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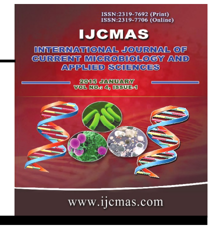

Original Research Article

Inhibitory action of extract of ankado (*Calotropis gigantea*) leaves on mild steel corrosion in hydrochloric acid solution

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A B S T R A C T

Keywords

Adsorption, Ankado, Corrosion, Hydrocloric acid, Inhibition effect, Mild Steel

The influence of Ankado leaves extract on corrosion through mild steel in 1M HCl has been studied using weight loss measurements and electrochemical techniques. The inhibition efficiency of Ankado leaves was found to vary with concentration, temperature and immersion time. Good inhibition efficiency (IE) was evidenced in acid solutions, the inhibition efficiency was found to be 96.10% in 1M HCl of the 1.25% inhibitor concentration. The adsorption of these compounds on the steel surface for acid was found to obey Temkin's adsorption isotherm. The values of activation energy and free energy of adsorption indicated physical adsorption on mild steel surface. The potentiodynamic polarization data have shown that compounds studied are mixed type inhibitors.

Introduction

The study of corrosion of mild steel in hydrochloric acid is a subject of practical significance and many engineering applications since the acid is highly corrosive and extensively used in industrial operations. Hydrochloric acid is generally used for the removal of undesirable scale and rust in several industrial processes. Thus, inhibitors are one of the most convenient methods for protection against corrosion, particularly in acid solutions to prevent unexpected metal dissolution and acid consumption1. Most of the well known acid inhibitors are organic compounds containing hetero atoms such as nitrogen, sulfur, oxygen. Synthetic dyes (xylenol orange 2-3), synthetic drugs (Sulphathiazole4) and heterocyclic compounds are widely used as corrosion inhibitor. The majority of the reported inhibitors used in the industry is highly toxic, so they are very hazardous to the environment, expensive and non-environmentally friendly, due to these factors their applications are limited. Due to the toxicity of some corrosion inhibitors, there has been increasing search for green corrosion inhibitors5. Natural products of plant origin containing different organic compounds (e.g., alkaloids, tannins, pigments, organic, and amino acids) are known to inhibit action6-7. Inhibitors in this class are those that are environment friendly, less polluting, cheap, and easily available and are obtained from natural products such as plant extracts8. Extracts of natural products like Murraya koenigii9, Nypa fruticans wurmb10, Emblica officinalis11, Phyllanthus amarus12, black pepper extract13, khillah seeds14, Ficus carica15, piper guinensis16, fenugreek seeds and leaves17, Nyctanthes arbortristis 18, Caffeic acid 19, etc. have been tested as corrosion inhibitors for metals. These plant extracts are low cost, nontoxic, readily available, and ecofriendly substances. Therefore, the present study investigates the inhibiting effect of leaf extract of Calotropis gigantea, which is commonly known as Ankado in India. Inhibition effect of Ankado (Calotropis gigantea) on the corrosion of mild steel in 1 M HCl solution by weight loss and potentiodynamic polarization methods.

Experimental

Materials preparation

Mild steel contains Fe = 99.746; Mn = 0.100; C = 0.058; Al = 0.033; Si = 0.010; Cr = 0.008; Cu = 0.004; Ni = 0.0029; Mo = 0.002% were used in this study. Each sheet, which was 0.12 cm in thickness, was mechanically press-cut into coupons of dimension 3.5 x 3 cm with small hole of about 5 mm diameter near the upper edge. These coupons were used in the "as cut" condition, inhibition efficiency without further polishing, but were de-greased in absolute ethanol, dried in acetone, weighed and stored in a moisture-free desiccator prior to use.

All chemicals and reagents used were of analytical grade and used as source without further purification. The aggressive media were, respectively, 1, 2 and 3 M HCl solution. Ankado were used inhibitor in the concentration range 0.25 to 1.25%,

Weight loss method

The test specimens were immersed in 1, 2 and 3 M HCl solution with and without inhibitors. Only one specimen was suspended by a glass hook, in each beaker containing 230 ml of the test solution and was open to air at room temperature for 24 h duration. After the test, the specimens were rinsed with distilled water and dry it. Triplicate experiments were performed in each case and the mean values of the weight loss data are calculated and which is shown in figure-1.

To study the effect of temperature on corrosion rate, the specimen was immersed in 230 ml in 1 M HCl, with ankado as inhibitor concentration 0.25, 0.50, 0.75, 1.0 and 1.25% at solution temperatures of 313, 323 and 333 K for a period of 3 h. To study the effect of temperature, thermostat assembly with an accuracy of ± 0.5oaks was used. Wesley 20 and ASTM 21 pointed out that thermostatic controls to within ± 1oC usually are considered satisfactory. Inhibition efficiency (η %), energy of activation (Ea), heat of adsorption (Qads) free energy of adsorption (ΔG0ads), enthalpy of adsorption (ΔH0ads) and entropy of adsorption (ΔS0ads) were calculated and shown in Table-1.

Polarization

For polarization study, metal specimens of rectangular design having an area of 0.0932 dm2 were exposed to corrosive solutions. Mild steel was used as a working electrode, SCE was used as reference electrode and the auxiliary graphite electrode was placed in a 230 ml corrosive media through which external current was supplied automatically from the computerized polarization instrument. The change in potential was measured by potentiostate / galvanostate

(Gamry-Make, USA) on the potentiostate mode with 5 mg/ sec scan rate. Polarization has been taken with and without inhibitors in 1 M HCl. The curves show polarization of both the anodes and cathodes.

Results and Discussion

The results are presented in Tables 1 to 2 and Figs. 1 to 8. To assess the effect of corrosion of mild steel in HCl, ark of ankado is used as inhibitors.

The corrosion rate of mild steel in HCl was increased with the acid concentration which was shown in figure-1. The inhibition efficiency (η %) and degree of surface coverage (θ) at each concentration of ark of ankado leaves was calculated by comparing the corrosion loss in absence (Wu) and presence of inhibitor (Wi) using the relationships:

$$\eta\% = \left(\frac{Wu - Wi}{Wi}\right) X100 \quad (1)$$

$$\theta = \left(\frac{Wu - Wi}{Wi}\right) \quad (2)$$

As a constant inhibitor concentration, the inhibition efficiency decreases with the increase in acid concentration. At 1.25 % inhibitor concentration, the inhibition efficiency of ark of Ankado is 96.14, 88.95 and 82.04 % with respect to 1, 2 and 3 M acid concentration respectively. At a constant acid concentration, the inhibition efficiency of the ark of ankado increases with the inhibitor concentration, e.g. in 1 M HCl the inhibition efficiency was found to be 93.50, 94.31, 94.72, 95.94 and 96.14 % with respect to 0.25, 0.50, 0.75, 1.0 and 1.25 % inhibitor concentration respectively (Figure 1).

The temperature has significant influence on a metal corrosion rates. The effect of change in temperature on the corrosion rates of mild steel in 1 M HCl, the corrosion of Ark of Ankado was increased with rising temperatures. Corrosion rate was measured in 1 M HCl containing 0.25, 0.50, 0.75, 1.0 and 1.25 % inhibitor concentration at a solution temperature of 313, 323 and 333 K for an immersion period of 3 h. In 1M HCl solution with 1.25% inhibitor concentration, the inhibition efficiency for leaves of ankado ark was decreased corresponds to 92.48, 90.09 and 89.20 % at temperature 313, 323 and 333 K respectively (Figure-2).

In the present study general type of corrosion occurs predominately and less pitting. Plotting of log θ/1-θ versus log C (%), straight lines were obtained, indicating that the adsorption of the added inhibitors followed the Langmuir adsorption isotherm (Fig.3). Therefore, adsorption of these compounds is assumed to occur uniformly over the metal surface.

Plot a graph θ versus log C gives straight line (Figure-4) showing that the adsorption of the compound on the mild steel surface from 1 M HCl obeys also Temkin's adsorption isotherm. It is also found that the degree of adsorption of the inhibitors increases with their concentration.

For Freundlich's adsorption isotherm a plot of log [θ] against log C. Fig. 5, which is linear graph, was obtained, showing that the adsorption of ethanol extract of Ankado leaf on the surface of the mild steel obeys Freundlich's adsorption isotherm 22-23.

The values of the free energy of adsorption (ΔG0ads) were calculated with the slope of the following equation24.

$$LogC = L\log\left(\frac{\theta}{1-\theta}\right) - LogB \quad (3)$$

Where $LogB = -1.74 - \left(\frac{\Delta G^0_{ads}}{2.303RT} \right)$ and C is the inhibitor concentration. The mean ΔG^0_a values are negative almost in all cases and lie in the range of -34.56 to -36.63 kJ. mol^{-1} shown in Table-1. The most efficient inhibitor shows more negative ΔG^0_a value. This suggests that they be strongly adsorbed on the metal surface. This statement was supported by the work of Talati and Darji [25]. The values of heat of adsorption (Q_{ads}) were calculated by the following equation.

$$Q_{ads} = 2.303R\left[Log\left(\frac{\theta_2}{1-\theta_2} \right) - Log\left(\frac{\theta_1}{1-\theta_1} \right) \right] X \left[\left(\frac{T_1 T_2}{T_2 - T_1} \right) \right] \quad (4)$$

From Table -1, it is evident that in all cases, the (Q_{ads}) values are negative and ranging from -2.67 to -30.95 kJ. mol^{-1}. The negative values show that the adsorption, and hence the inhibition efficiency, decreases with a rise in temperature [26].

Mean 'Ea' value was calculated by using equation (5) for mild steel in 1M HCl is 38.32 kJ.mol-1 while in acid containing inhibitor, the mean Ea values are found to be higher than that of an uninhibited system (Table 1). Higher values of Ea in the presence of the extract which acts as inhibitor is a good indication of strong inhibiting action of the extract by increasing the energy barrier for the corrosion process. Higher values of Ea in the presence of extract can also be correlated with the increase in thickness of the double layer that enhance the Ea of the corrosion process 27. The values of Ea calculated from the slope of an Arrhenius plot (Figure 6) and using equation (5) are almost similar. Energy of activation (Ea) has been calculated from the slopes of log p versus 1/T (p = corrosion rate, T = absolute temperature) and also with the help of Arrhenius equation.

$$L\log \frac{P_2}{P_1} = \frac{Ea}{2.303R}\left[\left(\frac{1}{T_1} \right) - \left(\frac{1}{T_2} \right) \right] \quad (5)$$

Where p_1 and p_2 are the corrosion rate at temperature T_1 and T_2 respectively.
The enthalpy of adsorption (ΔH^0_{ads}) and entropy of adsorption (ΔS^0_{ads}) were calculated using the following equation (6) and (7).

$$\Delta H^0 ads = Ea - RT \quad (6)$$

$$\Delta S^0_{ads} = \frac{\Delta H^0_{ads} - \Delta G^0_{ads}}{T} \quad (7)$$

The enthalpy changes (ΔH^0_a) are positive, indicating the endothermic nature of the reaction suggesting that higher temperature favors the corrosion process [28]. The entropy (ΔS^0_a) values are positive, confirming that the corrosion process is entropically favorable [29].

Anodic and Cathodic polarization curves for mild steel in 1M HCl at 1.25 % inhibitor concentration of the presence and absence of inhibitors are shown in Fig.7. The value of the corrosion potential with inhibitors were found become more positive than the without inhibitors. Polarization study reveals that the inhibitors function as little anodic, but significant cathodic inhibitors, inhibitor functions as a mixed inhibitor. It is evident from the figure that cathodic tafel slopes (βc) remain almost unchanged with increasing inhibitor concentration. This indicates that hydrogen evolution is activation controlled and the addition of inhibitor did not change the mechanism of cathodic hydrogen evolution reaction 30-31. The values for the Tafel parameters obtained from this plot with and without inhibitors are given in Table-2.

The values of corrosion current densities in the presence and absence of inhibitor were obtained from the graph while percentage efficiency (η %) was calculated using the Equation (8). The inhibition efficiency from Tafel plots agrees well (within ± 4 %) with the values obtained from weight loss data.

$$\eta(\%) = \left[\frac{i_{corr}(u) - i_{corr}(i)}{i_{corr}(u)}\right] \times 100 \qquad (8)$$

The linear polarization study was carried out from cathodic potential versus OCP to an anodic potential of versus OCP with a sweep rate 0.01 V S^{-1} to determine the polarization resistance ($R_p{}'$). From the measured polarization resistance value, the inhibition efficiency has been calculated using the relationship:

$$\eta\% = \frac{Rp' - Rp^0}{Rp'} X\ 100 \qquad (9)$$

Where $R_p{}^0$ and $R_p{}'$ are the polarization resistance in the absence and in the presence of inhibitor, respectively.

Mechanism

Mild steel dissolves in acid solutions due to the hydrogen evolution type of attack. The reaction-taking place at the micro electrodes of the corrosion cell being represented as under,

$$Fe^{+2} \rightarrow Fe^{+3} + e^{-} \qquad (10) \quad \text{(anode)}$$

$$H^{+} + e^{-} \rightarrow H \qquad (11) \quad \text{(cathode)}$$

Followed by the reaction

$$H + H \rightarrow H_2 \qquad (12)$$

The following secondary reaction can also take place in acid solutions [32].

$$2M + 2H^{+} \rightarrow H_2 + 2M^{+} \,(13) \quad \text{(anode)}$$

$$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O \,(14) \quad \text{(cathode)}$$

Therefore, only if the hydrogen evolution type of attack is predominate and no other factors influence the corrosion process, corroded by the strong acid should be maximized.

The inhibitory mechanism is a separation process involving (i) the inhibitor is adsorbed on the surface of the metal forming a compact protective thin layer and (ii) the inhibitor forms a precipitate on the surface of the metal, acting on the aggressive media to form protective precipitates or remove the aggressive agents 33. Adsorption, on the other important notes can be described by two main types of interaction, which are physisorption and chemisorption, where 34-35 : • Physisorption: involves electrostatic forces between ionic charges or dipoles on the adsorbed species and the electric charge at the metal/solution interface. The heat of adsorption is low, thus, this adsorption is only stable at relatively low temperature.

Chemisorption: involves the charge transfer or sharing from the inhibitor molecules to the metal surface to form a coordinate type bond. This type of adsorption is known to have much stronger adsorption energy compared to the other mode of adsorption. Thus, such bond is more stable at higher temperature.

The de-localized π- electrons of inhibitors facilitate its strong adsorption on the mild steel surface leading to the outstanding corrosion inhibition.

As a constant inhibitor concentration, the inhibition efficiency of all inhibitors decreases as the concentration of acid increases. At all concentration of acid, as the inhibitor concentration increases inhibition efficiency increases and corrosion rate decreases. As the temperature increases corrosion rate increases in plain acid. Addition of inhibitors in corrosive media indicates that as the temperature increases corrosion rate increases while inhibition efficiency decreases. In all cases, the value of heat of adsorption (Qads) and the value of free energy of adsorption (ΔG0a) is negative.The Value of change of enthalpy (ΔH0a) and entropy of adsorption (ΔS0a) is positive. A mean value of 'Ea' in inhibiting acid is higher than the value of 'Ea' in acid only. In almost all the cases, the inhibition efficiency from Tafel plots agrees well (within ± 6 %) with the values obtained from weight loss data.

Table.1 Energy of activation (E_a), heat of adsorption (Q_{ads}) and free energy of adsorption (ΔG^0_{ads}) for mild steel in 1 M HCl containing inhibitors

Inhibitor Concentration	Mean E_a from Eq. (2) ($kJ.mol^{-1}$)	E_a from Arrhenius plot ($kJ.mol^{-1}$)	Q_{ads} ($kJ.mol^{-1}$)		Mean value ($kJ.mol^{-1}$)		
			313 –323 (K)	323-333 (K)	ΔG^0_{ads}	ΔH^0_{ads}	ΔS^0_{ads}
Blank	38.32	37.02	-	-	-	27.19	-
0.25	45.19	43.49	-3.75	-13.66	-36.63	37.91	0.231
0.50	45.44	43.74	-4.20	-13.16	-35.31	37.94	0.227
0.75	58.13	56.23	-30.95	-15.34	-34.81	39.97	0.231
1.00	45.24	43.66	-13.08	-2.67	-34.56	29.51	0.198
1.25	53.79	52.09	-25.46	-8.56	-34.83	34.87	0.215

Table.2 Polarization data and inhibition efficiency of Ankado for mild Steel in 1 M HCl.

Inhibitor concentration: 1.25% Ankado — Effective specimen area: 0.0932 dm²

System	E_{corr} (mV)	I_{corr} (A/cm²)	Rp (ohm)	Tafel slope (V/decade)			Inhibition efficiency (%)		
							Pol. Method		
				-βc	+βa	β	From I_{corr}	From Rp	Wt. loss method
Blank	-557	4.866×10^{-3}	12	5.751	1.436	2.64	-	-	_
Ankado	-333	1.935×10^{-05}	2280	4.806	5.048	5.67	99.60	99.47	96.14

Figure.1 Effect of inhibition efficiency of Ankado leaf extract for mild steel at different acid and inhibitor concentrations for 24 h at 301 K

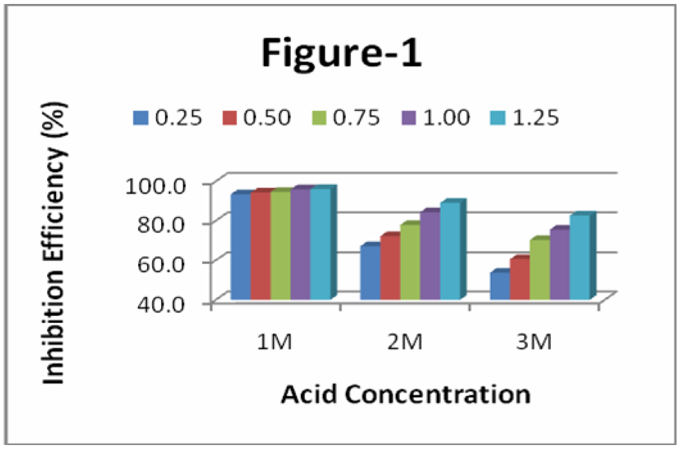


Figure.2 Effect of inhibition concentration of Ankado leaf extract for mild steel in 1M HCl at different temperatures for 2h

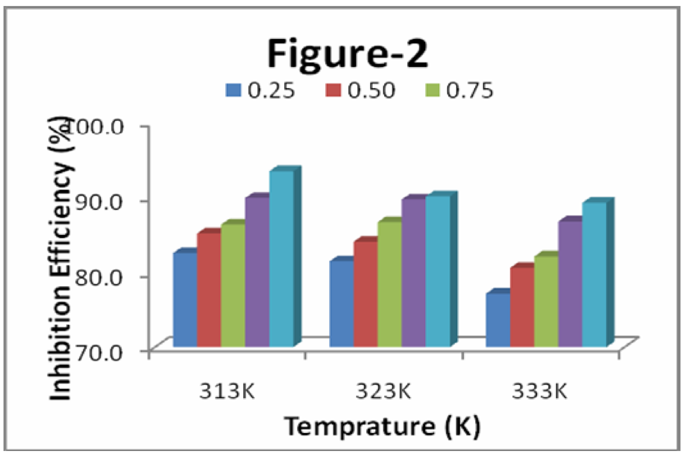


Figure.3 Plot of log (θ /1- θ) versus log C for Ankado leaf extract at different concentrations of HCl for 24 h at 301K

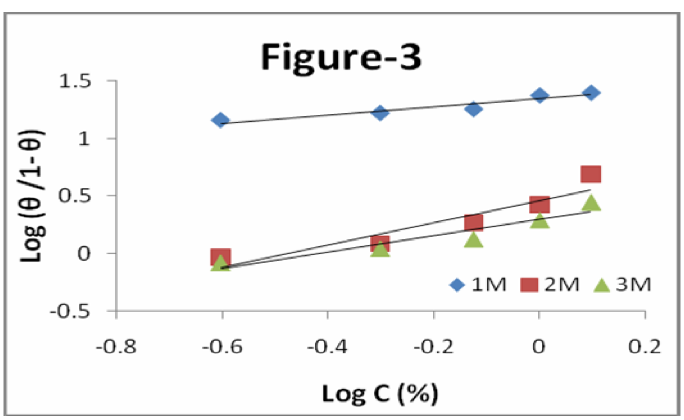


Figure.4 Plot of θ versus log C for Ankado leaf extract at different concentrations of HCl for 3h

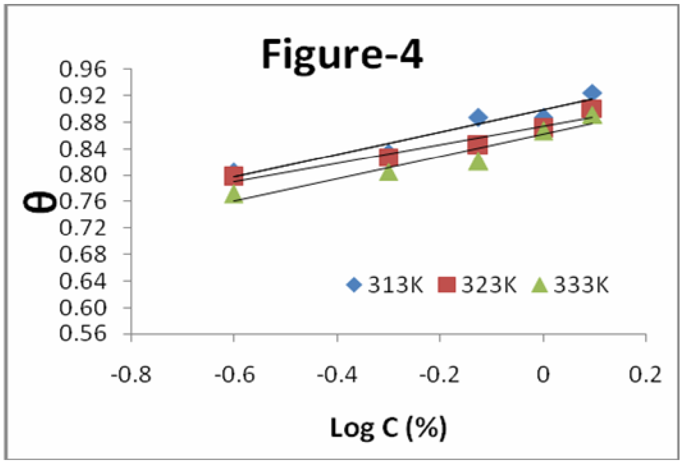


Figure.5 Plot of Log θ versus Log C for Ankado leaf extract at different concentrations of HCl for 3 h .

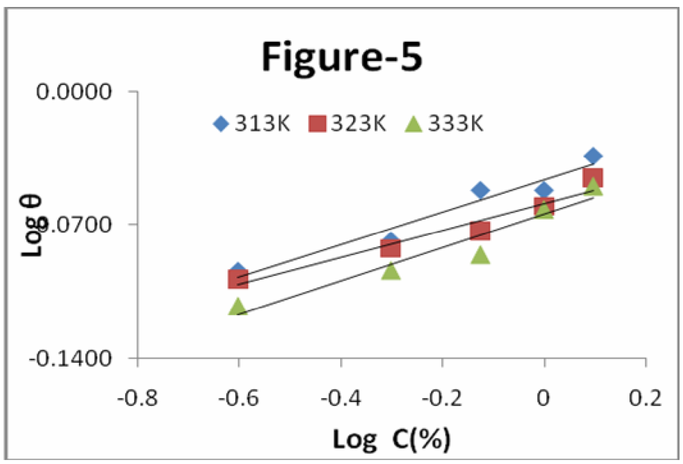


Figure.6 Arrhenius plots for corrosion of mild steel in 1 M HCl in absence and presence of Ankado leaf extract.

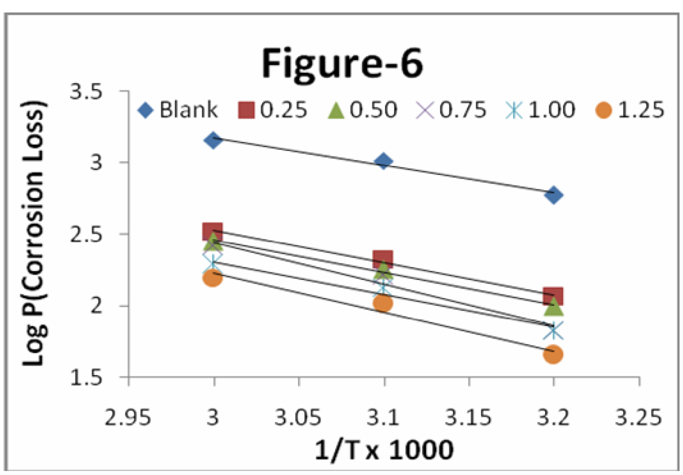


Figure.7(a) Polarisation curves for corrosion of mild steel in 1 M Hcl without inhibitors

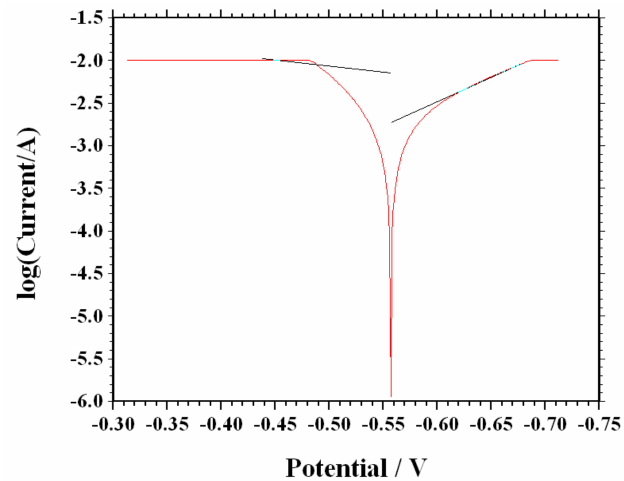
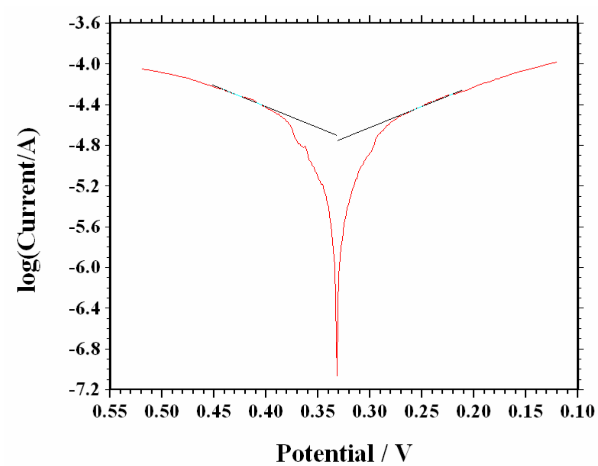


Figure.7(b) Polarisation curves for corrosion of mild steel in 1 M Hcl containing 1.25% ankado leaf extract inhibitors



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