins in ASS. Potentiodynamic polarization showed that the corrosion current (I_{corr}) values increased which was attributed to the specific dissolution of Zn for 50P coins (dezincification). The specific wear rate of the corroded minted coins demonstrated that the brass-plated layer was about three times larger than that of the nickel-plated layer. The surface morphology was shown for these coins after immersion in ASS followed by wear that increasing the immersion time, there was a consequent increase in the depth of the scratching of the two types of coins.

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References

1. Y. Salem, E.H. Mohamed, *Nucl. Instrum. Meth.* B, 461 (2019) 247–255
2. S.K. Ross, Routledge, London (2000) 114-242 CE.
3. W. Kapłonek, T. Mikolajczyk, D.Y. Pimenov, M.K. Gupta, M. Mia, S. Sharma, K. Patra, M. Sutowska, *Materials*, 13 (2020) 5371
4. J. Chen, Z. Li, A. Zhu, L. Luo and J. Liang, *Mater. Des*., 34 (2021) 618-623.

5. L. Robbiola, T. Tran, P. Dubot, O. Majerus and K. Rahmouni, *Corr. Sci*., 50(8) (2008) 2205-2215.
6. J.P. Thyssen, D.J. Gawkrodger, I.R. White, A. Julander, T. Menné and C. Lidén, *Contact Derm*., 68(1) (2013) 3-14.
7. G. N. Flint, *Contact Derm*., 39(5) (1998) 213-221.
8. C. Lidén, E. Röndell, L. Skare and A. Nalbanti, *Contact Derm*., 39(3) (1998) 127-131.
9. I. Rezić, L. Ćurković and M. Ujević, *Mater. Corr.,* 61(6) (2010) 524-529.
10. X. Wang, G. Herting, Z. Wei, I.O. Wallinder and Y. Hedberg, *Regul. Toxicol. Pharmacol*., 106 (2019) 15-26.
11. A. Julander, K. Midander, G. Herting, J.P. Thyssen, I.R. White, I.O. Wallinder and C. Liden, *Contact Derm*., 68(6) (2013) 323-330.
12. D.J. Gawkrodger, *Contact Derm*., 68(6) (2013) 321-322.
13. E. Nucera, D. Schiavino, A. Calandrelli, C. Roncallo, A. Buonomo, C. Pedone, C. Lombardo, V. Pecora, T. D. Pasquale, E. Pollastrini and G. Patriarca, *Br. J. Dermatol*., 150(3) (2004) 500-503.
14. I. Milošev and T. Kosec, *Appl. Sur. Sci.,* 254(2) (2007) 644-652.
15. C. Lidén, T. Menné and D. Burrows, *Br. J. Dermatol*., 134(2) (1996) 193-198.
16. H. Zhuang, C. Wang, F. He and Q. Song, *Chem. Pap*., 73(8) (2019) 1863-1869.
17. D. Mamania, M. R. Singh, *J. Appl. Spectrosc*., 86(5) (2019) 948-954
18. P. Verma, G. Lal, M. Singh, *Xray Spectrom*. (2021) 1-9
19. C.H. Liang, S.S. Wang, N.B. Huang and W. Peng, *Trans. Nonferrous Met. Soc*., 25(2) (2015) 654-660.
20. R. J. Rathish, S. Rajendran, J.L. Christy, B.S. Devi, S. Johnmary, M. Manivannan, K. Rajam, P. Rengan, *O. Corr. J*., 3(1) (2010) 38-44.
21. D. Saber, R. Abdel-Karim , A. A. Kandel, Kh. Abd El-Aziz, *Phys. Met. Metallogr*.,121(2) (2020) 188–194.
22. J.P. Randin, *J. Biomed. Mater. Res*., 22(7) (1988) 649-666.
23. Gh. A. Gaber, H.A. Aly, L. Z. Mohamed, *Int. J. Electrochem. Sci*., 15(8), (2020), 8229 – 8240.
24. L.Z. Mohamed, *Egypt. J. Chem*. 64(1) (2021) 133 – 142.
25. L.Z. Mohamed, G. Hamdy, Gh.A. Gaber, *Int. J. Electrochem. Sci*., 16 (2021) 210515.
26. R.G. Parr, R.A. Donnelly, M. Levy, W.E. Palke, *J. Chem. Phys.,* 68(8) (1978) 3801-3807.
27. A. M. El-Shamy, Y. Reda, K. M. Zohdy, , A.K. Eessaa, *Egypt. J. Chem*., 63(2) (2020) 579-597 (2020)
28. R.P. Nair, D. Griffin, N.X. Randall, *Wear*, 267(5-8) (2009) 823-827.
29. C. Liangi, S. Wang, N. Huang, P. Wang, *Trans. Nonferrous Met. Soc. China*, 25(2015) 654−660
30. T. Pavesi, J.C. Moreira, *Contact Derm*., (2020) 1–6
31. J. P. Randin, *Werks. Korros*., 38 (1987) 233-236
32. M.H. Staia, E.J. Castillo, E.S. Puchi, B. Lewis, H.E. Hintermann, *Surf. Coat. Technol*., 86-87 (1996) 598-602
33. A. Sharma, A.K. Singh, *Cent. Eur. J. Eng*., 1(3) (2011) 234-243
34. S. Caporali, U. Bardi, *Corrosion*, 68(2) (2012) 025001-1: 02001-8