International Journal of Advanced Materials Research
Vol. 5, No. 1, 2019, pp. 20-30
http://www.aiscience.org/journal/ijamr
ISSN: 2381-6805 (Print); ISSN: 2381-6813 (Online)

Assessment of Corrosion Inhibitory Potential of *Cordia millenii* Leaves Extract on Mild Steel in Acidic Medium

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Abstract

The corrosion inhibitory potential of Ethanol Extract of *Cordia millenii* (EECM) leaves on mild steel corrosion in 1M H_2SO_4 solution was investigated using gravimetric and electrochemical techniques. Experiments were performed by varying the immersion time, extract concentration and reaction temperature. The results obtained from weight loss method showed a decrease in the corrosion rate of mild steel as the extract concentration increases while the inhibition efficiency increases with extract concentration. The highest inhibition efficiency observed for EECM at 1.0g/L was 92%. Temperature studies revealed an increase in inhibition efficiency with rise in temperature and activation energies were found to decrease in the inhibited solutions compared to uninhibited solutions. A mechanism of chemical adsorption of the plant components on the surface of the metal is proposed for the inhibition behaviour. The Kinetic and thermodynamic parameters were calculated and discussed. The adsorption of the EECM on mild steel surface was in accordance with the Langmuir adsorption isotherm. The potentiodynamic polarization curves revealed that the inhibitor acts as mixed-type inhibitor. FTIR results indicate that EECM contains O and N atoms in functional groups (O-H, N-H, C=C, C=N, C=O, C-O) and aromatic ring which meet the general consideration of a typical corrosion inhibitor. SEM- EDX results revealed that the corrosion of mild steel in 1 M H_2SO_4 was retarded by EECM due to an adsorption film that appeared on the surface.

Keywords

Corrosion, Mild Steel, Electrochemical, Gravimetric, Inhibition, *Cordia millenii*

Received: February 28, 2019 / Accepted: April 8, 2019 / Published online: May 5, 2019

1. Introduction

The word corrosion is as old as the earth, but it has been known by different names. It is commonly known as rust which destroys the luster and beauty of objects by shortening their life span [1]. However, corrosion is a natural phenomenon commonly defined as the deterioration or destruction of metal surfaces caused as a result of chemical reactions between it, and the surrounding environmental conditions [2]. It is an extractive metallurgy in reverse which serves to return metals to their ore. It is typically an electrochemical process in which the corroding metal behaves like a small electrochemical cell. The study of mild steel corrosion phenomena has become important especially in acid solutions because of the increase industrial applications of acid media [3]. Acid solutions are widely used in industry for removal of undesirable scale and rust in metal finishing. The most important areas of application are acid pickling, industrial acid cleaning and heat exchangers. The use of inhibitors for the control of metals is one of the

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most practical approaches for preventing metal against corrosion especially in acid solutions in order to prevent unexpected metal dissolution and acid consumption [4]. Meanwhile, concerted efforts are being employed by scientists with a view to improving the life span of metallic and alloy materials by finding suitable compounds that could be used as anti-corrosion in various media to prevent the metal from being deteriorated. A lot of money is being expended every year due to corrosion which can be as high as 3.5% of the nation's GDP and losses due to corrosion could be around Rs 2.0 lakh crores per annum in India [5]. Corrosion costs manifest in the form of premature deterioration or failure necessitating maintenance and replacement of damaged parts. In the United States alone, the total direct cost of corrosion is estimated at about 300billion dollars per annum, which is about 3.2% of GDP. It was suggested that, if corrosion optimum management practices are put in place, about 25 to 30% of this total cost could be avoided [4, 5]. Aside from materials loss, corrosion interferes with human safety, disrupts industrial operations and possesses danger to environment. A way of controlling or preventing corrosion is not only timely but also important. Awareness to corrosion and adaptation of timely and appropriate control measures hold the key in the abatement of corrosion failures. Meanwhile, if corrosion is prevented, the colossal amount of money lost to corrosion can be used in other areas, such as creation of employment and road construction. In light of this, corrosion is an undesirable phenomenon that must be prevented. A corrosion inhibitor is a chemical compound which when added in small concentration to liquid or gas, decreases the corrosion rate of a material, typically, a metal or an alloy [6]. In some years back, synthesized chemicals from organic and inorganic compounds have been used as inhibitors in addressing the problem of corrosion of metals among other preventive corrosion methods [7]. Unfortunately, most of these synthesized chemical inhibitors are expensive and not eco-friendly due to their hazardous effects [8], since the safety to the environment is an essential tool for any inhibitor to be considered for use. For this purpose, natural products are considered desirable as a good source [6], because they are readily available, eco-friendly, renewable, cheap, inherent biodegradability and environmentally acceptable [9]. In addition, natural products yield versatile materials through chemical transformation with plethora of applications in corrosion resistance against various corrodents [10]. The *Cordia millenii* belongs to the family of Boraginaceae and is widely distributed in tropical Africa, found in close forests and old secondary formations. It is resistant to termite and dry-wood borer attack and moderately resistant to fungi attacks being commonly used for construction, joinery, interior trim, paneling, furniture, musical instruments including drums, boxes, toys, utensils tool handles, canoes and carving. It is suitable for boat building, cabinet work veneer, plywood and hardwood. Meanwhile, preliminary investigation showed that *Cordia millenii* leaves contains some phytochemicals which could make it function as a good corrosion inhibitor. However, literature search reveals that no study has been done on the inhibitive effects of *Cordia millenii* leaves extract on acid corrosion of mild steel. Thus, this study aims at investigating the inhibitive effects of *Cordia millenii* leaves extract on mild steel corrosion in acidic medium.

2. Experimental

2.1. Materials Specimen Preparation

The mild steel specimen used for this work had the following elemental composition of C: 0.215%, Si: 0.258%, Mn: 0.467%, S: 0.009%, Cr: 0.007%, Ni: 0.001%, Cu: 0.017%, Ti: 0.019% and others being Fe: 98.98%. It was mechanically sectioned into coupons of uniform dimensions of 19×16×4 mm at the Mechanical Engineering workshop of the Federal University of Technology, Akure. The coupons were polished with successively fine grades of emery papers until scratches-free surfaces were obtained and then washed thoroughly with distilled water, degreased with absolute ethanol and finally dried at room temperature before corrosion test was carried on them.

2.2. Preparation of Aggressive Solution

H_2SO_4 acid was used as aggressive solution for the study. It was prepared by dilution of 1M H_2SO_4 of analytical grade (98.77%) with double distilled water. 100 mL of the prepared solution was employed as the corroding medium for each metal in the study.

2.3. Preparation of Plant Extract

The leaves of *Cordia millenii* were cut into pieces and dried at room temperature. Thereafter, the leaves were pulverized and soaked in ethanol for five days. At the end of the extraction period, the extract was filtered and the filtrate was further subjected to evaporation using vacuum condenser. The crude extract obtained was used to prepare test solutions at concentrations of 0.2, 0.4, 0.6., 0.8 and 1.0g/L.

2.4. Weight Loss Experiment

The gravimetric technique was carried out as previously described [11, 12]. Briefly, the pre-cleaned mild steel coupons were immersed in 100 mL of 1M H_2SO_4 solution with and without addition of different concentrations of *Cordia milleniii* extract for 4 hours. After the immersion period, the coupons were washed with distilled water, dried and re-weighed using 4-digit Electronic Analytical balance. The weight of the mild steel coupons before and after the immersion was calculated and taken as the weight loss. From the weight loss results, Corrosion Rate (CR), Inhibition Efficiency (I.E) and Surface coverage (θ) were calculated using equations 1, 2 and 3 below.

$$\text{CR } (\text{gh}^{-1}\ \text{cm}^{-2}) = \text{CR} = \frac{\Delta W}{At} \qquad (1)$$

Where CR is the Corrosion Rate, ΔW = is the weight loss (W_1-W_2)

W_1 = initial weight of the coupon before immersion in g, W_2 = final weight of the coupon after immersion in g, A = is the area of the mild steel coupon in cm^2, t = is the immersion period of time in hours

$$\text{I.E } (\%) = 1 - \left(\frac{C_{Rinh}}{C_{Rblank}}\right) \times 100 \qquad (2)$$

Where, I.E is the Inhibition Efficiency, CR_{inh} is the corrosion rate in the presence of the inhibitor, CR_{blank} is the corrosion rate in the absence of the inhibitor

$$\text{Surface coverage } (\theta) = 1 - \left(\frac{C_{Rinh}}{C_{Rblank}}\right) \qquad (3)$$

2.5. Electrochemical Measurements

Electrochemical cell is a conventional three-electrode Pyrex glass cell. The electrochemical testing of inhibitors provides the significant benefit of short measurement time and vital information about the mechanism of inhibition. In the electrochemical study, potentiodynamic polarization (PDP) analysis was carried out using AUTOLAB PGSTANT 204N instrument in Metallurgical and Material Engineering (MME) Department, FUTA. In study this; the mild steel specimens of geometric area of $1cm^2$ for the experiment was embedded in Teflon holder using epoxy resins as the working electrode. A Platinum wire was used as an auxiliary electrode while a saturated silver chloride was used as reference electrode and acid solution of 1M H_2SO_4 as the electrolyte. Prior to the experiment, each of the working electrodes (pre-cleaned mild steel) was dipped in the test solution for 10 minutes in order to attain open circuit potential (OCP) for the study system. The Potentiodynamic polarization (PDP) study was carried out from cathodic potential of -250mV to an anodic potential of +250mV with a scan rate of 10mv/s. Tafel lines extrapolation method was used for detecting corrosion current (Icorr) and corrosion potential (Ecorr) values.

The I.E (%) values from PDP measurement were calculated using equation below

$$\eta_p\ (\%) = (1 - CR_0 / CR_I) \times 100 \qquad (4)$$

Where, CR_0 and CR_I are the corrosion current densities with and without of extracts respectively.

3. Results and Discussion

3.1. Weight Loss Measurement

3.1.1. Effect of Extract Concentrations on Corrosion Rate

The rate of corrosion of mild steel in 1M H_2SO_4 decreased with increasing in the extract concentration of *Cordia millenii* as shown in Figure 1. This indicates that the rate of corrosion of mild steel in acid solution is dependent on the amount of inhibitor present suggesting that the presence of inhibitor in the acid solution was responsible for the decrease in the corrosion rate of mild steel in the acid solution. This can be further explained on the basis that as the concentration of the extract increases, there is an increase in the amount of adsorbed phytochemical constituents of the extract on the mild steel surface which causes a barrier for mass transfer, thus preventing the further corrosion. This result showed that the inhibitory potential of the extract on mild steel is concentration dependent which is in good with the previous reports [13-15].

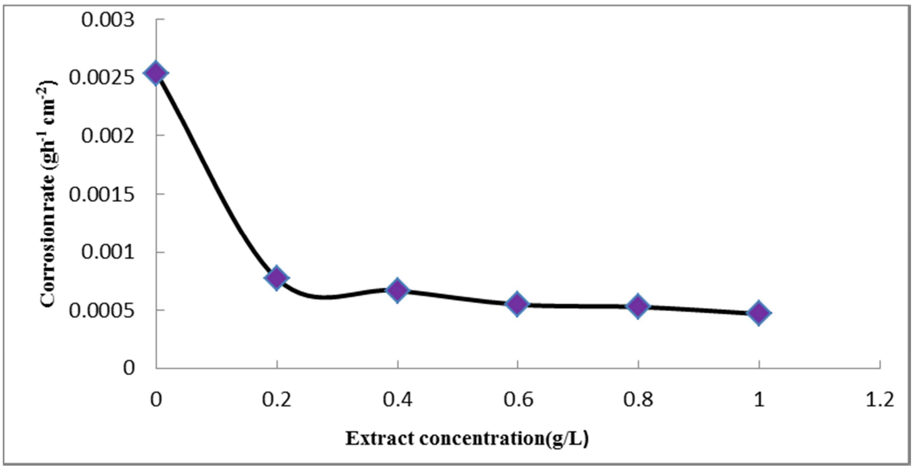

Figure 1. Effect of concentration of EECM on the corrosion rate of mild steel in 1M H_2SO_4.

3.1.2. Effect of Extract Concentration on Inhibition Efficiency on Mild Steel

According to Figure 2, it is evident that the inhibition efficiency increases with a corresponding increase in concentration of the extract. This could be as a result of adsorption of organic compounds of the extract unto the mild steel surface which block the reaction sites, and protects the mild steel from further attack by the ions in the corrosive medium. Previous studies have shown that increase in inhibition efficiency with increase in inhibitor concentration can be explained on the basis of increased adsorption of the extract molecules on the metal surface [16]. This indicates that the increase in the degree of metal surface coverage by adsorbed inhibitor species in acid solution reduces the surface area that is available for the attack by the aggressive ions in the acid solution and hence results into increase in the inhibition efficiency of the extract.

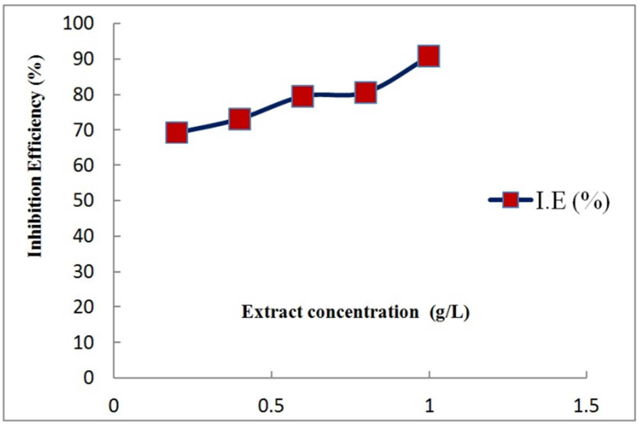

Figure 2. Effect of extract concentration of *Cordia millenii* Inhibition Efficiency on mild steel in 1M H_2SO_4.

3.1.3. Effect of Temperature on Corrosion Rate

The effect of temperature on the corrosion rate of mild steel in the absence and presence of various concentrations *of Cordia millenii* in 1M H_2SO_4 solution was studied at various temperature values ranging from 303K to 343K. From the results obtained as shown in Figure 3, the rate of corrosion of mild steel with and without different concentrations of the inhibitor increases with increasing temperature. This is expected because increase in the temperature increases the average kinetic energy of the reacting molecules which leads to increase in the rate of corrosion of the mild steel. However, it can be observed from the Figure that the corrosion rate of mild steel in the inhibited acid solution is much more decreased than the corrosion rate in the uninhibited acid solution. This is plausible because decrease in the corrosion rate of the inhibited acid solution is indicative of the mitigating effect of inhibitors on the corrosion rate of mild steel [17].

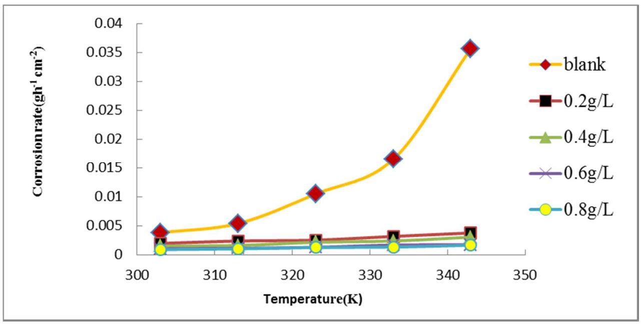

Figure 3. Effect of *Cordia millenii* extract on the Corrosion Rate of mild steel coupons in 1M H_2SO_4 at different temperature.

3.1.4. Effect of Temperature on Inhibition Efficiency

The inhibition efficiency of EECM leaves on mild steel in 1M H_2SO_4 solution at various temperature values is shown in Figure 4. According to the Figure, the inhibition efficiency of the extract increases with increase in the temperature at different extract concentration. Previous investigators have described increase in inhibition efficiency with temperature as being suggestive of chemical adsorption mechanism while decrease in inhibition efficiency with analogous increase in temperature indicates physical adsorption mechanism [18]. In this study, it can be inferred that the mechanism of adsorption of EECM on mild steel is chemical adsorption due to an increase in inhibition efficiency with increasing temperature This indicates that the stability of adsorbed film on the mild steel in acid solution is strongly influenced by temperature involving charge sharing or transfer from the inhibitor molecules to the metal surface in order to form a co-ordinate covalent type of bond [19, 20].

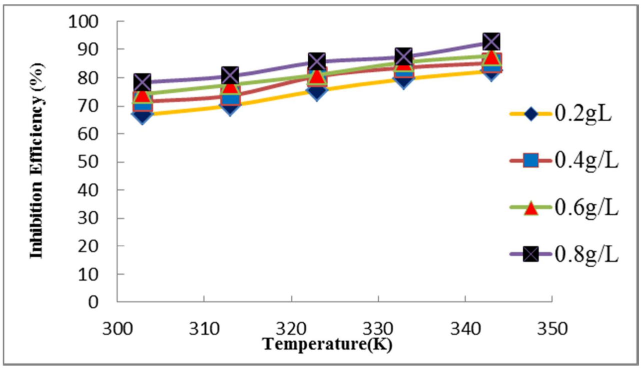

Figure 4. Effect of Inhibition Efficiency of EECM on mild steel in 1M H_2SO_4 at various temperature.

3.2. Kinetic Studies

The kinetics of the mild steel corrosion in 1M H_2SO_4 with and without different concentrations of the inhibitor was studied at 303K by fitting the corrosion data into different rate laws. In this present study, the initial weight of mild steel coupon at time 't' is designated as 'W_1, the final weight is designated as W_2 while the weight loss after time 't' as ΔW and the weight of the metal after time t is designated as (W_i-ΔW). As shown in Figure 5., a plot of ln (W_i -ΔW) against time according to equation (5) showed a linear variation which confirms a first order reaction kinetics with respect to the corrosion of mild steel in 1M H_2SO_4 solutions in the presence and absence of EECM. The linearity of the curves in the inhibited and uninhibited solutions implies that its presence does not change the kinetics of the corrosion reaction though it significantly reduces its rate constant as presented in Table 1.

The rate constants were deduced from the slope of the graph as shown in Figure 5 and the half-lives were calculated based on equation 6.

$$\ln (W_i - \Delta W) = -k_1 t + \ln W_i \tag{5}$$

$$t_{1/2} = \frac{0.693}{k} \tag{6}$$

The calculated values for rate constant and the half-life at different concentrations of the extract are listed in Table 1.

As the concentration of the extract increases, the half-life of the metal also increases suggesting increasing in inhibition efficiency of the extract with extract concentration. This provides corroborates the earlier assertion that as the concentration of the extracts increases, the corrosion rate of the mild steel decreases thereby resulting into higher inhibition efficiency [21].

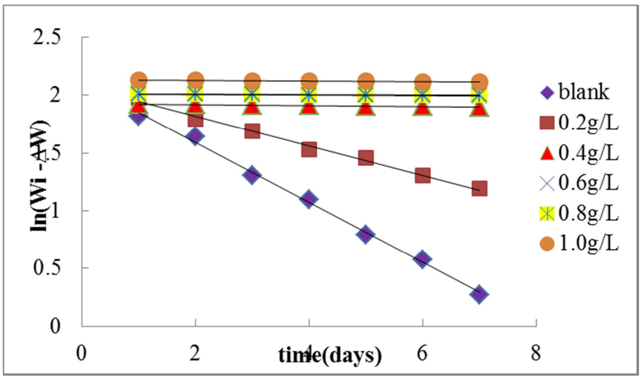

Figure 5. Variation of ln (W_i -ΔW) against time (days) for mild steel coupons in 1M H_2SO_4 solution containing EECM at 303k.

Table 1. The calculated values of rate constant, k and half-life ($t_{1/2}$) of the corrosion reactions for mild steel in 1M H_2SO_4 solution in the absence and presence EECM.

Concentration (g/L)	Blank	0.2	0.4	0.6	0.8	1.0
Rate Constant (day^{-1})	0.0525	0.0331	0.0080	0.0072	0.0050	0.0044
Half-life (day)	13.20	20.93	86.62	96.25	138.60	157.50

3.3. Thermodynamic Evaluation

In order to establish the stability of adsorbed film of inhibitors on the surface of mild steel as well as activation parameters of the corrosion process of mild steel in 1M H_2SO_4 solution, weight loss measurement was carried out at various temperatures ranging from 303K to 343K in the absence and presence of inhibitor concentrations ranging from 0.2g/ L to 0.8g/L for a period of 3hours immersion period.

The Arrhenius equation for the log of Corrosion Rate (C_R) is a linear function of temperature and is given as:

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

Where E_a is the apparent activation energy, A is the Arrhenius pre-exponential factor and R is the general gas constant.

An alternative formulation of equation (7) is given as:

$$C_R = \left[\frac{RT}{Nh}\right] \exp\left[\frac{\Delta S^o}{R}\right] \exp\left[\frac{-\Delta H^o}{RT}\right] \tag{8}$$

Where, h is the Plank's constant, N is the Avogadro's number, T is the absolute temperature (Kelvin),ΔS^o is the entropy of activation and ΔH^o is the enthalpy of activation. Arrhenius plots of the corrosion rate of mild steel in 1M H_2SO_4 solution against 1/T (Log Corrosion Rate as a function of 1/T) in the absence and presence of EECM concentrations ranging from 0.2g/100 mL to 0.8g/100 mL at various temperatures were plotted given a straight line graph as shown in Figure 6. The values of activation energy $E_{a,}$ from the slope $\frac{-Ea}{2.303RT}$ of the straight lines as well as the thermodynamic parameters values of ΔS^* and $\Delta H^*$from the slope $\left(\frac{-\Delta H^o}{2.303RT}\right)$ and the intercept (log$\left(\frac{RT}{Nh}\right) + \frac{\Delta S^o}{2.303R}$) of the straight lines graph in Figure 7 were computed and the results obtained are listed in Table 2.

Table 2. Activation parameters for mild steel corrosion rate in 1M H_2SO_4 in the absence and presence of different concentrations of EECM at various temperatures.

Concentration (g/L)	Blank	0.2	0.4	0.6	0.8
Ea (kJ/mol)	51.18	20.22	15.61	14.92	14.78
ΔH (kJ/mol	50.55	16.09	13.57	11.94	10.39
ΔS (kJ/mol K	-0.2108	-0.1877	-0.1976	-0.205	-0.2112

Inspection of the values of activation energy listed in Table 2 shows that the values are lower in the inhibited solutions than the uninhibited solutions. The decrease in apparent activation energy in the inhibited solutions compared to uninhibited solutions is frequently interpreted as being suggestive of chemical adsorption while the reverse is attributed to physical adsorption mechanism [22]. In the present study, the lower activation energies in the inhibited solutions compared to uninhibited solution suggests chemical adsorption of EECM on the surface of the mild steel in acidic solution. This assertion is corroborated by the increase in the inhibition efficiency of the extract with increasing temperature as shown in Figure 4.

The positive signs of enthalpies (ΔH) in the absence and presence of the extract in acidic medium reflect the endothermic nature of the adsorption of mild steel dissolution process. This indicates that the dissolution of metals is mitigated by the extracts through endothermic reaction process. It is also evident from the Table, that the activation enthalpies vary in the same manner with activation energies. The shift towards negative values of activation entropies (ΔS^*) imply that the activated complex in the rate determining-step represents an association between the metal and the inhibitor, rather than dissociation step suggesting a decrease in disordering takes place on going from reactant to activated complex [8].

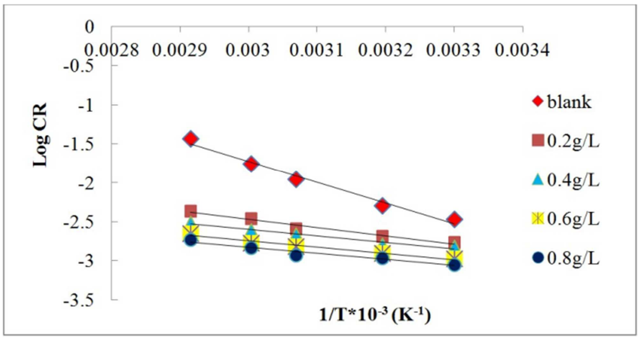

Figure 6. Arrhenius plot of Log CR against 1/T for mild steel at different concentrations of EECM in 1M H_2SO_4.

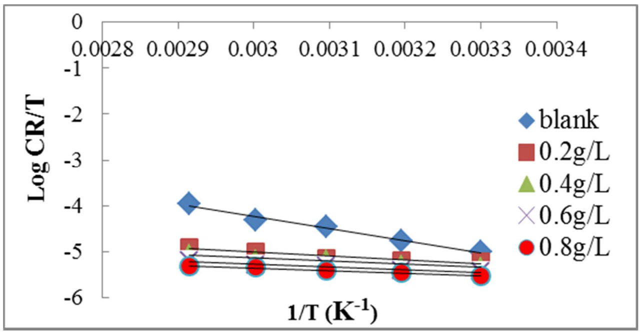

Figure 7. Eyring transition state plot for mild steel in 1M H_2SO_4 in the presence and absence of EECM at different concentrations.

3.4. Adsorption Consideration

The nature of inhibitor interaction on the corroding surface during corrosion inhibition of metals has been deduced in terms of adsorption characteristics of inhibitor. The inhibition of the corrosion of mild steel in acidic sulphate solution with addition of various concentrations of the extract can be explained by the adsorption of the components of the plant extract on the metal surface [23]. The percentage inhibition efficiency (I.E%) of mild steel is directly proportional to the fraction of the surface covered by the adsorption molecule (θ). Therefore, the adsorption isotherm provides important clues regarding the relationship between the surface of the metal covered with the adsorbed species and the concentration of extract in solution.

The general form of isotherm is given as;

$$f(\theta, x)\exp(-2a\theta) = KC_{inh} \qquad (9)$$

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 [24].

In this study, the values of the surface coverage (θ) at various concentrations of the inhibitor in 1M H_2SO_4 solution for the extracts were plotted as C_{inh}/θ vs C_{inh} and the adsorption parameters derived from the plot are listed in Table 3. The plots are linear as revealed by the regression coefficient (r^2) with slope equal to unity. The r^2 obtained with strong positive values being close to +1 suggests that the adsorption process of the extracts on mild steel in 1M H_2SO_4 solution occupied typical adsorption site on the metal surface with the strong linear association between the adsorbate molecules and adsorbent surface [16].

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (10)$$

Table 3. Calculated parameters from Langmuir adsorption plot for EECM for mild steel in 1M H_2SO_4.

Temperature (K)	Slope	R^2	Kads (gL^{-1})
303	1.20	0.9982	19.68
313	1.18	0.9986	24.64
323	1.13	0.9985	26.92
333	1.10	0.9998	32.85
343	1.99	0.9987	52.64

The intercept obtained from the graph was related to inverse of equilibrium adsorption constant (K_{ads}) in Equation 10 which is related to the Gibbs free energy of adsorption (ΔG_{ads}) as employed by the previous investigators [11, 12].

$$K_{ads} = \frac{1}{55.5}\exp\left[\frac{-\Delta G^{\circ}_{ads}}{RT}\right] \qquad (11)$$

This equation can also be expressed as:

$$\Delta G^{\circ}_{ads} = -2.303RT \, Log \, (55.5K_{ads}) \quad (12)$$

Where, ΔG°_{ads} is the Gibbs free energy of adsorption, K_{ads} is the equilibrium constant for the adsorption phenomenon, R is the universal gas constant, T is the thermodynamic temperature (kelvin) and the value of 55.5 is the molar concentration of water in solution. The Gibbs free energy of adsorption (ΔG_{ads}) for the EECM in 1M H_2SO_4 solution was calculated according to equation (12). The calculated values for K_{ads} and ΔG_{ads} are presented in Table 4.

Table 4. The values of equilibrium adsorption constant and Gibbs free energy of adsorption for mild steel corrosion in 1M H_2SO_4 at different temperatures.

Temperature (K)	**303**	**313**	**323**	**333**	**343**
Kads (g L^{-1})	19.68	24.83	26.92	32.85	52.64
ΔG (kJ mol^{-1})	-17.62	-18.79	-19.63	-20.79	-22.76

Inspection of Table 4 shows that the values of ΔG^{0}_{ads} are negative indicating that the adsorption of EECM on mild steel surface takes place spontaneously. It could also be observed from the Table that the values of K_{ads} increase with increasing temperature which suggests a strong adsorption interaction between the extracts and the mild steel surface in 1M H_2SO_4 solution. According to Bentiss et al, the higher the values of K_{ads}, the stronger and more stable is the adsorbed layer formed on the mild steel surface which usually results in the higher inhibition efficiency of the extract [24]. Hence, favourable adsorption and higher inhibition efficiency of the extract was established at high temperature.

3.5. Surface Morphology

The surface morphology was examined on mild steel after 24 hours of immersion in 1M H_2SO_4 solution in the absence and presence EECM in order to confirm the extent of change on the mild steel surface using a Scanning Electron Microscope (SEM). The SEM micrographs are shown in Figures 8a, b and c respectively. Figure 8a shows the SEM image of mild steel in its pristine condition before immersion in acid solution with a smooth and fine surface, indicating that the mild steel has not been damaged by any aggressive attack. Figure 8b shows the SEM image of mild steel after immersion in 1M H_2SO_4 solution without inhibitor. It is clearly observed from the image that the mild steel surface was severely damaged due to the absence of extract inhibitor in the acid media thereby resulting into rough surface with large number of pits. Figure 8c shows the SEM image of mild steel after immersion in 1M H_2SO_4 solution containing 1.0 gL^{-1} of extract inhibitor. It is observed that there is little acid corrosion product on the surface of the mild steel. The surface is covered by a uniform and dense film, which might be formed by the adsorption of the EECM molecules on the mild steel surface and can efficiently inhibit the corrosion of mild steel. To better understand the protection of the mild steel by the extract, the EDX results revealed that the percentage by weight of Fe in the metal before immersion is 98.98%. However, the percentage by weight of Fe in the metal reduces drastically to 63.5% after immersion in 1M H_2SO_4 solution without the inhibitor while the percentage by weight of Fe in the metal in 1M H_2SO_4 solution containing 1.0 gL^{-1} of extract inhibitor is 93.5%. Based on calculation, there is 5.5% reduction in the percentage by weight of Fe in the metal immersed in1M H_2SO_4 solution containing 1.0 gL^{-1} of inhibitor while 35.8% reduction in the percentage by weight of Fe in the metal immersed in1M H_2SO_4 without inhibitor. Thus, it is evident that the corrosion of mild steel in 1 M H_2SO_4 is retarded by EECM due to an adsorption film that appeared on the surface.

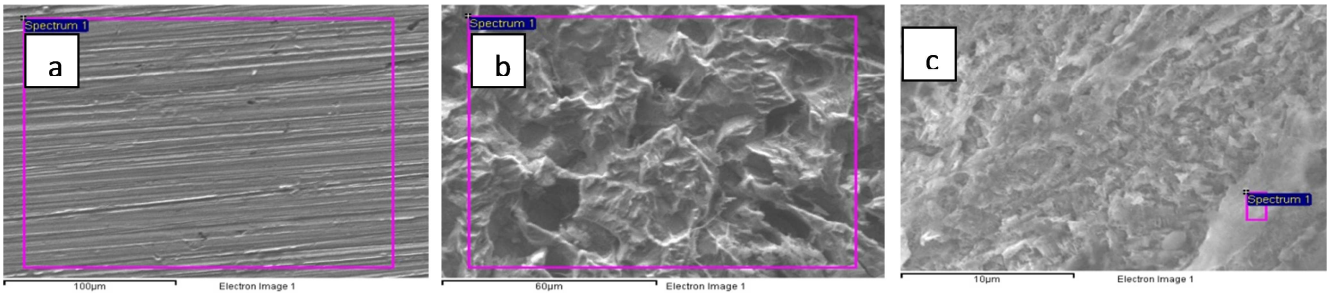

Figure 8. (a). SEM image of mild steel in its pristine condition before immersion in 1M H_2SO_4 solution; (b). SEM image of mild steel after immersion in 1M H_2SO_4 solution without EECM. (C). SEM image of mild steel after immersion in 1M H_2SO_4 solution containing 1.0 gL^{-1} of EECM.

3.6. Potentiodynamic Polarization Measurements

The potentiodynamic polarization curve for mild steel in 1M H_2SO_4 solution in the absence and presence of EECM is shown in Figure 9. It can be observed from the plot that the addition of EECM reduced the aggressive attack on the mild steel electrode [7]. Thus, the associated values of 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 calculated from the polarization Tafel curves and presented in Table 5. Inspection of Table 5 reveals that I_{corr} in 1 M H_2SO_4 without inhibitor is very high suggesting that the mild steel has been corroded by the acid. It should be noted that Icorr decreases with increasing EECM concentration and thus, the inhibition efficiency also increases with the EECM concentration which again suggests that EECM is a good inhibitor for mild steel corrosion in 1 M H_2SO_4. The EECM decreased the anodic current and also shifts the cathodic branches to lower values of current density at all investigated concentrations. This result indicates that EECM exhibits both cathodic and anodic inhibition effects. The Tafel slopes of b_c and b_a donot change remarkably upon addition of EECM, which indicates that the presence of EECM does not change the mechanism of hydrogen evolution and the metal dissolution process. An inhibitor can be classified as a mixed type inhibitor when the shift of corrosion potential in the presence of inhibitor with respect to that in the absence of inhibitor is less than 85mV [25]. From the results in Table 5, the changes of E_{corrr} are 26-33 mV compared to the blank which indicates that EECM acts as a mixed type inhibitor for the corrosion of mild steel in 1 M H_2SO_4 solution.

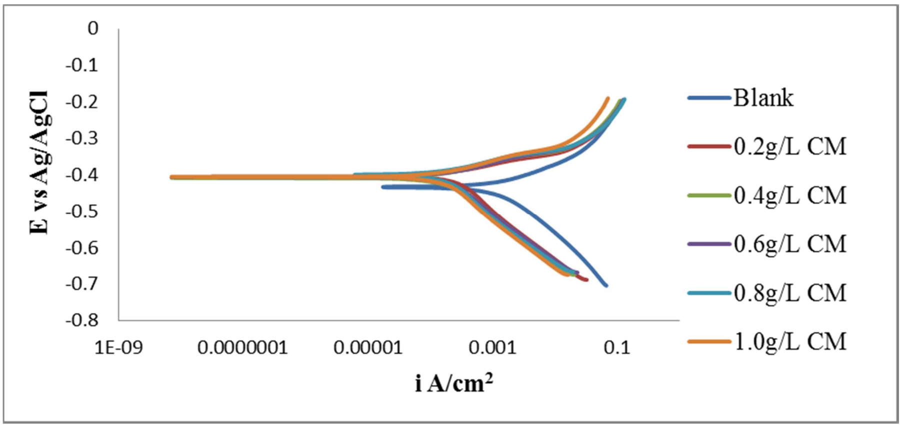

Figure 9. Tafel polarization curves for mild steel in 1M H_2SO_4 in the presence and absence of different concentration of *Cordia millenii.*

Table 5. Corrosion parameters obtained from electrochemical polarization measurements for mild steel in 1M H_2SO_4 in the absence and presence of EECM.

Concentration g/L	E_{corr} (mV vs SCE)	I_{corr} (μa/cm²)	β_a (mV/dec)	β_c (mV/dec)	I.E (%)
Blank	-434.083	1196	60.865	165.786	---------
0.2	-401.532	242.793	42.229	156.779	79.70
0.4	-408.493	200.438	56.555	163.229	83.24
0.6	-406.244	198.348	52.754	150.303	83.42
0.8	-400.289	185.066	51.570	162.140	83.69
1.0	-405.292	178.159	54.844	163.912	85.10

3.7. Fourier Transform-Infra Red Measurement

The inhibition performance of plant extract is normally ascribed to the presence of organic compounds containing polar functions with N, S, O atoms as well as conjugated double bonds or aromatic rings [26]. In this study, FTIR spectrometer is employed to identify whether there are functional groups in EECM which meet the general requirements of a potential inhibitor. Figures 10 and 11 show the FTIR spectrum of EECM and spectrum of the surface film on the mild steel after immersion in 1 M H_2SO_4 containing the 1.0 g/L EECM, respectively. The strong absorption band at 3397 cm^{-1} is attributed to N-H or O-H stretching vibration and that at 2935 cm^{-1} is assigned to C-H stretching vibration [27]. The peak at 1635 cm-1 is related to stretching mode of C=N. and C=O. The absorption bad at 1548 cm^{-1} corresponds to Aromatic C=C stretch [28]. The peaks at 1252 cm^{-1} and 1125 cm^{-1} are attributed to C-OH bond stretching vibration and stretching mode of C-O-C in ethers, respectively. The absorption bands below 1000 cm^{-1} correspond to aliphatic and aromatic C-H group [29, 30]. These results indicate that EECM contains O and N atoms in functional groups (O-H, N-H, C=C, C=N, C=O, C-O) and aromatic ring. The FTIR peaks of EECM were also observed in the spectra of EECM adsorbed on the mild steel. Compared with the spectrum of the EECM powder shown in Figure 10, there was an upward shift in band at 3397 cm^{-1} to 3412 cm^{-1}. Further, the C-H stretching vibration at 2935 cm^{-1} shifted to 2943. The strong absorption band observed at 1635 cm^{-1} also shifted to 1641 cm^{-1} while the absorption band corresponding to aromatic C=C stretch at 1548 cm^{-1} shifts to 1476 cm^{-1}. The shifts of the vibrations to the higher wave numbers may be due to the formation of Fe^{2+}-EECM complex adsorbing on the mild steel surface, which reduces the rate of corrosion of the mild steel in acid. corrosion.

Thus, the FTIR results provide evidence of the adsorption of EECM unto the surface of the mild steel and thus preventing it from being corroded easily.

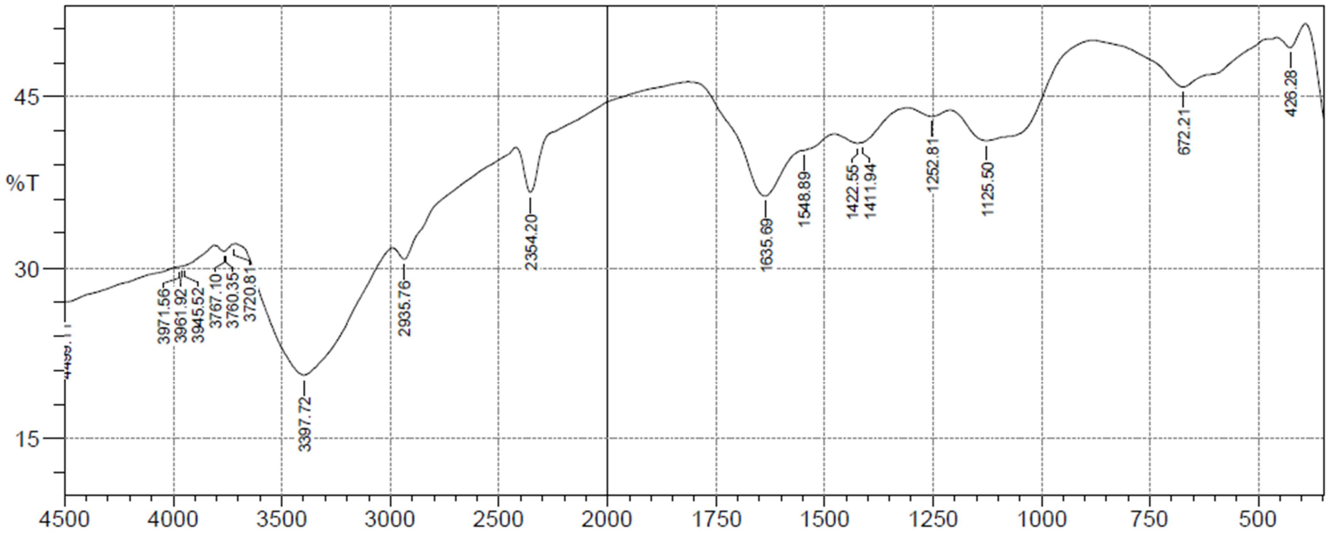

Figure 10. FT-IR spectrum of EECM.

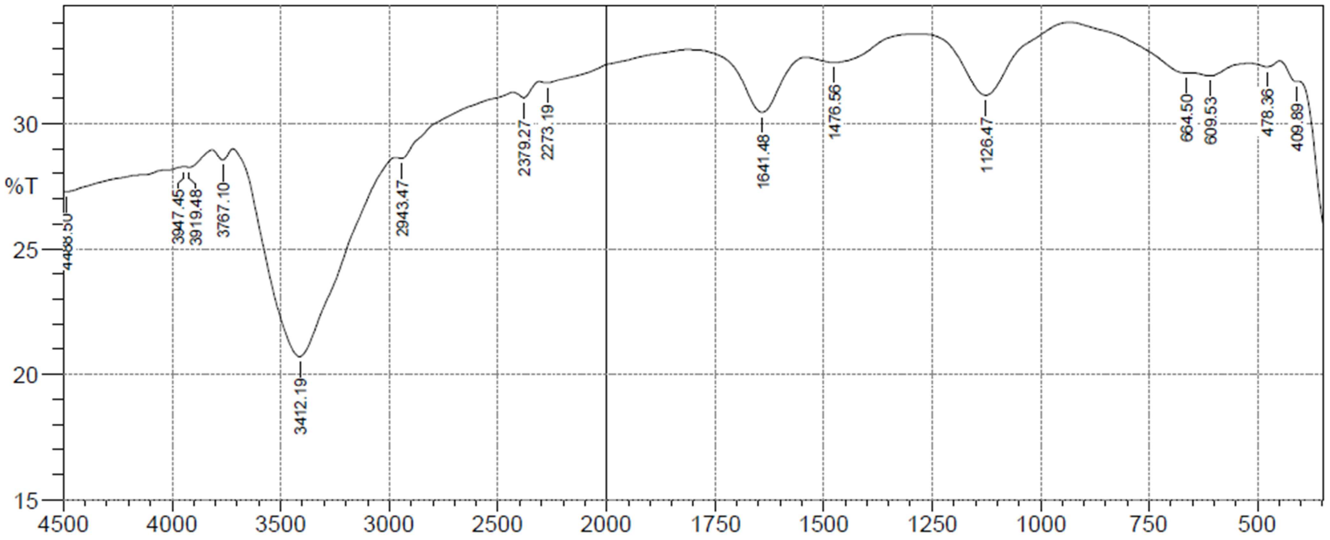

Figure 11. FT-IR spectrum of the dried solid adsorption product in 1M H_2SO_4 solution containing EECM and mild steel.

4. Conclusion

The extract of *Cordia millenii* acts as an effective green inhibitor of mild steel corrosion in 1 M H_2SO_4. Inhibition efficiency of the extract increases with increase in concentration of the extract and also with increase in the temperature. Polarization measurements have shown that EECM functions as a mixed-type inhibitor affecting both the anodic and cathodic reactions. Corrosion inhibition is mainly achieved through chemical adsorption of different compounds in the extract unto the mild steel surface. The adsorption of EECM on the surface of the mild steel in 1M H_2SO_4 obeys Langmuir adsorption isotherm and is a spontaneous and exothermic process accompanied by a decrease in entropy. The FT-IR spectra indicate that EECM contains O and N atoms in functional groups (O-H, N-H, C-O, C=O, C-H) and aromatic rings which meet the general consideration of a typical corrosion inhibitor. Kinetics of the reaction follows a first order reaction and the half-lives of the metal increase as the concentration of the extract increases. SEM-EDX confirms that the corrosion of mild steel in 1 M H_2SO_4 is retarded by EECM due to an adsorption film that appeared on the surface.

Acknowledgements

The technical assistance of members of staff of Chemistry Department and Materials and Metallurgical Department of the Federal University of Technology Akure is gratefully acknowledged.

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