

OPTIMIZATION OF THE INHIBITION EFFICIENCY OF BITTER KOLA LEAF EXTRACT AS CORROSION INHIBITOR OF MILD STEEL IN H₂SO₄.

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ABSTRACT

This work is on the optimization of the inhibition efficiency of bitter kola leaf extract as corrosion inhibitor of mild steel in H₂SO₄. Gravimetric method was employed in the corrosion inhibition study. It was supplemented by Fourier transform infrared (FTIR) spectrophotometric and scanning electron microscopic analyses of the plant extract and mild steel surface respectively. Response surface methodology (RSM) was applied in the optimization process. Central composite design tool of design expert software 9 was used to evaluate the effects and interactions of four variables of acid concentration (AC), inhibitor concentration (IC), temperature (T) and time (t) on the inhibition efficiency of the extract. Analysis of variance (ANOVA) was used to study the data generated. From the analyses of the experimental results, it was observed that there was a synergy among the functional groups of O-H, C-H, C=C and N-H in the corrosion inhibition process. Bitter kola leaves extract exhibited optimum inhibition efficiency of 83.56 % obtained at optima acid concentration of 1.2 M, inhibitor concentration of 0.9 g/l, temperature of 300 K and time of 21 hours. The extract is highly efficient in surface treatment of the mild steel in H₂SO₄ medium.

Keyword: Corrosion inhibitor; Optimization; Bitter kola leaf extract; Mild steel; H₂SO₄.

1.0 INTRODUCTION

Previously, the use of chemical inhibitors like imidazoline, oxides, resin in protection of metals against corrosion was successful, but due to their harmful effect to the environment and high cost of preventing corrosion in industries, there is need to focus research on suitable alternatives from renewable, eco-friendly and biodegradable sources. Agricultural by-products are been discarded as waste but they can be converted to wealth (put into economic use) as corrosion inhibitor. Many metals and alloys used in industries are prone to different mechanisms of corrosion due to their exposure to different aggressive environments. Acid solution such as H₂SO₄ and HCl are used for removal of undesirable scale and rust in several industrial processes. Acid solutions are often used in industry for cleaning, descaling and pickling of steel structure these processes are normally accompanied by considerable dissolution of metal quality [1, 2]. The most acceptable method of protecting metals and alloys against corrosion is the application of inhibitor in contact with the surface in order to inhibit the corrosion reaction and reduce the corrosion rate.

It has become imperative to look towards nature for “clean” solutions to the world’s energy demands. Green inhibitors are biodegradable, non-toxic and contain no heavy metals. Plants products are inexpensive, renewable and readily available. The extracts from the leaves, barks, seeds, fruits and roots comprise of mixtures of organic compounds containing nitrogen, sulphur and oxygen atoms. Some of the plant organic compounds have been reported to function as effective inhibitors of metal in different aggressive environments [3–8]. The choice of an appropriate inhibitor for a particular application is restricted by a number of factors [9]. Attempt has been made in using response surface methodology (RSM) in optimization of inhibition efficiency of plant extract [10]. There is need to consider up to for four factors in the experimental design. The aim of this work is to examine the corrosion inhibitive property of bitter kola leave extract and optimize its application as corrosion inhibitor of mild steel. Bitter Kola plant is perennial herb which belongs to *Asteracea* family. Plant extract is of interest because of its tremendous pharmaceutical and industrial applications [11].

2.0 MATERIALS AND METHOD

Fresh leaves of bitter kola (BKL) were collected from Uli in Anambra State of Nigeria. The leaves were sun-dried for four days and then ground into powder form to increase its surface area. During the extraction process, 30 grams of BKL powder were measured and soaked in 1000ml of ethanol for 48hrs. The mixture was filtered. The filtrate obtained is a mixture of the plant extract and the ethanol. Distillation process was applied to separate the solvent from the extract. The stock solution of the extract was weighed and stored for the corrosion inhibition study. The chemicals, ethanol and H₂SO₄, used for the study were of analytical grade.

2.1 Metals Preparation

Corrosion tests were performed on mild steel with the following compositions P (0.02%), Mn (0.11%), Si (0.02%), S (0.02%) Cu (0.01%), C (0.23%), Ni (0.02%), Cr (0.01%) and Fe (99.56%). Prior to corrosion tests, the mild steel was mechanically cut into (5cm x 4cm x 0.1cm). The surface of each coupon was polished using different emery papers to expose shining polished surface. To remove organic impurities, the coupons were degreased with acetone, washed with distilled water and allowed to dry in air.

2.1.1 FTIR Analysis of the Bitter kola Leaf Extract and Corrosion Product.

Fourier transform infrared (FTIR) spectrophotometer (SHIMADZU Model IR affinity-1, S/N A213747013651) was used to identify functional groups of the pure extract of bitter kola leaf and corrosion product. To obtain the corrosion product, mild steel was immersed in 1.2 M H₂SO₄ medium containing bitter kola extract. After the corrosion study, the pure extract and corrosion product (acid medium, extract of bitter kola leaf and corroded particles from the mild steel) were collected with sample bottle. Variations of the FTIR peak numbers were analyzed so as to identify appropriate functional groups for the corrosion inhibition process.

2.2 Weight Loss (Gravimetric) Method

2.2.1 Weight loss method using one factor at a time

Adapting one factor at a time, weight loss methods was carried out at different temperatures and with various concentrations of bitter kola leave extract. In this method, observing standard protocol [10, 12], weighed mild steel coupon was immersed in 250ml beaker containing 200ml of 1.2M H₂SO₄. Also, other mild steel coupons were separately immersed in 250ml beakers containing 1.2M H₂SO₄ with various concentrations of bitter kola leave extract.

The variation of weight loss was studied periodically at various temperatures in the uninhibited and inhibited medium with various concentrations of the BKL. At the end of corrosion study the coupons were taken out, immersed in acetone, scrubbed with brush, dried and reweighed. The weight loss (Δw), corrosion rate (CR), inhibition efficiency (IE) and degree of surface coverage were determined using the equations (1), (2) (3) and (4) respectively [10, 12].

$$\Delta w = w_i - w_f \quad (1)$$

$$IE\% = \frac{w_o - w_1}{w_o} \times 100 \quad (2)$$

$$E\% = \frac{w_o - w_1}{w_o} \times 100 \quad (3)$$

$$\theta = \frac{w_o - w_1}{w_o} \quad (4)$$

Where w_i and w_f are initial and final weight of mild steel samples respectively, w_i and w_o are the weight loss values of mild steel samples in presence and absence of the extract.

2.2.2 Optimization of the Inhibition Efficiency

Using response surface methodology (RSM), the inhibition efficiency of the extract was optimized by central composite design (CCD) tool of Design Expert Software 9. The independent variables selected for this study were acid concentration (0.3 M - 1.2 M), inhibitor concentration (0.3g/l - 0.9 g/l), temperature (300 K – 324 K) and time (7 hr – 21 hr). A total of 30 runs of experiments were conducted for the weight loss, corrosion rate and inhibition efficiency. The experimental design matrix is presented in Table1.

Table 1: The Experimental Design Matrix

Std	Run	Factor 1, Acid Conc. (M)	Factor 2, Inhibitor Conc. (g/l)	Factor 3, Temperature (K)	Factor 4, Time (hr)
5	1	0.3	0.3	324	7
6	2	1.2	0.3	324	7
27	3	0.75	0.6	312	14
17	4	0.3	0.6	312	14
28	5	0.75	0.6	312	14
30	6	0.75	0.6	312	14
2	7	1.2	0.3	300	7
13	8	0.3	0.3	324	21
15	9	0.3	0.9	324	21
14	10	1.2	0.3	324	21
1	11	0.3	0.3	300	7
16	12	1.2	0.9	324	21
3	13	0.3	0.9	300	7
22	14	0.75	0.6	324	14
8	15	1.2	0.9	324	7
10	16	1.2	0.3	300	21
12	17	1.2	0.9	300	21
18	18	1.2	0.6	312	14
19	19	0.75	0.3	312	14
25	20	0.75	0.6	312	14
21	21	0.75	0.6	300	14
7	22	0.3	0.9	324	7
9	23	0.3	0.3	300	21
24	24	0.75	0.6	312	21
11	25	0.3	0.9	300	21
4	26	1.2	0.9	300	7
26	27	0.75	0.6	312	14
20	28	0.75	0.9	312	14
29	29	0.75	0.6	312	14
23	30	0.75	0.6	312	7

2.3 Scanning Electron microscopy.

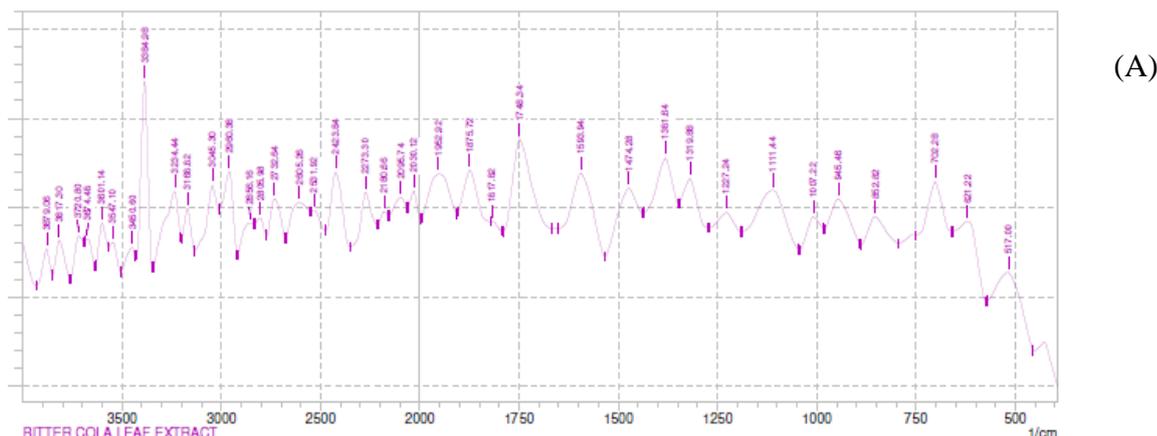
Morphological observations of the corroded mild steel samples were carried out at Chemical Engineering Department, Ahmadu Bello University, Zaria using the scanning electron microscope (SEM of type phenom Prox, model no MVE016477830, manufactured by Phenom World Eindhoven, Netherlands). The samples of the mild steel in the inhibited and uninhibited media were examined to ascertain the level of the corrosion inhibition process.

3.0 RESULTS AND DISCUSSION

3.1 Spectroscopy analysis of bitter kola leaves extract and corrosion product.

Pure bitter kola leaves extract and corrosion product of mild steel in H₂SO₄ (with bitter kola leaves extract) were analyzed using FTIR spectrophotometer. The peaks of spectra of bitter kola leaves extract and corrosion product are

shown in Figures 1 and 2 respectively. The spectrum of each graph shows different peaks in the absorbance versus wave length relationship. The peaks and their corresponding intensities represent the functional group of the plant extract as expressed by other research work [13]. The functional groups of stretched O-H at 3601.14 cm^{-1} peak shifted to 3547.1 cm^{-1} . Other shifts in peaks were noticed in stretched C-H of alkyl, N-H bond of amines and stretched C=C functional groups. The shifts in peaks in the FTIR results were used to monitor the shifting mechanism of the functional group of the plant extract. It was observed that there was synergy among the functional groups in the corrosion control process.



(B)
Fig. 1: FTIR spectra of bitter kola leaf (A) and corrosion product (B).

The experimental data of weight loss and corrosion rate using one factor at a time are presented in Table 2. The inhibition efficiency increased with increase in concentration of the inhibitor (extract) but decreased with increase in temperature. This observation is in agreement with other research reports as contained in literature [10]. Maximum inhibition efficiency of 83.80 % was obtained at temperature of 300 K, inhibitor concentration (g/l) and time of 21 hours. The high value of the inhibition efficiency showed that the extract can be used for corrosion control of mild steel in H_2SO_4 medium.

Table 2: Gravimetric results of mild steel in 1.2M H_2SO_4 with bitter kola leaf extract

Time (hr)	Temp. (K)	I (g/L)	Wt. loss (g)	CR (g/cm 2hr)	IE(%)	SC	
21	300	0.0	1.79				
		0.3	0.74	1.762	58.66	0.5866	
		0.6	0.51	1.214	71.51	0.7151	
		0.9	0.29	0.690	83.80	0.8380	
	312	0.0	1.83	4.357			
		0.3	0.79	1.881	56.83	0.5683	
		0.6	0.62	1.476	66.12	0.6612	
		0.9	0.43	1.024	76.50	0.7650	
	324	0.0	1.88	4.476			
		0.3	0.94	2.238	50.00	0.5000	

		0.6	0.65	1.548	65.43	0.6543
		0.9	0.48	1.143	74.47	0.7447
14	300	0.0	1.32	4.714		
		0.3	0.59	2.107	55.30	0.5530
		0.6	0.41	1.464	68.94	0.6894
		0.9	0.27	0.964	79.55	0.7955
	312	0.0	1.51	5.393		
		0.3	0.72	2.571	52.32	0.5232
		0.6	0.54	1.929	64.24	0.6424
		0.9	0.37	1.321	75.50	0.7550
	324	0.0	1.69	6.036		
		0.3	0.87	3.107	48.52	0.4852
		0.6	0.63	2.250	62.72	0.6272
		0.9	0.44	1.571	73.96	0.7396
7	300	0.0	0.95	6.786		
		0.3	0.51	3.643	46.32	0.4632
		0.6	0.34	2.429	64.21	0.6421
		0.9	0.22	1.571	76.84	0.7684
	312	0.0	1.08	7.714		
		0.3	0.59	4.214	45.37	0.4537
		0.6	0.49	3.500	54.63	0.5463
		0.9	0.30	2.143	72.22	0.7222
	324	0.0	1.17	8.357		
		0.3	0.74	5.286	36.75	0.3675
		0.6	0.55	3.929	52.99	0.5299
		0.9	0.37	2.643	68.38	0.6838

I = Inhibitor concentration, CR = corrosion rate, IE = inhibitor efficiency, SC = degree of surface coverage.

3.2 Results of the weight loss method using RSM

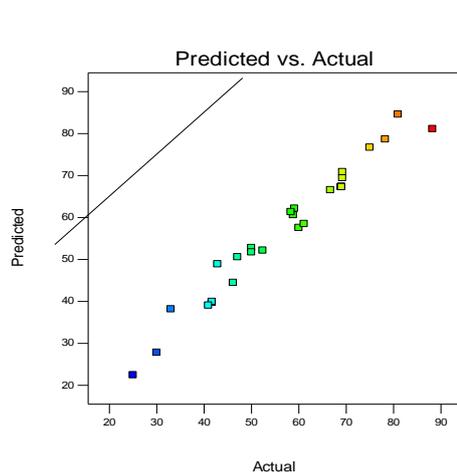
The results of weight loss, corrosion rate and inhibition efficiency as functions of acid concentration, inhibitor concentration, temperature and time are presented in Table 3. The corrosion rate increased with increase in acid concentration, temperature and time, while increased inhibitor concentration decreases the corrosion rate. The inhibition efficiency of the bitter kola leaves extract was dependent on acid concentration, inhibitor concentration, temperature and time. The analysis of inhibition efficiency of bitter kola leaves extract (inhibitor) on mild steel in H₂SO₄ medium is presented in Figure 2. The predicted versus actual inhibition efficiency plot showed a linear graph Figure 2 (A), indicating that the regression model is able to predict the inhibition efficiency of the extract. The 3-D surface plots (Figure 2, B-D) showed the relationship between the factors affecting the inhibition process and inhibition efficiency of the extract. The nature of the three dimensional surfaces suggest that there is interactions among the considered factors of the corrosion inhibition process.

Table 3: RSM Results of the Corrosion Inhibition Study

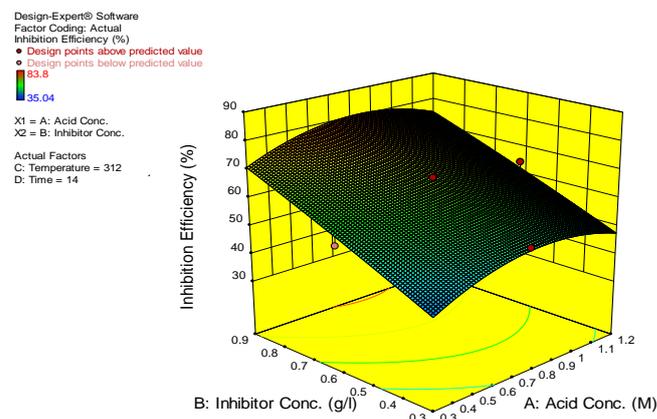
Std	Run	AC (M)	Factors			Responses		
			I C (g/L)	T(K)	Time(hrs)	WL (g)	CR (g/cm 2hr)	IE(%)
5	1	0.30	0.3	324	7	0.76	5.429	35.04
6	2	1.20	0.3	324	7	0.74	5.286	36.74
27	3	0.75	0.6	312	14	0.43	1.536	67.42
17	4	0.30	0.6	312	14	0.44	1.571	53.68

28	5	0.75	0.6	312	14	0.43	1.536	67.42
30	6	0.75	0.6	312	14	0.43	1.536	67.42
2	7	1.20	0.3	300	7	0.51	3.643	46.32
13	8	0.30	0.3	324	21	0.84	2	38.69
15	9	0.30	0.9	324	21	0.4	0.952	70.8
14	10	1.20	0.3	324	21	0.94	2.238	50
1	11	0.30	0.3	300	7	0.52	3.714	45.26
16	12	1.20	0.9	324	21	0.48	1.143	74.47
3	13	0.30	0.9	300	7	0.23	1.643	75.79
22	14	0.75	0.6	324	14	0.56	2	64.33
8	15	1.20	0.9	324	7	0.37	2.643	68.38
10	16	1.20	0.3	300	21	0.74	1.762	58.66
12	17	1.20	0.9	300	21	0.29	0.69	83.5
18	18	1.20	0.6	312	14	0.54	1.929	64.24
19	19	0.75	0.3	312	14	0.62	2.214	53.03
25	20	0.75	0.6	312	14	0.43	1.536	67.42
21	21	0.75	0.6	300	14	0.33	1.179	72.73
7	22	0.30	0.9	324	7	0.39	2.786	66.67
9	23	0.30	0.3	300	21	0.54	1.286	51.35
24	24	0.75	0.6	312	21	0.5	1.19	69.51
11	25	0.30	0.9	300	21	0.27	0.643	75.68
4	26	1.20	0.9	300	7	0.22	1.571	76.84
26	27	0.75	0.6	312	14	0.43	1.536	67.42
20	28	0.75	0.9	312	14	0.28	1	78.79
29	29	0.75	0.6	312	14	0.43	1.536	67.42
23	30	0.75	0.6	312	7	0.38	2.714	60.82

AC = acid concentration, I = Inhibitor concentration, T = Temperature, IE = inhibitor efficiency, WL = weight loss, CR = corrosion rate



(A)



(B)

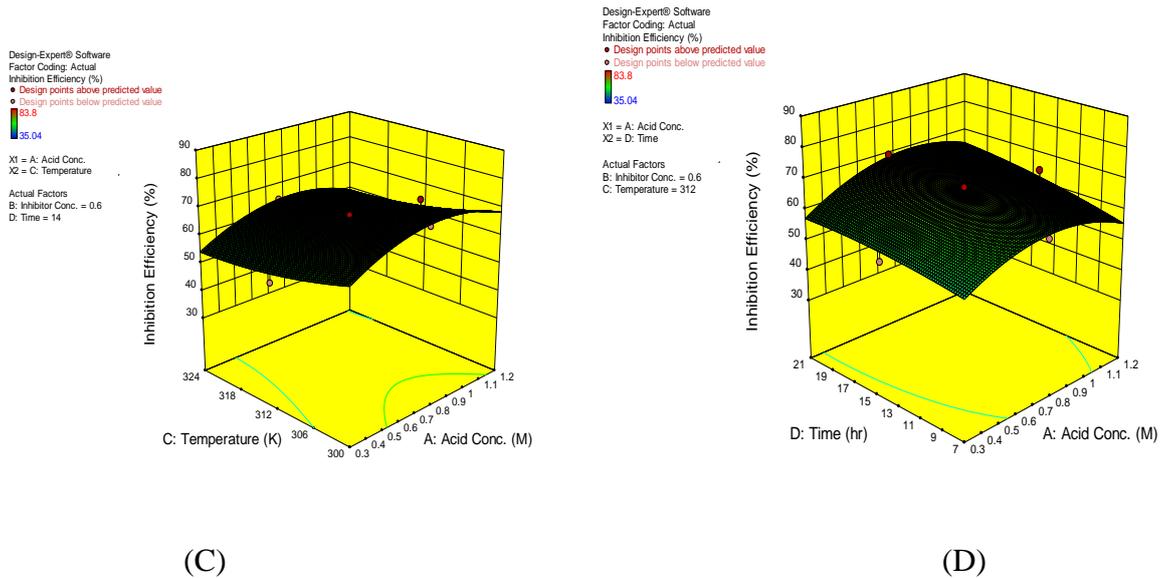


Figure 2. Inhibition efficiency and factors of the inhibition process.

The mathematical model of inhibition efficiency (IE) of bitter kola leaves extract as a function of the considered factors is expressed by Equation (5). A quadratic model described the relationship between the inhibition efficiency and the factors of acid concentration (A), inhibitor concentration (B), temperature (C) and time (D). The model in terms of coded factors predicted the response for given levels of each factor. The coded model showed the relative impact of the factors. From the analysis of variance (ANOVA), the model F-value of 130.92 implies the model is significant (Table 4). Values of "Prob> F" less than 0.0500 indicate model terms are significant. The "Pred R-Squared" of 0.9541 is in reasonable agreement with the "Adj R-Squared" of 0.9843; the difference is less than 0.2. Quadratic model is adequate for the description of the inhibition efficiency with the considered factors of the inhibition process. The optimum inhibition efficiency of 83.56 % was obtained at optima acid concentration of 1.2 M H₂SO₄, inhibitor concentration of 0.9 g/l, temperature of 300 K and time of 21 hours (Figure 3).

$$IE (\%) = +66.95 + 2.58*A + 14.23* B - 4.52*C + 3.39* D - 0.43*AB + 0.054*AC + 1.56* AD + 0.58* BC - 1.14 * BD + 0.12* CD - 7.52* A^2 - 0.57* B^2 + 2.05* C^2 - 1.31* D^2 \quad (5)$$

Table 4: ANOVA results for response parameter

ANOVA for Response Surface Quadratic model

Analysis of variance table [Partial sum of squares - Type III]

	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Model	4813.78	14	343.84	130.92	< 0.0001	Significant
<i>A-Acid Conc.</i>	120.13	1	120.13	45.74	< 0.0001	
<i>B-Inhibitor Conc.</i>	3644.30	1	3644.30	1387.57	< 0.0001	
<i>C-Temperature</i>	367.21	1	367.21	139.81	< 0.0001	
<i>D-Time</i>	207.33	1	207.33	78.94	< 0.0001	
<i>AB</i>	2.92	1	2.92	1.11	0.3081	
<i>AC</i>	0.046	1	0.046	0.018	0.8962	
<i>AD</i>	38.69	1	38.69	14.73	0.0016	

<i>BC</i>	5.43	1	5.43	2.07	0.1710
<i>BD</i>	20.84	1	20.84	7.93	0.0130
<i>CD</i>	0.21	1	0.21	0.081	0.7804
A^2	146.49	1	146.49	55.78	< 0.0001
B^2	0.84	1	0.84	0.32	0.5801
C^2	10.90	1	10.90	4.15	0.0597
D^2	4.48	1	4.48	1.70	0.2114
Residual	39.40	15	2.63		
<i>Lack of Fit</i>	39.40	10	3.94		
<i>Pure Error</i>	0.000	5	0.000		
Cor Total	4853.18	29			

Design-Expert® Software
 Factor Coding: Actual
 Overlay Plot

Inhibition Efficiency
 ● Design Points

X1 = A: Acid Conc.
 X2 = B: Inhibitor Conc.

Actual Factors
 C: Temperature = 300
 D: Time = 21

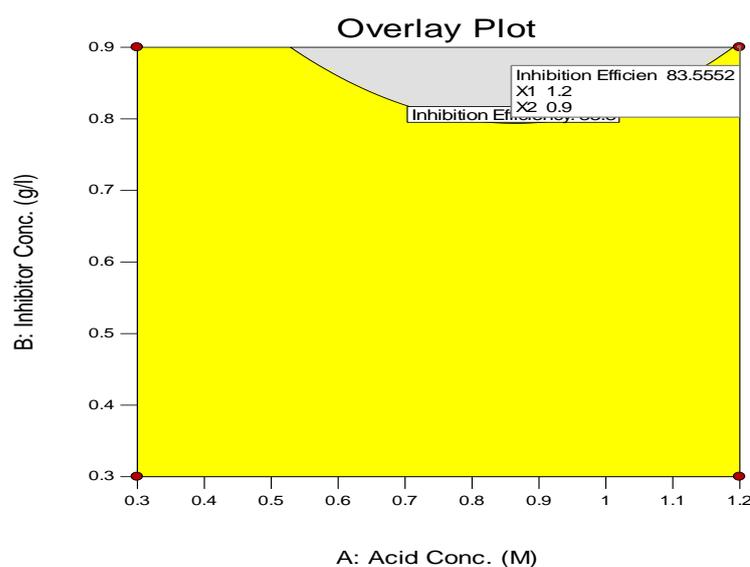
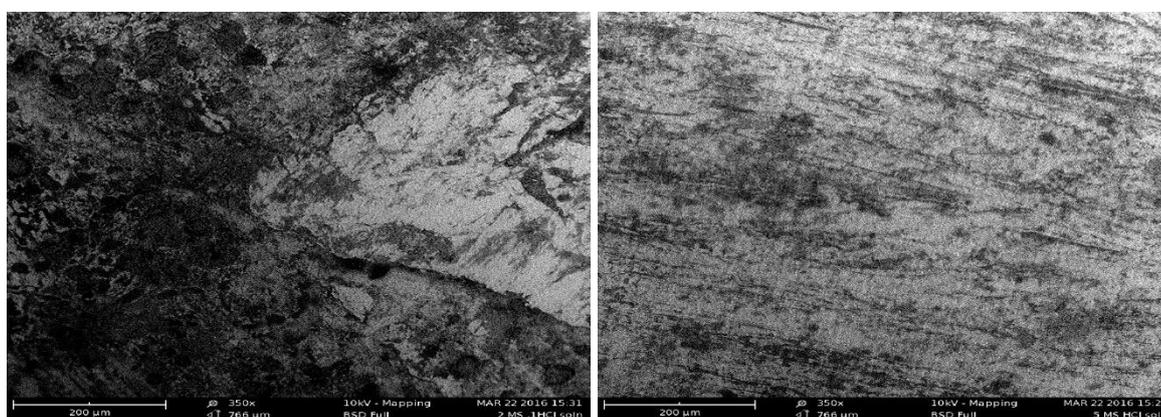


Figure 3. The overlay plot of the optimization result

3.3 Scanning Electron Microscopy

The scanning electron microscopic result is shown in Figure 4. It provided insight on the morphological observations of the corroded mild steel in absence of inhibitor (A) and in the presence of inhibitor (B). In the absence of the inhibitor, the mild steel was strongly damaged, while a smooth layer was observed in the inhibited mild steel. There was a formation of a protective film layer which implies that the adsorption of the plant molecules on the surface of the mild steel occurred according to the mechanism of physical adsorption.



(A)
 (B)
 Figure 4: Mild steel before (A) and after (B) application of inhibitor

CONCLUSION

Based on the analysis of the results, it can be inferred that:

1. It was observed that there was synergy among the functional groups of O-H, C-H, C=C and N-H in the corrosion inhibition process.
2. Bitter kola leaves extract exhibited optimum inhibition efficiency of 83.56 % was obtained at optimum acid concentration of 1.2 M H₂SO₄, inhibitor concentration of 0.9 g/l, temperature of 300 K and time of 21 hours.
3. Bitter kola leave extract is highly efficient in surface treatment of the mild steel in H₂SO₄ medium.
4. A quadratic model adequately explains the relationship between inhibition efficiency and the considered factors of the inhibition process.

REFERENCES

1. Oguzie, E. E., (2008), Corrosion Science, Vol. 50, pp. 2993 – 2998.
2. Kang, W. T, Mohd, J. K. and Chuan, W. O. (2012), Corrosion Science, Vol. 65, pp. 152-162.
3. Zucchi, F. and Omar, I. H. (1985), Surface Technology, Vol. 24, pp. 391 – 399.
4. El-Etre, A. Y., Abdallah, M. and El-Tantawy, Z. E. (2005), Corrosion Science, Vol. 47, pp. 385 – 396.
5. El-Etre, A. Y. (2003), Corrosion Science, Vol. 45, pp. 2485 – 2494.
6. Li, Y., Zhao, P., Liaqng, Q. and Hou, B. (2005), Applied Surface Science, Vol. 252, pp. 1245 – 1254.
7. Abdallah, M. (2004), Corrosion Science, Vol. 46, pp. 1981 – 1988.
8. Gunasekaran, G., and Chauhan, L. R. (2004), Electrochimica Acta, Vol. 49, pp. 4387 – 4394.
9. Oguzie, E. E., Iheabunike, Z. O., Oguzie, K. L., Ogukwe, C. E., Chidiebere, M. A., Enenebeaku, C. K. and Akalezi, C. O. (2013), Journal of Dispersion Science and Technology, Vol. 34, pp. 516 – 527.
10. Onukwuli, O. D., and Omotioma, M. (2016), Journal of Chemical Technology and Metallurgy, Vol. 51 (3), pp. 302 – 314.
11. Iwu, M., Ducan, A. and Okonji, C. (1999), New Antimicrobials of Plant Origin, Alexandria Press, pp. 457- 462.
12. Negm, N. A., Kandile, N. G., Badr, E. A. and Mohammed M. A. (2012), Corrosion Science, Vol. 65, pp. 94 – 103.
13. Furniss, B. S., Hannaford, A. J., Smith, P. W. G. and Tatchell, A. R. (1989), Vogel's Textbook of Practical Organic Chemistry, 5th Edition, Longman Group, UK, pp. 1412 – 1422.