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Corrosion inhibition for carbon steel in sea water using aqueous olive extract

Khulood Abid Saleh Al-Saadie*, Mohannd Kadhem Alshujery
University of Baghdad, College of Science, Department of Chemistry, Baghdad, (IRAQ)
E-mail: khulood_abid@yahoo.com

ABSTRACT

In this work potentiostatic study for the corrosion inhibition of carbon steel(C.S) was studied in saline water using hot water extracted of Olive using four extracted concentrations (1, 2, 3 and 4 ppm) at temperatures range 298-328K. Inhibition efficiency I% results show that all chooses concentrations gave about I% 99%. Thermodynamic functions of corrosion processes were calculated from experimental polarization data and the interpretation of the results reveals that Olive extract obey Langmuir adsorption isotherm. Polarization curves indicate that Olive extract act as anodic - type inhibitor at low concentration and cathodic - type inhibitor at higher concentration. The small values of the equilibrium constant of the adsorption-desorption process K_{ads} refer to physical adsorption process. The values of free energy of adsorption ΔG^o_{ads}, enthalpy ΔH^o_{ads} and entropy ΔS^o_{ads} were negative indicating the spontaneous and exothermic adsorption process as well as Olive extract retained the metal ions and reducing the dissolution of steel.

KEYWORDS

(Olea europaea L.) leaves extract;
Inhibition of carbon steel;
Saline medium.

INTRODUCTION

The desire to reduce corrosion problem is a prime strategic objective for industry. Since decades ago man has succeeded in modifying the environment among other methods through the injection of substances that can reduce the rate of corrosion, the uses of inhibitors are an important method for protecting materials against corrosion[1-3]. various types of organic inhibitors have been published[4]. The molecules most often used as corrosion inhibitors are nitrogen, sulphur, oxygen and phosphorus containing compounds[5-7].

These substances are generally called inhibitors; corrosion inhibitors are substances which when added in small concentrations to corrosive media decrease or prevent the reaction of the metal with the media[8]. They function through adsorption on metal surface to form a thin film, giving the surface a certain level of protective layer.

Many researchers report that the inhibition effect mainly depends on some physicochemical and electronic properties of the organic inhibitor which relate to its functional groups, steric effects, electronic density of donor atoms, and orbital character of donating electrons, and soon[9, 10]. the interest to use some tropical plant extract as inhibitor come to our mind after the fact that several countries have already introduced restriction on the use of some of the most harmful heavy metal compound & biocides and more strict regulation on their use are under completion both at the EU- and international level[11], Plant extracts have become important because they are environmentally acceptable, inexpensive, readily available and renewable sources of materials, and ecologically acceptable.

The aim of present work involves extract natural inhibitor using hot water for Olive in Saline water at temperature range 298-328K using potentiostatic measurements to study the corrosion inhibition of C.S., extracts of plant materials contain a wide variety of organic compounds. Most of them contain hetero atoms such as P, N, S, O. these atoms coordinate with the corroding metal atom (their ions), through their electrons. Hence protective films are formed on the metal surface and hence corrosion is prevented.

EXPERIMENTALPART

Chemicals and materials

C.S.(C45) was used as metallic materials with chemical Composition as described in the TABLE (1)

The chemical which used in this work include some regents are listed in TABLE (2) with their purity and origin.

Sample preparation

piece of C.S. (C45) of (0.5 mm) thickness was mechanically cut into circular sample with dimensions of 2.5 cm in diameter then: C.S sample surface was polished with emery paper in different sizes (600, 800,1200, 2000). Then washed by water, distilled water and finally with ethanol. The Specimen was kepted in desiccators for protecting and preventing them from oxidation.

Plant extract preparation

Plant leave were collect, washed,dried, grounded and kept at a laboratory temperature until use, for the preparation of aqueous extract (50) grams of olive powder were taken, placed in the conical flask containing (500) cm^3 of Hot Distilled water, mixed by magnetic stirrer for (30) minutes. After that the solution stand in the laboratory temperature for 24h, then it well be filtrated using Buchner apparatus, Then four concentration of aqueous extract[1,2,3,4]ppm were prepared in saline medium (3.5%NaCl) each concentration was studied at four different temperatures 298,308,318 and 328 K. Figure 1 show the FTIR spectra of Olive extract

The aqueous extract of Olive contains polyphenolic compounds with an antioxidation potential, so it was used historically in folk remedies[12]. Among these phenolics, the major constituents of the leaf extract are oleuropein ($C_{25}H_{32}O_{13}$) and hydroxytyrosol (3,4dihydroxyphenylethanol). 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 Figure 2

Electrochemical measurements

The experiments were performed in a classical three electrode electrochemical cell. C.S (C45) of

TABLE 1 : Chemical composition for C.S. (C45)

Grade	*% C*	*% Si*	*% Mn*	*%S*	*% P*	*%Ni*	*%Cr*	*%Mo, Cr+Ni*	*% Fe*
C45	0.42-0.50	<0.40	0.50-0.80	<0.045	<0.045	0.40	<0.40	<0.10	97.31-97.69

TABLE 2 : Chemical materials

Raw Material	*Molecular Formula*	*Supplier*	*Purity*
De ionized Water	H2O	University of Baghdad/College of Science/Laboratory of service	high degree of purity/empty of additional
Ethanol (EtOH	C2H5OH	GCC	99.9%
Sodium Chloride	NaCl	BDH	99.5%

(0.5 mm) thickness with dimensions of 2.5 cm in diameter was used as the working electrode and platinum electrode as a counter electrode and silver-silver chloride electrode as a reference electrode. Prior to each experiment, the working electrode surface was polished with emery paper. The electrochemical system consists of potintostate device (Germany, Mlab 2000), corrosion cell (1000 ml) and electrodes with a computer and MLabSci software were used for data acquisition and analysis (Srimathi, et al.2010). To determine the open circuit potential(OCP) of the specimens, the specimens have been immersed for (15 Min) in the synthesized sea water (3.5% NaCl)in different temperatures (298,308,318 and 328)K to reach the steady state between the specimen’s material and electrolytic solution. The change in potential according to the current were determined during (15min), and time step equal to 60 seconds for each specimens. After reaching the steady state condition, the determined potential is known as corrosion potential or free potential or open circuit potential.

RESULTS AND DISCUSSION

Potentiostatic polarization measurements

Anodic and cathodic polarization curves for the corrosion of C.S. (C45) in 3.5% NaCl, alone and containing different concentration of Olive (at 298K is shown in Figure 3 the curves show polarization

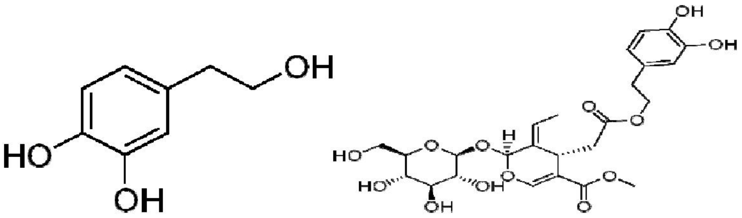

Figure 1 : Structure of hydroxytyrosol and oleuropein

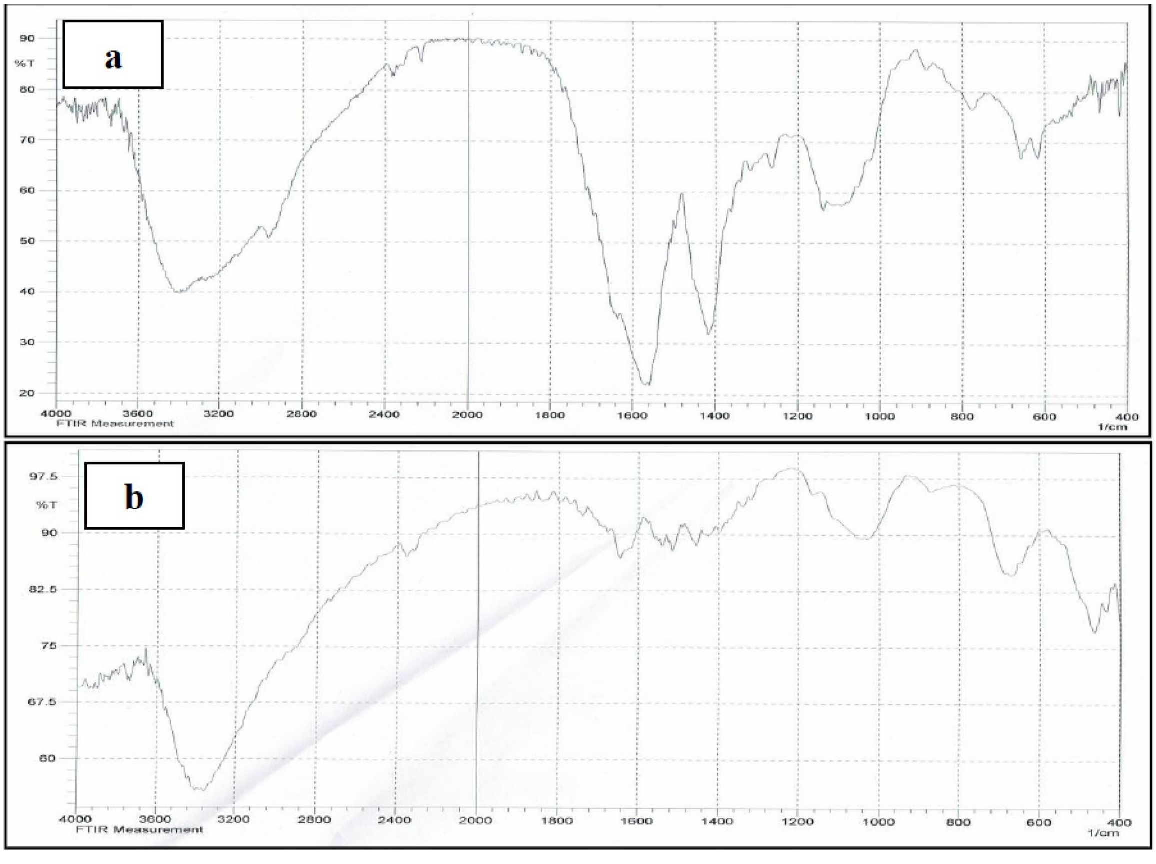

Figure 2 : FT-IR spectra of (a) aqueous olive extract before operation (b) film formed on the surface of C.S

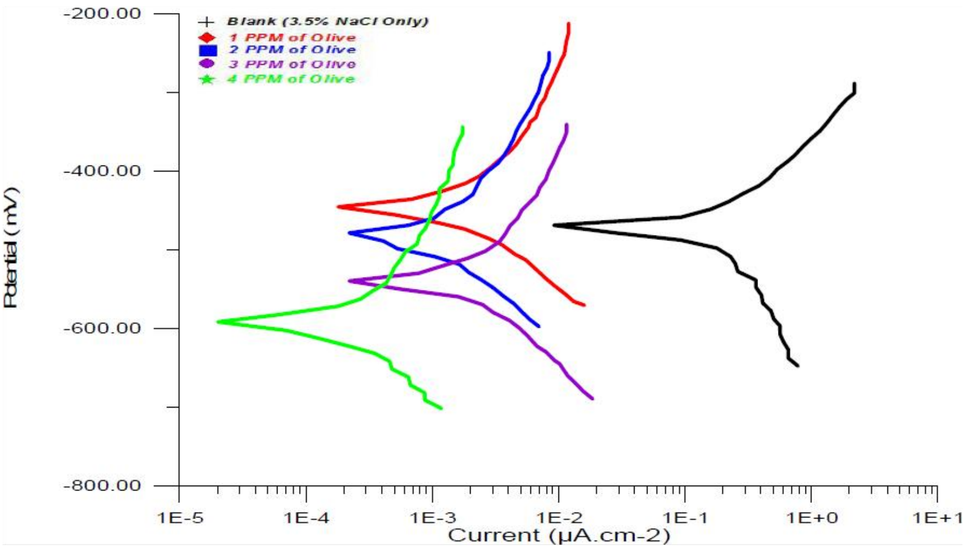

Figure 3 : Polarization plots of carbon steel in 3.5% NaCl for various concentrations of olive at 298K

TABLE 3 : Corrosion data of carbon steel in 3.5% NaCl at absence and presence different olive concentrations at temperature ranges 293 - 323K

Olive /ppm	T/K	- Ecorr mV	icorr/µA.cm^{-2}	- βc /mV.dec^{-1}	βa /mV.dec^{-1}	I%	θs
3.5% NaCl	298	520.00	168.72	243.9	107.2		
	308	573.50	201.57	179.1	104.2		
	318	622.00	220.34	140.3	82.2		
	328	651.00	280.34	137.3	79.6		
1	298	466.00	0.4824	59.1	54.6	99.714	0.997
	308	518.10	0.6661	45.6	51.9	99.670	0.997
	318	576.50	1.48	64.9	89.5	99.328	0.993
	328	597.40	1.55	62.7	69.7	99.447	0.994
2	298	489.60	0.4516	58.1	93.2	99.732	0.997
	308	545.30	0.5821	56.8	77.2	99.711	0.997
	318	574.00	0.8387	78.5	61.6	99.619	0.996
	328	595.10	0.8317	56.7	63.2	99.703	0.997
3	298	540.00	0.4978	49.7	52.4	99.705	0.997
	308	582.80	0.60907	51.2	54.2	99.698	0.997
	318	595.50	1.1	81.4	54.3	99.501	0.995
	328	602.20	1.21	62.5	50.7	99.568	0.996
4	298	361.80	0.046	61.6	41.8	99.973	0.9997
	308	399.60	0.0868	56.6	52.3	99.957	0.9996
	318	443.90	0.1136	64.8	63.5	99.948	0.9995
	328	502.90	0.118	51.7	74.1	99.958	0.9996

of both, the cathodic and anodic process.

The extrapolation method for the polarizations curves was applied and the data for corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic and anodic Tafel slopes (bc and ba) and percentage inhibition efficiency (%I) are show in TABLE (3). Inhibition efficiency %I can be determine using the following eq.[13]

$$\%I = I_{corr\ un} - I_{corr\ i} / I_{corr\ un} * 100 \quad (1)$$

Where $I_{corr\ un}$ and $I_{corr\ i}$ are the uninhibited and inhibited corrosion current densities, respectively, which evaluated by extrapolated cathodic and anodic Tafel lines to corrosion potential

Tafel plots Figure 3 revel that the corrosion potential (E_{corr}) of the working electrode in the solution containing corrosion inhibitor shifted to More noble value at low concentration and shifted to more active value when concentration of inhibitor increased more than 3 ppm, compared to that of blank, implying that the Olive inhibitor act as anodic - type inhibitor at low concentration and cathodic inhibitor at higher concentration[14].

Corrosion kinetic and thermodynamic activation parameters

In order to study the effect of temperature on the inhibition efficiencies of Olive, potentiostatic polarization measurements were carried out in the temperature range 298–328K in absence and presence of different inhibitor concentration. The various corrosion parameters obtained are listed in TABLE - 4. The obtained data suggests that Olive get adsorbed on the C.S surface at all temperatures studied and corrosion rates increased in absence and presence of inhibitor with increasing temperature in 3.5% NaCl solutions. Corrosion of metal is generally accompanied with cathodic reaction; rise in temperature usually accelerates the corrosion reactions which results in higher dissolution rate of the metal. Inspection of TABLE -3 showed that corrosion current density increased with increasing temperature both in uninhibited and inhibited solutions while the inhibition efficiency of Olive slightly change with temperature. In order to calculate activation parameters for the corrosion process, Arrhenius Eq. (2) and transition state Eq. (3) were used[15].

$$\mathbf{Log\ CR} = \log \mathbf{A} - \frac{\mathbf{Ea}}{\mathbf{2}}\mathbf{.303RT} \qquad (2)$$

$$\mathbf{Log}\frac{\mathbf{CR}}{\mathbf{T}} = \log\left(\frac{\mathbf{R}}{\mathbf{Nh}}\right) + \frac{\Delta S^*}{\mathbf{2}}\mathbf{.303R} - \frac{\mathbf{\Delta H^*}}{\mathbf{2}}\mathbf{.303RT} \qquad (3)$$

Where CR is the corrosion rate, Ea is the apparent activation energy, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is temperature, A is the Arrhenius pre-exponential factor, h is the Plank's constant (6.626 x 10^{-34} Js), N is the Avogadro's number (6.022 x 10^{23} mol^{-1}), ΔS* is the entropy of activation and ΔH* is the enthalpy of activation.

The plot of log CR against 1/T is presented in the slope of the line is (-Ea / 2.303 R) and the intercept of the line extrapolated gives log A.

The apparent activation energy (Ea) at optimum concentration of Olive was determined by linear regression between log CR and 1/T Figure 4 and the result is shown in TABLE -4.

Straight lines were obtained from the plot of log CR/T vs. 1/T showed in Figure 5. with the slope of (-ΔH* / 2.303 R) and an intercept of [(log (R/Nh) + (ΔS*/2.303 R)] from which the values of ΔH* and ΔS*, respectively were calculated

Adsorption isotherm behavior

The adsorption isotherm can be determined by assuming that inhibition effect is due mainly to the adsorption at metal/solution interface. Basic information on the adsorption of inhibitors on the metal surface can be provided by adsorption isotherm. In order to obtain the isotherm, the fractional surface coverage values (θ) as a function of inhibitor concentration must be obtained. The values of θ can be easily determined by the ratio %I/100, where %I is inhibition efficiency obtained by potentiostatic method so it is necessary to determine empirically

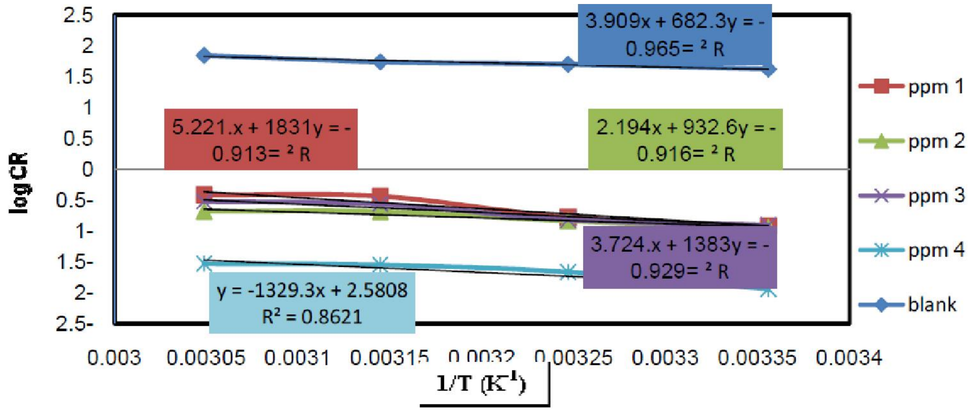

Figure 4 : Plot of log CR versus 1/T for the corrosion of C.S in 3.5%NaCl containing various olive concentrations

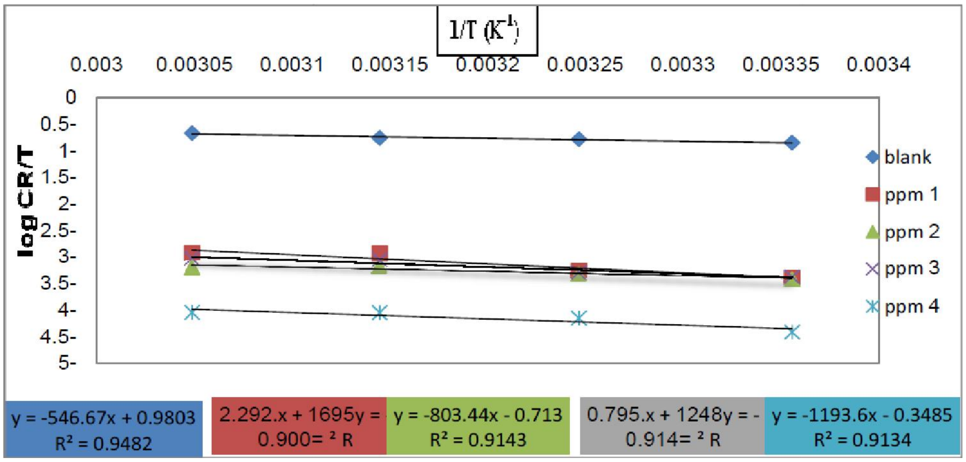

Figure 5 : Arrhenius plots of log CR/T vs. 1/T for the corrosion of C.S in 3.5%NaCl in the absence and the presence of olive

TABLE 4 : Activation parameters E_a, ΔH^o_{ads} and ΔS^o_{ads} for the C.S dissolution in 3.5% NaCl in the absence and the presence of olive concentration

C_{inh}	ΔH/kJ.mol^{-1}	-ΔS/ kJ.mol^{-1}.K^{-1}	Ea/kJ.mol^{-1}	A Molecules.cm^{-2}.S^{-1}
without	10.467	0.179	13.065	4.89E+27
1ppm	32.468	0.154	35.066	1E+29
2ppm	15.384	0.184	17.982	9.91E+25
3ppm	23.898	0.182	26.496	3.19E+27
4ppm	22.854	0.192	25.452	2.29E+26

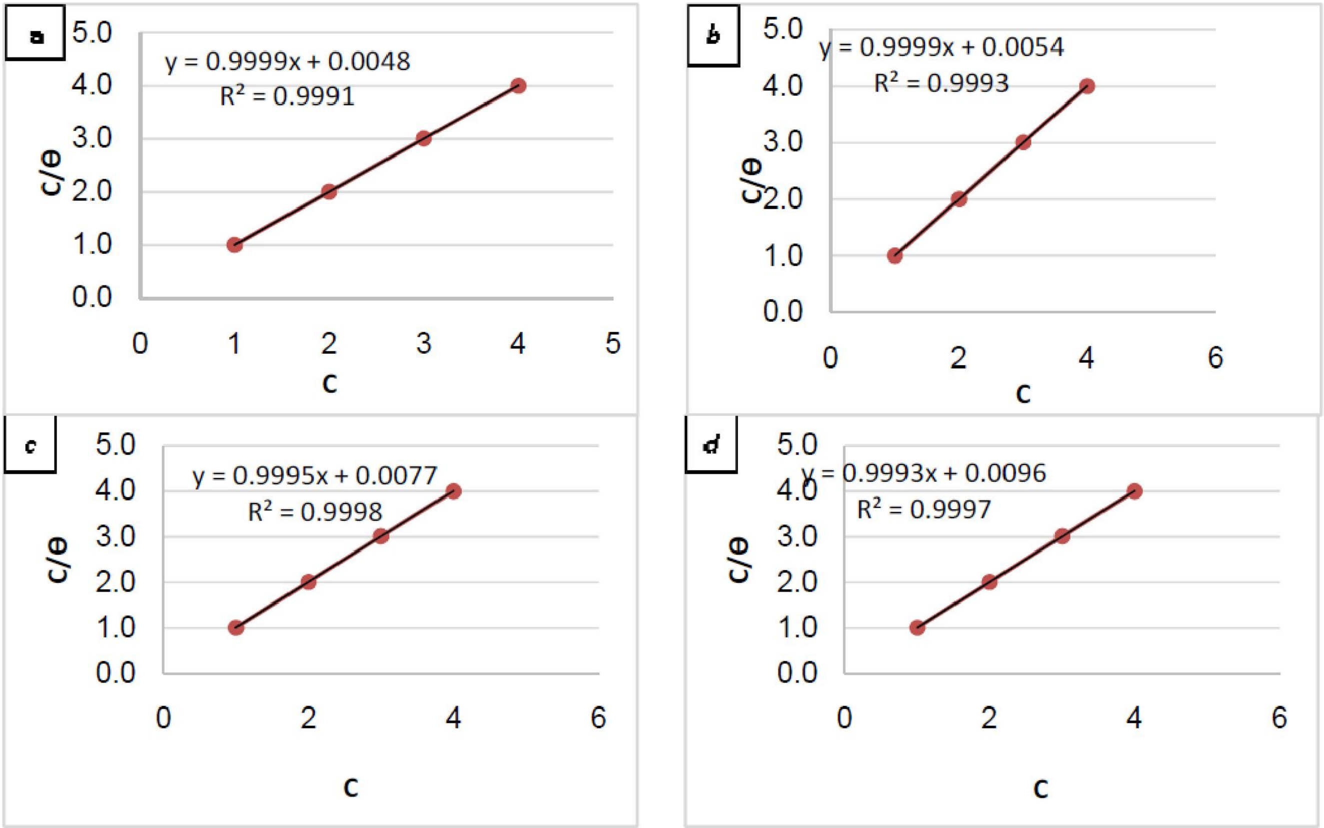

Figure 6 : Langmuir isotherms plots for the adsorption of Olive on carbon steel (a) at 298K, (b) at 308K, (c) at 318K & (d) at 328 K Figure

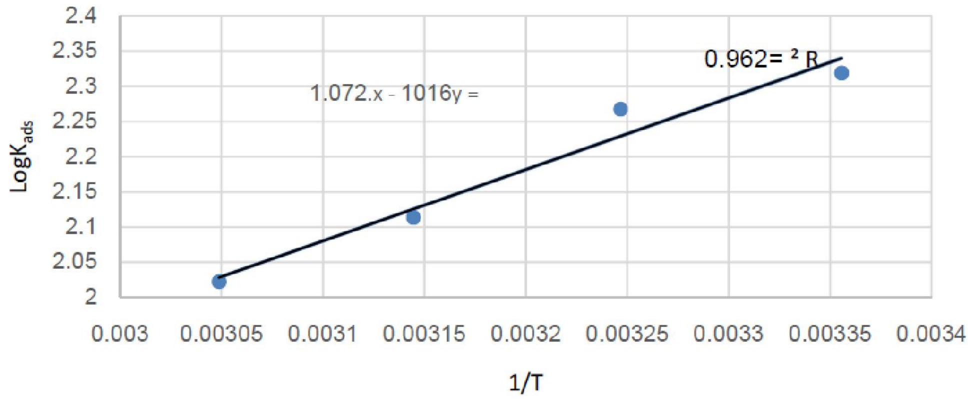

Figure : 7 Plot of log K_{ads} versus 1/T

TABLE 5 : Langmuir adsorption parameters for the adsorption of olive on the surface of carbon steel

T/K	*K_{ads}*	*-ΔG/KJ.mol^{-1}*	*-ΔH/KJ.mol^{-1}*	*ΔS/KJ.mol^{-1}*	*R^2*
298	208.3333	-87.3919	19.4688	0.012871	0.9991
308	185.1852	-89.6712			0.9993
318	129. 8701	-91.9505			0.9998
328	104.1667	-94.2298			0.9997

which isotherm fits best to the adsorption of inhibitors on the C.S surface. Several adsorption isotherms (viz., Frumkin, Langmuir, Temkin, Freundlich) were tested and the Langmuir adsorption isotherm was found to provide the best description of the adsorption behavior of this inhibitor. The Langmuir isotherm is given by following equation (4). (16), as shown in TABLE(5):

$$C/\theta = (1/k_{ads}) + c \qquad (4)$$

Where C is the inhibitor concentration, K_{ads} is the equilibrium constant of the adsorption process, and θ is the surface coverage. Plot C/θ Versus C yields a straight line, Figures-5 with regression coefficient, R^2, almost equal to 1. This suggests that Olive in present study obeyed the Langmuir isotherm and there is negligible interaction between the adsorbed molecules. Free energy of adsorption was calculated using the following relations[17].

$$K_{ads} = \frac{1}{55.55}\, Exp\left(\frac{-\Delta G_{ads}}{RT}\right) \qquad (5)$$

$$-\Delta G_{ads} = -2.303RTlog(55.55K_{ads}) \qquad (6)$$

$$logK_{ads} = \frac{-\Delta H_{ads}}{2.303RT} + \frac{\Delta S_{ads}}{2.303R} + \frac{\log 1}{55.5} \qquad (7)$$

The free energy of adsorption (Gads), is calculated from Eq. (6). The negative value of the free energy of adsorption and the high values of the adsorption constant indicate a spontaneous adsorption of these inhibitors on C.S and increase as the percentage inhibition increases. This means that the inhibitive action of this substance results from the chemical adsorption of these molecules on the surface of C.S.

CONCLUSIONS

Olive leaf extract acts as a good corrosion inhibitor for C-steel in 3.5% NaCl 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 anodic inhibitor at low concentration and work as cathodic inhibitor at more than 3 ppm concentration.
- The inhibition efficiency decreases with increasing temperature.

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