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Investigation of green corrosion inhibitor efficiency in different solutions at different pH and temperature

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Abstract-The effect of ginkgo biloba inhibitor on the corrosion of carbon steel in citric acid was studied by potentiodynamic polarization. The effects of temperature (30, 40, and 50) ˚C, concentrations of ginkgo biloba inhibitor (0, 50, 100, 200 and 500) ppm and acid concentration (1%, 3% and 5%) were studied. The corrosion potential, corrosion current, the cathodic Tafel slope (βc) and corrosion rate were measured. The results reveal that ginkgo biloba inhibition efficiency increases with the concentration of inhibitor and decreases with temperature rising. The adsorption of ginkgo biloba inhibitor on carbon steel surface followed the Langmuir isotherm.

Keywords: **Ginkgo biloba, Carbon steel, Corrosion inhibitor, Citric acid, Polarization, Adsorption.**

I. INTRODUCTION

The inhibition effect of Ginkgo leaves extract (GLE) on the corrosion of cold rolled steel (CRS) in 1.0–5.0 M HCl and 0.5–2.5 M H_2SO_4 solutions was investigated by potentio dynamic polarization technique. The results show that GLE is a good inhibitor, and exhibits better efficiency in 1.0 M HCl than 0.5 M H_2SO_4. The adsorption of GLE on CRS surface obeys Langmuir adsorption isotherm. GLE acts as a mixed-type inhibitor in 1.0 M HCl, while a cathodic inhibitor in 0.5 M H_2SO_4 [1].

Inhibition of carbon steel corrosion by some thiophene azodyes (1-3) in 2 M HCl was investigated by potentiodynamic polarization technique. The inhibition efficiency increased with increase in inhibitor concentration but decreased with increase in temperature. The thermodynamic parameters of corrosion and adsorption processes were calculated and evaluated. The potentiodynamic polarization measurements indicated that the inhibitors are of mixed type. The adsorption of these inhibitors was found to obey Langmuir adsorption isotherm [2].

II. MATERIALS AND METHODS

A. Specimen preparation

Cylindrical carbon steel specimens of 6mmdiameter were used. Each specimen was covered with epoxy (sikadur-32) to prevent corrosion on covered area. Only the cross sectional area at the rod exposed (0.2827cm^2). Before each experiment the specimen scraped by emery paper of different grades (200, 400 and 600) under running tap water. Then washing with distilled water, dried with tissue paper, washing with ethanol, dried with tissue paper and finally put in dissicator until used.

B. Preparation of inhibitor

The leaves of ginkgo biloba were used. The prepared leaves (100grams) mixed with the extraction solution and blended for half an hour at room temperature .An extraction solution of 240cm of distilled water and 60cm of methanol alcohol was used .The mixture filtrate by cloth and the filtrate dried by an oven at 50^{o}C for 24 hours.

C. Preparation of test solution

Three concentration (1, 3 and 5) g citric acid per 100ml at distilled water were used. Five concentrations at Ginkgo biloba (0, 50, 100, 200 and 500) ppm were used. Citric acid a molecular weight of 192.12 g/mole and density of 1.665g/cm3 respectively.

D. Experimental procedure

1-The tests carried out at temperature (30, 40 and 50 ^{o}C), water bath was used to obtain the required temperature.
2-Three electrode corrosion cell was used. Ag-AgCL as a reference electrode and platinum as a counter electrode.
3-In each experiment the current and the potential changed stepwise by varying the rheostat.
4-One minute was usually allowed for each reading of current and potential.
5-EACH TEST WAS REPEATED TWICE AT SAME CONDITIONS AND USING FRESH ELECTROLYTE.

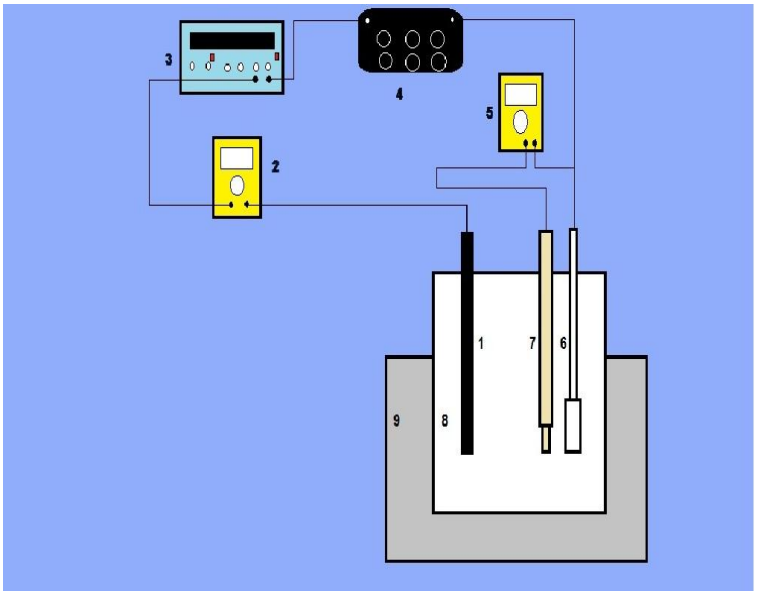

Fig 1: Schematic diagram of electrical circuit.
1-platinum electrode, 2- ammeter, 3- power supply, 4-Rheostate, 5- voltmeter, 6- working electrode (carbon steel), 7-reference electrode (Ag-Agcl electrode) , 8- Pyrex beaker, 9-water bath.

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III. RESULTS AND DISCUSSION

A. Effect of Inhibitor Concentration on corrosion Current

The efficiency of the inhibitors increases with increasing the concentration of inhibitor. A further increase of inhibitor concentration does not change the protective effect significantly [3]. The main constituents of Ginkgo biloba inhibitor are ginkgolides, amino acids and flavonoids which exhibit the inhibition efficiency. These compounds contain hetero atoms like O, N atoms in functional groups (N–H, C–O, O-H and C=O) and O-herterocyclic rings which meets the general properties of ideal corrosion inhibitors for prevent the corrosion of carbon steel. The components of inhibitor are adsorbed on the steel surface showed in table 1 [1]

B. Effect of acid Concentration on corrosion Current

The corrosion current increases with acid concentration increasing at all temperatures [3]. The corrosion inhibitor efficiency decreases with acid concentration increases by at all temperatures. The acid concentration increasing increases the dissociation of inhibitor and decrease the surface coverage with adsorbed inhibitor. The hydrogen adsorption increased due to the acid concentration increasing and increases the hydrogen evolution [4].

C. Effect of temperature

When temperature increase, the corrosion rate increases due to the hydrogen evolution over potential decreases. The Arrhenius equation is often expressed the relationship between the temperature and corrosion rate.

$$\ln i_{corr} = A + -\frac{Ea}{RT} \qquad (3.1)$$

Where R is the molar gas constant, A is the Arrhenius factor, Ea is the activation energy and T is the temperature of the solution. The plot of ln i_{corr} versus 1/T is showed in figure (3.1). In this plots, the slope (-Ea/R) and an intercept of Aware obtained. The inhibition efficiency decreases with increasing temperature, which shows that the inhibitive film formed on the metal surface is less protective at higher temperatures and more of desorption of inhibitor molecules from the metal surface.

Efficiency of inhibitor (η) % decreases with increase in temperature therefore the activation energy (Ea) of inhibited solution more than the activation energy Ea of uninhibited solution. The phenomenon of physical adsorption occurs in the first stage as shown in appendix B-1. Increasing thickness of the double layer with higher values of Ea in the presence of inhibitor which enhances the Ea of the corrosion process and increasing energy barrier for the corrosion process, emphasizing the electrostatic character of the inhibitor's adsorption on the carbon steel surface.

$$i_{corr} = \frac{RT}{Nh} \exp\left[\frac{-\Delta H}{RT}\right] \exp\left[\frac{\Delta S}{R}\right] \qquad (3.2)$$

N is the Avogadro's number, h is the Planck's constant, ΔS° is the entropy of activation and ΔH is the enthalpy. Plotting ln (icorr/T) versus (1/T) is showed in figures (3.2) . In these plots, the slope (-ΔH/R) and an intercept of $\left(\ln\frac{R}{Nh} + \frac{\Delta s}{R}\right)$ are obtained. ΔHads and ΔSads were calculated from the graph. The positive values of ΔHads mean the adsorption of inhibitor on carbon steel surface is an endothermic process and indicates that there is a chemical adsorption as shown in table 2.

D. Adsorption isotherm

The mechanism of the interaction between the carbon steel surface and the inhibitor may be using explained adsorption isotherms. The surface coverage (θ) values for various concentrations of inhibitor in citric acid solution were obtained from polarization measurements. The surface coverage (θ) could be written as

$$\theta = \frac{\eta(\%)}{100} \qquad (3.3)$$

The adsorption of inhibitor on the carbon steel surface represented by a modified Langmuir adsorption isotherm equation suggested by Villamil et al. can be given by the following:

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \qquad (3.4)$$

Where n is a constant, θ is the surface coverage, K_{ads} is the equilibrium constant of the adsorption process and C is the concentration of inhibitor . Figure.3 showed plot of $\frac{C}{\theta}$ versus C with slopes were greater than unity and correlation coefficient (R^2) was used to calculate the best fit isotherm. This means that the adsorption of inhibitor on carbon steel followed the Langmuir isotherm. The equilibrium constant of the adsorption process (K_{ads}) can calculate from the intercepts of the straight lines on the y-axis $\left(\frac{C}{\theta}\right)$. The standard free energy of adsorption (ΔG_{ads}) was calculated from equation:

$$\Delta G = -RT\ln K_{ads} C_{H2O} \qquad (3.5)$$

Where the concentration of water in solution are 999 (g/l), R is the gas constant (8.314 J/K mol) and T is the absolute temperature (K) . The negative sign of the standard free energy of adsorption ($\Delta G°_{ads}$) indicate the spontaneous adsorption of inhibitor on carbon steel surface. ΔG^{o}_{ads} was increased where becomes less negative with the increase of temperature which indicates the occurrence of exothermic process as shown in table .3). The values ΔG_{ads} are within the range (-20−-40) kJ mol^{-1} indicating that the adsorption of inhibitor on carbon steel surface classified as mixed type adsorption i.e., chemisorption (molecular) and physisorption (ionic).

E. Fourier transforms infrared (FTIR) spectroscopy of ginkgo biloba inhibitor

Figure 4 shows the FTIR spectroscopy of ginkgo biloba inhibitor. The strong band at 3269.71 cm^{-1} is attributed to N–H or O–H stretching. The band at 2924.43 cm^{-1} is related to C–H stretching vibration, and that at 2363.87cm^{-1} is O=C=O stretching vibration. The strong band at 1600.18 cm^{-1}

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could be assigned to C=C and C=N stretching vibration. The C–H bending in –CH3 is found to be at 1393 cm^{-1}. The absorption bands at 1238.55 cm^{-1} are due to the framework vibration of aromatic ring. Besides these, there is an absorption band at 1028.4 cm^{-1}, which can be assigned to the C–N or C–O stretching vibration. The absorption bands below 1000 cm^{-1} correspond to aliphatic and aromatic C–H group. This result indicates that GLE contains oxygen and nitrogen atoms in functional groups (N–H, C=O, C=N, C=C, C–N, O–H, C–O, O=C=O) and aromatic ring, which meets the general consideration of typical corrosion inhibitors.

IV. CONCLUSION

The main conclusions drawn from these studies are drawn:

1. Ginkgo biloba inhibitor is a good eco-friendly green inhibitor for the corrosion control of carbon steel in citric acid solution.
2. Inhibition efficiency of the ginkgo biloba increases with increase in the concentration of the inhibitor.
3. Inhibition efficiency of the ginkgo biloba decreases with increase in the temperature.
4. The adsorption of ginkgo biloba inhibitor on the surface of carbon steel follows Langmuir adsorption isotherm.
5. Energy of activation value suggests that ginkgo biloba undergoes physical adsorption on the surface of carbon steel.
6. The values ΔH_{ads} mean the adsorption of inhibitor on carbon steel surface is an endothermic process and indicates that there is a chemical adsorption.
7. The values ΔG_{ads} indicating that the adsorption of inhibitor on carbon steel surface classified as mixed type adsorption i.e., chemisorptions and physisorption.

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APPENDIX

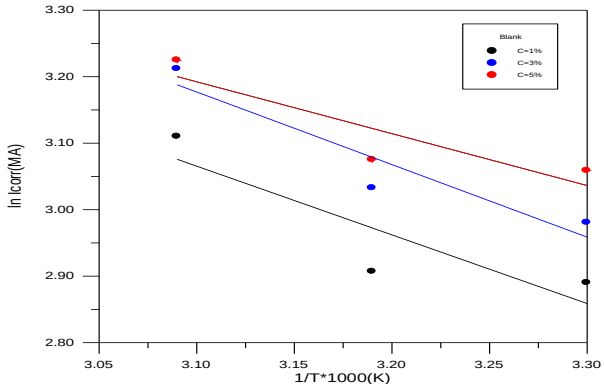

Fig 2.Arrhenius plots for carbon steel dissolution in different concentration of acid in the absence of inhibitor.

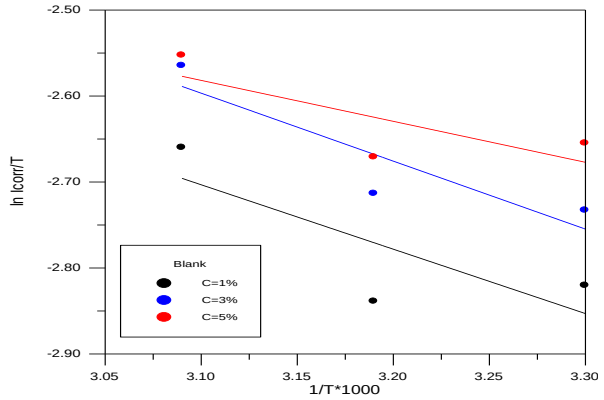

Fig 3. Transition state plot for the corrosion of carbon steel in different concentration of acid at absence of inhibitor.

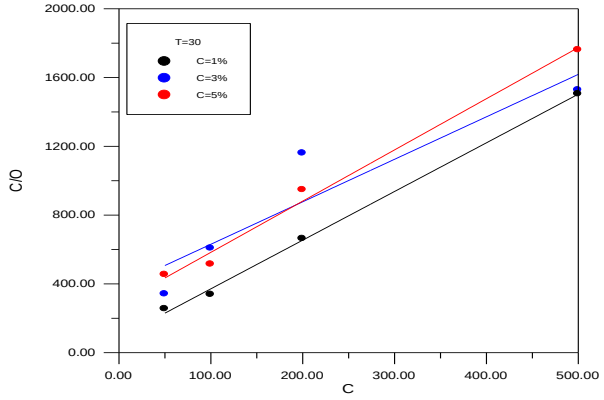

Fig 4.Langmuir isotherm adsorption model on the carbon steel surface of ginkgo biloba in citric acid at 30 ^{o}C.

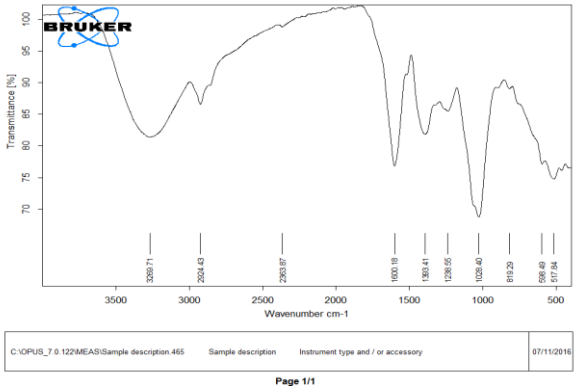

Fig 5. Fourier transforms infrared (FTIR) spectroscopy of ginkgo biloba inhibitor.

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Table 1: Values of Corrosion Current Density and Cathodic tafel slope of Polarization Curves at Different Temperatures, concentration of citric solution and Inhibitor Concentration

.

Temperature	Concentration	Inhibitor concentration (ppm)	Corrosion current avarage (μA)	Cathodic tafel slope (βc)
30	1%	0	18.05	174.75
30	1%	50	14.5	160.7
30	1%	100	12.7	132.258
30	1%	200	12.6	125.9
30	1%	500	12.05	210.9
30	3%	0	19.7	114.35
30	3%	50	16.8	151.615
30	3%	100	16.45	115.8
30	3%	200	16.3	107.3
30	3%	500	13.25	138.4
30	5%	0	21.3	109.5
30	5%	50	18.95	104.685
30	5%	100	17.15	103.58
30	5%	200	16.8	102.2
30	5%	500	15.25	93.008
40	1%	0	18.3	116.65
40	1%	50	17.9	144.4
40	1%	100	17.61	168.85
40	1%	200	16.65	148.13
40	1%	500	16	178.
40	3%	0	20.75	142.4
40	3%	50	18.9	116.285
40	3%	100	18.85	117.25
40	3%	200	16.6	159.8
40	3%	500	16.5	147.27
40	5%	0	21.65	100.935
40	5%	50	21.5	121.1
40	5%	100	21.25	117.35
40	5%	200	21.15	109.95
40	5%	500	20.2	
50	1%	0	22.5	133.8
50	1%	50	19.15	144.86
50	1%	100	18.25	158.3
50	1%	200	17	119.8
50	1%	500	17	124.24
50	3%	0	24.85	108.94
50	3%	50	21	121.
50	3%	100	19.55	113.535
50	3%	200	19.2	140.6

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50	3%	500	18.65	118.8
50	5%	0	25.15	98.9
50	5%	50	24.05	126.035
50	5%	100	24	82.5
50	5%	200	21.85	84.05
50	5%	500	20.5	188.77

Table 2: Activation Energy and the enthalpy in the absence and presence of ginkgo biloba with different concentrations and different concentration of citric acid solution.

		Ea	ΔH_{ads}
1%	Blank	8.4658	7.0049
	50ppm	14.58	10.8269
	100ppm	12.0029	9.4839
	200ppm	11.101	8.556
	500ppm	13.74	11.2
3%	Blank	9.07	6.5739
	50ppm	8.83	6.2163
	100ppm	13.55	4.28
	200ppm	6.44	3.89
	500ppm	6.83	11.099
5%	Blank	11.086	3.9624
	50ppm	6.515	6.927
	100ppm	10.516	10.826
	200ppm	13.43	7.97
	500ppm	11.89	9.344

Table 3. Thermodynamic parameters at different concentration of citric acid solution and different temperature

Temperature	30 °C			40 °C			50°C		
Concentration of acid	1%	3%	5%	1%	3%	5%	1%	3%	5%
ΔG_{ads}	-26.14	-22.1	-23.31	-19.55	-25.092	-14.91	-20.55	-27.88	-20.45