THE INHIBITORY ACTION OF BITTER LEAF EXTRACTS ON MILD STEEL CORROSION IN AN ACIDIC MEDIUM

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Abstract

With the use of the weight loss technique and the response surface approach (RSM),the main process parameters of the leaf extract of bitter leaf on mild steel corrosion in an acidic medium were examined. An atomic absorption spectrophotometer (AAS) was used to quantify the elemental compositions of metals. In order to verify that the bitter leaf extract contained organic components such alkaloids, tannins, terpenes, glycosides, saponins, and flavonoids that helped the extract function as an effective inhibitor, phytochemical analysis was carried out. An acidic medium's corrosion rate was studied in relation to many parameters, including inhibitor concentration, time, and temperature influence. The iron content of mild steel is determined by the presence of phytochemical components and functional groups in the extract, which give it an effective inhibitory effect. Studies from the experimental design of bitter leaf showed that the optimal inhibition efficiency was 83.9 percent at 47.3^{0}C, inhibitor concentration of 12.10 mg/mol, and time of 7.50s. These findings indicate that bitter leaf extract is a potent inhibitor.

Key words: Better leaf, acidic medium, corrosion rate and weight loss, Optimization.

INTRODUCTION

BACKGROUND OF THE STUDY

In addition to being a major financial burden, corrosion can present major concerns to public safety and the environment (Xiaogang Li et al., 2015). China's overall yearly cost of corrosion is estimated to be roughly 2127.8 billion RMB (310 billion USD), or 3.34 percent of GDP, based on a recent study (Baorong Hu et al., 2017). The yearly corrosion cost is estimated to be in the neighborhood of $2.50 trillion if the world economy experiences the same level of damage. Organic corrosion mitigation strategies are the most widely used and successful forms of protection; they account for two thirds of all anti-corrosion expenditures (Evrim et al., 2016, Fan Z et al., 2018).

The economy has consistently experienced downturns due to the corrosion of metallic constructions. Nonetheless, given their cost and physical characteristics, metallic materials appear to be used in building going forward. Crucially, the use of iron and its alloys in building presents significant challenges for corrosion experts and the manufacturing sector. Particularly due to frequent interaction with mineral acids as CH_3COOH, H_2SO_4, HCl, etc. Because most industrial environments have an acidic influence, external corrosion affects exposed parts of metallic structures more (Ejekeme et al., 2015 and Othaki et al., 2020). According to Ngobiri et al., (2013) and Othaki et al., (2020), the corrosive industrial fluids they transport have an impact on the interior metallic surfaces. Material deterioration due to an interaction with its surroundings is known as corrosion.

There exist multiple techniques for managing corrosion in building materials. The methods most commonly applied to pipelines, underground storage systems, and offshore facilities are cathodic production technique, organic and metallic protective coating, corrosion-resistant alloys, plastics, and polymers, and corrosion inhibitors (Ajayi et al., 2011).

STATEMENT OF THE PROBLEM

Numerous studies on corrosion have been conducted with acids such as sulfuric acid and hydrochloric acid, but not enough study has been done on the inhibitory effect of bitter leaf extracts to interest industry in their use. This is the investigation's main emphasis.

AIM AND OBJECTIVE OF THE RESEARCH

The purpose of this research is to conduct a corrosion inhibitory action utilizing extracts from bitter (Vernonia amygdalina) leaf, exposure period, and temperature, at a constant concentration of acid. Response surface methodology (RSM) will be used to assess the effectiveness of this action on corrosion prevention.

Specific objectives are:

1. To investigate and characterize the process of extracting sap from the bitter (vernonia amygdalina) leaf.
2. To use an Atomic Absorption Spectrometer (AAS) to ascertain the mild steel's metallic composition.
3. To research how mild steel corrodes in an acidic (HCl) environment.
4. Through the use of the weight loss method, ascertain the effects of process parameters, bitter leaf extract concentration, time and temperature on the rate of mild steel corrosion, and optimize the inhibition process through the application of surface methodology (RSM).

SIGNIFICANCE OF THE STUDY

(1) The purpose of this study is to offer the best circumstances possible for the usage and application of locally obtained plants as corrosion inhibitors in both the oil and non-oil sectors.

(2) Corrosion control has the potential to significantly extend component life in the oil and gas and marine industries, which results in even bigger advantages like lower maintenance costs

(3) By advancing the method for creating environmentally friendly inhibitors that are sustainable, it will also highlight the field that the government and business community should support.

MATERIALS:

Bitter leaf (Vernonia_amygdalina) will be collected from Amokwe, Udi, Enugu State, Nigeria. The mild steel coupon would be purchased from Kenyatta Market, Enugu state, Nigeria. The analytical grade of acid will be purchased from Gerald Chemicals Ltd Ogbete Main Market, Enugu, Nigeria.

The equipment AAS, SEM, weighing balance, beakers, heating mantle and water bath, desiccators, ethanol, stop-watch, shall be used for analysis.

METHODS:

Extraction of juice from the leaves

The plants leaves will be washed thoroughly with water to remove unwanted material. The samples will be dried, pulverized, and weighed. The weighed inhibitors will be stored in desiccators prior to use. 60g each of the ground samples will be mixed with ethanol tightly covered to prevent evaporation and kept for 48 hours. Then the extracts will be filtered to obtain high yields of the concentration. The filtered solutions will be heated in rotary evaporator setup to expel the ethanol at 70°C for 20 min.

Characterization of the extracts

The phytochemical laboratory analysis of the extracts will be carried out at Projects Development Institute, PRODA, Enugu, Nigeria while phytochemical instrumentation analysis will be carried out at NARICT , Zaria, Nigeria and results will be printed from spectroscopy, to identify the compounds, functional groups and their structures. The laboratory analysis be done using American Society for Testing and Materials (ASTM International D4903). The instrumentation tests:

Fourier Transformation Infrared (FTIR-8400S) spectroscopy analyses will be used to characterized bitter(vernonia_amygdalina) leaf extracts for identification of all active functional groups present in the extracts.

Phytochemical analysis

For the phytochemical analysis of ethanol and aqueous extracts of the plant samples, the method reported by Eddy and Ebenso (2008) will be employed. For the identification of saponin, frothing test and Na_2CO_3 test will be adopted. For the identification of tannin, bromine water and ferric chloride tests will be used. For the identification of cardiac glycodises, Leberman's and Salkowski's tests will be adopted and for the identification of alkaloid, dragendorf, Hagger and Meyer reagents will be used.

3.2.4. Preparation of Metal Specimen

The mild steel obtained will be analyzed to determine the metallic compositions using AAS. It will be used to prepare for corrosion experiment by adopting the method employed by Awe *et al.*, (2015). The mild steel specimens will be mechanically cut into dimension of 3.0cm x 3.0cm with 1.5mm thickness (with a surface area of 9.0 cm^2). Prior to all, the mild steel will be mechanically polished with series of emery paper from 400 to 1200 grades to sufficiently remove any mill scale on the sample of mild steel. The specimen will be washed thoroughly with distilled water, degreased with absolute ethanol, dipped into acetone to avoid corrosion and dried in air. The dried specimens will be stored in desiccators before use.

Experimental Procedure

Weight loss measurements will be conducted under total immersion using 250 ml capacity beakers containing 100 ml prepared solution of acid(HCl) at 30°C to 70°C which shall be maintained in a thermostatic water bath using method employed by Awe *et al.*, (2015). The mild steel shall be weighed and dropped in different concentrations of acid with the aid of acid resistance plastic clip at the required conditions. The coupons will be retrieved at a certain time interval such as 2s, 4s, 6s, 8s and10s. After each exposure time, the mild steel coupons shall be removed, washed thoroughly to remove the corrosion product with emery paper, rinsed with distilled water and dried in acetone as previously explained. The mild steel was re-weighed to determine the weight loss, in gram by the difference of mild steel weight before and after immersion. The procedure will be repeated with different concentration of inhibitors in the solution. The corrosion rates (g/cm^2h) in the absence and presence of the inhibitors will be determined. The variations of factors used in the experiment are shown in Table 1. Weight loss will be calculated by finding the difference between weight of each coupon before and after immersion as reported by Awe *et al.*, (2015).

$$\Delta W = W_b - W_a \quad (1)$$

W_b is the weight before immersion; W_a is the weight after immersion. While the corrosion rate (g/cm^2h) in absence and presence of inhibitors shall be calculated using equation 2

$$CR = \frac{\Delta W}{At} \quad (2)$$

Where ΔW is the weight loss (g) after exposure time t (h), A is the area of the specimen (cm^2), t is time of exposure in hours and CR is the corrosion rate at each exposure time. The corrosion rate obtained in the absence and presence of inhibitor shall be used to calculate inhibition efficiency (IE %) as in equation 3.

$$IE(\%) = \frac{CR_1 - CR_2}{CR_1} \times 100 \quad (3)$$

Where IE (%) is inhibition efficiency, CR_1 is the corrosion rate of mild steel in absence of inhibitors; CR_2 is the corrosion rate of mild steel coupons in the presence of inhibitors.

Optimization of the inhibition process using response surface methodology (RSM)

Design Expert software (version 10) shall be used in this study to design the experiment and to optimize the inhibition conditions. The experimental design employed in this work is a two-level-four factor full factorial design, including 30 experiments. Concentration of the extract

(%v/v), exposure time (hour), and temperature (^oC) at constant acid chloride medium were selected as independent factors for the optimization study. The response chosen was inhibition efficiency, IE (%) obtained from corrosion inhibition of mild steel alloy using selected plant extracts. Six replications of centre points were used in order to predict a good estimation of errors and experiment were performed in a randomized order. The actual and coded levels of each factor are as shown. The coded values were designated by −1 (minimum), 0 (centre), +1 (maximum), −α and +α. Alpha is defined as a distance from the centre point which can be either inside or outside the range. It is noteworthy to point out that the software uses the concept of the coded values for the investigation of the significant terms, thus equation in coded values was used to study the effect of the variables on the responses. The empirical equation is represented as shown in Equation 1:

$$Y = \beta_0 + \sum_{i=1}^{4} \beta_i X_i + \sum_{i=1}^{4} \sum_{j=i+1}^{4} \beta_{ij} X_i X_j + \sum_{i=1}^{4} \beta_{ii} X^2{}_i \qquad (1)$$

Where Y is the response factor (corrosion rate), x_i = the ith term of independent factor, $ß_o$= intercept, $ß_i$ = linear model coefficient, $ß_{ii}$ = quadratic coefficient for the factor i, and $ß_{ij}$ = linear model coefficient for the interaction between factors i and j.

The coded values of the process variables were determined using Equation (2):

$$x_i = \frac{X_i - X_0}{\Delta X} \qquad (2)$$

Where x_i = coded value of Ithvariable, X_i = un-coded value of the Ithtest variable and X_o = un-coded value of the Ithtest variable at center point, ΔX =change/intervals between the un-coded values. Selection of levels for each factor was based on the experiments performed.

Table 1: Range of each factor in actual and coded form for corrosion inhibition of in acidic medium.

Factor	Units	Low level	High level	-α	+α	0 level

Conc. of Extract (A)	(mg/100ml)	10(-1)	20(+1)	5(-2)	25(+2)	15
Exposure time , (B)	Hours	4(-1)	8(+1)	2(-2)	10(+2)	6
Temperature (C)	°C	40(-1)	60(+1)	30(-2)	70(+2)	50

Table 2: Experimental design Matrix for corrosion inhibition of mild steel

Run order	Conc. of extract (%v/v) A		Exposure Time (Hours) B		Temperature (ºC) C		IE Of Bitter (vernonia amygdalina) leaf (%)
	Coded	Real	Coded	Real	Coded	Real	
1	-1	10	-1	4	-1	40	
2	+1	20	-1	4	-1	40	
3	-1	10	+1	8	-1	40	
4	+1	20	+1	8	-1	40	
5	-1	10	-1	4	+1	60	

6	+1	20	-1	4	+1	60	
7	-1	10	+1	8	+1	60	
8	+1	20	+1	8	+1	60	
9	-1	10	-1	4	-1	40	
10	+1	20	-1	4	-1	40	
11	-1	10	+1	8	-1	40	
12	+1	20	+1	8	-1	40	
13	-1	10	-1	4	+1	60	
14	+1	20	-1	4	+1	60	
15	-1	10	+1	8	+1	60	
16	+1	20	+1	8	+1	60	
17	-2	5	0	6	0	50	
18	+2	25	0	6	0	50	
19	0	15	-2	2	0	50	
20	0	15	+2	10	0	50	
21	0	15	0	6	-2	30	
22	0	15	0	6	+2	70	
23	0	15	0	6	0	50	
24	0	15	0	6	0	50	
25	0	15	0	6	0	50	
26	0	15	0	6	0	50	
27	0	15	0	6	0	50	
28	0	15	0	6	0	50	
29	0	15	0	6	0	50	
30	0	15	0	6	0	50	

RESULTS AND DISCUSION

Discussion and Results

Extraction yield from leaves

Bitter leaf extracts weighing 45g were made from 65g of dried leaves. With yields of 69%, all leaves have a considerable amount of extract that can be utilized as green inhibitors (Ebenso et al., 2008).

An examination of the phytochemicals

Table 3 lists the photochemical constituents of ethanol-extracted bitter leaf extracts. The ethanol extracts of the leaves included anthraquinone but not saponin, tannin, terpenes, flavonoids, perpenoids, glycosides, or alkaloids. The phytochemical contents in the ethanol extracts of these leaves may have contributed to the suppression of mild steel corrosion since the majority of these phytochemicals possessed heteroatoms or electron-rich linkages in their chemical structures, which enhanced their electron-donating ability. Similar findings have been reported by other studies regarding the inhibition of mild steel and aluminum corrosion by ethanol extracts of some plants.(Ebenso et al., 2008; Lot et al., 2009) discovered that bitter leaf ethanol extracts included anthraquinone but not saponin, tannin, terpenes, flavonoids, perpenes, glycosides, or alkaloids.

Table 3. Phytochemical Constituents of Ethanol Extracts of Leaves

S/N	**Phytochemicals**	**Bitter leave Extract (%w/w)**
A	Saponins (%w/w)	6.94
B	Terpenes (%w/w)	12.76
C	Tannins (mg/100g)	15.41
D	Flavonoid (%w/w)	3.93
E	Phlobatannins	-

	(%w/w)	
F	Anthraquinones (%w/w)	-
G	Glycoside (mg/100g)	2.46
H	Alkaloids (%w/w)	8.44

MILD STEEL METALLURGICAL COMPOSITION

Scientists employed atomic absorption spectroscopy (AAS) (wt%) to assess the composition of mild steel sheet. Similar findings on mild steels with Mn: 0.90, P: 0.69, C: 0.50, Si: 0.06, and Fe: 97.86 (wt%) were reported by (Hawraa Khaleeli and Amjed, 2018).

Time's Influence on Mild Steel Corrosion Rate

Under the following circumstances, Figure 1 illustrates how time affects the pace at which mild steel corrodes both with and without inhibitors: 30 degrees Celsius, 1.5 milliliters of acid, and 10 milligrams per 100 milliliters of inhibitor Without an inhibitor, corrosion progressed quickly, achieving a 0.02 g(cm2 hr) corrosion rate after around 10 hours. The increase in the medium's corrosion rate may be due to the coupon's electrons being lost. Due to the production of different corrosion products on the surface of the corroded surface, the metal corroded more in an uncontrolled acid solution, changing color gradually from translucent to brownish (Amitha Rani and Bharathi, 2012). The corrosive nature of the acid may be the cause of this. Coupons made of metal coated in bitter leaf extracts rusted more initially, then less. The findings demonstrated that, in comparison to the uninhibited acid, better corrosion inhibition performance was obtained in the presence of the extracts used as the inhibitor (Dubey and Singh, 2021).

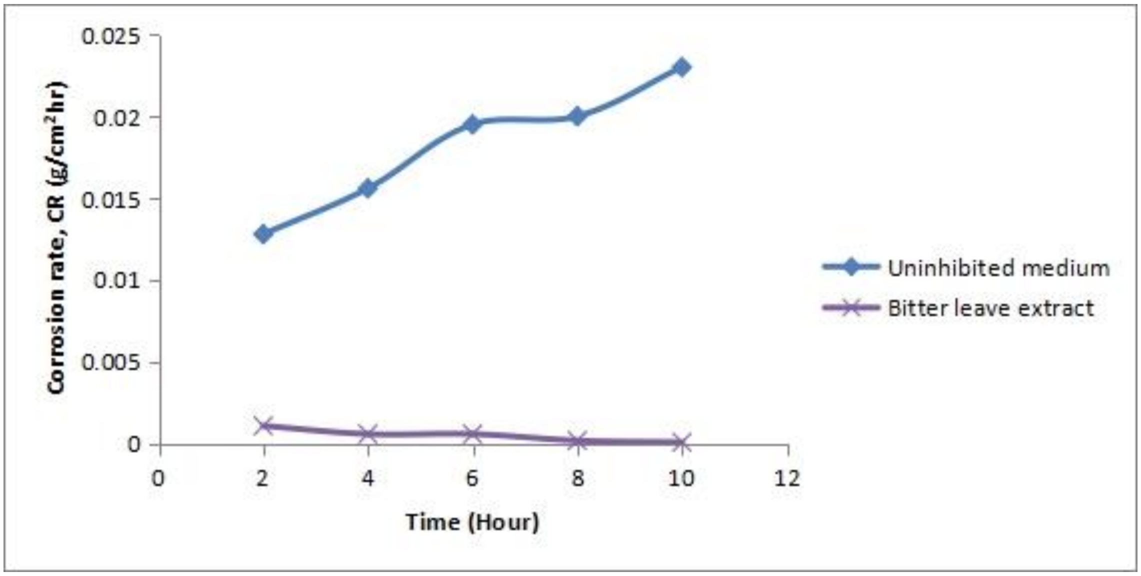


Figure 1: Time's Influence on mild Steel Corrosion rate in the presence and absence of various inhibitors.

Effect of inhibitor concentration on corrosion rate

As the concentration of bitter leaf extracts increased, the mild steel's rate of corrosion in the medium reduced. This might be because, as the extract concentration rises, more extract components adsorb on the mild steel surface, creating a barrier to mass transfer and stopping more corrosion. This outcome is consistent with findings from Patel et al. (2014), which indicate that an increase in inhibitor concentration also causes a decrease in the rate of corrosion.

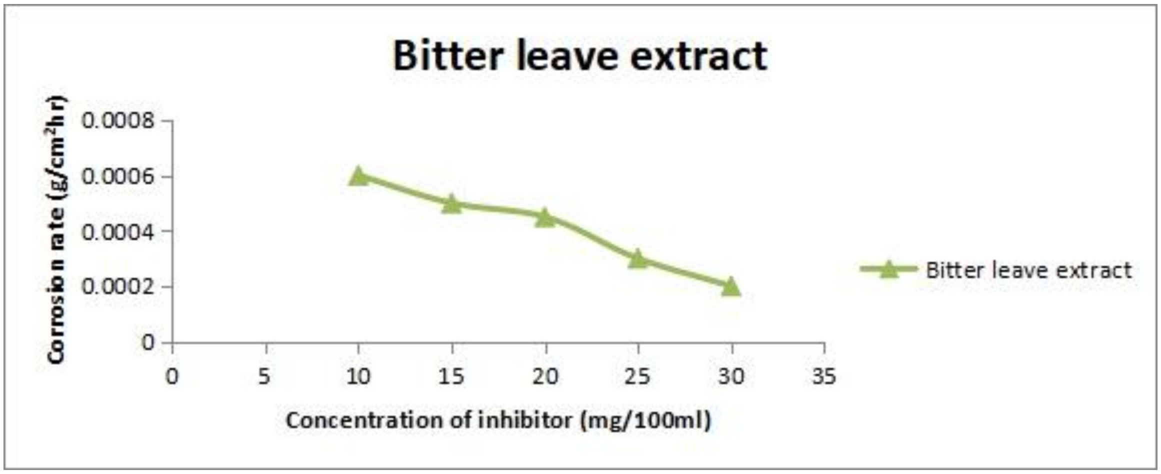


Figure 2 shows the effect of inhibitor concentration on mild steel corrosion rate in the presence and absence of various inhibitors.

The influence of temperature on the rate of corrosion

Figure 4 illustrates the influence of temperature on the rate of mild steel corrosion in free acid and in the presence of different amounts of the inhibitor (plant extract). The temperature range studied was 30 to 70 degrees Celsius. It was found that the rates of mild steel corrosion in both the presence of an inhibitor and in a free acid solution increased with temperature. This is to be expected since the average kinetic energy of the interacting molecules increases with temperature, which also increases the rate of mild steel corrosion. For instance, compared to an unrestricted acid solution, the corrosion rate decreased more in the inhibited acid solution. The constrained acid solution outperformed the uninhibited acid solution because the plant extract reduced the rate at which mild steel corroded. The study's findings showed that mild steel corrodes less quickly as leaf extract content rises (NorZakiah and Karimah, 2014). This implies that adding more leaf extract boosts the mild steel's ability to suppress growth in acidic media.

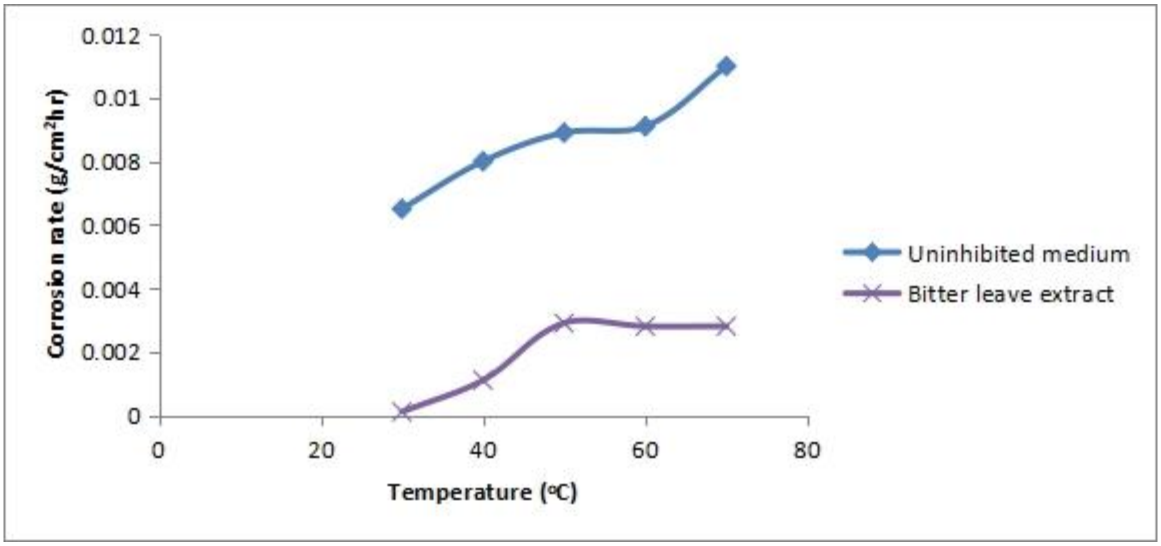


Figure 3 shows the effect of temperature on mild steel corrosion rates in the presence and absence of various inhibitors.

SURFACE MORPHOLOGICAL STUDIES OF THE MILD STEEL.

The surface morphology of mild steel was investigated using a sigma field emission scanning electron microscope. Images of the mild steel surface in its untreated state and with inhibitors present are shown in Figs. 4 and 5, respectively. As stated by Muthukrishnan and associates (2014). SEM images are useful for examining surface contaminations, providing qualitative chemical assessments, and identifying crystalline structures (Anadabe et al., 2018; Odejobi and Akinbulumo, 2016). It was demonstrated that there was an observable structural difference between the extracts and mild steel in the uncontrolled medium due to a quickly oxidized surface (Leelavathi and Rajalakshmi,2013, Mousavi et al.,2011, Munis et al.,2020, Olawale et al.,2018, Pal et al., 2019). Chang et al. (2020), Fu et al. (2010), Shukla et al. (2009), and Vijayalakshmi et al. (2011) state that the mild steel specimen submerged in the inhibitor's presence had a smoother surface covered in adsorbed inhibitor, indicating that the specimen was in better condition. The metal surface submerged in blank acid solutions, on the other hand, was uneven and had a cracked, pitted appearance.

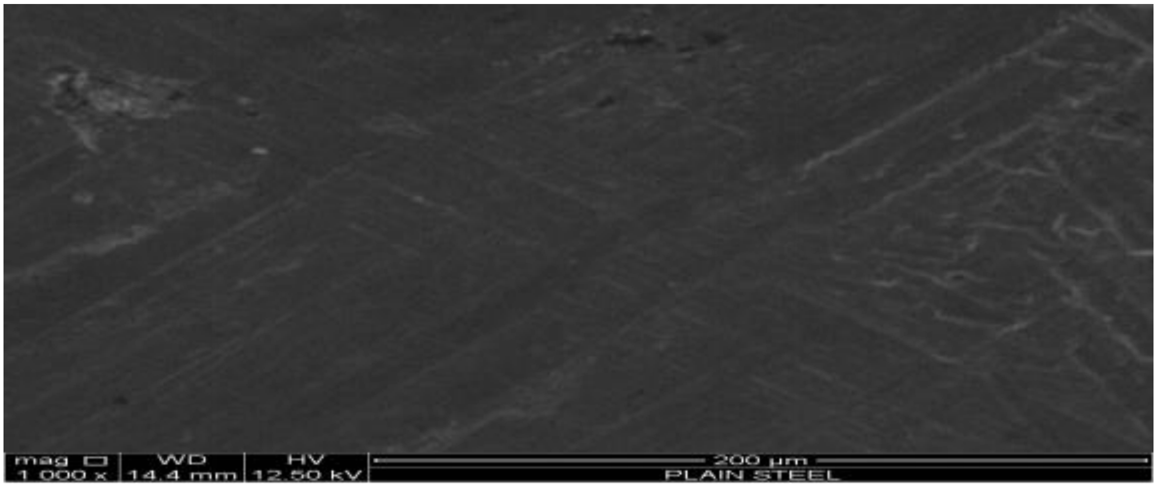
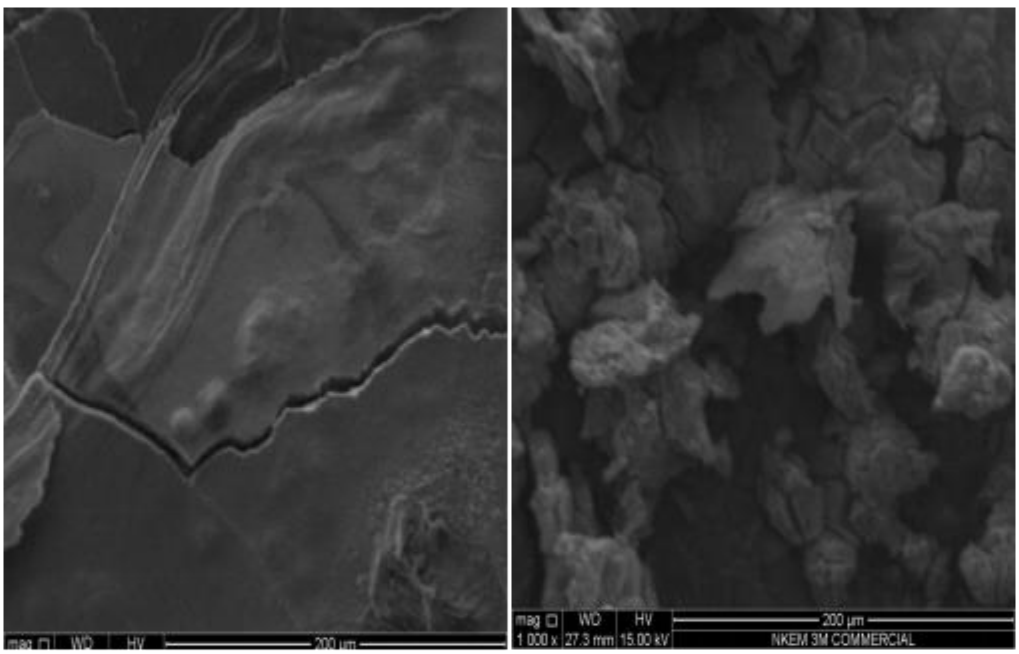


Fig. 4: SEM images of mild steel coupon



(a) Absence of inhibitor **(b) Presence of inhibitor**

Fig. 5: SEM images of absence and presence of Bitter leaf.

Conclusion:

The study comes to the conclusion that bitter leaf ethanol inhibits mild steel corrosion in acidic environments. The ethanol extract of the leaf's inhibitory activity was caused by the photochemical components of the extracts. The inhibitor concentration of 19.39 mg/100 ml, the time of 6.56 h, and the temperature of 48.90C are the optimal values. Under optimal circumstances, the inhibition efficiency in bitter leaf inhibited acid media was 88.8%. This implies that in an acidic environment, leaf extract can stop mild steel from corroding. The study concludes that environmentally acceptable inhibitors are always preferred over innocuous organic inhibitors.

RECOMMENDATIONS

Nigeria ought to use the opportunity presented by the economic viability of producing environmentally friendly inhibitors and applying them to stop metal corrosion. To control or lessen corrosion, oil companies and other industrial sectors could use green inhibitor techniques. To support technical domestication and industrialization, the government ought to provide greater funding for research on green corrosion inhibitors.

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