

Curcuma Zedoaria Extract as a Novel Corrosion Inhibitor for Mild Steel in 0.5 M H₂SO₄

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Abstract

In this study, *curcuma zedoaria* extract was investigated as a mild steel (MS) corrosion inhibitor in 0.5 M H₂SO₄ solution by conventional methods of weight loss (WL), electrochemical impedance spectroscopy (EIS) and polarization at 25 °C. The highest percentage of inhibition was obtained for the concentration of 0.5 g/l of *curcuma zedoaria* extract. The results of polarization method showed that *curcuma zedoaria* extract acts as a mixed inhibitor. Examination of MS immersion time by weight loss method showed that with increasing immersion time, the inhibitory effect decreases in low concentrations of *curcuma zedoaria* extract but in higher concentrations of *curcuma zedoaria* extract (concentration 1.0 g/L), the inhibitory effect remains almost constant over time. The effect of temperature on the performance of *curcuma zedoaria* extract by electrochemical polarization method in the temperature range of 35-65 °C shows a decrease in inhibition percentage with increasing temperature. Adsorption of *curcuma zedoaria* extract molecules on the surface of MS at all studied temperatures follows the Langmuir adsorption isotherm. Using the results of kinetic and thermodynamic calculations, the adsorption of molecules of *curcuma zedoaria* extract on the surface of MS physical adsorption type was observed.

Keywords

Corrosion Inhibitor; Mild Steel; Green Extract; H₂SO₄; Polarization; Electrochemical Impedance Spectroscopy.

1. INTRODUCTION

Corrosion is a destructive phenomenon that has adverse effects on the economy and industry [1]. The corrosion resistance of different metals varies due to the difference in the percentage composition of their constituent alloying elements [2]. Mild steel is widely used when it requires a large amount of steel due to its cost-effectiveness. However in the acid pickling process, it is strongly damaged. A common way to prevent corrosion of metals is to use corrosion inhibitors. Tetrahydroacridines [3], graphene oxide [4], surfactant of polyoxyethylene sorbitan trioleate [5], imidazoline [6], 2-amino-4-(5-hydroxy-3-methyl-1H-pyrazole-4-yl)-4H-chromene-3-carbonitrile, abbreviated by name (PCP) [7], chitosan functionalized aminotriazolethiol [8], and 5- aminoindazole loaded into MgAl-LDHs (magnesium aluminum layered double hydroxides) nanocontainer [9], are examples of corrosion inhibitors in different corrosive environments. In recent years, much emphasis has been placed on the use of natural and environmentally friendly inhibitors [10–19]. Notwithstanding of the large number of inhibitory compounds, there are some things to consider when choosing the right inhibitor; including, the

toxicity of inhibitors can have dangerous effects on living organisms, and their economic value when inhibitors are expensive or in large quantities. Herbal extracts are one of the best and most compatible alternatives to traditional corrosion inhibitors [11–14,20]. *Calotropis procera* [21], *Ferula hermonis* [22], *Cannabis sativa* [23], Jujube shell [24], cauliflower [25], *Glycyrrhiza glabra* [26], *Artichoke* [27], and Peach Pomace [28] extracts have been described as effective inhibitors for various metals in the last two years.

Curcuma zedoaria, which has been selected as an effective inhibitor in this study, is a perennial plant that is widely used in traditional medicine due to its anti-inflammatory, anti-cancer and anti-bacterial properties[29–32]. *Zedoary*, white turmeric, or temu putih with the scientific name of *curcuma zedoaria* belongs to the *Zingiberaceae* family. The use of the plant as a spice is very rare today and most people use *Curcuma longa* and *Zingiber officinale* instead. The plant has yellow flowers with green and red leaves. These leaves are often large and up to one meter high. The plant has an underground stem that makes it a large rhizome with numerous branches. *Zedoary* has extraordinary medicinal and therapeutic

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properties. This plant is used as a spice, flavoring and even part of pickles and salads in South and Southeast Asia as well as India. The taste of this plant is very bitter and spicy and it smells like mango. The zedoary plant is grown in humid tropical and subtropical regions. This plant is found in abundance in India and Indonesia; but now it can be seen in the US, state of Florida. Zedoary was introduced to Europeans by Arab traders in the sixth century. Zedoary plant is used to treat inflammation of the body. This plant is anti-inflammatory and improves joint pain. It is also used as housing. This plant is used in traditional medicine to relieve headaches, abdominal pain, toothaches and other chronic pain. The main rhizome is nearly ovoid with a yellow brown to yellow-red color. It contains the greatest volume of curcuminoids, i.e., curcumin (1), demethoxycurcumin (2), and bisdemethoxycurcumin, compared with other *Curcuma* species.

Preliminary studies have shown that *Curcuma zedoaria* extract has not been used as a corrosion inhibitor of MS in sulfuric acid. For this purpose, in this study, the possibility of using this extract as a green compound and effective corrosion inhibitor in 0.5 M sulfuric acid medium was evaluated. *Curcuma zedoaria* extract was introduced for this research due to having the mentioned active constituents. These constituents are predicted to adsorb on the surface of the steel MS and have a protective role.

2. EXPERIMENTAL

The chemicals purchased for the research are: sulfuric acid with a degree of Analytical purity, with specifications: density of 1.83 kg/L and a percentage of purity of 98%, and ethanol with a purity of 96% purchased from Merck.

To prepare 25 ml of 0.5 M H_2SO_4 solution, the calculated amount of 98% sulfuric acid solution was poured into a 25 ml volumetric balloon and made up to volume with distilled water.

The extract was prepared according to the method proposed in reference [30]. Macroscopic and microscopic characteristics of the plant were examined and confirmed in the botany department of Tooba Company.

To prepare 25 mL of the 0.5 M H_2SO_4 solutions containing 0.1, 0.2, 0.3, 0.4 and 0.5 g/l of the extract, the calculated amount of the extract was weighed with a digital scale with an accuracy of

0.0001 g. It was then dissolved in a beaker by adding a minimum of ethanol. Then the required amount of H_2SO_4 to reach a concentration of 0.5 M was calculated and added to it.

In this study, mild steel was used. The composition of the percentage of constituent elements of the studied metal is shown in Table 1. To use the metal in the experiments, they were first cut to the size of 1 cm².

In weight loss measurements, metal pieces are immersed in corrosive solutions. To do this, a hole is made at a distance of 0.2 cm from the upper edge of the cut metal pieces in dimensions of (1.0×1.0×0.1) cm³. For perform weight loss method, after preparing the surface of each sample and polishing it, it is weighed by an analytical scales with an accuracy of 0.1 mg. The plastic wires are then passed through a hole embedded in the piece and suspended inside containers containing the blank solution and the extract solution at different concentrations. The samples are then taken out of the solution after a certain time and weighed again after drying. Measurements are repeated three times by weight loss method and the average results are reported.

For electrochemical studies of impedance and polarization, metal parts must be designed in such a way that it can be electrically connected to the device. So that only one side of the surface of the metal piece is in contact with the corrosive solution. To achieve this goal, first a coated copper wire (the cover of the two ends of which is cut by 1 cm) was soldered to a metal piece in the dimensions of 1 cm² by soldering wire and oil. After ensuring the connection of the copper wire with the metal piece, the metal piece was placed in a box with a length, width and height of 1.25 cm. It was adjusted so that the metal piece was 0.25 cm away from the four sides of the box and was fixed in this case. The box was then filled with two-component epoxy resin. After 8 to 10 hours, the resin dries and hardens and the box can be separated from the resin. Before each measurement, the surfaces of metal pieces were polished with sandpaper numbers 600, 800, 1000, 1200 and 1500, washed with double distilled water and degreased with ethanol.

A three-electrode cell with a working electrode (electrode prepared in previous paragraph), a platinum auxiliary electrode, and an Ag/AgCl reference electrode was used for electrochemical measurements.

Table 1. Composition of percentage of mil steel constituent elements.

C	Si	Mn	P	S	Cr	Ni	Al	Cu	Nb	Ti	V	Fe
0.52	0.0027	0.23	0.006	0.01	0.012	0.04	0.056	0.067	0.0032	0.0021	0.0015	Remaining of 100

All experiments were performed under ambient conditions without stirring the solution. The electrochemical system used is an AUTOLAB potentiostat/galvanostat system model PGSTAT12 made by ECOCHEMIE company which has GPES software in polarization method and FRA software in EIS method. For corrosion studies of this research, two methods of polarization and EIS have been used. Measurements by these two methods should be performed after the potential has stabilized at a constant value to avoid errors due to potential changes during the measurement. For this purpose, the prepared electrode is placed in the desired solution and after connecting the electrodes to the device, it is necessary to wait until the potential is fixed. The numerical value of the potential after it is fixed is called the open circuit potential (OCP). Chrono potentiometric method can be used to observe these changes. In this method, potential changes are plotted over time. The part of the curve where the potential change over time is negligible is known as the OCP potential.

For polarization measurements, the working electrode was first placed in the test solution for the time required for the potential to reach the steady state of open circuit potential (E_{OCP}). Then, the potentiodynamic curves of polarization with a scan rate of 0.50 mV s^{-1} in the potential range of -500 to $+500 \text{ mV}$ relative to the E_{OCP} were obtained. In order to investigate the mechanism of action of the extract and calculate the activation energy of the corrosion process, polarization curves at different temperatures (35 to 65°C) were obtained for the blank solution and solutions containing different concentrations of the extract. Polarization measurements were performed at different temperatures in a double-walled cell connected to a thermostat. The immersion time of the sample in the corrosive environment at temperatures of 35 to 65°C is about 20 minutes. EIS measurements also begin after the time required to fix the OCP time has elapsed. EIS was measured in the frequency range of 100 kHz to 0.10 Hz by applying a potential of 5 mV to the open circuit potential (OCP). That is, a sinusoidal excitation with the mentioned amplitude is created on the open circuit potential, and after determining the actual and apparent resistance during this excitation, which has different values at different frequencies, these two resistors appear in the spectrum relative to each other.

3. RESULT AND DISCUSSION

3.1. Weight loss measurement

One of the methods used to measure the corrosion rate and determine the percentage of inhibition is the weight loss method. Corrosion rate (v) was calculated using the following equation:

$$v_{corr} = \frac{m_1 - m_2}{St} \quad (1)$$

In this equation, m_1 and m_2 are the weight of the piece before and after corrosion in mg, S is the total surface area of the piece in terms of cm^2 , and t is the immersion time in terms of hours.

After calculating the corrosion rate, the percentage of inhibition (η_{WL}) at different concentrations of inhibitors and surface coverage (θ) were calculated from the following equations:

$$\eta_{WL}(\%) = \left(1 - \frac{v_{corr}}{v_{corr}^0}\right) \times 100 \quad (2)$$

$$\eta_{WL}(\%) = \theta \times 100 \quad (3)$$

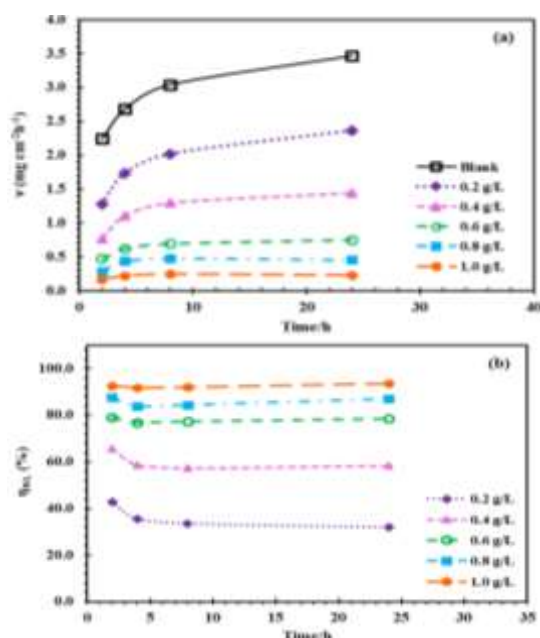
In the above relation, v_{corr} and v_{corr}^0 are the corrosion rates of steel piece in the absence and presence of extract, respectively.

Weight loss experiments were measured at 2, 4, 8 and 24 hours in the absence and presence of different concentrations of the extract at 25°C and the results are shown in Table 2. According to the results of Table 2, with increasing the concentration of *curcuma zedoaria* extract, the v_{corr} of MS in H_2SO_4 solution decreases and the percentage of inhibition increases. The reason for this behavior is attributed to the adsorption of molecules in the *curcuma zedoaria* extract on the surface of MS by increasing the concentration of the *curcuma zedoaria* and thus increasing the covering on the surface of the MS. For better comparison of the results of Table 2, diagrams of changes of v_{corr} and η_{WL} with time are drawn in Figs. (1a and b). Comparing the results in the Table 2 and diagrams mentioned above, it can be concluded that for concentrations lower than the *curcuma zedoaria* extract, a decrease in the η_{WL} is noticeable over time. For example, in an acid solution containing 0.2 g/l extract, the η_{WL} after 2 and 24 hours of immersion was 42.8 and 31.8, respectively. On the other hand, a comparison of changes in the percentage of inhibition for higher concentrations of the extract (for example, a solution of 1.00 g/l of the *curcuma zedoaria* extract) shows that the η_{WL} remained almost constant (change from 92.6% for 2 hours to 93.5% for 24 hours). A small increase in η_{WL} over time is described due to the more complete coverage of the electrode surface with the *curcuma zedoaria* extract molecules and the improvement in the formation of the protective film over time.

Table 2. Corrosion parameters obtained from weight loss method for 1018LCS in 0.5 M H₂SO₄ without and with various concentration of *curcuma zedoaria* extract after different immersion times.

Time	C (g/L)	v (mg cm ⁻² h ⁻¹)	θ	η_{WL} (%)
2	Blank	2.242	-	-
	0.2	1.280	0.4287	42.9
	0.4	0.766	0.6582	65.8
	0.6	0.469	0.7905	79.1
	0.8	0.282	0.8743	87.4
	1.0	0.165	0.9264	92.6
4	Blank	2.68	-	-
	0.2	1.730	0.355	35.5
	0.4	1.106	0.587	58.7
	0.6	0.621	0.768	76.8
	0.8	0.436	0.837	83.7
	1.0	0.219	0.918	92.8
8	Blank	3.042	-	-
	0.2	2.019	0.336	33.6
	0.4	1.298	0.573	57.3
	0.6	0.692	0.773	77.3
	0.8	0.477	0.843	84.3
	1.0	0.245	0.920	93.0
24	Blank	3.471	-	-
	0.2	2.363	0.319	31.9
	0.4	1.446	0.583	58.3
	0.6	0.748	0.784	78.4
	0.8	0.454	0.869	86.9
	1.0	0.227	0.935	93.5

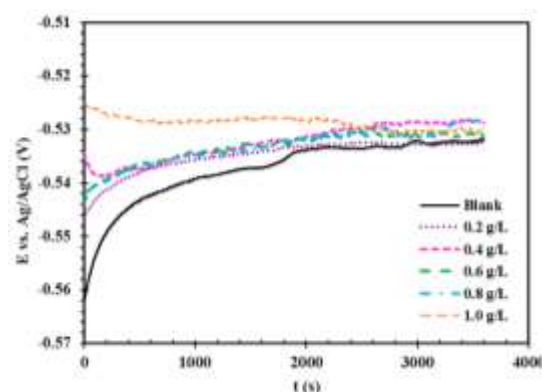
without and with various concentration of *curcuma zedoaria* extract after different immersion times.

**Fig. 1.** The diagrams ((a) variation of WL of MS in the absence and presence of different concentrations of *curcuma zedoaria* extract and ((b) η_{WL} relative to immersion time in 0.5 M H₂SO₄ solution.

3.2. Determining the stabilization time of OCP

In this section, potential changes in terms of time were plotted using the chrono potentiometric method. The results are shown in Fig. 2. The

maximum potential displacement in the presence of the *curcuma zedoaria* extract in H₂SO₄ solution is 10 mV. In the presence of *curcuma zedoaria* extract, the potential of the system reaches a steady state in less time. While, in the absence of *curcuma zedoaria* extract, the time to reach steady state potential is longer. The reason for faster stabilization of the potential in the presence of the extract can be attributed to the formation of a protective layer on the surface and thus achieving faster stability of the system.

**Fig. 2.** Open circuit potential changes with time for soft steel electrode in 0.5 M H₂SO₄ solution in the absence and presence of different concentrations of *curcuma zedoaria* extract.

3.3. EIS measurements

The corrosion of MS in 0.5 M H₂SO₄ without and with *curcuma zedoaria* extract was investigated by EIS at 25°C. The Nyquist curves are shown in Fig. 3. The equivalent circuit of Fig. 3(b) corresponds to the experimental results. The EIS spectrum has a large capacitance semicircle at high frequencies and a small inductor loop at low frequencies. The presence of inducers at low frequencies may be attributed to the relaxation process resulting from the adsorption of components such as H⁺ and SO₄²⁻ on the electrode surface or the dissolution of the metal surface at low frequencies [33]. The impedance spectra are modeled by the device simulation software and the relevant parameters are given in Table 3. The value of R_{ct} indicates the amount of resistance of electron transfer on the surface and is inversely proportional to the corrosion rate. The η_{EIS} (%) is calculated using the values of R_{ct} from Equation 4.

$$\eta_{EIS}(\%) = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \times 100 \quad (4)$$

R_{ct} and R_{ct(inh)} are the resistance of electron transfer for blank and solutions containing of the *curcuma zedoaria* extract, respectively. The CPE (constant phase element) is used instead of the capacitor and symbolizes of all the factors influencing the surface non-uniformity due to surface roughness, impurities, distribution of active regions, formation of porous layers, and adsorption of inhibitors, etc. CPE impedance is expressed by Equation (5).

$$Z_{CPE} = \frac{1}{Y_0 (j\omega)^n} \quad (5)$$

In this relation Y₀ is a value of CPE and n (−1 ≤ n ≤ 1) is equal to the non-uniformity coefficient of the surface. For curves that have the appearance of a recessed semicircle, 0.5 ≤ n ≤ 1. The capacity of the double layer C_{dl} for the circuit containing CPE is calculated from the following equation.

$$C_{dl} = Y_0 (\omega_{\max})^{n-1} \quad (6)$$

In this relation, ω_{max} = 2πf_{max} is the highest frequency of the imaginary part of the impedance.

Adsorption of molecules on the surface of metal is associated with a decrease in the capacity of the C_{dl}, that results in an increase in the thickness of the C_{dl} or a decrease in the dielectric constant. Table 3 shows that with increasing the concentration of the *curcuma zedoaria* extract, the values of R_{ct} increase and the values of C_{dl} and the corrosion rate decrease. The decrease in C_{dl} is the result of a decrease in the dielectric constant or an increase in the thickness of the double layer. This can be analyzed as the inhibitory molecules replacing the adsorbed water molecules at the solution/metal boundary and increasing the thickness of the bilayer thereby reducing the capacity of the bilayer.

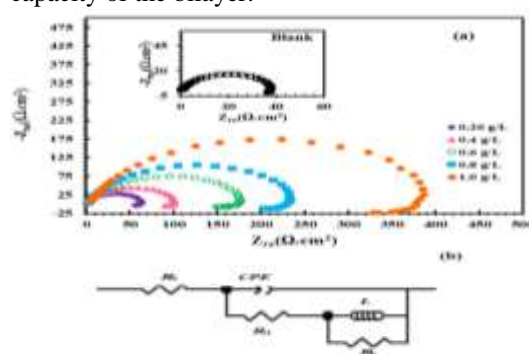


Fig. 3. (a) Nyquist curves and (b) equivalent circuit of MS surface in 0.5 M H₂SO₄ solution without and with different concentrations of *curcuma zedoaria* extract at 25 °C.

3.4. Measurements using polarization curve

In the Tafel extrapolation method, it is also possible to measure very low rates, the value of which can be calculated according to the location of the intersection along the linear region of the Tafel curves. In order to achieve the mentioned curves, after preparing the electrodes and adjusting the device conditions and also with the GPES software, the desired Tafel diagrams were obtained. Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic and anodic Tafel slopes (b_a and b_c) and the percentage of relevant inhibitions are obtained by extrapolation of Tafel lines.

Table 3. Electrochemical parameters derived from EIS measurements for MS corrosion in acid solutions without and with different concentrations of *curcuma zedoaria* extract at 25 °C.

Concentration(g/L)	R _s (Ω.cm ²)	R _{ct} (Ω.cm ²)	CPE		C _{dl} (μF cm ²)	η _{EIS} (%)
			Q(μΩ ⁻¹ s ⁿ cm ⁻²)	n		
Blank	0.31	33.2	590.6	0.79	489.3	-
0.2	0.42	61.9	166.8	0.82	154.6	43.13
0.4	0.68	100.6	118.3	0.84	91.4	65.01
0.6	1.50	170.3	77.0	0.84	64.4	79.33
0.8	1.29	267.9	50.5	0.85	48.8	86.86
1.0	2.90	408.4	41.4	0.86	33.7	94.16

Also, the η_{pol} (%) can be calculated according to Equation 7.

$$\eta_{\text{Pol}}(\%) = \left(1 - \left(\frac{I_{\text{corr}}}{I_{\text{corr}}^0}\right)\right) \times 100 \quad (7)$$

The results of this study are shown in Table 4 and Fig. 4. According to Table 4, with increasing the concentration of the *curcuma zedoaria* extract, the η_{pol} (%) as well as the surface coverage (θ , $\theta = \eta_{\text{pol}}/100$) increases and the I_{corr} decreases. As can be seen from the Tafel curve in Fig. 4, in the presence of the *curcuma zedoaria* extract compared to the blank solution, the current density decreased in both cathodic and anodic branches, and this behavior indicates the effect of the *curcuma zedoaria* extract on both cathodic and anodic reactions and *curcuma zedoaria* extract is of mixed type (cathodic-anodic).

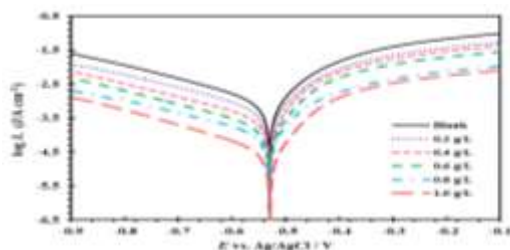


Fig. 4. Polarization curves obtained from 1018LCS surface in 0.5 M H₂SO₄ solution without and with different concentrations of *curcuma zedoaria* at 25 °C.

Table 4. Polarization parameters and inhibitory percentages, for corrosion of MS, in 0.5 M H₂SO₄ without and with different concentrations of *curcuma zedoaria* extract at 25 °C.

Concentration (g/L)	E_{corr} (V, vs. Ag/AgCl)	$-b_c$ (V dec ⁻¹)	b_a	I_{corr} ($\mu\text{A cm}^{-2}$)	θ	η_{pol} (%)
Blank	-0.53	0.252	0.089	909.1	-	-
0.2	-0.53	0.277	0.095	527.0	0.420	42.04
0.4	-0.529	0.214	0.088	313.7	0.655	65.50
0.6	-0.53	0.176	0.067	176.0	0.806	80.64
0.8	-0.531	0.278	0.084	95.1	0.895	89.54
1.0	-0.529	0.179	0.065	38.2	0.958	95.80

Table 5. Polarization parameters and inhibitory percentages, for corrosion of MS, in 0.5 M H₂SO₄ without and with different concentrations of *curcuma zedoaria* extract at different temperatures.

Temperature(°C)	Concentration(g/L)	E_{corr} vs. Ag/AgCl(V)	I_{corr} ($\mu\text{A cm}^{-2}$)	θ	η_{pol} (%)
35	Blank	-0.527	959.2	-	-
	0.2	-0.524	570.80	0.405	40.49
	0.4	-0.530	364.12	0.620	62.04
	0.6	-0.531	203.27	0.788	78.81
	0.8	-0.525	129.18	0.865	86.53
	1.0	-0.535	59.14	0.938	93.83
45	Blank	-0.529	5895.4	-	-
	0.2	-0.524	3650.85	0.381	38.07
	0.4	-0.519	2460.97	0.583	58.26
	0.6	-0.518	1350.39	0.771	77.09
	0.8	-0.520	1002.27	0.830	83.00
	1.0	-0.519	527.04	0.911	91.06
55	Blank	-0.532	7767.0	-	-
	0.2	-0.537	4998.64	0.356	35.64

The values of b_a and b_c for the *curcuma zedoaria* extract remain almost constant, indicating that the extract does not affect the kinetics of the hydrogen gas evolution reaction at the cathode and that it does not interfere with the dissolution mechanism; Therefore, in practice, the extract has only played the role of surface coating [21].

3.5. Investigation of temperature

The influence of temperature on the parameters of the corrosion of MS in 0.5 M H₂SO₄ without *curcuma zedoaria* extract and with different concentrations of the *curcuma zedoaria* extract was studied using the polarization method (Fig. 5 and Table 5) in the temperature range of 35 °C to 65 °C. The corrosion parameters of Table 5 show that when the temperature increases, I_{corr} increases in the presence and absence of *curcuma zedoaria* extract, but the *curcuma zedoaria* extract has inhibitory properties at all the studied temperatures and with increasing temperature, the inhibitory percentage values for the extract decrease; The fact that the percentage of inhibition decreases with increasing temperature was explained by the fact that at high temperatures there is probably no specific interaction between the iron surface and the inhibitor [10].

65	0.4	-0.541	3376.30	0.565	56.53
	0.6	-0.539	1973.53	0.746	74.59
	0.8	-0.54	1570.32	0.798	79.78
	1.0	-0.546	867.29	0.888	88.83
	Blank	-0.540	9391.8	-	-
	0.2	-0.544	6366.07	0.322	32.22
	0.4	-0.545	4338.87	0.538	53.80
	0.6	-0.549	2865.13	0.695	69.49
	0.8	-0.552	1939.79	0.793	79.35
	1.0	-0.558	1233.17	0.869	86.87

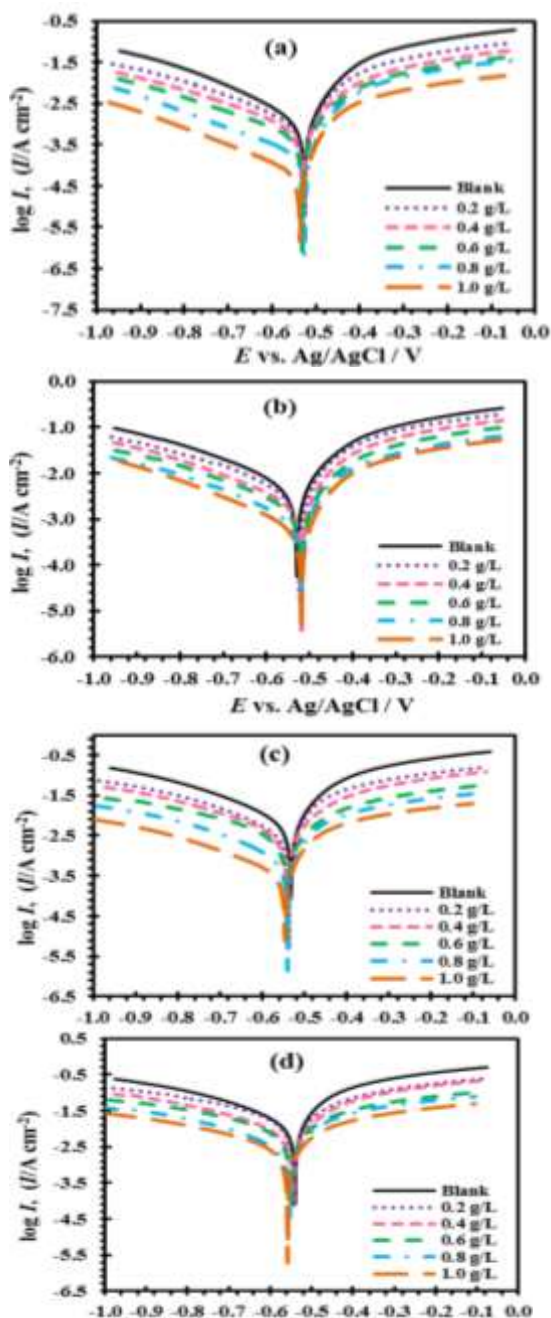


Fig. 5. Polarization curves obtained from MS surface in 0.5 M H₂SO₄ solution without and with different concentrations of *curcuma zedoaria* at (a): 35 °C, (b): 45 °C, (c): 55 °C and (d): 65 °C.

Adsorption isotherm was investigated to further understanding the mechanism of corrosion inhibitors. Adsorption isotherms determine the interaction of inhibitory molecules with active positions on the metal. The degree of surface coverage (θ) is calculated using the polarization calculations (in Tables 4 and 5) from the following equation.

$$\theta = \frac{\eta_{pol}(\%)}{100} \quad (8)$$

From a scientific point of view, it is necessary to determine which of the adsorption isotherms the surface coverage data corresponds to; because the results of the adsorption isotherm are benefit to determine the thermodynamic parameters. The isothermal model studied in this research is the most prominent extract of Tamkin, Framkin, Langmuir, Freundlich and Flory-Huggins isotherms. The R², correlation coefficient, was used to select the best adsorption isotherm according to the experimental results. Examination of the adsorption isotherm diagrams shows that the value of R² in the Langmuir curves is very close to one (Table 6). As a result, the extract studied in this study follows the Langmuir adsorption isotherm that is defined as follows.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (9)$$

Langmuir adsorption isotherm was obtained at different temperatures. The results are shown in Fig. 6.

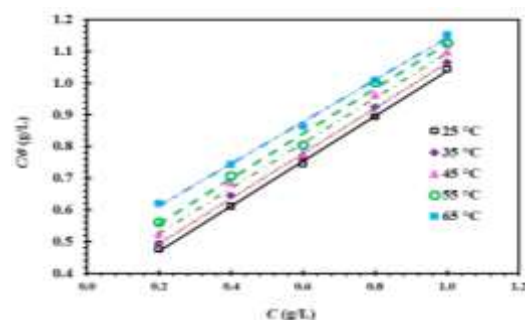


Fig. 6. Langmuir adsorption isotherm obtained from adsorption of *curcuma zedoaria* on the surface of MS in acidic solution 0.5 M H₂SO₄ solution at various temperatures.

Table 6. Thermodynamic parameters of adsorption of *curcuma zedoaria* on MS in 0.5 M H₂SO₄ obtained from Langmuir adsorption isotherm at different temperatures.

Temperature (°C)	Slope	Intercept	R ²	K _{ads} (L/g)	ΔG _{ads} ⁰ (kJ mol ⁻¹)
25	0.7095	0.3279	0.9991	3.050	-12.71
35	0.7117	0.3511	0.9981	2.848	-12.97
45	0.7115	0.3836	0.9926	2.607	-13.15
55	0.7121	0.413	0.9911	2.421	-13.36
65	0.6627	0.4798	0.9980	2.084	-13.35

Table 7. Thermodynamic parameters of adsorption of *curcuma zedoaria* on MS in 0.5 M H₂SO₄ obtained from Langmuir adsorption isotherm at different temperatures.

Concentration(g L ⁻¹)	E _a (kJ mol ⁻¹)	ΔH [*] (kJ mol ⁻¹)	-ΔS [*] (J mol ⁻¹ K ⁻¹)
Blank	54.60	51.96	14.29
0.2	60.35	57.71	1.37
0.4	68.65	66.02	24.70
0.6	76.12	73.48	43.98
0.8	79.16	76.52	247.79
1.0	85.13	82.49	64.58

The adsorption isotherm of the Langmuir type can represent the formation of a monolayer on the surface of MS as well as the occupation of the adsorption site by one or more inhibitory molecules. To investigate and determine the adsorption behavior of inhibitors using thermodynamic data, two main interactions should be considered, one is physical adsorption and the other is chemical adsorption. In physical adsorption, adsorption occurs because of electrostatic gravitational forces between ionic or bipolar charges on the adsorbed components (inhibitors) and the electrical charge on the metal-solution surface. In physical adsorption, heat absorption is low, so it is stable merely at low temperatures. Chemical adsorption is associated with the formation of a co-ordination bond by sharing charge or transferring charge from inhibitory molecules to the metal surface. In chemical type of adsorption, adsorption energy relative to physical type is stronger, therefore, at high temperatures is more stable. The ΔG_{ads} parameter is used to determine whether the inhibitory adsorption on the metal surface is of the physical or chemical adsorption type. Therefore, the K_{ads}, adsorption equilibrium constant, is achieved from the inverse of the intercept of the Langmuir adsorption isotherm curve. ΔG_{ads} can be calculated by determining the K_{ads} by using the following relation:

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}}{RT}\right) \quad (10)$$

The number 55.5 is the concentration of water in solution and is expressed in units of molarity.

The thermodynamic parameters obtained from the study of inhibitory adsorption processes are given in Table 6, which presents the slope, line correlation coefficients (R²) and K_{ads} obtained by plotting the C/θ values against C. Negative values of ΔG_{ads} indicate the spontaneity of the adsorption

process and indicate the tough and firm interaction of the adsorption layers on the surface. ΔG_{ads} values greater than -20 kJ/mol indicate the electrostatic interaction (physical adsorption) and values between -40 kJ/mol to -400 kJ/mol indicate chemical adsorption and co-ordination bond formation. ΔG_{ads} between -20 kJ/mol to -40 kJ/mol also indicate physico-chemical adsorption [10,18,26]. The values of ΔG_{ads} in Table 6 are greater than -20 kJ/mol, indicating a physical adsorption.

Kinetic parameters are activation energy E_a, enthalpy (ΔH^{*}) and entropy (ΔS^{*}) of activation, which are obtained in the presence of inhibitor and in the absence of inhibitor.

$$r = \lambda \exp\left(\frac{-E_a}{RT}\right) \quad (11)$$

In this relation E_a (kJ mol⁻¹) activation energy, λ frequency factor, T absolute temperature (K), R constant of gases, r is the corrosion reaction rate which it has a direct relationship with corrosion rate and I_{corr}. If there is a linear relationship between ln(I_{corr}) and 1/T, the E_a of the metal dissolution process can be calculated from the slope of the resulting lines. Fig. 7 (a) shows the linear relationship between ln(I_{corr}) and 1/T. E_a was obtained using the slope of the resulting lines and the results are reported in Table 7. The modified formula of Arrhenius equation is as follows:

$$r = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \quad (12)$$

In this relation, h is Planck's constant and N is Avogadro's number. Straight lines are attained from drawing (ln(I_{corr}/T)) to 1/T. The slope of the resulting line is -ΔH^{*}/R and the intercept is lnR/Nh+ΔS^{*}/R; Therefore, from the slope and intercept, the values of ΔH^{*} and ΔS^{*} are calculated and are given in Table 6. The positive values of

ΔH^* obtained in Table 7 show that the process of dissolving steel in H_2SO_4 solution is endothermic.

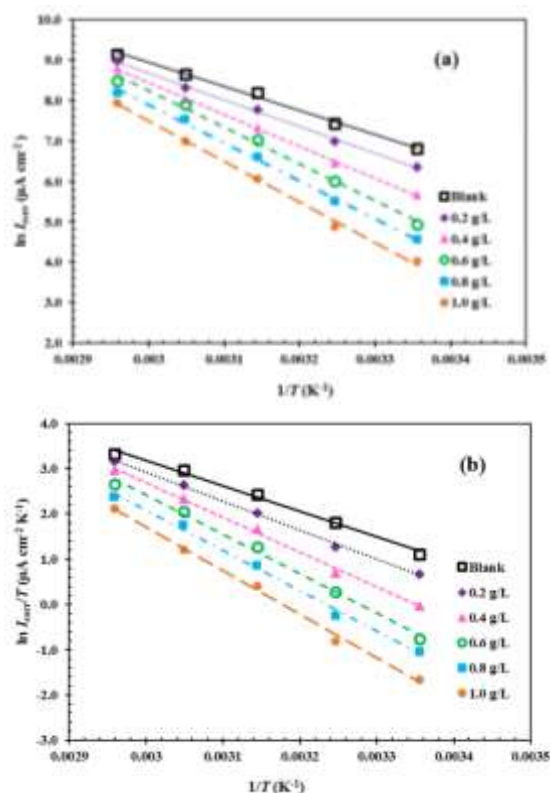


Fig. 7. Arrhenius curve obtained from drawing $\ln(I_{\text{corr}})$ versus $1/T$ (a) and $\ln(I_{\text{corr}}/T)$ versus $1/T$ (b) in the absence and presence of different concentrations of *curcuma zedoaria*: in 0.5 M H_2SO_4 solution.

So corrosion increases with increasing temperature. The negative sign ΔS^* indicates a greater tendency of the activated complex to accumulate, in comparison with the dissolution, at the rate-determining stage. Thus, with the transition of the reactants to the activated complex, the disorder is reduced. The results of Table 7 indicate that E_a is increased in the presence of the *curcuma zedoaria* extract. According to the above, higher amounts of E_a obtained with existence of the *curcuma zedoaria* extract in comparison with blank solution can be attributed to the physical adsorption of the *curcuma zedoaria* extract on the MS surface.

3.6. Inhibitory mechanism of *curcuma zedoaria* extract

The results of investigating the inhibitory effect of *curcuma zedoaria* extract on the surface of MS in various methods exhibited that by increasing the concentration of the *curcuma zedoaria* extract, the inhibition performance increased. Therefore, it is concluded that more molecules in the *curcuma zedoaria* extract can be adsorbed on the metal

surface. Therefore, the part of the metal surface that is directly attacked by the acid is reduced. In this section, the aim is to investigate how the surface is covered by extract molecules. Therefore, we select the main constituents in the extract and study the process of their adsorption on the surface. According to the results of the study of the extract of the most famous shoots, the most main constituents of *curcuma zedoaria* are polyphenol compounds, the most important of which are curcumin, demethoxycurcumin, and bisdemethoxycurcumin [30]. The structure of some of the polyphenol compounds of *curcuma zedoaria* extract is shown in Fig. 8. As can be seen from the structure of polyphenol compounds in Fig. 8, there are oxygen atoms, OH, OCH_3 groups, and aromatic rings in the structure of polyphenol compounds. Hydroxyl groups are protonated in an acidic environment.

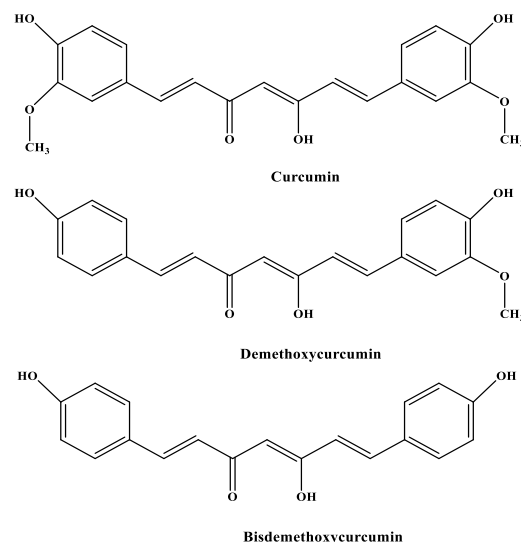
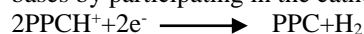


Fig. 8. Some chemical structure of *curcuma zedoaria* components.

Therefore, in the acidic environments of H_2SO_4 , polyphenol compounds get positive charge. The metal surface load in H_2SO_4 medium has been reported positively in articles [33]. In H_2SO_4 solution, acid anions SO_4^{2-} are first adsorbed on the surface of metal and the surface have negative charge relative to the solution and circumstances are provided for the adsorption of protonated compounds (electrostatic interaction). In other words, a synergistic effect is created between the SO_4^{2-} anion and the positively charged polyphenol compounds in the solution. As soon as corrosion begins, cationic polyphenol compounds (PPC) begin to attack cathodic sites and, given the following relationship, become free compounds bases by participating in the cathodic reaction.



Therefore, it will be possible to directly adsorb the polyphenol compounds in the *curcuma zedoaria* extract to the metal surface through donor-acceptor interactions type between the π electrons of heterocyclic compounds and the empty d orbitals of Fe surface atoms.

4. CONCLUSION

Examination of *curcuma zedoaria* extract at concentrations of 0.2, 0.4, 0.6, 0.8 and 1.0 g/l on the surface of MS in 0.5 M sulfuric acid showed that with increasing the concentration of the extract, the inhibition efficiency also increases and has the best inhibitory performance at a concentration of 1.0 g/l. The *curcuma zedoaria* extract acts as a mixed inhibitor (cathodic-anodic) in sulfuric acid medium. Since with increasing temperature, the amount of activation energy for solutions containing the extract has increased in comparison with the blank solution, it can be concluded that the adsorption of the *curcuma zedoaria* extract on the surface of MS in 0.5 M sulfuric acid is of physis adsorption type.

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عصاره Curcuma zedoaria به عنوان یک بازدارنده جدید خوردگی برای فولاد نرم در ۰/۵ مولار H_2SO_4

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چکیده

در این تحقیق، عصاره *curcuma zedoaria* به عنوان بازدارنده خوردگی استیل نرم در محلول ۰/۵ مولار سولفوریک اسید به روش‌های متداول کاهش وزن، طیف سنجی الکتروشیمیایی امپدانس و پلاریزاسیون در دمای $25^{\circ}C$ مورد بررسی قرار گرفت. بیشترین درصد بازدارندگی برای غلظت ۰/۵ گرم بر لیتر از عصاره *curcuma zedoaria* به دست آمد. نتایج روش پلاریزاسیون نشان داد که عصاره *curcuma zedoaria* به عنوان بازدارنده مختلط عمل می‌کند. بررسی زمان غوطه‌وری استیل نرم به روش کاهش وزن نشان داد که با افزایش مدت زمان غوطه‌وری اثر بازدارندگی در غلظت‌های کم عصاره *curcuma zedoaria* کاهش می‌یابد اما در غلظت‌های بیشتر از عصاره *curcuma zedoaria* (غلظت ۱/۰ گرم بر لیتر) اثر بازدارندگی با گذشت زمان تقریباً ثابت می‌ماند. بررسی اثر دما بر عملکرد عصاره *curcuma zedoaria* به روش الکتروشیمیایی پلاریزاسیون در محدوده دمایی $25-65^{\circ}C$ نشان دهنده کاهش در درصد بازدارندگی با افزایش دما است. جذب مولکول‌های عصاره *curcuma zedoaria* بر سطح استیل نرم در تمام دماهای مورد بررسی از هم دمای جذب لانگمویر پیروی می‌کند. با استفاده از نتایج محاسبات سینتیکی و ترمودینامیکی جذب مولکول‌های عصاره *curcuma zedoaria* بر سطح استیل نرم از نوع جذب فیزیکی مشاهده شد.

واژه‌های کلیدی

بازدارنده خوردگی؛ استیل نرم؛ عصاره سبز؛ H_2SO_4 ؛ پلاریزاسیون؛ طیف سنجی امپدانس الکتروشیمیایی.