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Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves

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Abstract

The inhibitive action of the aqueous extract of olive (*Olea europaea* L.) leaves toward the corrosion of C-steel in 2 M HCl solution was investigated using weight loss measurements, Tafel polarization, and cyclic voltammetry. It was found that the extract acts as a good corrosion inhibitor for the tested system. The inhibition efficiency increases with increasing extract concentration. The inhibitive action of the extract is discussed with a view to adsorption of its components onto the steel surface, making a barrier to mass and charge transfer. The adsorption of extract components onto the steel surface was found to be a spontaneous process and to follow the Langmuir adsorption isotherm. It was found also that such adsorption increases the activation energy of the corrosion process. The results of cyclic voltammetry showed that the presence of olive extract decreases the charge density in the transpassive region. The inhibition efficiency is greatly reduced as the temperature is increased.
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1. Introduction

Corrosion inhibitors are chemical compounds usually used in small concentrations whenever a metal is in contact with an aggressive medium. The presence of such compounds retards the corrosion process and keeps its rate to a minimum and thus prevents economic losses due to metallic corrosion. The chemical compounds that could be used for this purpose may be organic or inorganic. However, not just any chemical compound can be used as a corrosion inhibitor. There are some requirements that the compound must fulfill to do so. Regarding the chemical structure and chemical behavior, an inorganic compound must be able to oxidize the metal, forming a passive layer on its surface. On the other hand, a molecule of an organic compound must have some features that give it the ability to act as a corrosion inhibitor. Among these, the molecule may have a large structure, double bonds, an active center or group, etc. These features give the molecule the ability to

cover a large area of a metal surface with a firmly attached film.

Apart from the structural aspects, there are also economic and environmental considerations. Thus, since the whole subject of corrosion is about its destructive economical effect, the used inhibitor must be cheap. Furthermore, due to the recent increasing awareness of green chemistry, it must be a nontoxic and environmentally friendly chemical. One of the sources of these cheap and clean inhibitors is plants. Plant parts contain several compounds that satisfy the mentioned criteria. Many recent researches [1–8] have adopted this trend and carried out their work on naturally occurring substances. Promising results were obtained in previous work in this field. It was reported that Khillah extract inhibits steel corrosion in HCl solution with inhibition efficiency as high as 99% [1], while opuntia extract inhibits the corrosion of aluminum in the same acid with efficiency of about 96% [8].

This work is devoted to examining the aqueous extract of olive (*Olea europaea* L.) leaves as an inhibitor for corrosion of C-steel in 2.0 M HCl solution. Weight loss measurements, potentiostatic polarization, and cyclic voltammetry were used in the study.

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2. Experimental details

ASTM A573 Grade 70 low carbon steel was used in the present study. The chemical composition of this steel is 0.27% C, 0.85% Mn, 0.035% P, 0.035% S, 0.15% Si, and the remainder is iron. The steel specimens were taken from the tanks of Cairo Co. for petroleum refining.

Coupons of steel with dimensions (1, 1, 0.5 cm) and exposed surface area 4 cm^2 were used for weight loss measurements. For potentiostatic polarization experiments, a cylindrical rod of steel embedded in araldite with exposed surface area 0.38 cm^2 was used. The electrodes were polished with different grades of emery papers, degreased with acetone, and rinsed in distilled water before they were inserted into the test solution.

All chemicals used for preparing the test solutions were of analytical grade and the experiments were carried out at room temperature, $25 \pm 1\,°C$.

Dry olive leaves were finely divided and extracted in boiled water for 3 h. The filtrate was evaporated in a steam bath and the solid residue was left overnight in open air for complete dryness. A stock solution was prepared, by weight, from the collected solid and used to prepare the desired concentrations by dilution.

For weight loss measurements, the steel coupons were left hanging in the test solution for 1 day at $25 \pm 1\,°C$ before their loss of weight was recorded. The corrosion rate was calculated, in milligrams per square centimeter per hour (mg/(cm^2 h)), on the basis of the apparent surface area. The inhibition efficiency calculations were based on the weight loss measurements at the end of the whole exposure period. The results of the weight loss experiments are the mean of three runs, each with a fresh steel sheet and a fresh acid solution. The percentage of inhibition efficiency was calculated using the equation

$$IE = \left[\frac{(W - W_i)}{W}\right] \times 100, \tag{1}$$

where W and W_i are the corrosion rates of the steel coupons in the absence and presence of olive leaf extract, respectively.

Potentiostatic polarization and cyclic voltammetry experiments were carried out using a PS remote potentiostat with PS6 software for calculation of corrosion parameters (corrosion current density, corrosion potential, and Tafel constants) as well as current integration for charge density calculations. The corrosion parameters were calculated from the intercept of the anodic and cathodic Tafel lines. A three-compartment cell with a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode was used. The inhibition efficiency IE was calculated using the equation

$$IE = \left[\frac{(I - I_i)}{I}\right] \times 100, \tag{2}$$

where I and I_i are the corrosion current densities in free and inhibited acid, respectively.

3. Results and discussion

3.1. Weight loss measurements

The data of Table 1 represent the results obtained from weight loss experiments. Inspection of the table reveals that the rate of carbon steel corrosion is greatly reduced upon the addition of olive leaf extract. This behavior reflects the inhibitive effect of the extract toward the acid corrosion of the steel. The inhibition efficiency increases as the added extract concentration is increased. It reaches 91% for 900 ppm of the added extract.

3.2. Adsorption behavior

The inhibitive action of olive extract toward the acid corrosion of steel could be attributed to the adsorption of its components onto the steel surface. The adsorbed layer acts as a barrier between the steel surface and the aggressive solution, leading to a decrease in the corrosion rate. It follows that the inhibition efficiency (IE) is directly proportional to the fraction of the surface covered by the adsorbed molecules (θ). Therefore, (θ) is calculated using the relation $\theta = IE/100$, and the calculated values are presented in Table 1. The mode of variation of (θ) with the extract concentration specifies the adsorption isotherm that describes the system.

The aqueous extract of olive (*Olea europaea* L.) leaf contains polyphenolic compounds with an antioxidation potential, so it was used historically in folk remedies [9–11]. Among these phenolics, the major constituents of the leaf extract are oleuropein ($C_{25}H_{32}O_{13}$) and hydroxytyrosol (3,4-dihydroxyphenylethanol). Oleuropein is readily hydrolyzed to hydroxytyrosol and elenolic acid. The other polyphenols present include tyrosol, oleuropein aglycone, and gallic acid. The chemical structures of polyphenols are represented in Fig. 1 Because oleuropein is hydrolyzed into elenolic acid and hydroxytyrosol [12,13], the latter may play the major role in the inhibition process. Thus, the extract concentration is represented as hydroxytyrosol in the adsorption isotherm diagram. This representation enables the calculation of an approximate value of the molar free energy of adsorption. When extract concentration, as molar hydroxytyrosol (C), is plotted against (C/θ), a straight line with almost unit slope is obtained, as shown in Fig. 2. This behavior suggests that the olive compounds adsorbed onto the steel surface following the Langmuir

Table 1
Corrosion behavior of C-steel in free and inhibited 2 M HCl solutions as revealed from weight loss experiments

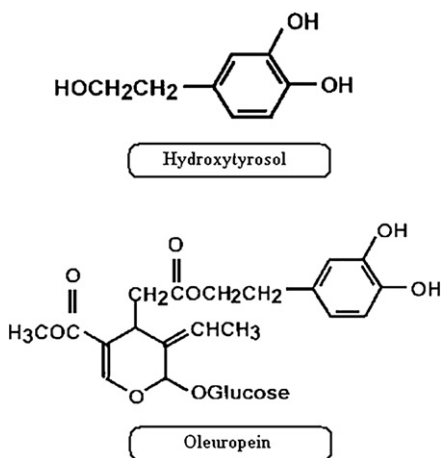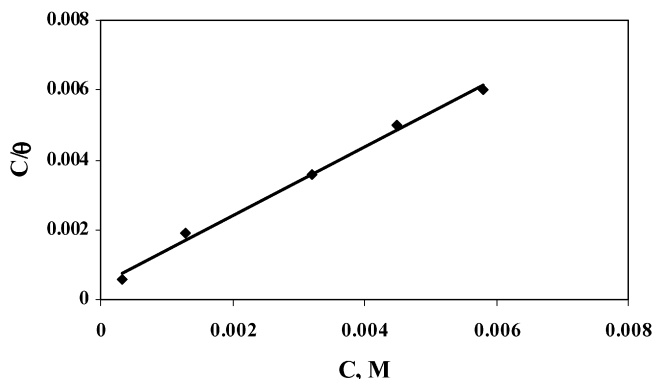| Extract conc. (ppm)	Extract conc. (as molar hydroxytyrosol)	Wt. loss (mg/(cm^2 h))	θ
–	–	0.56	–
50	0.00032	0.24	0.57
200	0.00128	0.18	0.68
500	0.0032	0.07	0.87
700	0.0045	0.06	0.90
900	0.0058	0.05	0.91

Fig. 1. Structure of hydroxytyrosol and oleuropein.

Fig. 2. Langmuir isotherm for adsorption of olive leaf extract components, represented as hydroxytyrosol, onto steel surface in 2 M HCl solution.

adsorption isotherm. According to the Langmuir adsorption isotherm, there are no interaction forces existing between the adsorbed molecules, and the energy of adsorption is independent of the surface coverage (θ).

The Langmuir adsorption isotherm could be represented using the equation [14]

$$\frac{C}{\theta} = \frac{1}{k} + C, \tag{3}$$

where K is the adsorption constant and

$$\ln k = \ln \frac{1}{55.5} - \frac{\Delta G^{\circ}_{ads}}{RT}, \tag{4}$$

where ΔG°_{ads} is the standard free energy of adsorption, where one molecule of water is replaced by one molecule of inhibitor and the numerical value (1/55.5) in the equation stands for the molarity of water. The calculated value of free energy of adsorption was found to be -28.74 kJ/mol. The negative sign indicates that the adsorption of olive components onto the steel surface is a spontaneous process. It is well known that values of ΔG_{ads} on the order of -20 kJ/mol or lower indicate a physical adsorption, while those of -40 kJ/mol or higher involve charge sharing or a transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond [15]. The obtained value of ΔG_{ads} suggests a strong physical adsorption of olive leaf extract components onto the steel surface in HCl solution.
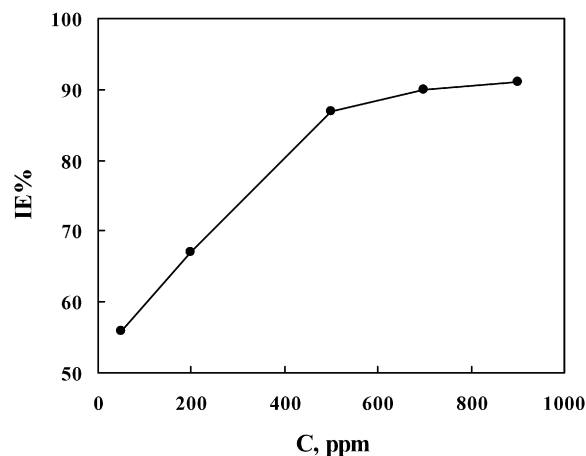

Fig. 3. Relation between inhibition efficiency and olive leaf extract concentration.

The phenolic compounds adsorb on the steel surface through the lone pairs of electrons of the oxygen atoms forming a covering film. Inspection of the phenolic structures in Fig. 1 reveals that the oxygen atoms almost surround the aromatic rings of the phenolics. This arrangement of the oxygen atoms may lead to the conclusion that the phenolic compound is forced to be adsorbed horizontally onto the steel surface. This adsorption gives rise to a large covered surface area with a small number of adsorbed molecules. Therefore, high inhibition efficiency could be obtained by relatively low concentrations of the extract. At the same time, the increase of extract concentration above a certain value has little effect on the inhibition efficiency. This conclusion is confirmed by the fact that the inhibition efficiency does not increase linearly with extract concentration, as shown in Fig. 3. As revealed from the figure, the inhibition efficiency maintained almost constant values for extract concentrations above 500 ppm.

3.3. Polarization studies

The cathodic and anodic polarization curves of C-steel in solutions of 2 M HCl devoid of and containing different concentrations of olive leaf extract were recorded at a scanning rate of 5 mV/s and are represented in Fig. 4. Inspection of the figure reveals that the polarization curves are shifted toward more negative potentials and less current density upon addition of olive extract. This result confirms the inhibitive action of the olive extract toward acid corrosion of C-steel.

The corrosion parameters of C-steel in 2 M HCl solutions devoid of and containing different concentrations of olive leaf extract were calculated from polarization curves and presented in Table 2. Inspection of the data of the table revealed that the corrosion potential shifts to more negative values with increased concentrations of olive extract. Moreover, the corrosion current density decreases markedly on addition of the extract. The magnitude of this decrement increases as the concentration of the extract is increased. Therefore, the inhibition efficiency increases with increasing extract concentration. Further inspection of the table reveals that both the anodic and cathodic Tafel constants increase with increasing extract concentration. This
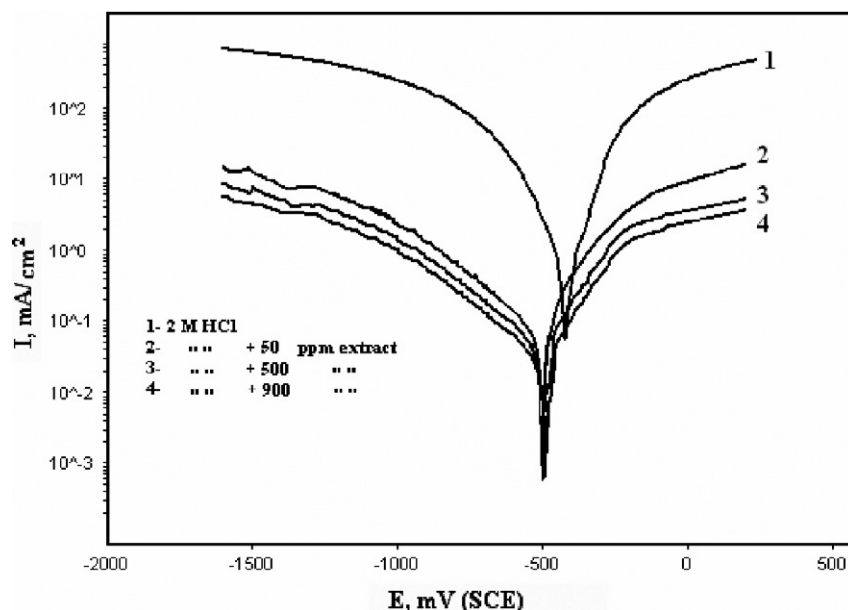
Fig. 4. Anodic and cathodic polarization curves of steel in solutions of 2 M HCl free and inhibited by different concentrations of olive leaf extract.
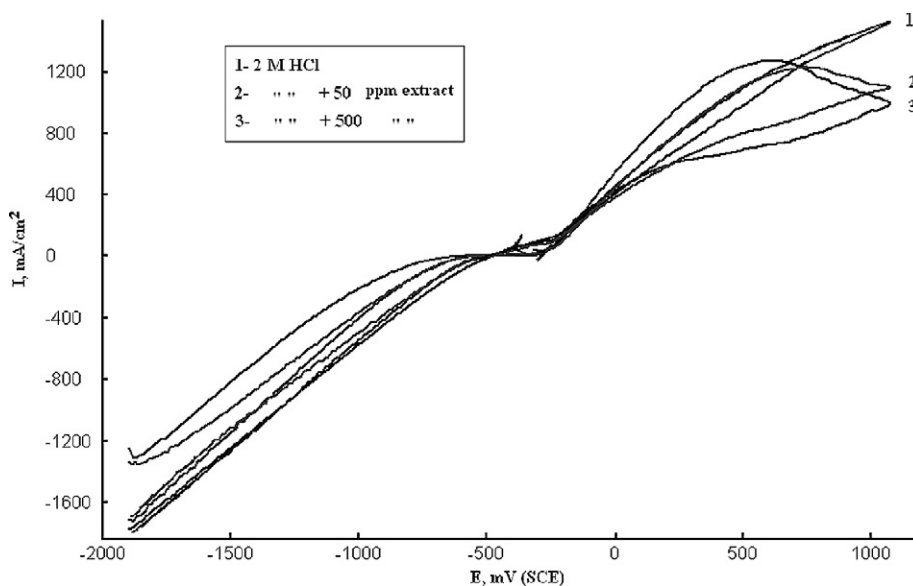

Fig. 5. Cyclic voltammetry of C-steel in 2 M HCl solution free and inhibited by different concentrations of olive leaf extract. Scanning rate = 10 mV/s.

Table 2
Corrosion parameters of C-steel in solutions of 2 M HCl, free and inhibited by different concentrations of olive leaf extract, at 298 K

Inh. conc. (ppm)	E_{corr} (mV)	I_{corr} (mA/cm^2)	IE%	β_a	$-\beta_c$
–	−468	0.42	–	110	204
50	−510	0.12	71	121	254
200	−512	0.07	83	145	271
500	−516	0.05	88	153	308
700	−520	0.04	90	178	318
900	−523	0.03	93	191	342

result suggests that the presence of the extract affects the anodic dissolution of steel as well as the cathodic reduction of hydrogen ions. Therefore, it could be concluded that the molecules of extract absorb onto both anodic and cathodic sites of the steel surface. This behavior indicates that the extract acts as a mixed inhibitor.

3.4. Cyclic voltammetry

The cyclic voltammograms of C-steel in solutions of 2 M HCl devoid of and containing different concentrations of olive leaf extract were recorded and are represented in Fig. 5. The potential was started at −1900 mV and swept in the positive direction up to oxygen evolution at a scanning rate of 10 mV/s. Inspection of Fig. 5 reveals that the anodic branches of the steel in free and inhibited acid solutions exhibit a very narrow passive region with no anodic dissolution peaks. The transpassive region and the onset of oxygen evolution start in both solutions at almost the same potential; about −350 mV.

Table 3
Corrosion parameters of C-steel in solutions of 2 M HCl free and inhibited by 500 ppm of olive leaf extract at different temperatures

Temp. (K)	Solution	E_{corr} (mV)	I_{corr} (mA/cm^2)	IE%	β_a	$-\beta_c$
298	Free	−390	0.42	–	88	129
	Inhibited	−516	0.05	88	153	308
313	Free	−395	0.57	–	81	121
	Inhibited	−439	0.16	72	66	168
323	Free	−400	0.74	–	69	119
	Inhibited	−417	0.32	57	78	140
333	Free	−412	0.83	–	55	115
	Inhibited	−428	0.63	24	76	136
343	Free	−392	0.99	–	51	110
	Inhibited	−401	0.92	7	63	120

Fig. 6. Arrhenius plot for steel corrosion in 2 M HCl solution free and inhibited by 500 ppm of olive leaf extract.

Further inspection of the curves of Fig. 5 reveals that upon the onset of the transpassive region the current still rises up until the potential is reversed, in the case of steel in free acid solution. On the other hand, the current of the transpassive region decreases in the presence of the extract, forming a broad anodic peak. The formation of such a peak could be attributed to the adsorption of the extract components on the steel surface. The values of charge density of the transpassive region were calculated for the three tested solutions and found to be 109, 102, and 99 C for free, 50, and 500 ppm of extract, respectively. It is obvious that the charge density decreases with increasing extract concentration. This result could be interpreted in view of the adsorption of extract components onto the steel surface. The adsorbed molecules form a barrier for charge and mass transfer.

3.5. Effect of temperature

The effect of temperature on the corrosion of C-steel in free and inhibited 2 M HCl solutions was studied using potentiostatic polarization in the range of 25–70 °C. The acid solutions were inhibited by addition of 500 ppm of olive leaf extract. The corrosion parameters calculated from the polarization curves are given in Table 3. Inspection of Table 3 reveals that the corrosion potential shifted to a more active potential as the temperature was increased. Moreover, the corrosion rate of steel in both free and inhibited acid media increased as the temperature was increased. However, the inhibition efficiency of the olive extract decreases markedly with increasing temperature. This result supports the idea that the adsorption of extract components onto the steel surface is physical in nature. Thus, as the temperature increases, the number of adsorbed molecules decreases, leading to a decrease in the inhibition efficiency.

The activation energies of the corrosion process in free and inhibited acid were calculated using the Arrhenius equation [16],

$$k = A \exp \frac{E_a}{RT}, \tag{5}$$

where E_a is the activation energy, A is the frequency factor, T is the absolute temperature, R is the gas constant, and K is the rate constant, which is directly proportion to the corrosion current (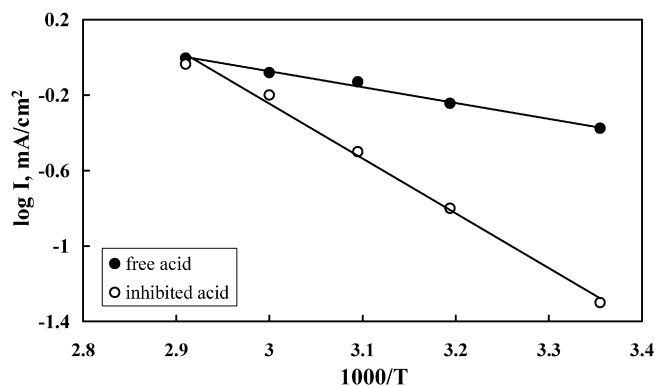I_{corr}). Plotting $\log I$ versus $1/T$ gives a straight line, as revealed by Fig. 6. The values of activation energy calculated using the lines of Fig. 6 are 3.02 and 10.41 kJ/mol for free and inhibited acid solutions, respectively. The obtained results suggest that olive leaf extract inhibits the corrosion reaction by increasing its activation energy. This could be done by adsorption onto the steel surface, making a barrier to mass and charge transfer. However, such types of inhibitors perform good inhibition at ordinary temperature, with considerable loss in inhibition efficiency at elevated temperatures [17].

4. Conclusions

– Olive leaf extract acts as a good corrosion inhibitor for C-steel in 2 M HCl solution.
– The inhibition action of the extract was attributed to the physical adsorption of its phenolic compounds, mainly oleuropein and hydroxytyrosol, onto the steel surface.
– The extract acts as a mixed inhibitor.
– The inhibition efficiency decreases with increasing temperature.
– The presence of extract increases the activation energy of the corrosion process.
– The presence of extract decreases the charge density in the transpassive region.

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