J. Mater. Environ. Sci. 5 (5) (2014) 1557-1564
ISSN : 2028-2508
CODEN: JMESCN

Study of the behavior of Moroccan coin ½ DH in a simulated sweat solution and 3% NaCl

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Received 14 Feb2014; Revised 27 May 2014; Accepted 27 May 2014

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Abstract

The copper-nickel alloy is known for its good corrosion resistance in different environments. It also has good mechanical properties. This alloy has been used for the manufacture of coins for the first time in the United Kingdom in 1947. In this work, we studied the behavior of one of the most used pieces of Moroccan currency (the coin of ½ DH type 2002) in different medium: acidic or neutral (artificial sweat, 3% NaCl and 3% NaCl at pH = 2). This coin is composed of 75% copper and 25% nickel. The results showed by Atomic Absorption Spectrophotometer and electrochemical measurements that the coin ½ DH resists in a neutral medium (artificial sweat and 3% NaCl). The amounts of Ni^{2+} and Cu^{2+} released after seven days of the two media is: $[Cu^{2+}]_{\text{(Sueur Artificial)}} = 37.8$ mg / l $[Ni^{2+}]_{\text{(Sueur Artificial)}} = 11.9$ mg / l, $[Cu^{2+}]_{\text{(3\% NaCl)}} = 59.1$ mg / l and $[Ni^{2+}]_{\text{(3\% NaCl)}} = 16.1$ mg / l. Therefore, its manipulation is not very dangerous. Against, in the solution of 3% NaCl at pH = 2, the quantity Ni^{2+} and Cu^{2+} released is significant, $[Cu^{2+}]_{\text{(3\% NaCl)}} = 59.1$ mg / l and $[Ni^{2+}]_{\text{(3\% NaCl)}} = 16.1$ mg / l. Furthermore, we found that the coin releases more copper than nickel in the three medium. This confirms the trend to substitute cupronickel alloy by nickel or steel nickel coated.

Keywords: Coins, Copper-nickel, Sweat, 3% NaCl, Corrosion

1. Introduction

For decades, the man uses coins as an intermediary of trade and contracts. The coins were made of bronze, gold, silver and copper-nickel alloy since 1850 [1-2]. This evolution in the choice of metal or alloy is the result of a compromise between corrosion resistance and wear resistance and also the ease of implementation and low cost. Currently, the alloys of nickel and copper are the most used.

Nevertheless, it is well known that the direct contact of nickel with the skin can cause allergic reactions when it is easily released [3-4]. Free nickel ions are the source of the outbreak of dermatitis in susceptible individuals [5]. Nickel sensitivity increases with the exposure time, it can reach a third of the population in the main risk group, namely women wearing jewelry such as nickel objects [6]. Some authors believe that in industrialized countries more than 10% of women and 2% of men suffer from more or less severe this allergy [7]. These observations are at the origin of a European legislative regulation and implementation of the Nickel Directive in the EU (94/27/EC) [8]. The conclusions of studies on the euro coins are contradictory. Some have asserted that they release more nickel that the ancient national currencies such as the franc with a greater risk to human health [9]. Other studies suggest that euro coins do not pose a significant risk to human health due to a too brief contact with the skin [10]. Moreover, the copper can also cause some of the symptoms such as platelets decreased, the deterioration of pancreatic function.

In this study, our aim is to determine the behavior of the coin ½ DH, one of the most used in Morocco, in contact with different solutions and then evaluate the amount of released ions.

2. Materials and Methods

2.1. Composition of coins

The composition of the coins varies with different vintages outputs on the market. Table 1 gives the nominal characteristics of components Moroccan currency ½ DH compared to parts 1 DH, since the first vintage (1965) until the 2002 [11].

Table 1: Nominal characteristics of parts of Moroccan currency ½ DH.

Denomination	Aspect	Composition in surface %	Diameter (mm)	Weight (g)
1 DH 1965, 1968 et 1969	White	Ni100	24	**6**
1 DH 1974, 1987 et 2002	White	Cu75 Ni25	24	**6**
½ DH 2002	White	Cu75 Ni25	21	**4**

Front **Back**

Fig. 1: Photograph of the piece of Moroccan currency ½ DH 2002 version [12]

2.2. Preparation of samples

Parts ½ DH studied are used. Before putting them in contact with the solutions: artificial sweat NaCl 3% and 3% NaCl at pH = 2 using the method described in BS EN [13], each piece has been pre-treated:

- Distilled water at pH≈6
- 3wt% NaCl at pH= 6,45 (similar to a marine environment).
- Artificial sweat

The artificial sweat solution used for metal release immersion tests was prepared similar to EN1811, using 0.5 wt% sodium chloride, 0.1 wt% lactic acid, 0.1 wt% urea and normal ultrapure water.The pH of the solution was adjusted to pH 6.5 using 1 wt% ammonia solution. The artificial sweat solution was stored in darkness and used within 3 hr of preparation.

- Temperature study is 26 ± 1 °C
- Slight polishing, rinsing with distilled water, degreasing with acetonedrying in the open air and weighing to determine the initial mass.

2.3. Experimental Protocol

The kinetic study was carried out in two different ways by monitoring over time:

- Weight loss of the contact: We immersed, at room temperature, a coin ½ DH for various times: 1, 5, 7, 10, 15, 20, 25, 30, 35, 40 and 45 days in 50 ml each of three solutions.

Then, the parts are rinsed with distilled water, dried in open air and weighed (weight of the final determination). Thus, a change in mass was determined:

$$\Delta m = \text{initial weight} - \text{final weight}$$

- The change in the concentration of Ni^{2+} and Cu^{2+} ions in the supernatant solution: Metal components (copper and nickel) released in the leachate were determined by Atomic Absorption Spectrophotometer with a device type Unicam 929 AA Spectrometer.

- Electrochemical measurements were carried out in a conventional three-electrode glass cell with a platinum counter electrode and (Ag/AgCl) as reference. All tests were performed in continuously stirred conditions at room temperature; all tests were performed at 308 K. Potentiodynamic curves-polarization experiments were undertaken by (Radiometer-analytical PGZ 100) and controlled with analysis software (Voltamaster 4). The mild steel electrode was maintained at open circuit conditions (corrosion potential, Ecorr) for 1 h and thereafter pre-polarized at -1200 mV for 15 min. After this scan, the potential was swept to anodic potentials at 300mv. The cathodic branch was always determined first; the open-circuit potential was then re-established and the anodic branch determined. The anodic and cathodic polarization curves were recorded by a constant sweep rate of 1 mV s−1.

3. Results and Discussion

3.1. Weight variation

The Weight variation (Δm) coins ½ DH type 2002 for the three series of measurements is given in Table 2. First, we note that it follows the same pattern in the three environments considered.

Thus, we find a weight loss in three phases based on the time of immersion of the coin (fig 2). During the first 24 hours, we observe a slight loss of weight. Then, on the second day, we record a linear increase in Δm, more or less rapidly depending on the medium. In solutions of artificial sweat and 3% of NaCl, the weight loss is multiplied by five between the first and second day of immersion, while in 3% NaCl acidified, it is multiplied by a factor of 9. This evolution was maintained until the twentieth day (Table 2). Indeed, the slope of this straight is much greater in the case of the 3% NaCl solution at pH = 2 (Table 3).

Table 2: Change in ½ DH coin weight (Δm) in artificial sweat, NaCl 3% and NaCl 3% at pH = 2 as a function of time

Immersion time (Days)		**1**	**5**	**7**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**
Δm (mg)	**artificial sweat**	1,7	8,9	13,1	32,7	72,3	114,5	131,5	140,4	146,6	147,7	148,2
	3% NaCl Neutral	2,2	11,4	21,3	46,3	87,2	130,6	145,3	154,2	158,8	159,4	159,8
	NaCl 3% at pH=2	3	27	90,8	223	415	607	681	732	755	760	762

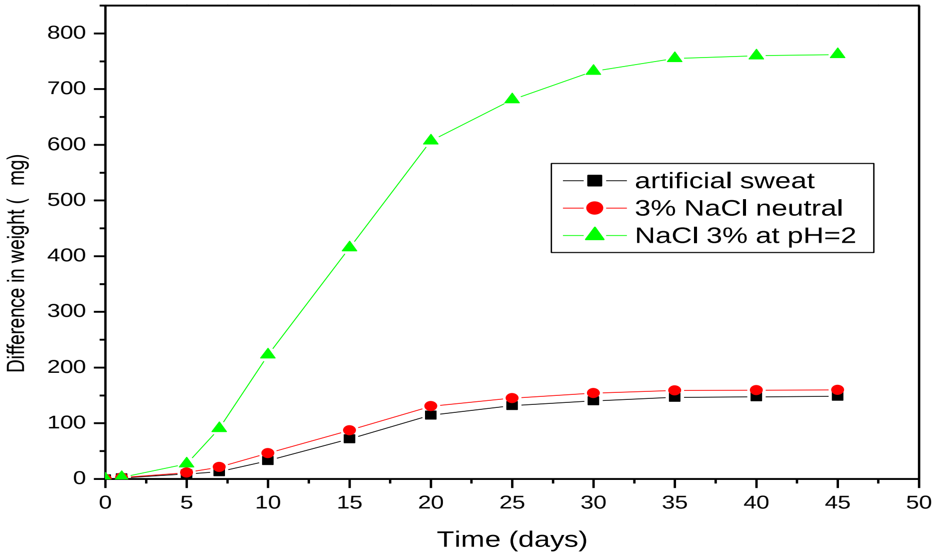

Fig.2: Evolution of the weight loss of the coin ½ DH 2002 during the immersion time in artificial sweat, NaCl 3% and NaCl 3% at pH = 2

Table 3: Slope of the weight variation in artificial sweat, NaCl 3% and NaCl 3% at pH = 2 (In the range of 5 to 20 days)

Medium	Slope (mg / day)
NaCl 3% solution at pH = 2	38,7
NaCl 3% solution	7,9
The artificial sweat solution	7,0

Beyond the 20th day, weight loss becomes practically independent of immersion time of the coin in the different solutions. In fact, Figure 1 shows a plateau at 148 in the artificial sweat mg, 160 mg in 3% NaCl and 760 mg in 3% NaCl at pH = 2. This would be attributed to the formation of corrosion products on the surface of the coin that would slow down the deterioration. Nevertheless, we still find that in the most aggressive (3% NaCl at pH = 2) medium weight loss recorded is five times larger compared to neutral medium. This indicates that the piece of ½ DH is degraded in the acidic medium.

3.2. Potentiostatic measures

Previous results were confirmed by measurements of corrosion potential and corrosion current by the stationary method in the three medium (Table 4).

- We observe that the attack is much greater in the NaCl 3% solution acidified. Thus, the corrosion potential is more cathodic and the corrosion current is much higher in this medium. We record a corrosion current of around 1 $\mu A.cm^{-2}$ in solutions of artificial sweat and NaCl 3% and 25 $\mu A.cm^{-2}$ for the NaCl 3% solution acidified at pH = 2.
- We also observe that Ecorr of the coin ½ DH Type 2002 in the 3% NaCl solution at pH = 2 is more negative compared to 3% NaCl and in artificial sweat, because potential slightly more cathodic and the Alloys with Ni content < 30% show relatively higher corrosion, was approved by W. A. Badawy and all [14].

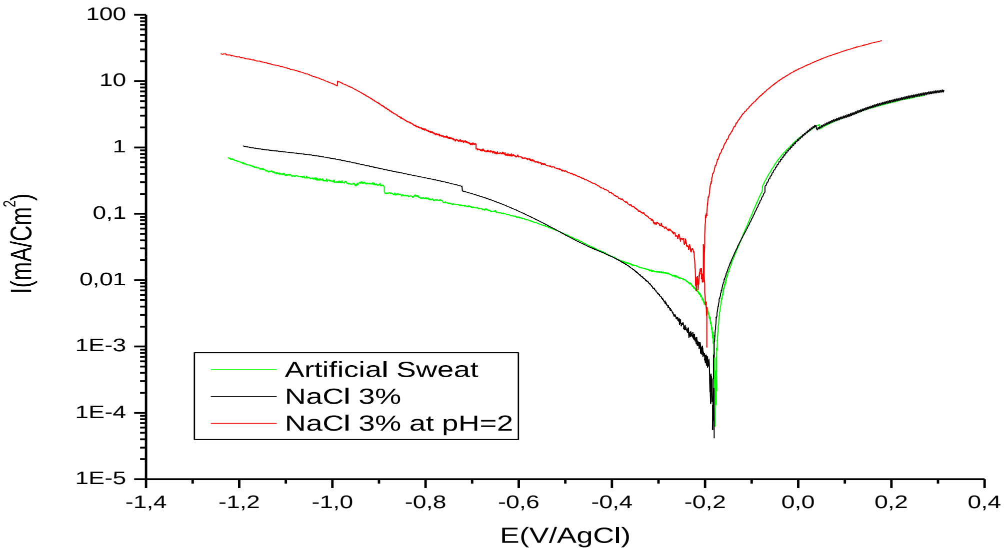

Fig.3: Polarization curves of the coin ½DH Type 2002 in the artificial Sweat, 3% NaCl and 3% NaCl at pH=2

Table 4: Corrosion potential and corrosion current in the three medium

Medium	**Ecorr** (mV/Ag/AgCl/KCl)	**Icorr** ($\mu A.cm^{-2}$)
The artificial sweat solution	-180	0.9
NaCl 3%	-180	1.2
NaCl 3% at pH=2	-200	25

3.3 SEM Observations

The observations in SEM of samples immersed in the three media also showed a much severe attack in the medium 3% NaCl at pH 2 (SEM micrographs 3-6)

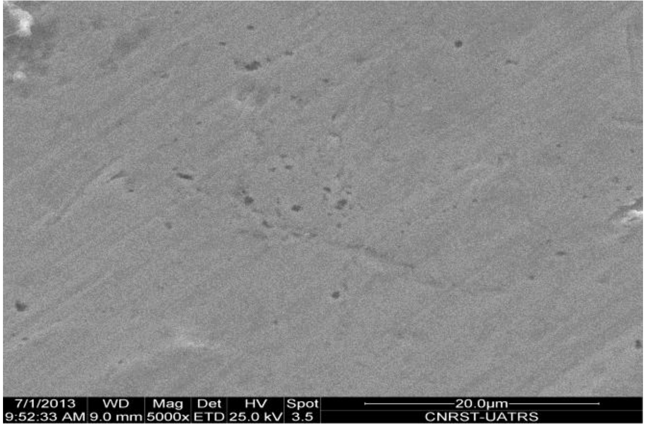

Fig.4: SEM micrograph of new coin not attacked (reference)

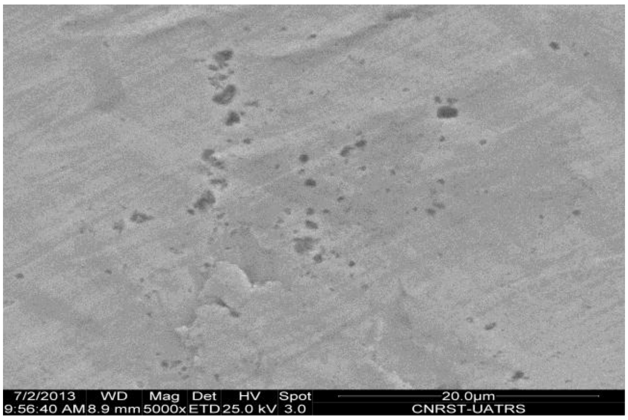

Fig.5: SEM micrograph of coin immersed in artificial sweat for 7 days

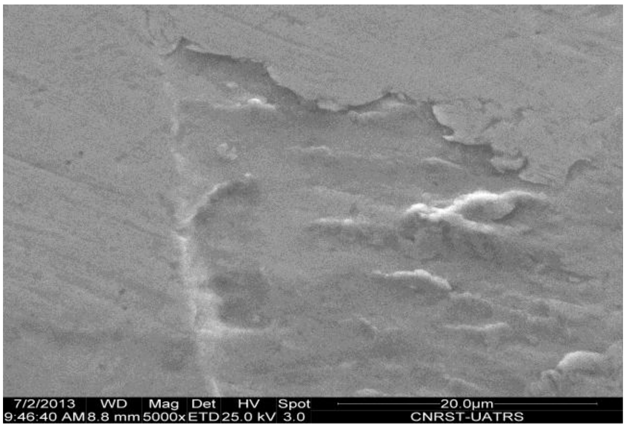

Fig.6: SEM micrograph of coin immersed in NaCl 3% for 7 days

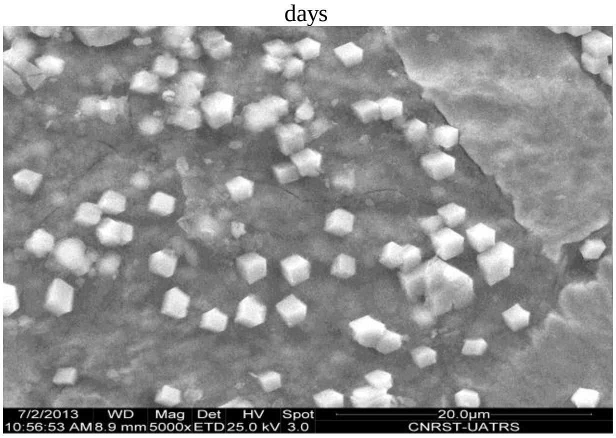

Fig.7: SEM micrograph of Coin immersed in NaCl 3% à pH = 2 for 7 days

When we observe the samples surface after immersion in the three medium compared to the reference state (Fig.3), we realize a more or less pronounced degradation. In the artificial sweat medium, piece of ½ DH is slightly attacked confirming its strength (Fig. 6). This attack intensifies slightly in medium NaCl 3%, the surface becomes roughened (Fig. 7). By against, in 3% NaCl at pH = 2, there is a degradation of the coin with nodules at the surface (Fig 6).

3.4. Concentration of copper and nickel in various media

It was interesting to follow the concentration of metal ions in solution to determine oxidation kinetic of each element constituting the piece of ½ DH.

3.4.1. Copper concentration

The copper concentrations in the artificial sweat, NaCl 3% and NaCl 3% at pH=2 as a function of the immersion time are reported in Table 5.We note, in a first time, a very slow copper oxidation during five days for the three solutions and it explained by the formation of a protective film [15]. Then, the kinetic accelerates between five and twenty days. The evolution becomes almost linear in the three mediums studied. Finally, it reaches a plateau due to the presence of a film formed by the corrosion products which protects the coin. Concentrations reach the following values:

- in artificial sweat : [Cu] = 270,4 mg/l ;
- in NaCl 3% : [Cu] = 296,9 mg/l
- in NaCl at pH = 2 : $[Cu]_{(NaCl\ 3\%\ à\ pH=2)}$ =1547,7 mg/l.

Table 5: Evolution of copper concentration in the artificial sweat, NaCl 3% and 3% NaCl at pH = 2 as a function of immersion time

Immersion time (Days)		**1**	**5**	**7**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**
[Cu] (mg/l)	**artificial sweat**	3.6	24.2	37.8	94.5	167.9	225.3	248.1	259.2	265.5	269.4	270.4
	NaCl 3% Neutral	4.2	31.9	59.1	119.7	192.2	250.9	273.1	286.7	293.7	295.3	296.9
	NaCl 3% at pH=2	5.9	62.1	186.2	629.6	1028.5	1267.2	1390.3	1490.5	1534.6	1546.2	1547.5

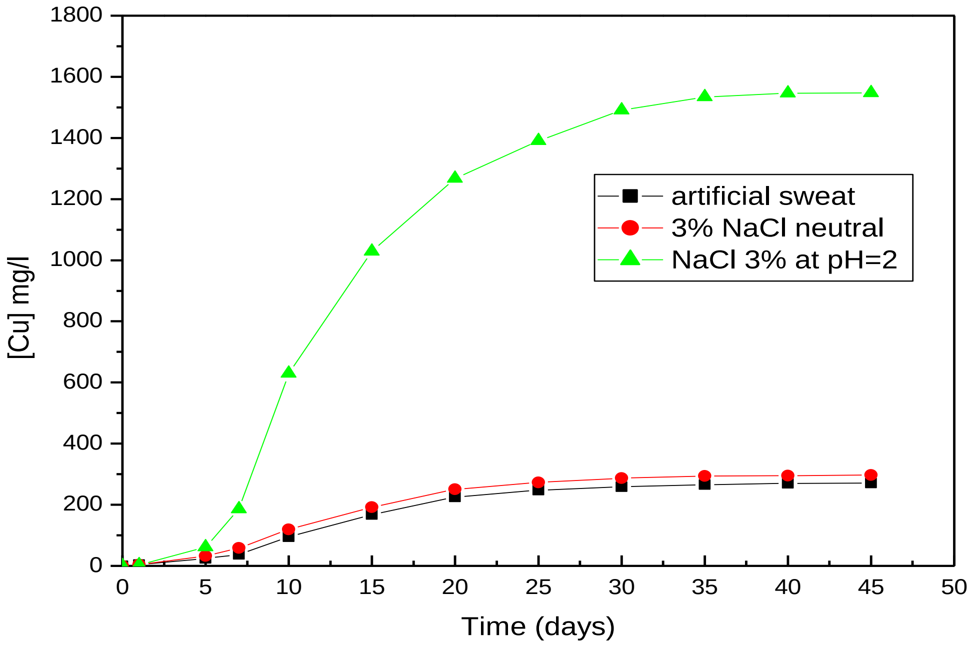

Fig.8: Evolution of the copper concentration released by the coin ½ DH Type 2002 in the artificial sweat, 3% NaCl and 3% NaCl at pH = 2

3.4.2. Nickel concentration

Table 6 includes the nickel content as a function of immersion time in artificial sweat solution, 3% NaCl and 3% NaCl at pH = 2.

Immersion time (Days)		**1**	**5**	**7**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**
[Ni] (mg/l)	**artificial sweat**	1,2	8,4	11,9	31,2	54,7	72,4	80,9	86,3	90,2	91,1	91,5
	NaCl 3% Neutral	1,5	10,8	16,1	38,5	63,4	83,7	89,8	94,3	97,8	98,2	98,6
	NaCl 3% at pH=2	3,1	22,4	60,8	207,2	349,3	418,2	459,1	492,3	507,3	512,0	512,6

Tableau 6: Evolution of nickel concentration in the artificial sweat, NaCl 3% and NaCl 3% at pH = 2 as a function of immersion time

We note that the evolution of the nickel content in the media studied goes through three phases. In the first stage, there is a slow release of nickel in the three medium for five days. The second phase lasted fifteen days where we recorded an accelerated release of nickel ions especially in the 3% NaCl solution at pH = 2 (five times more than other solutions). From the twentieth day, the evolution of released nickel reached a level of saturation. Metal dissolution would be blocked by the formation of corrosion products on the surface:

- in artificial sweat : [Ni] = 91,5 mg/l
- in NaCl 3% : [Ni] = 98,6 mg/l
- in NaCl at pH = 2 : [Ni] =512,6 mg/l

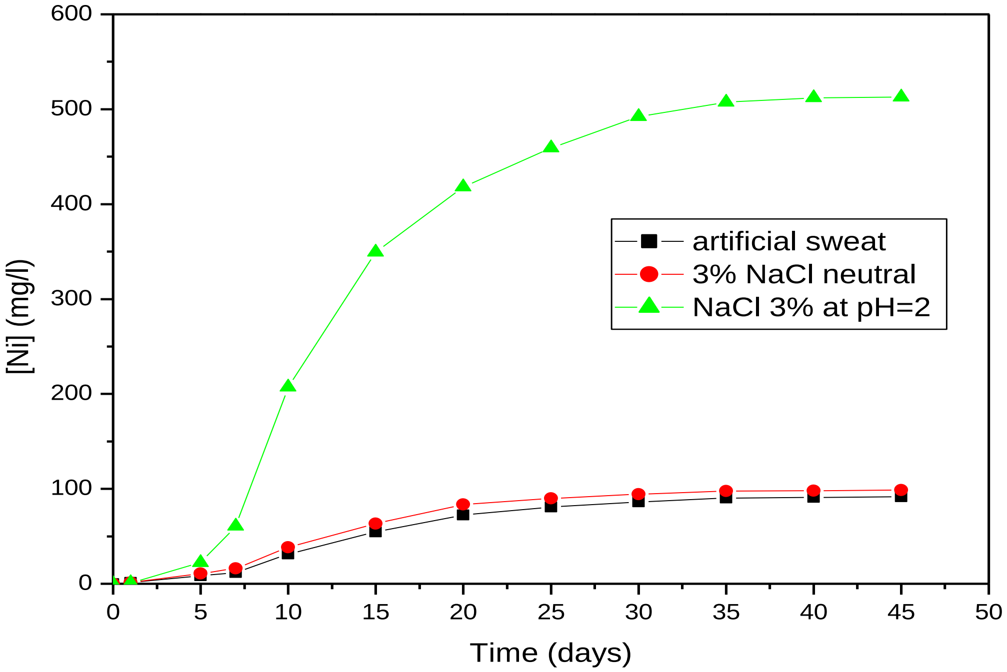

Fig.9: Evolution of the nickel concentration released by the coin ½ DH Type 2002 in the artificial sweat, NaCl 3% and 3% NaCl at pH = 2

Conclusion

Our study showed that the coin ½ DH presents a fairly good resistance in solutions of artificial sweat and 3% NaCl. As against, in a 3% NaCl solution at pH = 2, it has some damage. Thus, we recorded a five times higher mass loss in NaCl 3% medium acidified by the other two solutions. This result was confirmed by measurements of corrosion current and observations by scanning electron microscope. Similar results were found by Sławomir Smolik and All in studies on parts of European currencies (Euro 1 and 2) and Poland (PLN 2 and 5 PLN) [16].

Nevertheless, we will point that mass loss reached a nevel probably due to the formation of corrosion products on the surface of the part that block oxidation. Indeed, Colin and al showed that Cu_2O is the principal composed in the surface of Cu-Ni alloys exposed to synthetic sweat [17]. However, other studies have shown, by XPS measures, the existence of the oxygen in position 1s indicate the presence of hydroxide at the surface, might nickel hydroxide [18]. These observations were confirmed by N. Marya and all who mentioned that the Cu-Ni alloys are covered by an oxide / hydroxide porous layer which does not allow a total surface protection but slows the corrosion process [19]. Also we showed that the coin ½ DH releases much more copper than nickel during its immersion in the three solutions chosen. This confirms the decisions taken in 2012 by the leaders to refrain from the Ni-Cu in Moroccan coin and opt for a nickel coating on steel.

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(2014) ; http://www.jmaterenvironsci.com