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Characterization of E*uphorbia Hirta* Leaf as Eco-Friendly Inhibitor for Protection of Mild Steel in Acidic Environment

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Abstract

I The feasibility of using extract of *Euphorbia hirta* (*EH*) as green inhibitor for mild steel was studied using gravimetric and characterization techniques in 0.5 M hydrochloric acid. The concentration of inhibitor, temperature and time were varied in the range of 0–18 g/L at 3 g/L interval, 30–70°C at 10°C interval and 2-12 days at 2 days interval. Characterizations of the extract were done by qualitative and quantitative analyses, Fourier transforms infrared (FT-IR) and gas chromatography–mass spectrometry. Scanning electron microscope attached with energy dispersive spectroscopy (SEM/EDS) was used to analyse the surface morphology of the samples before, during and after corrosion tests. The results showed that corrosion rate decreased with increase in inhibitor concentration and time, and maximum inhibition efficiency of 98.79% at optimum concentration of 15 g/L and increased with increase in temperature from 30-70°C. The phytochemical constituents, FT-IR and GC–MS revealed some elements which are capable of Aliphatic cyanide/nitrile, C≡N· Aliphatic bromo compounds, C-Br, ($C_{16}H_{28}O$), and ($C_{25}H_5Br_2$), chemical bonds/functional groups (NH_2) etc which were responsible for the protection of mild steel inhibition in the medium. The SEM/EDS of the coupon without the extract was rough, severe pits, cracks and dissolution of intermetallic occurred at the surface, whereas there was an improvement in the surface morphology of mild steel with green inhibitor (smooth). The inhibitor served as an alternative to synthetic inhibitors which are expensive, cancerous and environmental unfriendly. The values of inhibition efficiency obtained are well above the minimum acceptable limit of 70% required of a good inhibitor. It can therefore be used in the formulation of paints.

1. Introduction

The consumptions of oil and natural gas account for over 60% of all global energy demands. It is obvious that the conventional method of extracting fossil fuels will not cease within the next decades. For years, corrosion has been a major problem in various industries especially in oil and gas and has caused approximately 80-90% failures in this sector [1]. The consequences of these forms of corrosion are obvious, varying from huge material losses to unhealthy environment and possibly death. Corrosion control and prevention can be carried out using suitable methods such as synthetic and eco-friendly inhibitors, cathodic protection, anodic protection, metallic coating, alloying, etc which have been successfully developed to extend the service lifespans of these structures in such corrosive environments [2, 3]. Corrosion occurred in different forms in structures made of mild steel during service in various environments.

The use of chemical inhibitors is often the most practical and cost-effective means of corrosion mitigation. However, most of these synthetic inhibitors such as chromates, nitrates, borates, molybdates had proved good anticorrosive action but highly toxic to both human beings and environment. An alternative has to be searched to replace the expensive and toxic synthesized corrosion inhibitors because of environmental regulations in order to promote the sustainable greenness to the atmosphere [2, 4]. The issue of toxicity has led to the use of naturally occurring substances in order to find low-cost and non-hazardous inhibitors. Plant extracts have become important as an environmentally acceptable, readily available and renewable source of materials for a wide range of corrosion prevention formulations [5]. Therefore, finding naturally occurring substances as corrosion inhibitors is a subject of great practical significant.

Extracts of plants contain organic compounds such as N, O, P and S atoms which are considered to be effective corrosion inhibitors. The effectiveness of organic inhibitors, however, depends on the nature and the condition of the metallic surface, the chemical composition and structure of the inhibitor [6-8]. All plant products are organic in nature and their constituents are tannins, organic and amino acids, saponins, alkaloids, flavonoids, glycosides and pigments are known to exhibit inhibiting action [6–10].

This work is designed to carry out the possibility of using *Euphorbia hirta* (*EH)* leaf commonly known as garden spurge leaf as green corrosion inhibitor, which is a non-toxic, cheap, environmentally friendly for mild steel protection in 0.5 M HCl solution. The objectives of this research work were to characterize the coupons before and after corrosion tests using Scanning Electron microscopy with energy dispersive spectroscopy (SEM/EDS). The extract was also characterized by quantitative and qualitative analyses, Fourier Transform Infrared Spectroscopy (FT-IR) and GC-MS respectively.

2. Experimental Design

2.1 Materials preparation

The mild steel coupon used for this study was obtained from a steel manufacturer company in Port Harcourt, Rivers State. The chemical composition of mild steel samples in weight percent is shown in Table 1.

Table 1: Chemical composition of mild steel

Element	Fe	C	Si	Mn	P	S	Co	Mo	Ni	Al	Cu
% Wi.	99.01	0.17	0.033	0.423	0.018	0.014	0.05	0.014	0.19	0.002	0.015

2.2 Solution Preparation

Solutions of 0.5 M HCl was prepared by diluting of analytical grade with double distilled water. Extracts were dissolved in the acid solution at the required concentrations (g/L). The solution in the absence of inhibitor was taken as blank (0) for comparison purposes [11]. The test solutions were freshly prepared before each experiment by adding *Euphorbia hirta* extract directly to the corrosive solution. Concentrations of *Euphorbia hirta* extract used were: 0, 3, 6, 9, 12, 15, and 18 g/L respectively. Experiments were performed in triplicate to ensure good results.

2.3 Preparation of inhibitor

Seven hundred grams of *Euphorbia hirta* leaf (Figure 1) after cleanings in water and dried at room temperature was extracted in 1.5 L of 70% ethanol and 30% distilled water as solvent and followed by

maceration method. The extract and the final stage of collecting the liquid at 100 °C before evaporation were presented in figure 1. The concentration of the stock solution was expressed in terms of (g/L) and the concentration of 3-18 g/L of the extract was prepared [12].

Figure 1: *Euphorbia hirta* leaf

2.4 Determination of Phytoconstituents of the Leaf Extract

The phytochemical constituents were determined by quantitative and qualitative methods. The analyses were carried out at the Multi-Users Laboratory, Ahmadu Bello University, Zaria, Nigeria.

2.5.1 Characterizations of Leaf Extract by Fourier transforms infrared (FT-IR)

Prepared small quantity of *EH* powdered sample was then exposed to infrared radiation. The sample molecules selectively absorb radiation of specific wavelength which causes the change of dipole moment of the sample molecules [16]. The commonly used region for infrared absorption spectroscopy was from 4000 to 400 cm−1. This is because the absorption radiation of within this region. Fourier transforms infrared (FT-IR) spectroscopy was carried out to identify the active ingredients (chemical bonding and functional groups) present in the extract. It was carried out using a Shimadzu 8400S spectrophotometer at the Multi-Users Laboratory, Ahmadu Bello University, Zaria. The spectra were recorded, and the interpretations were carried out using a standard library [13].

2.5.2 Characterizations of Leaf Extract by Gas chromatography-mass spectrometry (GC-MS)

About 1 mL of each of the concentration of the extract was analyzed by GC-MS using QP 2010 Plus Schmadzu Product equipped with two fused-silica capillary columns (60 m × 0.22 mm), film thickness at National Research Institute for Chemical Technology, Zaria. Conditions under which was carried out are: column oven temperature 80 °C, injection temperature 250 °C, injection mode: split flow control mode: linear velocity, pressure: 108.0 kPa, total flow: 6.2 mL/min column flow: 1.58 mL/min, linear velocity: 46.3 cm/s, split ratio: 1.0. GC-MS was carried out and their chromatography mass spectrometry and compounds present in the extract were obtained accordingly [14, 15]. It was carried out at the Multi-Users Laboratory, Ahmadu Bello University, Zaria

2.6 Corrosion Measurement Methods

2.6.1 Gravimetric Measurements

The weight loss experiments were carried out in accordance with the methods reported elsewhere [16-19]. Coupon specimens with dimensions of 4 cm × 3 cm × 1 cm were abraded with various grades of wax coated emery papers from 600 to 1600 grit. Specimens were degreased in absolute ethanol,

dried in acetone, accurately weighed and stored in moisture-free desiccators prior to use to avoid reaction with atmospheric air. In gravimetric experiments, pre-weighed coupons were immersed in 0.5 M HCl solution without and with inhibitor concentrations of 0-18 g/L *EH* leave extracts at interval of 3 g/L and for 12 days at an interval of 2 days for withdrawal. The experiments were carried out using calibrated thermostat at temperatures 30, 40, 50, 60, and 70°C, respectively. After the time elapsed, the specimens were removed, washed with distilled water, dried with acetone and re-weighed accurately. To ensure the reproducibility of the weight loss results, each experiment was performed in triplicate and mean values were used. From the weight loss obtained, corrosion rate, inhibition efficiency (IE%) and the surface coverage (θ) were computed using the following relationships according to Equations (1-3) [14].

$$\text{Corrosion rate (mpy)} = \frac{534W}{DAT} \quad (1)$$

where W, D, A and t will be in units of milligrams, grams per cubic centimetre, square inches and hours, respectively. Inhibition efficiency (IE %) and surface coverage (θ) were calculated from the following equations:

$$\text{Inhibition efficiency (IE \%)} = \frac{CRa}{CRp} x \frac{100}{1} \quad (2)$$

$$\text{Surface coverage } (\theta) = \frac{CRa - CRp}{CRa} \quad (3)$$

2.5 Characterization of the coupons

The mild steel surface was prepared for Scanning Electron Microscopy attached with Energy Dispersive Spectroscopy (SEM/EDS) studies by taking the specimens from the optimum concentrations of the inhibitor. The mild steels at the optimum were washed with distilled water, dried and analysed for morphological studies of the coupons before and after corrosion tests. The instrument model used for the studies was JOEL JSM 5900LV operating at 5 kV accelerating voltage with a magnification of 5000 [20, 21].

3. RESULTS AND DISCUSSION

3.1 Phytoconstituents of the *Euphorbia hirta (EH)* extract

The detailed results of phytochemical constituents present in the extract by quantitative and qualitative analyses showed that it contains Saponins, Tannins, Alkaloids, Flavonoids, Glycosides and Volatile oil. Tables 2 and 3 presented the quantitative and qualitative analyses of *Euphorbia hirta (EH)* extract respectively.

Table 2: Quantitative analysis of ***Euphorbia hirta*** *(EH)* extract

Leaves	Alkaloids (%)	Tannins (mg/100g)	Saponins (%)	Flavonoids (%)	Glycosides (mg/100g)	Volatile oil (%)
EH	11.56	1673	8.34	8.34	978	3.78

Table 3: Qualitative analysis of ***Euphorbia hirta*** *(EH)* extract

Leaves	Alkaloids	Tannins	Saponins	Flavonoids	Glycosides	Volatile oil
EH	++	++	++	++	++	++

++: presence

From the results, the constituents can be adsorbed onto the metallic surface by blocking the active corrosion site or reduce the evolution of hydrogen gas at the cathode. This may be attributed to the facts that some of these phytoconstituents contain heteroatom such as O, Br, and both aromatic and functional groups. This agrees with earlier research reported [19, 22].

3.2 Fourier Transforms Infrared (FT-IR) Spectroscopy results

Figure 2 and Table 4 showed the IR absorption spectra and their functional groups. The prominent peaks obtained from the FT-IR spectroscopy for the *Euphorbia hirta* extract were presented in table 4, these also confirm the previous works [19, 23]. The inhibitor showed an effective anticorrosion potential and the results clearly indicated that the inhibition mechanism involved blockage of the mild steel by inhibitor molecules via adsorption. In general, the phenomenon of adsorption was influenced by the nature and surface charge of the metal, by the type of aggressive electrolyte and by the chemical structure of inhibitors.

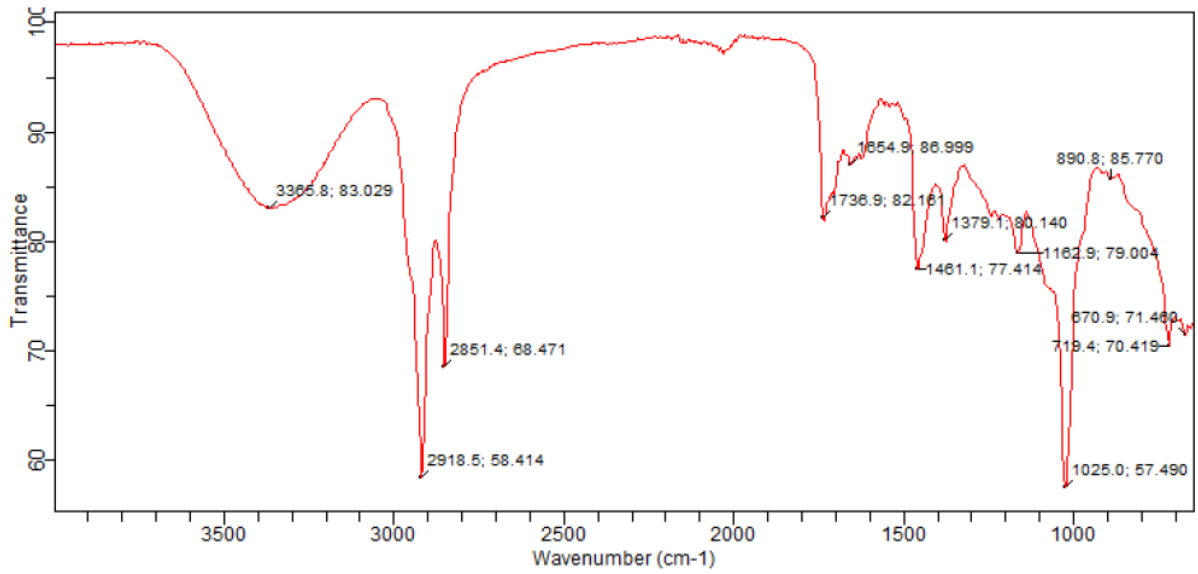

Figure 2: IR absorption spectrum

Table 4: Prominent peaks obtained from reflectance FTIR spectroscopy for *EH* extract

S/No	Frequency range (cm^{-1})	Band assignments
1	3365.8	Aliphatic primary amine, NH_2 stretch
2	2851.4	Aliphatic cyanide/nitrile, $C\equiv N^-$ stretch
3	2918.5	Methyne CnH_{2n-2} stretch
4	1854.9	Five-membered ring anhydride
5	1756.9	Alkyl carbonate
6	1379.1	Phenol or tertiary alcohol, OH bend
7	1461.1	Methylene C-H bend
8	1162.9	Organic sulphates
9	890.8	Vinylidene C-H out-of-plane bend
10	719.4	Methylene —(CH2)n— rocking ($n \geq 3$)
11	690.9	Aliphatic bromo compounds, C-Br stretch
12	1025	Primary amine, CN stretch

3.2.1Gas Chromatography-Mass Spectrometry (GC-MS) analysis

GC–Mass Spectrum of *Euphorbia hirta (EH)* is also presented in figure 3. The compounds identified in the ethanol distillate were presented in Table 5 and the structures of the compounds identified in the *EH* extract is also similar to the findings [1, 2, ,24].

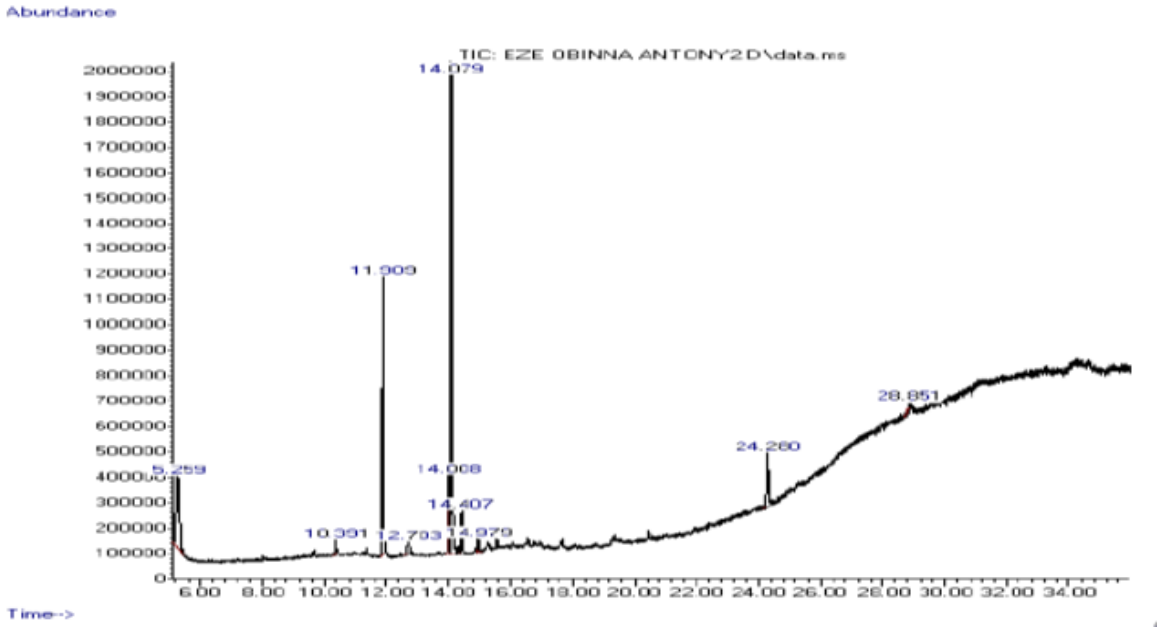

Figure 3: GC- Mass Spectrum of *Euphorbia hirta (EH)*

The table revealed the presence of 17-Octadecadienal ($C_{18}H_{32}O$), 9,12-Octadecadienoic acid ($C_{18}H_{32}O_2$) and 7,11-Hexadecadienal ($C_{16}H_{28}O$) at R. time of 5.259 respectively. Others are 26-oate, erythro-9,10-Dibromopentacosane ($C_{25}H_5Br_2$) at R. time of 28.814. 9-Octadecene, 1-[3-(octadecyloxy) propoxy] -($C_{39}H_{78}O_2$) also occurred at R. time of 28.851. The functional groups obtained from the GC-MS has an anticorrosion property capable of mitigating the corrosion in such an environment as reported by [25, 26]. The extract contains oxygen atoms, hydroxyl, aromatic rings and hydrocarbon which are the centres of adsorption. However, adsorption involving organic molecule at the metal solution interface may occur in any of the following ways: (*i*) the electrolytic attraction between charged molecule and the charged metal; (*ii*) interaction of unshared electron pairs in the molecules with the metal; (*iii*) interaction of s electrons with metal; (*iv*) combination of the above [27, 28].

3.3 Effect of *Euphorbia hirta extract* on mild steel

Weight loss measurements were performed on mild steel immersed in 0.5 M HCl solution with and without (*EH*) extract for 12 days. The results obtained in the absence and the presence of the inhibitor at various concentrations were presented in Figure 4. The inhibition efficiency increases with the increasing in inhibitor concentration, which could be due to the increases in the mass and charge transfer to the mild steel surface leading to the adsorption of inhibitor molecules and reduction in the metal dissolution as shown in the plant characterizations by both FT-IR and GC-MS spectroscopies. Further increase in the inhibitor concentration causes little or negligible change and the highest inhibition efficiency occurred at the optimum concentration of the inhibitor (15 g/L). Owing to the acidity of the corrosive medium, the extract which contains the phytochemical constituents, functional groups from both the FT-IR and GC-MS respectively could not remain in the solution in its free base state and may exist as neutral species or in its cationic form which were presented in tables 4 and 5 respectively. This assertion also agrees with the findings of the previous studies [28, 29].

Table 5: The chemical compounds identified in the ethanol distillate of *Euphorbia hirta (EH) leaves* extract by GC-MS analysis

Pk#	RT	Area %	Library/ID	Ref#	Molecular Formula	Molecular weight g/mol
1	5.259	15.62D	9,17-Octadecadienal, 9,12-Octadecadienoic acid, 7,11-Hexadecadienal	125003 140137, 98680	$C_{18}H_{32}O$ $C_{18}H_{32}O_2$ $C_{16}H_{28}O$	264 280 236
2	10.391	0.74 D	Cyclohexadecane, 9-Eicosene, 5-Eicosene	87836, 140276, 140275	$C_{16}H_{32}$ $C_{20}H_{40}$ $C_{20}H_{40}$	224 280 280
3	11.909	19.26D	Hexadecanoic acid, methyl ester, Hexadecanoic acid, methyl ester, Hexadecanoic acid, methyl ester	130820, 130813, 130822	$C_{17}H_{34}O_2$ $C_{17}H_{34}O_2$ $C_{17}H_{34}O_2$	270 270 270
4	12.703	1.99 D	cis-Vaccenic acid, Oleic Acid, Hexadecanoic acid, ethyl ester	142073 142071 144304	$C_{18}H_{34}O_2$ $C_{18}H_{34}O_2$ $C_{18}H_{36}O_2$	282 282 284
5	14.008	6.00 D	11,14-Octadecadienoic acid, methyl ester, 9,15-Octadecadienoic acid, methyl ester, Methyl 10-trans,12-cis-octadecadie noate	153884 153899 153874	$C_{19}H_{34}O_2$ $C_{19}H_{24}O_2$ $C_{19}H_{34}O_2$	294 294 294
6	14.079	44.37 D	9-Octadecenoic acid, methyl ester, 9-Octadecenoic acid, methyl este	155754, 155721	$C_{19}H_{36}O_2$ $C_{19}H_{36}O_2$	296 296
7	14.407	3.67 D	Methyl stearate, Heptadecanoic acid, 16-methyl-, methyl ester, Methyl stearate	157881 157956 157885	$C_{19}H_{38}O_2$ $C_{19}H_{38}O_2$ $C_{19}H_{38}O_2$	298 298 298
8	14.979	1.38 D	7,10,13-Hexadecatrienoic acid, methyl ester, 7,10,13-Hexadecatrienoic acid, methyl ester, Cyclododecyne	124916 124917 35042	$C_{16}H_{26}O_2$ $C_{16}H_{26}O_2$ $C_{12}H_{20}$	250 250 164
9	24.280	6.15 D	Squalene, Squalene, 5,9,13-Pentadecatrien-2-one,6,10,1-4-trimethyl	243219 243217 123157	$C_{30}H_{50}$ $C_{30}H_{50}$ $C_{18}H_{30}O$	410 410 262
10	28.814	0.35 D	Methyl (25RS)-3.beta.-hydroxy-5-cholesten-26-oate, erythro-9,10-Dibromopentacosane, Rhodopin	250932 267311 271155	$(C_{27}H_{44})3$ $C_{25}H_5Br_2$ $C_{40}H_{58}O$	1104 465 554
11	28.851	0.48 D	Cholest-4-ene, 3.beta.-(methoxymethoxy)-, Methyl(25RS)-3.beta.-hydroxy-5-cholesten-26-oate, 9-Octadecene, 1-[3-(octadecyloxy)propoxy]-	250967 250932 272301	$C_{29}H_{52}O_2$ $C_{27}H_{42}O_4$ $C_{39}H_{78}O_2$	432 430 578

The high inhibition efficiency recorded was possibly due to the fact that Cl^{-1} was hydrated in HCl and this can be poorly adsorbed onto the metal surface leaving more active sites for the adsorption of the inhibitor – neutral species – and thus inhibition efficiency increased with increase in concentrations of the inhibitor in HCl medium. Hence, it can be concluded that while adding the inhibitor to HCl solution the anions like COOH, OH present in the inhibitor solution, and the unshared pair of electrons present

on the various hetero atoms present in the functional groups like Br=O, O–H, O–H, got adsorbed on the mild steel. These observations also confirm the works of [30, 31].

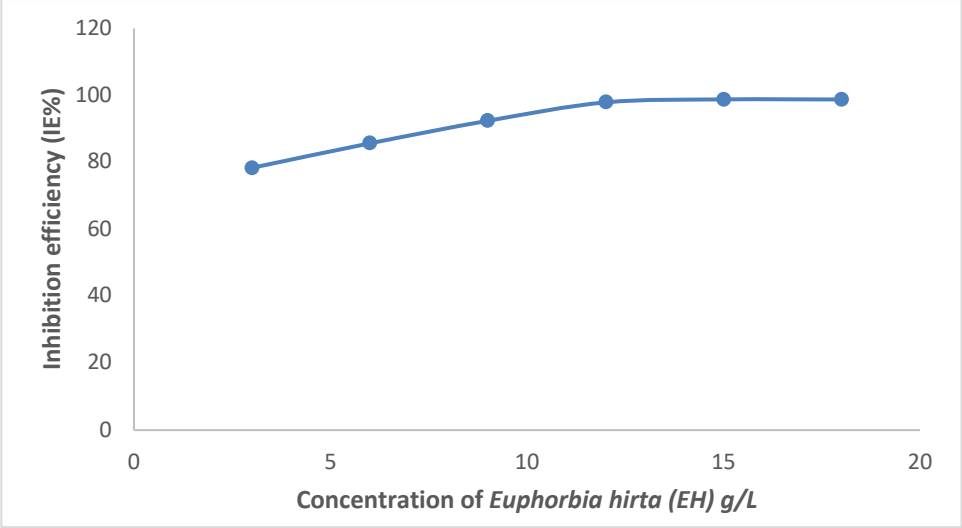

Figure 4: Variation of inhibition efficiency (% IE) with inhibitor concentration at 303 K

3.4 Effect of Temperature on Inhibition Efficiency

The temperatures effect on the inhibition efficiency investigated on mild steel at range of 30- 70°C were shown in Figure 5. The inhibition efficiency decreases with increase in temperature. At higher temperature, the hydrogen evolution increases on the metal surface and leads to desorption of the adsorbed inhibitor film from the metal surface as noted. It could also be attributed to an increase in the rates of ionization and diffusion of active species in the corrosion process. These phenomena also confirm to the previous findings of [32,33].

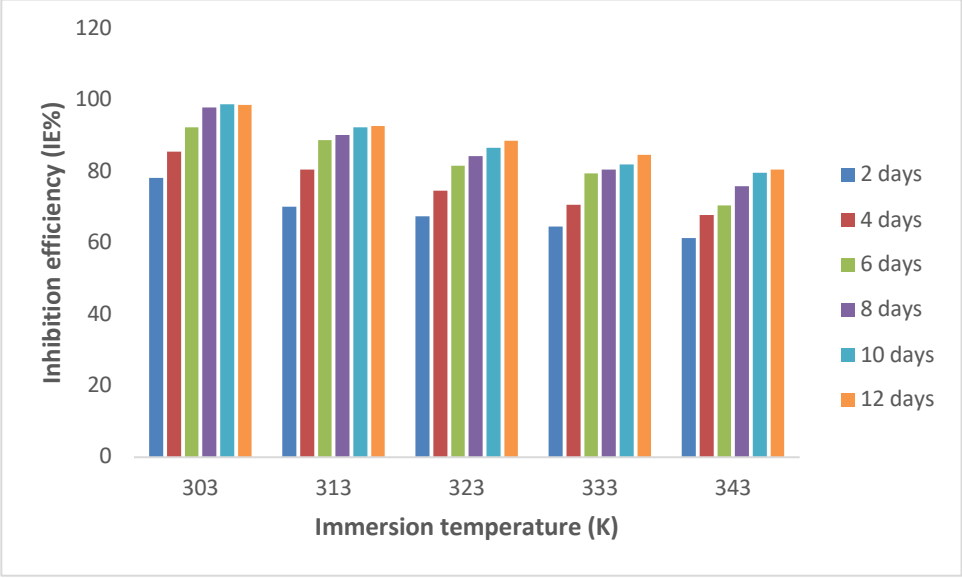

Figure 5: Variation of inhibition efficiency (% IE) with concentration of inhibitor at different temperatures (30-70°C)

3.5 Surface morphological analyses

The morphology of mild steel samples as received, without and with optimum concentrations of *Euphorbia hirta (EH)* in hydrochloric acid solutions were presented in figures 6a-6c respectively.

Figure 6a presented the SEM/EDS of mild steel as-received sample in a polished state, figure 6b is the polished sample in the presence of 0.5 M HCl solution without extract. Finally, figure 6c represented the polished sample in 0.5 M HCl solution with the optimum concentration of *EH* extract. The surface of the coupon in figure 6a was completely smooth, without any indentations except the polished surface that was revealed. In figure 6b, the pits initiation commenced which is often linked to the presence of local defects at the metal surface such as flaws in the oxide or segregation of alloying elements, presence of aggressive anions such as chlorides in the environment. Pit initiation occurs on the alloy surface passivated by an oxide film due to the damage caused by passivation of the electrolyte resulting in anodic reaction on the metal surface while the unexposed protective surrounding becomes the cathode leading to localized corrosion [34]. As the time progresses, growth of pits increases from the SEM evaluation, it is clear that the corrosion resistance decreases which confirmed that weight loss results obtained is in agreement with each other and similar to the findings [35, 36]. In figure 6c, the coupon exposed to corrodent in the presence of optimum concentration of 15 g/L was less rough and most of the elements present were enhanced in the presence of the extract. Hence, the propagation of pits in the material was impeded by the adsorption of the inhibitor on mild steel surface. Comparing the morphologies of 6b and 6c, the mild steel lost some of its component elements to corrosion in 0.5 M HCl solution without extract. The difference could be an indication of oxygen bearing active components in the extract adsorbing onto the metal surface and seems to be a confirmation to the earlier assertion that the extract active components compete for direct adsorption on mild steel surface [2]. The adsorption of components of *EH* leaves extract could be attributed to their functional groups obtained from phytoconstituents, FT-IR, and GC-MS results. The *EH* can be considered to be good and effective corrosion inhibitor of material in acid and similar to the previous findings [14, 26].

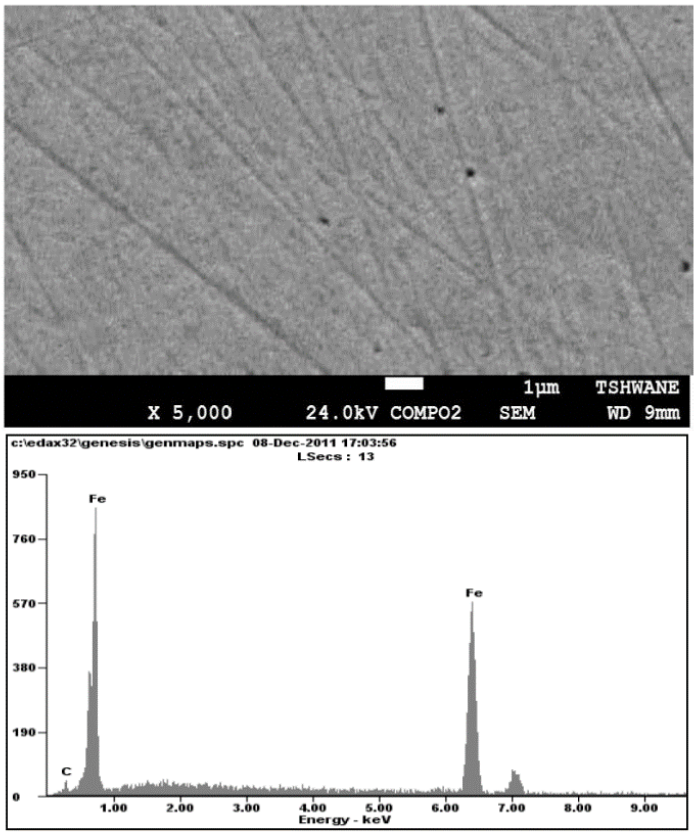

Figure 6a: SEM/EDS of as-received mild steel coupon

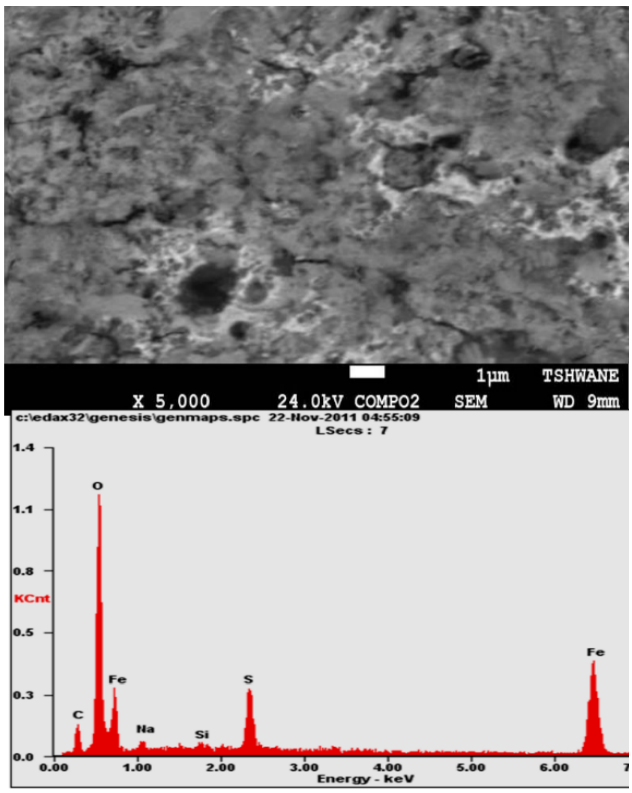

Figure 6b: SEM/EDS of mild steel in 0.5 M HCl in the absence of *EH* extract for 12 days

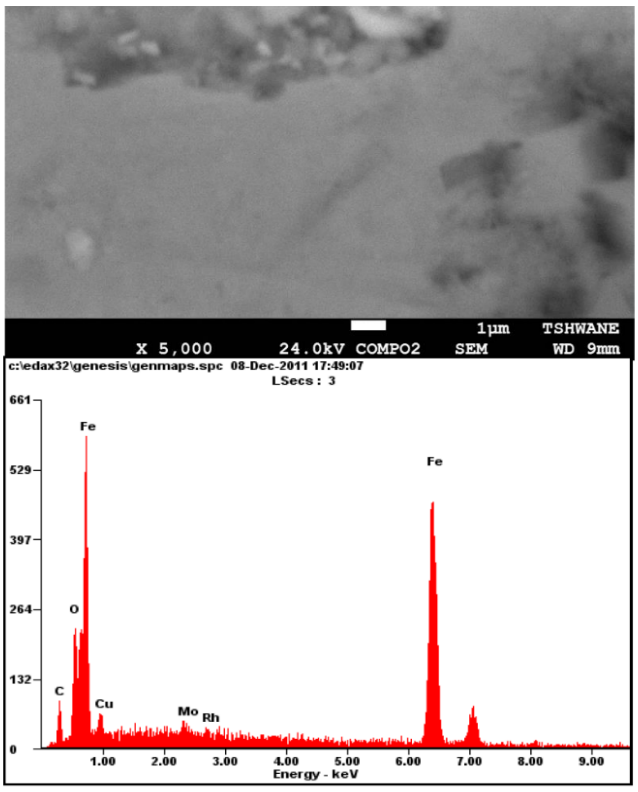

Figure 6c: SEM/EDS of mild steel at the optimum of 15 g/L of *EH* extract for 12 days

Conclusions

From the work carried out, the following conclusions can be drawn:

1. *Euphorbia hirta (EH)* extract had acted as an efficient anti-corrosive agent for mild steel in 0.5 M HCl solution. At the optimal concentration of 15 g/L, it can increase the lifespan of the mild steel by 98.79%, and this can be utilized in both oil and gas industries.
2. The gravimetric weight loss technique showed the inhibiting effect of *EH* with percentage inhibition efficiency of 98.79% at 15 g/L at 30°C but decreased to 79.76% at 15 g/L at temperature of 70°C.
3. The phytoconstituents, FT-IR and GC-MS revealed some major constituents which formed a protective thin film layer preventing the discharge of hydrogen ion (H^+) ions in the presence of acidic solution.
4. The SEM/EDS morphologies of the adsorbed protective films on the mild steel surface confirmed the high performance of inhibitive effect of the active components in *Euphorbia hirta (EH)* extract.

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