OPTIMIZATION AND EFFECT OF INHIBITIVE ACTION OF VERNONIA AMYGDALINA AND AZADIRACHA INDICA LEAVE EXTRACTS ON CORROSION OF MILD STEEL IN ACIDIC MEDIUM: AN INNOVATIVE APPROCH

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Abstract:

The major process parameters of plant extracts of Veroninia Amigdanina and Azadirachta Indica on mild steel corrosion in acidic medium (HCL) were investigated by the weight loss technique and optimized using the central composite design (CCD) of response surface approach (RSM).The elemental compositions of metal were determined using an Atomic Absorption Spectrophotometer(AAS).Phytochemical analysis results confirmed the presence of organic constituents such as Alkaloids, Tannins, Terpenes, Glycosides, Saponins, and Flavonoids, which made the Veroninia Amigdanina and Azadirachta Indica plant extracts act as a good inhibitor and functional groups using ASTM International and a Fourier Infrared Spectrometer, respectively. The result of system variables such as inhibitor concentration, time, effect of temperature and medium concentration on corrosion rate in an acidic (HCL) medium was studied. The results show that iron is the main component of mild steel, and that a lack of phytochemical components and functional groups in the extracts makes them effective inhibitors. The highest inhibition efficiency was 95.1 percent, temperature: 47.90C, inhibitor concentration: 18.84mgmol, time 5.55s, medium concentration 1.67mgmol, and 83.9 percent, temperature: 47.30C, inhibitor concentration: 12.10 mgmol, time 7.50s, according to studies from the experimental design of Veroninia Amigdanina and Azadirachta Indica. Within Veroninia Amigdanina and Azadirachta Indica inhibited acid media, the best feasible conditions yielded inhibition efficiency of 96.2 percent and 84.85 percent, respectively. This suggests that Veroninia Amigdanina and Azadirachta Indica leaf extracts can help.

Key words: Optimization, Inhibitors, Veroninia Amigdanina, Azadirachta Indica Hydrochloric acid, corrosion rate and weight loss.

INTRODUCTION

BACKGROUND OF THE STUDY

Corrosion is a significant financial burden that can also pose serious safety and environmental risks (Xiaogang Li et al., 2015) . According to a recent study, China's total annual cost of corrosion is around 2127.8 billion RMB (310 billion USD), or 3.34 percent of GDP (Baorong Hu et al., 2017) . If the global economy experiences is in the same proportion, the annual corrosion cost comes in the range of $2.50 trillion. The most effective form of protection is organic, extensively utilized corrosion mitigation strategy, accounting for two-thirds of all anti-corrosion expenditures (Fan Z et al., 2018) .Corrosion of metallic structures has persistently been a source of down turn to the economy. However, the use of metallic materials for construction presently seems inevitable due to its physical properties and cost. Importantly, iron and its alloy, used for construction poses a great challenge for corrosion scientists and manufacturing industries. More so as a result of regular contact with mineral acids such as HCl, H_2SO4, CH_3COOH, etc. The exposed part of a metallic structure is more affected by external corrosion due to acidic effect of most industrial environment (Ejekeme et al., 2015 and Othaki et al., 2020). While the inner metallic surfaces are affected by the corrosive industrial fluids they convey (Ngobiri et al., 2013 and Othaki et al., 2020). Corrosion is the destruction of material by a reaction with its environment. The petroleum industry is one of the most affected by corrosion due to the presence of numerous corrosive substances in the crude oil, which affect equipment and pipelines from the extraction of crude oil to the transportation of final products (Ashworth, et al., 2001and Olawale et al., 2018**).** Corrosion can be defined as an irreversible reaction of a material with the environment, which usually (but not always) results in a degradation of the material or its properties. It is the inevitable deterioration (thermodynamically favored) of materials by the chemical interaction with their environments. It is the returning of the materials to its original form (stable state) to the mother earth (Moudgil, 2014). There are several aspects of corrosion: the material, the environment, and the material properties (Uhlig, 2000; Fontana, 1999; Bardal, 2003). The rate and extent of corrosion depend mainly on the nature of the metal and the nature of the environment(Krishnamurthy et al., 2014).Thus the position of the metal in the galvanic series; relative areas of the anode and cathode; purity of the metal; physical state of the metal;

nature of the oxide film; solubility of the products of corrosion; temperature; humidity; pH; nature of the electrolyte; concentration of oxygen and formation of oxygen concentration cells affect corrosion (Bardal, 2003; Roberge, 2008). The degradation of metals has a negative influence on the populace and is apparently an issue of concern as it influences the economic cost and also creates safety awareness from the damages such as in pipelines, building, bridges, waste water system, and even our residence. A recent study in USA of industrial sectors, predicts the cost of corrosion would rise over $1.1 trillion in 2016 (Joshua.,2016).These estimates were based on a landmark study by NACE (National Association of Corrosion Engineers) that estimated (direct) corrosion costs were $276B in 1998 as reported in the NACE Corrosion Costs Study(Lewis,2000; Ngobiri,2013).

Several methods used in the controlling of corrosion in structures are available. The most frequently used techniques include organic and metallic protective coating; corrosion resistant alloys, plastics and polymers; corrosion inhibitors and cathodic production technique which are used on piping, underground storage system and offshore facilities (Ajayi et al., 2011).

STATEMENT OF THE PROBLEM

Over the years, a lot of researches have been done on the area of corrosion. Several authors have carried out research on corrosion in acidic medium like hydrochloric acid, sulphuric acid etc but sufficient work is yet to be done on the optimization and effect of corrosion inhibition activities using the Vernonia_amygdalina (bitter leaf) and azadiracha indica (neem leaf) plant extracts, to draw industrial attention towards application. This is the focus of this study.

AIM AND OBJECTIVE OF THE RESEARCH

The aim of this research efforts is to carry out an optimization of corrosion inhibition activities using concentration of the vernonia_amygdalina (bitter leaf) and azadiracha indica (neem leaf) plant extracts, exposure time, and temperature, at constant concentration of acid and evaluate its performance on prevention of corrosion using response surface methodolgy (RSM): an innovative approach.

Specific objectives are:

1. To study the extraction of juice from the vernonia_amygdalina (bitter leaf) and azadiracha indica (neem leaf) plant.
2. To characterize the vernonia_amygdalina (bitter leaf) and azadiracha indica (neem leaf) plant extracts using analytical and instrumentation (ASTM International and Fourier Transform Infra-Red Spectrophotometer, FTIR methods).
3 To determine the metallic compositions of the mild steel using Atomic Absorption Spectrometer, AAS.

4. To study the corrosion behavior of mild steel in acidic (HCl) environment.

5. To determine the effects of process parameters, concentration of the vernonia amygdalina (bitter leaf) and azadiracha indica (neem leaf) plant extracts, exposure time, and temperature, at constant concentration of the medium on the rate of corrosion of

mild steel using the weight loss method and to optimize the inhibition process using response surface methodology (RSM).

Research Questions

1. How can we extract juice from the , vernonia_amygdalina (bitter leaf) and azadiracha indica (neem leaf)?

2. How can we characterize the vernonia_amygdalina (bitter leave) and azadiracha indica (neem leaf) extract using analytical and instrumentation (American System for Testing and Material "ASTM" International and Fourier Transform Infra-Red Spectrophotometer, FTIR methods)?

3. What is the metallic composition of the mild steel using atomic absorption spectrometer?

4. What is the corrosion behavior of mild steel in acidic environment?

5. What is the effect of process parameters, concentration of the vernonia_amygdalina (bitter leave) and azadiracha indica (neem leaf) extract, exposure time, temperature, and concentration of the medium on the rate of corrosion of mild steel using the weight loss method and to optimize the inhibition process using response surface methodology (RSM)?

SCOPE OF THE STUDY

This work is restricted to synthesis of corrosion inhibition using vernonia_amygdalina (bitter leaf) and azadiracha indica (neem leaf) plant extracts and optimization studies. The rate of corrosion using weight loss method .

SIGNIFICANCE OF THE STUDY

(1) This study aims to achieve and promote the use of locally sourced plants as corrosion inhibitors and provide optimum conditions for their use and application in the oil and non-oil sectors.

(2) If corrosion is control it reduces the overall economic cost: corrosion of metals costs U.S. economy almost $300 billion per year at current prices. Approximately one-third of these costs could be reduced by broader application of corrosion-resistant materials and the application of best corrosion related technical practices such as locally sourced plants as corrosion inhibitors.

(3) If corrosion is control it creates a certain level of safety from the areas such as in pipelines, building, bridges, waste water system, and even our residence, but if corrosion is not controlled, it will serve as a threat to the environment and mankind, so effective corrosion control methods should be implemented to prevent damaging effects of corrosion.

(4) The benefits of corrosion management in the oil and gas industry and also the marine industry can dramatically increase component life, which leads to much greater benefits such as reduced maintenance costs.

(5) It will also expose the area worthy of investment by government and industrialist by developing the technique for production of sustainable green inhibitors.

(6) This study, optimization of mild steel corrosion inhibition of vernonia amygdalina (bitter leaf) *and* azadiracha indica (neem leaf) extracts in acidic medium using central composite design of response surface methodology, is expected to suggested means of producing green inhibitors through conversion of wastes from plant to wealth and their management in the environment.

LITERATURE REVIEW

Corrosion can be viewed as a universal phenomenon, omnipresent and omnipotent. It is there everywhere; air, water, soil and in every environment, we encounter. Since the discovery of metals, human beings have been trying to understand and control corrosion, learning the processes that take place to make even the smallest corrosion reactions and how in turn it relates to human health is interesting (Leelavathi et.,al, 2013; Kerri, 2013). Certain environments offer opportunities for these metals to combine chemically with elements to form compounds and return to their lower energy levels(Shrei et al., 2000). Most metals corrode on contact with water, air, acids, bases, salts, oils. Aggressive metals will also corrode when exposed to gaseous materials like acid vapours, formaldehyde gas, ammonia gas, and sulphur containing gases (Tromans et al., 2001) .

ECONOMIC IMPACT OF CORROSION

It is a general belief that corrosion is a universal foe that should be accepted as an inevitable process. As products and manufacturing processes are becoming more complex and the penalties of corrosion failures have become more costly and has generated an increased awareness, (Procter 2000; Perez,2004; Ita, 2004) underscores the above assertion and further argues that corrosion is like corruption, when both are left uncontrolled, they eat deep into the fabrics of a nation's economy in an irreversible manner that recovery most often becomes an unrealizable mirage. More so, it is estimated that an average of 10% of the total world's metal output is lost to corrosion. This affects the economy of a nation and her assets: infrastructures, transportation, utilities, nuclear and military facilities, and production and manufacturing plants (Rawat et al., 1984; Rajendra et al,2000; Rawat et at., 2004).

REVIEW OF RELATED WORKS IN OPEN LITERATURE

According to Deng et al.,(2014), the corrosion inhibition by Dendrocalamus brandisii leaves extract (DBLE)/major flavonoid of cold rolled steel (CRS) in trichloroacetic acid (Cl_3CCOOH) solution was investigated by weight loss, electrochemical techniques. The results show that DBLE is a good inhibitor, and the maximum inhibition efficiency is higher than 95%. According to . Muthukrishnan et al.,(2014), hyptis suaveolens leaf extract (HSLE) as corrosion inhibitor in 1 M H_2SO_4 was evaluated using mass loss measurement as well as potentiodynamic polarization and electrochemical impedance spectroscopy measurements. Maximum inhibition efficiency of HSLE in 1 M H_2SO_4 was found to be 95 %. According to Onukwuli et al.,(2016), The optimization of inhibition efficiency of mango (mangnifera indica) extract as inhibitor of mild steel in 1.0M H2SO4 using response surface methodology is presented. The corrosion inhibition study was carried out using thermometric, gravimetric (one factor at a time and response surface methodology) and potentiodynamic polarization methods. The inhibition efficiency was concentration, temperature and time dependent. Mango extract exhibited the optimum inhibition efficiency of 74.09 % (at optima inhibitor concentration of 0.97g l-1, temperature of 305.33 K and time of 22.76 h). According to Omotioma et al., (2017), Pawpaw leaves extract was examined as anti-corrosion agent for aluminium in hydrochloric acid medium. The extract and corrosion product were analyzed using Fourier transform infrared spectrophotometer (FTIR). Optimum inhibition efficiency of 80.58% was obtained at inhibitor concentration of 0.961 g/l, temperature of 311.459 K and time of 3.932 hrs. The extract is a mixed-type inhibitor that can control both cathodic and anodic corrosion. According to Awe et al.,(2015), The inhibitive ability of Bitter leaf (Vernonia amygdalina) root extract was investigated on corrosion of mild steel in 1.5 M Sulphuric acid solution using weight loss, hydrogen evolution and thermometric measurements at temperature ranges of 30-60°C. The inhibitor exhibit excellent inhibition efficiency on mild steel corrosion in H_2SO4 solution as 90 %, 84.82 %, 79.65 % and 76.90 % of inhibition efficiency achieved with addition of 0.5 g/l concentration of bitter leaf root extract (BLRE) at 30°C, 40°C, 50°C and 60°C temperature respectively .According to Alan et al.,(2020), the plant extracts obtained corrosion inhibition efficiencies above 60%, most of them around 80–90%. According Oyewole et al.,(2021), The corrosion inhibition of mild steel in 0.5M H_2SO_4 solution was studied in the presence of Corchorus olitorius stem extract as inhibitor, which gave an inhibition efficiency of 94.34%.According to Evrim et al.,(2016), the inhibitory effect of the methanol gentiana olivieri and its fractions on the corrosion of mild steel in a 0.5 M HCl solution were investigated using potentiodynamic polarization and electrochemical impedance spectroscopy(EIS), EIS results showed maximum inhibition efficiency (93.7%) at an inhibitor concentration of 800 mg/L. According to Olawale et al.,(2018), the evaluation of groundnut leaves extract as corrosion inhibition on mild steel in 1M sulphuric acid, the optimum Inhibition efficiency was predicted to be 85.9% .According to Demian et al.,(2021), the seed extract of Piper guineense (PGS) was investigated as an eco-friendly and cost-effective anticorrosion agent for the protection of Q235 carbon steel in acid chloride medium, using a sequence of experimental and computational techniques. The extract was found to sustain its remarkable anticorrosion efficiency (> 98%) for prolonged time intervals (up to 144 h) without replenishment. According to Othaki et al.,(2020),inhibition of pipeline Steel Corrosion in 0.5M H_2SO_4 using Coltyledon of Chysophyllum Albidum.The result obtained showed that the inhibition efficiencies of the extracts are 94% with 5g/L at 303k and 52.2% with 1g/L at 333k.

However, there is no consensus regarding which method assesses corrosion levels of structures most accurately, that is why the technique for corrosion detection will remain an issue no matter how corrosion inhibition is being carried out (Peckner, 2000; Onene et al,. 2006 and Olasehinde et al., 2013). Evidence cum literatures have shown that no research work has been done on this issue of optimum conditions for inhibition of mild steel in acidic medium using vernonia amygdalina (bitter leaf) and azadiracha indica (neem leaf) plants extracts, this is the gap between the previous works and current research.

RESEARCH METHODOLOGY

MATERIALS:

Vernonia_amygdalina (bitter leaf) and azadiracha indica (neem leaf) will be collected from Amokwe, Udi, Enugu State, Nigeria. The mild steel coupon would be purchased from Kenyatta Market, Achara Layout, Enugu, Nigeria. The analytical grade of acid will be purchased from Gerald Chemicals Ltd Ogbete Main Market, Enugu, Nigeria.

The equipment AAS, FTIR, 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 was washed thoroughly with water to remove unwanted material. The samples will be dried, pulverized, and weighed. The weighed inhibitors were stored in desiccators prior to use. 60g each of the ground samples was mixed with ethanol tightly covered to prevent evaporation and kept for 48 hours. Then the extracts were filtered to obtain high yields of the concentration. The filtered solutions were 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 were carried out at Projects Development Institute, PRODA, Enugu, Nigeria while phytochemical instrumentation analysis were carried out at NARICT , Zaria, Nigeria and results were printed from spectroscopy, to identify the compounds, functional groups and their structures. The laboratory analyses were done using American Society for Testing and Materials (ASTM International D4903). The instrumentation tests:

Fourier Transformation Infrared (FTIR-8400S) spectroscopy analyses were used to characterized vernonia_amygdalina (bitter leaf) and azadiracha indica (neem leaf) plant 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) were employed. For the identification of saponin, frothing test and Na_2CO_3 test were adopted. For the identification of tannin, bromine water and ferric chloride tests were used. For the identification of cardiac glycodises, Leberman's and

Salkowski's tests were adopted and for the identification of alkaloid, dragendorf, Hagger and Meyer reagents were used.

Fourier Transform Infra-red (FTIR) analysis

The method employed by Wang et al., 2005 and Yuliet et al., 2014, were adopted to carry out FTIR analysis of ethanol extracts of plant samples and that of the corrosion products using BUCK model 500 M infra red spectrophotometer. The samples were preparad using KBr and the analysis were done by scanning the sample through a wave number range of 400 to 4000 cm^{-1}.

3.2.4. Preparation of Metal Specimen

The mild steel obtained was 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 were 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 was 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 were washed thoroughly with distilled water, degreased with absolute ethanol, dipped into acetone to avoid corrosion and dried in air. The dried specimens were stored in desiccators before use.

Experimental Procedure

Weight loss measurements were 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 was weighed and dropped in different concentrations of acid with the aid of acid resistance plastic clip at the required conditions. The coupons were retrieved at a certain time interval such as 2s, 4s, 6s, 8s and10s. After each exposure time, the mild steel coupons were 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 was repeated with different concentration of inhibitors in the solution. The corrosion rates (g/cm^{2}h) in the absence and presence of the inhibitors were determined. The variations of factors used in the experiment are shown in Table 1. Weight loss was calculated by finding the difference between weight of each coupon before and after immersion as reported by Awe *et al.*, (2015).

$$\Delta W = W_b - W_a \tag{1}$$

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

$$CR = \frac{\Delta W}{At} \tag{2}$$

Where ΔW is the weight loss (g) after exposure time t (h), A is the area of the specimen (c���^{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 inhibitors were used to calculate inhibition efficiency (IE %) as in equation 3.

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

Where ���E (%) is inhibition efficiency, ���R_1 is the corrosion rate of mild steel in absence of inhibitors; ���R_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) was 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 i^{th} 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):

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

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 vernonia amygdalina (%)	IE of Azadirachta Indica leaf extract (%)
	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		

3.1.Yield of extract from the leaves

42g of Veroninia Amigdanin leave extract and 35g of Azadirachta Indica leave extract were obtained respectively from 60g each of the dried leaves of Veroninia Amigdanin and Azadirachta Indica leaves. These represent 70% and 58% yield respectively, showing that all leaves have good quantity of extract which can serve as green inhibitors Awe *et al*., (2015).

3.2.Phytochemical analysis

Table 4: shows the photochemical constituents of ethanol extracts of Veroninia Amigdanin and Azadirachta Indica leave extract. The results indicates that saponin, tannin, terpenes, flavanoid, perpenes, glycoside and alkaloids were present while anthraquinone is absent in the leaves ethanol extracts. The chemical structures of most of these phytochemicals contained electron rich bond or hetero atoms that facilitated their electron donating ability; hence the inhibition of the corrosion of mild steel by ethanol extracts of these leaves may be attributed to the phytochemical constituents of the extracts. Similar results have been reported by other researchers for the inhibition of the corrosion of mild steel and aluminium by ethanol extract of some plants. Similar results was obtained by(Ebenso et al.,2006, El-Shamy et al.,2020), indicating the results of ethanol extraction of Veroninia Amigdanin and Azadirachta Indica (neem) leaves such as saponin, tannin, terpenes, flavanoid, perpenes, glycoside and alkaloids were present while anthraquinone is absent in the leaves ethanol extracts (Alaneme et al.,2015, Hassan et al.,2016, Makkar et al.,1996).

Table 4. Phytochemical Constituents of Ethanol Extracts of Leaves

S/N	Phytochemicals	Veroninia Amigdanin leave Extract (%w/w)	Azadirachta Indica leave Extract (%w/w)
1	Saponins (%w/w)	6.23	6.61
2	Terpenes (%w/w)	12.47	9.59
3	Tannins (mg/100g)	13.60	9.59
4	Flavonoid (%w/w)	3.17	5.84
5	Phlobatannins	-	-

	(%w/w)		
6	Anthraquinones (%w/w)	-	-
7	Glycoside (mg/100g)	2.05	1.59
8	Alkaloids (%w/w)	8.54	6.34

3.3.METAL COMPOSITION OF MILD STEEL

Mild steel sheet was analyzed using Atomic absorption spectroscopy *(*AAS) to determine the composition (wt %).It could be observed from Table 5 that iron is the dominant metal that make up the mild steel. Similer observation was made by (Nnanna et al.,2013, Prasanna et al.,2016) on the mild steel composition such as Mn: 0.89, P: 0.67, C: 0.51 Si: 0.05, Fe: 97.86 (wt %).

Table 5: Metal Composition of Mild steel Using *Atomic Absorption Spectroscopy (AAS)*

Metals	Composition (Wt %)
Magnesium	0.89
Phosphorus	0.70
Carbon	0.49
Silicon	0.05
Iron	97.87

3.3.1.Effect of time on corrosion rate of mild steel

Figure 1 depicts the effect of time on corrosion rate of mild steel in existence and non- existence of inhibitors at certain Conditions: Temp = 30^{o}C, acid conc. = 1.5M, inhibitor conc. = 10mg/100ml) From the figure, it can be observed that corrosion rate was rapid and progressive in absence of inhibitor, at about $10\ hours$ the corrosion rate was $0.02\ g/cm^2hr$. The increase in corrosion rate in the medium may be adduced to the loss of electrons from the coupon. It was also observed that the metal corroded more in uninhibited acid solution with progressive color change from transparent solution to brownish solution due to the release of various forms of corrosion products suspected to be Fe_2O_3, Fe_2O_4 and $Fe(OH)_3$ that were formed on the surface of the corroded surface (Ghali et al.,2007, Ebenso et al.,2008). This may be as a result of corrosive nature of acid. The corrosion of metal coupons smeared with inhibitors pawpaw leave extract and neem leave extracts initially increased and then decreased. This may be as a result of the adsorptions of the inhibitors which were gradually increasing initially and on long exposure of the metal in the inhibitor solution which there by inhibited the corrosion at about $10 hours$ the corrosion rate are $0.0007\ g/cm^2hr\ and\ 0.00032\ g/cm^2hr$. for the two inhibitors. The corrosion rate of mild steel in uninhibited medium was higher than when in an inhibited medium.

This was in agreement with (Omotioma and Onukwuli,2017, Awe el al.,2015) results obtained in immersion of mild steel coupon in concentration of hydrochloric acid (HCL) at different time in the absence and presence of the two leaves extracts, there corrosion rate are $0.021\, g/cm^2hr$and $0.00061\, g/cm^2hr$ at about $10hours.$The results obtained reviewed that there is more corrosion inhibition performance achieved in the presence of the extracts used as the inhibitor compared to the uninhibited acid (Prasanna et al.,2016, Hawraa Khaleeli et al., 2018).

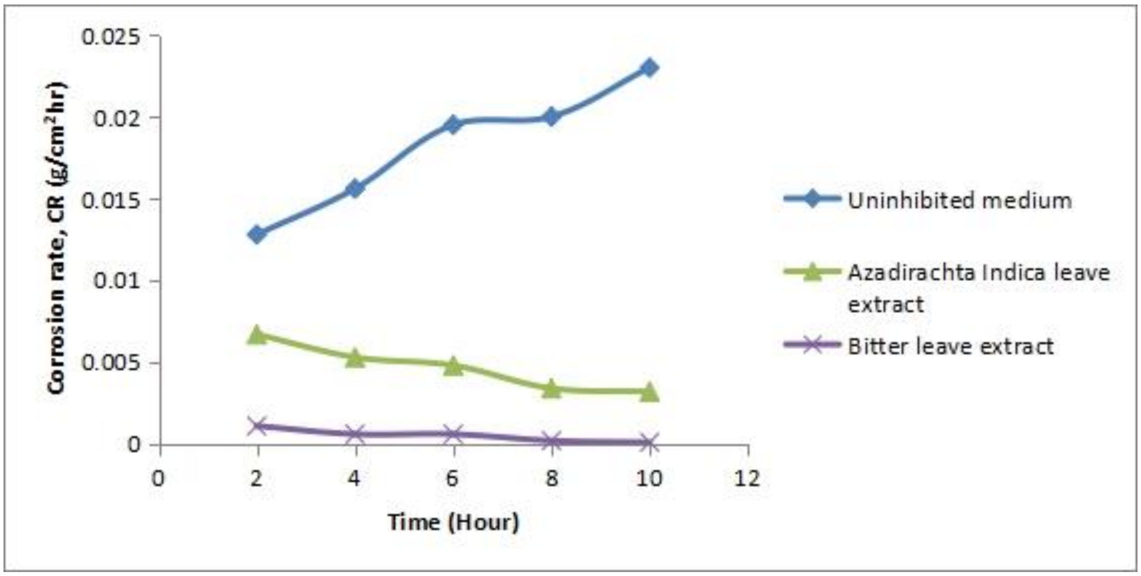

Fig. 1:Effect of time on corrosion rate of mild steel in the presence and absence of different inhibitors.

3.3.3. Effect of concentration of inhibitor on corrosion rate

The variation of corrosion rate of mild steel in acidic medium in the non-existence and existence of various concentrations of ethanol extracts pawpaw leave and neem leaves extract were studied at certain conditions such as Temp = 30ºC, time = 6H, acid conc. = 2M, the graph shown in Figure 3. It was observed from the figure that the corrosion rate of mild steel in the medium decreased such as $0.0006g/cm^2hr$, $0.0005g/cm^2hr$, $0.00045g/cm^2hr$, $0.0003g/cm^2hr$, $0.0002g/cm^2hr$, with increase in the concentration of the extract such as 5M, 10M, 15M, 20M, 25. This could be that as the concentration of the extract increase, there is was increase in the number of adsorption of the extract constituents on the surface of the mild steel which makes a barrier for mass transfer and prevents further corrosion. This result is in consonance with the findings (Patel et al.,2014, Baran et al., 2014 and Hawraa et al.,2018). where the decreases in the corrosion rate are $0.00060 g/cm^2hr$, $0.00051 g/cm^2hr$, $0.00043 g/cm^2hr$, $0.00031 g/cm^2hr$, $0.00021 g/cm^2hr$ with same increase in the concentration of inhibitors.

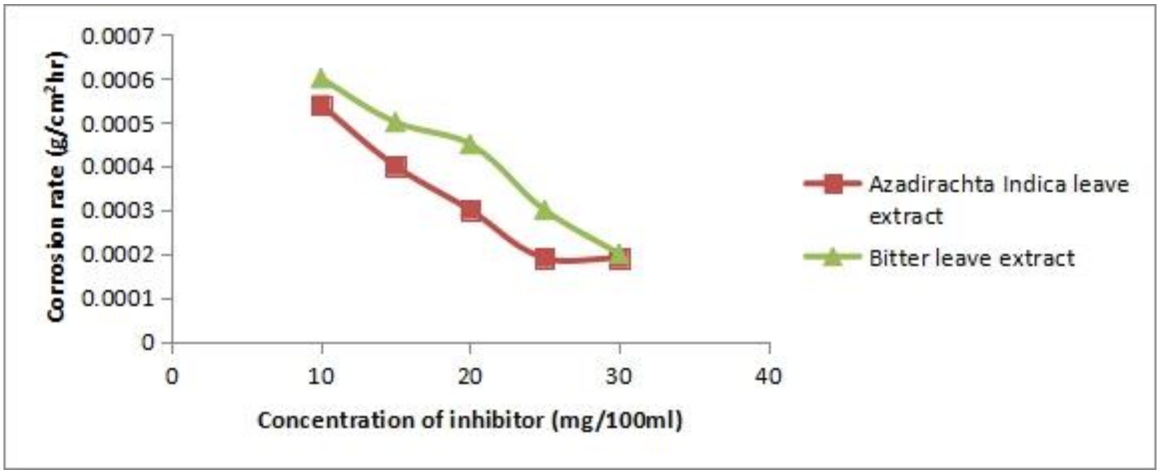

Fig 3.Effect of concentration of inhibitor on corrosion rate of mild steel in the presence and absence of different inhibitors.

3.3.4. Effect of temperature on corrosion rate

The outcome of temperature on the corrosion rate of mild steel in free acid and in the existence of different concentrations of the inhibitor (plant extract) was studied in the temperature range of 30^{o}Cto 70^{o}C with certain Conditions: Time = 6H, acid conc. = 2M, inhibitor conc. = 15mg/100ml as shown in Figure 4. It was found that the rates of corrosion of mild steel in free acid solution and in the existence of inhibitor increased with increase in temperature. This is expected because as temperature increase, the rate of corrosion of mild steel also increased as a result of increase in the average kinetic energy of the reacting molecule such as the corrosion rate decreased more for inhibited acid solution than the uninhibited acid solution with the values as $0.0054 g/cm^2hr$, $0.0052 g/cm^2hr$, $0.0067 g/cm^2hr$, $0.0043 g/cm^2hr$, $0.0041 g/cm^2hr$. The decrease in the corrosion rate for $0.0065 g/cm^2hr$, $0.0080 g/cm^2hr$, $0.0089 g/cm^2hr$, $0.0091 g/cm^2hr$ $0.0110 g/cm^2hr$ .However, the inhibited acid solution compared to the uninhibited was as a result of the mitigating effect of the plant extract on the corrosion rate of the mild steel. This result was in agreement with (Vasudha et al.,2014, Gaber et al 2020) findings at the same temperature range with decrease in the corrosion rate as$0.0055 g/cm^2hr$, $0.0056 g/cm^2hr$, $0.0043 g/cm^2hr$, $0.0040 g/cm^2hr$, $0.0039 g/cm^2hr$ the results achieved in the studied the effect of rising concentration of the leaves extract on the corrosion rate of mild steel in concentration of acid (HCL). The studied results showed that the corrosion rate of the mild steel decreases with the increase in the different concentration of the leaves extract (NorZakiah et al.,2014). This indicates that the increase of the leaves extract increases the inhibition efficiencies of the mild steel in acidic medium (Leelavathi et al., 2013, Okafor 2007, Siddiqui et al 1984)

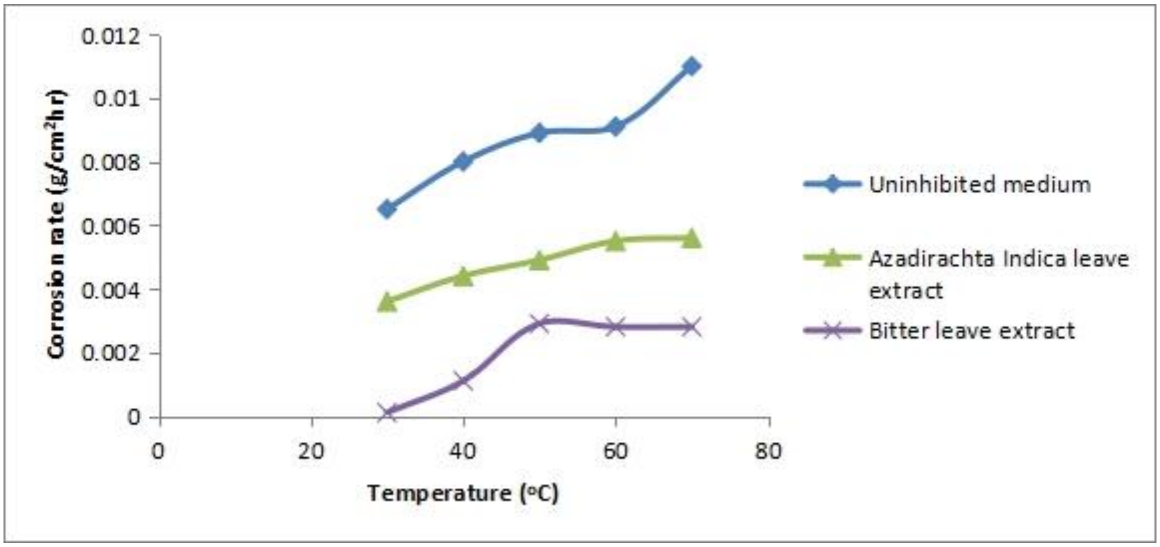

Fig.4 Effect of temperature on corrosion rate of mild steel in presence and absence of different inhibitors.

3.3.5.Three Dimensional Surface Plots of interaction effect of parameters for corrosion inhibition efficiency of carica papaya (pawpaw) leaf extract in acidic medium.

The 3D response surface plots were generated to estimate the effect of the combinations of the independent variables on the corrosion inhibition efficiency in acidic medium. The plots are shown in Figure 5 to 9.

A quadratic regression equation that fitted the data is:

$$Y_{BLE} = 94.93 + 3.06A + 3.55B - 5.62C + 0.089D - 5.48AB + 3.95AC - 0.62AD + 3.92BC + 0.95BD + 0.36CD - 2.22A^2 - 3.50B^2 - 11.02C^2 - 0.73D^2 \quad (13)$$

The model reduced to Equation 14 below after removing the insignificant terms.

$$Y_{BLE} = 94.93 + 3.06A + 3.55B - 5.62C - 5.48AB + 3.95AC - 0.62AD + 3.92BC + 0.95BD - 2.22A^2 - 3.50B^2 - 11.02C^2 - 0.73D^2 \quad (14)$$

Figure 5 displays the reliance of corrosion inhibition efficiency on concentration of inhibitor (extract) and exposure time. As can be perceive from the figure, % corrosion inhibition efficiency increases as both the exposure time and concentration of inhibitor increase. The increase in inhibition efficiency stayed at 92.88% as exposure time and concentration of inhibitor increased beyond 6hr and 15mg/100ml (Enekwe et al.,2020, Zaafarany 2013). This may be attributed to the positive significance of both variables (Equation 13). Similarly it can be observed from other researchers that inhibition efficiency increased with extract concentration by up to 85.49% at 100 g/l. This occurrence may be because, as the inhibitor increased, the amount of phytochemical compounds adsorbed on the metal surface increased (Okewole and Adesin ,2020, Olasehinde et al., 2012) .

Figure 6 displays the reliance of corrosion inhibition efficiency on concentration of inhibitor and temperature. It can be seen from the figure (Lewis 2000, El-Shamy et al.,2020) , % corrosion inhibition efficiency increases as concentration of inhibitor increases and temperature decrease. This could be as a result of negative significance of temperature which does not favour the adsorption of the inhibitor to stop corrosion (Hmamou.,2012, Box et al., 1978).

Figure 7 displays the reliance of corrosion inhibition efficiency on exposure time and temperature. It can be seen from the figure (Enekwe et al.,2020, Sanjay et al.,2009) that % corrosion inhibition efficiency increases as the temperature decreases and exposure time increases. This could be that adsorption of inhibitor on the mild steel was not favoured by temperature increase at all time considered (Hmamou.,2012 Box et al., 1978).

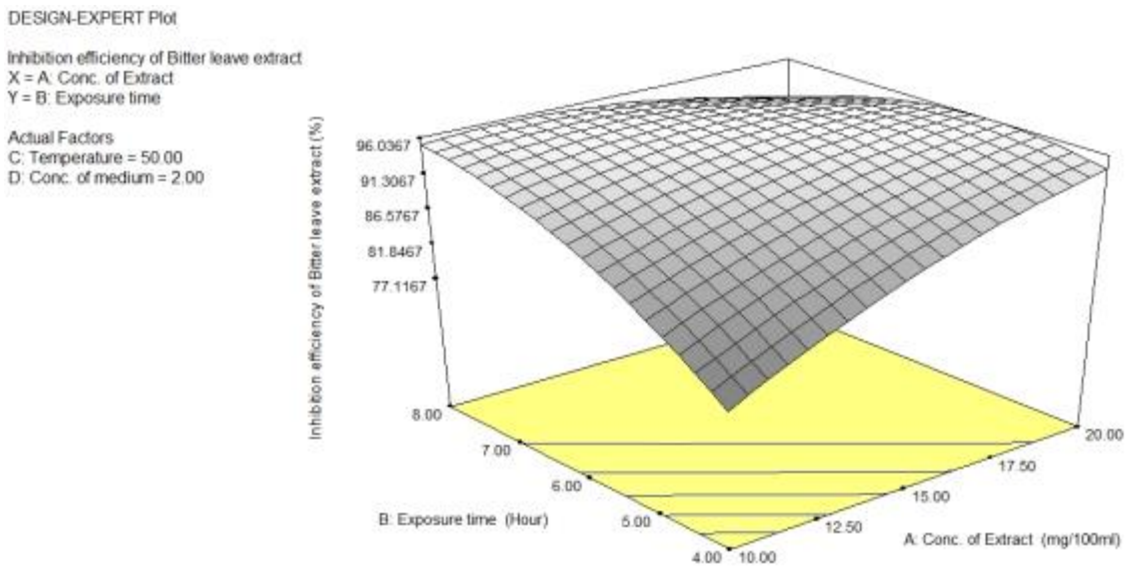

Figure 5: 3D plot showing the effect of concentration of inhibitor and exposure time on the corrosion inhibition efficiency of Veroninia Amigdanin (bitter) leaves *extract*.

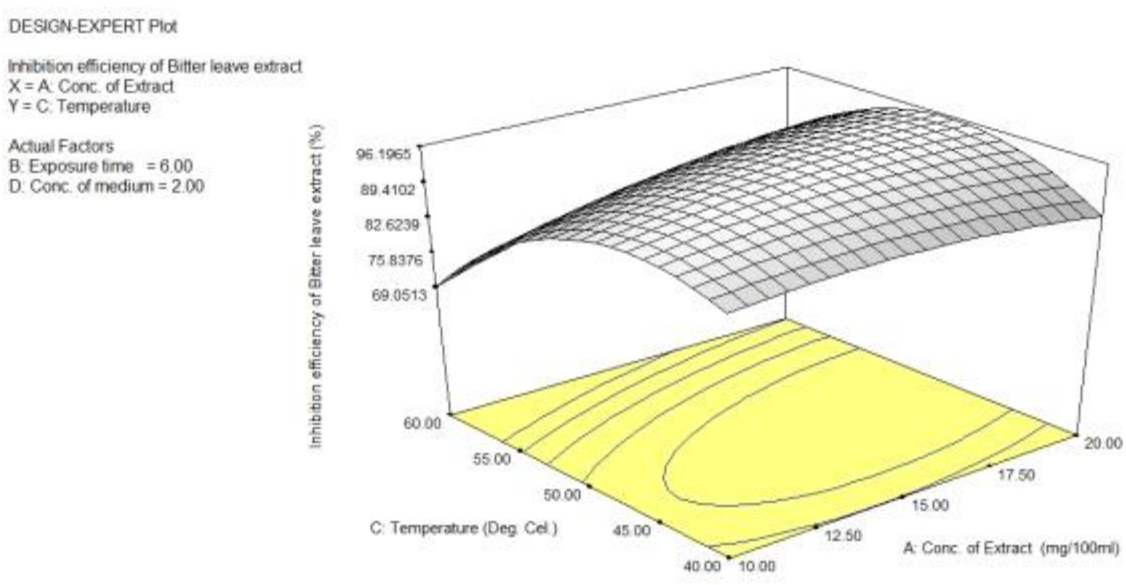

Figure 6 : 3D plot showing the effect of concentration of inhibitor and temperature on the corrosion inhibition efficiency of Veroninia Amigdanin(Bitter) leaves *extract*.

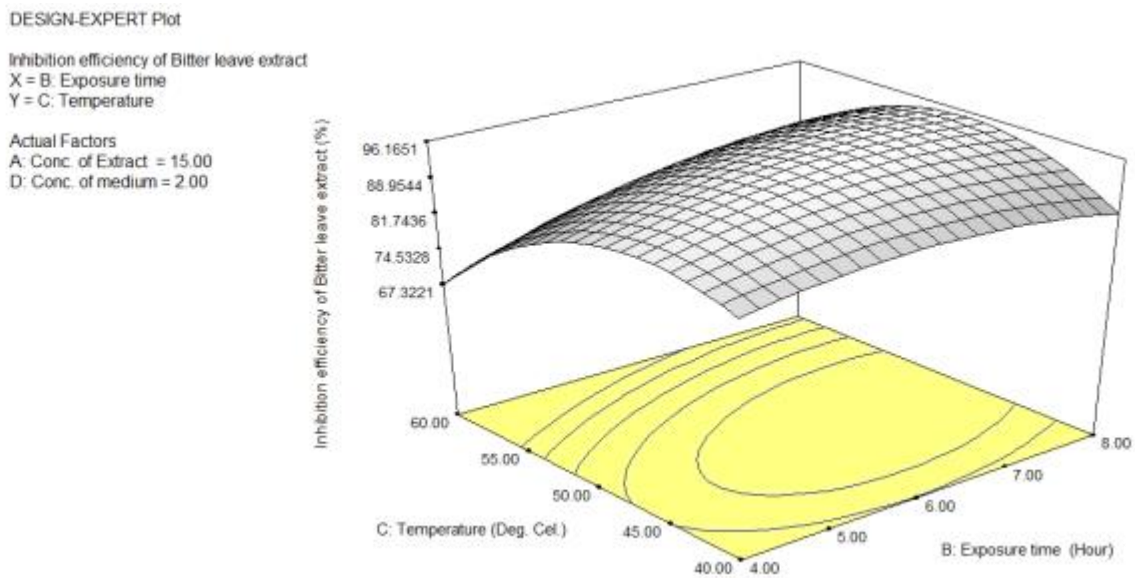

Figure 7 : 3D plot showing the effect of temperature and exposure time on the corrosion inhibition efficiency of Veroninia Amigdaninn (Bitter) leaves *extract*.

3.3.6.**Three Dimensional Surface Plots of interaction effect of parameters for corrosion inhibition efficiency of Azadirachta indica leaves extract in acidic medium**

The 3D and contour response surface plots were generated to estimate the effect of the combinations of the independent variables on the corrosion inhibition efficiency in acidic medium. The plots are shown in Figure 11 to 16.

A quadratic regression equation that fitted the data is:

$$Y_{AILE} = 82.58 + 3.13A + A^{2}.26B - B^{2}78C + (C^{2}8D - 5D^{2}3AB + 3.81AC - 1.02AD + 4.10BC + 0.69BD + 0.50CD - 2.50 \quad - 3.75 \quad - 10.88 \quad - 0.70 \qquad (15)$$

Figure 8 displays the reliance of corrosion inhibition efficiency on concentration of inhibitor (extract) and exposure time. As can be observed from the figure (Enekwe et al.,2020, Hmamou.,2012, Sanjay et al.,2009, , Zaafarany 2013), % corrosion inhibition efficiency increases as both the exposure time and concentration of inhibitor increase. The increase in inhibition efficiency stayed constant (80.42%) as exposure time and concentration of inhibitor increased beyond 6hr and 15mg/100ml. . This may be attributed to the positive significance of the both variables (Equation 15).

Figure 9 displays the reliance of corrosion inhibition efficiency on concentration of inhibitor and temperature. As can be observe from the figure(Enekwe et al.,2020, Hmamou.,2012, Sanjay et al.,2009, , Zaafarany 2013) , % corrosion inhibition efficiency increases as concentration of inhibitor increases and temperature decrease. This could be as a result of negative significance of temperature which does not favour the adsorption of the inhibitor to stop corrosion.

Figure 10 displays the reliance of corrosion inhibition efficiency on exposure time and temperature. As can be observe from the figure, % corrosion inhibition efficiency increases as the temperature decreases and exposure time increases. This could be that adsorption of inhibitor on the mild steel was not favoured by temperature increase at all time considered (Enekwe et al.,2020, Hmamou.,2012, Sanjay et al.,2009, , Zaafarany 2013) .

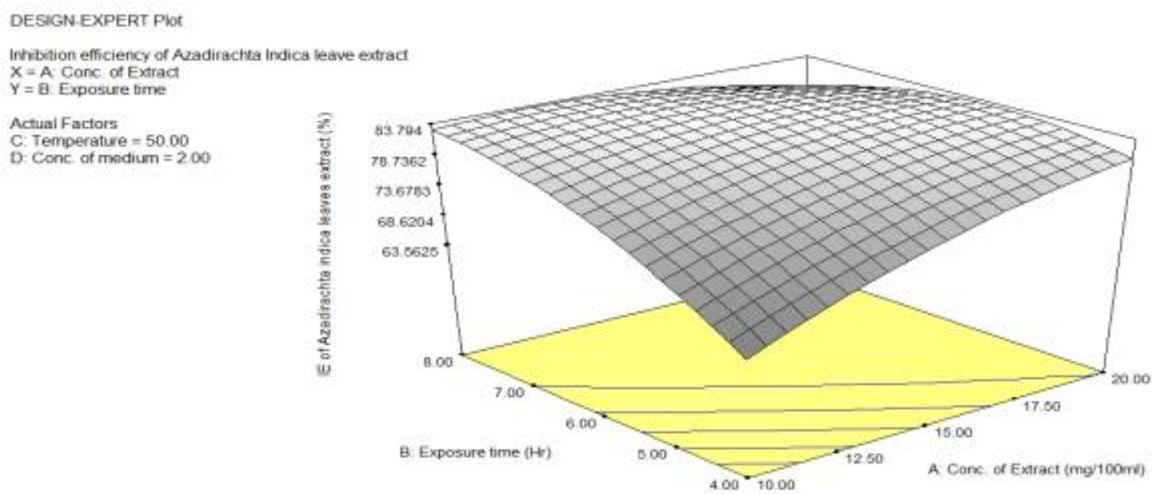

Figure 8 : 3D plot showing the effect of concentration of inhibitor and exposure time on the corrosion inhibition efficiency of Azadirachta indica leaves extract.

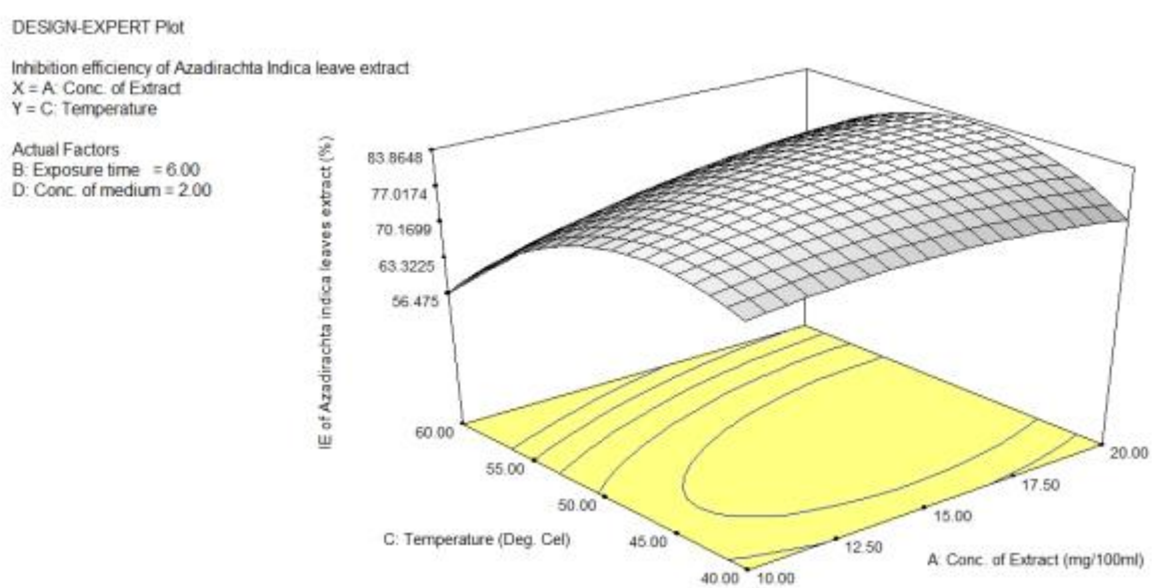

Figure 9: 3D plot showing the effect of concentration of inhibitor and temperature on the corrosion inhibition efficiency of Azadirachta indica leaves extract.

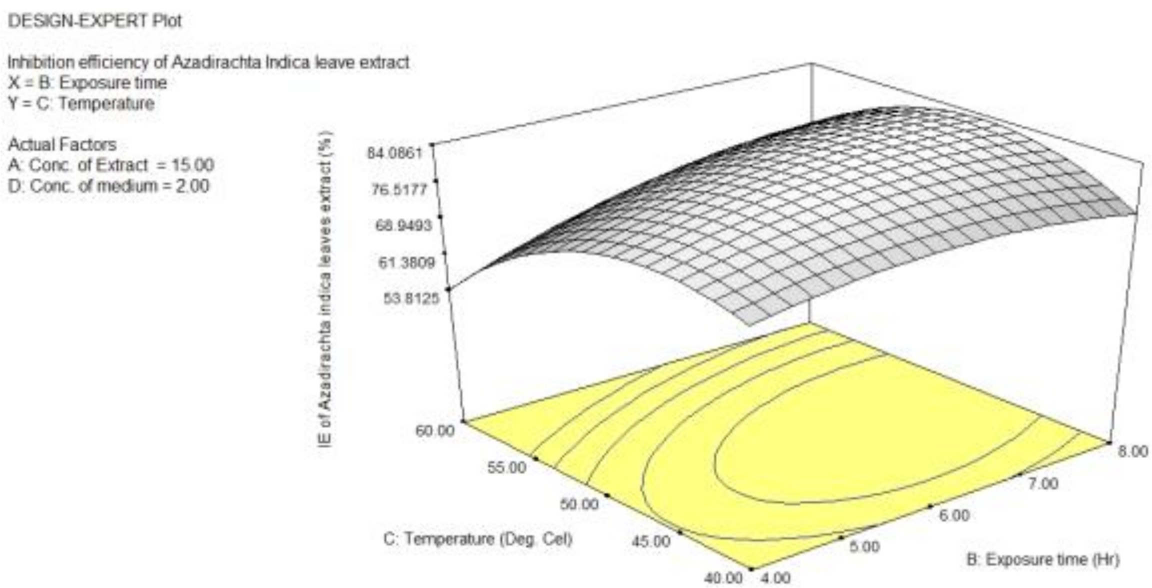

Figure 10: 3D plot showing the effect of temperature and exposure time on the corrosion inhibition efficiency of Azadirachta indica leaves extract.

3.3.6. Optimal Conditions for corrosion inhibition of Veroninia Amigdaninn (Bitter) leave extract

According to Igwilo et al.,2021**,** Optimization is concerned with selecting the best among the entire set by efficient quantitative methods. The goal of optimization however, is to find the values of the variables in the process to yield the best value of the performance criterion.

The inhibitive effect of Veroninia Amigdaninn (Bitter) leave extract was optimized using CCD of RSM and the following optimal conditions were obtained: concentration of inhibitor is 18.84mg/100ml, time is 5.55hr, temperature is 47.9^{o}C. The inhibition process under the obtained optimum operating conditions was carried out in order to evaluate the precision of the model; the experimental value and predicted values are shown in Table 6. Comparing the experimental and predicted results, it can be seen that the error between the experimental and predicted is 0.5%, therefore it can be concluded that the generated model has sufficient accurancy to predict the corrosion inhibition efficiency. Similar result was obtained by (Challouf et al., 2016, Davis and Fraunhofe,2003, Gaber et al.,2020, Peasura,2005) such as concentration of inhibitor is 18.77mg/100ml, time is 6.35hr, temperature is 48°C and acid concentration is 2.2M.

Table 6.Results of the Model Validation (Experiment 1 Indicates the Optimum Inhibition Process Conditions and Corrosion Inhibition Efficiency of Veroninia Amigdanina Extract in Acidic Medium

Experiment	Concentration ofinhibitor/extract (mg/100ml) A	Exposure time (Hour) B	Temperature (°C) C	Experimental inhibition efficiency %	Predicted inhibition efficiency (%)
1	18.84	5.55	47.9	95.1	96.4

3.3.8..Optimal Conditions for corrosion inhibition of Azadirachta indica leaves leave extract

The inhibitive effect of Azadirachta indica(neem) leave extract was optimized using CCD of RSM and the following optimal conditions were acquired: concentration of inhibitor is 12.30mg/100ml, time is 7.90hr, temperature is 47.4°C. The inhibition process under the acquired optimum operating conditions was carried out in order to evaluate the precision of the quadratic model; the experimental value and predicted values are shown in Table 7 Comparing the experimental and predicted results, it can be seen that the error between the experimental and predicted is 2.0%, therefore it can be concluded that the generated model has sufficient accurancy to predict the corrosion inhibition efficiency. This was a similar result obtained by(Challouf et al., 2016, Davis and Fraunhofe,2003, Gaber et al.,2020, Peasura,2005) , such as concentration of inhibitor is 12.10mg/100ml, time is 7.50hr, temperature is 47.3°C and acid concentration is 2.37M.

Table 7: Results of the Model Validation (Experiment 1 Indicates the Optimum Inhibition Process Conditions and Corrosion Inhibition Efficiency of Azadirachta indica leaves Leave Extract in Acidic Medium)

Experiment	Concentration of inhibitor/extract (mg/100ml) A	Exposure time (Hour) B	Temperature (°C) C	Experimental inhibition efficiency (%)	Predicted inhibition efficiency (%)
1	12.10	7.50	47.3	82.9	84.9

3.3.9. SURFACE MORPHOLOGICAL STUDIES OF THE MILD STEEL.

The surface morphology of the mild steel was studied using Sigma Field Emission Scanning Electron Microscope and the images at 200µm of the plain mild steel surface and its surface in absence and presence of inhibitors respectively are shown in Figures 11, 12 and 13. (Muthukrishnan et al., 2014). SEM picture helps in examining surface contaminations, provides qualitative chemical analyses and identifies crystalline structures (Anadebe et al.,2018, Odejobi and Akinbulumo 2016). It was observed that there is structural distinction of the mild steel in non-existence and existence of the extracts with, a rapidly oxidized surface in the uninhibited medium (Leelavathi and Rajalakshmi,2013, Mousavi et al.,2011, Munis et al.,2020, Olawale et al.,2018, Pal et al.,2019,). The SEM images also revealed that the mild steel specimen immersed in presence of inhibitor is in better condition having a smooth surface covered with adsorbed inhibitor while the metal surface immersed in blank acid solutions is rough and appeared like full of pits, cracks and cavities (Chang et al.,2020,Fu et al.,2010, Shukla et al.,2009, Vijayalakshmi et al.,2011)

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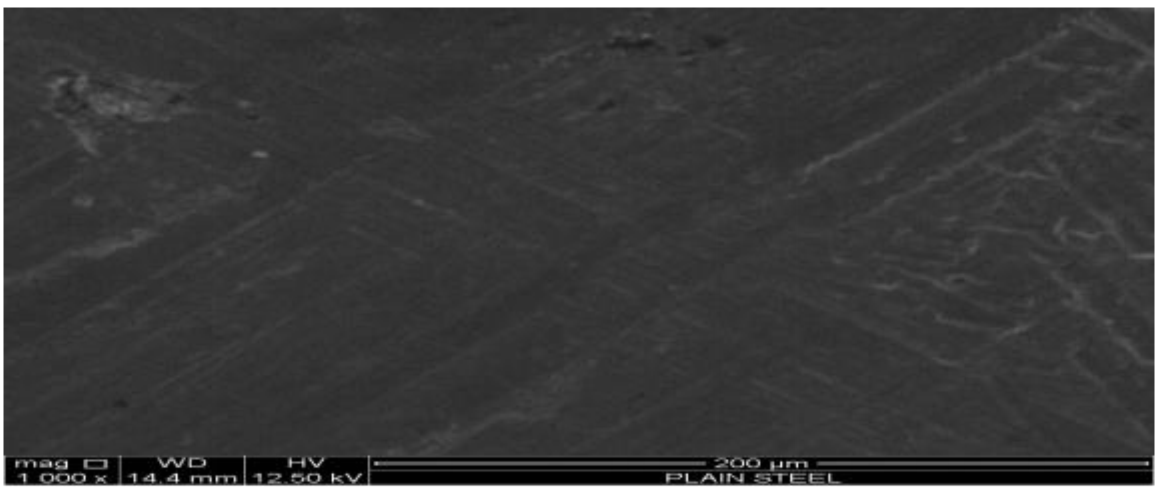
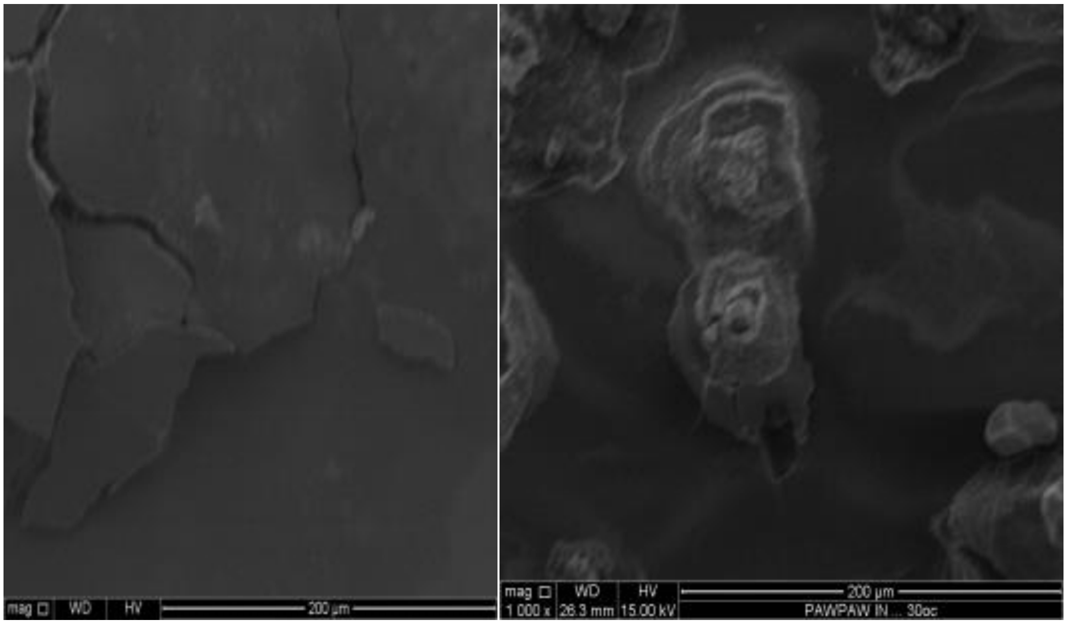
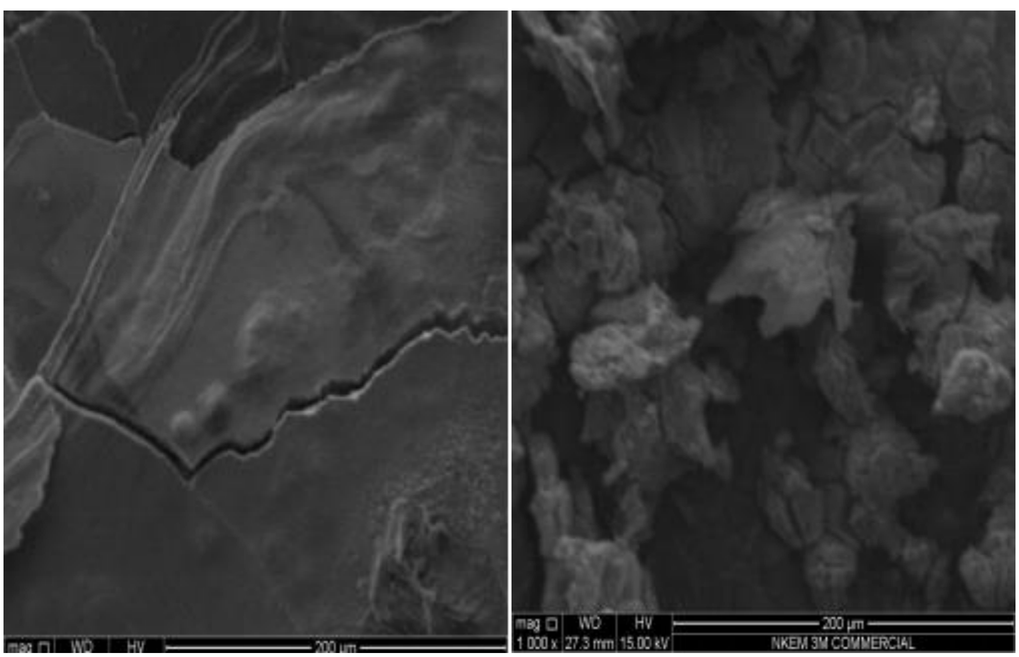


Figure 11: SEM images of mild steel coupon



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

Figure 12: SEM images of absence and presence of Veroninia Amigdaninn(BLE).



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

Figure 13: SEM images of absence and presence of Azadirachta indica(AILE).

4.0.Conclusion

It can be concluded from the study that ethanol extract of Veroninia Amigdaninn and of Azadirachta indica leave are adsorption inhibitors for the corrosion of mild steel in acidic medium. The inhibition efficiency of ethanol extracts of the leaves was due to the photochemical constituents of the extracts. The optimal conditions are: concentration of inhibitor 18.38mg/100ml, time, 5.55h, and temperature 47.9°C, concentration of inhibitor 12.30mg/100ml, time, 7.90h, temperature 47.4°C. The optimal conditions obtained gave inhibition efficiencies of 96.4% and 84.9% % in Veroninia Amigdaninn leave extract and Azadirachta indica leave inhibited acid media respectively. This signifies that leaves extracts can inhibit corrosion of mild steel in acidic medium. The study has shown that environmentally acceptable inhibitors are always preferred over nontoxic organic inhibitors.

RECOMMENDATIONS

The economic viability of producing environmentally acceptable inhibitors and their usage for corrosion inhibition of metals should be harnessed in Nigeria. Industrial sector such as oil companies should take up measures to use green inhibitor in minimizing or controlling corrosion. More research on green corrosion inhibitors should be sponsored by government to encourage domestication of the technology and enhance industrialization.

Abbreviations:

AAS	Atomic Absorption Spectrometer
ASTM	American Society for Testing and Materials
AILE	Azadirachta Indica Leaves Extract(neem)
FTIR	Fourier Transform Infra-Red Spectrophotometer
BLE	Veroninia Amigdaninn leave extract(bitter leave)
SEM	Scanning Electron Microscope

REFERENCES

Anadebe CV,Onukwuli D.O, Omotioma M, et al.(2018). Optimization an electrochemical study on the control of mild steel corrosion in hydrochloric acid solution with bitter kola leaf extract as inhibitor. S. Afr. J. Chem.2018; 71:51–61.

Ajayi, O.O., Omotosho, O.A.and Ifepe, V.O., (2011). Acid Failure of Mild Steel in 2MSulphuric Acid in the Presence of Vernonia amygdalina .*Journal Mater.Environmental Science.* 2 (2), 186-195.

Alaneme KK, Daramola YS, Olusegun SJ, et al.(2015). Corrosion inhibition and Adsorption characteristics of rice husk extracts onmild steel immersed in 1M H2SO4 and HCl solutions. *Int. J. Electrochem. Sci.* 50,3553–3567.

Ashworth, C. J. and Booker, L., (2001). *Cathodic protection theory, Institution of Corrosion Science and Technology*, New York: McGraw-Hill.

Awe, I., Caroline, A. S., Ibrahim, H. K., Kareem ,A. G.and Adams, S. M (2015).Inhibitive Performance of Bitter Leaf Root Extract on Mild Steel Corrosion in Sulphuric Acid Solution.*American Journal of Materials Engineering and Technology*. 3(2), 35-45.

Bardal, E., (2003).*Corrosion and Protection.Springer.*New York..131-132.

Baran E, Cakir A, Yazici B(2016).. Inhibitory effect of Gentian a Olivier extracts on the corrosion of mild steel in 0.5M HCl: electrochemical and phytochemical evaluation. Arab. J. Chem.12, 4303–4319.

Baorong. Hu, Xiaogang. Li, Xiumin. Ma, Cuiwei. Du, Dawei. Zg, Meng. Zg , Weichen.Xu Dongzhu. Lu, Fubin. Ma. *The cost of corrosion in China, npj Mater. Degr* 1(2017)1:4.

Bendahou M.A, Benadellah M.B and Hammouti B.B (2007). A study of Rosemary oil as green corrosion inhibitor for steel in 2M H3PO4. Pigment and Resin Technology.

35,9-10.

Box G.E, Hunter W.G and Hunter J.S.(1978). Statistics for experimenters: an introduction to design, data analysis, and model building.1,JSTOR.

Brunner J.H.(1994). Direct spectrophotometer determination of saponin. Journal of Animal Chemistry. 1994; 34: 1314-1326.

Busayo T.A, Emmanuel O.F, Julius A.U, et al.(2020). Corrosion Control of Mild Steel in Sulphuric Acid by Athyrium filix-femina Leaf Extract Green Inhibitor. Chemical Science Review and Letters Research Article. Chem Sci Rev Lett .2020; 9: 869-88.

Challouf H, Souissi N, Messaouda M.B, et al(2016). Origanum majorana extracts as mild steel corrosion green inhibitors in aqueous chloride medium. J. Environ. Protect.7:532–544.

Davis D.G, Fraunhofer J.A.(2003). Tobacco Plant Extracts as Environmentally Benign Corrosion Inhibitors. Mater. Perform.42:56–59

Evrim .B, Ahmet .C, Yazici B, (2016). Inhibitive effect of Gentiana olivieri extracts on the corrosion of mild steel in 0.5M HCl: Elecrtrochemical and photochemical evaluation. Arabin Journal of Chemistry. 12(8), 1-16.

Ejikeme,P.M; Umana, S.G; Menkiti, M.C; Onukwuli, O.D, (2015).Inhibition of mild steel and aluminium corrosion in 1M H2SO4 by leaves extract of African breadfruit. *International Journal of material and chemistry* 5(1), 14-23.

Ebenso, E.E., Ekpe, U.J., Umoren, S.A., Jackson, E., Abiola, O.K., and Oforka,N.C., (2006). Synergistic effect of halide ions on the corrosion inhibition of aluminium in acidic medium by some polymers,*Journal of Applied Polymer Science.*100 (4), 2889-2896.

Ebenso E.E, Eddy O.N and Odiongenyi O.A.(2008). Corrosion inhibitive properties and adsorption behavior of ethanol extract of piper guinensis as a green corrosion inhibitor for mild steel in H_2SO_4. African Journal of Pure and Applied Chemistry. 2, 107-115.

El-Naggar, M.M., (2007). Corrosion Inhibition of Mild steel in acidic medium by some Sulfa drugs compound.*Corrosion Science*, 49, 2226-2236.

Enekwe C.B,Chime T.O, Osoka E.(2020). Optimization and Effect of leaves Extracts on Corrosion of mild Steel in acidic medium. *International journal of Bioscience, Biochemistry and Bioinformatics*.10,117-126.

Fan. Z, Pengfei. J.U , Pan. Me , Huang. Ya , Gu. Li , Li. Xi, (2018).Self healing mechanisms in smart protective coatings, *A review Corrosion Science* 144:74-88.

Fontana, M.G., (1999). *Corrosion Engineering,(3rd ed)*. New York: McGraw-HillBook.

Gaur, B and Srinivasan, H.S., (2002).Corrosion of metals and alloys in Methane Sulphonic acid,*British Corrosion Journal*, 34 (1): 63-72.

Gaber M.A, Rahal T.H, Beqai T.F.(2020). Eucalyptus leaf extract as a eco-friendly

corrosion inhibitor for mild steel in sulfuric and phosphoric acid solutions. *Int. J. Integrated Care.* 11,123–132.

Hassan K.H, Khadom A.A and Kurshed N.H (2016). Citrus aurantium leaves extract as a

sulfuricacid. *S. Afr. J. Chem. Eng*. 22, 1–5.

Hawraa Khaleeli A and Amjed A.A (2018). The Effect of Temperature and Inhibitor on Corrosion of Carbon Steel in Acid Solution under Static Study. *International Journal of Applied Research.*13:3638-3647.

Ita, B.I.,(2004). 4-Formylmorpholinehydrazone and 4-Formylmorpholine: A New Corrosion Inhibitors for Mild Steel in 0.1MHCl solution.*Proceedings of Chemical Society of Nigeria*. 34, 52-56.

Joshua,E.J.,(2016). Cost of corrosion Annually in the US over $1.1 Trillion.*Analysis by G2MT laboratories*.20(2).

Krishnamurthy, N., Vallinayagam, P.,and Madhavan, D., (2014).*Corrosion of steels and environment (3rd ed)*. PHI Learning Pvt Ltd .

Kerri, B., (2013). *Corrosion Engineering: Principles and Solved Problems(3rded)*.New York John Wiley and Sons.

Lewis, l., (2000).Corrosion resistance of technical ceramics.*International Journal of corrosion*, 2(4) 187-198.

Leelavathi, S and, Rajalakshmi, R., (2013).Dodonaea viscosa (L.) Leaves extract as acid Corrosion inhibitor for mild Steel – A Green approach.*Journal of Material and Environmental Science*, 4(5), 625-638.

Loto CA.(2003). The effect of bitter leaf extract on the inhibition of mild steel in HCl and H2SO4, *Corrosion Prev. & Control.* 50,43-49.

Mahalakshmi, D.; Hemapriya, V.; Subramaniam, E.P.; Chitra, S.,(2019). Synergistic effect of antibiotics on the inhibition property of aminothiazolyl coumarin for corrosion of mild steel in 0.5 M H2SO4. *J. Mol. Liq*. 284, 316–327. [CrossRef]

Moudgil, H.K., (2014). *Textbook of Physical Chemistry. New York:* PHI Learning Pvt.Ltd. Science.

Mousavi M, Mohammadalizadeh M, Khosravan A.(2011). Theoretical investigation of corrosion inhibition effect tof imidazole and its derivatives on mild steel using cluster model. *Corros. Sci.*2011;53:3086–3091

Munis A, Zhao T, Zheng M, et al.(2020). A newly synthesized green corrosion inhibitor imidazoline derivative for carbon steel in 7.5% NH4Cl solution. *Sustain Chem. Pharm.*2020;169

Nnanna A.L, Owate O.I and Nwadiuko C.O,et al.2013. *International Journal of materials and*

Chemistry.(3)10-16.

Ngobiri, NC; Akaranta, O; Oforka, NC; Oguzie, EE; Ogbulie, SU, (2013). Inhibition of pseudoanaerobic corrosion of pipeline steel in pipeline water using biomsa-derived molecules, *Advances in materials and corrosion.* 2, 20-25.

Njoku I. D, Njoku C.N, Lgaz .H, Okofor P.C, Oguzie E.E, Ying Li, (2021). Corrosion protection of Q235 steel in acidic-chloride media using seed extracts of Piper guineense. *Journal of Molecular liquids.* 330(2021)115619.

Odejobi O.J,and Akinbulumo O.A. Modeling and Optimization of the inhibition Efficiency of Euphorbia heterophylla Extracts Based Corrosion Inhibitor of Mild Steel Corrosion in Hcl Media Using a Response Surface Methodology.2016; 54: 217-232.

Okewole A.O, Adesina A.O.(2020). Kinetic and thermodynamic study of corrosion inhibition of mild steel in 1.5 M HCl medium using cocoa leaf extract as inhibitor. *Journal of Applied Science and Environmental Management.* 24,37-47.

Olawale,o., Idefob,C,K, Ogunsemi,B.T,Bello,J.O et al.,(2018). Evaluation of Groundnut leave extract as corrosion inhibitor of mild steel in 1M sulphuric acid using Response Surface Methodology(RSM). *International Journal of Mechanical Engineering Technology(IJMET)*. 9(11),829-841.

Onukwuli, O.D., Monday, O., 2016. Optimization of the inhibition efficiency of mango extract as corrosion inhibitor of mild steel in 1.0M H2SO4 using response surface methodology. *J. Chem. Technol. Metall*. 51 (3), 302–314.

Omotioma, M., Onukwuli, O.D.,(2017). Evaluation of pawpaw leaves extract as anticorrosion agent for aluminium in hydrochloric acid medium. Niger. *J. Technol*. 36 (2), 496–504.

Oyewole, O., Oshin, T.A.,and Atotuoa, B.O.,2021. Corchorus olitorius stem as corrosion inhibitor on mild steel in sulphuric acid. Journal homepage:www.cell.com/heliyon. *Heliyon* 7(2021) e06840.

Okafor C.P.(2007).'Eco-friendly corrosion inhibitors: inhibitive action of ethanol extracts of Garcinia kola for the corrosion of mild steel in H2SO4 solutions', Pigment Resin Technol. 36,34-42.

Olasehinde ,E. F., Olusegun S. J., Adesina, A. S., Omogbehin S. A, and Momoh-Y.H., (2013). Inhibitory Action of Nicotiana tabacum Extracts on the Corrosion of Mild Steel in HCl: Adsorption and Thermodynamics Study. *Nature and* Science, 11(1), 83-90.

Onen, A.I., (2006). Influence of Halide ions on the Corrosion Inhibition of Aluminium in H_2SO_4 using Alizarin Red. *Nigerian Journal of Polymer Science and Technology,*5 (1): 357-371.

Othaki, E.P. and Ngobiri, N.C.,(2020). Inhibition of pipeline Steel Corrosion in 0.5M H_2SO_4 using Coltyledon of Chysophyllum Albidum. *J.App. Sci. Environ. Manage*.24(4) 691-697.

Pal S,Lgaz S, Tiwari P, et al.(2019). Experimental and theoretical investigation of aqueous and methanolic extracts of Prunus dulcis peels as green corrosion inhibitors of mild steel in aggressive chloride media. *J. Mol. Liq*. 276:347–361.

Peckner, D., and Bernstein, I.M., (2000). *Handbook of Stainless Steel.* New York: McGraw-Hill.

Procter, R.P.M., (2000). *Effects of Metallurgical structure on Corrosion*.,(*3rd ed).* Great Britain: Butterworth Heinemann.

Prasanna .M.B, Praveen .M.B, Hebbar N, et al. 2016. Inhibition study of mild steel corrosion in 1M hydrochloric acid solution by 2-chloro 3-formyl quinolone. Int J Ind. Chem. 7, 9–19.

Pourbaix, K., (2002). *Corrosion of Metals: Physicochemical Principles and CurrentProblems.* New York: John Wiley and Sons .

Perez, N., (2004). *Electrochemistry and Corrosion Science, (2nd ed).* Oxford Butterworth-Heinemann.

Rajendra, S., Apparao, B.V., and Palaniswamy, N.,(2000).Mechanism of Corrosion Inhibition by the 2-Chloroethyl phosphonic acid-Zn^{2+} system. Anti-corrosion. Methods and materials.*Journal of Material and Environmental Science,*47: 147-158.

Rawat, N.S., Udayabhanu, G., and Arora, R.K., (1985).Mechanism of Corrosion Inhibition of Mild Steel in Acid Medium.*Transactions* SAEST, 20 (2): 104-109.

Roberge, P.R., (2008). *Corrosion Engineering: Principles and Practice.*New York: McGraw-Hill.

Sanjay SK, Ackmez M, Gargi J, et al.(2009). Corrosion inhibition of Neeem (Azadiracha indica) leaves extract as a green corrosion inhibitor for Zinc in H_2SO_4. 2: 47-51.

Strehblow, K.O and Oforka, N.C., (2004). Inhibition of Corrosion of Mild Steel in HCl using Leaves Extract of Nypa Fruticans Wurmb. Material Letter.58 (11): 57-68.

Shreir, L.L., (2000). *Basic Concepts of Corrosion.(3rd ed).*Great Britain: Butterworth Heinemann.

Shreir, L.L, Jarman RA,and Burstein, G.T., (2000). Corrosion: 1(3rd ed). Oxford Butterworth-Heinemann.

Shukla SK, Singh AK, Ahamad I, et al(2009).. Streptomycin: A commercially available drug as corrosion inhibitor for mild steel in hydrochloric acid solution. Material Letters. 63:819-822.

Siddiqui S, Faizi S and Siddiqu S.B (1984). Studies on the chemical constituents of Azadirachita bindica.A. Juss (Meliaceae):Isolation and structure of a new nortriterpenoid nimolicinol, Heterocycles, 22:295.

Tromans,,E.and Helmult, K., (2011). *Corrosion of Metals, Physicochemical Principlesand Current Problem.* Great Britain: Butterworth Heinemann.

Uhlig, H.H., (2000).*Corrosion and Corrosion Control (3rded).* New York: John Wiley and Sons.

Vasudha VG, Priya SK, (2014). Corrosion inhibition of mild steel in H2SO4 media using Polyalthia longifolia leaves. *Chem. Sci. Rev. Lett.* 2, 435–443.

Vijayalakshmi PR, Rajalakshmi R, Subhashini S.(2011). Corrosion inhibition of aqueous extract of Cocos nucifera– Coconut palm-petiole extract from destructive distillation for the corrosion of mild steel in acidic medium. Portugaliae Electrochimica Acta. 29: 9- 21.

Wang, W., Free, M.L., andHorsup, D., (2005). Prediction and Measurement of Corrosion Inhibition of mild steel by imidazoline in brine solutions. *Metallurgical andMaterial Transactions*,36(2),335-341.

Xiaogang. Li Dawei. Zg , Zhiyong. Lu, Zhong. Li, Cuiwei. Du, Chaofang. Dg, (2015). Materials science: *share corrosion data* . *Nature* 527:441-442.

Yuliet, E. M.S., and Abdullah, R.M., (2014). Kinetic study of corrosion Inhibition Aluminium in Chloroacetic acids. *Bulletin of Chemical Society ofFrance.*3: 297-309.

Yadav, P.N.S., (1999). Molecular Structure of Heterocyclic compounds and their Inhibitive Action for Corrosion of Grade 1100 Aluminium in dilute HCl. *British Corrosion Journal,*34 (1): 51 -56.

Zaafarany I.(2013). Corrosion inhibition of mild steel in hydrochloric acid Solution using cationic surfactant olyel-amido derivatives, *International Journal of Electrochemical Science*. 2013; 8: 9531-9542.

Zumdal, Z. A.,(2010).*Principles of Corrosion Engineering and Corrosion Control.* New York: John Wiley and Sons.