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Synergistic effect and statistical model of *terminalia avicennioides* as anti-corrosion inhibitor of steel pipelines in acidic environment

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Abstract

Investigation of *Terminalia avicennioides (Ta)* extract as corrosion inhibitor for steel pipelines in acidic medium using gravimetric method with and without (0.5 M KI^-) and statistical modelling was carried out. Qualitative analysis was used to determine the phytochemical constituents in the extract. The inhibitor concentration, temperature and time were varied in the range of 2.5-15.0 g/l at 2.5 g/l interval, 35-80 °C at 15 °C interval and 12- 72 hours at 12 hours interval in a static solution. A scanning electron microscopy (SEM) technique was used to characterize the coupon surfaces. A statistical design for the corrosion process was carried out to determine which parameters (inhibitor concentration, temperature and exposure time) that were statistically significant using ANOVA. The results revealed the presence of tannins, saponins, glycosides, flavonoids, alkaloids with reasonable amounts. Inhibition efficiency results without and with KI^- at the optimum concentration of 10 g/l were 94.86% and 99.12%. Langmuir adsorption isotherm was followed. E_a in the presence of inhibitor is greater than in the absence of inhibitor at all the temperatures studied, less than 80KJ/mol and physiorption in nature. The surface of the steel pipeline at optimum point of 10 g/l had smooth surface compared to the surface in the absence of the inhibitor. The ANOVA results showed that the inhibitor was the most significant parameter having the highest statistical influence of 78.39% followed by time (11.09%) and temperature (10.43%). These results therefore confirmed the high inhibition efficiency values obtained in the presence of the inhibitor earlier.

Keywords: Terminalia avicenoides, Potassium iodide, Corrosion inhibition, Gravimetric method, Phytochemical constituents.

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1. Introduction

Sulphuric acid is being produced than any other chemicals in the world. It is being used directly or indirectly in nearly all industries and is a vital commodity in national economy. The consumption rate of sulphuric acid, like steel production or electric power could be used as a yardstick to judge economic conditions of nation [1-2]. Pickling of steel and other metals, manufacture of fertilizers, dyes, drugs, pigments, explosives, synthetic detergents, rayon, and other textiles, petroleum refining, metal refining and production of rubbers give rise to the corrosion of equipment [3]. However, these constructional materials such as steel pipelines had been subjected to dissolution when exposed to high concentration of sulphuric acid solution. Deterioration and weakness of the constructional material can cause serious problems that had lead to the losses of lives and equipment, so it becomes imperative to protect materials against corrosion in such aggressive environments [4]. Protection of this constructional material from being corroded is not only important for increasing the lifespan of materials, but also important in protecting our environments from hazards resulting from the disasters [5]. However, an important approach adopted for the protection of this material against corrosion is by the use of inhibitors which is one of the numerous ways of mitigating corrosion in any environments [6].

The use of chemical inhibitors is often the most practical and cost effective means of corrosion mitigation. However, most of these synthetic inhibitors such as chromates, nitrates, borates, molybdates had proved good anticorrosive action but highly toxic to both human beings and environment [7]. An alternative has to be searched to replace the expensive and toxic synthesized corrosion inhibitors because of environmental regulations in order to promote the sustainable greenness to the atmosphere. The issue of toxicity has led to the use of naturally occurring substances in order to find low-cost and non-hazardous inhibitors.

Plant extracts have become important as an environmentally acceptable, readily available and renewable source of materials for a wide range of corrosion prevention formulations. Therefore, finding naturally occurring substances as corrosion inhibitors is a subject of great practical significance [8]. Extracts of plants contain organic compounds such as N, O, P and S atoms which are considered to be effective corrosion inhibitors. The effectiveness of organic inhibitors however, depends on the nature and the condition of the metallic surface, the chemical composition and structure of the inhibitor [9]. All plant products are organic in nature and their constituents are tannins, organic and amino acids, saponins, alkaloids, flavonoids, glycosides and pigments are known to exhibit inhibiting action [10-17].

The use of organic inhibitors in acid solutions cannot be complete without mentioning the phenomena of synergism. This effect has been observed since the earliest days of inhibitor technology and continues to be a potent tool in the development of acid inhibitors for specialized uses [18,19]. The synergistic inhibition between halide ions and some organic compounds have been investigated [20-22].

Terminalia avicennioides is a much-branched shrub or a small tree; it can grow from 2 - 12 metres tall. The tree is harvested from the wild for local use as a medicine and source of materials. It has potential use as a pioneer to restore woodland and also for stabilizing the soil. A decoction of the root is taken by draught and by enema to remedy diarrhoea and dysenteries [23].

In the present work, inhibitive action of *Terminalia avicennioides* as ant-corrosion behaviour of steel pipelines in 0.5 M acidic medium in the presence of potassium iodide as synergy at (35-80 °C) was investigated using gravimetrical weight loss method. The results obtained were compared with that obtained by synergy and statistical model results.

2. Experimental

2.1 Solution Preparation

Weight loss studies of the sized coupons were conducted in 0.5 M H_2SO_4 and 0.5 M KI^- prepared in double distilled deionized water, with or without different concentration of the inhibitor.

2.2 Preparation of inhibitor

Six hundred grams of *Terminalia avicennioides* roots after cleanings in water and dried was extracted in 1.5 L of 70 % ethanol and 30 % distilled water as solvent and followed by maceration method. The extract and the final stage of collecting the liquid at 100 °C before evaporation were presented in Figure 1. The concentration of the stock solution was expressed in terms of (g/l) and the concentration of 2.5g/l – 15g/l) of the extract was prepared [17].

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Fig. 1. *Terminalia avicennioides* roots and the extraction process

2.3 Weight loss method

The coupons used for this research was cut from steel pipeline with the following compositions presented in Table 1 of size 24 x 2 mm. The specimens were abraded with various grades of wax coated emery papers from 600 - 1800 grits and degreased in absolute ethanol, dried in acetone, weighed and stored in moisture-free desiccators prior to use to avoid reaction with atmospheric air. Shimadzu Corporation, Model AUW120D was used to weigh the samples. The metal coupons were then suspended with the help of glass hooks into beakers containing 200 mL of corrosive electrolyte for complete immersion test. The potassium iodide (0.5 M KI^-) was then added to the solution of 0.5 M H_2SO_4 already prepared. The corrosion rate of each specimen in mmpy, inhibition efficiency and surface coverage were determined using equations (1-2) according to the methods [1,2].

$$Corrosion\ Rate\ (CR) = \frac{KW}{dat} \qquad \ldots .1$$

Where CR is corrosion rate (mm/yr), W is weight loss (g), D is the density (g/cm^3), A is the area (cm^2) and T is time and K is a constant equal to 87500.

Where W is the weight loss (g), W_i is the initial weight (g) and W_f is the final weight (g).

$$\text{Inhibition efficiency (IE \%)} = \frac{CRo}{CRi} \times 100 \qquad \ldots .\ 2$$

where CRo and CRi are corrosion rates in the absence and presence of inhibitors, respectively.

Table 1. Chemical Composition of Steel pipeline coupon

Element	Fe	C	Si	Mn	P	S	Co	Mo	Ni	Al
% Wt	Reminder	0.25	0.51	0.72	0.015	0.014	0.041	0.013	0.182	0.001

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The synergy was evaluated by the following parameters in equation 3 [20]

$$S_p = \frac{I-I_{1+2}}{I-I'_{1+2}} \quad \ldots . 3$$

where $S_{p=}$ Synergy parameter, $I_{1+2} = (I_1 + I_2) - (I_1 . I_2)$,
I_1 = inhibition efficiency of the extract,

I_2 = inhibition efficiency of the coupon in the presence of the iodide;
I'_{1+2} = inhibition efficiencies of the coupon in the presence of the extract and iodide.

2.4 Characterization of the coupons:

A Philips model XL30SFEG Scanning Electron Microscope with high resolution was used to study the morphology and chemical analysis of the corroded steel pipelines surfaces. The surface morphology of the coupons before and after corrosion was characterized [15].

2.5 Development of mathematical model

To investigate which of the corrosion parameters that significantly controls the corrosion rate studied the standard L8 orthogonal array was adopted in the design of the experiment. 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 Tables 2 and 3 respectively. The model equation was obtained by representing the corrosion rate value by CR, which is a function of the three variables as expressed in equation (4) below:

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

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 in equation 5. Hence the general model is written as;

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

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 [27].

Table 2. Factorial design of the corrosion rate

Factors	Low level	High level
Temperature (A)	35 ^{o}C	80 ^{o}C
Inhibitor (B)	0	15 (g/l)
Time (C)	12 hours	72 hours

Table 3. 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)

3. Results and Discussion

Table 4 shows the qualitative and quantitative analyses of phytochemical constituents present in the root extract of *Terminalia avicenoides*.

Table 4. The qualitative and quantitative analyses of phytochemical constituents

Terminalia avicenoides (Ta)	Tannins	Saponins	Flavonoids	Glycosides	alkaloids	Volatile oil
	+	+	-	+	+	+
	15.10±0.01	3.23±0.03	0.000	0.65±0.12	1.34±0.03	0.65±0.24

3.1 Effect of Inhibitor concentration

Corrosion rates of the steel pipeline coupons in 0.5 M H_2SO_4 were evaluated in the absence and presence of solutions and the results obtained were presented in Table 5. Corrosion rate increases with increase in temperature and decrease with increase in the plant extract. Compared to the inhibited solution, corrosion rate was higher in the free acid solution, which implies that the *Terminalia avicennioides* extract actually retarded the pipeline steel corrosion. The effectiveness of the extract is concentration dependent and corrosion rate on the other hand decreases as concentration of the extract increases. Similar trends have been reported in literatures [19,20]. The variation of corrosion rates with temperature was in the sequence of 80 ^oC >65 ^oC > 50 ^oC >35 ^oC. It can be attributed to the rate of chemical reaction occurring during corrosion process and a well known fact that increase in temperature brings more chemical reaction hence, decrease in the surface coverage [18].

Inhibition efficiency (% IE) increases with increase in inhibitor concentration and decreases with increase in temperature (Table 5) and illustrated in Figure 2. Maximum inhibition efficiency of 94.86% was obtained from weight loss at 303 K. This efficiency maybe attributed to electrostatic interactions between its charged sites of the organic phytochemicals such as tannins, alkaloids, saponins, volatile oil [19,21].

Table 5. Optimum values of Corrosion rate and Inhibition efficiency from weight loss on steel pipeline at 35, 50, 65 & 80 °C.

Extract (g/l) (TA)	Corrosion Rate (mmpy)				Inhibition Efficiency (IE %)			
Temp. (K)	308K	323K	338K	353K	308K	323K	338K	353K
Blank (0)	30.78	34.65	39.56	40.89	-	-	-	-
2.5	3.63	6.70	9.71	12.01	88.21	80.65	75.43	70.61
5.0	3.04	7.40	10.43	14.06	90.11	78.63	73.61	65.61
7.5	2.62	7.73	11.02	14.49	91.48	77.67	72.12	64.56
10.0	1.58	8.53	11.81	15.39	94.86	75.36	70.31	62.34
12.5	1.82	9.55	12.59	15.54	94.10	72.41	68.16	61.98
15.0	2.27	10.32	13.79	16.30	92.61	70.20	65.14	60.12

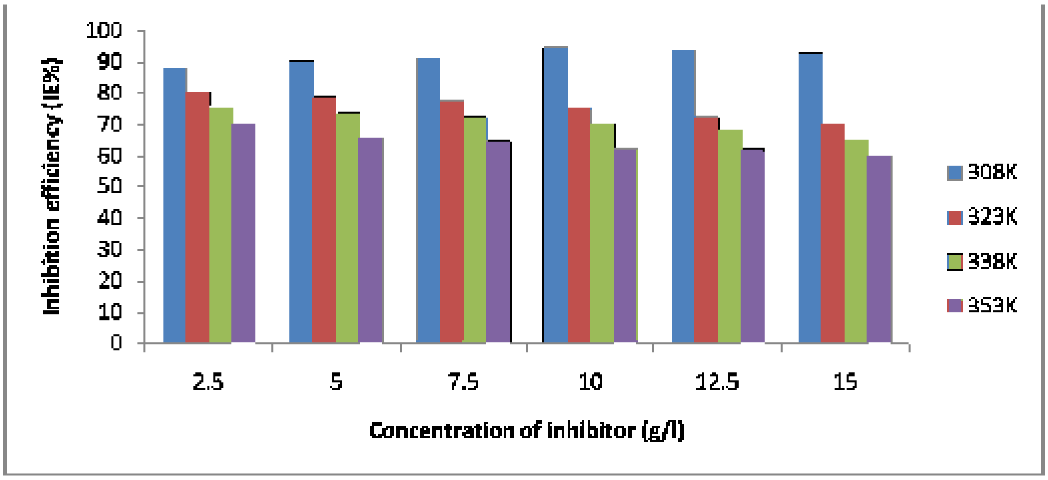

Fig. 2. Variation of Inhibition efficiencies (IE %) with different concentration of *TA* at different temperatures (35, 50, 65 and 80 °C) in 0.5 M H_2SO_4

3.2 Effect of immersion time

To assess the stability of inhibitive properties of the extract on a time scale, weight loss measurements were performed in 0.5 M H_2SO_4 in the absence and presence of the extract at 2.5- 15.0 g/l concentrations. The effect of immersion period on steel pipeline corrosion inhibition by *Terminalia avicennioides* (TA) was studied for 12, 24, 36, 48, 60 and 72 hours immersion time in 0.5M H_2SO_4 at 35 °C were summarized in Table 6 and illustrated in Figure 3. It shows that inhibition efficiency of the extract increased with increasing immersion time from 12 to 72 hours and decrease with increase in temperature. The increase in inhibition efficiency up to 36 hours reflects the strong adsorption of constituents present in the extract (tannins, alkaloids, Volatile oil), resulting in a more protective layer formed on steel pipeline-sulphuric acid solution interface [12]. Thus, the extract effectively inhibits the samples in 0.5 M sulphuric acid solution.

Table 6. Effect of immersion time on percentage inhibition efficiency of mild steel in 0.5 M H_2SO_4 at 35 °C in the presence of optimum concentrations of the extract

Name of the plant extract with optimum concentrations	Inhibition efficiency (IE %)					
	Immersion time (Hours)					
	12	24	36	48	60	72
10 g/l of *(TA))*	70.12	88.97	94.86	94.77	94.32	93.99

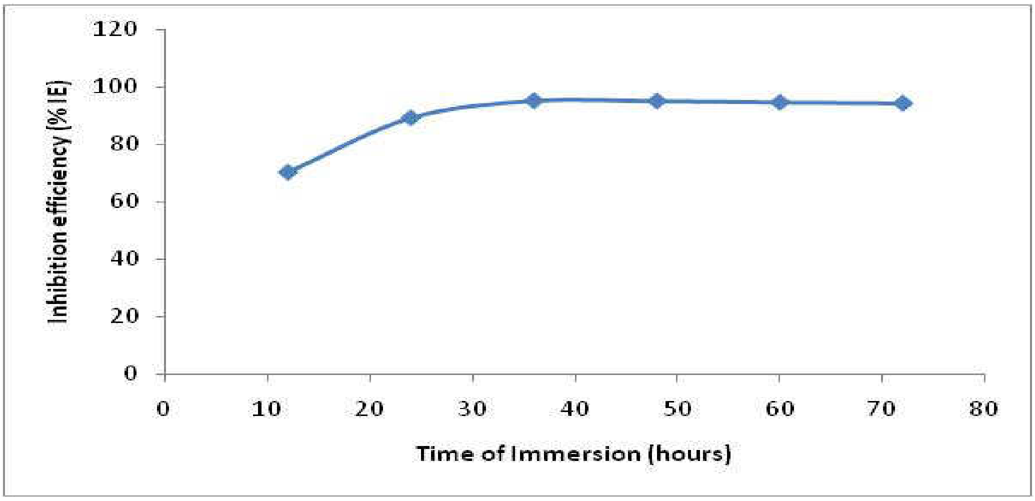

Fig. 3. Variation of inhibition efficiency of *Terminalia avicennioides* extract in 0.5 M H_2SO_4 with immersion time of the solution

3.3 Synergism considerations

The synergistic parameters were calculated using the relation initially given by [20] in equation 5 to evaluate its synergistic effects on the protection of steel pipelines in sulphuric acid at different temperatures. The results obtained from the equation 5 were presented in Table 7 and illustrated in Figure 4. There was decrease in corrosion rates from 35-80 ^oC and inhibition efficiencies of the system were enhanced.

Table 7. Synergistic parameters (Sp) for different concentrations of *TA* extract at 35, 50 and 65 and 80 ^oC in 0.5 M H_2SO_4

Conc. of Inhibitor (g/l)	S_p			
	35 ^oC	50 ^oC	65 ^oC	80 ^oC
2.5	1.53215	1.42356	1.39032	1.29752
5.0	1.83457	1.82389	1.79654	1.68564
7.5	1.97654	1.95483	1.93482	1.86564
10.0	2.09456	2.00529	1.96432	1.88765
12.5	2.26543	2.14567	2.07894	1.976555
15.0	2.45674	2.35467	2.17654	2.0009879

The halide ions introduced into the solution change the situation and the mechanism of action of anion-active substances was connected with the fact that adsorbed anion-active substances created connecting bridges between metal atoms and organic cations. It was assumed that many organic inhibitors in acidic electrolytes become protonated, changing into cations according to the scheme [21]. According to the previous works, if S_1 approaches 1, it implies no interaction between the inhibitor compound existences, if $S_1 > 1$, it implies synergistic effects between the inhibitor and the halide and if $S_1 < 1$, the antagonistic interaction prevails, which may be attributed to competitive adsorption [22]. From the studies presented in Table 7, there were synergistic effects between the extract and halide ion investigated and greater than 1. It was observed that the inhibitive effects of halide ions increase in the order of $Cl^- < Br^- < I^-$ [20].

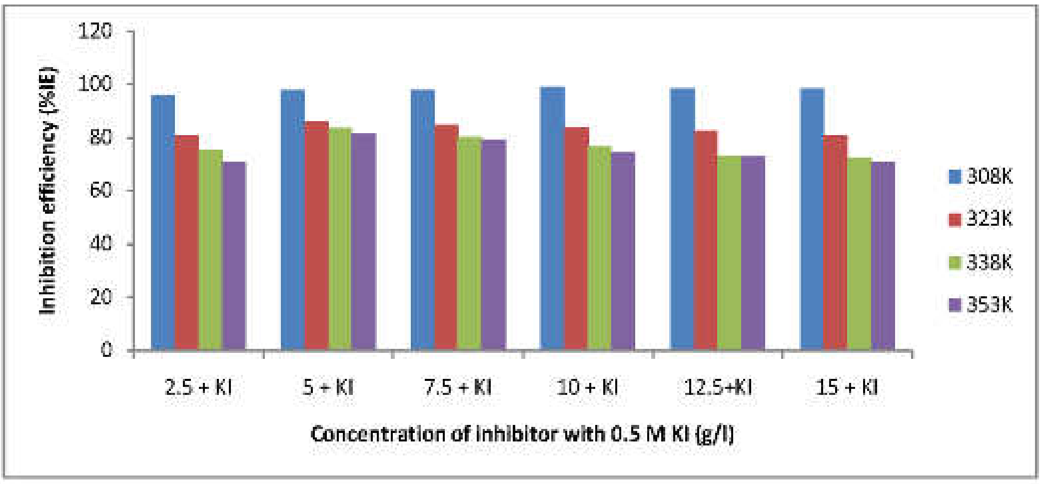

Fig. 4. Variation of Inhibition efficiencies (IE %) with different concentration of *TA* at different temperatures (35, 50, 65 and 80 ^{o}C) in the presence of 0.5 M KI

3.4 Effect of temperature

Temperature investigation was carried out in order have an idea about the stability of the inhibitor films deposited during protection at various temperatures studied. From the weight loss results presented in Table 5, the effect of temperature on inhibition efficiency and activation energy of corrosion process was carried out. It was observed that corrosion rates decreases with increase in temperature. The increase in corrosion rate on temperature increase can be attributed to the etching, rupture and desorption of inhibitor molecules at higher temperature and physorption in nature [22].
However, the dependency of corrosion rate on temperature can be best represented by the Arrhenius equation given in equation 6 [23]:

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

Table 8. Activation energy for steel pipelines dissolution in 0.5 M H_2SO_4 in the absence and presence of an optimum concentration (10 g/l) of inhibitor

Inhibitor	Ea (KJmol^{-1})
Blank	5.65
Inhibitor	44.37

Where Ea is the apparent activation energy, R is the molar gas constant, T is the absolute temperature (K) and A is the Arrhenius pre-exponential factor, known as frequency factor.
Figure 5 shows the plot of log (CR) against 1/T for corrosion of steel pipelines in 0.5 M H_2SO_4 solution giving straight line with regression coefficient (R^2) value close to one. It is also clear from Table 10 that the value of Ea is higher in the presence of inhibitor than in its absence. This increase of Ea in presence of inhibitor indicated the adsorbed inhibitor film on steel pipelines surface increases the energy barrier for corrosion reaction [12].

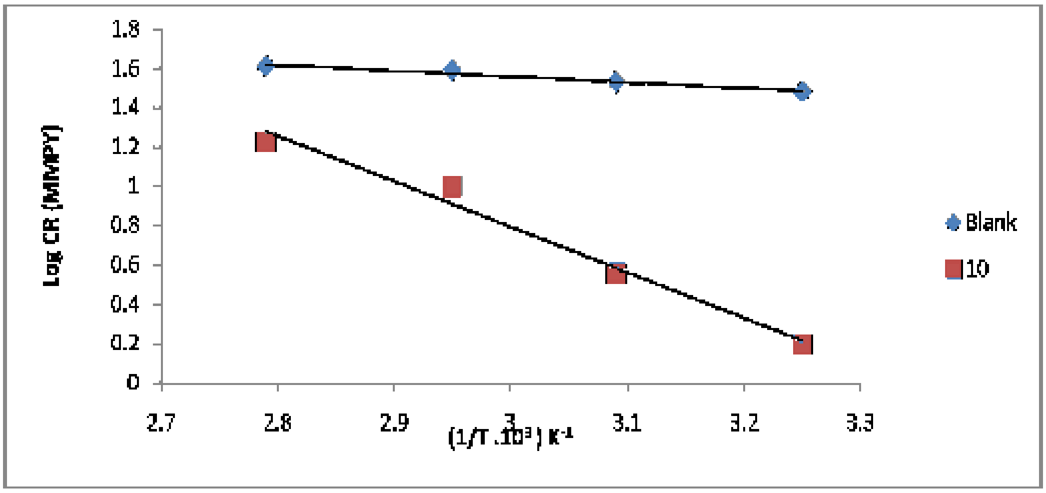

Fig. 5. Arrhenius plots for steel pipelines in 0.5 M H_2SO_4 solution in the absence and presence of optimum concentrations at 35-80 °C of *TA*

3.5 The Adsorption Isotherms

Adsorption isotherm gives the relationship between the coverage of an interface with the adsorbed species and the concentration of species in solution. The use of adsorption isotherms provides useful insight into the corrosion inhibition mechanism. The values of the degree of surface coverage (θ) were evaluated at different concentrations of the inhibitor in 0.5 M H_2SO_4 solution. Attempts were made to fit θ values to various adsorption isotherms (El-Awady, Freundlich, Frumkin, Temkin and Langmuir models) as described elsewhere [22-24]: The inhibitor was found to obey Langmuir isotherm with a plot of C/θ vs. C which was linear. From the figure 6, the adsorption of different concentrations of *Terminalia avicennioides* extract on the surface of steel pipelines was found to obey Langmuir adsorption isotherm. The phytochemical constituents of *terminalia avicennioides* showed that these compounds were hydrolysable and can easily be adsorbed on the metal surface via the lone pair of electrons present on their oxygen atoms and make a barrier for charge and mass transfer leading to decrease the interaction of the metal with the corrosive environment and as a result, the corrosion rate of the metal decreased with increase in the extract [15]**.** The formation of film layer essentially blocks discharge of H^+ and dissolution of metal ions was then satisfied. Acid pickling inhibitors containing organic N, S and OH^- groups behave similarly to inhibit

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corrosion [17]. It follows that inhibition efficiency (IE) is directly proportional to the fraction of the surface covered by the adsorbed molecules (θ). Therefore, (θ) with the extract concentration specifies the adsorption isotherm that describes the system.

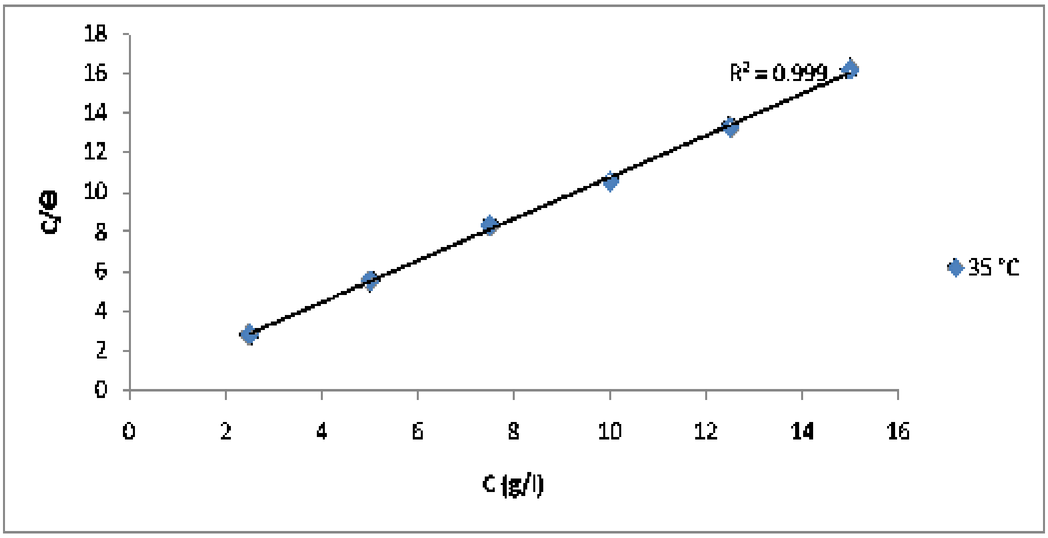

Fig. 6. Langmuir adsorption isotherm plot for the adsorption of various concentrations of plant extract on the surface of steel pipeline in 0.5 M H_2SO_4 solution

3.6 Surface Examination Studies

Philips model XL30SFEG scanning electron microscope (SEM) was used to examine the action of the inhibitor on the steel pipeline specimens with the magnification of 1000X. The coupons after immersion in 0.5 M H_2SO_4 solution for thirty six hours at 35 °C in the absence and presence of optimum concentration of the plant extract were investigated using SEM. The SEM images at different coupons were obtained at optimum concentrations. From figure 7, the images obtained showed more pits were found in SEM image of steel pipelines immersed in 0.5 M H_2SO_4 solution in the absence of the inhibitor. SEM image of steel pipelines immersed in 0.5 M H_2SO_4 solution in the presence of the plant extract shows the presence of a protective film over their surfaces and the protective film form was uniform [26]. The SEM morphologies of the adsorbed protective films on the steel pipelines surface have confirmed the high performance of inhibitive effect of the plant extract [5,9].

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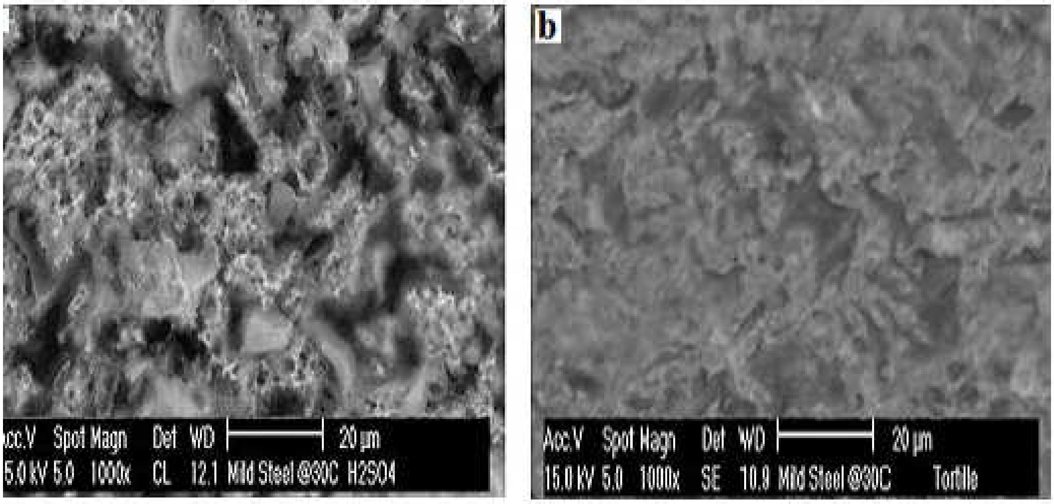

Fig. 7. SEM microstructure of steel pipelines immersed in a) 0.5M H_2SO_4 b) 0.5M H_2SO_4 with 10 g/l *Terminalia avicennioides*

3.7 Analysis of variance and the effects of parameters on the corrosion rate

The results of ANOVA for the corrosion rate were presented in Tables 9 and 10 respectively. The results showed that the inhibitor was the most significant parameter having the highest statistical influence of 78.39% 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 [27]. The coefficient of determination (R^2) being 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%), then high correlations with the experimental values established. The developed mathematical model equation for the corrosion behaviour of the steel pipelines in the acidic environment with the presence of the extract can be expressed in equation 7:

$$CR\ (TA) = 39.58 + 7.33A - 19.85B - 7.56C - 2.60BC - 1.31ABC \quad \ldots .7$$

From Table 10 and equation 7, inhibitor (-19.85) is the most important variable followed by time (-7.56) in the corrosion control studied. Similar results have been observed [27]**.** Cconfirmation test carried were presented in figure 8. Residual variation estimated for the corrosion was in the range of -2.12 to 2.12. Hence, the regression models developed has demonstrated feasible and effective way to predict the corrosion rate of the steel pipeline investigated and also reported [28].

Table 9. Analysis of Variance (ANOVA) for corrosion rate in the presence of *Terminalia avicennioides* extract

Source of variation	Sum of Squares	Degreeof Freedom (DF)	Mean Square	$F_{cal} = \frac{Ms}{ErrorMs}$	F-value	F (%)
Main effect						
A	430.12	1	430.12	47.07	0.0206	10.43
B	3150.59	1	3150.59	344.75	0.0029	78.39
C	457.53	1	457.53	50.07	0.0194	11.09
Interaction						
BC	54.29	1	54.29	5.94	0.1351	1.32
ABC	13.73	1	13.73	1.50	0.3451	0.33
Residual	18.28	2	9.14			0.44
Cor.Total	4124.54	7				100

Table 10. Effect of the variables at 95% confidence level for *Terminalia avicennioides* 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	-2.60	1	1.07	-7.20	1.99
AC, 1.00	-1.31	1	1.07	-5.91	3.29

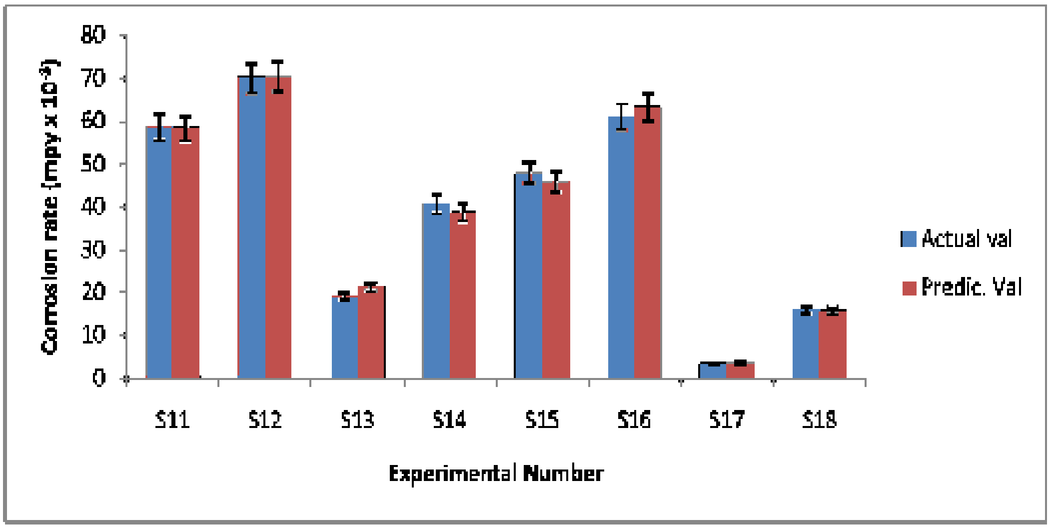

Fig. 8. Variation of experimental number with corrosion rate for mild steel with *Terminalia avicennioides*

4. Conclusions

From the research work carried out so far, the followings can be drawn:

1. The root extract of *Terminalia avicennioides* acts as good and efficient inhibitor for corrosion of pipeline steel in 0.5 M H_2SO_4 acid. The plant extract obeys Langmuir adsorption isotherm and physorption in nature.
2. The mechanism involved in this study is the phytochemical constituents in the plant extract was adsorbed on the steel pipelines surface forming a protective thin film layer preventing the discharge of hydrogen ion (H^+) ions.
3. The SEM morphology of the adsorbed protective film on the steel pipelines surface confirmed high performance of inhibitive effect of the plant extract.
4. Results obtained from weight loss method were very much in good agreement with that of statistical model showing that inhibitor was the most important variable.
5. The result of the synergy is greater than one and the corrosion rate was drastically reduced.

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