



Kinetics and Thermodynamic Study of Corrosion Inhibition of Mild Steel in 1.5M HCl Medium using Cocoa Leaf Extract as Inhibitor

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ABSTRACT: This study examined the corrosion inhibition of mild steel in 1.5M HCl solution using cocoa leaf extract as an inhibitor. The effect of inhibitor concentrations, kinetics, and time of immersion were undertaken at 30°C while the thermodynamic parameters were determined with temperature range of 35°C – 55°C. FTIR result indicated that the actual adsorption of the inhibitor is as a result of donation of single pair of electrons on oxygen to the vacant d – orbitals of the metal (mild steel) that leads to the formation of complexes on the mild steel surface. The corrosion rate decreased from 1.64 g/cm²hr to 0.09gm/cm²hr in the presence of inhibitor used. However, increased in temperature showed a decreased in inhibition efficiency this resulted to an increase in rate of corrosion. Half – life of the corrosion kinetics ranges from 49.71 – 53. 15hr which is directly proportional to the inhibitor concentrations. Activation energy E_a , enthalpy (ΔH°), and entropy (ΔS°) calculated showed good interactions. The enthalpy of activation ranges from 63.28kJ/mol to 97.55kJ/mol. Rise in activation energy with inhibitor concentration confirmed the physical (physisorption) adsorption mechanism for the corrosion of mild steel surface. Endothermic nature of the corrosion process is ascertained with the positive value of ΔH° obtained.

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Corrosion behaviour of steels has received a considerable amount of attention as a result of its industrial importance. Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment. Corrosion is often thought of only in terms of rusting and tarnishing. However, corrosion damage occurs in other ways as well, resulting, for example, in failure by cracking or in loss of strength or ductility. The term corrosion is sometimes also applied to the degradation of plastics, concrete, and wood, but generally refers to metals. The most commonly used metal is iron (usually as steel). Corrosion can cause disastrous damage to metal and alloy structures causing economic consequences in terms of repair, replacement, product losses, safety, and environmental pollution. There are several ways of preventing corrosion and the rates at which it can propagate with a view to improving the lifetime of metallic and alloy materials. Corrosion inhibitors are widely used in industry to reduce the rate corrosion of different metals and alloys that are in contact with aggressive environments (acid solution). Acid solutions are often used in industry for cleaning and pickling of steel structures, processes that are normally accompanied by considerable dissolution of the metal. Corrosion inhibitor is a substance which, when added

in small concentration to an environment, effectively reduces the rate of corrosion of a metal exposed to that environment. A useful method to protect metals and alloys in aggressive environments against corrosion is to add some species to the solution in contact with the surface in order to inhibit the corrosion reaction and reduce the rate of corrosion (Oguzie, 2008). Many studies have been carried out to find suitable compounds to use as corrosion inhibitors. Use of inhibitors is one of the most practical and environmentally method for protection of mild steel and metals against corrosion, especially in acid solutions, to prevent unexpected metal dissolution and acid consumption (Sorcha, 2008). Most of these compounds in used as corrosion inhibitors are synthetic chemicals that may be very expensive and hazardous to human, aquatic life and environment at large. It is very important to use cheap, environmentally, and safe to handle compounds for use as corrosion inhibitors. These natural organic compounds are either synthesized or extracted from aromatic herbs, spices, and medicinal plants. Plant extracts are seen as an incredibly rich source of naturally synthesized chemical compounds that can be used as a corrosion inhibitor and are also biodegradable in nature. In very many cases, the

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corrosion inhibitive effect of some of these plants extracts has been attributed to the presence of tannin in their chemical constituents (Loto, 2003). Due to environmental laws and regulations on the use of toxic chemicals, and heavy metal – based inhibitors are being curtailed (Touir *et al.*, 2009). This has led to several attempts on the development of green corrosion inhibitors from plant extracts (Abiola *et al.*, 2007). The inhibitive action of these extracts was attributed to the presence of organic compounds in their chemical constituents and the blocking of the metal surface via adsorption of these organic compounds onto the surface of metal in acidic solutions. *Theobroma Cacao* belongs to the stercoaliaceae family known as cocoa trees. However, mild steel is referred to as low carbon steel which is generally used in chemical and process industries because it is reasonably cheap to produce and has a good toughness, ductility, weldability, and machinability; thus it can be used in different applications such as design of tank, pipelines, and fabrication of reactor vessels fabrication. The inhibitive effect of cocoa leaves (*Theobroma Cacao*) and kola nut (*Cola Acuminata*) extracts on the corrosion of mild steel in seawater and marine environment at room temperature was investigated by Urnoru *et al.*, (2006). The results showed that kola nut and cocoa leaves extracts are potential inhibitors of mild steel corrosion.

MATERIALS AND METHODS

Materials: The cocoa leaves were collected from Ugbomro community located in Effurun, Delta State, Nigeria. Mild steel was procured from accredited iron sheet dealer in Effurun. Macerator apparatus, HANNA model pH – 211 (pH meter), Genlab oven model Mino/75/f (oven), weighing balance of model (BH – 600), and beakers, were employed for this corrosion study. Hydrochloric acid, acetone, and ethanol solutions used were of analytical grades and were gotten from a qualified chemical dealer in Effurun, Delta State, Nigeria. Distilled water was procured from the Department of Chemical Engineering Laboratory, Federal University of Petroleum Resources, Effurun Delta, State, Nigeria for sample preparation and solutions.

Pre-treatment of sample and sample characterization: The dried cocoa leaves were used as obtained. This was washed to remove dirt and later sun dried in the oven at 60°C for a period of 24 hours to remove inherent moisture in the leaves. Subsequently, this was shredded to a particle size of 0.143µm. The sample was stored in a desiccator prior to use.

Fourier Transform Infrared Spectroscopy (FTIR): Cocoa leaf of 0.143µm particle size was examined with FTIR spectroscopy (Buck Scientific model 530) with the range 500 - 4000 cm⁻¹ (wavelength) to identify the functional group. The background material used in the analysis is potassium bromate (KBr).

X – Ray Fluorescence Analysis (X – RF): The elemental compositions of the mild steel used were observed with X – RF oxford machine.

Analysis of the phytochemical constituents in cocoa leaf extract: Screening of physico – chemical properties and phytochemical constituents of cocoa leaf extract were carried out to identify the active constituents present the cocoa leaf extract. The qualitative and quantitative methods of (Okwu, 2001; Rahilla *et al.*, 1994; Sofowora, 1993; and Herbone 1973) were used for these analyses.

Extraction of cocoa leaf extract: 500g cocoa leaf sample was poured in 1L macerator containing 70% v/v of ethanol. The mixture was stirred in the macerator for 4days. The resulting aliquot was subsequently filtered by using Whatman filter paper. The filtrate was transferred to a rotary evaporator at temperature between 54 – 55°C to obtain the extract concentrate. The resultant extract was then stored in an air tight container and kept in a desiccator before used.

Experimental procedure (Weight loss Measurements): The effect of time of immersion and temperature were carried out using weight loss measurement. The effect of temperature was carried out at 308K, 318K, and 328K. The corrosion study was carried out using the method described by Nwigbo *et al.*, (2012). The mild steel coupon having dimension of 2cm x 3cm x 0.12cm were polished with abrasive paper, greased to inhibit corrosion, degreased with ether of petroleum and thereafter rinsed with distilled water and dried. The mild steel coupon was suspended with the aid of a thread in 100 mL beaker that contains 100 ml of 1.5M HCl with various concentrations of the inhibitor. At time intervals of 24, 48, 72, 96, and 120 hours, the inhibitor concentrations used are 0.1g/L, 0.3g/L, 0.5g/L, 0.7g/L, 0.9g/L, 1.1g/L and 1.3g/L at temperature of 30°C. Each coupon after corrosion study was inserted in distilled water and dipped in methanol solution which was scrubbed to remove remaining acids, and residual inhibitor concentration. Thereafter, the mild steel was washed thoroughly with washing liquor, rinsed with distilled water and thereafter dried in acetone before it is reweighed.

Efficiency of inhibitor determination: The efficiency of corrosion inhibition was obtained using the equation below

$$E(\%) = \frac{W_0 - W_1}{W_0} \times 100 \quad (1)$$

Where, W_0 is the loss in weight in uninhibited medium (blank), and W_1 is the loss in weight in inhibited medium.

Determination of weight loss: The weight loss of the mild steel coupon was determined using equation 2 below;

$$\text{Weight loss, (g)} = W - W_i \quad (2)$$

Where, W is the initial weight of the mild steel coupon, W_i is the weight of the mild steel coupon after corrosion study.

Determination of rate of corrosion: The corrosion rate of the mild steel by the inhibitor was calculated using the equation below;

$$CR (\text{gcm}^{-2}\text{h}^{-1}) = \frac{\Delta W}{At} \quad (3)$$

Where, ΔW is the weight loss in (g), A is the area of the Mild steel in (cm^2), and t is the exposure time, (hr).

Determination of surface coverage: The degree of surface coverage (θ) is calculated from the weight loss measurement results using equation (4) below;

$$\text{Surface coverage } (\theta) = \frac{W_0 - W_i}{W_0} \quad (4)$$

Where; W_0 is the weight loss in the absence of the inhibitor, W_i is the weight loss in the presence of the inhibitor.

RESULTS AND DISCUSSION

Characterization of Cocoa leaf extract: Table 1 shows the presence of tannin, flavonoids, saponin and anthraquinone in the cocoa leaf extract. These phytochemicals has the capacity to enhance the process of corrosion inhibition of mild steel in acidic medium. The presence of these compounds has been reported to promote the corrosion inhibition of mild steel in aggressive acid media (Umoren *et al.*, 2006). This also corroborates the work of (Nwigbo *et al.*, 2012; Prithiba *et al.*, 2014; Owate *et al.*, 2014). Figure1 shows the FTIR of cocoa leaf extract with regions of wavelength $\leq 1500 \text{ cm}^{-1}$ being regarded as the fingerprint region while regions ranging from $1500\text{-}3000 \text{ cm}^{-1}$ wavelength are regarded as diagnostic or functional group region. It is this region that indicates the functional group present in the sample.

Table 1 Phytochemical Analysis of Cocoa Leaf Extract

Chemical constituents	Indicator of Presence
Alkaloid	+
Terpenoid	-
Phenol	+
Sterols	-
Flavonoid	++
Cardiac glycoside	+
Glycoside	-
Tannin	++
Phytosterol	+
Saponins	++
Anthraquinones	+
Reducing sugar	-
Steroids	-

++: Abundance, +: Trace, -: Absent

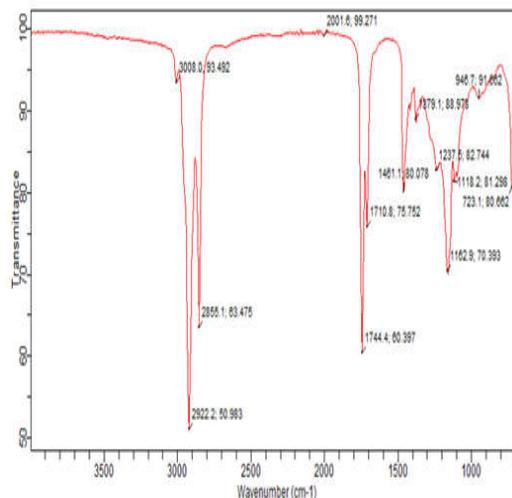


Fig. 1 FTIR Spectroscopy of the cocoa leaf extract

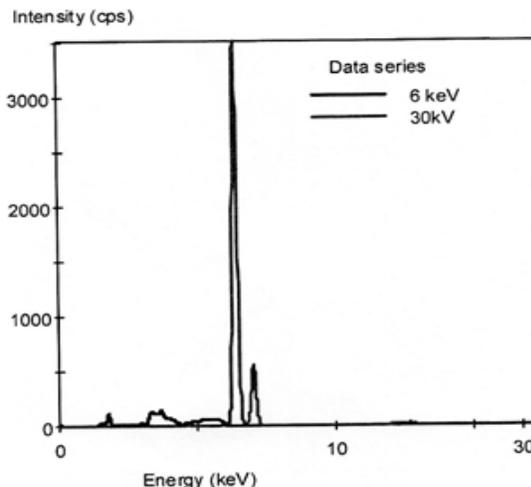


Fig. 2: X – ray Fluorescence spectra of mild steel sample

The wave number 2922.2 cm^{-1} gives a sharp shape that shows the presence of C – H bond present in the sample. The wavenumber of 2855.1 cm^{-1} infers the presence of a C – H alkyl bond. 1744.4 cm^{-1} and 1710.4 cm^{-1} depicts the carbonyl group which is a functional group composed of a carbon atom double-

bonded to an oxygen atom C=O but carbonyl stretch that is saturated with strong conjugation is noticed in 1710.4cm^{-1} (Pongpiachan, 2014). 1279.1cm^{-1} falls within the wavenumber ($1080 - 1360\text{cm}^{-1}$) which gives C - N stretch that belongs to amine functional group (Pongpiachan, 2014). The alkene band (C - H) sp^2 functional group is noticed in 3008.01cm^{-1} . Aromatic overtones of ring bend were seen in wave number 2001.8cm^{-1} . The presence of aromatic and amine functional groups present in the cocoa leaf extract confirms cocoa leaf extract as good corrosion inhibitors on mild steel.

Table 2 Result of the X - RF Analysis

Elements	Concentration, (mg/kg)	Abundance, (%)
Magnesium	698.068	0.341
Aluminium	623.737	0.304
Silicon	388.45	0.190
Sulphur	133.15	0.065
Chlorine	63.787	0.031
Calcium	453.855	0.221
Titanium	256.058	0.125
Chromium	136.308	0.067
Manganese	415.195	0.203
Iron	201548.523	98.362
Cobalt	125.519	0.061
Bromine	61.979	0.030

Weight loss measurements (Gravimetric measurements): The weight loss of the mild steel metal was determined with various inhibitor concentrations using equation 2 above and plotted in figure 3. It can be seen in figure 3 that there is a reduction in weight loss of the metal coupons in the presence of the inhibitor in comparison to the one without the inhibitor. It is revealed that the weight loss of the coupons decreased as inhibitor concentration is increased with immersion time.

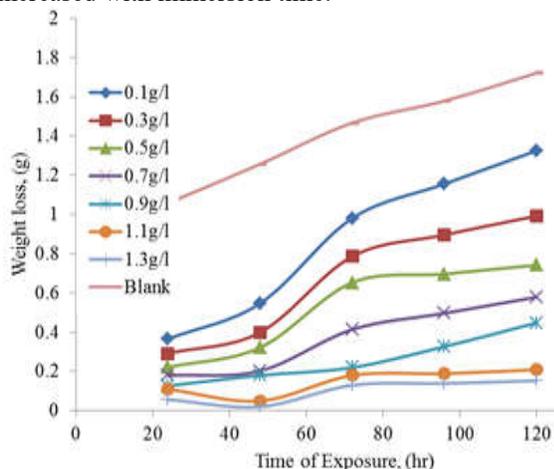


Fig. 3: Weight loss against exposure time

This can be attributed to the fact that with increased in inhibitor concentrations larger number of molecules is adsorbed on the surface of mild steel metal which

results in larger coverage of the metal surface by the inhibitor thus making it very difficult for more corrosive attack. The weight loss of mild steel in the absence of cocoa leaf extract inhibitor was much greater compared to the weight loss in the presence of the inhibitor. The inhibition efficiency of cocoa leaf extract was determined with different concentrations of inhibitor by using equation 1 above and the results plotted in figure 4.

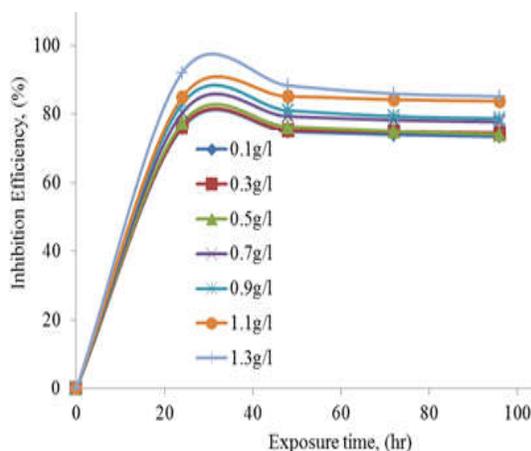


Fig. 4: Inhibition efficiency against exposure time

It has been reported that the inhibitive mechanism of organic compounds is based on their ability to be absorbed at surface of corroding metals. The efficiency of inhibition of the cocoa leaf extract increase with different inhibitor concentrations considered but decreased with time of exposure. The Prolonged time of exposure, long for soaring rate of loading the adsorbed inhibitor on the mild steel metal surface, this results in a constant film that prevents further corrosion of the surface of metal. The reduction in inhibitor efficiency can also be attributed to desorption of the phytochemical constituents from the metal surface (Oguzie *et al.*, 2006). This increased the area that will be available for corrosive attack by the hydrochloric acid. The inhibition efficiency increased at time of exposure of 24hours but thereafter it is reduced as evidenced in figure 4. In this work, the maximum inhibition efficiency that was reached is 92.08% with 1.3g/l of cocoa leaf extract. This can be attributed to the fact that the concentration of inhibitor is highest which can protect the mild steel surface form the aggressive hydrochloric acid environment. At this condition, the surface coverage is the highest with 0.9208 in comparison to others. Large surface areas of mild steel are covered by the film of inhibitor and thus reducing the reaction sites available on the mild steel surface. As a result, this in return giving the least corrosion rate of $0.087\text{g}/\text{cm}^2\text{hr}$ due to the presence of inhibitor that provide film barrier to corrosive agents.

High inhibition efficiency observed at 24hours of immersion suggests that adsorption of cocoa leaf extract inhibitor on the mild steel surface was accomplished within 24hour of immersion; subsequently the mild action of the acid medium was gradually felt other than the inhibitor adsorbed, thus leading to reduced efficiency in inhibition with increased time of exposure. This result corroborate with the works of (Ijuo *et al.*, 2016; Elyn, 2011; Ihebroke, *et al.*, 2010; Ismail *et al.*, 2011). Similar trends were observed by other researchers. Salah, (2016) observed that inhibition efficiency of the drug inhibitor on mild steel in hydrochloric acid increased by increasing the immersion time up to 6 hour, and thereafter it barely increased. Singh and Quraishi (2010), noticed that the inhibition efficiency of Mannich bases on the corrosion of mild steel in hydrochloric acid solution was found to increase with time up to 12 hour, and thereafter remained almost constant. Figure 5 depicted the rate of corrosion of mild steel in the absence and presence of an inhibitor in the presence of hydrochloric acid. It can be observed that the rate of corrosion of mild steel in the presence of the inhibitor is reduced compared to the one without inhibitor. The corrosion rate increased with time of immersion but decreased with increased in inhibitor concentration.

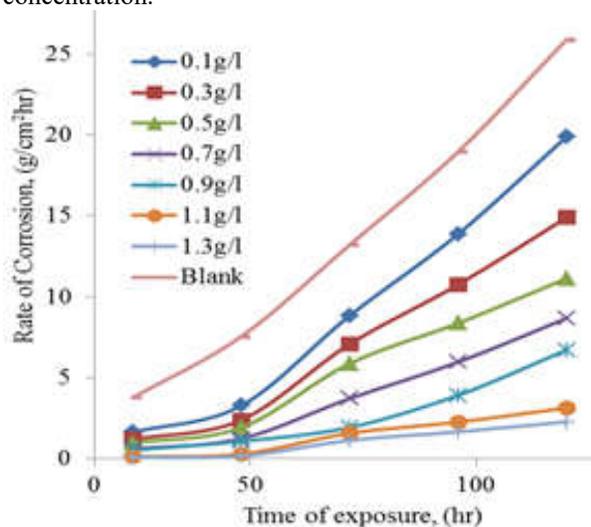


Fig. 5: Rate of corrosion against time of exposure

Kinetics and Thermodynamics of the corrosion process: Rate constant and half – life: The corrosion reaction is a heterogeneous reaction which is composed of anodic reactions at the same or different rate (Olasehinde *et al.*, 2013). The first order kinetics was employed and evaluated using integral method of analysis. This is given by equation 5 below;

$$-\log (\Delta W) = \frac{K_1 t}{2.303} \quad (5)$$

Where ΔW is the weight loss in (g), k_1 is the first order rate constant in (hr^{-1}), and t is the immersion time in (hr). The half - life of this corrosion study was gotten from equation (6), Njoku *et al.*, (2014).

$$\text{Half-life expression, } t_{1/2} = \frac{0.693}{K_1} \quad (6)$$

Figure 6 showed the plot of $-\log$ (weight loss) against exposure time in (hours) in the presence and absence of cocoa leaf extracts inhibitor. The rate constant, and half-life parameters are tabulated in Table 2. The plot showed a linear relationship between the slope, k (the rate constant), thus confirmed a pseudo – first order kinetics on the corrosion of mild steel in hydrochloric acid using cocoa leaf extract as an inhibitor. It was evidenced in table 2 that as the half-life of the kinetic corrosion process increased with inhibitor concentration. The high value of correlation coefficient obtained showed that the experimental value fitted well to the first order kinetics. This result is in conformity with reports of (Ijuo *et al.*, 2016; Olasehinde *et al.*, 2013).

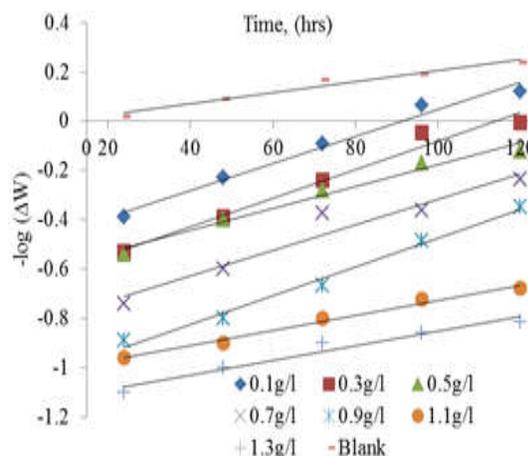


Fig. 6. Kinetics plot of first order reaction

Table 2 Half – life and rate constant parameters at various concentrations of cocoa leaf extract

Conc.	Rate constant, k (hr^{-1})	Half – life, (hr)	R^2 value
Blank	0.013941	49.71	0.963
0.1g/l	0.013841	50.07	0.9804
0.3g/l	0.013573	51.06	0.975
0.5g/l	0.013466	51.46	0.9762
0.7g/l	0.013396	51.73	0.9383
0.9g/l	0.013281	52.18	0.9883
1.1g/l	0.013082	52.97	0.9863
1.3g/l	0.013039	53.15	0.9863

Effect of temperature on corrosion: The effect of temperature on corrosion inhibition of cocoa leaf extract on mild steel in 1.5M hydrochloric acid was investigated for 6hours at 0.1g/l,0.3g/l and 0.5g/l inhibitor concentrations in temperature range 35°C –

55°C. Figure 7 gives the effect of temperature on the rate of corrosion process in the absence and presence of inhibitor. The rate of corrosion is higher in medium without inhibitor compared to the one that has inhibitor. As temperature is increased the rate of corrosion also increased due to the fact that the process of corrosion occurred rapidly at higher temperature due to the hot-movement of inhibitor molecules that weakening the adsorption capacity on mild steel surface (Shivakumar and Mohana, 2012; Norzila and Anis, 2015). On the other hand, the inhibition efficiency of the inhibitor decreases with increased in temperature for both absence and presence of inhibitor. This confirmed the physisorption adsorption of the corrosion process that resulted from desorption of adsorbed inhibitor as a result of higher rate of hydrogen evolution due to increased agitation of solution.

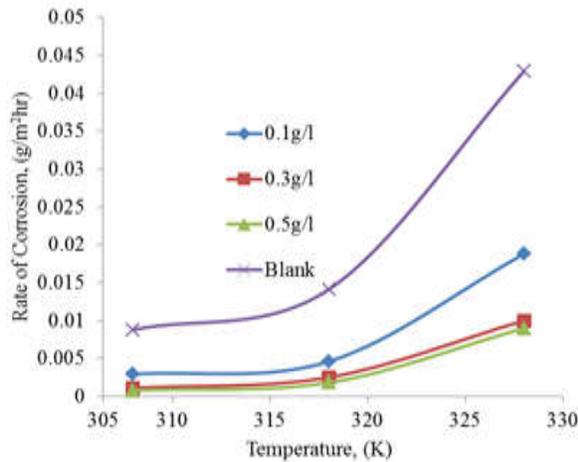


Fig. 7. Effect of Temperature on rate of corrosion of mild steel

Thermodynamic properties such as Activation Energy (E_a), Enthalpy (ΔH°) and Entropy of Activation (ΔS°) are studied so as to ascertain the mechanism of adsorption process involved in the corrosion process. In other to calculate the thermodynamic parameters like enthalpy (ΔH_{ads}), and entropy (ΔS_{ads}) of corrosion process in the presence and absence of cocoa leaf extract inhibitor in hydrochloric acid environment the transition state theory equation given by equation 8 was used (Mouheddin *et al.*, 2018; Ogoke *et al.*, 2009).

$$\log \left(\frac{C_R}{T} \right) = \left[\log \left(\frac{R}{Nh} \right) + \frac{\Delta S^\circ}{2.303R} \right] - \frac{\Delta H^\circ}{2.303RT} \quad (7)$$

Where h is the Planck's constant (6.626176×10^{-34} Js), N is the Avogadro's number, ($6.022 \times 10^{23} \text{ mol}^{-1}$), R is the Universal gas constant (8.314 J/Kmol) and T is the temperature of the medium. The plot of $\log (C_R/T)$ against $1/T$ is seen to be linear in Fig. 8 from which (ΔH°) and (ΔS°) values were deduced from the slopes and intercept of the graph respectively and listed in

table 3. Arrhenius equation represented by equation (8) was used to calculate the activation energy E_a in the presence and absence of cocoa leaf extract inhibitor.

$$\log C_R = \log A - \frac{E_a}{2.303RT} \quad (8)$$

Where C_R is the rate of corrosion, E_a is the apparent activation energy, R is the universal gas constant, T is the absolute temperature, and A is the frequency factor. The Arrhenius plot of $\log C_R$ against reciprocal of absolute temperature ($1/T$) is shown in Fig. 9 which gives a straight line with slope of $-E_a/2.303R$ from which the activation energy of the corrosion process was determined and listed in Table 3. The enthalpy of activation (ΔH°) and the entropy of activation (ΔS°) for the corrosion of mild steel in 1.5 M HCl were obtained from the transition state theory equation expressed as equation (8).

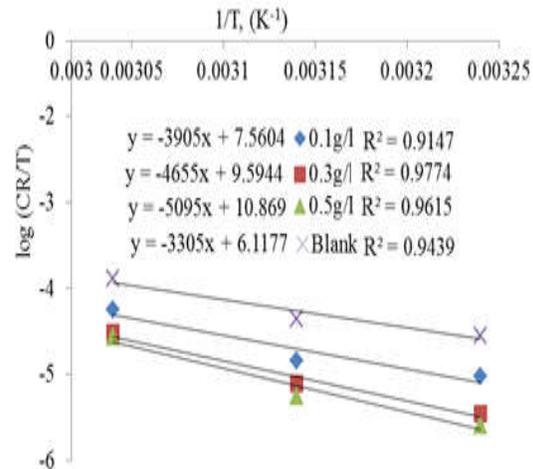


Fig. 8: Transition state for the corrosion of mild steel in absence and presence of inhibitor

Based on Table 3, the values of corrosion activations increased with inhibitor concentration of cocoa leaf extract. This trend is also consistent with that observed with inhibition efficiency and temperature. The value of E_a (activation energy) in blank solution is 65.87 kJ/mol and rise as concentration of inhibitors are increased from 0.1 g/l (77.45 kJ/mol) to 0.5 g/l (100.14 kJ/mol). This is due to the physical barrier produced by the adsorbed molecules on the surface of mild steel. This will increased the least energy required for corrosion reaction to occurs. Additional inhibitors will produce stronger film barriers on the mild steel surface. The trend of increasing E_a values as with inhibitor concentrations has been reported by other researchers on studies on various plant extract such as jujube leaves (Sivakumar and Mohana, 2012), black pepper (Quraishi *et al.*, 2009), sunflower leaves (Cang *et al.*, 2012), and piper nigrum extract (Norzila

and Anis, 2015). It has been reported that lower E_a value in the presence of inhibitors in comparison to the blank is attributed to chemical adsorption (Solomon *et al.*, 2010; Thirumoolan *et al.*, 2014; Mouheddin *et al.*, 2018). Since, the E_a increased in the presence of inhibitor compared to the blank, the mechanism of corrosion can be ascribed to physical adsorption (physisorption) mechanism. The corrosion reaction will be pushed away on the surface site and occurs at the uncovered parts of mild steel when inhibitors are added in hydrochloric acid solution thus giving a higher value of E_a (Quraishi *et al.*, 2009). In this study, the increasing values of E_a obviously showed a physical adsorption of inhibitor molecules on mild steel surface occurred. Physical adsorption happens due to the electrostatic force between negatively charged metal surface and positive charged of organic species (Norzila and Anis, 2015). The activation entropy (ΔS°) in the absence and presence of cocoa leaf extract inhibitor was positive. This can be interpreted to mean that the activated complex in the rate determining step represents dissociation rather than association step, implying that during the adsorption process, an increase in the degree of orderliness takes place when moving to the activated complex from the reactants. The increased in inhibitor concentration, the more associated is the order of activated complex entangled in the rate determining step of the corrosion reaction. Hence, orderliness is increased as reactants are transformed to activated complex (Nooshabadi and Ghandchi, 2015). The enthalpy of activation (ΔH°) values in the presence and absence of inhibitor are positive, close and exhibited the same trend noticed in E_a . From literature, the negative sign of (ΔH°) has been clearly associated with an exothermic adsorption process that can either be physisorption or chemisorption or combination of both. However, the positive sign is connected to endothermic adsorption process which is credited to physisorption. The positive sign of the enthalpy of activation as obtained in the present study reflects the endothermic nature of the process of steel dissolution.

Table 3 Thermodynamic parameters for mild steel in the presence and absence of inhibitor

Concentration of Inhibitor	E_a (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
Blank	65.87	63.28	297.10
0.1g/l	77.45	74.77	324.72
0.3g/l	91.81	89.13	363.66
0.5g/l	100.14	97.55	388.07

Adsorption isotherm: Three different adsorption isotherms were tested so as to obtain more knowledge about the interface between the mild steel surface and inhibitor. The isotherms tested are Langmuir,

Freundlich, Temkin, and El - Awady adsorption isotherms. The linear regression coefficient of determination (R^2) was used to adjudge the model that best fit the experimental values. Langmuir relationship is represented by equation (9)

$$\frac{C}{\theta} = \frac{1}{K} + C \quad 9$$

Where K is the equilibrium constant of adsorption (M⁻¹) which was employed to obtain the Gibb's free energy, C is the inhibitor concentration, g/L, and θ is the degree of surface coverage (Rajendran *et al.*, 2000; Nnanna *et al.*, 2014). A plot of C/ θ against C as depicted in figure 10 gave a reciprocal of intercept as the adsorption constant. Using the K value determined from the Langmuir isotherm relationship, the standard Gibb's free energy of adsorption ΔG_{ads}° (kJ/mol) value at temperature range 35°C – 55°C was determined according to equation (10) below:

$$\Delta G_{ads}^\circ = -RT \ln (55.5K) \quad 10$$

Where R is the gas constant (8.314J/mol), T is the temperature (K), and 55.5 is the standard molar of water in the solution (Cheng *et al.*, 2007).

Temkin isotherm: This is expressed in equation (11);

$$\theta = \frac{1}{f} \ln(K_{ads}C) \quad 11$$

Equation 11 can be re - written as

$$\theta = \frac{1}{f} \ln C + \frac{1}{f} \ln K \quad 12$$

Where θ is a linear function of $\ln C$ (Nnanna *et al.*, 2009), K is the equilibrium constant of adsorption, (L/g), C is the inhibitor concentration, (g/L), and f is a coefficient of inhomogeneity connected with the range of inhomogeneity C by equation 13.

$$f = C/RT \quad 13$$

A plot of θ against $\ln C$ gives a straight line as indicated in figure 11, if Temkin isotherm is follow. Freundlich isotherm. The fitting of non – ideal system can be done sometimes by fitting the experimental data to Freundlich adsorption isotherm as seen in figure 12 (Yaro and Khadom, 2008). This is expressed in equation 14:

$$\theta = KC^n \quad 14$$

Equation 14 can be re – written as

$$\ln \theta = \ln K + n \ln C \quad 15$$

A plot of $\ln \Theta$ against $\ln C$ should give a straight line. Where Θ is the degree of surface coverage, C is the inhibitor concentration, g/L, K is the adsorption constant which is a measure of adsorption capacity, (L/g), and n is the positive constant called the Freundlich exponent which talks about the intensity of adsorption process on the mild steel surface.

El-Awady isotherm: This model is also referred to as the kinetic/thermodynamic model and is written as follows;

$$\log \left(\frac{\theta}{1 - \theta} \right) = \log k + y \log C \quad 16$$

Where y represents the number of inhibitor molecules occupying one active site of the metal surface, Θ is the degree of surface coverage, C is the inhibitor concentration, g/L.

A plot of $\log(\Theta/1-\Theta)$ against $\log C$ as shown in figure 13 can be used to determine the associated parameters such as the reciprocal of y which is used to describe the number of active sites on the surface occupied by one molecule of the inhibitor. It can be related to the binding constant, B , according to equation (17).

$$B = k^{1/y} \quad 17$$

When $1/y > 1$, each inhibitor molecule is believed to occupying more than one active site on the metal surface and vice – versa (Fouda and Ellithy, 2009).

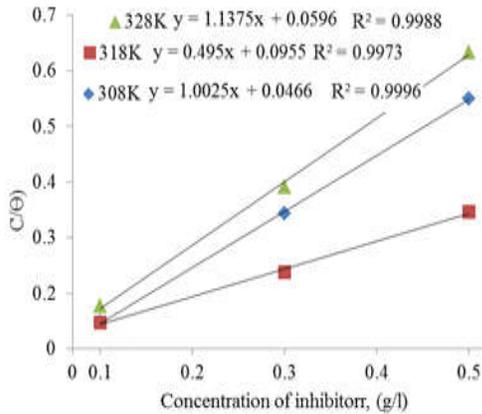


Fig 9. Langmuir isotherm for adsorption of cocoa leaf extract inhibitor on mild steel surface

Based on Table 4 – 7, the R^2 values obtained from the linear regression of the experimental data showed they are close to unity which suggested that the adsorption of cocoa leaf extract molecules onto the surface of mild steel is strongly fitted to Langmuir, and El – Awady isotherms.

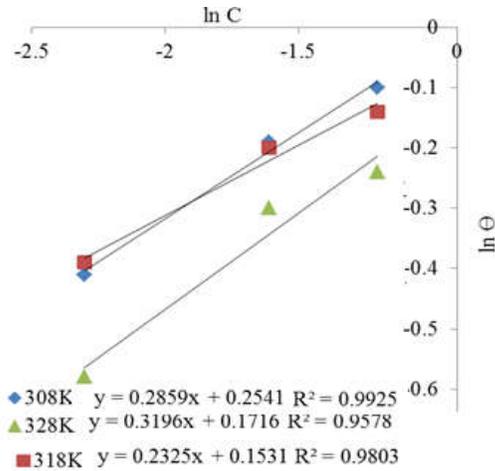


Fig 10. Freundlich isotherm for adsorption of cocoa leaf extract inhibitor on mild steel surface

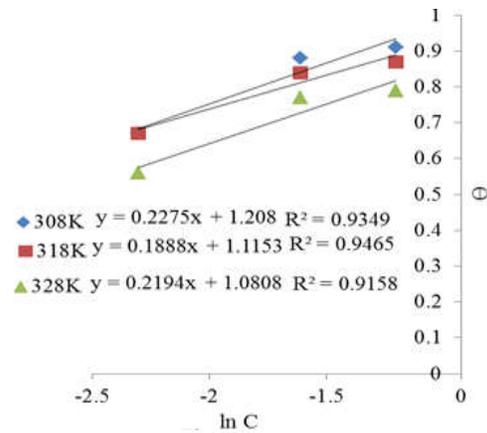


Fig 11. Tempkin isotherm for adsorption of cocoa leaf extract inhibitor on mild steel surface

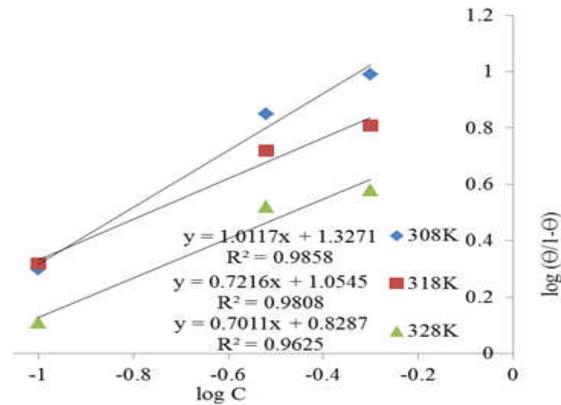


Fig 12. El-Awady isotherm for adsorption of cocoa leaf extract inhibitor on mild steel surface

Though, the Langmuir plot is linear with good correlation coefficient values, the slopes are greater than 1 this indicated a variation from an ideal Langmuir adsorption equation (Mouheddin *et al.*, 2018; Solomon *et al.*, 2010). This implied that there is

an interaction between surface of mild steel metal and species of adsorbed inhibitor molecules. The value of intensity adsorption shown in Table 5 is lesser than unity which indicated moderate adsorption. Table 6 showed the Temkin isotherm model parameters where the effect of indirect adsorbate (inhibitor)/adsorbate (inhibitor) interactions with the metal surface on the adsorption process was confirmed. The ΔG°_{ads} values obtained ascribed chemisorption nature of Temkin isotherm. From Table 7, the value of reciprocal of y gotten for 0.1g/L of inhibitor concentration at 308K temperature is less than unity; this showed that each molecule of the inhibitor occupied less than one active site on the metal surface. The value of $1/y$ obtained for 0.3g/L, and 0.5g/L inhibitor concentration at 318K and 328K respectively is greater than 1 which showed each molecule of the inhibitor is believed to occupy more than one active site on the metal surface (Fouda and Ellithy, 2009). The calculated values of ΔG°_{ads} listed in Tables 4, 5, and 7 are in the range -10.93 – 18.64kJ mol⁻¹.

Table 4 Langmuir Adsorption Isotherms Parameters

Temp., (K)	K _{ads} (L/g)	R ²	ΔG (KJmol ⁻¹)
308	21.46	0.9996	-18.14
318	10.47	0.9973	-16.83
328	16.78	0.9988	-18.64

Table 5 Freundlich Adsorption Isotherm Parameters

Temp. (K)	K _{ads} (L/g)	R ²	n	ΔG (KJmol ⁻¹)
308	1.289	0.9925	0.2859	-10.93
318	1.165	0.9803	0.2325	-11.02
328	1.187	0.9578	0.3196	-11.42

Table 6 Temkin Adsorption Isotherm Parameters

Temp, (K)	K _{ads} (L/g)	R ²	f	ΔG (KJmol ⁻¹)
308	202.42	0.9349	4.396	-23.88
318	460.73	0.9465	5.319	-26.83
328	137.72	0.9158	4.557	-24.38

Table 7 El - Awady Adsorption Isotherm Parameters

Temp (K)	K _{ads} (L/g)	R ²	y	B	ΔG (KJmol ⁻¹)
308	21.24	0.9858	1.0117	20.50	-18.11
318	11.34	0.9808	0.7216	28.94	-17.04
328	6.74	0.9625	0.7011	15.19	-16.16

These value less negative than -20kJmol⁻¹, from literature value of $\Delta G^{\circ}_{ads} = -20\text{kJmol}^{-1}$ or less suggested physisorption that involved electrostatic interaction between charged molecules whereas those in the order of -21 to -40 kJ mol⁻¹ or more is taken as chemisorption that involved transfer or sharing of charge from the inhibitor to the surface of metal to form a kind of co-ordinate bond (Yaro and Khadom, 2008; Roy *et al.*, 2014). From the values of ΔG°_{ads} obtained in this work, it can be inferred that mechanisms of adsorption of cocoa leaf extract on

mild steel surface might involve two types of interface namely physisorption and chemisorption. It can be thought that adsorption occurred first in the metal surface due to physisorption as a result of effective adsorption of molecules of water on the mild steel surface. The unused part of the water molecules adsorbed on the metal surface water is complemented by a chemical interaction between the metal surface, and the inhibitor that showed chemisorption adsorption process.

Conclusion: In the present work, cocoa leaf was extracted and characterized using phytochemical analysis, and FTIR while the mild steel was characterized using the X – RF for elemental compositions. FTIR result indicated that the actual adsorption of the inhibitor is as a result of donation of single pair of electrons on oxygen to the vacant d – orbitals of the metal that leads to the formation of complexes on the metal surface. Kinetics and thermodynamic studies were carried out to estimate the binding/adsorption mechanism of the molecules of inhibitor onto the surface of the mild steel. It was observed that the maximum inhibition efficiency of 92.08% was attained when the inhibitor concentration is 1.3g/l at 24hours time of immersion due to higher surface coverage of the extract on mild steel surface (0.9208). However, the lowest inhibition efficiency of 72.63% was recorded at 0.1g/l which is the lowest concentration of inhibitor used due to lower surface coverage value of 0.7263. Corrosion inhibition of the cocoa leaf extract on mild steel surface occurred by physical adsorption mechanism. This was proved with the values of activation energy that was obtained in inhibited medium which is higher than in the blank solution.

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