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Olive mill wastewater (OMW) as corrosion inhibitor for copper in NaCl solution

M. Masmoudi[*], C. Rahal, M. Bouaziz, R. Abdelhedi
Laboratory of Electrochemistry and Environment, Sfax National Engineering School (ENIS) BPW 3038 Sfax. University of Sfax. Tunisia.

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[*]*Corresponding Author. E-mail: med_mmasmoudi@yahoo.fr (+216 27 75 23 24)*

Abstract

OMW is greatly enriched in hydroxytyrosol (HT) and slightly in tyrosol. This compound acts as mixed-type corrosion inhibitor for copper in 3 % NaCl solution. The molecules of this inhibitor physically adsorbed onto both anodic and cathodic sites of the copper surface. Adsorption of this inhibitor on the copper surface obeys the Langmuir adsorption isotherm. The free energy of adsorption (-30.50kJ mol^{-1}) reveals a strong physical adsorption of the HT on the metal surface. The exceptional effect of this inhibitor is above E_{corr}. The passivation range greatly increases upon addition of inhibitor and increases further with increasing HT concentration.

Keywords: Olive Mill Wastewater, Hydroxytyrosol, Corrosion, Copper.

1. Introduction

Olive mill wastewaters (OMWs) have a direct impact on the environment due to the aesthetic degradation caused by their strong odor and dark color and due to their high organic fraction [1]. However, in the last years OMWs have received increasing attention for the presence of high added value compounds, such as antioxidant substances and phenols OMWs can be considered as an inexpensive, potential source of high added value powerful natural antioxidants comparable to some synthetic antioxidants commonly used in the food industry [2-6]. Consequently, several valorization approaches have been investigated to recover fine bioactive chemicals from OMWs that can be exploited for pharmaceutical, nourishment and cosmetic applications. Numerous works were used some natural extract, containing phenolic compounds, as a corrosion inhibitor [12-19]. Promising results were obtained in this field.

This work is devoted to examining the stored Olive mill wastewaters (hydroxytyrosol) as an inhibitor for corrosion of pure copper in NaCl 3% solution.

2. Materials and methods

2.1. HPLC analysis

The identification of phenolic compounds was carried out using HPLC system (Ultimate 3000, Dionex, Germany).The HPLC system was equipped with a pump (LPG-3400SD), column oven and diode-array UV/VIS detector (DAD-3000RS). The output signal of the detector was recorded using Dionex ChromeleonTM Chromatography Data System. The separation was executed on an Inertsil ODS-4 C18 colomn (5µm, 4.6 x 150 mm) maintained at 35 °C. The flow rate was 1.5 mL/min, the injection volume was 20 µL and the detection UV wavelength was set at 280 nm. The mobile phase used was 0.1% acetic acid in water (A) versus 0.1% acetic acid in acetonitrile (B) for a total running time of 25 min and the following proportions of solvent B were used for the elution: 0-5 min: 10%; 5-10 min: 10-100%; 10-20 min: 100% and 20-25 min: 100-10%.

2.2. Potentiodynamic polarization measurements

Pure copper (99.99%) was used for sample preparation. The electrolyte was a 3 wt% NaCl solution prepared using distilled water. The concentration range of OMW stored for 2 years ranges from 40 to 200 g/L and corresponds to HT concentration range from 0.66 to 3.30 mmol/L.

The potentiodynamic polarization measurements were carried out in the potential range from -400 to 760 mV/SCE, depending on the current density evolution, with a scanning rate of 0.5 $mV.s^{-1}$. A Potentiostat Galvanostat Radiometer's Electronic controlled by the software VoltaLab was used. An electrochemical cell with a three-electrodes configuration was used; pure copper, platinum foil and a Saturated Calomel Electrode (SCE : XR110, Radiometer-Analytical) were used as a working, counter and reference electrodes, respectively.

3. Results and discussion

3.1. Identification and quantification of phenolic monomers in OMW

Representative chromatogram of OMW, obtained after HPLC analysis is given in Figure 1. This chromatogram shows several peaks corresponding to different phenolic monomers. From the retention time comparison and with co-elution with standards, it was deduced that the stored OMW were greatly enriched in 3,4-dihydroxyphenylethanol (HT) and slightly in tyrosol. This may be explained by the hydrolysis of the secoiridoid derivatives having in part in their structure HT and tyrosol [17].

As expected, HT is the major polyphenol compounds in the stored OMW, it is about 2.54 g/L. However, the concentration of tyrosol does not exceed 0.775 g/L.

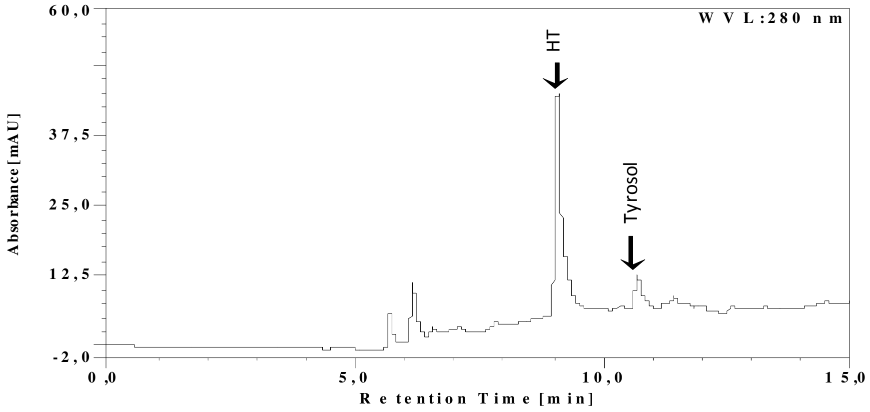


Figure 1: HPLC chromatogram of stored OMW.

3.2. Effect of HT concentration on the electrochemical behaviour.

3.2.1. Potentiodynamic polarization measurements.

The cathodic and anodic polarization curves of copper in NaCl 3wt % solutions without and with different concentrations of stored OMW years are represented in Figure 2. Inspection of this figure reveals that the potentiodynamic polarization curves are slightly shifted toward more negative potential and less current density upon addition of OMW, containing principally hydroxytyrosol (HT) as mentioned above. This result confirms the inhibitive action of the HT toward corrosion of copper. The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (J_{corr}), cathodic (β_c) and anodic Tafel (β_a) slopes, polarization resistance (R_p), corrosion rate (*CR*) and inhibition efficiency (*IE, %*) are listed in Table 1.

The values of J_{corr} and E_{corr} are obtained from the extrapolation of anodic and cathodic Tafel lines located next to the linearized current regions. The R_p values are calculated as follows [18],

$$R_p = \frac{\beta_c \beta_a}{2.303(\beta_c + \beta_a) J_{corr}} \qquad (1)$$

The values of corrosion rate (*CR*, millimeters per year ($mm.y^{-1}$)) are calculated using the expression [9],

$$CR = 3.268 \times 10^3 \frac{J_{corr}}{\rho} \frac{MW}{Z} \qquad (2)$$

Where *MW* is molecular weight of copper in g, ρ is the density of Cu in $g.cm^{-3}$ (=8.92) and Z is the number of electrons transferred in the Cu corrosion reaction. While, the inhibition efficiency (*IE, %*) of the HT effect on corrosion resistance was calculated using the following equation [19]:

$$(IE)\% = \left(1 - \frac{J'_{corr}}{J_{corr}}\right) \times 100 \qquad (3)$$

Where J_{corr} and J'_{corr} are the corrosion currents density without and with wastewater, respectively.

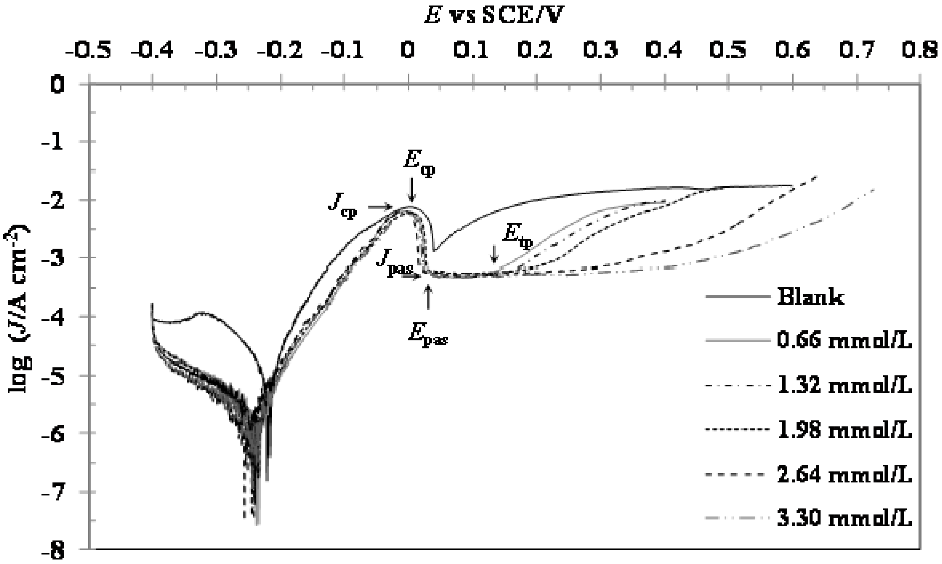


Figure 2: Potentiodynamic polarization curves of copper in NaCl 3wt % solutions devoid of and containing different concentrations of HT.

Table 1: Electrochemical parameters and degree of surface coverage obtained from Figure 2.

Solutions		**Parameters**							
OMW conc. (g/L)	**HT conc. (mmol/L)**	**E_{corr} (mV/SCE)**	**$-\beta_c$ (mV/dec)**	**β_a (mV/dec)**	**J_{corr} (μA/cm^2)**	**R_p (kΩcm^2)**	***CR* (mm/year)**	***IE.* (%)**	**θ**
Blank	Blank	-218	101	55	15.85	0.97	0.184	-	
40	0.66	-233	175	67	3.80	5.54	0.044	76.03	0.760
80	1.32	-240	163	60	3.98	5.52	0.046	74.89	0.749
120	1.98	-241	181	62	3.39	5.91	0.039	78.61	0.786
160	2.64	-248	150	60	2.45	7.75	0.028	84.54	0.845
200	3.30	-253	180	59	2.51	7.79	0.029	84.16	0.842

Inspection of Table 1 and Figure 2 reveals that the values of the anodic Tafel slop remain almost unchanged upon the addition of the HT and both cathodic (β_c) and anodic Tafel (β_a) depend slightly on the HT concentration. The HT compound affects the anodic dissolution of copper as well as the cathodic reduction reactions. Compared with the blank, the E_{corr} values move slightly in the negative direction, and all the displacement are less than 35 mV/SCE, which confirm that the HT compound acts as mixed-type corrosion inhibitor [14]. The decrease of J_{corr} upon addition of the inhibitor, leading to a decrease of *CR* and an increase of both R_p and the *IE*. Nevertheless, all the corrosion parameters depend slightly on the HT concentration.

Figure 2 shows also that the copper in the blank solution reaches passivity in a typical active-passive transition. The specimen in wastewater chloride solution featured much wider potential range of full passivation, which provides additional protection at high values of anodic potential. The values of some other parameters obtained from Figure 2 are listed in Table 2. The comparison of anodic behaviour of the copper has shown that the addition of the HT performs an improvement in corrosion resistance, especially above E_{corr} value. Indeed, a further increase in potential's values towards positive direction has revealed the beginning of corrosion in all specimens, related to dissolution of the metal. The specimens get successively covered with a passive film until the beginning of critical passivation potential, E_{cp}, at the critical current density of passivation, J_{cp}. Above the value of E_{cp}, a sudden decease in current density appears, below J_{cp}, to the value of full passivation start current density, J_{pas}, and the potential of full passivation start, E_p, what is related to passive film sealing (increasing its thickness). The shift of E_{cp} and E_p values towards negative potentials proves higher corrosion resistance of the copper upon addition of inhibitor. Nevertheless, all the corrosion parameters are almost independent on the HT concentration. The lower value of J_{pas}, in the presence of HT, proves a better tightness on the passive layer formed on the copper surface. When the potential of full passivation finishes, E_{tp} is reached. After this, the passive film continuity is damaged and the metal gets trans-passivated. Further inspection of Table 2 reveals also that the trans-passivation potential, E_{tp}, greatly increases upon addition of inhibitor and increases further with increasing inhibitor concentration.

Table 1: Characteristic passivation parameters obtained from Figure 2.

Solutions	Parameters				
HT conc. (mmol/L)	E_{cp} (mV/SCE)	J_{cp} (mA.cm^{-2})	E_p (mV/SCE)	J_p (mA.cm^{-2})	E_{tp} (mV/SCE)
Blank	7	7.94	40	1.32	47
0.66	1	6.31	26	0.62	109
1.32	1	6.17	27	0.55	130
1.98	3	6.03	32	0.63	184
2.64	-8	6.46	31	0.56	275
3.30	0	5.89	31	0.53	483

3.2.2. Adsorption behaviour

It is widely accepted that organic molecules inhibit corrosion by adsorption at the metal/solution interface. The adsorption of compounds can be described by two main types of interaction: physical adsorption and chimisorption [20]. A direct relationship between inhibition efficiency (*IE. %*) and the degree of surface coverage by the adsorption molecules (θ).Therefore, θ is calculated using the relation $\theta = IE/100$, and the calculated values are added in Table 1.

As described above, the major constituents of the OMW is the hydroxytyrosol (HT). The latter may play the major role in the inhibition process. Thus, the concentrations used in the adsorption isotherm diagram (Figure 3) were the HT concentrations in the different test solutions. Surface coverage data were tested by Langmuir adsorption isotherm, which can be expressed by the following equation (4) [21]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (4)$$

Where θ is the degree of the coverage on the metal surface, C is the HT concentration (mmol.L^{-1}) and K_{ads} is the equilibrium constant of adsorption-desorption process (mol^{-1}L). The latter is related to the standard free energy of adsorption (ΔG^0_{ads}) according to relation (5) [22]:

$$\Delta G^0_{ads} = -RT \ln(55.5 K_{ads}) \qquad (5)$$

where R is the molar gas constant (8.314 J mol^{-1}K^{-1}) and T is the absolute temperature (K).

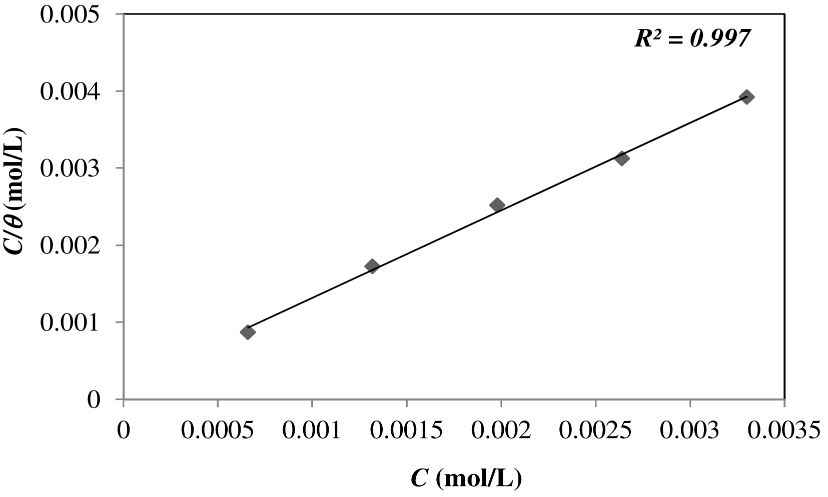
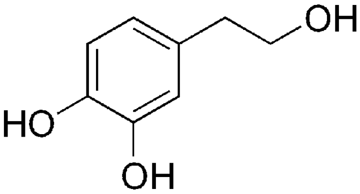


Figure 3: Langmuir adsorption isotherm of HT on the copper surface.



hydroxytyrosol (HT).

Figure 3 represents the Langmuir adsorption plot of HT on the copper surface. The best fitted straight line is obtained for the plot of C/θ versus C. The correlation coefficient ($R^2 = 0.997$) is very close to 1 and confirms that the adsorption of HT on the copper surface in NaCl solution obeys the Langmuir adsorption isotherm.

The value of ΔG^0_{ads} was calculated as about -30.50kJ mol^{-1}, which suggests a strong physical adsorption of HT onto the copper surface in NaCl solution [22]. Adsorption is essentially due to the presence of the three hydroxyl groups and aromatic ring.

Conclusion

The main conclusions of this study are summarized below:

- HT is the major polyphenol compounds in the stored OMW.
- The HT compound acts as a mixed-type corrosion inhibitor, suppressing both anodic and cathodic reactions.
- The full passivation range greatly increases upon addition of inhibitor and increases further with increasing HT concentration.
- The free energy of adsorption reveals a strong physical adsorption of the HT on the copper surface.

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