

# ASSESSING THE POTENTIAL OF *Caesalpinia Bonducella* LEAF Ethanol EXTRACT IN 1M H<sub>2</sub>SO<sub>4</sub> SOLUTION FOR CORROSION INHIBITION AND ADSORPTION

<sup>2</sup>Akinjokun, A. I., <sup>1</sup>Oyewumi M. S., <sup>1</sup>Oladele E. P., <sup>1</sup>Esho, J. I., <sup>3</sup>Adeniyi B. O.,  
<sup>1</sup>Olasehinde E. F.

<sup>1</sup>Department of Chemistry, The Federal University of Technology, Akure, Nigeria

<sup>2</sup>Department of Chemical Sciences, Joseph Ayo Babalola University, Ikeji Arakeji, Nigeria

<sup>3</sup>Department of Chemical Science and Technology, Federal Polytechnic Ede, Nigeria

## Correspondence

epoladele@futa.edu.ng,  
peaceademme@live.com

## History

Received: 31/12/2024

Accepted: 26/03/2025

Published: 30/05/2025



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## ABSTRACT

The corrosion inhibition and adsorption properties of *Caesalpinia bonducella* leaf ethanol (CBLE) extract, a low-cost and sustainable corrosion inhibitor on low-carbon steel coupon in 1M H<sub>2</sub>SO<sub>4</sub> solution were studied using weight loss and potentiodynamic polarization measurements. The surface morphology and the organic functional moieties of the extract were obtained from Scanning Electron Microscopy (SEM) and Fourier Transform Infrared spectroscopy (FTIR) data, respectively. The highest Inhibition efficiencies of 73.34% and 82.35% were obtained at 303K and 343K, respectively and at 0.8 g/L extract concentration. Corrosion inhibition occurred by the formation of CBLE extract adsorption films onto the coupon's surface. The adsorption process can be best described by the Langmuir isotherm and chemisorption mechanism. Thermodynamic studies further showed that corrosion inhibition of the steel coupons in an acidic solution mediated by CBLE extract is endothermic and spontaneous. Electrochemical studies showed that the extract is adaptable in that it acts as a mixed-mode inhibitor with a prevalence of cathodic effectiveness

**Keywords:** *Caesalpinia bonducella*, Corrosion, Mild Steel, Electrochemical, Gravimetric, Inhibition.

## 1 | Introduction

In many industrial chemical processes, particularly those associated with the use of acidic electrolytes/solutions, corrosion of metallic components has been identified as a major cause for concern due to its associated negative economic and environmental impacts (Buchweishaija, 2009). These concerns are related to the cost of replacement or repairs of corroded components and the release of

potentially toxic metal ions into the environment. To prevent these problems, a diminutive amount (Singh *et al.*, 2011) of a certain class of chemicals called “corrosion inhibitors” is added to the metal's surfaces (Cao *et al.*, 2022; Loto *et al.*, 2021). Corrosion inhibitors are organic compounds containing abundant pie bond systems and heteroatoms which allow them to bind to the metal surface through the formation of a thin film adsorption layer (Pandey *et al.*, 2018; Hijazi *et*

*al.*, 2015). Although chemical inhibitor formulations with high inhibition efficiencies are commercially available, their use is limited by high cost and toxicity (Ng *et al.*, 2022; Verma *et al.*, 2018). As a result, many research efforts are currently centered on finding affordable inhibitors made from sustainable feedstock. Several studies have reported that plant extracts with chemical functionalities similar to those found in conventional chemical inhibitors can function as low-cost, eco-friendly and sustainable corrosion inhibitors –(Arockia *et al.*, 2020; Helen *et al.*, 2014; Miralrio and Espinoza Vázquez, 2020; Olasehinde *et al.*, 2022). Extracts from several plants such as *Datura mete* seed (Sathiya *et al.*, 2014; Singh *et al.*, 2016), *aloe vera* (Singh *et al.*, 2016), *alchornea laxiflora* (Oluwafemi *et al.*, 2019; Olasehinde *et al.*, 2015), *Garcinia kola* (Ikeuba *et al.*, 2013) among others have been studied and found to have great potentials as green and low-cost inhibitors.

*Caesalpinia bonducella* is a shrub (Nallagouni *et al.*, 2021) commonly found growing on its own in the tropics. Its use as an important component of herbal concoctions has been widely documented in the treatment of bacterial and fungal infections; as an anti-diabetic, analgesic, and anti-tumor agent (Billah *et al.*, 2013; Chakrabarti *et al.*, 2005; Pandey *et al.*, 2018; Devi *et al.*, 2008; Kumar *et al.*, 2019; Nazeerullah *et al.*, 2012; Shukla *et al.*, 2009, 2010). The efficacy of plant extract in corrosion inhibition has been reported to be dependent on many variables including the type of corrosion medium, nature of corrosion inhibitors and extracting solvent (Salleh *et al.*, 2021; Hijazi *et al.* (2015). Meanwhile, preliminary investigation showed that *Caesalpinia bonducella* leaf 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 *Caesalpinia bonducella* leaves ethanol extract on

acid corrosion of mild steel. Therefore, this study attempts to investigate the inhibitive effects of CBLE on mild steel corrosion in 1M H<sub>2</sub>SO<sub>4</sub> solution. It should be noted that despite the effectiveness and relatively low toxicity of ethanol as extractant, care must be taken during the extraction due to its flammability which can pose a fire risk during extraction.

## 2. | Materials and methods

### 2.1 | Materials Preparation

Mild steel was obtained from School of Engineering workshop, Oba-kekere, FUTA and the chemical composition was determined at universal steel, Ogba, Lagos State. The mild steel specimen 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%. The steel was cut into coupons of dimension ranging from 8 mm to 9 mm in height and 8 mm in diameter. Each coupon was polished mechanically using emery papers, washed thoroughly with distilled water, degreased with ethanol and finally dried at room temperature prior to the corrosion test. The leaves of *Caesalpinia bonduc* were obtained from Aramoko-Ekiti in Ekiti State and authenticated at Crop, Soil and Pest Department, Federal University of Technology, Akure.

### 2.2 | Preparation of Plant Extract

The leaves of *Caesalpinia bonducella* (LCB) were cut into pieces and washed with distilled water, air-dried, and pulverized into powder using a laboratory blender. The LCB powder was thereafter extracted with ethanol (98% w/v) (1g: 5 mL) for 96 h. The extract was concentrated by evaporating the solvent to dryness on a thermostated water bath at 78 °C to obtain the *Caesalpinia bonducella* leaf ethanolic (CBLE) extract. Extract with masses ranging from 0.2 – 0.8

g were weighed and then dissolved separately in 1000 mL 1M H<sub>2</sub>SO<sub>4</sub> solution for use as the media for the corrosion study.

### 2.3 | Characterization

The IR spectrum of the CBLE extract was recorded using a PerkinElmer 1600 FTIR spectrometer (Sehmi *et al.*, 2020). A dried sample (0.5g) of the CBLE extract was powdered with KBr to form IR transparent pellets and used in spectrum collection. The surface morphology of the steel coupon before and after immersion for 4 h at room temperature in the corrosive test media containing 0 % w/v and 0.8 % w/v CBLE extract in 1M H<sub>2</sub>SO<sub>4</sub> solution surface was viewed using a Scanning Electron Microscope.

### 2.4 | *Caesalpinia bonducella* ethanolic extract corrosion inhibition estimation

#### 2.4.1 | Weight loss measurements

The difference in weights of the steel coupons before and after immersion in corrosion media expressed as weight-loss was utilized in determining the extent of corrosion inhibition – (Cao *et al.*, 2022; Ikeuba *et al.*, 2022; Loto *et al.*, 2021; Sehmi *et al.*, 2020; Wang *et al.*, 2020). Effects of parameters such as CBLE extract concentration (in gL<sup>-1</sup>) and solution temperature (in Kelvin) on corrosion inhibition were investigated to obtain information on the effectiveness of CBLE extract as a viable inhibitor of corrosion.

The effect of extract concentration was investigated by dipping pre-weighed steel coupon into each of five 250 mL beakers containing 100 mL of 1M H<sub>2</sub>SO<sub>4</sub> at 298K for 4 h in addition to 0 % (w/v), 0.2% (w/v), 0.4% (w/v), 0.6% (w/v) and 0.8% (w/v) CBLE extract. The effect of temperature was studied by immersing pre-weighed coupons in 100 mL corrosion media containing 0 % (w/v), 0.2% (w/v), 0.4% (w/v), 0.6% (w/v) and 0.8% (w/v) CBLE extract in 1M

H<sub>2</sub>SO<sub>4</sub> contained in 250 mL beakers in a thermostated water bath maintained at 303 – 343 K for 4 h. The corrosive test media with 0 % (w/v), and 0.2 – 0.8 % (w/v) CBLE extract is designated as the blank and inhibited solution respectively.

At the end of each experimental run, the steel coupons were retrieved from the acidic media and re-weighed after thorough washing with distilled water and acetone – (Umoren *et al.*, 2016). The coupons weight loss data were used to compute corrosion rate,  $C_R$  (mgcm<sup>-2</sup>.h<sup>-1</sup>), inhibition efficiency,  $\eta$  (%), and surface coverage,  $\theta$  using Eqs. 1-3 (Olasehinde *et al.*, 2022; Sehmi *et al.*, 2020; Verma *et al.*, 2016).

$$C_R = \frac{\Delta w}{At} \quad (1)$$

where  $\Delta w = w_0 - w_1$

$$\eta (\%) = \left(1 - \frac{C_{R(inh)}}{C_{R(blank)}}\right) \times 100 \quad (2)$$

$$\theta = \frac{\eta}{100} \quad (3)$$

Where  $A$  = surface area of the steel coupon (in cm<sup>2</sup>),  $t$  = time of steel coupon's immersion in the corrosive media (in sec.),  $\Delta w$  = difference in steel coupon's weight (in g),  $w_0$  = initial weight of the steel coupon and,  $w_1$  = weight of steel coupon after immersion in the corrosive media for the stipulated time.

#### 2.4.2 | Potentiodynamic Polarization (PPP) Curves measurement

Tafel or PPP curves were measured in the blank and solutions containing the extract and recorded at 298 K on a 3 electrodes AUTOLAB PGSTAT 204N system consisting of platinum foil, standard silver/silver chloride electrode and the steel

coupon (circular with surface area = 1 cm<sup>2</sup>) designated as the counter/auxiliary, reference and working electrodes respectively. The curves were recorded between -250 mV and +250 mV (vs, OCP) at a scan rate of 1.0 mV. s<sup>-1</sup> after the coupon's initial immersion in the acidic media for about 30 minutes. Linear segments of the anodic and cathodic Tafel curves were extrapolated from the corrosion potential ( $E_{\text{corr}}$ ) to obtain the current density ( $i_{\text{corr}}$ ) from which inhibition efficiency ( $\eta$  %) was calculated using Eq.4 (Olasehinde, Agbaffa, Adebayo, & Enis, 2022; Verma *et al.*, 2016)

$$\eta(\%) = \frac{(i_{\text{corr}(\text{blank})} - i_{\text{corr}(\text{inh})})}{i_{\text{corr}(\text{blank})}} \times 100 \% \quad (4)$$

Where ( $i_{\text{corr}(\text{blank})} - i_{\text{corr}(\text{inh})}$ ) is the corrosion current density (in  $\mu\text{Acm}^{-2}$ ) in the blank and inhibited solution respectively.

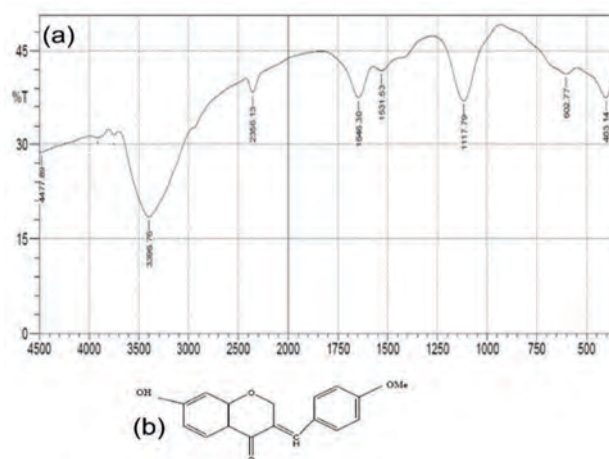
### 3.0 | Results and Discussion

#### 3.1 | Characterization

The FTIR spectrum of CBLE extract is presented in Figure 1a and showed a sharp peak at 3396 cm<sup>-1</sup> which could be due to O-H or N-H bond stretching vibration. The peaks at 1646 cm<sup>-1</sup>, 1531 cm<sup>-1</sup> and 2356 cm<sup>-1</sup> could be due to C=O, C=C, and C-H bonds stretching vibration in aromatic ring. Furthermore, the peaks at 1117 cm<sup>-1</sup> could be due to C-O bond stretching vibration of aromatic ether while =C-H and C-H bonds bending vibration could be responsible for peaks < 1000 cm<sup>-1</sup>. These results indicate that CBLE contains O and N atoms in functional groups (O-H, N-H, C=C, C=N, C=O, C-O) and aromatic ring. These peaks are consistent with those reported for bonducellin (Figure 1b), a major compound isolated from CBLE (Hijazi *et al.*, 2015).

#### 3.2 | Assessment of Weight Loss

Figures 2a-e show that corrosion rate ( $C_R$ ) and

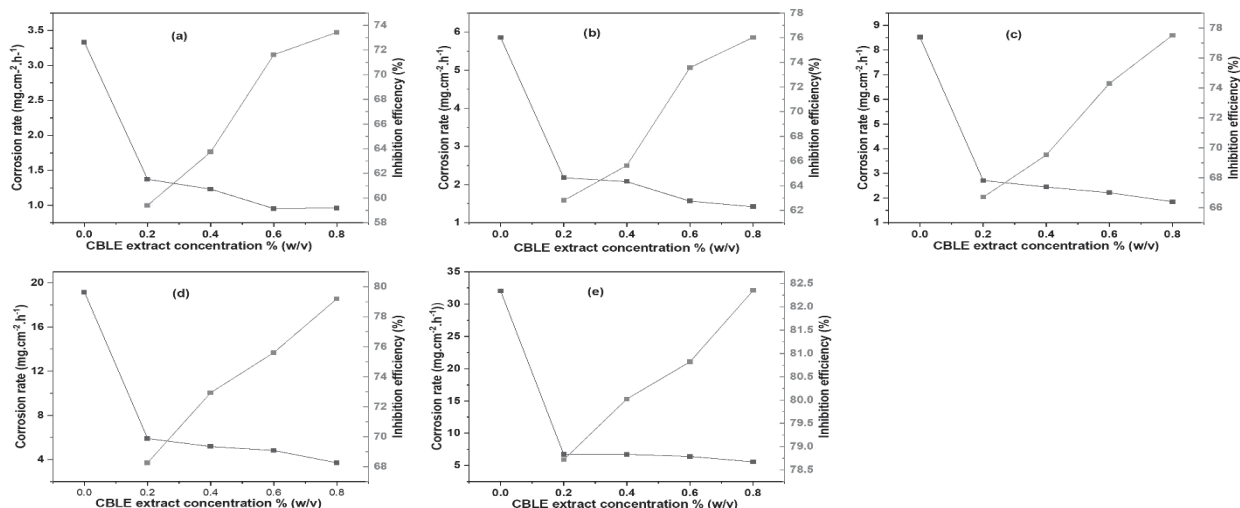


**Figure 1 | (a) FTIR spectrum of ethanolic extract of *Caesalpinia bonducella* leaf, and (b) structure of bonducellin, an important compound in CBLE extract**

corrosion inhibition (IE%) vary with CBLE extract concentration and temperature. A significant decrease and increase respectively in the rate of corrosion ( $C_R$ ) and inhibition efficiency (IE%) is seen with increasing concentrations of CBLE extract (Figures 2a-e). Similar trends have been reported by previous studies (Adebayo *et al.*, 2019a; Olasehinde *et al.*, 2015; Olasehinde *et al.*, 2022; Olasehinde *et al.*, 2022; Singh *et al.*, 2016; Verma *et al.*, 2018). These studies suggest that the observed variation in  $C_R$  and IE (%) with increasing concentration of the CBLE extract could be connected to the enhanced adsorption and coverage of the steel coupon's surface with adsorbed films of corrosion-inhibiting natural molecules found in the extract (Salleh *et al.*, 2021).

Though the corrosion rate increased with increasing solution temperature, the rate is nonetheless reduced by the extract (Figure 2). Furthermore, inhibition efficiency (%) increased with increasing solution temperature indicating the propensity of the CBLE extract to inhibit corrosion (Figure 2). Inhibition efficiency increased from 59.41 % at 303 K to 78.72% at 343 K in 0.2 % (w/v), from 63.74 % at 303 K to 80.02% at 343 K in 0.4 % (w/v), from 71.61 % at 303 K to 80.82 at 343

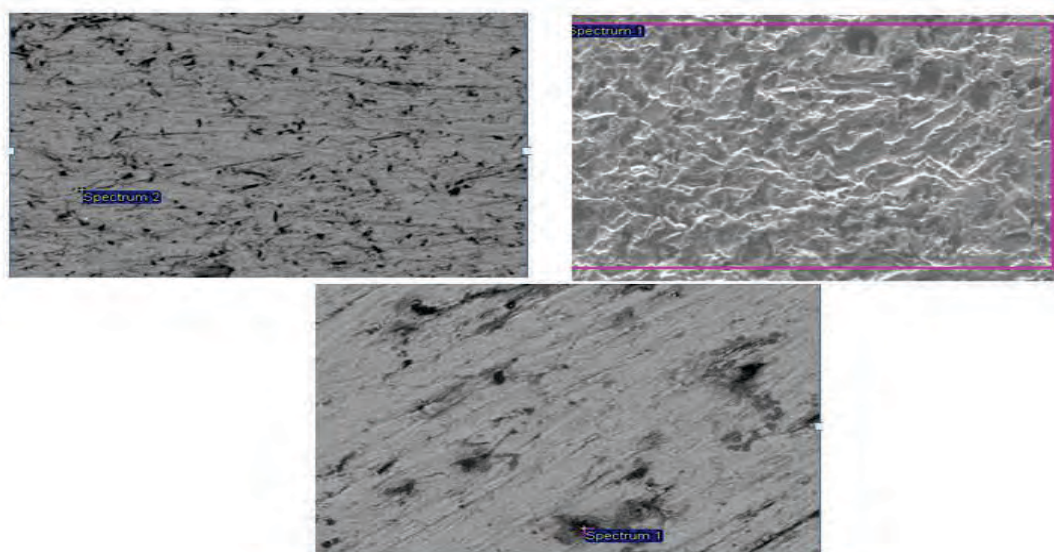




**Figure 2 | Variation in corrosion rate and inhibition efficiency with CBLE extract concentration in 1M H<sub>2</sub>SO<sub>4</sub> at (a) 303 K, (b) 313 K, (c) 323 K, (d) 333 K, and (e) 343 K**

K in 0.6 % (w/v), from 73.43 % at 303 K to 82.35 % at 343 K in 0.8 % (w/v) (Figure 2). This trend may be as a result of increased stability of the adsorbed thin film CBLE extract molecules on the metal surface or association between the metal surface and the adsorbed extract thin film with increasing solution temperature (Sehmi *et al.*, 2020); this trend has been ascribed to chemisorption (– Devi *et al.*, 2020; Sehmi *et al.*, 2020; Umoren *et al.*, 2018; and Verma *et al.*, (2016).

Figures 3 (a) – (c) shows the SEM images of the steel coupon surface before and after immersion in the corrosion media. The unevenness of the steel coupon surface morphology (Figure 3(b)) attests to the aggressive attack by the blank acidic solution. In contrast, the surface morphology of steel coupon immersed in the inhibited corrosion medium (Figure 3c) is noticeably preserved thus implying that CBLE extract significantly reduces



**Figure 3 | SEM Images of steel coupon (a) before immersion in blank and inhibited, (b) after immersion in blank, and (c) after immersion in inhibited solutions**

or inhibits corrosion.

### 3.3 | Adsorption isotherm and thermodynamic

#### 3.3.1 | Adsorption isotherms

Surface coverage data obtained from the weight-loss experiments were fitted to Freundlich, Langmuir, and Temkin isotherm models. According to Langmuir isotherm model, the adsorption of inhibitor molecules is by monolayer adsorption onto uniform sites of the steel coupons surface. The adsorbed inhibitor molecules do not interact with one another (Akinjokun *et al.*, 2023; Oladipo *et al.*, 2021). The linear version of the Langmuir isotherm equation is depicted in Eq.5 (Akinjokun *et al.*, 2023; Oladipo *et al.*, 2021):

$$\frac{C_{inh.}}{\theta} = \frac{1}{K_{ads}} + C_{inh.} \quad (5)$$

where  $C_{inh}$  is the concentration of CBLE extract;  $K_{ads}$  represents the equilibrium adsorption constant while  $\theta$  is the surface coverage of steel coupon with the CBLE extract (inhibitor). Estimation of  $K_{ads}$  at different inhibitor concentrations was determined from the intercepts  $\left(\frac{1}{K_{ads}}\right)$  of  $\frac{C_{inh.}}{\theta}$  versus  $C_{inh}$  (Figure 4a).

Freundlich isotherm model, an empirical model for systems with heterogenous surfaces presupposes that the inhibitor (CBLE extract) adsorbs to various sites with different affinities (Akinjokun *et al.*, 2023). The Freundlich isotherm linear expression is as shown in Eq. 6:

$$\log \theta = \log K_f + \frac{1}{n} \log C_{inh} \quad (6)$$

where  $\theta$  = surface coverage,  $C_{inh}$  = concentration of inhibitor,  $K_{ads}$  and  $n$  (dimensionless) are characteristic Freundlich's isotherm constants related to the intensity and capacity of adsorption. The values of  $n$  and  $K_f$  was calculated from the

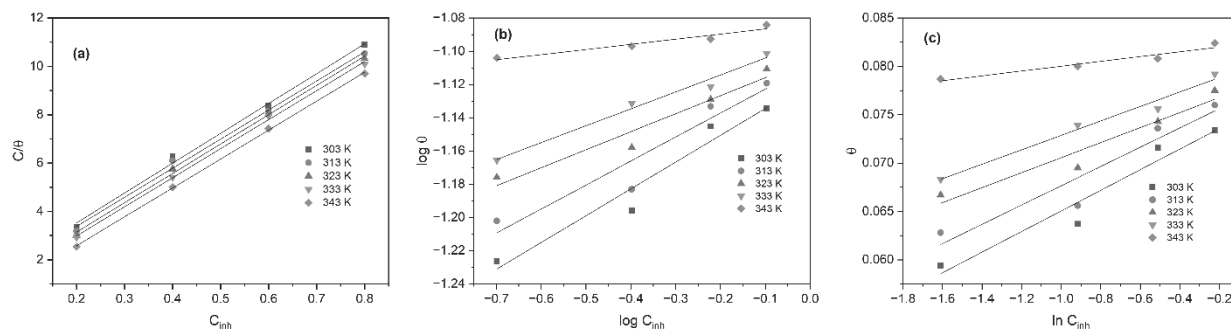
slope, and intercept of  $\log \theta$  versus  $\log C_{inh}$  plots (Figure 4b).

According to Temkin's isotherm, adsorbent and adsorbate interactions cause the heat of adsorption to drop linearly with adsorbent surface coverage (Musah *et al.*, 2022). The Temkin isotherm linearized equation is depicted by Eq. 7:

$$\theta = B \ln A_T + B \ln C_{inh} \quad (7)$$

where  $B = \frac{RT}{b_T}$ ;  $C_{inh}$  = concentration of the inhibitor (CBLE);  $\theta$  = surface coverage;  $b_T$  and  $A_T$  are respectively Temkin's heat constant of adsorption ( $\text{J.mol}^{-1}$ ) and isotherm ( $\text{L}^{-1} \cdot \text{g}$ ) while  $R$  and  $T$  = gas constant ( $8.314 \text{ J.mol}^{-1} \cdot \text{K}^{-1}$ ) and absolute temperature (in K) respectively. Temkin's constants,  $b_T$  and  $A_T$  were estimated from the slope and intercept of  $\theta$  versus  $\ln C_{inh}$  plots (Fig. 4c).

The goodness of fit of experimental data to the applied models was confirmed using the coefficients coefficient ( $R^2$ ) proximity to unity (Oladipo *et al.*, 2021). Examination of the estimated values of the coefficients coefficient ( $R^2$ ) obtained from Fig. 4 as shown in Table 1 revealed that Langmuir's isotherm with the highest  $R^2$  values ranging from 0.9951 to 0.9976 (Table 1) provides the best fit for the data. It could also be observed from the Table that the values of  $K_{ads}$  increase with increasing temperature which suggest a strong adsorption interaction between the extracts and the mild steel surface in 1M  $\text{H}_2\text{SO}_4$  solution. Further, an increase in  $k_f$  and  $b$  with increasing temperature suggest an endothermic adsorption process, where heat is absorbed during adsorption. (Salleh *et al.*, 2021; Verma *et al.*, 2016; Wang *et al.*, 2020; Sehmi *et al.*, 2020; Umoren *et al.*, 2018).



**Figure 4 | (a) Langmuir, (b) Freundlich and, (c) Temkin adsorption plots**

**Table 1 | Estimated values of coefficient coefficient ( $R^2$ ) and calculated parameters for Langmuir, Freundlich and Temkin adsorption plots**

Langmuir isotherm			Freundlich isotherm		Temkin isotherm		
Temp.(K)	K <sub>ads</sub>	$R^2$	b (kJ/mol)	$R^2$	k <sub>f</sub>	1/n	Intercept
303	9.46	0.9963	17.15	0.9495	0.083	0.161	0.9424
313	10.30	0.9951	19.62	0.9117	0.094	0.144	0.9048
323	14.08	0.9976	26.34	0.9432	0.105	0.108	0.9354
333	16.12	0.9988	28.35	0.9812	0.108	0.103	0.9791
343	54.73	0.9997	77.68	0.9366	0.118	0.030	0.9330

### 3.3.2 | Thermodynamic parameters

Furthermore, the thermodynamic parameter,  $\Delta G_{ads}^o$  for the adsorption of CBLE extract was determined at the studied temperatures from Eq.8 (Adebayo *et al.*, 2019b):

$$\Delta G_{ads}^o = -RT \ln(55.5 * K_{ads}) \quad (8)$$

The estimated values of  $\Delta G_{ads}^o$  at the studied temperatures are all negative and varied from -22.74 kJ.mol<sup>-1</sup> to -45.58 kJ.mol<sup>-1</sup> (Table 2) and

confirms that CBLE extract corrosion inhibition occur spontaneously (Olasehinde *et al.*, 2022; Kumar & Mohana, 2014). Adsorption processes are frequently classified as physisorption or chemisorption based on the values of  $\Delta G_{ads}^o$  process with  $\Delta G_{ads}^o$  values  $\leq 20$  kJ.mol<sup>-1</sup> and between -20 kJ.mol<sup>-1</sup> and -40 kJ.mol<sup>-1</sup> are classified respectively as physisorption and chemisorption – (Olasehinde *et al.*, 2022; Umoren *et al.*, 2018; Verma *et al.*, 2016). Therefore, the adsorption of CBLE extract to the metal surface (Table 2) can be said to occur through a chemisorption process which involves the formation of chemical bonds

**Table 2 | Calculated CBLE extract adsorption parameters**

Temperature (K)	$K_{ads}$ (mol. L <sup>-1</sup> )	$\Delta G_{ads}^{\circ}$ (kJ.mol <sup>-1</sup> )	$\Delta H_{ads}^{\circ}$ (kJ.mol <sup>-1</sup> )	$\Delta S_{ads}^{\circ}$ (J.mol <sup>-1</sup> . K <sup>-1</sup> )
303	9.46	-22.74		
313	10.30	-24.38	+33.76	-164.70
323	14.08	-28.45		
333	16.12	-31.58		
343	54.73	-45.58		

between the extract and the metal surface via charge transfer (Sehmi *et al.*, 2020; Verma *et al.*, 2018).

Adsorption enthalpy,  $\Delta H_{ads}^{\circ}$  was computed from Van't Hoff thermodynamic model (Eq. 9) (Umoren *et al.*, 2016):

$$\ln K_{ads} = \frac{-\Delta H_{ads}^{\circ}}{RT} + \text{Constant} \quad (9)$$

where  $K_{ads}$  = equilibrium adsorption constant (mol. L<sup>-1</sup>) and  $\Delta H_{ads}^{\circ}$  = enthalpy of adsorption (kJ.mol<sup>-1</sup>) under the specific conditions highlighted in this study.

An estimated  $\Delta H_{ads}^{\circ}$  value of +33.76 kJ.mol<sup>-1</sup> was obtained (Table 2) from the slope of  $\ln K_{ads}$  versus 1/T linear plot (Figure 3a) for CBLE extract adsorption unto the metal surface. According to the literature, processes with  $\Delta H_{ads}^{\circ}$  values > 0 are endothermic and attributable to chemisorption whereas processes with  $\Delta H_{ads}^{\circ}$  < 0 are exothermic and could occur either by physisorption, chemisorption, or a combination of the two processes (Jafari *et al.*, 2013). The endothermic nature of the adsorption of CBLE extract is

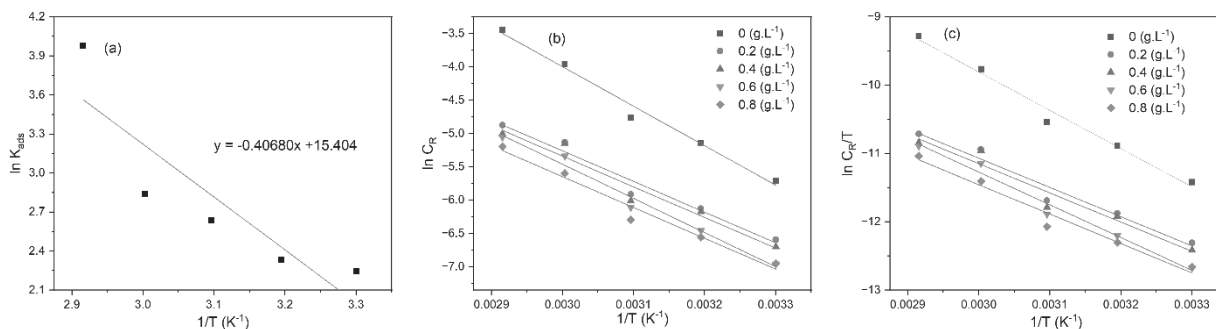
demonstrated by the positive values of positive  $\Delta H_{ads}^{\circ}$  (Table 2). To further understand the relationship between temperature and CBLE extract corrosion inhibition capacity, estimation of activation energy,  $E_a$  is necessary (Ansari & Quraishi, 2018).  $E_a$  for the adsorption of CBLE extract in corrosion inhibition was evaluated from Eq. 10 –'(Umoren *et al.*, 2016):

$$\ln C_R = \frac{-E_a}{RT} + \ln A \quad (10)$$

where A=Arrhenius pre-exponential constant. The linear relationship exhibited in  $\ln C_R$  versus 1/T plots confirms that a linear relationship exists between corrosion rate and temperature (Fig. 5b). In this study,  $E_a$  is lower in the inhibited (with CBLE extract) compared to the blank test media (Table 3).

According to Eddy *et al.* (2009), chemisorption and physisorption are typically credited with the inhibition process in which the activation energy values in inhibited solutions are respectively lower than, and higher than in the blank test media. Therefore, CBLE extract-mediated corrosion inhibition investigated in this study could be





**Figure 5 | Plot of (a)  $\ln K_{ads}$  versus  $\frac{1}{T}$ ; (b)  $\ln C_R$  versus  $\frac{1}{T}$ , and  $\ln\left(\frac{C_R}{T}\right)$  versus  $\frac{1}{T}$  for the corrosion inhibition CBLE extract in 1M  $H_2SO_4$  solution.**

**Table 3 | Thermodynamic CBLE extract adsorption activation parameters**

$C_{inh}(g.L^{-1})$	$E_a(kJ.mol^{-1}K^{-1})$	$\Delta H^*(kJ.mol^{-1})$	$\Delta S^*(J.mol^{-1}K^{-1})$	$E_a - \Delta H(kJ.mol^{-1})$	$Q_{ads}(kJ.mol^{-1})$
Blank	49.40	46.74	-81.37	2.66	-
0.2	36.13	33.44	-132.22	2.68	+17.93
0.4	37.16	34.48	-129.65	2.68	+17.49
0.6	42.39	39.72	-114.47	2.68	+9.64
0.8	38.62	35.95	-127.52	2.68	+10.68

attributed to chemisorption as indicated by CBLE concentration-dependent reduction of the estimated  $E_a$  values in the inhibited test media (Table 3).

The CBLE extract-mediated corrosion inhibition activation enthalpy and entropy in 1M  $H_2SO_4$  by was also estimated from Eq. 11:

$$\ln\left(\frac{C_R}{T}\right) = \left[\ln\left(\frac{R}{hN_A}\right) + \frac{\Delta S^*}{R}\right] - \frac{\Delta H^*}{RT} \quad (11)$$

where  $h$  = Planck's constant,  $N_A$  = Avogadro's number while  $\Delta H^*$  and  $\Delta S^*$  is the change in activation enthalpy and entropy. The calculated values of  $\Delta H^*$  and  $\Delta S^*$  at different CBLE extract concentrations are enumerated in Table 3. Estimated enthalpy of activation values of +33.44, +34.48, +39.72 and +35.94  $kJ.mol^{-1}$  respectively in the acid test media containing 0.2, 0.4, 0.6 and 0.8

% (w/v) are not significantly different from the standard enthalpy of adsorption ( $\Delta H_{ads}^o = 33.76$   $kJ.mol^{-1}$ ) estimated from Van't Hoff model (Table 3). In addition to this, the positive values of  $\Delta H^*$  again affirm the earlier claims of the endothermic nature of CBLE extract adsorption unto the metal surface via chemical interactions (Goulart *et al.*, 2013). A closer look at the estimated thermodynamic parameters,  $E_a$  and  $\Delta H^*$  shows that  $E_a$  values are generally greater than  $\Delta H^*$ ; this trend is synonymous with corrosion processes accompanied by the release of hydrogen gas – ' (Umoren *et al.*, 2016) associated with a decrease in the solution volume. This also agrees with the thermodynamic relationship described by Eq. 12 (ref.) that there is a difference between the estimated values of  $E_a$  and  $\Delta H^*$  (Table 3):

$$E_a - \Delta H^* = R * T \quad (12)$$

The mean of the difference ( $2.67 \text{ kJ.mol}^{-1}$ ) is similar to the product of the universal gas constant,  $R$  ( $8.314 \text{ J.mol}^{-1}\text{K}^{-1}$ ) and  $T$  ( $298\text{K}$ ) ( $2.48 \text{ kJ.mol}^{-1}$ ) (Table 4). Furthermore,  $\Delta S^*$  decreased with increasing concentration of CBLE extract (Table 4). This is indicative of a decrease in disorderliness on metal surfaces in the inhibited solutions (Essien *et al.*, 2018; Thommes *et al.*, 2015).

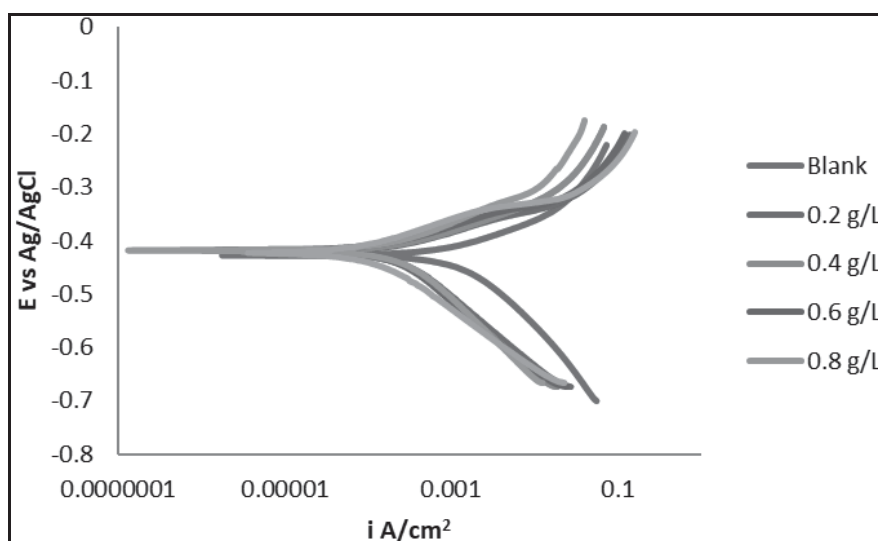
### 3.3 | Potentiodynamic Polarization Measurements

Values of characteristic parameters such as  $i_{\text{corr}}$ ,  $E_{\text{corr}}$ ,  $\beta_c$  and  $\beta_a$  were obtained by extrapolating the linear portions of the polarization curves (Verma *et al.*, 2016) for the CBLE extract-mediated corrosion inhibition in  $1\text{M H}_2\text{SO}_4$  at  $298 \text{ K}$  (Figure 6) and are presented in Table 6. The corrosion inhibition efficiency of CBLE extract was estimated using Eq. 13:

$$\eta(\%) = \frac{i_{\text{corr(Blank)}} - i_{\text{corr(inh)}}}{i_{\text{corr(Blank)}}} \times 100 \quad (13)$$

where  $i_{\text{corr(Blank)}}$  and  $i_{\text{corr(inh)}}$  is the current density in the blank and inhibited solution with  $0.8 \text{ g.L}^{-1}$  CBLE extract.

From the results,  $E_{\text{corr}}$ ,  $i_{\text{corr}}$ , and  $\beta_a$  decreased in value with increasing CBLE extract concentration (Table 4). Corrosion current density ( $i_{\text{corr}}$ ) decreased from  $1038 \mu\text{A.cm}^{-2}$  in the blank test media to  $168.2 \mu\text{A.cm}^{-2}$  in the inhibited test media (Table 4) due to an appreciable suppression of (i) corrosion arising from the dissolution of the metal surface and (ii) the evolution of hydrogen gas on the anodic and cathodic reactions (Helen *et al.*, 2014). The decrease in  $i_{\text{corr}}$  could also be due to the increase in the adsorption of inhibitor molecules on the surface of the MS thereby inhibiting the transfer of charge from the anodic and cathodic reaction (Olivares *et al.*, 2006). Inhibition efficiency increased from 73% to 83.30% with increasing CBLE extract concentration and decreasing current density (Table 4). Although the corrosion potential  $E_{\text{corr}}$  decreased with CBLE extract concentration, the decrease observed in  $E_{\text{corr}}$  values in the inhibited and blank solution decides the mode of inhibition. When the magnitude of shift is greater than  $85 \text{ mV}$ , it is then inhibition mode is either anodic or cathodic. However, when the shift  $< 85 \text{ mV}$ , inhibition mode is mixed-type. In this study,  $E_{\text{corr}}$  shift was  $< 85 \text{ mV}$  (Table 4) thus implying that CBLE extract inhibits



**Figure 6 | Potentiodynamic polarization curves for CBLE extract-mediated corrosion inhibition**

Table 4 Potentiodynamic polarization parameters for CBLE extract mediated corrosion inhibition in 1M H<sub>2</sub>SO<sub>4</sub> solution

$C_{inh}$ (g.L <sup>-1</sup> )	$E_{corr}$	$i_{corr}$	$\beta_a$	$\beta_c$	$C_R$	IE
	(mV)	( $\mu$ A.cm <sup>-2</sup> )	(mV.dec <sup>-1</sup> )	(mV.dec <sup>-1</sup> )	(mm.y <sup>-1</sup> )	(%)
Blank	-428.7	1038	66.68	120.24	12.06	
0.2	-422.1	273.3	62.43	151.68	3.17	73.00
0.4	-420.5	231.6	55.82	141.18	2.50	77.7
0.6	-471.3	177.5	55.41	123.24	1.91	82.9
0.8	-419.2	168.2	58.28	126.24	2.90	83.8

steel coupon corrosion through deceleration of both cathodic and anodic reactions. However, the higher values of  $\beta_c$  relative to  $\beta_a$  for all extract concentrations (Figure 6) indicates that corrosion inhibition by the extract is predominantly via reduction of cathodic reactions. Thus, CBLE extract can be classified as a dual mode inhibition with mainly cathodic effectiveness (Helen *et al.*, 2014).

4 | Conclusion

This study investigated corrosion inhibition of *Caesalpinia bonducella* leaf ethanolic (CBLE) extract on mild steel coupons in 1M H<sub>2</sub>SO<sub>4</sub> using weight loss and potentiodynamic polarization measurements. Corrosion rate decreased with CBLE extract concentration and increased with temperature. The positive values of transition state

enthalpy indicate that the corrosion process is endothermic while the negative values of standard entropy are indicative of a decrease in disorderliness at the metal/solution interface. The values of the standard Gibbs free energy, ( $\Delta G^\circ$ ) ranged from -22.74 kJ.mol<sup>-1</sup> to -45.58 kJ.mol<sup>-1</sup>. The mechanism of sorption of CBLE extract to the steel coupon surface is chemisorption. The adsorption of the extract can be described by Langmuir's isotherm while electrochemical measurements showed that CBLE extract has a high cathodic effectiveness.

Acknowledgments

The authors acknowledge the technical assistance provided by the Corrosion Laboratory of the Federal University of Technology, Akure.

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