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Application of Cosmetic Argan Oil as green Corrosion Inhibitor for Copper in phosphoric acid medium

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Abstract
Cosmetic Argan Oil (CAO) was tested as inhibitor for copper corrosion in 2 M H_3PO_4 containing 0.3M of NaCl. The techniques used in this work were weight loss measurements and potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS). The inhibition efficiency was found to increase with inhibitor content to attain 97% for CAO at 7g/L. Inhibition efficiency E (%) obtained fromgravemitric and electrochemical methods are in reasonably good agreement. Results confirm the performance of copper in phosphoric medium containing CAO.

Keywords: *Corrosion; Copper; Inhibition; Argan oil***.**

Introduction
Phosphoric acid is produced in large quantities in Morocco. It is widely used in industries, for example, in the food industry, acid pickling, acid cleaning and acid desalting.
Copper is used widely in industry, because of his good thermal conductivity and mechanical properties. Copper is a relatively noble metal. Nevertheless, it reacts easily in ordinary environments containing oxygen. Thus, the study of its corrosion inhibition has attracted much attention. Copper corrosion depends not only on the nature of the environment but also of the condition of use on materials. Most work on copper corrosion reveals that the presence of aggressive elements such as chloride and sulfide accelerates the corrosion of this metal [1–3]. The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media [4].Large numbers of organic compounds were studied and are being studied to investigate their corrosion inhibition potential. All these studies reveal that organic compounds especially those with N, S and O showed significant inhibition efficiency [5–15]. But, unfortunately most of these compounds are not only expensive but also toxic to living beings. It is needless to point out the importance of cheap, safe inhibitors of corrosion. Plant extracts are environment friendly, bio-degradable, non-toxic, easily available and of potentially low cost. Most of the naturally occurring substances are safe and can be extracted by simple procedures. Recent literature is full of researches which test different extracts for corrosion inhibition applications. The examples are numerous such as Argan Hulls [16], Thymus capitatus [17-18], Fenugreek [19], Artemisia [20], Hibiscus sabdariffa [21], Oxandra asbeckii [22], Citrus paradise [23] and Anacyclus pyrethrum L. [24].
In this work, the inhibitive action of cosmetic argan oil (CAO), as an inexpensive, eco-friendly, naturally occurring substance, on the corrosion of copper in 2 M H_3PO_4 solution containing 3.10^{-1} M NaCl has been studied by electrochemical techniques potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

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2. Materials and methods

2. 1 Weight loss measurements

Gravimetric methods were conducted on copper test samples of a total surface of 12 cm^2. All experiments were carried out under total immersion in 75 ml of test solutions. Mass loss was recorded by an Analytical balance. Prior to each gravimetric or electrochemical experiment, the surface of the specimens was polished successively with emery paper up to 1200 grade, rinsed thoroughly with acetone and bidistilled water before plunging the electrode in the solution. Pure copper samples (99%) were used. The experiments were carried out in 2M H_3PO_4 medium containing different concentration of NaCl; it was prepared by dilution of Analytical Grade 84% H_3PO_4 with bidistilled water and pure NaCl.

2.2 Electrochemical tests

The current–voltage characteristics are recorded with a potentiostat PGZ100 piloted by Voltamaster soft-ware. The scan rate is 30 mV/min and the potential is ranged from catholic to anodic potentials. Before recording each curve, the working electrode is maintained with its free potential of corrosion E_{corr} for 30 min. The polarisation curves are obtained from −800 mV/SCE to 500 mV/SCE. We used for all electrochemical tests a cell with three electrodes and double wall thermostats (Tacussel Standard CEC/TH). Saturated calomel (SCE) and platinum electrodes are used as reference and auxiliary electrodes, respectively. The working electrode is in the form of a disc from pure copper of the surface 1 cm^2.

3. Results and discussion

3.1 Weight loss, corrosion rates and inhibition efficiency

Gravimetric measurements of the copper immersed in 2 M H_3PO_4 + 3.10^{-1} M NaCl in the absence and presence of the inhibitors at various concentrations (Table 1). In the same table, it summarizes Inhibition efficiency values E_w (%) of CAO at different concentrations. We noted that E_w (%) was calculated as follows:

$$E_W(\%) = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100 \qquad (1)$$

where W_{corr} and W'_{corr} are the corrosion rate of copper in 2 M H_3PO_4 + 3.10^{-1} M NaCl in the absence and presence of CAO inhibitor, respectively.

Table 1: Copper weight loss data and inhibition efficiency of CAO in 2 M H_3PO_4 + 0.3 M NaCl

Concentration (g/L)	**W'_{corr}(mg.j^{-1}. dm^{-2})**	**E_w(%)**
0	162	-
1	62	62
5	26	84
7	3	98

It is clear that the corrosion rate W'_{corr} decreases with the increase of concentration of the tested inhibitors and in turn the inhibition efficiency (E_w%) increases to attains 98% at 7g/L of CAO. From weight loss measurements, we can conclude that CAO is a good inhibitor.

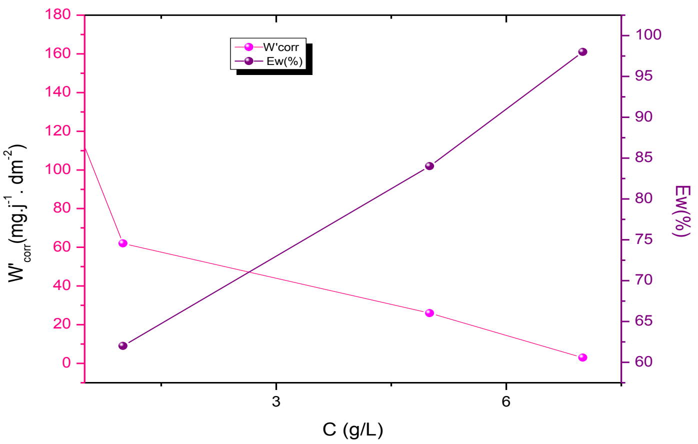

Figure 1. Variation of corrosion rate (W'_{corr}) and inhibition efficiency (E_w) of corrosion of copper in 2 M H_3PO_4 + 3.10^{-1} in the presence of CAO.

3. 2 Polarization curves

The cathodic and anodic polarization curves of the copper immersed in 2 M H_3PO_4 + 3.10^{-1}M NaCl in the presence and absence of at different concentrations at 298 K are presented in Fig. 2. Values of the associated electrochemical parameters are given in Table 2.

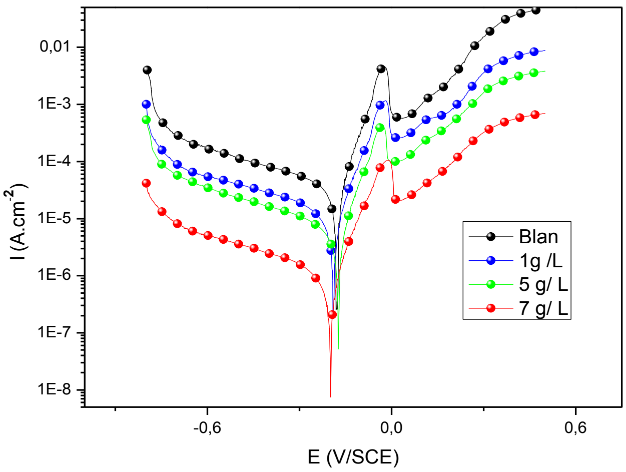

Figure 2: Cathodic and Anodic polarisation curves of copper in (2M H_3PO_4+ 3.10^{-1}M NaCl) in the presence of Cosmetic Argan oil at different concentrations.

In this case, the inhibition efficiency is defined as follows:

$$E_i(\%) = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100 \qquad (2)$$

where I_{corr} and I'_{corr} are the uninhibited and inhibited current density, respectively.

The examination of Fig. 2 and Table 2 reveals that the corrosion current (I_{corr}) decreased prominently and inhibition efficiency increased with inhibitor concentration. The presence of CAO does not remarkably shift the corrosion potential (E_{corr}) and hence, it can be said to be a mixed type inhibitor in (2M H_3PO_4+ 3.10^{-1}M NaCl).We also remark that the cathodic current–potential curves give rise to parallel Tafel lines, which indicate that hydrogen evolution reaction is activation controlled and that the addition of the CAO does not modify the mechanism of this process [25]. The inhibition efficiency reaches 95% at 7g/l of oil tested. Consequently, CAO is a good inhibitor.

Table 2: Electrochemical parameters of copper at various concentrations of COA in (2M H_3PO_4+ 0.3M NaCl) and the corresponding inhibition efficiency

CAO (g/l)	**E_{corr} (mV/SCE)**	**I_{corr} (µA/cm^2)**	**b_c (mV/dec)**	**Ei (%)**
0	-177	36	-297	-
1	-192	14	-487	61
5	179	7	-486	81
7	-195	2	-471	95

3.3. Electrochemical impedance spectroscopy measurements

The corrosion behavior of copper in the acidic solution in the absence and presence of inhibitor was also investigated by the EIS method at 298 K. The inhibition efficiency can be calculated by the following formula:

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$$E_{Rt}\% = \frac{(R_t - R_t^0)}{R_t} \times 100 \qquad (3)$$

Here $\boldsymbol{R_t}$ and $\boldsymbol{R_t^0}$ are the charge transfer resistances in inhibited and uninhibited solutions respectively.
The values of the charge transfer resistance were calculated by subtracting the high frequency intersection from the low frequency intersection [26]. TThe corresponding Niquist diagrams are represented in figure 3. Double layer capacitance values C_{dl} were obtained at the frequency (f_{max}), at which the imaginary component of the Nyquist plot is maximum, and calculated using the following equation.

$$C_{dl} = \frac{1}{\omega . R_t} \quad \text{with} \quad \omega = 2\pi\, f_{max} \qquad (4)$$

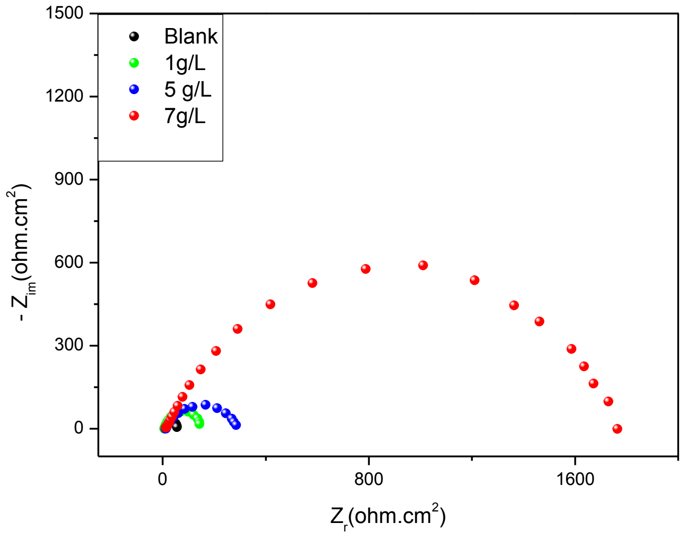

Figure 3. Nyquist diagrams for copper electrode in (2M H_3PO_4+ 3.10^{-1}M NaCl) with and without C*AO* after 30min of immersion at E_{corr}.

The impedance parameters derived from this investigation are given in Table 3. It is worth noting that the presence of inhibitor does not alter the profile of impedance diagrams which are almost semi-circular (Fig. 3), indicating that a charge transfer process mainly controls the corrosion of copper. In fact, the presence of inhibitor enhances the values of R_t in the acidic solution. On the other hand, the values of C_{dl} decreased with an increase in the inhibitor concentration. This was due to an increase in the surface coverage by this inhibitor, resulting into an increase in the inhibition efficiency. Thus, the change in C_{dl} values was caused by to the gradual replacement of water molecules by the adsorption of the organic molecules on the metal surface, decreasing the extent of metal dissolution [27].

Table 3. Impedance parameters for corrosion of copper in (2M H_3PO_4+ 3.10^{-1}M NaCl) at various concentrations of CAO.

CAO (g/l)	R_t(Ω.cm^2)	f_{max}(Hz)	C_{dl}(μF/cm^2)	E_{RT} (%)
0	51	63	49	-
1	141	40	28	64
5	281	22	25	82
7	1755	11	08	97

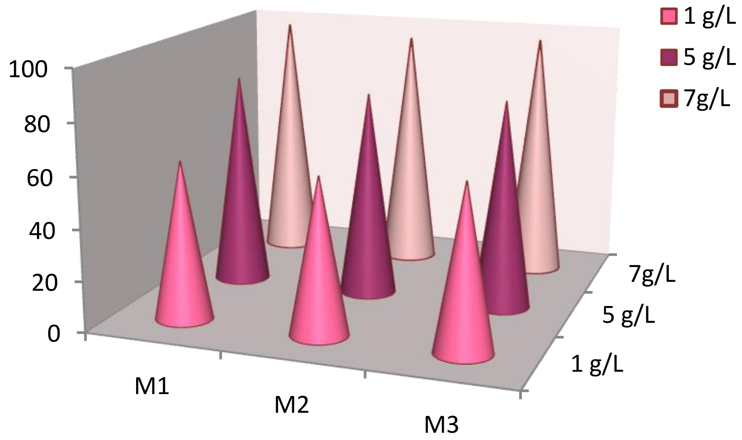

Figure 4 . Comparison of inhibition efficiency (E %) values obtained by weight loss(M1), (M2) and EIS methods (M3).

A comparison may be made between inhibition efficiency E (%) values obtained by different methods (weight loss, polarization curves and EIS methods). Figure 4 shows a histogram that compares the E (%) values obtained. One can see that whatever the method used, no significant changes are observed in E (%) values. We can then conclude that there is a good correlation with the three methods used in this investigation at all tested concentrations and that Cosmetic Argan Oil is an efficient corrosion inhibitor.

Conclusion

From the above results and discussion, the following conclusions are drawn:

- Cosmetic Argan Oil acts as a good inhibitor for the corrosion of copper in 2M $H3PO_4$ + 0.3M NaCl.
- The inhibition efficiency of CAO increases with the concentration to attain a maximum value 97 % at 7g/L.
- CAO is a mixed inhibitor and its molecules block both the anodic and cathodic sites of the metal surface.
- The results obtained from weight loss measurements and potentiodynamic polarisation are in reasonably good agreement.

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