Inhibition Effect of Eucalyptus leaf extract on low carbon steel in dilute H2SO4 acid at room and high temperatures.

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Abstract

Corrosion inhibitors are currently a beneficial technique to maintain or reduce corrosion problems in equipment, therefore the development of all non-toxic, natural, and low-cost inhibitors is in high demand. The extract of eucalyptus leaves was employed as a mild steel corrosion inhibitor in this study at various H2SO4 concentrations (0.5, 1, and 1.5 molarity). The effect of temperature on the corrosion behavior of mild steel was also examined. Electrochemical polarization test methods were used to explore this. The extract inhibition efficiency and mild steel corrosion rate were calculated. The results suggest that the extract could be one of the most effective mild steel corrosion inhibitors. The inhibitor efficiency was also shown to decrease when temperature and H2SO4 concentration increased.

Keywords: Eucalyptus leaves extract , Electrochemical polarization , mild steel , inhibitor efficiency

1. Introduction

Corrosion will always occur since practically, in the Earth's atmosphere, every metal and alloy is unstable. One of the biggest reasons of industry overhead costs is the maintenance and repair of damaged and worn out equipment and parts, which is caused by chemical contact with their environment. In general, proper corrosion control and monitoring can prevent a significant amount of the loss. The addition of inhibitors to metallic surfaces, even at modest quantities, is one of the best ways to limit the rate of metallic corrosion. [1-6]. Due to its unique physical and mechanical features, such as ductility, huge strength, weldability, and the ability to heat treat for diverse mechanical properties, mild steel is one of the most commonly used materials for petroleum pipelines . Mild steel is often constructed in such a way that it can meet the stringent needs and services needed, such as for a petroleum transmission pipeline that is sensitive to a number of parameters such as the content of the petroleum product travelling through it, the temperature and pressure of the contents [7]. Because of the existence of massive corrosive substances in crude oil, which have an emotional impact on pipelines and equipment, petroleum production might be hindered by corrosion [8]. The inclusion of inhibitors, which can be found in even modest amounts, is one of the finest ways to lower the pace of metallic corrosion. However, there are a few factors that can help you choose the right inhibitor. These considerations include the cost and amount of the inhibitor, long-term toxicological impacts on the environment, and the inhibitor's ability to treat corroded surfaces, as well as the availability and stability of the inhibitor under various situations [9]. One of the most effective strategies for shielding metallic surfaces against corrosion is to employ corrosion inhibitors (inorganic & organic).The inorganic inhibitors operate as anodic inhibitors, whereas the organic inhibitors build a protective coating on the metal surface by adsorbing their molecules, resulting in corrosion resistance [10,11]. Organic compounds with heteroatoms in their molecules, such as nitrogen, sulphur, or oxygen, and an aromatic ring in their molecules have a substantial influence on the extent of adsorption on the surface of the metal, and may therefore be employed as corrosion inhibitors [12]. They are poisonous and dangerous to humans and the environment, and their synthesis is frequently costly. As a result, the development of non-toxic, environmentally friendly, green corrosion inhibitors is seen as critical and ongoing. Recently, there has been a surge in interest in using naturally occurring compounds and extracts that meet the criteria for usage as effective corrosion inhibitors [13].

Eucalyptus is an Australian native genus of the Myrtaceae family, with approximately 900 species and subspecies, making it one of the world's most important and widely planted genera. It is grown for its timber, pulp, and medicinal and therapeutic essential oils[14]. **Tezeghdenti et al. [15]** Using weight loss measures and several electrochemical methods, researchers investigated the corrosion prevention effect of a methanolic extract of Eucalyptus globulus leaves for corrosion control of carbon steel in a 1 M H2SO4 solution. It was discovered that E. The extract of globulus acts as a mixed type inhibitor. They discovered that the Langmuir adsorption isotherm is obeyed by this green inhibitor. The current study investigates the impact of methanolic Eucalyptus leaf extract on mild steel corrosion in sulfuric acid solutions. The effect of acid anions, sulfate, and the inhibitory efficacy of Eucalyptus leaf extract for mild steel corrosion management will be revealed. The researchers wanted to see how temperature affected the inhibitor's effectiveness[16-23]

2 . EXPERIMENTAL

Electro-chemical Tafel testing approach and chemical test of composition analyses are used to investigate the effects of eucalyptus leaf extract on mild steel samples that have been corroded in three concentration levels of Sulfuric acid mediums (0.5, 1, and 1.5 molarity) at different temperatures (25C, 60C).

2.1 Materials

a) **The mild steel samples**

Before each test, mild steel discs having a diameter of 25 mm and a thickness of 1.5 mm were cut into small discs to fit into the holder of the potentiostat device's working electrode, which was immersed in the preparation solution .Furthermore, emery sheets were used to polish each sample. Table 1 shows a sample with chemical composition. This test was done at State Company for Inspection and Engineering Rehabilitation (SIER)

TABLE 1: THE CHEMICAL ANALYSIS OF MILD STEEL SAMPLE

	C%	Si%	Mn%	P%	S%	Cr%	Mo%	Ni%	Cu%	Al%	Fe%
Element%	0.0429	0.00059	0.296	0.0066	0.0257	0.0277	0.0029	0.0281	0.0422	0.0138	Bal.

b) **Eucalyptus leaf extract**

The leaves of the Eucalyptus tree are collected and washed to remove any dirt. After that, 100 gm of eucalyptus leaves were mixed with 500 ml of methanol and fractional distillation was performed for 1 hour to obtain 120 ml of extraction, which was then filtered.

2.2 Electrochemical measurements

In a traditional 3-electrode electrolysis cell,electrochemical measurements were done. The working electrode (which contains the test material of interest) had a disc form that has been cut from mild steel samples with thicknesses of 1.5 mm and a diameter 25 mm the area exposed to the corrosion is 0.78 cm^2 surface area. A calomel electrode that has been saturated (SCE) as well as graphite rod were used as a reference and auxiliary electrode.The electrochemical cell is then filled with a electrolyte solution. Also, the experiments have been utilized at two different temperature (25°C and 60°C) and utilizing the software program of Gamry work frame to record the experiment data. Recorded Data might be saved and after that, analyzed with the software of Gamry Echem Analyst.

Figure1. The electrochemical device

2.3 Solutions preparation

The H2SO4 solution (0.5, 1M, 1.5M) was made by diluting analytical H2SO4 with distilled water. The solution tests are made before to the experiment by mixing the extract with the corrosive solution directly.

2.4 Eucalyptus extract composition

The compounds in the sample were detected and characterized using GC-MS analysis ; this test identified all of the chemical components detected in Eucalyptus leaf extracts. The extraction of Eucalyptus leaves yielded 12 chemicals, the most important of which is: 1,8-Cineole (7.50%) , 1,2,3-Benzenetriol (6.00%) , Benzyl benzoate (17.47%) , Cyclononasiloxane, octadecamethyl- (20.90%) as shown in Table-2.

TABLE-2 THE COMPOUND OF GC-MS ANALYSIS

No	RT (min)	Area%	Name	Quality	CAS Number
1	7.654	7.50	1,8-Cineole	99	000470-82-6
2	10.928	2.20	Benzoic acid	91	000065-85-0
3	11.146	3.60	4-Terpineol	97	000562-74-3
4	11.457	4.40	.ALPHA. TERPINEOL	90	000098-55-5
5	12.064	2.90	2,3-DIHYDRO-BENZOFURAN	70	000000-00-0
6	15.66	6.00	1,2,3-Benzenetriol	87	000087-66-1
7	20.039	5.00	Globulol	93	000000-00-0
8	20.189	8.00	γ-Gurjunene	90	022567-17-5
9	20.397	5.90	2,6-Dideutero pyridine-4-carboxylic acid	35	055090-48-7
10	23.204	17.47	Benzyl benzoate	98	000120-51-4
11	35.169	20.90	Cyclononasiloxane, octadecamethyl-	90	000556-71-8
12	42.973	5.30	Vouacapenic acid	11	019941-59-4

3. RESULT AND DISCUSSION

The data of each test were recorded and then discussed in order to determine its significance. According to the findings of the tests below, the extract is an efficient mild steel corrosion inhibitor.

3.1 Electrochemical polarization test

Tafel extrapolation is a common polarization method for measuring corrosion rates, and it is a faster experimental methodology than traditional weight-loss estimation.

3.1a Electrochemical polarization test at (25 ºC)

Mild steel polarization curves in various concentrations of H_2SO_4 obtained without and with the inhibitor are shown in Figures below.

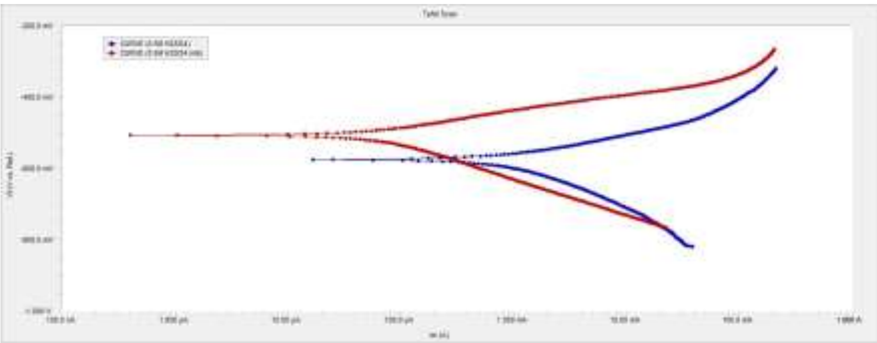

Figure 2. Tafel Tests for 0.5 Molarity of H_2SO_4 (with and without inhibitor)at 25℃

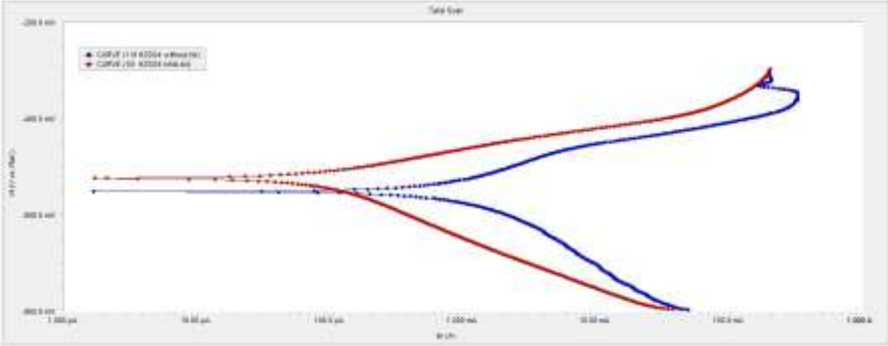

Figure 3. Tafel Tests for 1 Molarity of H_2SO_4 (with and without inhibitor)at 25°C

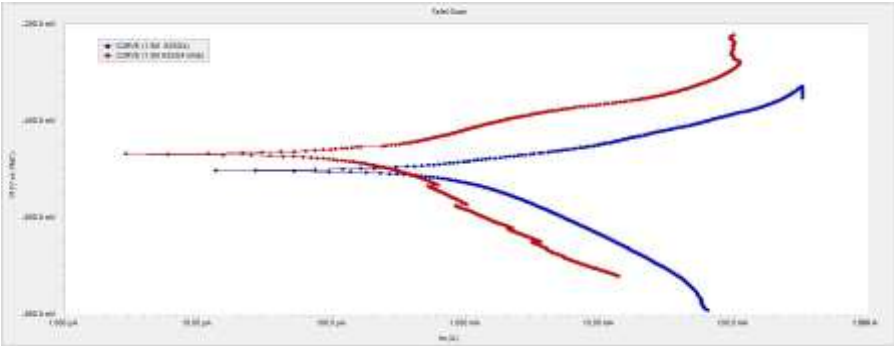

Figure 4. Tafel Tests for 1.5 Molarity of H_2SO_4 (with and without inhibitor)at 25°C.

Table 3 includes electrochemical characteristics such as icorr (corrosion current density), Ecorr (corrosion potential), ßc (cathodic Tafel slope), and ßa (anodic Tafel slope), as well as the inhibitor's inhibitory efficacy (percent EI). The addition of an inhibitor shifted the polarization curves to lower current levels, as shown in the figures above, showing the inhibition tendency of eucalyptus leaf extract. The inhibition efficiency was determined in this situation by utilizing the corrosion rate as follows:

$$ŋ\% = \frac{Wcorr - WH}{Wcorr} \quad ……(1)$$

ŋ% represents the percentage of the inhibitor efficiency, WH represents the rate of the Corrosion in (mmpy) with inhibitor, and Wcorr represents the rate of Corrosion without inhibitor in (mmpy).

Table 3. Parameter values of the Tafel testing for 0.50, 1.0, 1.50M of the H_2SO_4 with and without eucalyptus leaf extract.

Environment	Ecorr(mV)	Corrosion rate(mmpy)	Icorr (µA)	Aβ V/decade	Cβ V/decade	Efficiency □
0.5M H2SO4	-575.0	5.305	383.0	47.90e-3	90.50e-3	86%
0.5M H2SO4 Inhibitor	-506.0	741.3e-3	53.50	53.10e-3	98.00e-3	
1M H2SO4	-550.0	7.446	538.0	75.30e-3	76.70e-3	84%
1M H2SO4 inhibitor	-523.0	1.169	84.40	56.20e-3	115.6e-3	
1.5M H2SO4	-503.0	9.575	691.0	48.40e-3	111.9e-3	75%
1.5M H2SO4 inhibitor	-469.0	2.374	171.0	61.30e-3	112.5e-3	

Table 3 shows that applying eucalyptus extract reduced corrosion current density (icorr). However, it is possible that the pace of electrochemical reaction was slowed due to the creation of a layer on the surface caused by molecule adsorption. This adsorption phenomena might be explained by the synergistic impact of diverse organic compounds in corrosion inhibitors, or by an interaction between the components of the inhibitor's chemical makeup and the steel surface, which encouraged the creation of an inhibitory layer. As a result, the active components of eucalyptus leaf extract mentioned in table 2 limit mild steel dissolving ,they are the cause of film deposition by absorption because they are carbohydride that do not dissolve in aqueous solution. The anodic and cathodic Tafel slopes, ßa and ßc, were both different from the blank values. Further examination of the table reveals that adding the extract changes both the anodic and cathodic Tafel constants, demonstrating that the plant extract has an impact on both cathodic and anodic reactions, with the cathodic curves being more impacted. As a result of these findings, we were able to determine the inhibitory efficiency (%EI) reaching the maximum value of 86% at o.5M of H2SO4 at room temperature.

3.1b Electrochemical polarization test at (60 ºC)

Corrosion is influenced by the medium's composition and temperature. At high temperatures, electrochemical tests were carried out. In the absence and presence of eucalyptus leaf extract, the influence of temperature in the 60 ºC range on the electrochemical parameters of mild steel is indicated in Table 4. These findings show that when the temperature rises, the corrosion rate of mild steel in both free and inhibited acidic medium increases. However, the inhibition efficiency of the eucalyptus leaf extract decreases significantly. This finding backs up the theory that extract component adsorption on the mild steel surface was purely physical. As a result, the quantity of adsorbed molecules reduced as the temperature rose, lowering the inhibitory efficiency. The desorption of adsorbed inhibitor molecules from the metal surface causes this action.

Figures below shows Tafel tests for Mild Steel specimen, the temperature of the medium was maintained at 60◦ C using water bath. in three concentrations of H_2SO_4 without and with inhibitor .Fastest cathodic reaction is in the state of acid without adding the inhibitor for all concentrations of H_2SO_4, which means that the corrosion rate will be high, while the slowest occure when the inhibitor used which means that a low corrosion rate is occurred.

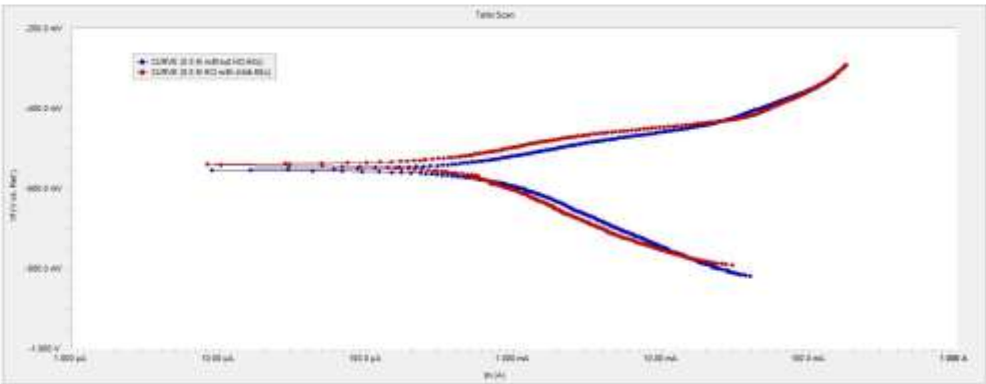

Figure (5) Tafel Tests for 0.5 Molarity of H2SO4 (with and without inhibitor)at 60℃

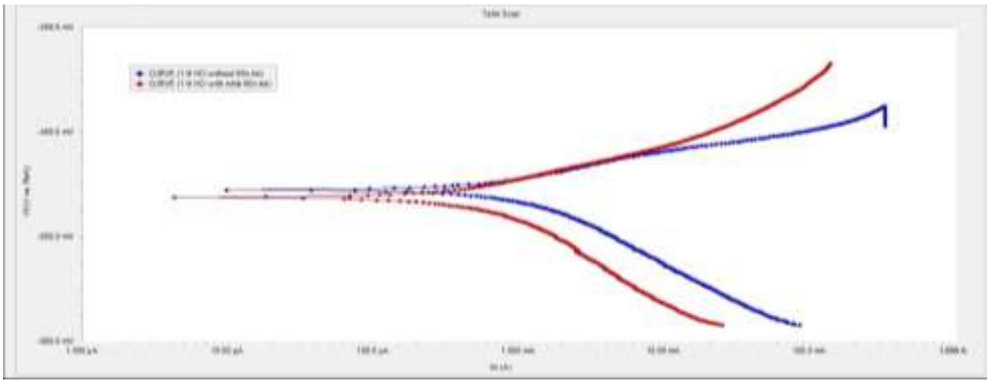

Figure 6 Tafel Tests for 1 Molarity of H2SO4 (with and without inhibitor)at 60℃

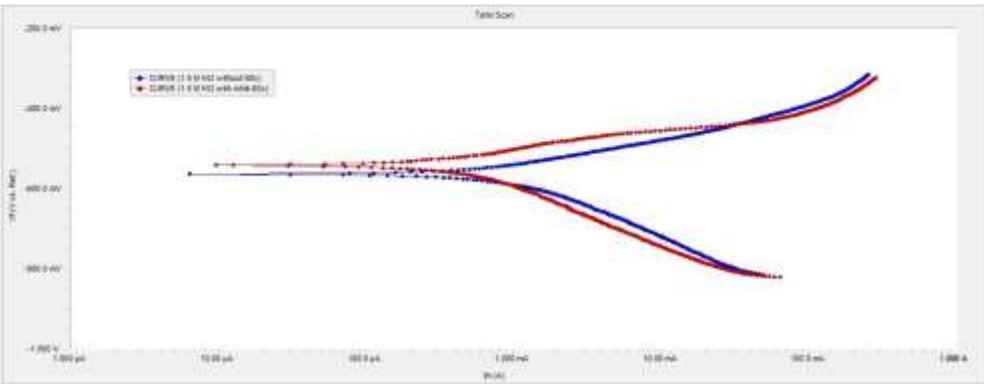

Figure 7 Tafel Tests for 1.5 Molarity of H2SO4 (with and without inhibitor)at 60℃

In general, CR increases with temperature, and various changes occur on the inhibited metal surface, such as fast etching and desorption of inhibitor, as well as breakdown and/or rearrangement of the inhibitor itself .The effect of higher temperatures is to speed up a chemical reaction .In addition, temperature has a negative effect on the %IE. As the temperature rises, the dynamic energy of the inhibitor molecules rises as well . The inhibitors' adsorption on the metal surface has significantly decreased . As mentioned in Table 2, the components of the extract are effective at room temperature, but their effect is less at high temperatures because they are volatile and evaporate with high temperature, this is turn impedes and slows the formation of the protective film of inhibitors on the metal surface, so their effect was weak at high temperatures, which reduces the efficiency of the inhibitor. Because the strength of the inhibitor molecules' interaction with the metal surface reduces as temperature rises, this behavior is typical of a physisorption mechanism.

Table 4. Parameter values of the Tafel testing for 0.50, 1.0, 1.50M of the H_2SO_4 with and with no eucalyptus leaf extract.

Environment	Ecorr(mV)	Corrosion rate(mmpy)	Icorr (µA)	Aβ V/decade	Cβ V/decade	Efficiency □
0.5M H2SO4	-535.0	16.18	1.170	47.30e-3	125.6e-3	**67%**
0.5M H2SO4 inhibitor	-524.0	5.191	375.5	35.00e-3	87.20e-3	
1M H2SO4	-522.0	26.05	1.880	36.10e-3	120.3e-3	**59%**
1M H2SO4 inhibitor	-516.0	10.60	765.0	69.30e-3	118.1e-3	
1.5M H2SO4	-541.0	61.70	4.450	74.70e-3	165.4e-3	**52%**
1.5M H2SO4 inhibitor	-501.0	29.32	2.120	109.0e-3	143.8e-3	

Figure 8 illustrates the variation of efficiency of inhibitor with different concentrations of acid solution for the corrosion inhibition of low carbon steel in at a given temperatures of 25ºC and 60ºC. The vertical curve indicates that the efficiency of the inhibitor was high at room temperature and decreasing with increasing concentration of H2SO4 ,this is due to the rapid sedimentation of compounds for weak aqueous solutions and its effect decreases with the increase in the strength of the acidic solution .also, From the result it can be seen that the efficiency of inhibitor for low carbon steel decrease with increase in temperature.

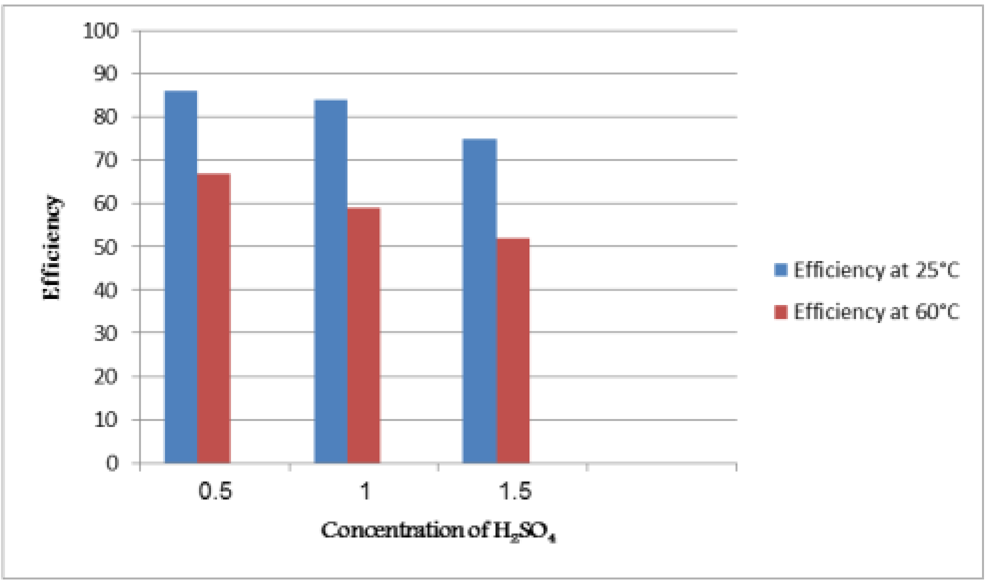

Figure 8. Relationship between % efficiency of inhibitor in different concentrations of H_2SO_4 at 25°C and 60°C.

Conclusions

1. The extract of Eucalyptus utilized as natural corrosion inhibitor.
2. The presence of certain phytochemical components in the Eucalyptus leaves extract, which is adsorbed on the surface of the mild steel metal, causes the inhibition.
3. The inhibitor efficiency related to the Eucalyptus extract decreased with the increase in H_2SO_4 concentration at room temperature.
4. The carbohydrate substances contained in the components of the extract are responsible for the formation of a protective film on the surface of the metal, they are affected by temperature and evaporate, losing their effectiveness.
5. The inhibitory effectiveness reduced as the temperature rose due to greater dissolving of mild steel at higher temperatures.

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