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Research Article

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Corrosion inhibition of carbon steel in 1M HCl solution by *Ruta graveolens* extract

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ABSTRACT

The inhibition property of Ruta graveolens extract (RGE) on the corrosion of carbon steel in 1M HCl solution was investigated using potentiodynamic polarization and weight loss techniques. The percentage inhibition increased with the increase of the concentration of the extract. At a concentration of 2.0g/l, the percentage inhibition reached about 94.34% at 25°C duration 6 hours. The inhibition efficiency decreased with the increase of temperature. The results showed that the adsorption of the extract on the carbon steel surface obeys Langmuir isotherm. Also the activation parameters, apparent activation energy (E_a), the enthalpy of activation (ΔH_a) and entropy of activation (ΔS_a) for the corrosion of carbon steel in 1M HCl in the absence and presence of RGE were calculated and discussed.

Key words: Carbon steel, Hydrochloric acid, Corrosion inhibition, *Ruta graveolens*, Adsorption

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INTRODUCTION

Corrosion is the deterioration of metal by chemical attack or reaction with its environment. It is a constant and continuous problem, often difficult to eliminate completely [1]. The use of inhibitors is one of the best options of protecting metals against corrosion in various fields of application as acid pickling and acid descaling [2]. The inhibitors employed are varied and some have been found to be severe to health and the environment at large. Thus efforts are now directed towards formulation of modern environmentally safe inhibitors in which plant extracts have become important as eco-friendly, economical, readily available and renewable sources of effective corrosion inhibitors. The present study aimed at investigating the inhibitive properties of ethanol extract of *Ruta graveolens* plant leaves on the corrosion of carbon steel in 1M HCl solution.

EXPERIMENTAL SECTION

Specimen preparation

Metal used for the study was carbon steel of composition (wt. %) Si (2), Mn (0.4), C (0.368), S (0.1), Cr (0.07), Mo (0.012) and Fe (97.05). Carbon steel specimens of size 5.6 cm x 2.5 cm x 0.3 cm containing a small hole of 3 mm diameter near the upper edge were employed for the weight loss test. For electrochemical study, carbon steel circular strips of the same composition with an exposed area of 1 cm^2 were used. Before each test, the specimen was subsequently ground with 60 and 1200 grit grinding papers, cleaned by distilled water and acetone.

Preparation of plant extract

Fresh leaves of *Ruta graveolens* plant was used in this study. The leaves were washed with tap water several times followed by distilled water. After one day the leaves were dried more in an electric furnace for 10 – 20 min and grounded to powder form. Limited weight (grams) of the powder of leaves was immersed in 60 ml of ethanol for three days. After three days the solution was filtered and used as natural corrosion inhibitor in 1M HCl solution.

Weight Loss and Electrochemical Measurements

In the weight loss experiments, a clean weighed carbon steel coupon was immersed completely in 100 ml of the electrolyte (hydrochloric acid and treated water) in the absence and presence of the inhibitor. After specified period of time each specimen was taken out of the test solution, washed with distilled water, dried and weighed. The experiments were performed for various parameters such as:

1. Extract concentration variation (0.4, 0.8, 1.2, 1.6 and 2.0).
2. Temperature variation (25, 45, 65℃).

Potentiodynamic polarization measurements were carried out using computerized electrochemical analyzer model 35415. The carbon steel specimen was used as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The polarization measurements were made to evaluate the corrosion current, corrosion potential and Tafel slopes. A luggin capillary arrangement was used to keep the reference electrode close to the working electrode. 400 ml of the electrolyte was added to the test cell and the luggin capillary was filled with the same test solution. Ten minutes was given for each experiment to attain the steady state open circuit potential [3]. Then the carbon steel specimen was polarized to about ± 200 mV anodically and cathodically from the open circuit potential to obtain the corrosion potential, corrosion current and Tafel slopes [4].

RESULTS AND DISSCUSION

Effect of RGE Concentration

The electrochemical parameters, anodic Tafel constant (β_a), cathodic Tafel constant (β_c), corrosion potential (E_{corr}), corrosion current density (i_{corr}) and the corresponding inhibition efficiencies for the corrosion of carbon steel in 1M HCl solution without and with different concentrations (0.4 – 2 g/l) of RGE at 25℃ are illustrated in table (1). Also figure (1) shows the anodic and cathodic potentiodynamic polarization curves for the previous tests. As expected, the polarization curves of the carbon steel were considerably modified when RGE is added. Indeed, both cathodic and anodic reactions of carbon steel electrode corrosion were inhibited with the increase of RGE concentration. This result suggests that RGE addition reduces anodic dissolution and also retards the hydrogen evolution reaction [5]. The corrosion current density of carbon steel in 1M HCl solution reduced from 231.98 $\mu A/cm^2$ to 19.65 $\mu A/cm^2$ and the corrosion inhibition efficiency increased to 91.5% in the presence of 2 g/l of RGE at 25℃ . In general, the increase in the inhibition efficiency could be attributed to the increase coverage of the surface area of the carbon steel by RGE molecules as it blocks the available sites for reaction on the surface [6].

Table1. Electrochemical parameters of corrosion inhibition by RGE

RGE (g/L)	β_a (mV/Dec)	β_c (mV/Dec)	E_{corr} (mV)	i_{corr} ($\mu A/cm^2$)	I.E %
0.0	79.4	-123.1	-403.8	231.98	----
0.4	87.0	-150.2	-411.3	27.82	88.0
0.8	93.4	-125.0	-424.6	25.36	89.0
1.2	81.9	-120.9	-416.0	24.10	89.6
1.6	78.2	-107.3	-415.8	22.23	90.4
2.0	87.0	-108.5	-424.4	19.65	91.5

Also corrosion rates of carbon steel samples were determined in 1M HCl solution at various concentration of RGE for 6 hours of immersion at 298 K. Table (2) shows the values of inhibition efficiencies (I.E) and corrosion rates (C.R) obtained from weight loss test at different RGE concentrations. It is observed that the inhibition efficiency increases with increasing concentration of the plant extract which is an indication of the adsorption of constituents of the phytochemicals present in the RGE on the surface of the metal thereby reducing the surface area available for corrosion, thus inhibiting the rate of dissolution of the metal in the acid. The maximum inhibition efficiency (94.34%) was obtained at 2 g/l.

Table2. Weight loss data for 6 hours immersion time at 298 K

RGE (g/L)	Weight loss (mg/cm^2)	C.R (mg/cm^2.hr)	I.E %
0.0	2.82	0.4700	-----
0.4	0.29	0.0483	89.7234
0.8	0.26	0.0433	90.7872
1.2	0.25	0.0416	91.1489
1.6	0.19	0.0316	93.2765
2.0	0.16	0.0266	94.3404

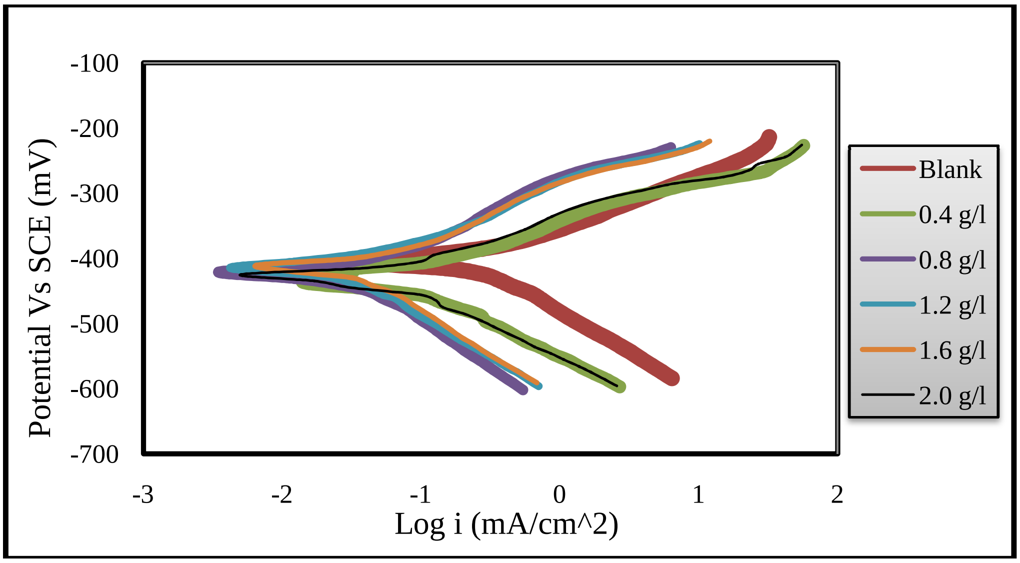

Figure1. Tafel polarization plots

Adsorption isotherm is very useful in determining the adsorption characteristics of an inhibitor. Values of degree of surface coverage calculated from weight loss measurements were used to fit curves to Langmuir isotherm. The assumptions of Langmuir adsorption isotherm is represented by equation (1) [7]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh} \ldots (1)$$

Where C_{inh} is the concentration of the inhibitor θ is degree of surface coverage of the inhibitor and K is the adsorption equilibrium constant. Plotting C_{inh}/θ against C_{inh} gives a straight line with unit slope value (Fig.2) indicating that adsorption of RGE inhibitor molecules from HCl solution on carbon steel surface follows Langmuir adsorption isotherm. From this result it could be concluded that there is no interaction between the molecules adsorbed at the metal surface [8].

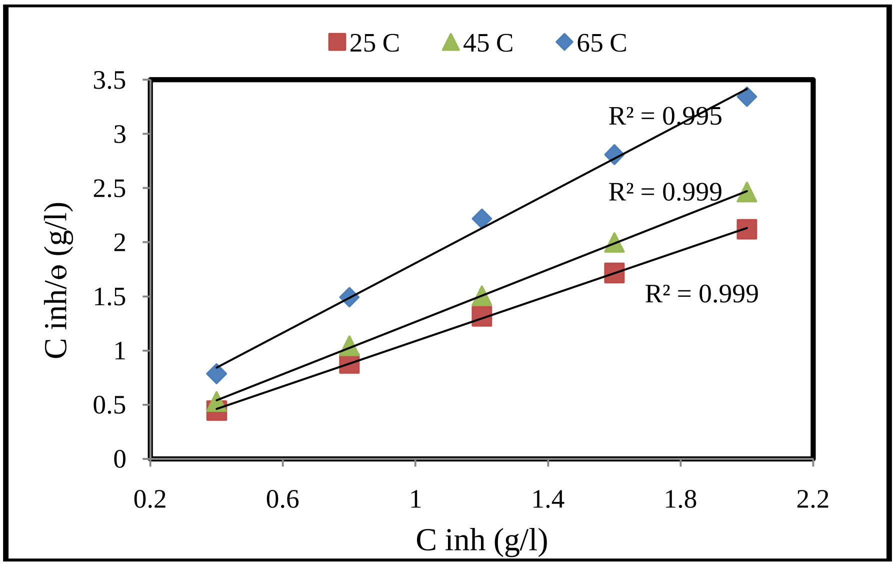

Figure2. Langmuir adsorption plots for carbon steel in 1M HCl containing different concentrations of GRE

Effect of Temperature

The influence of temperature on the corrosion behavior of carbon steel in HCl solution was studied in the absence and presence of different concentrations of RGE at 25, 45 and 65℃ duration 6 hours. As shown in table (3) the corrosion rate of carbon steel in HCl solution in the absence and presence of the extract increases with the rise in temperature and the inhibition efficiency decreases when the temperature rises to 65℃. Decrease of inhibition efficiency with temperature rise attributed to increase in dissolution process of carbon steel and partial desorption of the inhibitor from the metal surface with temperature. These results indicate that the adsorption of the extract of the carbon steel surface obeys physical adsorption mechanism.

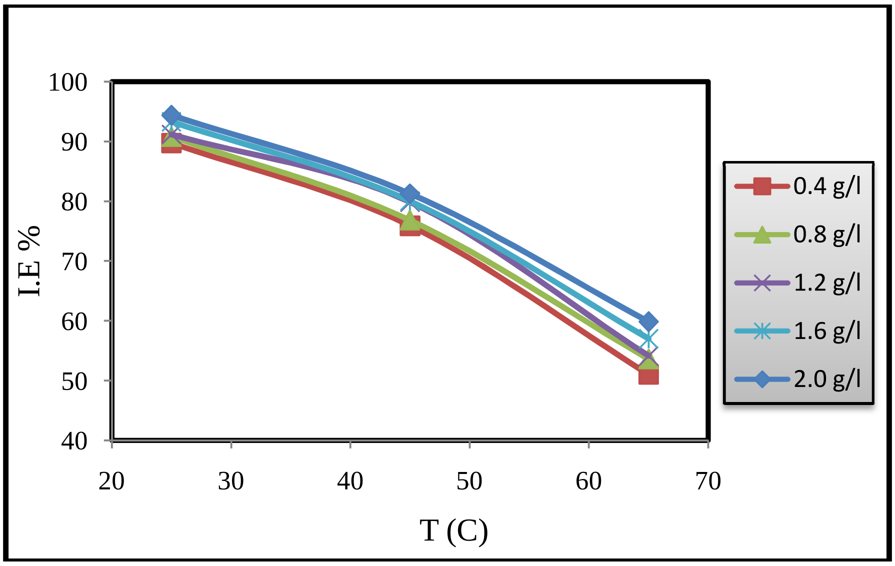

Figure3. Effect of temperature on inhibition efficiency of RGE

Table3. Effect of temperature on the corrosion parameters of carbon steel in 1M HCl at various concentration of GRE duration 6hr

RGE (g/L)	T (℃)	Weight loss (mg/cm^2)	C. R (mg/cm^2.hr)	I.E %
0.0	25	2.82	0.4700	----
	45	9.87	1.6450	----
	65	39.48	6.5800	----
0.4	25	0.29	0.0483	89.7234
	45	2.38	0.3966	75.8905
	65	19.33	3.2216	51.0395
0.8	25	0.26	0.0433	90.7872
	45	2.29	0.3816	76.8024
	65	18.33	3.0550	53.5714
1.2	25	0.25	0.0416	91.1489
	45	1.99	0.3316	79.8419
	65	18.11	3.0183	54.1291
1.6	25	0.19	0.0316	93.2765
	45	1.97	0.3283	80.0425
	65	16.98	2.8300	56.9908
2.0	25	0.16	0.0266	94.3404
	45	1.85	0.3083	81.2583
	65	15.86	2.6433	59.8282

Activation Parameters of Inhibition Process

The apparent activation energy (E_a), the enthalpy of activation (ΔH_a) and entropy of activation (ΔS_a) for the corrosion of carbon steel in 1M HCl solution in the absence and presence of RGE were calculated from Arrhenius equation and Arrhenius transition state equation [9]:

$$\log \mathrm{C.R} = -\frac{E_a}{2.303RT} + \log j \ldots \ (2)$$

$$\log \frac{\mathrm{C.R}}{T} = \left[\log \frac{R}{Nh} + \frac{\Delta S_a}{2.303R}\right] - \frac{\Delta H_a}{2.303RT} \ \ldots \ (3)$$

Where C.R is the corrosion rate, R is the universal gas constant, T is the temperature, K is the Arrhenius pre-exponential constant, N is Avogadro’s number and h is Planck’s constant. A plot of logarithm corrosion rate of carbon steel obtained from weight loss measurements versus the reciprocal of absolute temperature ranges (25, 35 and 65℃), gives a straight line as shown in figure (4) with slope $-E_a/2.303R$. On the other hand, a plot of $\log \mathrm{C.R}/T$ versus $1/T$gives a straight line (figure (5)) with a slope equal to $-\Delta H_a/2.303R$ and an intercept of $\log R/Nh + \Delta S_a/2.303R$, from which the values of ΔH_a and ΔS_awere calculated. The values of E_a, ΔH_a and ΔS_a are listed in table (4). Inspection of table (4) shows that values of both E_a and ΔH_a obtained in presence of RGE are higher than those obtained in the blank solution. This observation further supports the proposed physical mechanism. On the other hand, the positive value of ΔH_a reflects the endothermic nature of the carbon steel dissolution process, while the increase of ΔS_a reveals that an increase in disordering takes place on going from reactant to the activated complex [9].

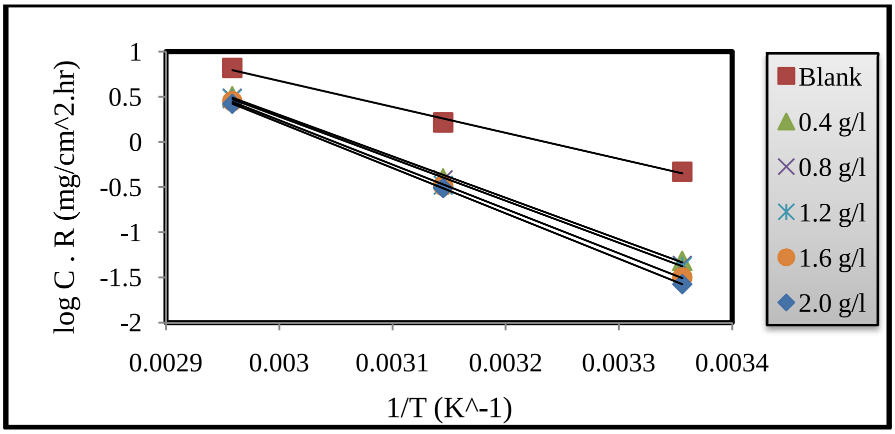

Figure4. Plot of log C.R against 1/T for carbon steel in 1M HCl in the absence and presence of different concentrations of RGE

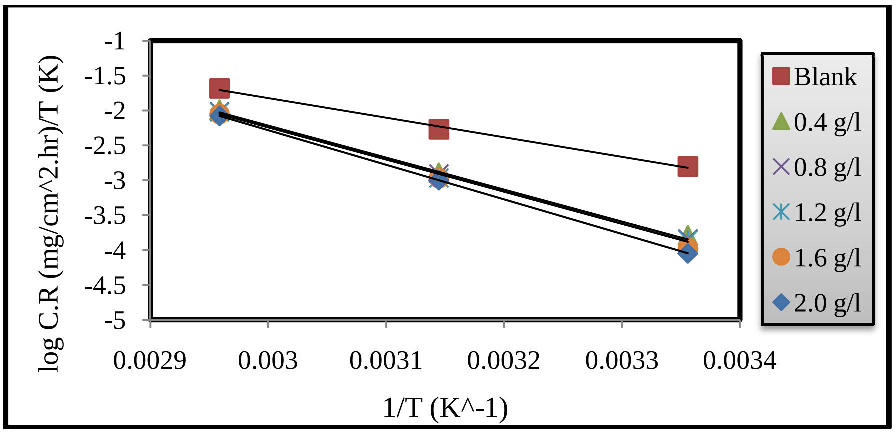

Figure5. Plot of log C.R/T against 1/T for carbon steel in 1M HCl in the absence and presence of different concentrations of RGE

Table4. Activation parameters

RGE (g/L)	E_a (KJ/mol)	ΔH_a (KJ/mol)	ΔS_a (J/mol.K)
0.0	55.1246	53.76517	-71.1856
0.4	87.8279	86.46849	19.55268
0.8	89.0342	87.67476	22.99916
1.2	89.5320	88.17259	23.95652
1.6	94.0699	92.71046	37.16805
2.0	96.2909	94.93153	43.48661

CONCLUSION

1. Results obtained from electrochemical and weight loss methods shows that the RGE acts as an inhibitor for corrosion of steel in hydrochloric acid media.
2. The inhibition efficiency of RGE increases with increasing RGE concentration.
3. The inhibitor acts by being adsorbed on the surface of carbon steel by physical adsorption mechanism.
4. The adsorption characteristics of this inhibitor follows Langmuir adsorption isotherm.
5. The effect of temperature study shows that the extract becomes less efficient at the highest temperature.
6. Activation energies were higher in the presence of RGE suggesting a physisorption mechanism.

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