

## Adsorption Studies on the Inhibitive Properties of Aqueous Extracts of *Theobroma cacao* (TC) Leaves on Mild Steel in 1.0 M HCl

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**Abstract:** Corrosion of mild steel is an impactful environmental process because the electrochemical degradation process operates to severely waste the usefulness of the metal. The consideration of the various industrial installations that use mild steel for their construction, the present investigation is aimed at employing *Theobroma cacao* leaf extract to protect against mild steel deterioration through the inhibition method with due consideration of the influence of factors such as temperature, concentration, time, etc. .. The results of the investigations indicated that aqueous extract of the cocoa leaf inhibited mild steel corrosion with efficiencies ranging from 63.36 – 77.64 % at 302K. However, maximum inhibition efficiency of 83.21 % was observed at extract concentration and temperature of 1000 ppm and 323 K respectively. The behaviour of the inhibitor showed pronounced patterns that supported a physicoadsorption mechanism and model fitness that is consistent with the Freundlich and El-Awardy adsorption models. The adsorption of the inhibitor was observed to prevent the diffusion of the acid unto the active sites that could have enhanced corrosion. An exothermic and spontaneous adsorption were upheld based on the positive values observed for the enthalpy change and the negative values of standard free energy of adsorption.

**Keywords:** Corrosion inhibition, Adsorption, Cocoa leaf extract

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### 1.0 Introduction

The global industrial setting can not be effective without metal components. However, these metals (such as mild steel) are highly prone to corrosion attack, especially when exposed to liquid aggressive medium (Eddy and Ita, 2011). Uses of excessive loss of valuable metals through corrosion attacks have been widely reported in several published literature. In the fertilizer, oil, metallurgical and other industries, corrosion mitigation is essential if the survival of such and related industries must be guaranteed (Ukpe, 2019). Mitigation measures may include anodic/cathodic protection, galvanizing, alloying, application of corrosion inhibitors, etc (etc). through (Eddy *et al.*, 2010; Kumar and Dhanda, 2020).

Corrosion is a naturally occurring process generally defined as the deterioration of metallic materials as a result of the electrochemical reaction between the metals and their surroundings that can be controlled by either modifying the anodic, cathodic or both anodic and cathodic reactions (Eddy and Ameh, 2021). Results of corrosion cost

studies for Africa are not readily available, however as of 2017 South Africa reportedly spent about \$83 million to tackle corrosion. In Nigeria, it was estimated that the oil and gas industry loses up to \$765 million yearly to the corrosion of oil pipelines (Muanya, 2017). Similarly, the annual cost of all forms of corrosion to the oil and gas industries in the US is \$13.4 billion (Adekunle, 2019; Aliyu *et al.*, 2022). Consequently, industrial facilities exposed to corrosion are often protected against corrosion by adopting several options including painting, oiling, cathodic and anodic protection, etc. However, these technologies are capital intensive, which effects may be insignificant to the industries. Concerning corrosive solutions, the use of natural and synthetic organic inhibitors is the most efficient technique to control or impede corrosion risks due to its economic benefits and excellent performance (Amin *et al.*, 2011; Chai *et al.*, 2020; Berrissoul *et al.*, 2020). Corrosion inhibitors are one of the most promising methods to overcome corrosion. The use of eco-friendly corrosion inhibitors is on rising progress because of the consistency of favourable reports and the zeal of designing better ones (Ansari and Quraish, 2010). Inhibitors used for corrosion are substances able to retard the rate of corrosion when added, by being adsorbed on the surface of the metal through the mechanism of physical or chemical adsorption (Douadi *et al.*, 2015). Naturally occurring substances, especially plant extracts as inhibitors for the corrosion of materials, have received attention worldwide as a replacement for synthetic ones, which have several detrimental effects on the environment and human beings (Ebenso *et al.*, 2008). In a bid to find a substitute for the synthetic corrosion inhibitors an era of green inhibitors emerges. Green Inhibitors are of plant origin and biodegradable and are void of heavy metals or other toxic substances and are less toxic, easily accessible, less expensive and biodegradable (Eddy *et al.*, 2010). They contain heterocyclic compounds containing hetero-atoms such as N, O, S, Pii multiple bonds, pi-electron, conjugated

system, aromatic system and high molecular weight with hydrocarbon parts attached to the polar group. in their structures, which allows easy adsorption onto the surface of the metal (Ebenso *et al.* 2010; Muthukrishnan *et al.*, 2017; Ameh and Eddy, 2019; Anand and Chitra, 2020; Iroha and Ukpe, 2020; Essien *et al.*, 2021)

Several plants extract have been reported to have inhibited corrosion rate in various corrosive environments and their corrosion inhibition properties are often attributed to their phytochemical constituents (Umoren and Ebenso, 2008; Deng and Li, 2012; Eduok *et al.*, 2012; Umoren *et al.*, 2013Kristianto *et al.* 2019)

*Theobroma Cacao* belongs to the Stercaliaceae family known as cocoa trees. 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). In this present work, the aqueous leaves extract of *Theobroma cacao* (TC) leafy is studied by gravimetric technique for its corrosion inhibition potentials on mild steel in 1.0 M HCl solution.

Given the expected environmental consequences, cost expectations and other problems that are presenting giving challenges to most inorganic or toxic corrosion inhibitors, there is a need to continuously search and document inhibitors of natural origin. Consequently, the present study is investigating the efficiency of leaf extract of *Theobroma cacao* as an inhibitor for the retardation of the corrosion of mild steel. Previous studies of the use of this plant as a corrosion inhibitor have been reported. Yetri *et al.* (2018), documented good inhibition efficiency for the peel extract of *Theobroma cacao* and reported favourable adsorption characters to account for the good efficiency. Onuegbu *et al.* (2020) also investigated the corrosion inhibition potential of cold water extract of *Theobroma cacao* pod with maximum efficiency of 99% at a concentration

## 2.0 Materials and Methods

### 2.1 Materials

Mild steel sheet was purchased from the Ariara market, Aba. The chemicals employed for all analyses were analar grade and were used as purchased. Elemental analysis was carried out to determine the percentage of elements present in the mild steel using atomic absorption spectrophotometer, Perkin Elmer Analytix, 200 model. Corrosion tests were performed on the mild steel of the following percentage composition: carbon (0.126%), manganese (0.181%), silicon (0.058%), phosphorous (0.033%), sulfur (0.029%), chromium (0.012%), molybdenum (0.012%), nickel (0.002%) and iron (99.547%). The mild steel was cut into several coupons with dimensions, 5.0 x 1.0 x 0.6 cm were used for the experiments. They were abraded with emery papers of variable grades, starting with a coarse one (#600) and proceeding to the finer grade (#1200). The coupons were degreased in absolute ethanol, dried in acetone and warm air, and stored in moisture-free desiccators before use.

The leafy parts of cocoa were collected from the Amaoba Community of Abia State, Nigeria. A voucher specimen of the plant was dried by air for six weeks, then pulverized with a pestle and mortar and kept in a desiccator in the laboratory. Five hundred grams of the air-dried and powdered leaf parts of the plant were boiled with deionized water three times at 60 °C for 1 h and allowed to cool before filtration. The aqueous extract was concentrated under a vacuum at 40 °C until all the solvents were completely removed. The dried plant aqueous extract was used for the corrosion inhibition experiments by preparing inhibitor test solutions in the concentrations: 100 ppm, 200 ppm, 400 ppm, 600 ppm, 800 ppm and 1000 ppm. This was achieved by transferring 0.05g, 0.10 , 0.15 , 0.20 , 0.25 and 0.30 g of the extract into 250 mL of 0.5 M HCl solution in glass jars (Eddy *et al.*, 2010; Momoh-Yahaya, 2012; Chahul *et al.* 2019; Amadi *et al.*, 2022).

### 2.4 Gravimetric measurement

The gravimetric study was conducted using the standard protocol for weight loss measurements. The respective test solution was made to come in contact with the aggressive solutions (acid media) respectively. The experiments were conducted at different temperatures. Each metal coupon was allowed to remain in the corrodent for a specified time before it was removed, washed (to remove the corrosion product) and re-weighed. The difference in weight before and after immersion was recorded as the weight loss. The result obtained from the weight loss test; the inhibition efficiency (%) of the inhibitor, the degree of surface coverage, and corrosion rates were calculated using equations 1, 2, 3, 4 respectively (Omotosho, 2016)

$$\Delta W = W_f - W_i \quad (1)$$

$$(\% \text{ I.E}) = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \times 100 \quad (2)$$

$$\theta = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \quad (3)$$

$$CR \text{ (mmpy)} = \frac{876\Delta W}{A \times T \times D} \quad (4)$$

where T is immersion time in an hour, W is weight loss in grams, A is the area of the sample (coupon) in square cm (cm<sup>2</sup>) and D is the density of metal in g cm<sup>-3</sup>. CR<sub>blank</sub> is the corrosion rate of the sample in an acid medium (HCl) and CR<sub>inh</sub> is the corrosion rate of the metal sample in the inhibitor and the acid. W<sub>i</sub> is the weight before immersion and W<sub>f</sub> is the weight after immersion

#### 2.4.1 Theoretical models

The rate constant of the corrosion rate at different concentrations and temperatures is calculated using the relation:

$$-\log(\text{weight loss}) = -\frac{kt}{2.303} \quad (5)$$

where k is the rate constant (hr<sup>-1</sup>) t is the time in hours. The required rate constant, k is evaluated from the slope of the plot of -log (weight loss) against t. The half-life is thus calculated using the relation:

$$t_{1/2} = \frac{\ln R}{k} = \frac{0.693}{k} \quad (6)$$

Activation energy (E<sub>a</sub>): Activation energy was calculated using the following Arrhenius equation (7) (Umoren *et al.*, 2008).

$$\log C_R = \log A - \frac{E_a}{2.303RT} \quad (7)$$

Where A is the Arrhenius pre-exponential factor,  $C_R$  is the corrosion rate, T is the absolute temperature in Kelvin and R is the universal gas constant. The slope of the graph plotted between  $\log C_R$  and  $1/T$  gives the values of activation energy at various studied temperatures. The values of enthalpy of activation ( $\Delta H$ ) and entropy of activation ( $\Delta S$ ) were obtained from the transition state equation (8) (Umoren *et al.*, 2016).  $\log \frac{C_R}{T} = \left[ \left( \frac{R}{hN} \right) + \left( \frac{\Delta S}{2.303 R} \right) \right] - \left[ \frac{\Delta H}{2.303 RT} \right]$  (8) where  $C_R$  is the corrosion rate, N is Avogadro's number, T is the absolute temperature and R is the universal gas constant, h is Planck's constant. A plot between  $\log \left( \frac{C_R}{T} \right)$  and  $\left( \frac{1}{T} \right)$  gives a straight line with a slope of  $\left( \frac{-\Delta H}{2.303} \right)$  and intercept of  $\left[ \log \left( \frac{R}{Nh} \right) + \left( \frac{\Delta S}{2.303} \right) \right]$  from which the values of enthalpy of activation ( $\Delta H$ ) and entropy of activation ( $\Delta S$ ) were calculated (Olasehinde *et al.*, 2013).

The Langmuir adsorption isotherm was established by plotting  $\log(C_{inh}/\theta)$  against  $C_{inh}$ , which is based on equation 9

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (9)$$

where  $C_{inh}$  is the concentration of the inhibitor in the bulk electrolyte,  $\theta$  is the degree of surface coverage and  $k_{ads}$  is the Langmuir adsorption constant. The Langmuir model applies to a single adsorption layer (monolayer) process and expects the slope value to be unity for

ideal fitting. From the Langmuir adsorption constant, the standard free energy of adsorption of the inhibitor was evaluated using the Gibb Helmholtz equation, that is equation 10

$$\Delta G_{ads}^0 = -RT \ln k_{ads} \quad (10)$$

Adsorption is spontaneous if the free energy change is negative. Free energy values are also an index for predicting the mechanism of adsorption. Values between 0 and -20 kJ/mol are typical for the physisorption mechanism. Above 40 kJ/mol, the values interpreted the chemisorption mechanism but both mechanisms for values between -20 and -40 kJ/mol.

The Freundlich adsorption isotherm given by equations (11) and (12) was established by plotting  $\log \theta$  against  $\log C_{inh}$

$$\theta = K_{ads} C_{inh} \quad (11)$$

$$\log \theta = \log(K_{ads}) + \frac{1}{n} \log C_{inh} \quad (12)$$

where  $\theta$  is the degree of surface coverage and  $C_{inh}$  is the concentration of the inhibitor,  $K_{ads}$  is the equilibrium constant in the adsorption process. A straight line is obtained between the logarithm of the degree of surface coverage ( $\theta$ ) and the logarithm of inhibitor concentration  $C_{inh}$  in Freundlich isotherm.  $\log K_{ads}$  is the intercept,  $\frac{1}{n}$  is equated to the slope of the plot and n is a positive Freundlich exponent which is the intensity of the adsorption process on the surface.

### 3.0 Results and Discussion

#### 3.1. Effect of immersion time

The weight loss study results indicated the increase in IE with an increase in time of immersion till 12 h. At 12 h, efficiency was a maximum of 85.73 and then decreased to 82.69 at 24 h. The best performance of the TC has been perceived at 12 h of immersion period with the entire concentration of the inhibitor. The variation of inhibition performance of TC with immersion time at various concentrations is shown in Fig.1

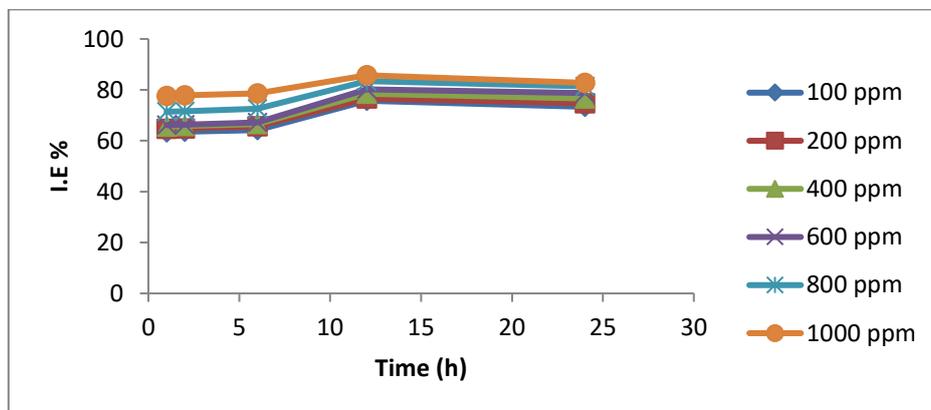
#### 3.2. Weight loss (WL) method

The WL of mild steel in an acidic solution at 25 °C in the absence and presence of a different concentration of TC after various immersion periods (1-24 h) is shown in Fig. 2. The WL was found to decrease as the TC concentration increases due to the formation layer on the MS surface. The adsorbed molecule isolates the metal from an acidic solution and inhibits the corrosion sites (Amadi *et al.*, 2020).

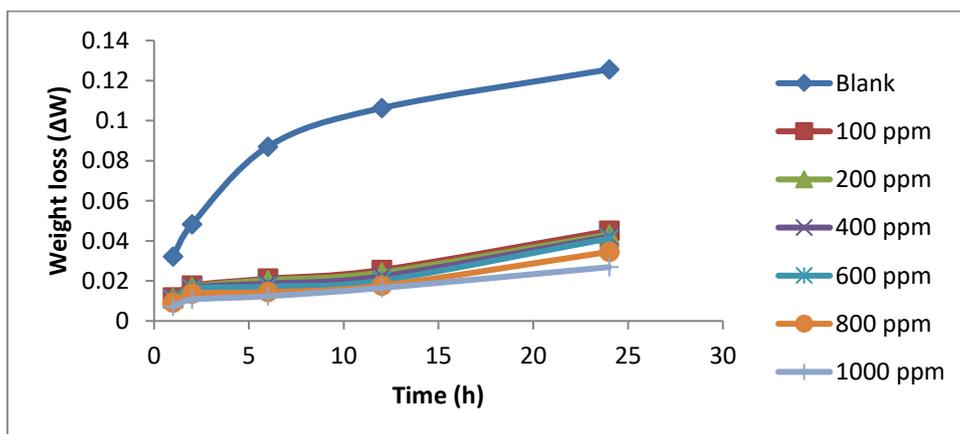
#### 3.3 Weight loss evaluation

Fig. 3, represents the weight loss against temperature for mild steel at temperatures 302K, 312K, 322K, 332K and 342K. An increase in extract concentration reduced the weight loss while an increase in temperature increased the mild steel weight loss. Plots

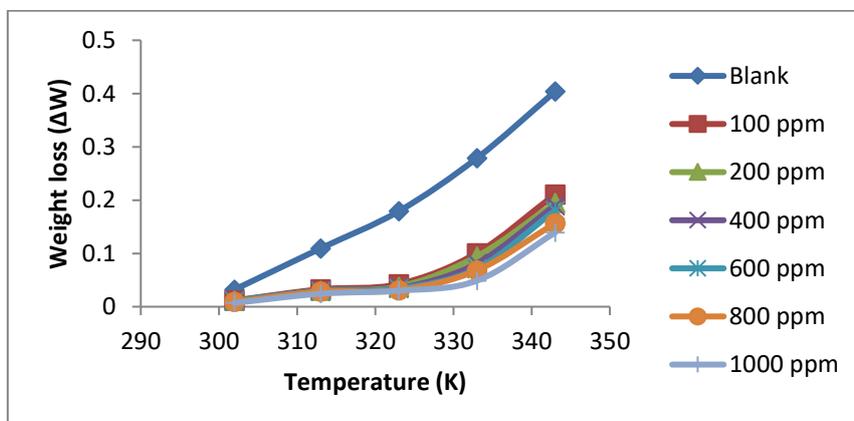
representing the variation of the corrosion rate with the temperature at various concentrations of the inhibitors are shown in



**Fig.1: Variation of inhibition efficiency with different immersion times of TC in 1.0 M HCl on the mild steel surface**



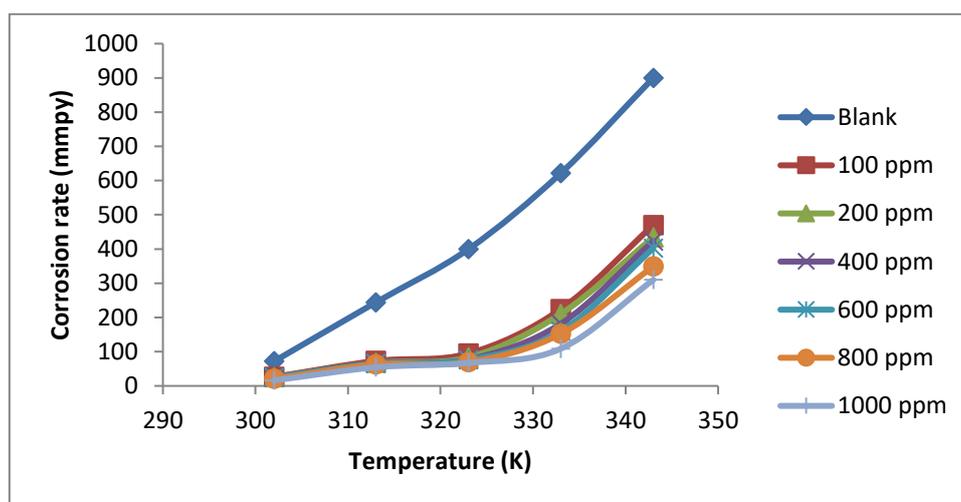
**Fig. 2: WL vs. time at 25°C for MS corrosion in 1.0 M HCl in the presence and absence of different concentrations of TC.**



**Fig. 3: Weight loss variation for TC at different temperatures in 1.0 M HCl**

Fig. 4. An increase in the concentration of extract reduced the corrosion rate while the increase in temperature increased the corrosion rate. Besides, an increase in temperature increased the susceptibility of the metal to corrosion (James *et al.*, 2007). Table 1, showed inhibition efficiency variation against different extract concentrations of mild steel in 1.0 M HCl at the various temperatures studied. An increase in extract

concentration increased the inhibition efficiency while a temperature increase reduced the efficiency of inhibition. Decreased inhibition efficiency at high temperatures was due to the increase in kinetic energy of the extracts, which makes adsorption between the extract and mild steel insufficient at the binding sites (Eddy *et al.*, 2015).

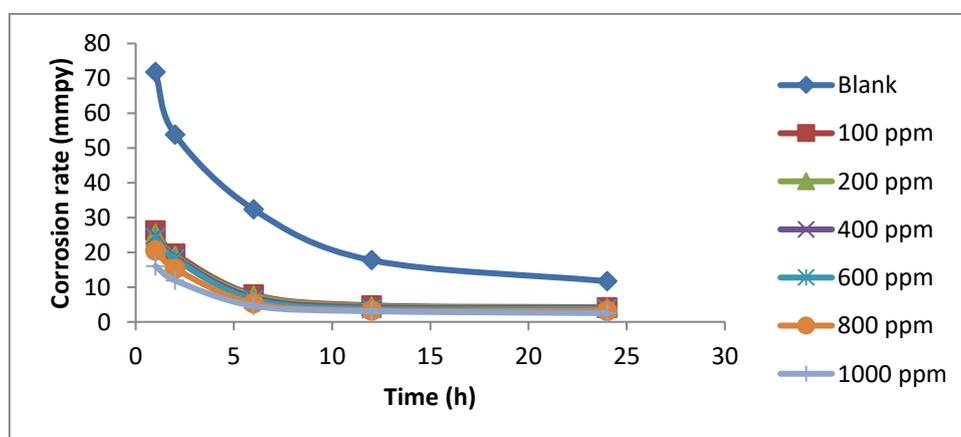


**Fig. 4: Variation of corrosion rate (CR) on mild steel with different concentrations of TC inhibitor in 1.0 M HCl at various temperatures (303–433 K) for an immersion time 5 h.**

**3.4: Effect of inhibitor concentration**

Mild steel corrosion parameters in a 1.0 M hydrochloric acid environment were evaluated from mass loss analysis data in the

presence and absence of various concentrations (100–1000 ppm) of the TC for various immersions (1–24 h) at 303 K and postulated in Fig. 5.



**Fig. 5: Variation of corrosion rate (CR) on mild steel with different concentrations of TC inhibitor in 1.0 M HCl at 303 K for various immersion times.**

A review of the data in Fig. 5, exhibits that protection efficacy increases with increasing the concentrations of TC to 500 ppm concentration and after 500 ppm concentration remains relatively steady and hence 500 ppm was considered as optimum concentration and the concentration was selected as 100 ppm to 500 ppm. On the other hand, the corrosion rate was decreasing with increasing the concentrations of TC to 1000 ppm. The inhibition efficiency of TC at 400 ppm concentration was found to be 95.1%, while it was 71.5% at 100 ppm concentration at 303 K (Garcia-Ochoa *et al.*, 2016; Verma *et al.*, 2015)

### 3.5. Effect of temperature

The corrosion rate increases with an increase in temperature while the protection efficacy of TC reduces with an increase in temperature (Amadi *et al.*, 2020). Such behaviour can be interpreted on the basis that the inhibitor exerts its action by adsorbing itself on the mild steel surface and an increase in temperature resulted in the desorption of some adsorbed inhibitor molecules leading to a decrease in the inhibition efficiency. The protection efficacy of TC was found to be significant at all concentrations and temperatures. Table 2 shows the presence of tannin, flavonoids, saponin and anthraquinone in the cocoa leaf extract (Okewale and Adesina, 2020). These phytochemicals can enhance the process of corrosion inhibition of mild steel in an 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).

Customarily, IE increases with the inhibitor concentration (Fig.6). But in acidic media, corrosion of metal is accompanied by the evolution of H<sub>2</sub> gas, which may be attributed to a rise in temperature which resulted in higher dissolution rate of the metal. It has been observed from Table 1 that IE increase with an increase in temperature up to 333 K

and beyond this decrease in efficiency was observed. The decrease in IE with temperature might be attributed to the desorption of the inhibitor molecule from the metal surface at higher temperatures (Essien *et al.*, 2021). When the temperature increased, CR increased which was due to the desorption of TC from the metal surface and exposure of more area of the metal surface to an acidic medium. The decrease in the adsorption at higher temperatures indicated the physical adsorption of the inhibitor (Iroha and Ukpe, 2020).

### 3.6. Thermodynamic and activation parameters

The Arrhenius equation (Eq. (7)) was used to compute the apparent activation energy (E<sub>a</sub>) for mild steel dissolving in 1.0 M HCl. The Arrhenius plot of log CR against  $\frac{1}{T}$  for mild steel corrosion in the presence and absence of inhibitor at concentrations 100–600 ppm is exhibited in Fig. 7. The activation energy was evaluated using the calculation E<sub>a</sub> = (slope) x 2.303R. Table 3 presents the E<sub>a</sub> value that was calculated and it shows that the activation energy value for the inhibited solution was higher than for the uninhibited solution and that this trend was maintained as the inhibitor concentration was increased. This demonstrates why the corrosion reaction energy barrier rises when inhibitor concentration rises (Wu *et al.*, 2019; Jawad *et al.*, 2020; Al-Amiery *et al.*, 2020). The unimolecular reactions are described by the following equation (Eq. (13)) from a thermodynamic and kinetic standpoint (Karthikaiselvi and Subhashini, 2014)

$$E_a = \Delta H_{ads} + RT \quad (13)$$

A plot between  $\log\left(\frac{CR}{T}\right)$  and  $\left(\frac{1}{T}\right)$  gives a straight line with a slope of  $\left(\frac{-\Delta H}{2.303}\right)$  and intercept of  $\left[\log\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S}{2.303}\right)\right]$ . It can be observed from Table 2, for the tested inhibitor, E<sub>a</sub> > ΔH by a value that is almost as RT. Therefore, Mild steel coupons corrode in 1.0 M HCl solution each in the presence or absence of various concentrations of the investigated inhibitor by a unimolecular reaction (Al-Amiery *et al.*, 2021; Yamin *et al.*, 2020).

**Table 1: Corrosion rate and inhibition efficiency of mild steel of TC leave extract for mild steel corrosion at various temperatures**

C. (ppm)	302 K		313 K		323 K		333 K		343 K	
	CR (mmpy)	IE (%)								
<b>Blank</b>	71.77	—	243.85	—	399.22	—	621.45	—	900.07	—
<b>100 ppm</b>	26.30	63.36	72.89	70.11	94.51	76.34	224.24	63.92	469.87	47.80
<b>200 ppm</b>	25.41	64.60	67.54	72.30	83.36	79.14	210.42	66.14	434.21	51.76
<b>400 ppm</b>	24.74	65.53	66.65	72.67	77.57	80.59	181.44	70.80	423.07	53.00
<b>600 ppm</b>	24.30	66.14	65.31	73.22	76.01	80.98	159.82	74.28	402.34	55.30
<b>800 ppm</b>	20.51	71.42	62.85	74.23	69.10	82.71	152.02	75.54	349.29	61.19
<b>1000 ppm</b>	16.05	77.64	54.39	77.70	67.09	83.21	108.76	82.50	309.83	65.58

The standard activation enthalpy ( $\Delta H$ ) and entropy standard activation ( $\Delta S$ ) values for the activation complex formation in the transition state were determined according to the transition state relation (Eq. (8)).

From Fig. 8, it is obvious that the plot of  $\log\left(\frac{CR}{T}\right)$  vs  $\left(\frac{1}{T}\right)$  gave a straight line with a slope of  $\frac{\Delta H}{2.303}$  and an intercept of  $\left[\log\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S}{2.303}\right)\right]$ , from which the thermodynamic activation parameters

$\Delta H$  and  $\Delta S$  were determined and summarized in Table 3. Also from Table 3, it is obvious the studied inhibitor has  $\Delta S$  with a positive value which suggests that the activated complex formation in the rate evaluating step depicts preferably dissociation than an association, implying that during the shift from reactants to activated complex, there is an increase in disorder (Al-Amiery *et al.*,2020; Eddy and Ameh, 2021).

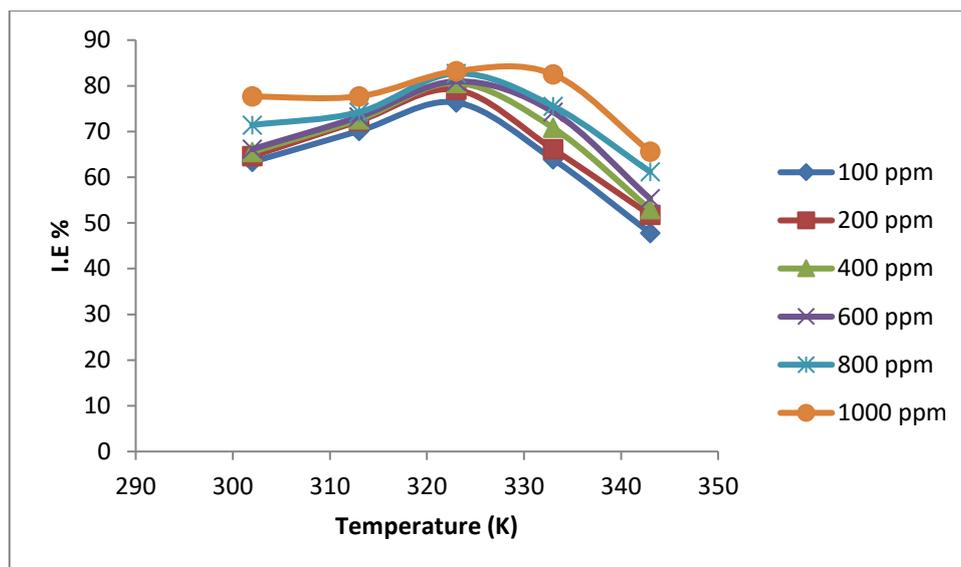
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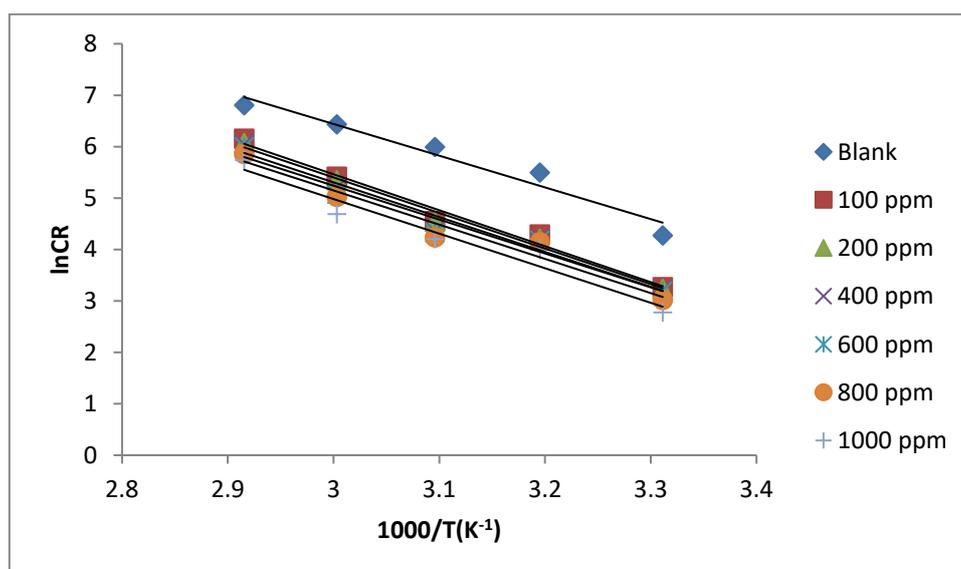
**Table 2; Phytochemical Constituents of Cocoa Leaf Extract**

Chemical constituents	Rating
Alkaloid	+
Terpenoid	-
Phenol	+
Sterols	-
Flavanoid	++
Cardiac glycoside	+
Glycoside	-
Tannin	++
Phytosterol	+
Saponins	++
Anthraquinones	+
Reducing sugar	-
Steroids	-

**Key:** ++ Abundance + Trace – Absent



**Fig. 6.** Variation of inhibition efficiency (IE%) on mild steel with different concentrations of TC inhibitor in 1.0 M HCl at various temperatures (303–343 K) for immersion time 5 h.



**Fig. 7.** Arrhenius plots of log CR versus  $1000/T$  for mild steel corrosion in 1.0 M HCl environment

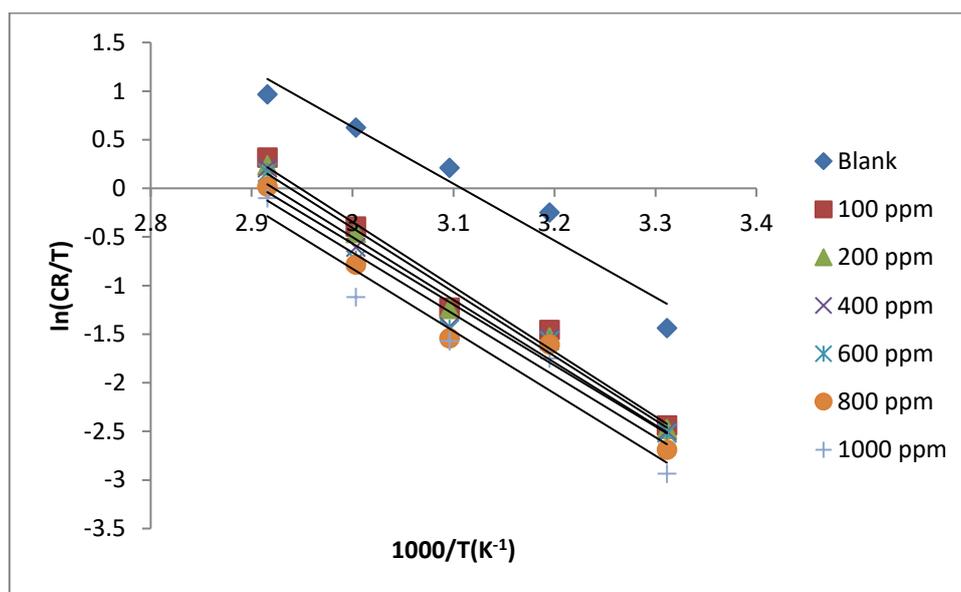
### 3.7 Kinetics study

Fig. 9 shows the plot of  $-\log W$  (weight loss) against immersion time in (hour) in the presence and absence of TC leaves extracts. The rate constant and half-life parameters are shown in Table 4. From the table, the corrosion rate constant values increased with an increase in the concentration of TC leaf extract. The values of the half-life decreased as the concentration of TC extract increases.

There is also a corresponding decrease in half-life values as the rate constant increases. This confirmed the first-order kinetics for the corrosion of mild steel in 1.0 M HCl. The correlation coefficient values obtained were close to unity showing that the experimental value fitted well to the first-order kinetics. Similar results had also been reported by (Olasehinde *et al.*, 2013; Ijuo *et al.*, 2016).

**Table 3: Activation and thermodynamic parameters of mild steel in 1.0 M HCl without and with TC leaves extract**

C (ppm)	Ea (KJ/mol)	ln β	ΔG (kJ/ppm)					ΔH (kJ/p pm)	ΔS (kJ/K/pp m)
			302 K	313 K	323 K	333 K	343K		
Blank	51.27	24.94	-129.18	-135.66	-141.54	-147.43	-153.32	48.59	588.65
100 ppm	58.13	26.44	-126.08	-132.69	-138.70	-144.72	-150.73	55.46	601.13
200 ppm	57.50	26.15	-125.83	-132.41	-138.40	-144.38	-150.36	54.83	598.22
400 ppm	56.25	25.60	-125.86	-132.40	-138.34	-144.28	-150.22	53.58	594.17
600 ppm	54.80	25.01	-125.84	-132.32	-138.21	-144.10	-150.00	52.12	589.26
800 ppm	55.32	25.11	-125.55	-132.04	-137.94	-143.84	-149.74	52.65	590.07
1000 ppm	55.94	25.17	-125.08	-131.58	-137.48	-143.37	-149.29	53.26	590.53



**Fig. 8. Transition state plots of log CR/T versus 1000/T for mild steel in 1.0 M HCl the environment at various inhibitor concentrations**

**3.8. Adsorption isotherm and adsorption parameters**

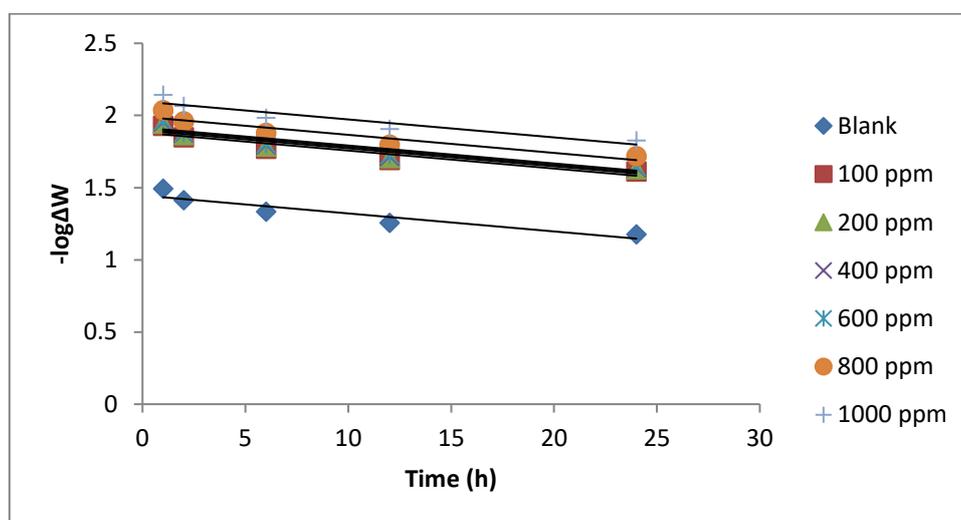
To gain more information about the mode of adsorption of the plant extract on the mild steel surface, the experimental data have been tested with several adsorption

isotherms. The weight loss temperature results were used to calculate the adsorption

isotherm parameters. The most frequently used isotherms are Langmuir, Frumkin, Temkin, Flory-Huggins and the thermodynamic/kinetic model of El-Awady isotherm. Inhibitor molecules were adsorbed on the metal surface if the interaction between the molecule and the metal surface was higher than that of the water molecule and the metal surface.

**Table 4: Half-life and rate constant parameters at various concentration leaves extract of TC at ambient temperature**

Conc.	Rate constant $k_1$ (hrs-1)	Half-life (hour)	Intercept	$R^2$ value
Blank	0.05112	13.5563	1.3482	0.7124
100 ppm	0.05021	13.8020	1.8558	0.9195
200 ppm	0.04974	13.9324	1.8704	0.9179
400 ppm	0.04794	13.9324	1.8915	0.9232
600 ppm	0.04951	13.9971	1.9133	0.9246
800 ppm	0.04951	13.9971	1.9849	0.9304
1000 ppm	0.05021	13.8020	1.9218	0.9218

**Fig. 9: Variation of  $-\text{Log } W$  (weight loss) versus Time (hour) in the presence or absence of TC leaves extract**

Several adsorption isotherms were plotted and Langmuir adsorption isotherm was found to be the best description of the adsorption behaviour. A plot of  $\frac{C_{inh}}{\theta}$  versus  $C_{inh}$  from weight loss data yielded a straight line as shown in Fig. 10. The values of the parameters obtained were shown in Table 5. From the results, the slopes and  $R^2$  values were close to unity which indicate strong adherence to Langmuir adsorption isotherm. These indicate an interaction among the adsorbed species on the surface of the mild steel. The values of  $\Delta G_{ads}$  obtained were

negative, ranging from  $-16.7793$  to  $-21.7915$   $\text{kJ mol}^{-1}$  and less than the threshold values of  $-40$   $\text{kJ/mol}$  which is required for the chemical

adsorption mechanism. Therefore this shows the spontaneous nature of the adsorption of inhibitor on the mild steel surface and the stability of the adsorbed layer on the surface of the mild steel. This is consistent with the physical adsorption mechanism. It has been postulated in the derivation of the Langmuir isotherm equation that adsorbed molecules did not interact with one another, but this was not true in the case of these extract molecules which could be adsorbed on the metal surface. The adsorbed species interact either by mutual repulsion or attraction and would affect the slope. The deviation of the slope could also be interpreted due to the changes in adsorption heat with increasing surface coverage which has also been ignored in the derivation of Langmuir isotherm (Oguzie *et al.*, 2004).

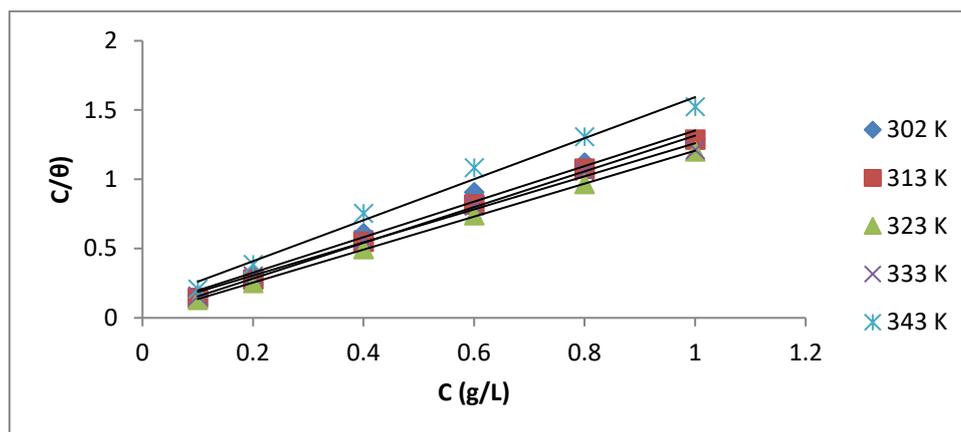


Fig. 10. Variation of  $C/\theta$  versus  $C_{inh}$  for Langmuir isotherm adsorption of TC leaves extract on the surface of mild steel

Table 5. Langmuir parameters for the adsorption of the inhibitor on the surface of mild steel

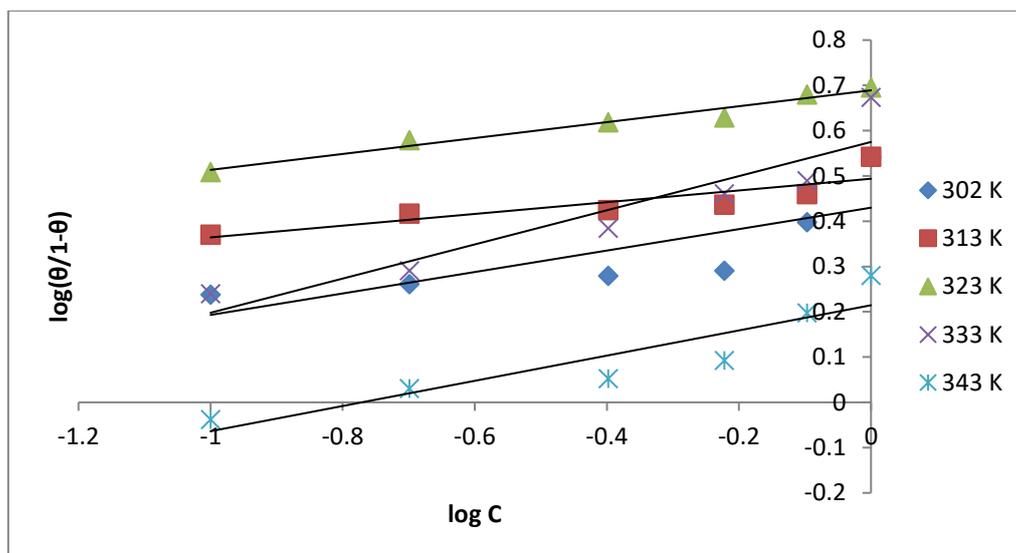
Temperature	$K_{ads}$	$-\Delta G_{ads}(\text{J mol}^{-1})$	$1/K_{ads}$	$R^2$
303	14.388	16779.30	0.0695	0.9882
313	38.462	19949.23	0.0260	0.9981
323	60.241	21791.49	0.0166	0.9998
333	14.948	18.607.40	0.0669	0.9935
343	8.826	17663.68	0.1133	0.9871

El-Awady isotherm: The experimental data have been then fitted into the modified form of Langmuir isotherm known as El-Awady isotherm which can appropriately represent the adsorption behaviour of the inhibitor onto the MS surface. El-Awady isotherm is given by (El-Awady et al., 1992)

$$\log\left(\frac{\theta}{1-\theta}\right) = \log k + y \log C \quad (14)$$

where  $y$  is the number of inhibitor molecules occupying one active site.  $\theta = (IE/100)$  is the surface coverage.  $C$  is the concentration,  $K$  is the constant related to the equilibrium constant of the adsorption process.  $K_{ads} = K^{1/y}$  and  $y$  represent the number of inhibitor molecules occupying a given site. The values of  $1/y$  calculated from the El-Awady model are given in Table 6. Generally, values of

( $\Delta G_{ads}$ ) up to  $-20 \text{ kJ ppm}^{-1}$  are consistent with the electrostatic interactions between the charged molecules and the charged metal (physisorption) while those around  $-40 \text{ kJ ppm}^{-1}$  or higher are associated with chemisorption as a result of sharing or transfer of electrons from plant extract molecules to the metal surface to form a coordinate type of bond (chemisorption) (Hosseini *et al.*, 2003). The values of  $\Delta G_{ads}$  listed in Table 5 indicate the physisorption of TC on the mild steel surface. Inspection of Table 5 revealed that  $\Delta G_{ads}$  value increases from  $-12$  to  $-15 \text{ kJ ppm}^{-1}$  with increasing temperature from 333 to 343 K. These results showed that inhibition efficiency increases with an increase in temperature (Ahamad and Quraish, 2010; Eddy *et al.*, 2022).



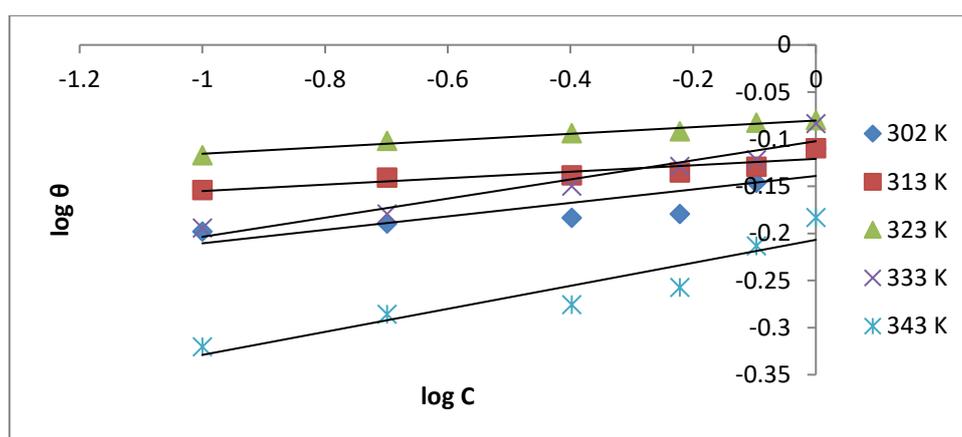
**Fig. 11:** El-Awardy isotherm plots for adsorption of TC on the mild steel surface in 1.0 M HCl solution.

**Table 6.** El-Awardy isotherm parameters for mild steel in the presence of leaves extract of TCat 302. 313, 323, 333 and 343 K

T(K)	Slope (y)	$K_{ads}$	1/y	$-\Delta G_{ads}(kJ/ppm)$	$R^2$
312	0.2368	2.6909	4.2230	12.5699	0.6213
313	0.1296	3.1175	7.7160	13.4106	0.7487
323	0.1757	4.8876	5.6915	15.0467	0.9691
333	0.3772	3.7584	2.6511	14.7852	0.8612
343	0.2781	1.6383	3.5958	12.8613	0.8318

Freundlich isotherm: The plot of  $\text{Log } \theta$  versus  $\text{Cin}^h$  from weight loss data yielded straight

lines as shown in Fig 12 and the parameters obtained in Table 7.



**Fig. 12:** Freundlich isotherm plots for adsorption of TC on the mild steel surface in 1.0 M HCl solution.

From the results,  $R^2$  values were close to unity which indicates strong adherence to

Freundlich adsorption isotherm. The values of  $\Delta G_{ads}$  obtained were also negative, ranging

from -8.10 to -10.65 kJ mol<sup>-1</sup> which is also less than -20.00 kJ mol<sup>-1</sup> and this supports the physical adsorption mechanism. The values of 1/n obtained which is the intensity of the adsorption process of mild steel surface shown in Table 7 are less than unity which indicates favourable adsorption (Okewale and Adesina, 2020). The values of 1/n also speak of the degree of heterogeneity of the adsorption surface. At 313 K temperature, the surface of the mild steel becomes more heterogeneous as the 1/n value (0.0342) gets

closer to zero (Itodo *et al.*, 2018). The comprehensive adsorption mechanism suggested in the work is thought to occur in succession. The first stage is physical adsorption due to the effective adsorption of molecules of water on the surface of mild steel, then complemented by a chemical interaction between the mild steel surface and the unused part of the water molecules which initiates the chemical adsorption process (Okewale and Adesina, 2020).

**Table 7. Freundlich isotherm parameters for mild steel in the presence of leaves extract of TC at 302, 313, 323, 333 and 343 K**

T (K)	n	1/n	K <sub>ads</sub>	-ΔG <sub>ads</sub> (kJ/ppm)	R <sup>2</sup>
312	13.9860	0.0715	0.7259	9280.12	0.6674
313	29.1545	0.0342	0.4550	8402.57	0.7847
323	28.3286	0.0353	0.4436	8602.89	0.9712
333	9.8425	0.1016	0.7914	10471.90	0.9213
343	8.1900	0.1221	0.7549	10651.71	0.8686

#### 4.0 Conclusion

The following conclusions are derived from the investigation:

- (i) It has been established in this study that the *Theobroma cacao* (TC) leafy aqueous extract exerted an inhibiting effect on the acid corrosion of mild steel.
- (ii) It has been established in this study that the rate of corrosion decreases with an increase in concentrations of inhibitors, equally the corrosion rate increases with temperature in the studied media.
- (iii) The *Theobroma cacao* (TC) leafy aqueous extract maintained remarkable corrosion inhibition efficiency even with prolonged exposure time.
- (iv) The adsorption of the extracts on the mild steel surface in 0.1 M HCl solutions respectively obeys Langmuir and Freundlich isotherms.
- (v) The presence of this TC in the acid media increases the activation energy of the corrosion process which indicates physical adsorption.

#### 5.0 Conclusion

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### Declarations

The authors declare that they have no conflict of interest

### Data availability

All data used in this study will be readily available to the public

### Consent for publication

Not Applicable

### Availability of data and materials

The publisher has the right to make the data Public.

### Competing interests

The authors declared no conflict of interest.

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**Authors' contributions**

Okoche K. Amadi: Designed, supervised and discussed the work.

Onyinyechi U. Akoh: plotted the graphs and calculated the parameters of the graphs

Godson C. Eric: Carried out the bench work under Okoche K. Amadi's supervision