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GREEN CORROSION INHIBITION AND ADSORPTION CHARACTERISTICS OF MAIZE HUSK POLAR EXTRACT ON MILD STEEL IN HCL ACID ENVIRONMENT

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Abstract

This research is directed to the use of green corrosion inhibitor (maize husk polar extract) in controlling corrosion on mild steel. Inhibition and adsorption properties of *Maize Husk Polar* Extract, corrosion inhibition efficiency of mild steel in 1.5M of HCL solution at various exposure time, MHPE concentration was investigated at atmospheric temperature using weight loss test (gravimetric analysis) method with Vacuum rotary evaporator at 79°C The result gotten from the vacuum rotary evaporator is 23.99% concentration (mg/100g) from 600.52grams of Maize Husk. Phytochemical analysis revealed the presence of Alkaloids, Flavonoids, Phenolics, Phenolics, Phytates, Saponins, Terpenoids, Anthocyanins, Steroids, and Tannins in the extract. The behavior of MHPE is spontaneous and the physical adsorptions obeys Fourier Transform Infrared Spectroscopy (FTIR), results shows that Maize Husk Polar Extract contains possible compounds with complex structures which are responsible for corrosion inhibition. The results for 384 hours show that the inhibition efficiency increases significantly up to 93.6% for HCL (gravimetric analysis). MHPE appears to be a good inhibitor for corrosion control in HCL; FTIR analysis revealed the amount of detectable functional organic inhibitor in the corrosion product.

KEYWORDS: HCL, Maize Husk Polar Extract, (MHPE) Corrosion, Inhibitor, Fourier Transform Infrared Spectroscopy (FTIR).

1. Introduction

In many industrial operations, the addition of inhibitors to process fluids to minimize the rate of metal corrosion is very common. Chemicals are usually applied on metal surfaces as part of the final finishing procedures prior to plating, painting, or storage (Bentiss et al., 1999). According to (Patricia et al. 2017), the chemicals are capable of removing scales, soil and light rust from the metal surfaces. Apart from this, they often contained about 1 % organic corrosion inhibitors by volume of the acid such as hydrochloric acid. Synthetic inhibitors have been widely applied to protect metal surfaces against corrosion (Zhang et al., 2012; Markhali et al., 2013). However, these inhibitors are toxic, expensive with environmental and safety issues. Alternative sources including natural products, extracts from plants, and other environmental benign organic sources have been widely reported (Sharma et al., 2015). A corrosion inhibitor is a substance which when added in small concentrations to an environment, effectively reduces the corrosion rate of the metal exposed to that environment (Patni et al., 2013). Corrosion inhibitors are commonly added in small concentrations to acids, cooling water, steam and other environments; either continuously or intermittently to reduce corrosion. Corrosion inhibitors reduce the rate of corrosion by adsorption of ion molecules onto the metal surface, increasing or decreasing the anodic and/or cathodic reaction, decreasing the diffusion rate for reactants to the surface of the metal and decreasing the electrical resistance of the metal surface (Amitha et al., 2012) . Chemical based corrosion inhibitors have been successfully used to control the corrosion of metals and alloys in various media (Amuda et al., 2008; Loto et al., 2014; Guzman et al., 2009) . However, due to the high toxic nature of chemical based corrosion inhibitors (Ezemonye et al., 2006) , there is need to develop environmentally acceptable and inexpensive green corrosion inhibitors. Green corrosion inhibitors are cheap, ecologically friendly and possess no threat to the environment (Umoren et al., 2008) . There are numerous reports on the use of extracts from plants to control the corrosion of mild steel in several media. Plants represent a class of interesting source of compounds currently being explored for use in metal corrosion protection in most systems, as possible replacement of toxic synthetic inhibitors. Hence, maize husk polar extract has a good characteristic as a corrosion inhibitor owning to the fact that it contains inhibitive components such as phenols, tannins, saponins, anthraquinones, cardiacglycosides, and phlobatannin. There are virtually little or no reports in literature on the use of maize husk polar extract as a corrosion inhibitor on mild steel which necessitated this study.

2. Materials and Experimental Procedure:

Maize husk were bought from Mammy market in Warri, Nigeria, washed, cleaned of dirt's and chopped into small pieces, dried in the open air until they were properly dried, as shown on plate 1 and plate 2. This took 5 days. The dry peels were then ground with mechanical blender. 600.52g of maize husk was then put in a liter of macerator containing 80% methanol. The mixture was stirred in macerator for 1 day, and the result was subsequently filtered by using filter paper. The filtrate was put in a vacuum rotary evaporator at a temperature of 54°C to 55 $^{\circ}$C to obtain maize husk concentrate. The result of the extract was put in bottle**.** Analysis to determine the presence of tannin was conducted on the maize husk with a mixture of methanol and ferric chloride. The change in colour on maize husk to olive-green indicates the presence of tannin The crude extract of the maize husk was fractionated to obtain the polar extract. The phytochemical analysis of maize husk polar extract (MHPE) has the results shown in Table 1 . The fractionation was conducted using 15% of hexane, and 15% of ethyl acetate mixture. Finally, the remaining ethyl acetate fraction was obtained as the *polar extract of the maize husk*. This polar extract was then used as the corrosion inhibitor.

Method Employed in the Research Work

Gravimetric analysis (weight loss), FTIR of the corrosion product and the extract, adsorption, phytochemical analysis were the various methods employed for the purpose of this work. The maize husk polar extract is the green inhibitor identified and used for corrosion control in diluted hydrochloric acid (1.5mole of HCL). The presence of the most inhibitive property was identified. Vacuum rotary evaporator was used to determine the concentration of the extract at 79°C.

The efficiency of the inhibitor was calculated using the gravimetric analysis

The weight loss test method was used to study the corrosion inhibitor. The mild steel (specimens) were manually polished with silicon carbide abrasive paper, greased to avoid further corrosions and degreased with petroleum ether, washed in distilled water and dried.

Each metal coupon is size 2cm x 3cm x 0.12cm. Before polishing, a hole of about 0.4cm was drilled on each coupon. The coupon is suspended with the aid of nylon thread and glass
rod in a 100ml beaker with 100ml of the 1.5M HCl without and with different concentrations of the inhibitor. To prevent evaporation of solution and contamination, the corrosion vessel was covered with paraffin. At various time intervals in hours, and inhibitor concentrations in HCl solution at room temperature 30^0Cdipped in distilled water and immersed in methanol solution which was scrubbed with bristle brush, to remove residual acids, and inhibitors concentration and then washed with washing liquor (NaOH + Zn dust) thoroughly, rinsed with distilled water, and later dried in acetone before reweighed (Nwigbo et al., 2012). The effect of inhibitor concentration on corrosion was investigated by changing the initial inhibitor concentration in the ranges in HCl, at room temperature for different hours. Effect of time of exposure the effect of exposure time on corrosion was investigated in 1.5M HCl concentration.
Test for alkaloids
0.2g of extracts was shaken with 1% HCl for two minutes. The mixture was filtered and drops of Wagner’s reagent added. Formation of a precipitate indicated the presence of alkaloids.

Test for phenols
0.2g of extracts was dissolved in ferric chloride solution. A green or dirty green precipitate indicated the presence of phenolic compound

Test for saponins
0.2g of extracts was shaken with 5ml of distilled water in a test tube. Frothing which persists on warming was taken as evidence for the presence of saponins.

Test for tannins
0.2g of extracts was stirred with distilled water and filtered. Ferric chloride was added to the filtrate. A blue- black, green or blue-green precipitate was taken as an evidence for the presence of tannins.

Determination of corrosion rate and inhibitor efficiency

$$H = \frac{(W1 - W2)}{(A\ t)} \qquad (1)$$

Where:

H = Corrosion rate

W_1 = initial weight (before immersion)

W_2 = final weight (after immersion)

A = surface area of the sample

t = exposure time

Efficiency (IE) of each sample was calculated by using equation 2.

$$IE = \frac{(V0 - V1)}{V0} \qquad (2)$$

V_0 = corrosion rate without inhibitor

V_1 = corrosion rate with the addition of inhibitor

3. Results and Discussion

Table 1 Phytochemical Analysis

PARAMETERS	**VALUES**
Alkaloids (mg/100g)	++
Cardiac Glycosides (mg/100g)	-
Flavonoids (mg/100g)	+
Phenolics (mg/100g)	+
Phytates (GAE/g)	+++
Saponins (mg/100g)	++
Terpenoids (mg/100g)	+
Anthocyanins (mg/100g)	+
Steroids (mg/100g)	++
Tannins (mg/100g)	++

+++ = highly concentrated, ++ = concentrated, + = in trace; - absent or too little to identified qualitatively.

The presence of the Alkaloids, Flavonoids, Phenolics, Phytates, Saponins, Terpenoids, Anthocyanins, Steroids, and Tannins as depicted by the phytochemical test in Table 1 also enhance the process of corrosion inhibitor adsorption on the mild steel. This also corroborates the work of (Nwigbo et al., 2012; Prithiba et al., 2014; Owate et al., 2014). The presence of these compounds has been reported to promote the corrosion inhibition of mild steel in aggressive acid media (Umoren et al., 2006). Molecules containing nitrogen and acetylenic alcohols are claimed to form a film on the metal surface and can retard the metal dissolution process (an anodic reaction) as well as hydrogen evolution (a cathodic reaction) (Barmatov et al., 2012).

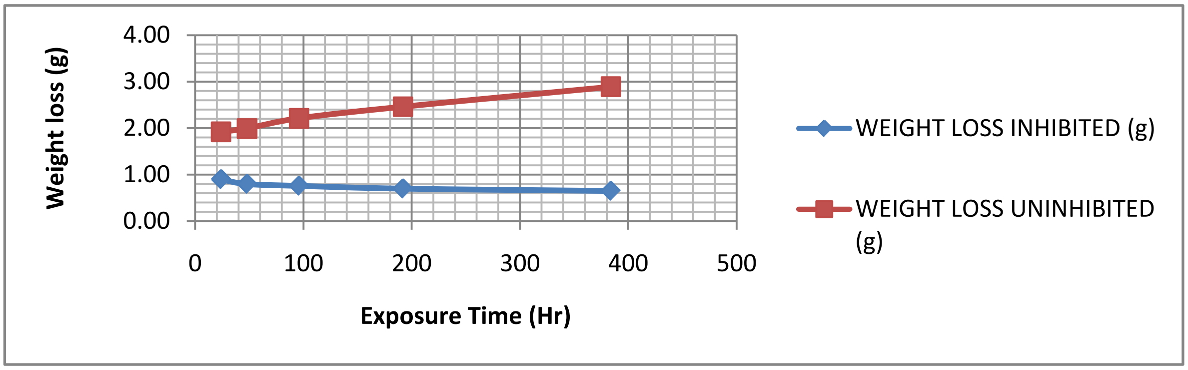

Fig. 1: 5ML^{-1} Concentration of Extract In 1.5M of HCL.

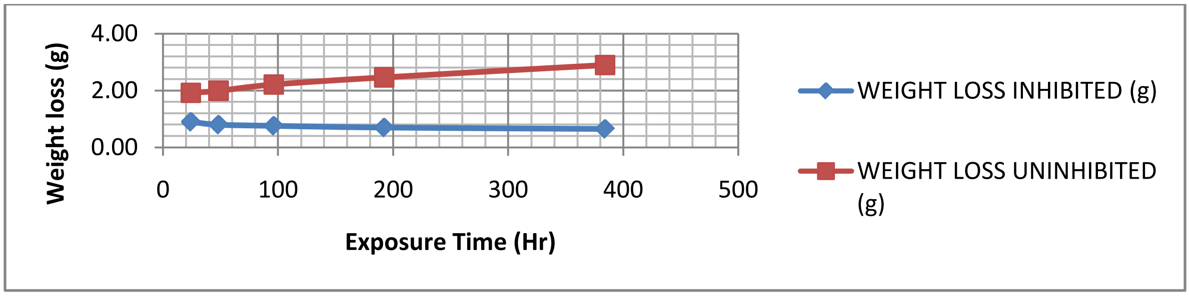

Fig. 2: 10ML^{-1} Concentration of Extract In 1.5M of HCL.

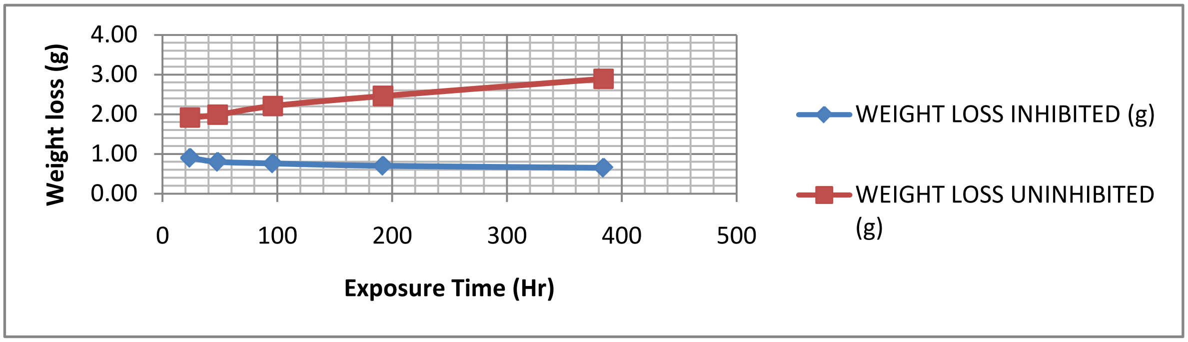

Fig. 3: 15ML^{-1} concentration of extract in 1.5M of HCL.

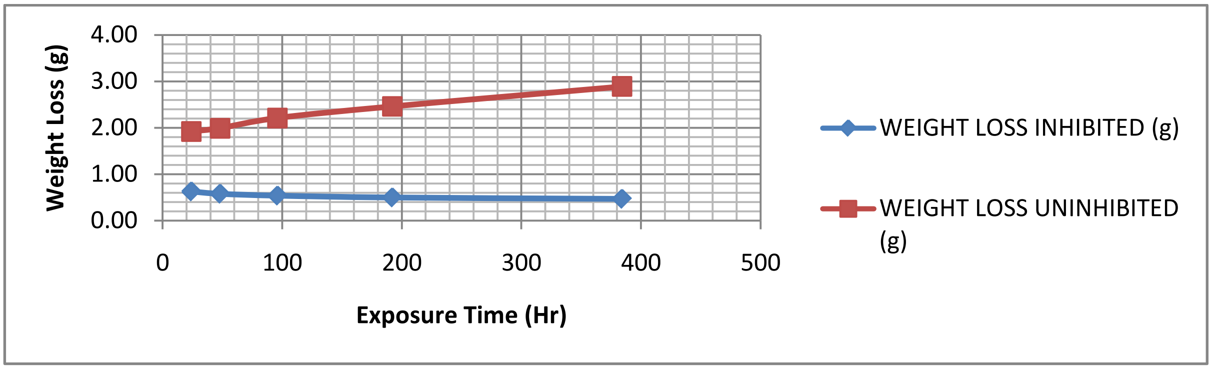

Fig. 4: 20ML^{-1} concentration of extract in 1.5M of HCL.

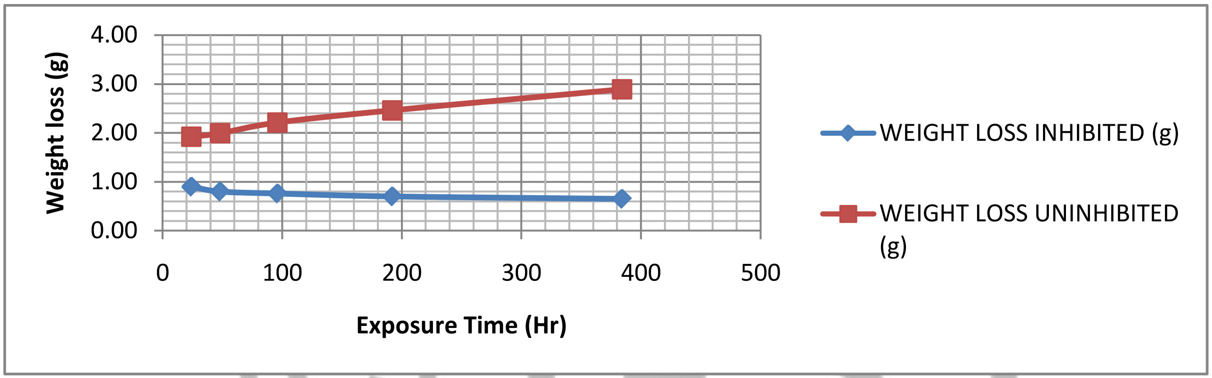

Fig. 5: 25ML^{-1}concentration of extract in 1.5M of HCL.

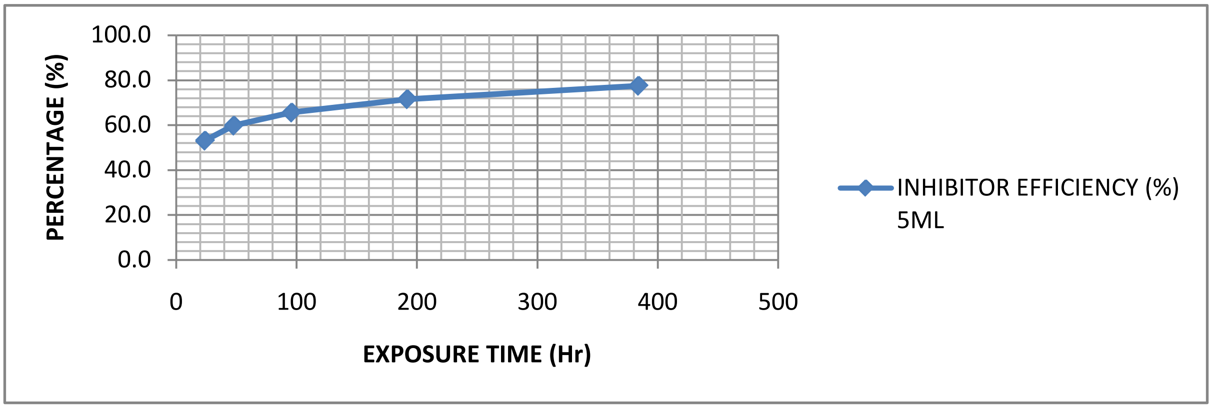

Fig.6: Inhibitor Efficiency (%), 5ML^{-1} concentration in 1.5M of HCL

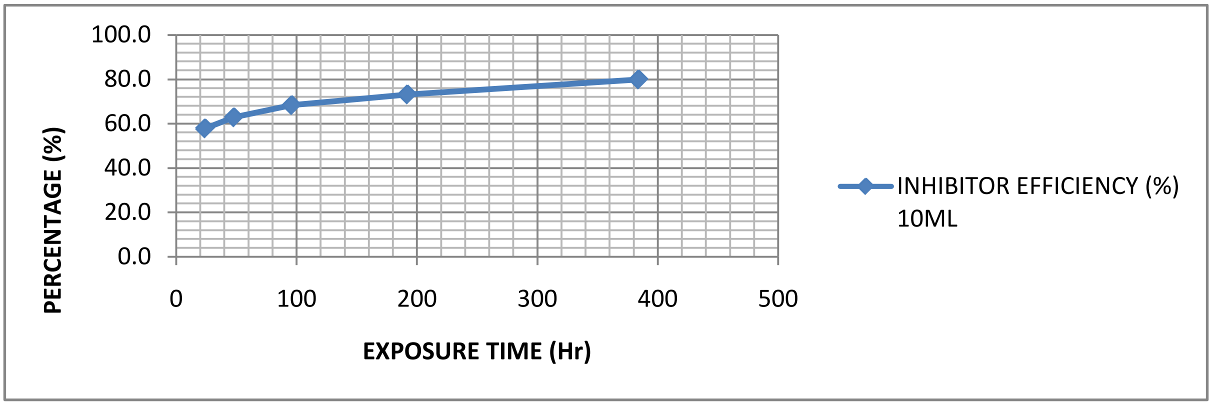

Fig.7: Inhibitor Efficiency (%), 10ML^{-1} concentration in 1.5M of HCL

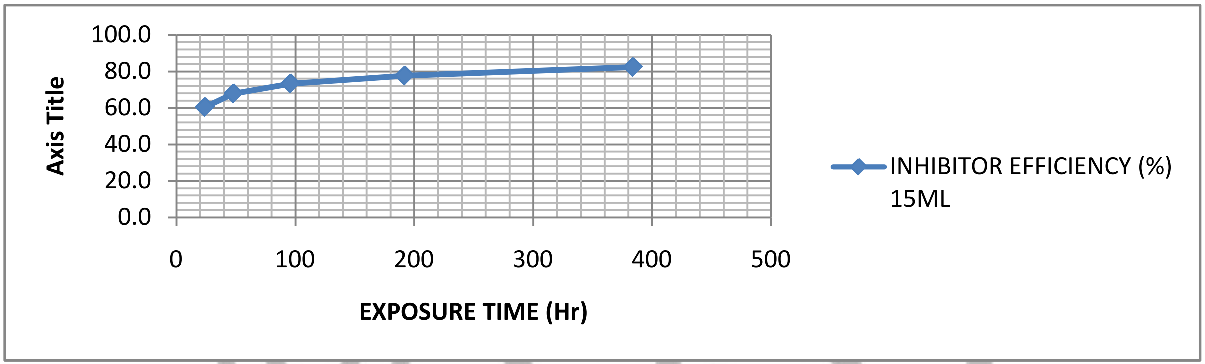

Fig.8: Inhibitor Efficiency (%), 15ML^{-1} concentration in 1.5M of HCL

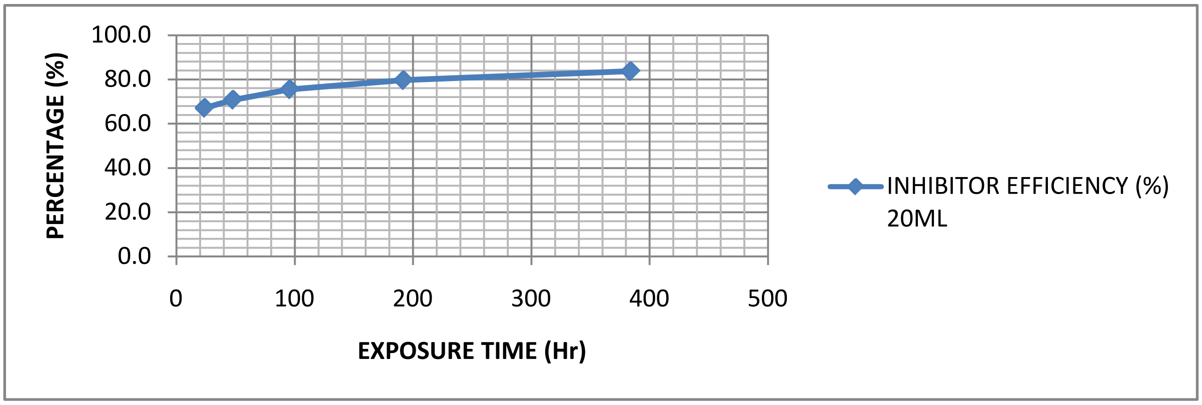

Fig. 9: Inhibitor Efficiency (%), 20ML^{-1} concentration in 1.5M of HCL

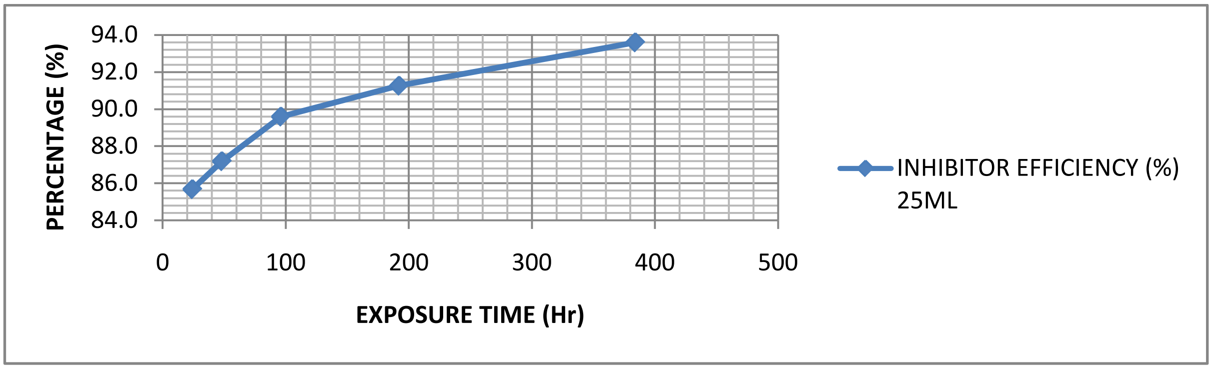

Fig.10: Inhibitor Efficiency (%), 25 ML^{-1} concentration in 1.5M of HCL

Figure 1 to fig.10 show the graphs displaying the effectiveness and compatibility of Maize Husk Polar Extract (MHPE), in the HCL medium solution. There is progressive decrease in weight loss of coupons as the concentration of the extract increases with time in the inhibited medium as compared to the un-inhibited medium (control). This is because maize husk polar extract contains compound with some complex structures that are responsible for corrosion inhibition and the Phytochemical Analysis are conformity to the fact. This complex compound prevents attack of corrosive ions on the metal surface, thus; decreasing the corrosion rate. The maize husk polar extract is a good natural inhibitor use to inhibit the corrosion rate of mild steel in the HCL medium

ADSORPTION ISOTHERM PARAMETERS

Table 2: Summary table for 1.5m of HCL with different concentration

Concentration of MHPE	Surface coverage at different time				
	24 hrs	48 hrs	96 hrs	192 hrs	384 hrs
5ml	0.50	0.80	0.91	0.96	0.99
10ml	0.55	0.81	0.92	0.97	0.99
15ml	0.58	0.84	0.93	0.97	0.99
20ml	0.65	0.85	.94	0.97	0.99
25ml	0.85	0.94	0.97	0.99	1.00

Table 3: Summary table for 1.5m of HCL with different concentration

MHPE	24 hrs		48 hrs		96 hrs		192 hrs		384 hrs	
C	θ	C/θ	θ	C/θ	θ	C/θ	θ	C/θ	θ	C/θ
5.00	0.50	10.00	0.80	6.30	0.91	5.50	0.96	5.20	0.99	5.10
10.00	0.55	18.20	0.81	12.30	0.92	10.90	0.97	10.30	0.99	10.10
15.00	0.58	15.60	0.84	17.90	0.93	16.10	0.97	15.50	0.99	15.20
20.00	0.65	30.80	0.85	23.50	.94	21.30	0.97	20.60	0.99	20.20
25.00	0.85	29.40	0.94	23.60	0.97	25.80	0.99	25.30	1.00	25.00

Langmuir Isotherm Plot for Adsorption of MHPE on Mild Steel, Temperature at 311K

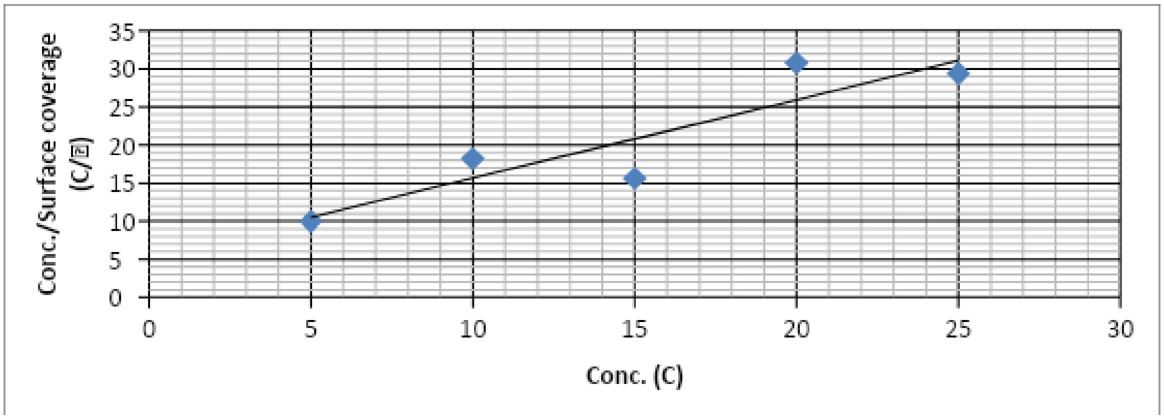

Fig.11: MHPE adsorption graph at 24hrs 1.5M HCL

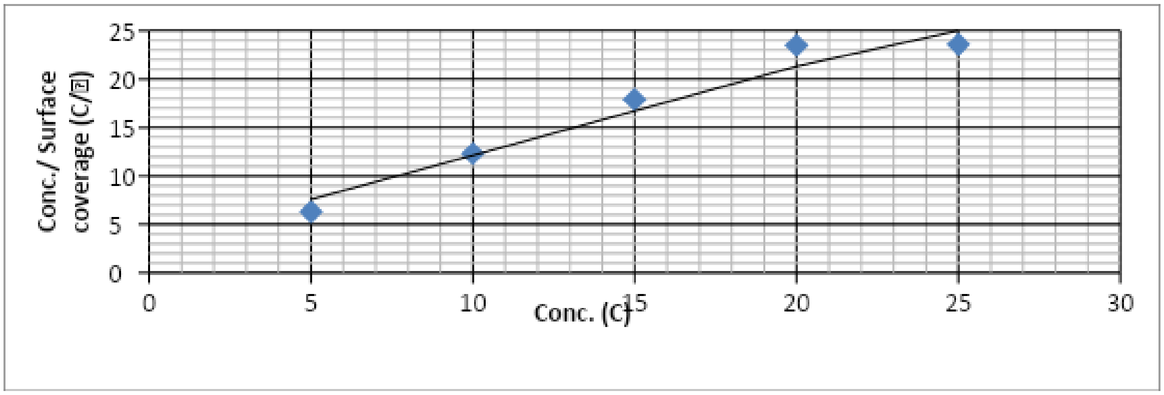

Fig.12: MHPE adsorption graph at 48hrs for 1.5M HCL

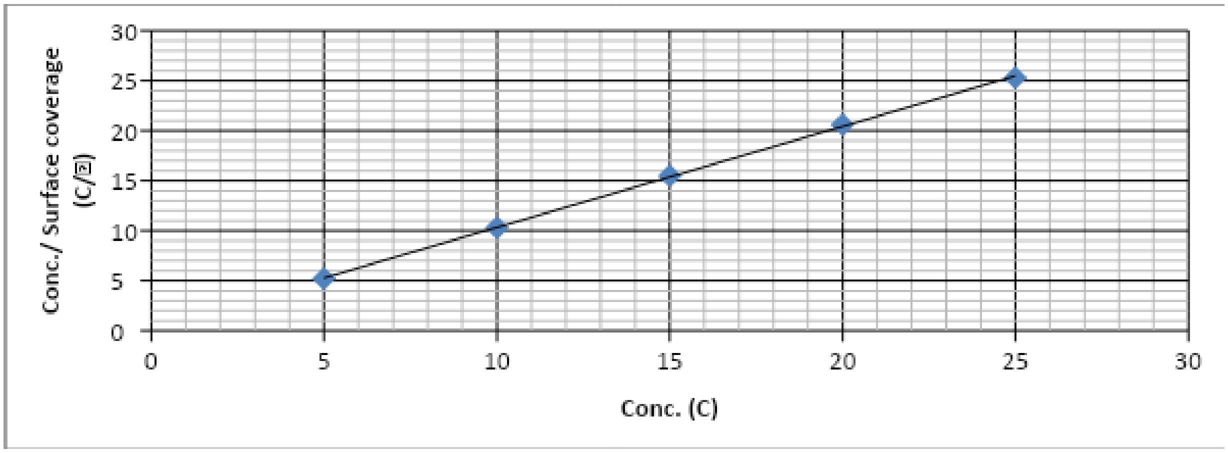

Fig.13: MHPE adsorption graph at 96hrs for 1.5M HCL

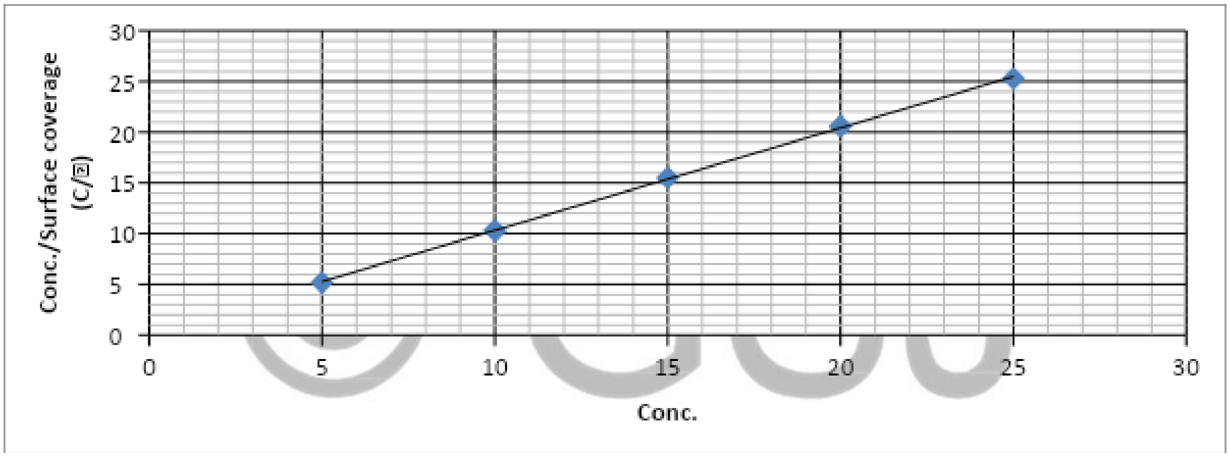

Fig.14: MHPE adsorption graph at 192hrs for 1.5M HCL

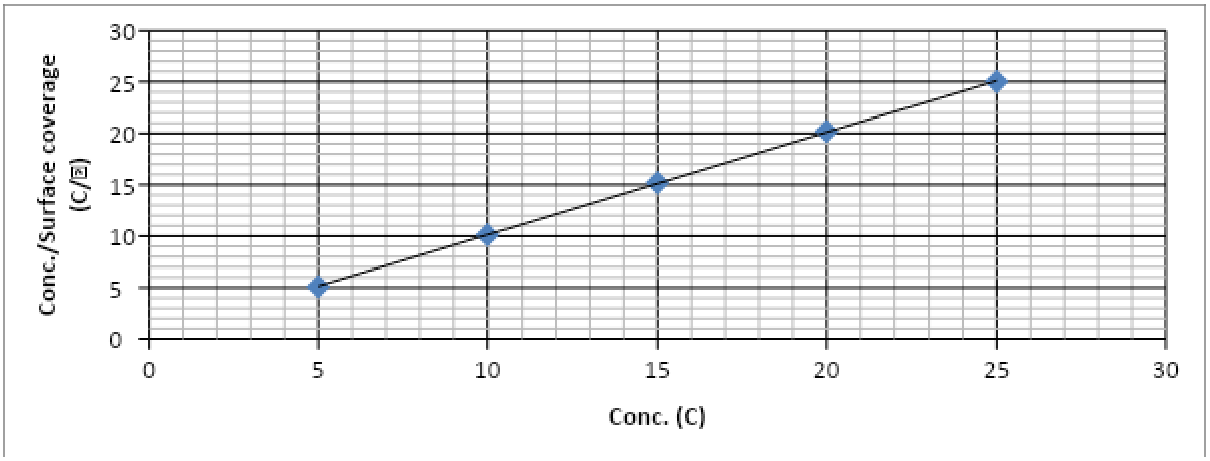

Fig.15: MHPE adsorption graph at 384hrs for 1.5M HCL

Figure 11 to figure 15, are various plots of Maize Husk Polar Extract Concentration (MHPE) with time t/乀 against concentration (C), from Table 2 and Table 3, straight line graphs were obtained and using the obtained value of this intercept fromC=c+ 1k, adsorption equilibrium constant, gotten from the intercept of the graph which is used to determine the adsorption process since it was assumed that the adsorption sites on the metal surface are uniformly distributed and energetically identical.

In 1.5M of HCL, the adsorption site on the metal surface are uniformly distributed and energetically identical and that maximum number of absorbed molecules per site is one, implying a case of monolayer adsorption and the model of adsorption.

Langmuir Absorption Parameters for Corrosion Inhibition

Table 5: Langmuir adsorption isotherm at different time for 1.5M of HCL

Time hours	K
24	0.1905
48	2.0000
96	1.0000
192	0.6667
382	0.0000

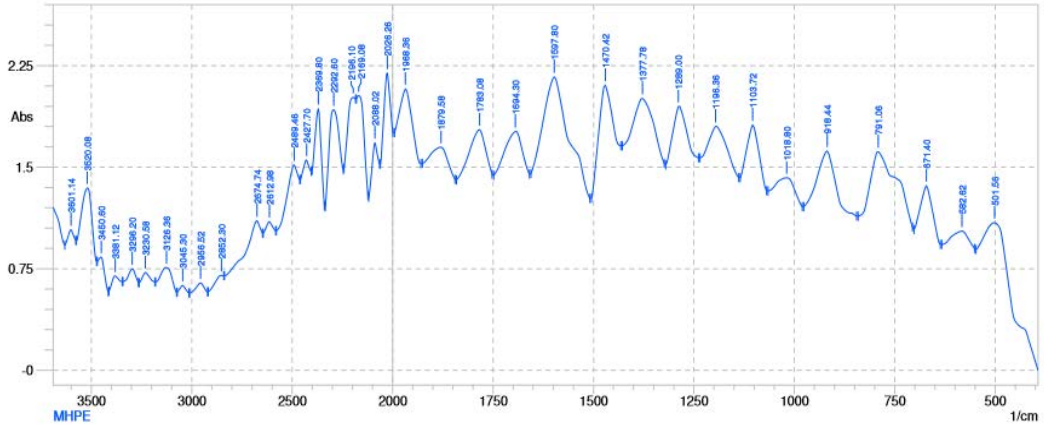

Fig.16: FTIR of MHPE.

Table 6: FTIR INTERPRETATION TABLE FOR MHPE

Peak position cm-1	Peak Intensity	Assignment
3601.14 3520.08	Sharp, weak	O-H free of Alcohols, Phenols
3450.6 3381.12 3296.2 3230.58 3126.36	Medium, broad	O-H or N-H Stretch of Alcohols, Phenols, Amines, Acids, carboxylics
3045.3 2956.52	Sharp, strong	C-H of Alkenes, Arenes, Alkyl groups
2196.1 2169.08	Sharp, variable	C= or N= of Alkynes, nitriles
1783.08 1289 1196.36	Strong	C-O stretch of Acids, halides, esters, Anhydrides
1597.8	Medium, strong	N-H bond of Amines, Amides
1470.42	Variable	C=C of Arenes, Alkenes
1377.78	Medium	C-H Stretch of methyl

1103.72	Strong	C-Stretch of ethers
791.06	Strong	C-H bond of $RCH=CR_2$

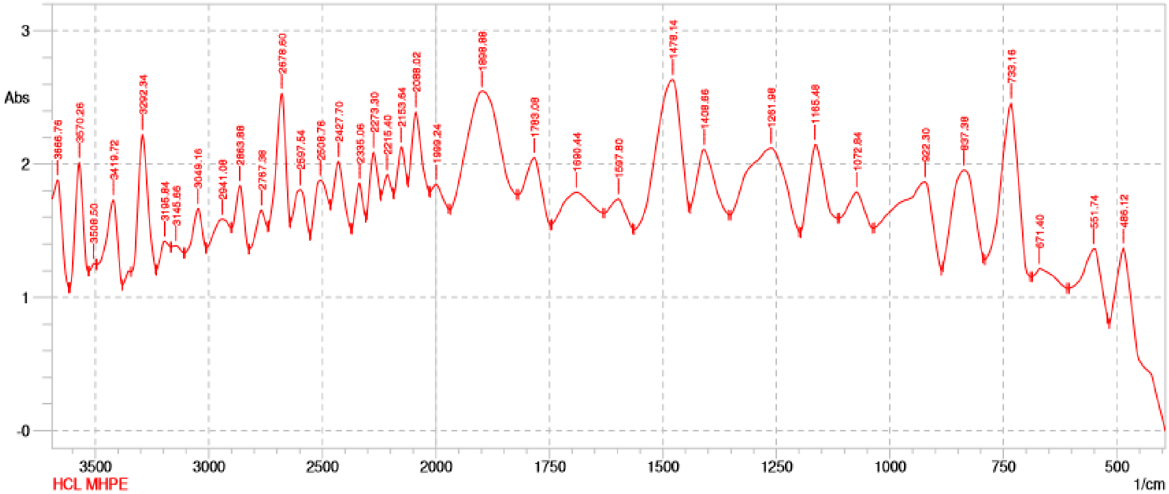

Fig.17: FTIR of Corrosion Product of 1.5M HCL

TABLE 7: FTIR INTERPRETATION TABLE FOR MHPE IN 1.5M OF HCL

Peak position cm-1	Peak Intensity	Assignment
3666.76 3570.26	Sharp, weak	O-H free of Alcohols, Phenols
3419.72 3292.34 3195.84 3145.66 3049.16 2941.08	Medium, broad	O-H or N-H Stretches of Alcohols, Phenols, Amines, Amides, Acids, carboxylic
2863.88 2767.38	Medium	C-H Stretch of Aldehydes, Alkyl groups
2215.4 2153.64	Sharp, variable	C= or N= for alkynes, nitriles
1690.44	Very broad	C=O Stretch of Amides

1597.8	Medium, strong	N-H bond of amides, amines
1478.14	Variable	C=C for Arenes
1261.98 1165.48	Strong	C-O Stretch for acids, esters, anhydrides
1072.84	Strong	C-Stretch for ethers
837.38	Strong	$RCH=CR_2$
733.16	Both strong	C-H bond for Mono-substituted benzene

Table 6 and table 7 above is an interpretation of figure 16 and figure 17 with various peak positions, peak intensity with corresponding assignment or functional group, thus; indicating the presence of the following (-OH,(Alcohols, Phenols), $-NH_2$, (Amines), -CHO, (Aldehyde) -COOH, (Carboxylics), $-NO_2$, (Nitriles), etc. in both the inhibitor and the corrosion product.

Maize Husk Polar Extract in 1.5mole of HCL, decreases or prevents the reaction of the metal with the medium. It reduces the corrosion rate by adsorption of ions/molecules onto metal surface, increasing or decreasing the anodic and/or cathodic reaction, decreasing the diffusion rate for reactants to the surface of the metal, decreasing the electrical resistance of the metal surface.

(–NH2, –NO2, –CHO, or –COOH) replacing H-atom attached to the C- central atom improve inhibition. However, the presence of a hydrophilic functional group (OH, NH, and NO) in the molecule increases the solubility of the inhibitors.

The inhibitive characteristics of such compounds derive from the adsorption ability of their molecules, with the polar group acting as the reaction center for the adsorption process. The resulting adsorbed film acts as a barrier that separates the metal from the corrodent, and efficiency of inhibition depends on the mechanical, structural, and chemical characteristics of the adsorption layers formed under particular conditions.

4. Conclusions

Corrosion behavior of mild steel in 1.5M of HCL solution, with and without *maize husk polar extract* (MHPE) at various exposure time at atmospheric temperature have been investigated. This study concludes that; the corrosion rate of mild steel decreases significantly with the increase in the volume maize husk polar extract (MHPE) concentration. The inhibition efficiency (IE) of MHPE reaches 93.6% in 1.5mole of HCL (Gravimetric analysis). The optimum efficiency is obtained at MHPE concentration of 25ML for exposure time of 384hours, (HCL) by weight loss method. The result gotten from the vacuum rotary evaporator is 23.99% concentration (mg/100g) from 600.52grams of Maize Husk. Phytochemical analysis revealed the presence of Alkaloids, Flavonoids, Phenolics, Phenolics, Phytates, Saponins, Terpenoids, Anthocyanins, Steroids, and Tannins in the extract. The behavior of MHPE is spontaneous and the physical adsorptions obeys Langmuir isotherm. Fourier Transform Infrared Spectroscopy (FTIR), results shows that Maize Husk Polar Extract contains possible compounds with complex structures which are responsible for corrosion inhibition of mild steel.

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