Research Article

Corrosion Control of Mild Steel in Sulphuric Acid by *Athyrium filix-femina* Leaf Extract Green Inhibitor

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Abstract
The inhibition potential of *Athyrium filix-femina* leaf extract (AF) on corrosion of mild steel in 1 M sulphuric acid solution was studied by gravimetric and electrochemical polarization techniques. Infrared spectra of the extract were studied. Morphology of metal coupons was examined by scanning electron microscope (SEM). Thermodynamic parameters such as activation energy, enthalpy and entropy, and Gibbs free energy of adsorption were determined. The results showed that the inhibition efficiency increased significantly by up to 85.49% (gravimetry) and 88.39% (electrochemical polarization) with increasing concentration of AF. However, the efficiency decreased slightly with increasing temperature in the range 303-343 K. The polarization curve showed that the inhibitor behaved as mixed inhibitor. AF was identified to contain compounds having functional groups of phenol, aromatic and ether. The adsorption model was found to obey Langmuir isotherm. The study showed that AF is effective in minimizing corrosion attack on mild steel in sulphuric acid.

Introduction

Iron and steel used in industrial processes involving acid cleaning, pickling and descaling, and drilling operations in oil and-gas exploration, undergo considerable corrosion [1]. Corrosion is a phenomenon which occurs naturally by the disintegration or destruction of metallic surfaces due to the chemical process between the metal and its surrounding environmental conditions [2].

The corrosion of iron and steel in acidic environments is reduced considerably by various methods. These include reduction in metal impurity content, use of some surface modification techniques and by the use of alloys. Also the use of corrosion inhibitors may be one of the most practical and economical. The inhibitor modifies the metal surface by the adsorbed organic molecules. In any case, the active corrosion sites on the metal surface are occupied by the adsorbed inhibitor and effectiveness of inhibitor will be determined by the energy released on forming the metal-inhibitor bond compared to the corresponding changes when the pure acid reacts with the metal [3].

Some synthetic organic (acetylenic alcohol, quaternary ammonium salts, hydroxy-benzylidene-amino-thioxo-thiazolidin-HBTT, dihydroxybenzy-lidenemethylquinolin trifluoro-thio-propano-hydrazides-HBTPH, alkaloids, butylmethlimi-dazolium chlorides-BMIC, polyethylenegly-colmethyl ether etc) and inorganic (butyl-methylimidazolium hydrogen sulphate-BMIMHSO$_4$, calcium gluconate etc) compounds have been used as corrosion inhibitors of metals but have been found to be non-biodegradable and toxic to both humans and the environment [4, 5]. This has led to research into the use of natural product plant extracts which are environmentally friendly and biodegradable. Extracts of leaves, roots, stems and flowers of plants have been studied and found to be efficient inhibitors of the corrosion of ferrous material in sulphuric, hydrochloric, phosphoric acid among others. Barreto *et al.* [6] studied the effectiveness of the extract of cocoa bark from *Theobroma cacao* to mitigate the corrosion of carbon steel 102 in 0.5 M HCl using weight loss and electrochemical methods and they reported an efficiency of 93% for 1.112 g/L extract. Anbarasi and Vasudha [7] studied the anticorrosion activity of *Cucurbita maxima* plant extract on mild steel in 1 M HCl. Loto *et al.* [8] investigated the effect of deanol on the corrosion of mild steel in dilute sulphuric acid mixed with sodium chloride. Also, extracts of *Biden pilosa* [9], Red Onion Skin [10], *Mimosa pudica* [11], *Juniperus procera* [4], and *Vernonia amygdalina* [12] have been studied as corrosion inhibitors of metals in aggressive environments. Interestingly, extracts of natural products such as leaves and seeds are known to contain several phytochemical substances, such as alkaloids, tannins, flavonoids, saponins, amino acids, ascorbic acids,

phenolic acids, pigments, resins, and triterpenoids which possess electronic structures similar to those of conventional organic corrosion inhibitors [1]. Such synthetic organic corrosion inhibitors have been reported to contain nitrogen, oxygen, sulphur, phosphorus, and multiple bonds or aromatic rings in their structures [13-16]. The number of lone pairs of electrons and loosely bound π-electrons in these functional groups are the key structural features that determine the inhibition efficiency [1]. *Athyrium filix-femina* is found in both temperate and tropical areas of the world and can grow successfully on many soils. The aim of this work, therefore, was to investigate the corrosion inhibition potential of ethanol extract of *Athyrium filix-femina* leaf as natural corrosion inhibitor for mild steel in sulphuric acid solution.

Experimental
Specimen and Material Preparation

The mild steel whose elemental composition has been reported earlier [17] was obtained commercially in Lagos, Nigeria. The steel sample was cut into coupons of dimensions $19 \times 16 \times 4$ mm, polished with emery paper, degreased in ethanol, dried and stored in dessicator. A stock solution of 1M H_2SO_4 was prepared for the experiment using analytical grade (98.77%) reagent and distilled water. Fresh *Athyrium filix-femina* leaf (**Figure 1**) collected from Ilara-Mokin, Ondo State, Nigeria, were cut separately into pieces and dried at room temperature. The dried leaves were ground into powder and soaked in ethanol for 5 days, after which the extract was filtered. The resulting filtrate was slowly evaporated to obtain crude extract. The extract was used to prepare five different concentrations ranging from 0.2-1.0 g/L in 1M H_2SO_4 solution.

Figure 1 Fresh Athyrium filix-femina leaf

Phytochemical Screening of the Crude Extract

The leaf extract of *Athyrium filix-femina* was qualitatively tested to identify the phytochemical constituents (saponins, steroids and triterpenoids, antraquinones, glycocydes, alkaloids and coumarins) according to standard methods [18]; and total flavonoids and tannins of the extract by reported methods [19, 20].

Gravimetry

In the gravimetric study, the pre-cleaned coupons were weighed (initial weight) before immersion in 100 mL of 1M H_2SO_4 solution for 4 hours; and in the presence of the leaf extract; after which, the coupons were retrieved, washed with distilled water, ethanol, and reweighed (final weight). The difference between the weight of the mild steel coupons before and after the immersion was the weight loss. The corrosion rate (CR, $gh^{-1} cm^{-2}$) was evaluated as,

$$CR = \frac{\Delta W}{At} \qquad (1)$$

Where ΔW = weight loss = $W_1 - W_2$, W_1 = initial weight of the coupon before immersion, W_2 = final weight of the coupon after immersion, A = area of the mild steel coupon, t = immersion time. The inhibition efficiency (I.E. %) was calculated as

$$\text{I.E.} = 1 - \left(\frac{CR_{inh}}{CR_{blank}}\right) \times 100 \qquad (2)$$

Where CR_{blank} is the corrosion rate without the inhibitor, CR_{inh} is the corrosion rate with the inhibitor. The surface coverage (θ) was obtained by

$$\theta = 1 - \left(\frac{CR_{inh}}{CR_{blank}}\right) \qquad (3)$$

Kinetic Study

Kinetic study was carried out by immersion of metal coupons in 1M H_2SO_4 solution containing different concentrations of the AF ranging from 0.2-1.0 g/L at room temperature. The experiment was performed by immersion of pre-weighed metal coupons in 100 mL of acid solution with the respective inhibitors and blank solutions. After 24 hours, the coupons were removed from the solutions, washed with distilled water, ethanol, and re-weighed. This was done progressively for 7 days.

Thermometric Study

The thermometric study was performed by immersing the pre-weighed mild steel coupons into beakers containing acidic solutions of 1 M H_2SO_4 in the absence (blank) and presence of extract of concentrations 0.2-0.8 g/L; subsequently the beakers with the contents were placed in a thermostated water bath. A digital thermometer was used to monitor the temperature of the bath as the temperatures were varied between 30-70 $^{\circ}$C (303-343 K) at 3 hours interval. At the end of immersion time, the metals were retrieved, washed with distilled water, rinsed in absolute ethanol; air - dried at room temperature and reweighed.

Fourier Transform Infra Red Study

FTIR spectra of AF and the corrosion products (in the absence and presence of the inhibitor) were obtained (KBr method) with a Pelkin Elmer Spectrum bx for the purpose of determining the functional groups of the compounds present in the extract. The study was carried out by scanning the samples through a wave number range of 400 to 4000 cm^{-1}.

Surface Morphology Study by SEM

The experiment was carried out by immersion of mild steel coupons in 1M H_2SO_4 in the presence and absence of the extract for 24 hours; after which, the coupons were retrieved, washed with ethanol and subsequently air-dried for SEM examination.

Electrochemical Studies

A three electrode cell assembly was used for the electrochemical study. The mild steel coupons of dimensions 1x1 cm^2 served as the working electrodes (WE). The mild steel coupons were embedded in a specimen holder using epoxy resin. A platinum wire was the auxiliary electrode while saturated silver chloride was the reference electrode. The electrolyte was 1M H_2SO_4 solution. The polarization curves were obtained with potentiostat AUTOLAB PG STAT 204 N system. The experiments were performed from -250 mV to +250 mV potential ranges at a scan rate of 10 mV/s. Before taking the polarization curves the WE was immersed in the test solution for 10 minutes at its corrosion potential to attain open circuit potential. Tafel lines extrapolation was used for detecting corrosion current (i_{corr}) and corrosion potential (E_{corr}) values. The I.E. (%) values from potentiodynamic polarization measurement were calculated using Equation 4.

$$\text{I.E.} = (CR_O - CR_I/CR_O) \times 100 \qquad (4)$$

Where, CR_I and CR_O are the corrosion current densities with and without extract inhibitor.

Results and Discussion
Phytochemical Analyses

The phytochemical analyses revealed the presence of triterpenoids, tannins, flavonoids, alkanoids, polyphenoids and

steroids in the AF. It has been reported that tannins, alkanoids, flavonoids and terpenoids of plant origin have good corrosion inhibitive capabilities [21, 22] and that the phytochemicals in plants that are effective for corrosion inhibition are those containing compounds that possess heteroatoms such as oxygen, nitrogen, phosphorus and sulphur in their heterocyclic carbon chain [20, 23]. These are adsorbed on the metal surface through which the protective films are formed [21]. Possession of suitable functional groups may also facilitate the transfer of electron from the inhibitor to vacant d-orbital of the metal [22].

Analyses of the FTIR Spectra

FTIR spectra were studied to gain knowledge of the interaction of molecules of the extract with the mild steel. **Figures 1** and **2**, respectively, show the infra-red spectra of the AF and mild steel corrosion product in the 1M H_2SO_4 solution with the extract. The following characteristic peaks were revealed in the AF (Figure 1); 3414 cm^{-1} (O-H broad of phenols), 2930 cm^{-1} (C-H stretch of alkenes), 1718 cm^{-1} (C=O stretch of ketones), 1642 cm^{-1} (C=O stretch of amides), 1067 cm^{-1} (C-O stretch of alcohols).
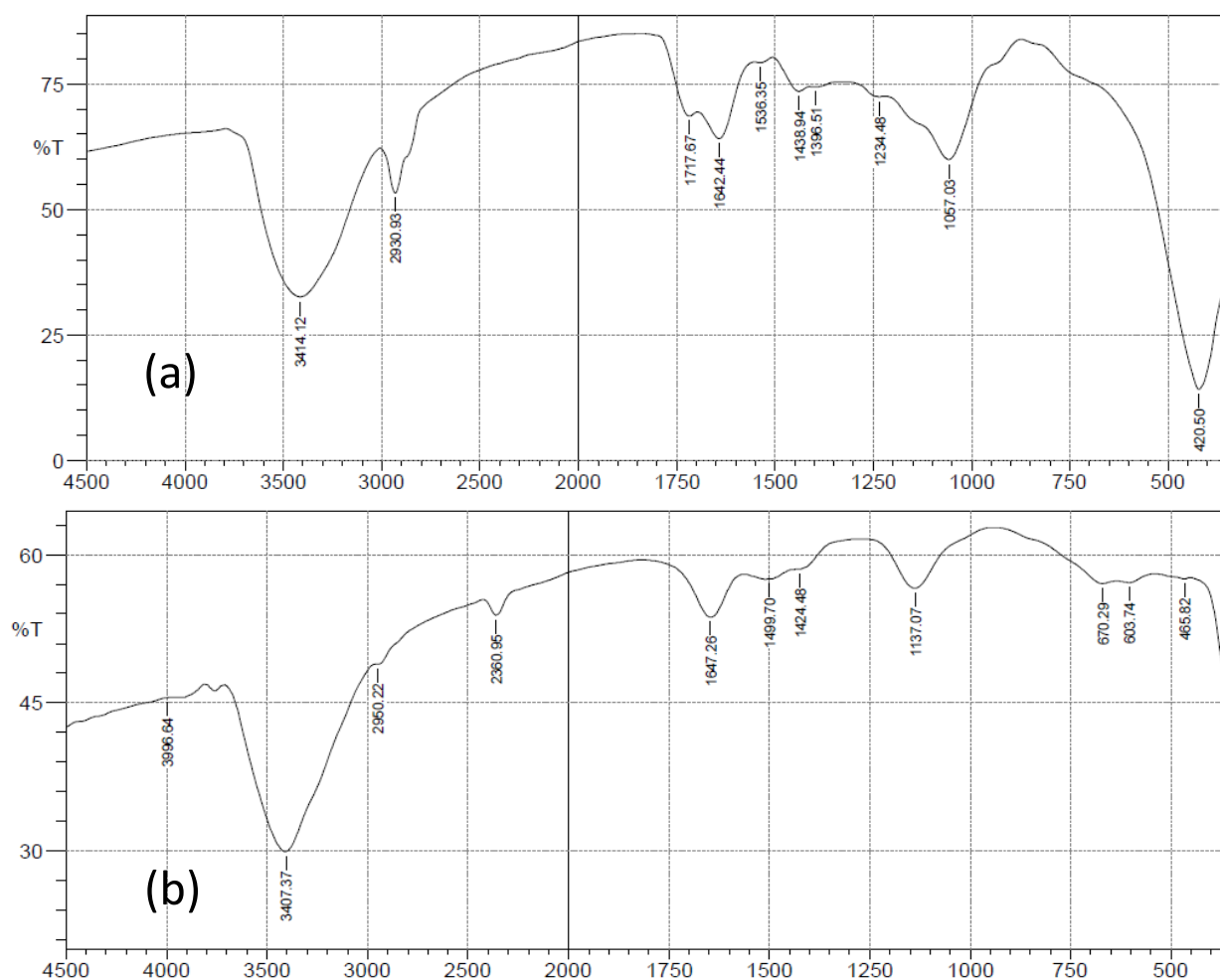

Figure 2 (a) FT-IR Spectrum of Ethanolic Extract of *Athyrium filix-femina*, (b) FT-IR Spectrum of the Dried Solid Adsorption Product in 1M H_2SO_4 Solution Containing Ethanolic Extract of *Athyrium filix-femina* and Mild Steel

The infra-red spectrum on the AF with dried adsorbed product in 1M H_2SO_4 (Figure 2) revealed the following characteristics: 3407 cm^{-1} (O-H stretch of phenols), 2950 cm^{-1} (C-H stretch of alkanes), 2360 cm^{-1} (C≡C stretch of alkynes), 1647 cm^{-1} (C=O stretch of amides), 1499 cm^{-1} (C=C stretch of aromatics), 1137 cm^{-1} (O-H stretch of alcohols). The broad peaks between 3300 cm^{-1} to 3500 cm^{-1} is assigned to the presence of superficial absorbed water, stretching mode of an OH or NH. In the AF spectrum, there was backward shift from 3414 cm^{-1} (broad) to 3407 cm^{-1} (sharp). Thus, presence of O-H stretching observed on the spectra of mild steel containing inhibitor suggests an interaction of the extract with the metal surface at this position [24]. Forward shift from 2930 cm^{-1} to 2950 cm^{-1} and 1642 cm^{-1} to 1647 cm^{-1}, was observed in Figures 1 and 2, respectively. These wave numbers correspond to stretching vibrations of C-H (alkanes); C=O (amides); C=C (aromatic rings); C≡C (alkynes) indicating that the plant extract

contained mixture of organic compounds that can facilitate the transfer of electron from the inhibitor molecule to vacant d-orbital of the metal [22]. These compounds were adsorbed on the mild steel surface thereby providing protection against corrosive environment. The peak at 1718 cm^{-1} (Figure 1) was observed in the AF without mild steel which correspond to stretching vibration of ketone, C=O. The stretching vibration could be as a result of electron cloud density shift from O atoms to co-ordinate with Fe^{2+} to form iron (II) oxide [25]. The peaks between 400 and 600 cm^{-1} were mainly due to Fe_2O_4 [24]. The changes in absorption bands imply that adsorption between extract and mild steel took place through these functional groups providing inhibition of corrosion of the mild steel.

Gravimetry
Effect of Concentration of Extract on the Corrosion rate of Mild Steel and the Inhibition Efficiency in 1 M H_2SO_4

Figure 3 shows the effect of concentration of ethanol extract of *Athyrium filix-femina* leaf on the corrosion rate of mild steel in 1 M H_2SO_4 as obtained in the gravimetric study. The corrosion rate of mild steel in 1 M H_2SO_4 decreased with increase in the extract concentration. This indicates that the rate of corrosion of mild steel in acid solution is dependent on the amount of inhibitor present which is in agreement with previous reports [12, 20, 26], meaning that corrosion resistance is enhanced. **Figure 4** shows the effect of extract concentration of *Athyrium filix-femina* leaf on inhibition efficiency on mild steel in 1 M H_2SO_4. It can be observed that inhibition efficiency increased with extract concentration by up to 85.49% at 1.00 g/L. This occurrence may be because, as the inhibitor increased, the amount of phytochemical compounds adsorbed on the metal surface increased [27, 28].
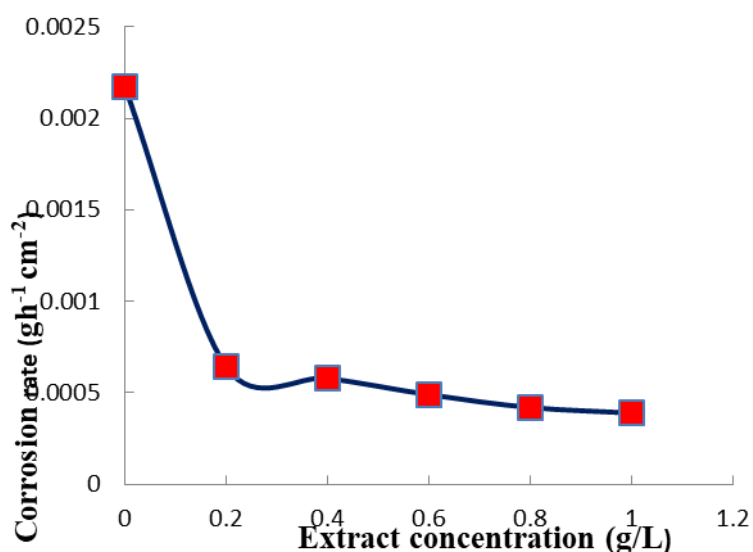

Figure 3 Effect of Concentration of Ethanolic Extract of *Athyrium filix-femina* on the Corrosion Rate of Mild Steel in 1M H_2SO_4
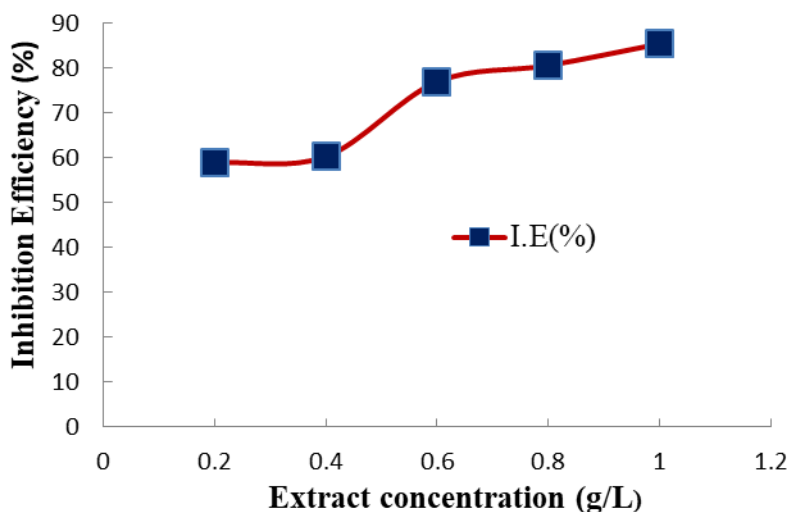

Figure 4 Effect of Extract Concentration of *Athyrium filix-femina* on Inhibition Efficiency on Mild Steel in 1M H_2SO_4

Effect of Temperature on Corrosion Rate

Weight loss measurement was carried out over a range of 303-343 K in presence and absence of the inhibitor for an immersion period of 3 hours (**Figure 5**). From the results, it is observed that the rate of dissolution of mild steel in the absence (blank solution) and presence of inhibitors increased with increase in the temperature. The result showed that the corrosion rate of mild steel in the presence of inhibitor is much decreased than the corrosion rate in the blank. The decrease in the corrosion rate of solution containing inhibitor is indicative of the mitigating effect of inhibitors on the corrosion rate of mild steel [29].
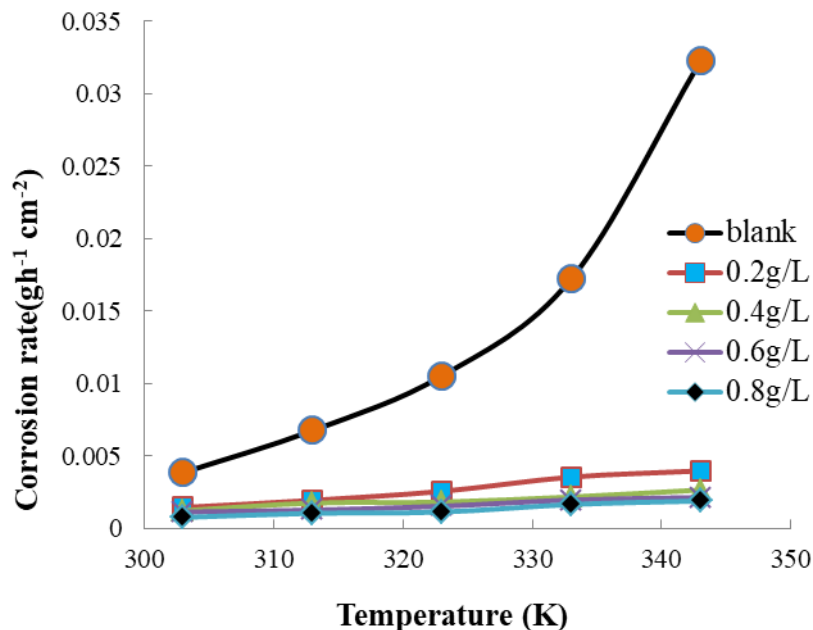

Figure 5 Effect of Temperature on Corrosion Rate

Corrosion Inhibition Kinetics

Kinetic analyses of corrosion inhibition data were considered by plotting $\ln(W_i - \Delta W)$ against time (days) (**Figure 6**). The plots showed a linear variation and confirm a pseudo first order reaction of mild steel in 1M H_2SO_4 in the absence and presence of AF. The rate constants (k_1) were calculated from the slope of the graph using Equation 5.

$$\ln(W_i - \Delta W) = -k_1 t + \ln W_i \qquad (5)$$

From the calculated rate constants, the half-life ($t_{1/2}$) values were evaluated according to Equation 6.

$$t_{1/2} = \frac{0.693}{k} \qquad (6)$$

The calculated rate constant and the half-life values, at different concentrations of the extract, are provided in **Table 1**. Here as the extract concentration increased, the rate constant decreased while the half-life increased consistent with [30]. The veracity of this observation is attributable to a similar trend previously reported on leguminous seeds [31].

Thermodynamic Studies

Figure 7 shows the Arrhenius plot of Log(CR) of mild steel in H_2SO_4 as a function of 1/T in the absence and presence of different concentrations of AF (0.2-0.8 g/L) according to equation 7.

$$Log(CR) = \frac{-Ea}{2.303RT} + LogA \qquad (7)$$

Where E_a is the apparent activation energy, A is the Arrhenius pre-exponential factor and R is the molar gas constant and T temperature (K).
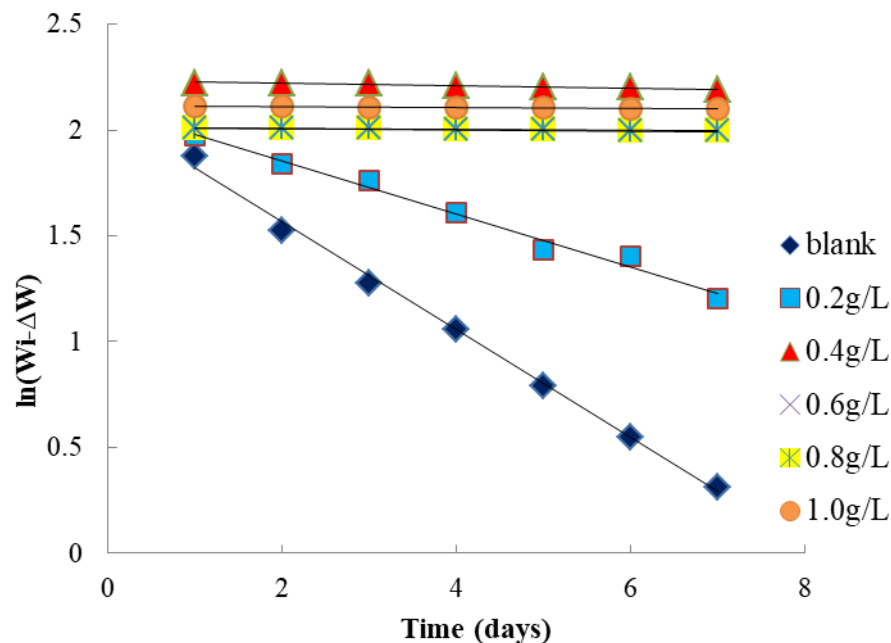The values of activation energy (E_a) were computed from the slope of Figure 7 and presented in Table 1.

Figure 6 Variation of ln(W$_i$ -ΔW) against time for Mild Steel Coupons in 1M H$_2$SO$_4$ Solution Containing Ethanol Extract of *Athyrium filix-femina* at 303K
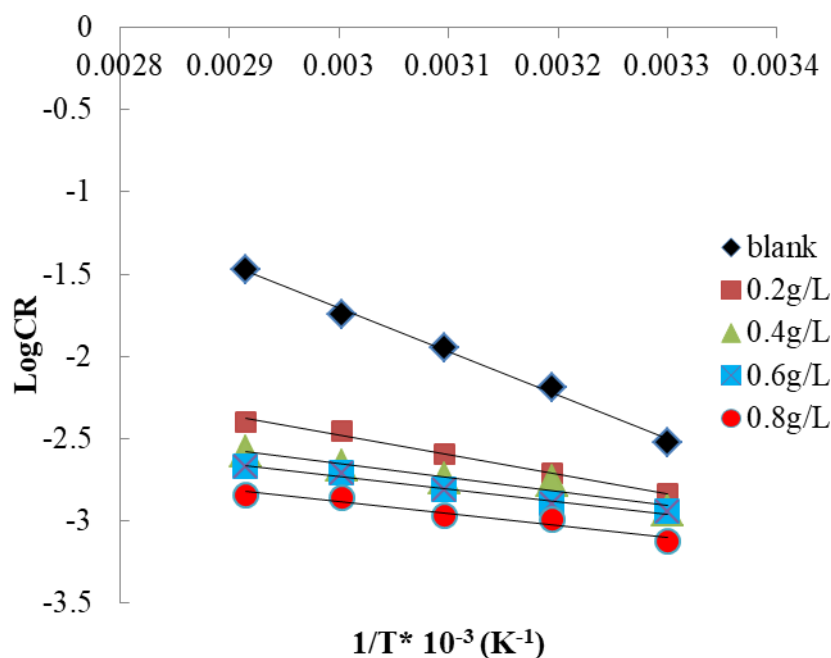

Figure 7 Arrhenius Plot of Log CR against 1/T for Mild steel at Different Concentrations of Ethanol Extract of *Athyrium filix-femina* in 1M H$_2$SO$_4$

Table 1 Kinetic and Thermodynamic Parameters of the Corrosion Reactions for Mild Steel in 1M H$_2$SO$_4$ Solution

Conc. of extract (g/L)	k (day^{-1})x10^{-3}	Half life (day)	ΔH^o (kJmol^{-1})	ΔS^o (kJmol^{-1})	E$_a$ (kJmol^{-1})
Blank	0.041309	16.7760	45.07812	-0.1944240	50.8472
0.2	0.020214	34.3832	18.03527	-0.1822598	22.7564
0.4	0.008982	77.1453	12.70949	-0.2010778	16.2038
0.6	0.006678	103.7736	11.76649	-0.2054604	14.8540
0.8	0.005067	136.7673	11.71384	-0.2069653	13.7994
1.0	0.003685	188.0597	-	-	-

The Eyring transition state explains the rate on the basis of thermodynamics through which the enthalpy and entropy of activation of the reactions are determined (Equation 9, **Figure 8**). Arrhenius equation can also be expressed as:

$$C_R = \left[\frac{RT}{Nh}\right] \exp\left[\frac{\Delta S^\circ}{R}\right] \exp\left[\frac{-\Delta H^\circ}{RT}\right] \qquad (8)$$

Where, h is the Plank's constant, N is the Avogadro's number, T is the absolute temperature (K), ΔS° is the entropy of activation and ΔH° is the enthalpy of activation. Equation 8 was further stated as

$$\text{LogCR/T} = \text{Log}\left(\frac{RT}{Nh}\right) + \frac{\Delta S^\circ}{2.303R} \frac{-\Delta H^\circ}{2.303RT} \qquad (9)$$

The thermodynamic values of ΔS° and ΔH° were calculated from the slope and intercept of Figure 8 and presented in **Table 2**.
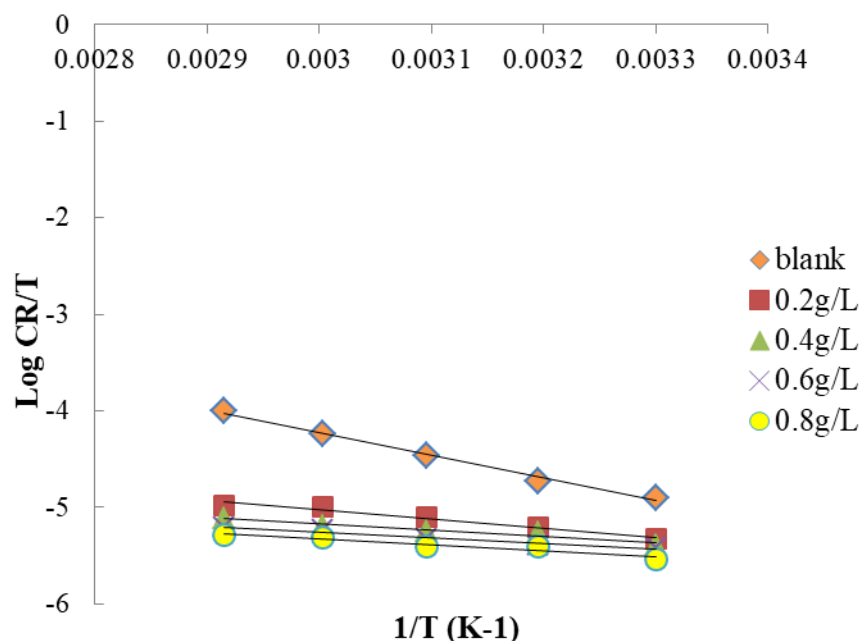

Figure 8 Eyring Transition State Plot for Mild Steel in 1M H_2SO_4 in the Presence and Absence of Ethanol Extract of *Athyrium filix-femina* at Different Concentrations

Table 2 Parameters Values of Adsorption Isotherm Models and Gibbs Free Energy for Ethanol Extract of *Athyrium filix-femina* in 1M H_2SO_4 at Various Temperatures

Temp. (K)	Freundlich			Temkin		Langmuir		ΔG_{ads} (kJmol^{-1})
	K_F	R^2	$1/n$	K_T	R^2	K_{ads}	R^2	
300	0.1409	0.9702	0.1029	23.3813	0.9666	15.0376	0.9992	-16.9492
313	0.1046	0.9034	0.1216	24.7514	0.9012	24.3891	0.9994	-18.7672
323	0.0712	0.9893	0.1185	25.0013	0.9869	28.4215	0.9992	-19.7780
333	0.0553	0.9205	0.1079	27.7641	0.9139	30.6410	0.9993	-20.5983
343	0.0359	0.9527	0.0728	46.7167	0.9037	55.5051	0.9986	-22.9114

It is evident from the obtained values in Table 1 that the value of activation energy (E_a) in the presence of the extract decreased as the concentration of the extract increased. The reduction in the activation energy E_a value in inhibited solution imply that the adsorption of the extract on mild steel has actually taken place, which indicates that the presence of inhibitors reduced considerably the activation energy of the corrosion process in acid solution as reported by [24]. It has been reported that decrease in apparent activation energy in the presence of extract inhibitor, as obtained in this work, suggests chemical adsorption mechanism [32-34].

The positive values of enthalpy (ΔH°) with and without extract in acidic medium suggest that the adsorption of the extract on mild steel was endothermic. "Adsorption processes with $\Delta S_{ads} < 0$, as obtained here are better described in terms of orderliness of the active species in the aggressive aqueous medium. Prior to adsorption, active ingredients

of the extracts are assumed to be more disordered (chaotic) in the bulk medium, but as the adsorption onto the metal surface progresses, orderliness gradually sets in leading to a decrease in entropy. The number of active molecules present in the bulk solution may have also decreased occasioned by involvement of much of the other molecules in the adsorption process, and hence the decrease in entropy" [35].

The equilibrium adsorption constant (K_{ads}) which is related to the Gibbs free energy of adsorption (ΔG_{ads}) as employed by previous investigators [21, 36, 37] is expressed as:

$$K_{ads} = \frac{1}{55.5} \exp\left[\frac{-\Delta G^{\circ}_{ads}}{RT}\right] \qquad (10)$$

Equation 10 can also be written as:

$$\Delta G^{\circ}_{ads} = -2.303RT \, Log \, (55.5K_{ads}) \qquad (11)$$

Where, ΔG°_{ads} is the Gibbs free energy of adsorption, K_{ads} is the equilibrium constant, R is the universal gas constant, T is the thermodynamic temperature (K) and the value of 55.5 is the molar concentration of water in solution.

The Gibbs free energy of adsorption (ΔG°_{ads}) for AF in 1M H_2SO_4 solution was calculated according to Equation 11 and presented in Table 1. The negative values of ΔG_{ads} indicate the spontaneity of the process and stability of adsorbed layer of the extract on mild steel in acid solution [25]. The increase in the values of K_{ads} with extract concentration as the temperature increased suggests a strong adsorption interaction between the extract and the mild steel surface in 1 M H_2SO_4 solution. According to Bentiss *et al.* [35], the higher the value of K_{ads}, the stronger and more stable the adsorbed layer forming on the mild steel surface which results in higher inhibition efficiency of the extract.

Generally, preliminary investigations have shown that the values of ΔG_{ads} up to -20 kJmol^{-1} are consistent with physisorption, while those negative values higher than -20 kJmol^{-1} are associated with chemisorption which involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond [29, 38]. In this study, the values of ΔG°_{ads} obtained for the AF on the corrosion rate of mild steel in 1M H_2SO_4 are in the range of physisorption [21]. The values of activation energy decreased with increase in extract concentration (Table 1).

Adsorption Isotherms

Corrosion inhibition of MS in acidic solutions by the inhibitors can be explained on the basis of molecular adsorption [39]. The adsorption processes of the inhibitor are influenced by the chemical structure of organic compounds nature and surface charge of the metal, the distribution of the charge in the molecule and type of aggressive media [40].

The general form of isotherm is given as:

$$f(\theta, x) \exp(-2a\theta) = KC_{inh} \qquad (12)$$

where $f(\theta, x)$ is the configuration factor which depends upon physical model and the assumption underlying the derivation of the isotherm. θ, is the degree of surface coverage, C_{inh} is the inhibition concentration, x is the molecular interaction parameter in the adsorbed layer of the surface and K is the equilibrium constant of adsorption phenomenon [41].

$$\theta = 1 - \left(\frac{C_{Rinh}}{C_{Rblank}}\right) \qquad (13)$$

Where, C_{Rblank} is the corrosion rate in the absence of the extract inhibitor, C_{Rinh} is the corrosion rate in the presence of the extract inhibitor.

The data obtained were correlated using Freundlich, Temkin and Langmuir adsorption isotherms.

Freundlich Isotherm

The empirical equation proposed by Freundlich is given as:

$$\theta = K_F \, C^{1/n} \qquad (14)$$

The linear equation (plotted in **Figure 9**) is expressed as:

$$Log\theta = LogK_F + 1/n\ LogC_{inh} \qquad (15)$$

Where, θ is the surface coverage, C_{inh} is the concentration of the extract inhibitor; K_F and $1/n$ are adsorption capacity and intensity respectively. The Freundlich constant K_F is the ratio of the amount of substance adsorbed to that in solution provided the Freundlich exponent is equal to 1. If the Freundlich exponent $(1/n)$ were less than 1, it would indicate that as sorbate (extract) concentration increased sorption of additional molecules on the solid surface would become more difficult [42].

The parameters obtained from the Freundlich isotherm are given in Table 2. The value of strength of adsorption, $1/n$ were less than 1 suggesting that the adsorption of extract on the mild steel was influenced by the increase in the extract concentration. This can be attributed to the presence of phytochemical species in the extract adsorbed on mild steel [20]. The regression coefficient R^2=0.9034-0.9893 and K_F=0.0359-0.1409 obtained from the Freundlich model suggest good association between the extract molecules and mild steel surface [36, 43].
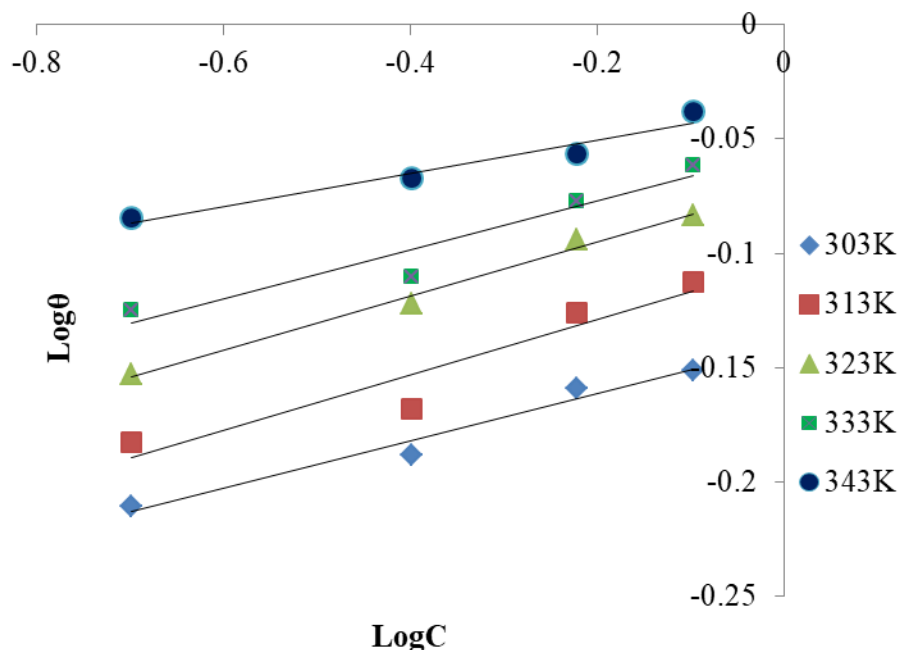

Figure 9 Freundlich Adsorption Isotherm for Ethanol Extract of *Athyrium filix-femina* on Mild Steel in 1M H_2SO_4 at Different Temperatures

Temkin Isotherm

Temkin explains that the heat of adsorption as a function of temperature of all the molecules in layer would linearly decrease with surface coverage rather than logarithmically (Equation 16). Temkin isotherm model is expressed as:

$$\theta = RT/b\ lnA + RT/b\ lnC_{inh} \qquad (16)$$

where, A is the Temkin adsorption equilibrium binding constant, b is the Temkin adsorption constant being related to the heat of adsorption, R is the universal gas constant and T is the temperature, C_{inh} is the concentration of the extract inhibitor [37]. Plots of θ against lnC_{inh} as shown in **Figure 10** produced straight line graph and Temkin coefficients (K_T and R^2) presented in Table 2. This observation provides evidence that the corrosion inhibition followed Temkin adsorption isotherm [36, 43]. Temkin constants increased with rise in temperature (Table 2). This indicates an inclination of adsorption towards chemisorption mechanism [21, 34, 37, 44].

Langmuir Isotherm

Langmuir isotherm is expressed as:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (17)$$

Where, θ is the surface coverage, K_{ads} is adsorption equilibrium constant and C_{inh} is the concentration of the extract inhibitor [43, 45].

The plot of C_{inh}/θ vs. C_{inh} (**Figure 11**) yielded straight line graph and adsorption coefficients (Table 2) showing that the corrosion inhibition on mild steel followed the Langmuir isotherm [45].

From the values in Table 2, it can be deduced that the best model fitted so far for this study was obtained with Langmuir isotherm (R^2=0.9986-0.9994). This implies that the adsorption process of the extract on mild steel in 1M H_2SO_4 occupied typical adsorption site on the metal surface with the strong linear association between the adsorbate molecules and adsorbent surface [46].
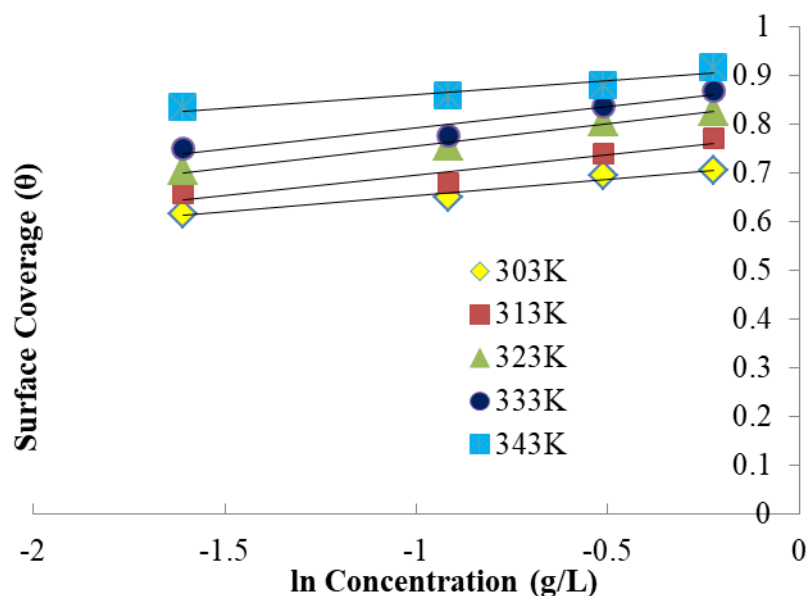

Figure 10 Temkin Adsorption Isotherm for Ethanol Extract of *Athyrium filix-femina* on Mild Steel in 1M H_2SO_4 at Different Temperatures
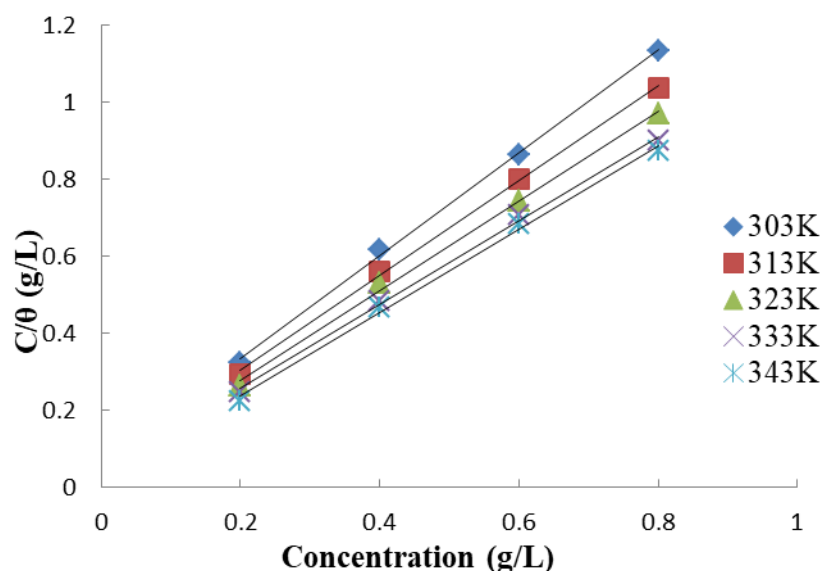

Figure 11 Langmuir Adsorption Isotherm for Ethanol Extract of *Athyrium filix-femina* on Mild Steel Corrosion Rate in 1M H_2SO_4 at Various Temperatures

SEM Surface Morphology

The SEM micrographs are shown in **Figures 12a-c** respectively. Figure 12a shows the SEM image of mild steel in its unspoiled condition before immersion in acid solution. Figure 12b shows the SEM image of mild steel after immersion in 1M H_2SO_4 solution without inhibitor. It is observed from the image that the mild steel surface was rough and highly damaged due to the direct attack of aggressive acid. Figure 12c shows the SEM image of mild steel after

immersing in 1M H_2SO_4 solution containing 1.0 g of extract. It can be observed that the metal surface is smoother when compared to the uninhibited sample (Figure 12b). The mild steel was covered by the inhibitor extract leading to the formation of a protective film on the metal surface that caused the reduction in the dissolution of mild steel in 1M H_2SO_4 solution [13]. It has been reported that the protective film acts as a barrier between the metal and the acidic medium by retarding the corrosion rate of the metal [22]. Thus, the surface morphology of the adsorbed protective film on the mild steel surface further confirmed the evidence of inhibition potentials of ethanol extract of *Athyrium filix-femina* leaf in retarding the corrosion rate of mild steel in 1 M H_2SO_4 solution [14]. Previous investigations gave similar report [28, 47].
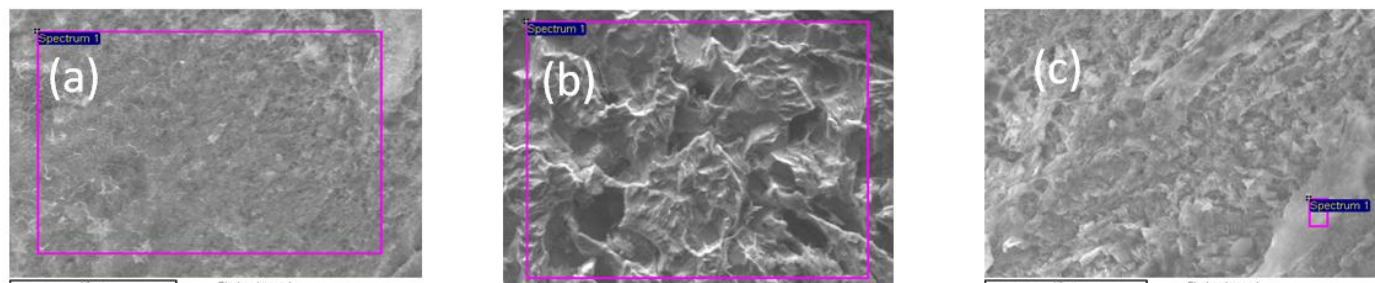

Figure 12 SEM Image of Mild Steel: (a) As Received Before Corrosion Study (b) Without Extract in 1M H_2SO_4 Solution (c) In the Presence of Extract in 1M H_2SO_4 Solution

Electrochemical Study

When a metal is immersed in a solution a negative charge occurs at the interface between the metal and the solution producing corrosion potential. The corrosion potential can be used to study the corrosion rate from polarization curves. The polarization curves for mild steel in 1 M H_2SO_4 solution in the absence and presence of *Athyrium filix-femina* leaf are shown in Figure 13. It can be observed from the graph that the addition of inhibitors prevented the aggressive attack on the mild steel electrode. The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current densities (i_{corr}), corrosion rate, anodic Tafel slope (β_a), cathodic Tafel slope (β_c) and inhibition efficiency (I.E%) were determined from the polarization Tafel curves and presented in **Table 3**.
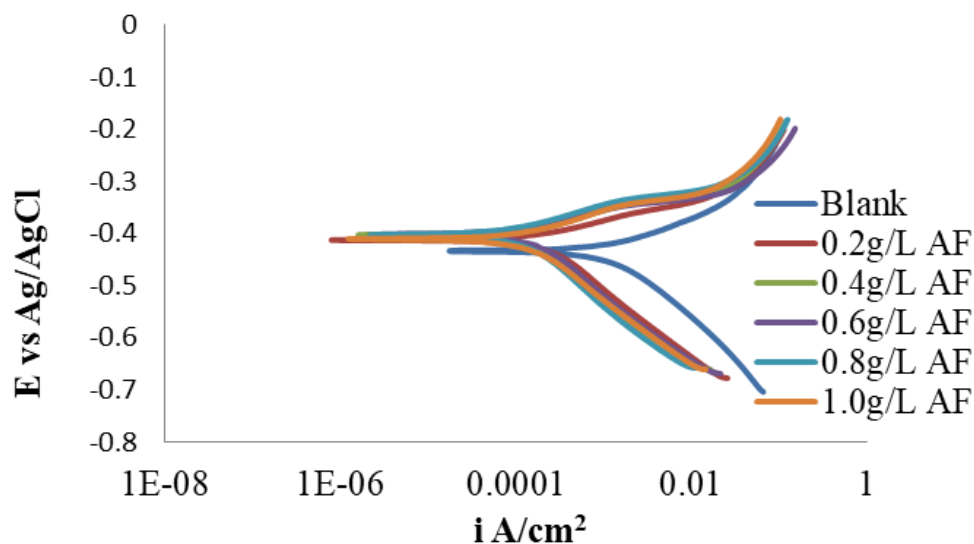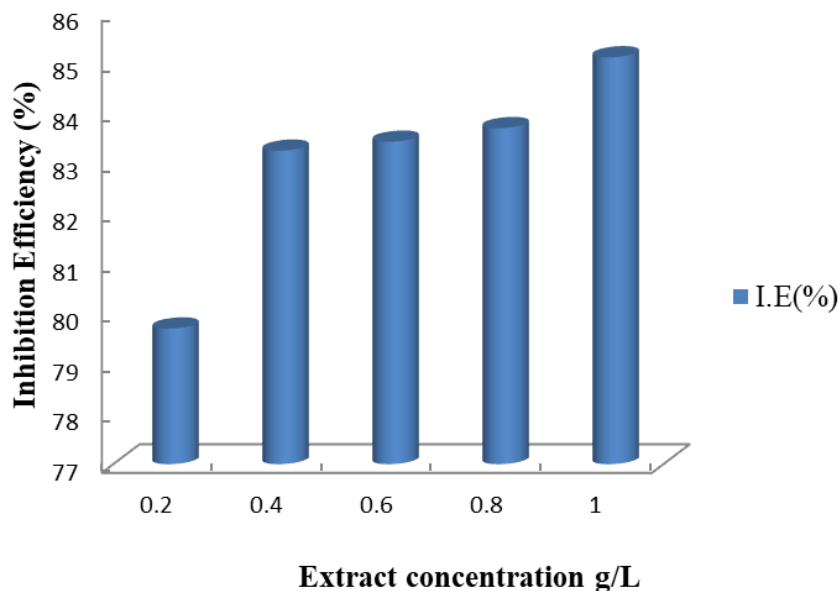

Figure 13 Tafel Polarization Curves for Mild Steel in 1M H_2SO_4 in the Presence and Absence of Different Concentration of *Athyrium filix-femina*

As can be seen from the data obtained from polarization curves (Table 3), the corrosion current density (i_{corr}) as well as the corrosion rate of the mild steel decreased considerably with increase in the extract concentration. The i_{corr} values were progressively decreased as the amount of inhibitor added to the acid solutions was increased. This was due to the constituents of the extract covering the surface of the coupons, thereby retarding the dissolution of the metal into the electrolyte.

Table 3 Corrosion Parameters Obtained from Electrochemical Polarization Measurements for Mild Steel in 1M H$_2$SO$_4$

Extract concentration g/L	E$_{corr}$ (mV)	i$_{corr}$ (µA/cm^2)	β$_a$ (mV/dec)	β$_c$ (mV/dec)	Corrosion rate (mm/y)	I.E (%)
Blank	-434.083	1196.000	60.865	165.786	13.8950	-
0.2	-412.336	205.814	49.522	124.101	2.3899	82.79
0.4	-402.647	159.523	60.435	166.271	1.8524	86.66
0.6	-401.356	158.998	55.773	140.873	1.8463	86.77
0.8	-409.108	145.108	72.480	165.436	1.6269	87.87
1.0	-410.108	140.817	65.153	139.013	1.5829	88.39

Figure 14 Effect of Potentiodynamic Polarization of *Athyrium filix-femina* Inhibition Efficiency on Mild Steel in 1M H$_2$SO$_4$

The inhibition efficiency increased as the concentration of extract was increased (**Figure 14**). This agrees with the results obtained in the gravimetric study. The increase in inhibition efficiency with increase in extract concentration can be explained on the basis of the amount of adsorption and the coverage of extract molecules on mild steel surface [46]. It can also be observed from the data that the decrease in the values of anodic Tafel slope (β$_a$) and cathodic Tafel slope (β$_c$) seems to be more pronounced with increase in the extract concentration compared to the values of corrosion potential (E$_{corr}$) which relatively remained the same with the uninhibited solution (blank) value. The change in anodic and cathodic Tafel slopes suggests that the extract acts as a mixed-type inhibitor (i.e. inhibits both cathodic and anodic reactions) [48, 49]. This indicates that the kinetic interaction of the extract on corrosion rate of mild steel in 1 M H$_2$SO$_4$ was controlled by the anodic dissolution mechanism and cathodic hydrogen evolution mechanism [50, 51]. Furthermore, the E$_{corr}$ did not change appreciably suggesting a mixed type inhibitor. The displacement of E$_{corr}$ was < 85 mV confirming a mixed type inhibitor [52].

Table 4 Comparison of Inhibition Efficiencies of *Athyrium filix-femina* with other Natural Inhibitors on Mild Steel Using 1 M H$_2$SO$_4$ by Gravimetry

Natural Products	Percentage Inhibition	References
Nypa fruticans wurmb leaves	74.48	[53]
Groundnut leaves	85.90	[54]
Sida acuta	85.00	[55]
Cordia milleni leaves	92.00	[17]
Zizyphus spina-Christi	90	[56]
Linum Usitatissimum seeds	95.5	[57]
Baphia nitida leaves	76.4	[58]
Sorghum vulgare leaves	72.03	[59]
Athyrium filix-femina leaf	85.49	This study

Comparison of Inhibition Efficiencies of Athyrium filix-femina with other natural inhibitors

Table 4 gives the result of comparative study of inhibition efficiency recorded from this study with other known green inhibitors. It is observed that the result obtained in this study compared favourably well with the results obtained from some other green inhibitors that have been applied to mild steel.

Conclusions

In the present study, *Athyrium filix-femina* leaf extracted with ethanol was successfully used as inhibitor for mild steel corrosion in 1 M H_2SO_4 acid solution. Inhibition efficiency was found to increase and corrosion rate decreased with increase in extract concentration and rise in temperature. Potentiodynamic polarization curves revealed anodic and cathodic mixed-type inhibitor. The phytochemical analysis revealed the presence of triterpenoids, tannins, flavonoids, alkanoids, polyphenoids, and steroids. The FTIR spectra showed that the functional groups present in the plant extract were those needed for corrosion prevention. Kinetics of inhibition showed pseudo first order reaction. Decrease in activation energy as concentration of extract increased implies the adsorption of extract on mild steel. Both physisorption and chemisorption apparently occurred in the corrosion inhibition whereas the isotherms studied showed that the best result was Langmuir model.

Acknowledgements

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