

Corrosion Inhibition of Ethanol Extract of Cassava (*Manihot esculenta*) Leaves on Mild Steel in Sulfuric Acid

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Abstract : The corrosion inhibition of mild steel in 0.5 M H₂SO₄ in the presence of ethanol cassava (*Manihot esculenta*) leave extract (ECLE) has been investigated using Fourier Transform Infra Red Spectroscopy (FTIR), Scanning Electron Microscopy (SEM)/ Energy Dispersive X-Ray (EDX), weight loss and potentiodynamic polarization methods. Analysis of the results showed that the addition of ECLE inhibits the corrosion of mild steel in 0.5 M H₂SO₄ and acts as a good inhibitor. Inhibition efficiency increases with increasing concentration of the ECLE and decreases with increasing temperature. The adsorption of the ECLE on the mild steel surface follows the Langmuir adsorption isotherm. Polarization measurements indicated that ECLE acts as a mixed inhibitor. The value of the free energy of adsorption indicated that the adsorption of inhibitor molecules was typical of physisorption.

Keyword : corrosion, inhibitor, *Manihot esculenta*, ethanol, mild steel.

Introduction

Mild steels are used for industrial applications but it is easily undergoes corrosion. Acids are used for pickling, descaling, acid cleaning, oil well acid in recovery and petrochemical process¹. The rate of corrosion destroyed a mild steel in acidic media is very high. The use of inhibitors is one of the most practical methods for protection steel against corrosion, especially in acidic media^{1,2,3}.

Most of the effective inhibitors used contain heteroatom such as O, N, S and multiple bonds in their molecules that they are adsorbed on the metal surface³. However, most of these compounds are not only expensive but also toxic to living beings. It is needless to point out the importance of cheap and safe inhibitors for corrosion of mild steel^{2,4,5}. The last few years, researcher in corrosion have reported the using of green corrosion inhibitors, such as *Toona sinensis* leaf extract⁴, *Water hyacinth* extract⁶, *Citrus sinensis L* leaf extract⁷, *Osmanthus fragran* leaf extract⁸, *Ligularia fischeri* extract⁹, and *Theobroma cacao* peels extract¹⁰.

The cassava leaves contain carotenoids, flavonoids, tannins, and terpenoid and carbohydrates^{11,12}. Leaves of cassava plant are large wasteful of flour production which can be used as a corrosion inhibitor and there was no literature report on studies of corrosion inhibition effect of the above plant extracts on mild steel in sulfuric acid media previously.

In this study, the effect of the ECLE on mild steel corrosion in 0.5 M H₂SO₄ solution was examined using weight loss method, thermodynamic polarization method, FT-IR and SEM/EDX methods.

Experimental

Sample preparation and solution

Mild steel used has a composition 0.195% C, 0.220% Si, 0.654% Mn, 0.013% Pb, 0.266% S, 0.079% Cr, 0.005% Mo, 0.057% Ni and the balance Fe. The mild steels were polished using sandpaper of different grades and cleaned with water, acetone and then dried before use. Corrosion inhibition tests were performed using spherical shape coupons with diameter of ± 2.5 cm and a thickness of 0.3 to 0.5 cm.

The cassava leaves were plucked from cassava farms in Ketaping, Pariaman, West Sumatera, Indonesia. The leaves were dried in a green house and shattered into powder. 500 g of leaf powder were extracted with ethanol for three days. The result was subsequently filtered by using filter paper. The solvent was evaporated using *rotary evaporator* and then dried by *freeze drier* to get solid mass as a corrosion inhibitor. The inhibition extract (ECLE) was put directly in 0.5 M H₂SO₄ with variations of the extract concentration are 0.1, 0.5, 1.0, 5.0, and 10 g/L.

Fourier Transform Infra Red (FTIR) Spectroscopy Analysis

Mild steels were soaked in 0.5 M H₂SO₄ by the addition of ECLE 10.0 g / L at room temperature for 3 days. The ECLE and the thin layer of corrosion product formed on mild steel surface were collected and analyzed with FT-IR technique using a Thermo Scientific FT-IR spectroscopy.

Scanning Electron Microscopy (SEM) / EDX Analysis

SEM and EDX confirmed the existence of a protective adsorbed film of the inhibitor on the mild steel. After exposure using to the sulfuric acid solution in the absence and presence of ECLE for three days, the mild steel surface morphologies were tested using Hitachi S3400N SEM/ EDX with EMAX software

Weight Loss Measurement

The weight loss measurement was carried out according to the method described previously^{5,13,14}. The mild steel was immersed in 0.5 M H₂SO₄ with the absence and presence of ECLE in various concentration. The weight loss method was performed in 303, 313, 323, and 333K for 6 hours. After immersion time, the specimens were taken out, cleaned by soft brush to remove the corrosion product. The weight loss was calculated as the difference in weight of the specimen before and after in immersion in corrosive solutions. The equation used as follows^{4, 15}

$$C_R = \frac{W_b - W_a}{S \cdot t} \quad (1)$$

Where C_R are corrosion rate, W_b dan W_a are the sample weight measured before and after soaking in a solution of corrosive. S is exposed area and t is time in hour.

Inhibitor Efficiency (η in %) is calculated by following equation^{5,15} :

$$\eta (\%) = \frac{C_{R(\text{blank})} - C_{R(\text{inh})}}{C_{R(\text{blank})}} \times 100 \% \quad (2)$$

C_{R (blank)} and C_{R (inh)} indicate corrosion rate the absence and presence of the inhibitor in the sulfuric acid.

Potentiodynamic Polarization

An EDAQ Potentiostat Electrochemical System was used in electrochemical measurements. A three electrode electrolyte cell was used, which had a platinum rod as a counter electrode, an Ag/AgCl electrode as a reference electrode, a mild steel cylindrical rod as the working electrode. The measurements were carried out in 0.5 M H₂SO₄ solutions in the absence and presence various concentrations of ECLE at room temperature, its polarization curve was calculated to obtain the relationship between the curve of potential (mV) to ln current (mA / cm²).

Results and Discussion

The FT-IR spectra of ECLE were recorded within the wavelength ranging between 4000 and 500 cm^{-1} using a FT-IR spectrometer. In Figure 1a, it shows strong broad band at 3385.35 cm^{-1} indicated to O-H stretching. The band at 1652.75 cm^{-1} is characteristic of C=O stretching vibration. The absorption band at 1065.38 shows C-O-C stretching vibration. In Fig 1b, the FT-IR spectrum appears the stretching frequencies shifting to 3407.07 cm^{-1} , 1654.54 cm^{-1} , and 1123.91 cm^{-1} for O-H, C=O, and C-O-C, respectively. These band shifts indicate interaction of mild steel with ECLE^{9,16}.

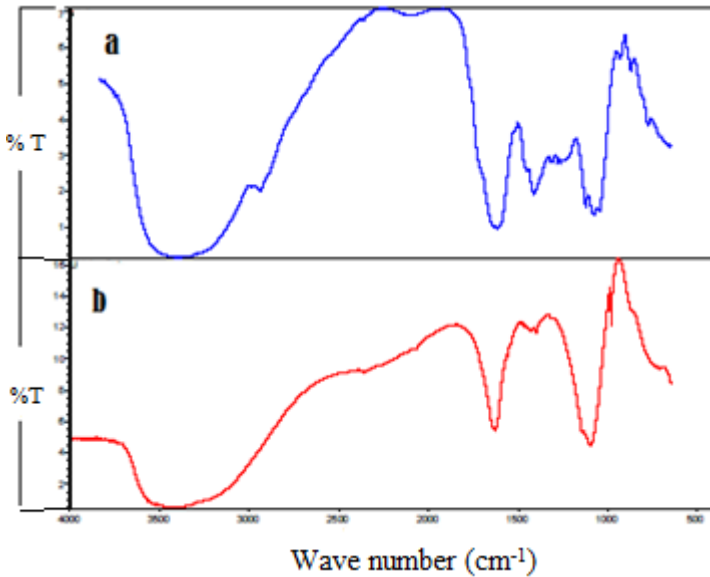


Figure 1. (a) FT-IR spectrum of ECLE. (b) FT-IR spectrum of ECLE adsorbed on mild steel surface

SEM and EDX Analysis

The mild steel surface before treatment is shown in fig. 2a, which is flat and non-porous. Fig. 2b exhibits that mild surface rough and porous in the absence of ECLE due to direct attack of aggressive acids¹⁷. The mild steel surface after being soaked in sulfuric acid with the presence of ECLE for 3 days is smoother than its absence. The presence of ECLE revealed the formation of an adsorbed film of ECLE on the mild steel surface and the absence of porous. Formation of a protective inhibitor film on the mild steel surface inhibits corrosion attack¹⁵.

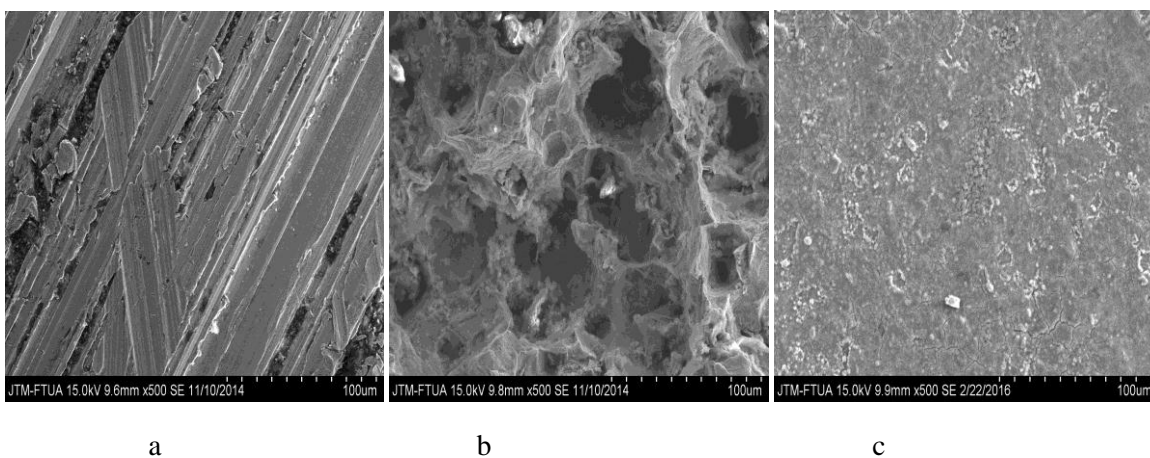


Figure 2. SEM image of the mild steel surface a) before treatment, b) after 3 days of immersion in 0.5 M H₂SO₄ and c) after 3 days of immersion in 0.5 M H₂SO₄ with the addition of 10 g/L ECLE.

The EDX were used to determine the elements present on the surface of mild steel and after 3 days of exposure in the absence and presence 0.5 M H₂SO₄. The presence of O element before treatment in table 1 was not detected on mild steel surface. Mild steel surface is soaked in H₂SO₄ with the addition of the ECLE as an inhibitor in table 1. It appears the formation of iron oxides resulting from corrosion of steel in 0.5 M H₂SO₄ solution, as evidenced by the presence of the oxygen content on the EDX^{17,18}. The presence of ECLE as an inhibitor in sulfuric acid solution increases the elements of carbon and oxygen. This increasing is due to the carbon and oxygen elements of ECLE covered the mild steel surface^{18,19}.

Table 1. Surface composition (wt %) of mild steel by using EDX

Treatment	Composition (wt %)		
	C	Fe	O
Mild steel	3.05	96.45	-
Mild steel after 3 days of immersion in 0.5 M H ₂ SO ₄	5.08	87.57	13.67
Mild steel after 3 days of immersion in 0.5 M H ₂ SO ₄ with the addition of 10 g/L ECLE	13.78	43.55	37.60

Intable. 1 showed that the carbon and oxygen content are increased upon adding ECLE to 0.5 M H₂SO₄ solutions. This increase in carbon and oxygen content is due to the carbon and oxygen elements of the adsorbed ECLE species¹⁸. This layer is surely due to the inhibitor, because of the high donation of the carbon and oxygen content observed in presence of ECLE. This high donation is not present on the mild steel surface exposed to uninhibited H₂SO₄ solutions¹⁹.

Corrosion Rate and Efficiency Inhibition of MildSteel

Effect of ECLE concentration on corrosion rate and inhibition efficiency in 0.5 M H₂SO₄ was shown in Fig.4. It has been showed that the corrosion rate of mild steel decreases with an increased in the concentration of ECLE and increases with an increase in temperature(Fig.3a). Inhibition efficiency increases with further increase in the concentration of the ECLE and decreases with an increase in temperature (Fig.3b).

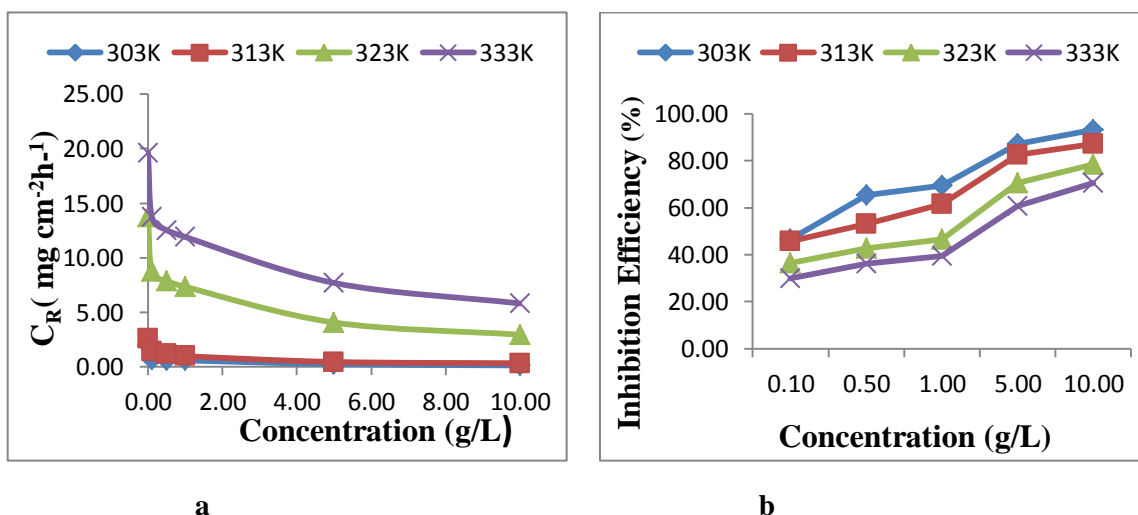


Figure 3 . Variations of the corrosion rate (a) and inhibition efficiency (b) of mild steel in 0.5 M H₂SO₄ with ECLE concentration at different temperature

This shows that ECLE acts as effective inhibitor even at low temperature. The existence of OH functional group of ECLE as a corrosion inhibitor interacts with mild steel to form a layer on the steel surface so as attack from corrosive ions in a solution of sulfuric acid to be blocked so that the corrosion rate is lowered^{4,5,9}. Inhibition efficiency decreases at high temperature due to increased rate of desorption of ECLE on the mild

steel surface¹⁹. The maximum inhibition efficiency of ECLE was 93.2% at a concentration of 10 g / L and temperature of 303 K.

Activation Energy Analysis

Calculation of activation energy for the corrosion reaction use Arrhenius equation¹⁵:

$$C_R = A \exp [-E_a / RT] \tag{3}$$

$$\ln C_R = \frac{-E_a}{RT} + \ln A \tag{4}$$

Where C_R is the corrosion rate, R is constant, T is the temperature, A is the pre-exponential factor, E_a is activation energy.

Fig.4 shows the Arrhenius straight lines of $\ln C_R$ vs $1/T$ for the mild steel in 0.5 M H_2SO_4 for the blank and various concentration of ECLE. Table 2 reveals that the value of activation energy in the presence of ECLE as a corrosion inhibitor has a higher value than the absence of corrosion inhibitor, which suggest that it acts as efficient inhibitor by forming a physical barrier to charge and mass transfer reaction. It is indicated that the adsorption of inhibitor is the physical adsorption (physisorption)^{15,21,22}.

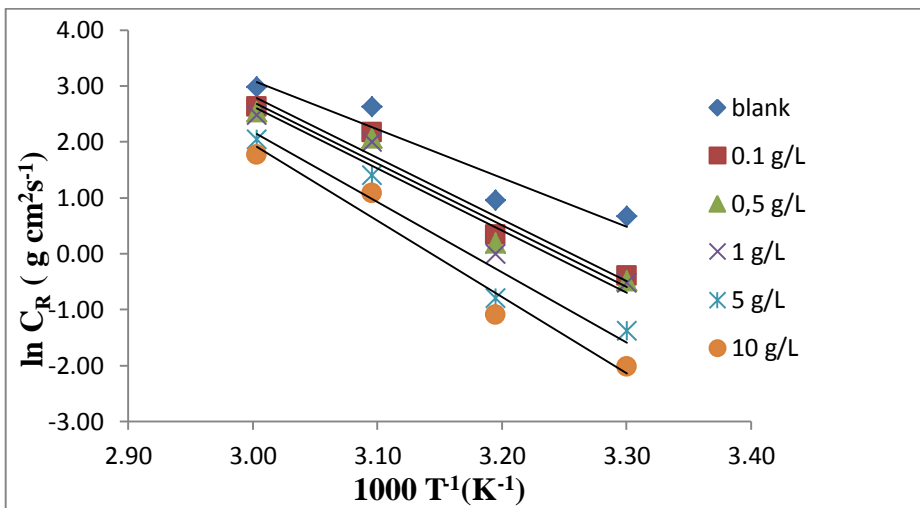


Figure 4. Arrhenius plots for the corrosion rate of mild steel in 0.5 M H_2SO_4 in the absence and presence of ECLE at different concentration.

Table 2. Value of activation energy with absence and presence ECLE

ECLE Concentration (g/L)	Activation energy (kJ/mol)
Blank	72.21
0.10	91.45
0.50	91.65
1.00	92.29
5.00	104.61
10.00	113.63

The ECLE covered the surface of the mild steel. Surface coverage value (θ) was studied at constant temperature and for different concentrations of ECLE in 0.5 M H_2SO_4 from weight loss measurements according to equation¹⁵:

$$\theta = \frac{C_{R(Blank)} - C_{R(Inh)}}{C_{R(Blank)}} \tag{5}$$

In 0.5 M H₂SO₄, ECLE adsorption follows the Langmuir isotherm that can be expressed as:^{9,15}

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (6)$$

Where C is the concentration of inhibitor, K_{ads} is adsorption equilibrium constant and θ is the surface coverage. In addition, the free energy of adsorption process ΔG_{ads} can be expressed^{9, 15}

$$K = \frac{1}{1000} \exp (- \Delta G_{ads}^0 / RT) \quad (7)$$

Where 1000 is the concentration of water in the solution in gL⁻¹, K = equilibrium adsorption constant, R = constant, and T = temperature.

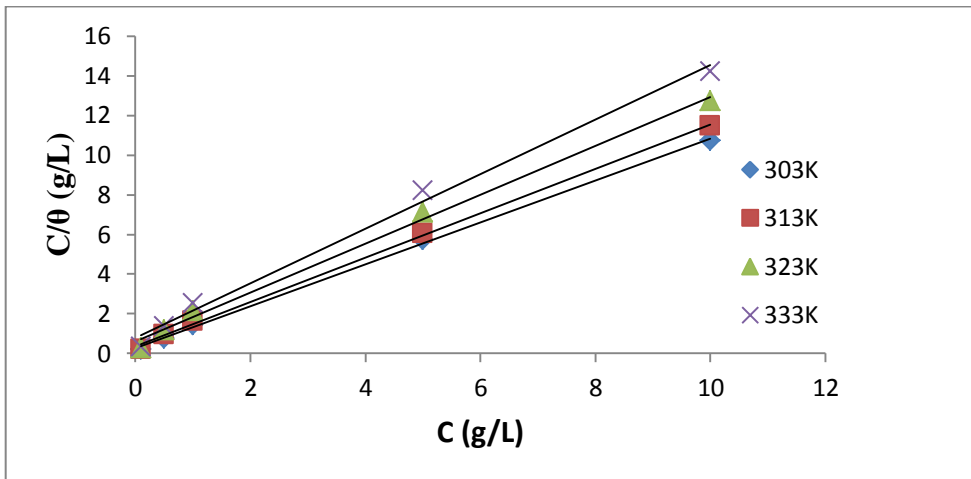


Fig 5. Langmuir isotherm adsorption of ECLE on the surface of mild steel at different temperatures.

K_{ads} and ΔG value are given in Table 3 at different temperatures. The equilibrium constant of the adsorption process (K_{ads}) increase with decreasing temperature in the range 303 – 333K. The negative value of ΔG⁰ in Table 3 shows the adsorption of ECLE on the mild steel surface spontaneously and physisorption. ΔG_{ads} value up to -20 kJ showed the interaction between molecules such as electrostatic forces or Van der Waals forces (physisorption) while those higher than -40 kJ involves the sharing or transfer of electrons on a metal surface to form a bond of coordination (chemisorption)²³.

Table 3 .Adsorption parameters derived from Langmuir adsorption isotherms for mild steel in 0,5 M H₂SO₄ at different temperatures

T (K)	K _{ads} (g/L)	ΔG ⁰ (kJ/mol)
303	3.58	-20.61
313	2.91	-20.76
323	1.70	-19.98
333	1.29	-19.84

Data values are shown in Table 3 in the form ΔG⁰ vs T a straight line is obtained from which change in standard adsorption enthalpy and standard adsorption can be derived, as shown in Fig.8. Intercept and slope of this plot yield ΔH_{ads}⁰ = -30.149 kJ / mol and ΔS = - 0.031 kJ / mol K. The negative value of ΔH is suggested as an exothermic process, which means that inhibition efficiency decreases with rising in the temperature. The sign of negative for entropy means that the process of adsorption is accompanied by a decrease in entropy²³.

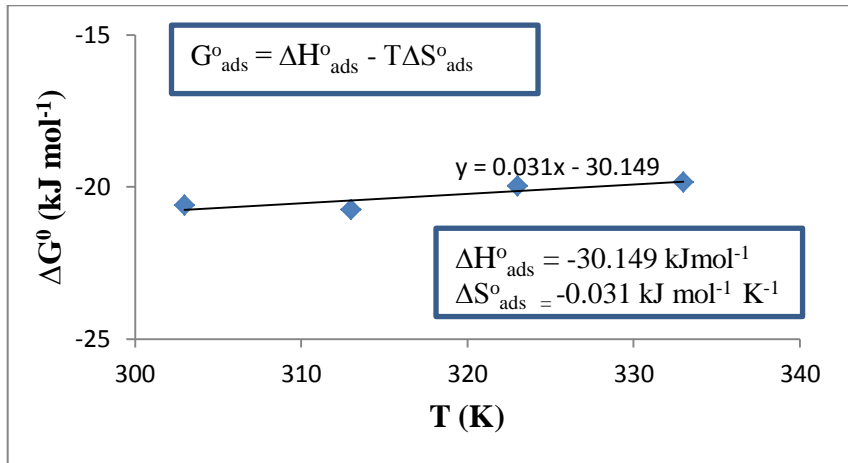


Figure 8. Plot of the standard free energy of adsorption vs T.

Potentiodynamic Polarization

Potentiodynamic polarization curves were measured for mild steel in 0.5 M H₂SO₄ with the absence and presence of ECLE (Fig.9). Potentiodynamic polarization measurement use Tafel slope of polarization curves to determine the corrosion current density (*I*_{corr}), corrosion potential (*E*_{corr}) and inhibition efficiency (IE%). Tafel slope of polarization curves is extrapolated to determine the corrosion current density (*I*_{corr}), corrosion potential (*E*_{corr}) and inhibition efficiency (% EI).

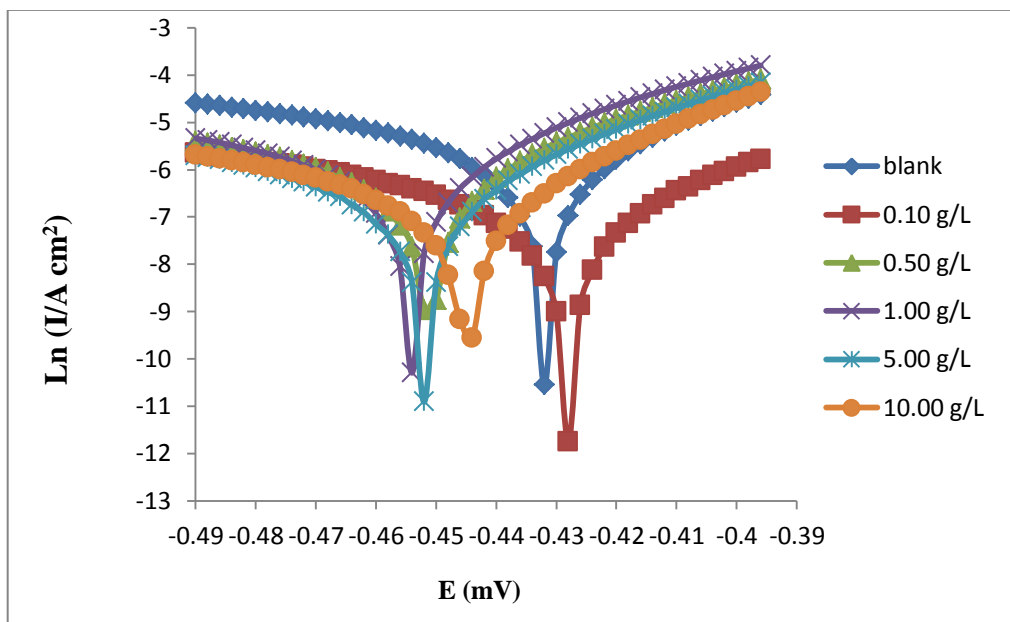


Figure 9. Potentiodynamic polarization curves for mild steel in 0.5 M H₂SO₄ without and with different concentrations of ECLE.

These data along with IE% are listed in Table 4. The addition of ECLE decreases the current density and increases the value of inhibition efficiency^{24, 25}. Inhibition efficiency can be reached at 10 g/L as high as 83.52%. Potentiodynamic polarization curves in Fig.9 reveals that the cathodic curves are shifted towards lower current density side with increase in ECLE concentration of 0.5 to 10 gL⁻¹. It shows that cathodic reaction is retarded on the addition of the inhibitor and it should be defined as cathodic inhibitor. But, in 10 gL⁻¹ ECLE shows a shift towards anodic curve, it is classified as a mixed type inhibitor. ECLE inhibit both cathodic reaction (hydrogen evolution) and anodic reaction (metal dissolution)^{14,15, 24}.

Table 4. Potentiodynamic polarization parameters for the corrosion of mild steel in 0.5 M H₂SO₄ solutions containing ECLE with different concentrations

Konsentrasi (g/L)	E _{corr} (mV)	Ln i/A	I _{corr} (mA)	(%)IE
Blank	-0.432	-2.869	6.7.10 ⁻⁵	
0.10	-0.428	-3.304	2.5.10 ⁻⁵	63.25
0.50	-0.452	-3.304	2.5.10 ⁻⁵	63.25
1.00	-0.455	-3.391	2.0.10 ⁻⁵	69.92
5.00	-0.453	-3.478	1.7.10 ⁻⁵	75.38
10.00	-0.455	-3.652	1.1.10 ⁻⁵	83.52

Conclusion

The ECLE can be used as green corrosion inhibitor for the mild steel in 0.5 M H₂SO₄. Inhibition efficiency increases with increasing concentration of the extract and decreases with increasing temperature. Polarization measurements indicated that ECLE acts as a mixed inhibitor. The value of the free energy of adsorption showed that the adsorption of inhibitor molecules was typical of physisorption. The adsorption of ECLE on mild steel surface obeys Langmuir adsorption isotherm. The adsorption process is an exothermic process accompanied by a decrease in entropy.

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