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A Study of The Green Corrosion Inhibition of *Acacia tortilis* Extract on Mild Steel-Sulphuric Acid Environment

I.Y. Suleiman[1], M. Abdulwahab[2],*, F.E. Awe[3]

[1]*Department of Metallurgical Engineering, Waziri Umaru Federal Polytechnic, Birnin Kebbi, Nigeria.*
[2]*Department of Metallurgical and Materials Engineering, Ahmadu Bello University, Zaria, Nigeria.*
[3]*Department of Applied Chemistry, Federal University, Dutsinma, Nigeria.*

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ABSTRACT

Studies was made on the effect of plant extract, Umbrella Thorn (*Acacia tortilis)* with mild steel using gravimetric and electrochemical corrosion techniques in 0.5 M H_2SO_4. Scanning electron microscope equipped with energy dispersive spectroscopy (SEM/EDS) was used to analyze the surface morphology of the sample. Linear regression equation and analysis of variance (ANOVA) were employed to investigate the influence of process parameters on the corrosion rate of the samples. From the result, corrosion rate increased with increase in temperature and decreased with increase in both inhibitor concentration and time. The maximum inhibition efficiency was 93.19% and 97.54% in the presence of KI addition. The adsorption of the molecules of the extract on the mild steel surface obeyed the Langmuir adsorption isotherm. The potentiodynamic polarization results showed that the green inhibitor acted as mixed-type inhibitor. The results from ANOVA showed that temperature, inhibitor concentration and time are statistically significant.

1. Introduction

Steel and steel-based alloys are widely employed in majority of engineering and structural applications such as acid pickling, cleaning and oil-well acidizing processes. In these service conditions, degradation of the material is reported. Accordingly, methods for improving/or controlling such occurrence becomes a research focus among. Over the years, development and identification of potential inhibitors for corrosion control in majority of environments have been subject of interest with a promising result output [1-3]. In that direction, the use of organic and inorganic substances as corrosion inhibitor to reduce the corrosion rate of metals and alloys have been widely reported [4-6].

However, in recent time, the use of synthetic chemicals as corrosion inhibitors have been identify to be are costly, non-environmentally friendly and some of them are not easily biodegradable. As such, search for natural inhibitors has gained recognition such as plant extracts that are environmental friendly, bio-degradable, non-toxic, less costly and easily available. The use of natural products as corrosion inhibitors in different media were also studied [7-9]. Many of these naturally occurring substances have been used with excellent result for different metals and alloys in some aggressive media.

Equally majority of plants are known to contain various types of constituents such as alkaloids, tannins, flavonoids, saponins and volatile oil. In such plants, their potentials as corrosion inhibitors have been accessed in acidic media by various authors [4, 10, 11]. In the present study, an attempt was made to examine *Acacia tortilis* extract as a potential green corrosion inhibitor for mild steel in 0.5 M H_2SO_4 medium using gravimetric, potentiodynamic polarization and scanning electron microscopy along with some statistical model to verify efficiency of the inhibitor developed.

2. Experimental Methods

2.1 Preparation of Plant Extract

The fresh leaves of Umbrella Thorn (*Acacia tortilis*) plant were washed by water, shade dried, pulverized and the extraction was done by ethanol. The extract was dried on water bath at 105 °C. Inhibitor concentrations were prepared in the range of 2-10% v/v and the concentration for synergistic of halide ions was 0.1-0.5 mM.

2.2 Preparation of Specimens

The mild steel used in this study has the following composition (wt %); C (0.17), Si (0.033), Mn (0.011), S (0.014), P (0.014), Ni (0.019), Cr (0.09), Mo (0.014), Cu (0.055), Al (0.05), Co (0.015) and the remainder iron (Fe) which was obtained from Ajaokuta Steel Company Ltd, Nigeria. The dimensions of the coupons were 20 mm x10 mm and were polished to a mirror finish using 240 down to 1200 grit and degreased with trichloroethylene. This was used for the weight loss method and surface examination studies. The specimen used for electrochemical method has dimension of 10 mm x 10 mm with the surface area of 1.33 m^2, polished with successive emery paper to mirror size and was made the working electrode.

2.3 Gravimetric Method

Experiments were conducted in the test solutions for 45 minutes progressively for 270 minutes between 30-70 °C in aerated solutions. In each experiment, the cleaned mild steel coupon was weighed and suspended with the aid of glass rod and hook in a beaker containing 100 mL acid solution with and without addition of different concentrations of leaves extract. The weight loss was taken as the difference between the weight at a given time and the initial weight of the test coupon determined using digital balance with sensitivity of ±1 mg (Shimadzu Corporation, Model AUW120D). The sample weights were measured in milligrams to 4 decimal places and was used to calculate the corrosion rate (CR) and inhibition efficiency (%IE).

$$\text{Corrosion rate} = \frac{534W}{DAT} \quad (1)$$

where W is the weight loss, D the density of the steel in g/cm^3, A is cross sectional area in cm^2 and T is the time in hour.

Inhibition efficiency (% IE) was obtained by:

$$IE = \frac{CR^{o}-CR^{\prime}}{CR^{o}}\ x\ 100 \quad (2)$$

where CR^o and CR^1 are the corrosion rates in the absence and presence of inhibitor respectively.

*Corresponding Author
Email Address: mabdulwahab@abu.edu.ng (M. Abdulwahab)

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2.4 Potentiodynamic Polarization Studies

The electrochemical studies were made using a three-electrode cell assembly in a 0.5 M H_2SO_4 static solution at 30 °C. The mild steel of 1.33 m^2 was the working electrode, platinum electrode was used as an auxiliary/ counter electrodeand standard calomel electrode (SCE) was used as reference electrode. Before each Tafel, the electrode was allowed to corrode freely and its open-circuit potential (OCP) was recorded as a function of time, that is, time necessary to reach a quasi-stationary value for the open-circuit potential. This steady-state OCP corresponds to the corrosion potential (E_{corr}) of the working electrode. The anodic and cathodic polarisation curves were recorded by a constant sweep rate of 20 mV min^{-1}. The inhibitor efficiency was calculated according to Eq. (3);

$$IE\ (\%) = \left[\frac{I_{corr} - I'_{corr}}{I_{corr}}\right] \times 100 \quad (3)$$

Where, I_{corr} and I'_{corr} are the corrosion current densities in case of the absence and presence of the inhibitor respectively.

2.5 Surface Analysis of the Coupons

The test coupons in the as-corroded condition were dried and the surface morphology was examined using a Philips model XL30SFEG scanning electron microscope with an energy dispersive X-ray with or without the plant extract using magnification of x1000 and x2000.

2.6 Development of Mathematical Model

The standard L8 orthogonal array was adopted in the design of the experiment in order to investigate which corrosion control parameters significantly affects the corrosion rate.The independently process parameters considered for the investigation are temperature, concentration and exposure time. Two levels of each of the three factors were used for the statistical analysis. The levels for the three factors are shown in Table1 and the treatment combinations for the two levels and three factors can be found in Table 2. The model equation was obtained by representing the corrosion rate value by CR, which is a function of the three variables as expressed in Eq. (4) below:

$$CR = f\,(A, B, C) \quad (4)$$

where A is the temperature, B is the inhibitor and C is the exposure time. The model selected includes the effects of first order main variables and second-order interactions of all variables. Hence the general model is written as;

$$CR = \beta_o + \beta_1 A_+ \beta_2 B_+ \beta_3 C_+ \beta_4 AB_+ \beta_5 AC_+ \beta_6 BC_+ \beta_7 ABC \quad (5)$$

Where β_o is average response of CR and $\beta_1, \beta_2, \beta_3, \beta_4, \beta_5, \beta_6, \beta_7$ are coefficients associated with each variable A, B, C and interactions. The test results were recorded against the standard order of sequence as shown in Table 3.

Table 1 Factorial design of the corrosion rate

Factors	Low level	High level
Temperature (A)	30 °C	70 °C
Inhibitor (B)	0	10% v/v
Time (C)	45 minutes	270 minutes

Table 2 Factorial design of the corrosion process with the treatment combinations

Experimental No.	Temperature level	Concentration level	Time level
1	-1	-1	-1
A	+1	-1	-1
B	-1	+1	-1
AB	+1	+1	-1
C	-1	-1	+1
AC	+1	-1	+1
BC	-1	+1	+1
ABC	+1	+1	+1

Coded= -1(low level), +1(upper level or high)

Table 3 Corrosion rate, Inhibition efficiency (%IE), and surface coverage (θ) for mild steel in 0.5 M H_2SO_4 solution with and without varying concentration of *Acacia tortillis* extract at 303 K for 4.5 h

Inhibitor concentration (% v/v)	Corrosion rate (mpy)	Inhibition efficiency (%IE)	Surface coverage (θ)
Blank	47.94	-	-
2	8.22	82.85	0.83
4	6.28	86.91	0.87
6	4.07	91.52	0.92
8	3.88	91.90	0.92
10	3.26	93.19	0.93

The sum of squares for main and interaction effects was calculated using Yates algorithm. The significant factors (main and interaction) were identified by analysis of variance (ANOVA) technique.

3. Results and Discussion

3.1 Effect of Inhibitor Concentration and Immersion Time

The effect of inhibitor concentration on inhibition efficiency in 0.5 M H_2SO_4 is presented in Fig. 1. The inhibition efficiency increased with increase in plant extract and the maximum inhibition efficiency of 93.19% was obtained at an optimum concentration of 10% v/v. Further increase in extract concentration did not show any significant change in the performance of the extract. The values of corrosion rate (CR), percentage inhibition efficiency (IE %) and surface coverage (Θ) at 303 K were summarized in Table 3.

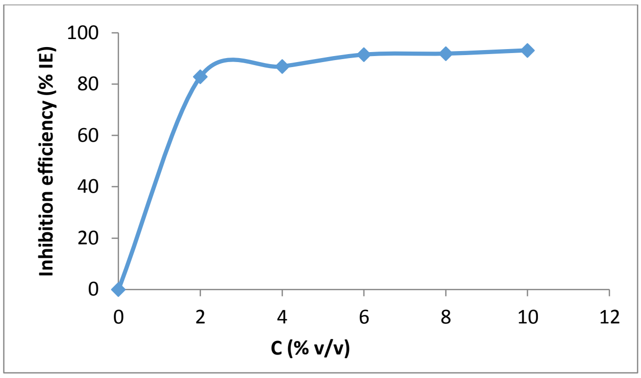

Fig. 1 Variation of inhibition efficiency against concentration of extracts at 30 °C

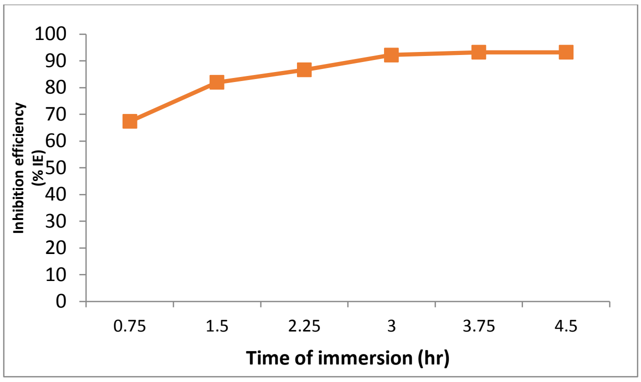

Fig. 2 Variation of inhibition efficiency against time of immersion in extract at 30 °C

Table 4 Effect of immersion time on percentage inhibition efficiency of mild steel in 0.5 M H_2SO_4Cl at 30 °C in the presence of optimum concentration of the *Acaciatortillis* extracts

Name of the plant extract with optimum concentration	Inhibition efficiency (%)					
	Time (h)					
	0.75	1.50	2.25	3.00	3.75	4.50
10% v/v of *Acaciatortillis*	67.37	81.94	86.62	92.20	93.19	93.18

The inhibition efficiencies were plotted against immersion time as seen from Fig. 2. The figure shows that inhibition efficiency of the extract was increased with increasing immersion time from 0.75 to 4.5 h. The increase in inhibition efficiency up to 4.5 h reflects the strong adsorption of constituents present in the extract on the mild steel surface, resulting in a protective layer formed at mild steel- sulphuric acid solution interface. It showed that maximum efficiency was at 3.75 h of immersion time which is sufficient for the pickling process [7, 9]. Effect of immersion time at 30 °C with an optimum concentration at 30 °C studied are given in Table 4.

3.2 Effect of Temperature Variation on the Corrosion Rate of Mild Steel Sample

The effect of temperature on the corrosion rate of mild steel in 0.5 M H_2SO_4 solution in absence and presence of 2-10% v/v *Acacia tortilis* was studied at different temperatures (303-343 K) by weight loss measurements during 4.5 h immersion time. It is obvious that the corrosion rate increases both in the uninhibited and inhibited with increase in temperature. The presence of inhibitor leads to decrease in the corrosion rate. %IE decreases with increase in temperature, meaning that the corrosion process is a temperature dependant.

The results obtained are presented in Table 5 and shown in Fig. 3. It can be seen that inhibition efficiency decreased with an increase in temperature. This might be due to increased rate of dissolution process of mild steel and partial desorption of the inhibitor from the metal surface with temperature. This occurrence has been reported [12].

Table 5 Effect of temperature on mild steel corrosion in the presence and absence of 6% v/v of *Acacia tortillis*extract for 4.5 h

Temperature (K)	Corrosion rate in the absence of inhibitor (CR°) mpy	Corrosion rate in the presence of inhibitor(CR') mpy	Inhibition efficiency (%IE)
303	47.94	2.80	94.16
323	54.21	10.71	80.23
343	60.99	20.95	65.65

In the presence of the extract, inhibition efficiency increased up to a temperature of 303 K and after that there was a decline from 323 to 343 K. Maximum inhibition efficiency was found to be 94.16% and minimum of 65.65% with 6% v/v concentration of *Acacia tortilis* extract in 0.5 M H_2SO_4. From the previous studies [13, 14], adsorption and desorption of inhibitor molecules continuously occur at the metal surface, and an equilibrium exists between these two processes at a particular temperature. This shows that there is an active-passive region in the corrosion process of mild steel in the studied environment. In this case, as the temperature increases, the rate of desorption of the inhibitor on the mild steel is higher than that of adsorption. Similar claim have been reported [15, 16].

Accordingly, the effect of temperature change in such condition of inhibited acid-metal reaction is not uncommon. This however was described earlier [17] as a complexreaction zone due to the changes that would occurred on the metal surface; such as rapid etching, desorption of inhibitor. Equally, the inhibitor itself may undergo decomposition reaction. In acidic solution, the corrosion rate is related to temperature by Arrhenius equation [18].

$$\text{Log}\,(CR) = -Ea/2.303RT + \text{A} \qquad (6)$$

where, *E*a is the apparent effective activation energy, *R* is the general gas constant and *A* is Arrhenius pre-exponential factor. A plot of log of corrosion rate obtained by weight loss measurement versus 1/*T* gave a straight line as shown in Fig. 4 (slope of -*E*a/2.303*R*). The values of activation energy are presented in Table 6. The data show that activation energy (*E*a) of the corrosion of mild steel in 0.5 M H_2SO_4 solution in the presence of extract is higher than that in the free acid solution. The increase in the apparent activation energy for mild steel dissolution in inhibited solution in this study may be interpreted as physical adsorption that occurs in the first stage. Similar to the report that explained an increase in the activation energy is attributed to an appreciable decrease in the adsorption of the inhibitor on the metal surface with increase in temperature [13, 19]. Similar views are held by [20, 21]. An alternative formulation of Arrhenius equation [22] is shown in equation (7) and represented in Fig. 5:

$$\text{CR} = \frac{RT}{Nh} \exp\left\{\frac{\Delta Sads}{R}\right\} \exp\left\{\frac{-\Delta Hads}{RT}\right\} \qquad (7)$$

From Table 6, the values of ΔH_a in the presence of *Acacia tortilis* are negative indicating the exothermic nature of the solution process suggesting that the dissolution of mild steel is slow as the concentration of the extract increases which indicates that inhibition efficiencies increases [23, 6]. The entropy (ΔS_a) is positive, this implies that the reaction was dissociation rather than association, meaning that disordering increases on going from reactants to the activated complex as suggested [24].

Table 6 Activation energy (Ea) and thermodynamic parameters for corrosion of MS in 0.5 M H_2SO_4 at 30, 50 and 70 °C containing different concentrations of *Acacia tortilis* extracts

Conc. (%V/V)	Activation energy (Ea) kJ/mol	Free energy of adsorption (Δ G) kJ/mol			Heat of adsorption (ΔH) J/molK	entropy change (Δ S) J/molK	K @ 30 °C	R2 @ 30 °C
		303K	323K	343K				
Blank	5.189	-	-	-	-	-		
2	32.876	14.604	15.454	16.559	14.514	48.24	5.9339	
4	32.971	12.933	13.771	14.385	14.609	42.73	3.0568	
6	33.335	11.97	12.824	13.746	14.973	39.55	2.0857	0.989
8	33.986	11.38	12.145	13.052	15.624	37.61	1.6502	
10	34.388	10.912	11.767	12.294	16.026	36.07	1.3705	

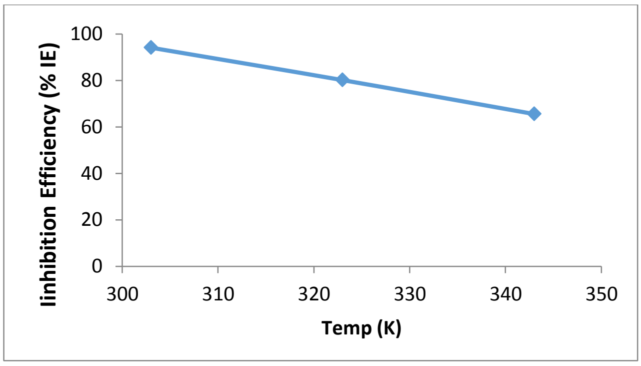

Fig. 3 Variation of inhibition efficiency of extracts with temperature in 0.5 M H_2SO_4 solution

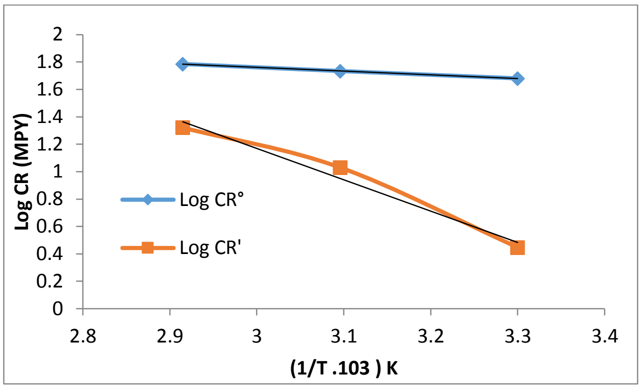

Fig. 4 Adsorption isotherm plots for log CR against 1/T

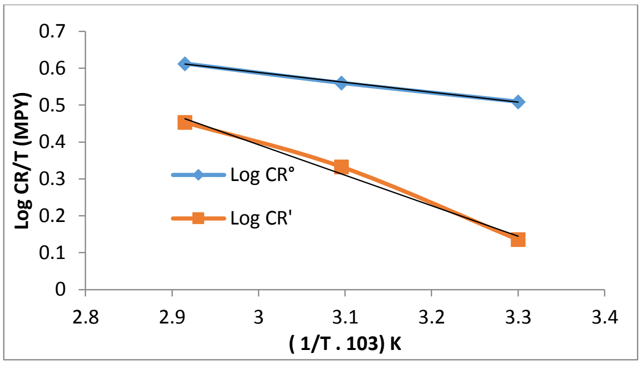

Fig. 5 Adsorption isotherm plots for log (CR/T) against 1/T

3.3 Potentiodynamic Polarization Measurement

The potentiodynamic polarization curves of the mild steel in 0.5 M H_2SO_4 solution without and in the presence of *Acacia tortilis* extract at varying concentrations is shown in Fig. 6. The increase in concentration of the extract led to both anodic and cathodic current inhibition, but the reduction in the cathodic current was more significant than that of the anodic current. This shows that the addition of *Acacia tortilis* reduces anodic dissolution and also retards the hydrogen evolution reaction.

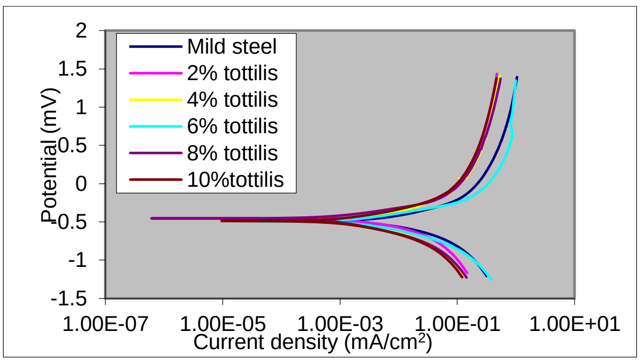

Fig. 6 Tafel plots of mild steel immersed in 0.5 M H_2SO_4 static solution without and with *Acacia tortillis* extractconcentrations at 30 °C

Table 7 gives the values of kinetic corrosion parameters as to the corrosion potential E_{corr}, corrosion current density I_{corr}, anodic and cathodic branches (ba and bc) and inhibition efficiency for the corrosion of mild steel in 0.5 M H_2SO_4 solution for the blankand in the presence of various concentrations ranging from 2-10% v/v of the extract.

The values of I_{corr} were found to decrease in the presence of inhibitor. The decrease in I_{corr} values can be due to the adsorption of the extract on the mild steel surface. It was observed that there was a small shift towards cathodic region in the values of E_{corr}. That is E_{corr} values are shifted positively which suggests that the extract functions as a mixed-type of inhibitor. In the entire concentrations ba and bc increased from 72 and 90 to 76 and 96 respectively suggesting that the inhibition is under mixed control, the effect of the inhibitor on the cathodic polarization is more pronounced than that of anodic polarization. This is similar to the previous studies reported elsewhere [25, 13].

Table 7 Potentiodynamic polarization parameters for mild steel in 0.5 M H_2SO_4 containing differentconcentrations of *Acaciatortillis*extract at 30 °C

Acacia T. (% v/v)	E_{corr} (SCE) (mV)	I_{corr} (mA/cm^2)	Tafel slopes mV/decade		Inhibition efficiency (IE %)
			b_a	b_c	
Blank (0)	-0.500	8.69	72	90	-
2.00	-0.480	0.78	73	93	91.02
4.00	-0.470	0.61	74	94	93.00
6.00	-0.460	0.70	75	95	91.90
8.00	-0.460	0.61	76	95	93.00
10.00	-0.460	0.52	76	96	94.01

The anodic and cathodic Tafel slopes (ba and bc) have a small change, indicating that the inhibiting action occurred by simply blocking the available anodic and cathodic active areas on the metal surface. The calculated inhibition efficiencies show that a good inhibition action of *Acacia tortilis* is obtained at the highest studied concentration comparatively. The anodic Tafel slopes, ba slowly decreases in the solution with *Acacia tortilis* extract indicating a small changes in the mild steel corrosion mechanism.

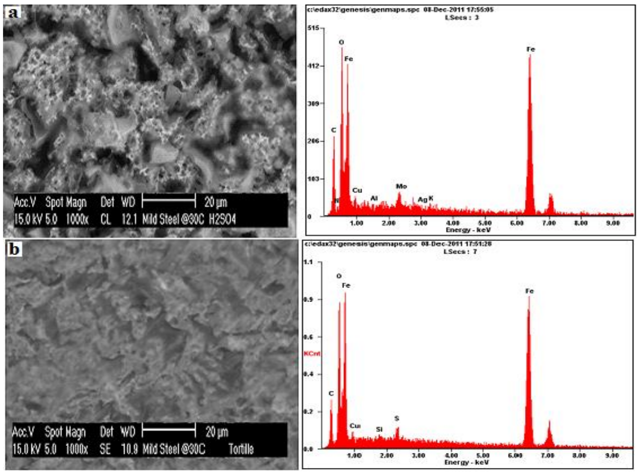

Fig. 7 SEM/EDX microstructure of mild steel immersed in a) 0.5M H_2SO_4 b) 0.5 M H_2SO_4 with 8% v/v of *Acacia tortilis*

3.4 Surface Morphology and Adsorption Isotherm

From the surface morphology of uninhibited mild steel-0.5 M H_2SO_4 interface in Fig. 7a, severe pits, cracks and selective dissolution of intermetallic occurred at the surface, whereas there was an improvement in the surface morphology of mild steel that was treated with the inhibitor. From the SEM-EDX evaluation, it is clear that the upraising value of O is due to the formation of the ferrous hydroxide. Such that the intensity is higher in the uninhibited sample (Fig. 7a and b). It is expected that some of the active constituent in the inhibitor form a protective thin layers and complexes on the mild steel surface.

The interactions between the *Acacia tortilis* extract and the mild steel surface was examined by the adsorption isotherm. The degree of surface coverage values for various concentrations of the extract in 0.5 M H_2SO_4 solution have been evaluated from the weight loss study. The dependence of fraction of the surface covered (θ) obtained by the ratios IE%/100 as a function of the extract concentration (C) was graphically fitted into Langmuir adsorption isotherms (Fig. 8). The Langmuir adsorption isotherm was found to be the best description of the adsorption behaviour of the studied plant extract as an inhibitor. That is, it obeys relationship;

$$\frac{C}{\theta} = \frac{1}{Kads} + C \qquad (8)$$

Where C is the inhibitor concentration; θ is the fraction of the surface covered, Kads is the adsorption coefficient. A higher correction factor (R^2) of 0.989 for Langmuir adsorption isotherm for *Acacia tortilis* extract was observed. The isotherm assumes that the adsorption of organic molecule on the adsorbent is monolayer and that the free energy of adsorption, ΔGads of the *Acacia tortilis* extract on mild steel surface can be determined using the equation reported [26].

$$\Delta G°ads = -RTln(55.5\ K) \qquad (9)$$

Where R is the universal gas constant and T is the absolute temperature. The value 55.5 in the above equation is the concentration of water in solution in molL^{-1}. The ΔGads value of *Acacia tortilis* extract was found to be -11.97 kJmol^{-1} at the optimum addition of 6% v/v. The negative value of the Δ*G*ads indicates the spontaneously adsorption of these molecules from H_2SO_4 solution to the metal surface. The value of Δ*G* ads around -20 kJmol^{-1} is consisted with the electrostatic interaction between charged organic molecules and the charged metal surface (physio sorption). This is in agreement with some observations elsewhere [27, 28].

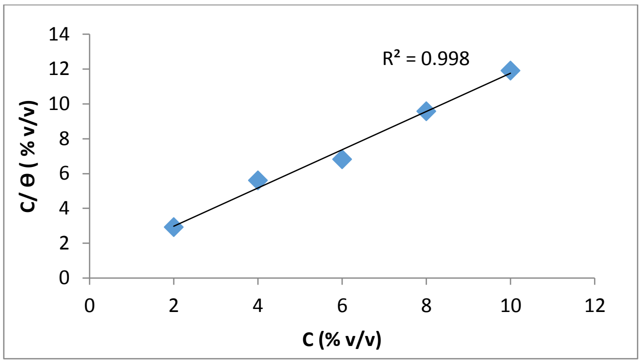

Fig. 8 Langmuir adsorption isotherm plot for the adsorption of *Acacia tortillis* extracts on the surface of mild steel in 0.5M H_2SO_4 solution at 303 K

Table 8 Synergism parameter S1 for various halides with *Acaciatortillis* by weight loss method at 30±1 °C

Name of the extract	Concentration (v/v)	Value of S_I (Halides)		
		KCl	KBr	KI
	2	1.77	1.7	1.68
	4	1.71	1.68	1.59
Acacia tortillis	6	1.68	1.62	1.52
	8	1.64	1.56	1.49
	10	1.59	1.47	1.40

3.5 Synergism Parameter

The increase in the inhibition efficiency of organic compounds in the presence of some anions have been observed previously [29] and was ascribed to synergistic effect. On that note, we considered it necessary to incorporate some halides in the environments. Table 8 shows the effect of 0.5 M KCl, KBr and KI on the inhibition efficiency of the system. The inhibition efficiency of the system increased in the presence of halide ions at the studied temperatures interval.

It was observed that halide ions are normally adsorbed on the surface of a corroding metal, which promote the adsorption of organic compounds by forming intermediate bridges between the positively charged metal surface and the positive end of the organic molecule [19]. Thus, the inhibitor is adsorbed on the metal by columbic attraction to the adsorbed halide ions on the metal surface.

SI value is found to be greater than unity, indicating the synergistic effect existing between the halide ions and *Acacia tortillis*. The inhibitive effect increases in the order Cl- < Br- < I-, which seems to indicate that the radii of halogen ions may also play a role. A similar trend was reported.

3.6 Analysis of Variance and the Effects of Parameters on the Corrosion Rate

ANOVA was used to determine the design parameters significantly influencing the corrosion rate (response). The results of ANOVA for the corrosion rate were presented in Table 9. This analysis was evaluated for a confidence level of 95%, that is for significance level of α = 0.05. From the results obtained, the inhibitor was the most significant parameter having the highest statistical influenceof 76.39% followed by time (11.09%) and temperature (10.43%). Since the F-value for the models was less than 0.05, then the parameter or interaction can be considered to be statistically significant [30]. The coefficient of determination (R^2) is defined as the ratio of the explained variation to the total variation and is a measure of the degree of fitness. For R^2 to approach unity, a better response model results is then indicated, which shows that it fits the actual data. The value of R^2 was 0.9291 (92.91%), thenhigh correlations with the experimental values established.The model was obtained from Eq. (5). The developed mathematical model equation for the corrosion behaviour of the mild steel in the acidic environment with the presence of the extract can be expressed as:

$$CR\ (AT) = 39.58 + 7.33A - 19.85B - 7.56C - 2.60BC - 1.31ABC \qquad (11)$$

The above equation can be used to predict the corrosion rate of the mild steel in the studied conditions. The constant in the equation is the residue. From the results in Table 10, inhibitor (-19.85) is the most important variable followed by time (-7.56) in the corrosion control in this study. Similar results have been observed [31].

Table 9 Analysis of Variance (ANOVA) for corrosion rate in the presence of *Acacia tortilis* extract

Source of variation	sum of squares	Degree of freedom (DF)	Mean Square	F_{cal} = M_S/Error M_S	F-value	F(%)
Main effect						
A	430.1	1	430.12	47.07	0.0206	10.43
B	3150	1	3150.59	344.75	0.0029	76.39
C	457.5	1	457.53	50.07	0.0194	11.09
Interraction						
BC	54.29	1	54.29	5.94	0.1351	1.32
ABC	13.73	1	13.73	1.5	0.3451	0.33
Resisdual	18.28	2	9.14			0.44
Cor. Total	4124	7				100

Table 10 Effect of the variables at 95% confidence level for *Acaciatortillis* extract

Factor	Coefficient estimate	Degree of freedom	Standard error	95% CI low	95% CI high
Intercept	39.58	1	1.07	34.98	44.18
A-Temp. 1.00	7.33	1	1.07	2.73	11.93
B-Inhibitor 1.00	-19.85	1	1.07	-24.44	-15.25
C-Time 1.00	-7.56	1	1.07	-12.16	2.96
AB 1.00	-2.6	1	1.07	-7.2	1.99
AC 1.00	-1.31	1	1.07	-5.91	3.29

Table 11 Comparison of the actual with the predicted result for mild steel using *Acaciatortillis*

Exp. No.	Temp. (°C)	Inhibitor (%v/v)	Time (mins)	Corrosion rate (mpy x 10^{-3}) Actual	Predicted	Residual
S11	1	1	-1	58.65	58.36	0.29
S12	1	1	-1	70.11	70.4	-0.29
S13	1	1	-1	19.14	21.26	-2.12
S14	1	1	-1	40.66	38.54	2.12
S15	1	1	1	47.94	45.82	2.12
S16	1	1	1	60.99	63.11	-2.12
S17	1	1	1	3.25	3.54	-0.29
S18	1	1	1	15.88	15.59	0.29

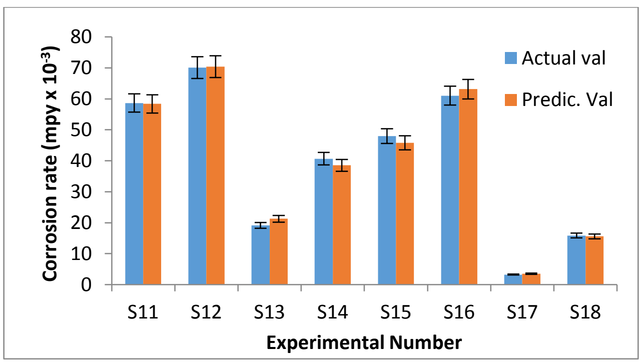

Fig. 9 Variation of experimental number with corrosion rate for mild steel with *Acaciatortillis*

Confirmation test was carried out and the results were presented in Table 11 and Fig. 9. Residual variation estimated for the Eq. (11) for corrosion is in the range of -2.12 to 2.12. This is similar to the report [32]. Hence, the regression models developed has demonstrated feasible and effective way to predict the corrosion rate of the mild steel investigated.

Figs. 10-11 showed the 3-D surface plots for corrosion rate of mild steel. These show the effect of temperature, inhibitor and time on the response on corrosion rate

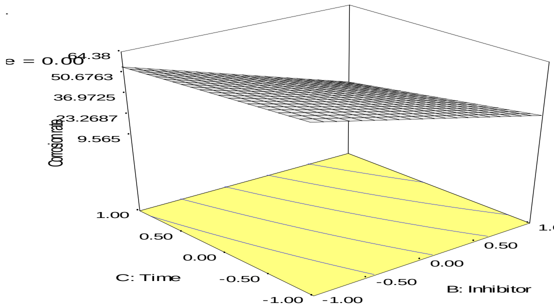

Fig. 10 3-D Surface plot of corrosion rate Vs time and inhibitor in the presence of *Acacia tortillis*

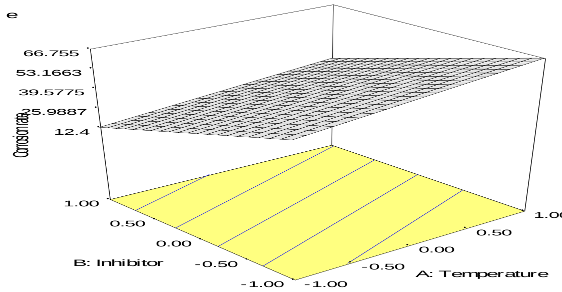

Fig. 11 3-D Surface plot of corrosion rate Vs inhibitor and temperature in the presence of *Acaciatortillis*

4. Conclusion

Acacia tortilis was found to be an efficient inhibitor for mild steel in 0.5 M H_2SO_4. Inhibition efficiency increased with increase in concentrations and decreased with rise in temperature and addition of halide ions synergistically increased the inhibition efficiency of the *Acacia tortillis* in the order of KCl < KBr < KI. The adsorption of the *Acacia tortilis* on the mild steel surface followed the Langmuir adsorption isotherm. Potentiodynamic polarization studies revealed that the extracts act through mixed modes of inhibition. The SEM morphology of the adsorbed protective film on the mild steel surface has confirmed the high performance of inhibitive effect of the plant extract. ANOVA results revealed that the parameters; temperature, concentration and time (A, B & C) are statistically significant. The results obtained by regression equations closely correlate each other which validate the corrosion rate equation developed. A good agreement between the predicted and actual corrosion rate was observed.

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