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Research Article

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Corrosion Inhibition of Mild Steel in Acidic Solution by *Combretum ghasalense* Leave and Root Extracts as a Green Inhibitor

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Abstract The inhibition of the corrosion of mild steel in HCl acid solution using leave and root extracts of *Combretum ghasalense* has been investigated using weight loss method. The temperature was varied from 30 °C, 40 °C, and 50 °C respectively over an exposure period of 24 hours. The inhibitor concentration was equally varied as 0.1, 0.2, 0.3, 0.4, and 0.5 g/l. The results obtained revealed that the inhibition efficiency decreased with increase in temperature. It has been found that the extracts act as a good corrosion inhibitor for mild steel in all concentrations of hydrochloric acid solution. The effect of temperature on the corrosion inhibition of the sample indicated an increase in the corrosion rate as temperature increased and subsequent decrease in the inhibition efficiency. Thermodynamic data calculated are suggestive of adsorption of inhibitor molecules onto the metal surface. The root was found to have inhibited the corrosion process than the leaves.

Keywords Hydrochloric acid, Mild steel, Adsorption, Inhibition efficiency, Weight loss

Introduction

Corrosion of mild steel is among the common forms of corrosion in acidic medium. Mild steel have been used in many industrial applications such as in automobiles, oil and gas, chemical industries. It was found that the metal corrodes when exposed to aggressive environments [1]. In many industrial applications, the stagnant solutions, water, fluid that remains in the pipes, containers are often sites for corrosion. Many lives and materials were lost due to corrosion, and in order to reduce the corrosion of metals different ways have been used. The use of inhibitor is an effective means for protecting metals from degradation in acidic media. It has been documented that an effective inhibitors are those that has in their structures compounds containing hetero-atoms such as oxygen, nitrogen, sulphur and phosphorus which allowed adsorption onto the surface of metal [2]. Many organic inhibitors exist but they are not ecofriendly to humans and environments due to their toxicity. Plant extracts of natural origin haven reported to be effective and contain O, N, P, and S in them and are readily available, cheap, non toxic [3]. Several authors have used different extracts of leaves, stems, roots, fruits, flowers, and seeds as inhibitors for steels [4, 5, 6]. The present study was carried out to see the effectiveness of controlling the corrosion of mild steel in acidic medium using *Combretum ghasalence* leave and root extracts as inhibitor.

Materials and Methods

Materials and Sample Preparation

Material used for the study were mild steel of the following composition (wt.%): Fe 99.30%, Mn 0.192%, C 0.076%, Si 0.026%, P 0.012%, Ni 0.050%, and Cr 0.050%. The mild steel was cut into different coupons of dimension 10 mm x 15 mm, and each coupon was polished with different size of emery paper grids from (600 – 1200), later degreased by washing with ethanol, rinsed with acetone and dried in air before they were preserved in a desiccators. All reagents used for the study were Analar grade and double distilled water was used for their preparation.

Plants Extraction

Samples of *Combretum ghasalense* leaves and roots were obtained from Malumfashi Local Government Area in Katsina State, Nigeria. The samples were shade dried ground and soaked in a solution of methanol for 72 hours. After 72 hours, the samples were filtered and the filtrates were further subjected to evaporation at 352 K in order to make it free of ethanol. The stock solutions of the extract so obtained were used in preparing different concentrations of the extract by dissolving 0.1, 0.2, 0.3, 0.4, and 0.5 g of the extract in 1L of 2.5M HCl respectively. The concentration of HCl used for the preparation of the inhibitor-acid solutions was 1M.

Phytochemical Screening

The phytochemical analysis of inhibitor sample was carried out to identify the presence of the chemical constituents: tannins, flavonoids, alkaloids, and saponins. The screening was done according to methods reported elsewhere [7, 8].

Weight Loss Method

The samples used for the weight loss was initially weighed and then completely immersed in 250 ml solution to perform the test. The beaker was inserted into a water bath maintained at a temperature of 30 ^oC. After 24 hours, each sample was withdrawn from the test solution, washed with distilled water and dried at room temperature before re-weighing. The difference in weight after the exposure time was taken as the weight loss. The effect of temperature on mild steel corrosion and corrosion inhibition was investigated by performing experiments in 1M HCl at 30 ^oC, 40 ^oC, and 50 ^oC for 24 hours. The experiment was repeated in triplicates to check the reproducibility of results. From the weight loss result obtained, corrosion rates were calculated using the following relationship:

$$\text{Corrosion rate, CR} = \frac{87.6W}{DAT} \text{ (mm/yr)} \quad (1)$$

Where W = weight loss in mg, D = density of the sample g/cm3, A = area of sample in cm, and T = exposure time in hours.

Corrosion inhibition efficiency (IE) was the calculated using the equation:

$$\text{IE \%} = \frac{CR_o - CR}{CR_o} \times 100 \quad (2)$$

CR_O = corrosion rate in the absence of an inhibitor

CR = corrosion rate in the presence of an inhibitor

and the degree of surface coverage, ϴ, was calculated using the equation:

$$\Theta = \frac{CR_o - CR}{CR_o} \quad (3)$$

Results and Discussion

Phytochemical Screening

Table 1 shows the result of the phytochemical analysis of *Combretum ghasalense* leave and root. The results obtained, indicate that saponnins, tannins, flavonoids and alkaloids are present in methanol extract of the plant. The inhibition efficiency of the extract is attributed to the phytochemical constituents [9].

Table 1: Phytochemical screening of *Combretum ghasalense* leave and root

Compounds	Leaves	Roots
Tannins	+	+
Alkaloids	+	+
Flavonoids	+	+
Terpenoids	+	-
Glycosides	_	+
Saponins	+	+

Key: Present (+), Absent (-)

Effects of inhibitor concentration on corrosion rate and inhibition

Tables 2 and 3 show the corrosion rate, inhibition efficiency, and surface coverage of mild steel in the absence and presence of *Combretum ghasalense* leaves and roots extracts in 1M HCl solution at 30 °C, 40 °C and 50 °C. The corrosion inhibitor efficiency of the plant extracts was determined in a test solution of 1M HCl on mild steel surface at different temperatures. Figures 1 and 2 show the corrosion rates against inhibitor concentrations of *Combretum ghasalense* leaves and roots. It is evident from the plots that corrosion rates decreased with increase in concentration of the extracts at all temperatures. However, the corrosion rate was observed to increase with increase in temperatures [10].

Table 2: Corrosion rate, Inhibition efficiency, and Surface coverage of Mild steel in the absence and presence of *Combretum ghasalense* leaves extract in 1M HCl solution at 30 °C, 40 °C and 50 °C

Temperature (°C)	Weight Loss (mg)	Inhibitor Concentration (g/l)	Corrosion Rate (mm/yr)	Inhibition Efficiency (IE)	Surface Coverage (Θ)
30	122.9	Blank	38.05	_	_
30	62.4	0.1	19.32	49.20	0.4920
30	39.1	0.2	12.09	68.26	0.6826
30	28.6	0.3	8.86	76.70	0.7670
30	20.8	0.4	6.45	83.04	0.8304
30	10.4	0.5	3.21	91.56	0.9156
40	190.8	Blank	59.07	_	_
40	116.7	0.1	36.14	38.81	0.3881
40	81.3	0.2	25.17	57.39	0.5739
40	60.1	0.3	18.61	68.50	0.6850
40	43.0	0.4	13.32	77.45	0.7745
40	27.8	0.5	8.60	85.44	0.8544
50	250.4	Blank	77.52	_	_
50	190.6	0.1	59.00	23.89	0.2389
50	135.1	0.2	41.84	46.03	0.4603
50	97.4	0.3	30.16	61.09	0.6109
50	64.9	0.4	20.12	74.05	0.7405
50	49.5	0.5	15.32	80.23	0.8023

Table 3: Corrosion rate, Inhibition efficiency, and Surface coverage of Mild steel in the absence and presence of *Combretum ghasalense* roots extract in 1M HCl solution at 30 °C, 40 °C and 50 °C

Temperature (°C)	Weight Loss (mg)	Inhibitor Concentration (g/l)	Corrosion Rate (mm/yr)	Inhibition Efficiency (IE)	Surface Coverage (Θ)
30	122.8	Blank	38.03	_	_
30	56.5	0.1	17.49	54.01	0.5401
30	34.3	0.2	10.62	72.07	0.7207
30	23.6	0.3	7.31	80.78	0.8078
30	13.8	0.4	4.26	88.80	0.8880
30	6.8	0.5	2.09	94.50	0.9450
40	190.8	Blank	59.07	_	_
40	104.4	0.1	32.31	45.30	0.4530
40	70.1	0.2	21.69	63.28	0.6328
40	47.3	0.3	14.65	75.20	0.7520
40	31.4	0.4	9.72	83.57	0.8357
40	22.0	0.5	6.81	88.47	0.8847
50	250.4	Blank	77.52	_	_
50	178.5	0.1	55.27	28.70	0.2870
50	135.3	0.2	41.89	45.96	0.4506
50	98.9	0.3	30.62	60.50	0.6050
50	62.0	0.4	19.20	75.23	0.7523
50	34.7	0.5	10.74	86.14	0.8614

The inhibition efficiencies and degree of surface coverage for both leaves and roots of *Combretum ghasalense* were calculated using the equations 2 and 3. The inhibition efficiencies increased with increase in inhibitor concentrations and decreases with increasing temperatures. This can be attributed to increase in corrosion rate due to desorption of inhibitor molecules from the surface of the metal at elevated temperatures which is also a suggestive of physical adsorption mechanism [11].

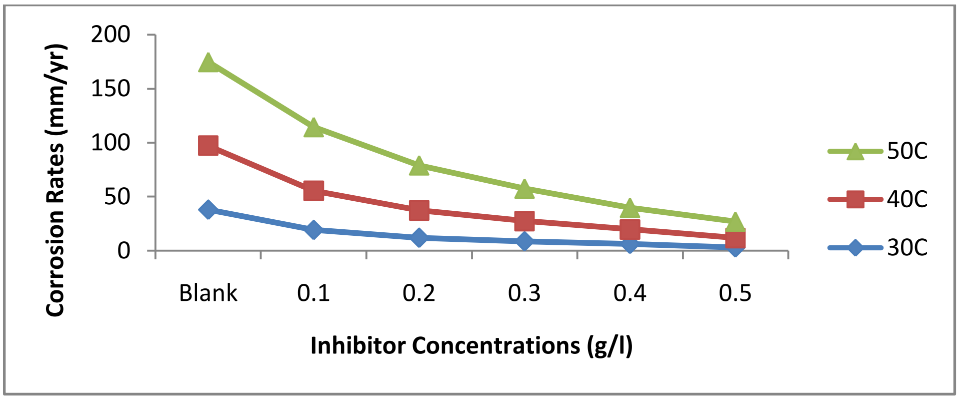

Figure 1: Corrosion Rates against Inhibitor Concentrations of Mild Steel in 1M HCl Solution in the Absence and Presence of Combretum ghasalense Leaves Extract

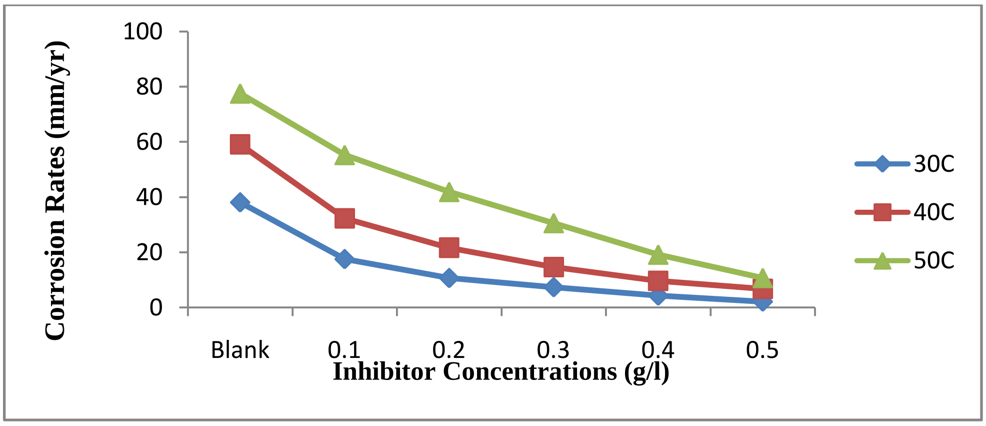

Figure 2: Corrosion Rates against Inhibitor Concentrations of Mild Steel in 1M HCl Solution in the Absence and Presence of Combretum ghasalense Roots Extract

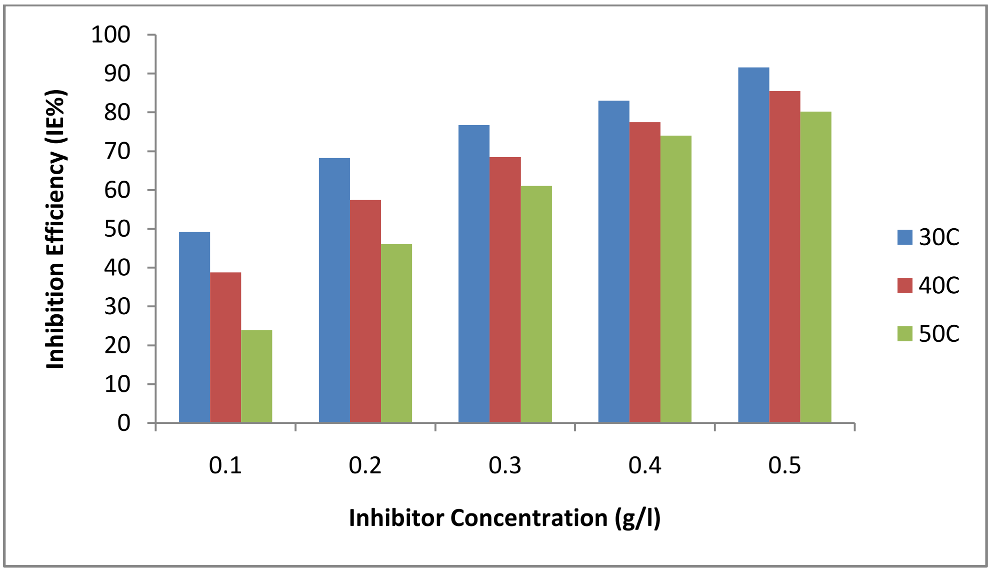

Figure 3: Inhibitor Efficiency against Inhibitor Concentration of Mild Steel in 1M HCl Solution in the Absence and Presence of Combretum ghasalense Leaves Extract

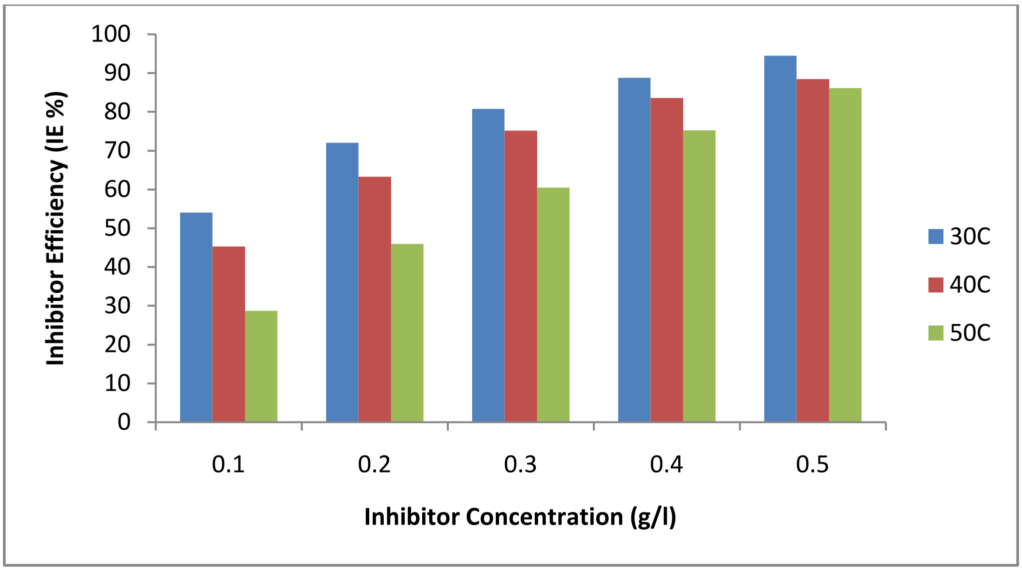

Figure 4: Inhibitor Efficiency against Inhibitor Concentration of Mild Steel in 1M HCl Solution in the Absence and Presence of Combretum ghasalense Roots Extract

Effect of Temperature

Temperature plays a significant role in the inhibitive mechanism of the corrosion process.

The effect of temperature on the corrosion of mild steel in the absence and presence of various concentration of *Combretum ghasalense* leaves and roots were investigated using the Arrhenius state equation shown in Equations (4 and 5) [12].

$$Log\ CR = Log\ A - \frac{Ea}{2.303\,RT} \quad (4)$$

$$Log\left(\frac{CR}{T}\right) = \left[Log\left(\frac{R}{NAh}\right) + \frac{\Delta Sa}{2.303\,R}\right] - \frac{\Delta Ha}{2.303\,RT} \quad (5)$$

Where CR is the corrosion rate of the metal, A is the Arrhenius or pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the temperature of the system. N_A is the Avogadro's constant, ΔSa is the entropy of activation and ΔHa is the enthalpy of activation. From Equation 4, plot of log CR versus reciprocal of absolute temperature, 1/T as presented in Figures 5 and 6 give a straight line with slope equal to $-\frac{Ea}{2.303\,R}$, from which the activation energy for the corrosion process can be calculated.

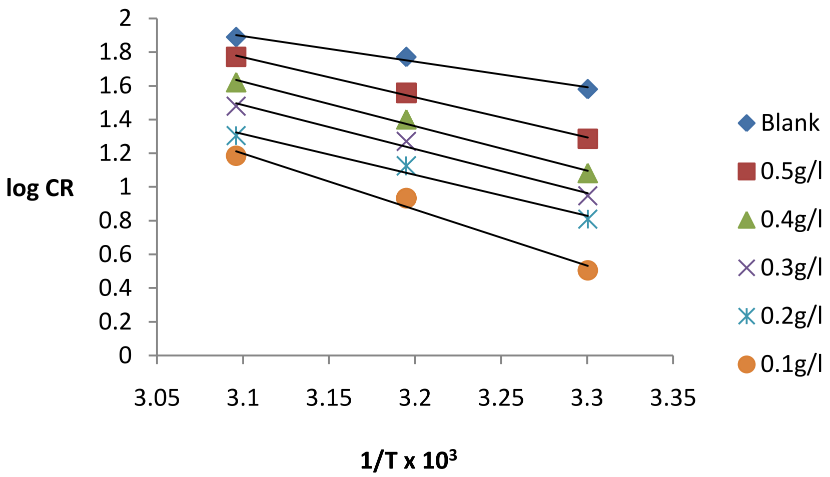

Figure 5: Variation of log CR with 1/T for the Corrosion of mild steel in 1M HCl solution in the absence and presence of Combretum ghasalense leaves extract

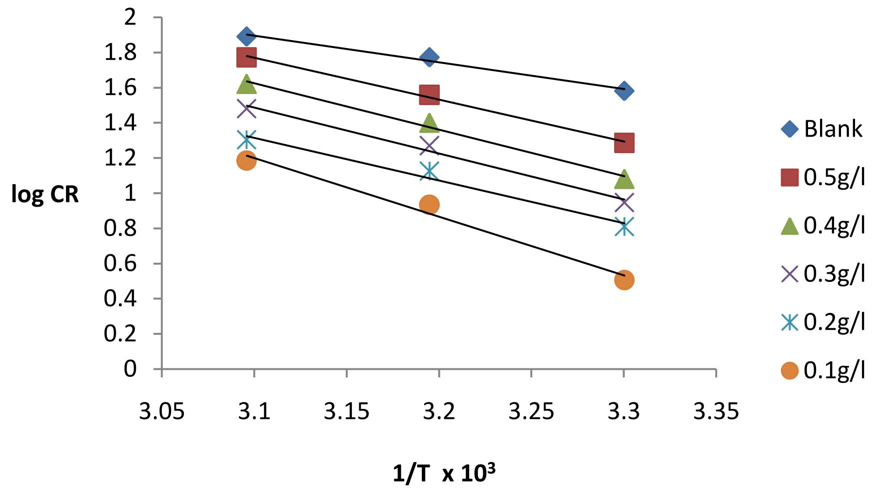

Figure 6: Variation of log CR with 1/T for the Corrosion of mild steel in 1M HCl solution in the absence and presence of Combretum ghasalense roots extract

From Equation (5), plot of $Log\ CR/T$ versus reciprocal of absolute temperature, $1/T$, as shown in Figures 7 and 8 give a straight line with slope equal to - $\frac{\Delta Ha}{2.303\,R}$ and intercept of $\left[Log\frac{R}{NAh}+\frac{\Delta Sa}{2.303\,R}\right]$, from which the enthyalpy and entropy of activation for the corrosion process can be calculated. Values of Ea, ΔSa, and ΔHa are presented in Tables 4 and 5. Figures 7 and 8 also show a linear relationship between the corrosion rate and the temperature of the environment.

The values obtained from the experiment show that the activation energies (ΔEa) were higher with the inhibited samples compared to uninhibited samples. This indicates the effectiveness of the inhibitor on the surface of the coupons since higher values of the activation energy leads to the lowering of the corrosion rates [13]. It has also been suggested that the higher the values of Ea in the presence of the plant extract than in its absence can be interpreted as an indication of adsorption effect and it showed that it is by physisorption [14]. The positive values of the enthalpy (ΔHa) reflect endothermic nature of the mild steel dissolution process which implies that the dissolution of steel became difficult. The ΔHa values increased in the presence of inhibitor than that obtained in the absence of inhibitor indicating protection efficiency. The entropy of activation (ΔSa) in the presence and absence of the inhibitor also has negative values which showed that the activated complex in the rate determining step represents an association rather than dissociation, which implies that a decrease in disordering took place on going from the reactant to the activated complex [12].

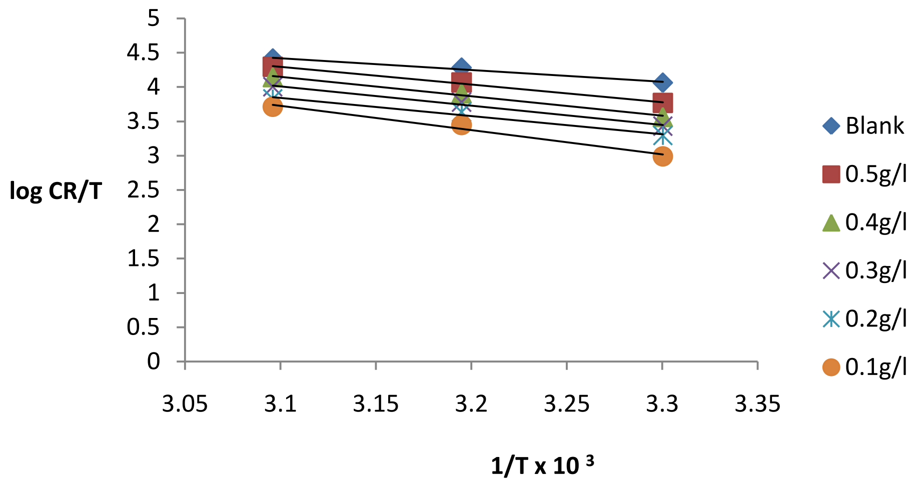

Figure 7: Variation of log CR/T with 1/T for the Corrosion of mild steel in 1M HCl solution in the absence and presence of Combretum ghasalense leaves extract

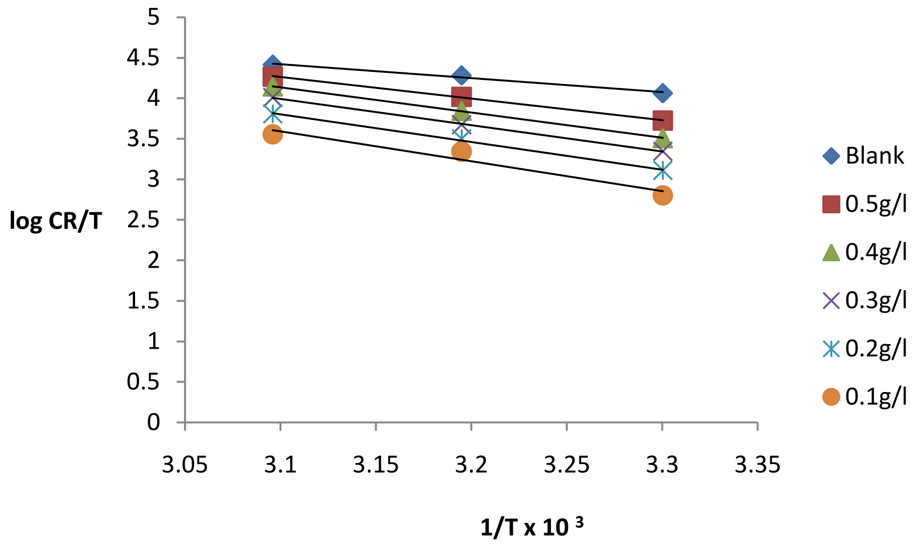

Figure 8: Variation of log CR/T with 1/T for the Corrosion of mild steel in 1M HCl solution in the absence and presence of Combretum ghasalense roots extract

Table 4: Activation energy parameters for the dissolution of mild steel in HCl in the absence and presence of different concentration of *Combretum ghasalense* leaves

Inhibitor Concentration	Ea (KJ/mol.)	ΔHa (kJ/mol.)	ΔSa (kJ/mol.)	Q_{ads} (kJ/mol.)
Blank	32.93	29.03	- 71.32	-
0.1	49.34	45.47	23.01	-45.85
0.2	50.30	46.39	- 28.58	- 37.63
0.3	53.84	49.94	- 14.32	- 30.12
0.4	54.47	50.59	- 9.61	- 21.97
0.5	67.67	63.74	-22.75	- 40.02

Table 5: Activation energy parameters for the dissolution of mild steel in HCl in the absence and presence of different concentration of *Combretum ghasalense* roots

Inhibitor Concentration	Ea (KJ/mol.)	ΔHa (kJ/mol.)	ΔSa (kJ/mol.)	Q_{ads} (kJ/mol.)
Blank	32.93	29.03	- 71.32	-
0.1	50.72	46.83	- 30.10	-43.61
0.2	59.74	55.83	16.88	- 46.64
0.3	62.13	58.25	-10.94	- 75.76
0.4	65.52	61.31	6.35	- 39.03
0.5	70.81	66.90	188.36	- 41.39

Conclusion

From the results of weight loss of corrosion rate of mild steel in acidic medium *Combretum ghasalense* leaves and root extracts as corrosion inhibitor, the following conclusions were drawn:

- The corrosion rate in the presence of the inhibitors decreases with increase in the concentration of the inhibitor
- The extracts can be used as inhibitor for mild steel in the studied medium
- The percentage inhibition efficiency (% IE) increased with increase in concentration of the inhibitor. However, it decreases with increase in temperature.
- The performance of the root extract as inhibitor is more than that of the leaves
- It has been established that the adsorption process followed a physisorption.

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Conflict of Interest

The authors did not have any conflict of interest associated with this work

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