



Theobroma Cocoa Dry Bean Extract as a Potential Green Inhibitor for Mild Steel in Acidic Medium

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ABSTRACT

Theobroma cocoa dry bean extract (CDBE) was prepared by Soxhlet extraction method and was characterized for its chemical constituents using Fourier Transform-Infrared Spectroscopy (FT-IR), Gas chromatography-Mass spectroscopy (GC-MS) and also by Thermogravimetric Analysis-Differential Scanning Calorimetry (TGA-DSC) techniques. FT-IR analysis gave information about the mostly like to be present functional groups in the extract. GC-MS analysis of the extract revealed the presence of important 07 chemical constituents with cis-13-octadecanoic acid as the major component. TGA-DSC study gave the idea about different stages of thermal decomposition of the chemical constituents present in the extract. CDBE was then tested for its ability to inhibit the corrosion rate of mild steel in 1.0M HCl solution medium by means of weight loss, Potentiodynamic polarization, and Electrochemical impedance spectroscopy (EIS) techniques. The weight loss experiments revealed the anticorrosive property of it on mild steel, which was found to increase with increase in the concentration of the inhibitor CDBE and decrease with an increase in temperature of corrosive medium. EIS results showed the adsorption of organic constituents present in the extract at the metal-solution interface. Potentiodynamic polarization studies revealed that CDBE functioned as a mixed type inhibitor. The surface morphological studies of mild steel surface were carried out by Scanning electron microscopy (SEM). The inhibition efficiency values obtained by electrochemical measurements were consistent with those from weight loss measurements and hence it can be proposed that CDBE as a potent inhibitor towards corrosion of mild steel under acidic conditions.

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INTRODUCTION

Phytochemistry is the science that deals with extraction, identification, separation and purification of the many different chemical constituents present in a plant. Plants are rich source of chemicals like alkaloids, glycosides, polyphenols, terpenes and volatile oils. Many of these are found to be bioactive and are expected to possess anti-oxidant, anti-bacterial, anti-microbial, anti-inflammatory and anti-arthritis properties [1].

Spectroscopy is a tool to provide a way for the development of new synthetic routes to identify compounds from its starting material in terms of quality and quantity. From the literature survey, it is evident that Mass spectroscopy, Nuclear Magnetic Resonance spectroscopy, Infrared spectroscopy, and Ultraviolet-Visible spectroscopy etc., play major role in giving an idea of the structure of a compound or identification of its chemical constituents [2-6].

Literature shows the study of chemical sample by *Thermogravimetric analysis* (TGA), *Differential*

Thermal Analysis (DTA) and *Differential Scanning Calorimetry* (DSC) analysis give information about thermal characteristics like melting temperature, heat of fusion, latent heat of melting, reaction energy and temperature also giving data about endothermic and exothermic processes [5, 6].

Corrosion is a phenomenon of deterioration of material surface due to physiochemical interaction between any exposed parts of the material with the surrounding oxygen. Corrosion is so posing a big challenge for the chemists and material scientists who are working to overcome the destruction of materials [7].

Mild steel is one of the widely used metals in industries related to the production of food, chemicals and nuclear power generation. The major problem with the mild steel is its dissolution in acid medium. In industry mild steel frequently come in contact with the acid solution during the acid pickling, acid descaling and acid cleaning processes. So controlling the dissolution of mild steel in aggressive medium is of great importance to protect the articles. Among the several methods

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employed to control the corrosion of mild steel, it has been found that use of corrosion inhibitors is one of the most promising method [8, 9].

Literature survey reveals that, use of organic inhibitors for the control of corrosion rate. The inhibition process is due to the presence of hetero atoms such as O, N, S and P in the organic inhibitor which allows the adsorption of the same on a metal surface [7-9]. However, most of the synthetic inhibitors used are found expensive, toxic to living kind and raise environmental issues. Due to this reason, investigation of less hazardous, more eco-friendly green inhibitors obtained from plants and natural products are used as corrosion inhibitors [10-17].

Theobroma Cacao L. commonly known as Cocoa is native of Amazon region of South America. *Cocoa* is mainly used in confectionery industries to produce chocolates and beverages. Being a tropical crop, India offers considerable scope for the growth of *cocoa* plant. Cocoa bean can be processed to get cocoa solids and cocoa butter. In India Cocoa is mainly grown in Southern India [18, 19].

Yuli et al. [20] have studied the corrosion inhibition efficiency of the cocoa extract on mild steel in hydrochloric acid. Othman et al. [18] have studied the antioxidant capacity and phenolic content of cocoa beans. These study showed that the *Cocoa* as a rich source of phenolic compounds, such as, flavanols, procyanidins and other flavanoids. Some of these chemical constituent possess O and N atoms in it which fulfil the requirements of a good inhibitor [18]. The pictures of *Cocoa* and dried *Cocoa* beans is shown in Figures 1 and 2.

In the present work, the dry *cocoa* bean's methanolic extracts was prepared using Soxhlet extract apparatus. It was then characterized using FT-IR [21], GC-MS [22] and thermal techniques [23] to get an idea about the presence of various anti-oxidative chemical constituents in them. Further its anticorrosive efficiency was checked using Weight loss, *Electrochemical Impedance Spectroscopy* (EIS) and *Potentiodynamic Polarization methods*. Surface morphological changes are analyzed using *Scanning Electron Microscopy* [24].

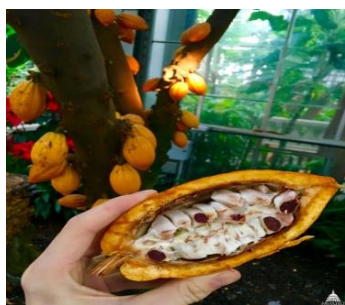


Figure 1. *Theobroma Cacao*



Figure 2. Dry Cocoa Bean

MATERIALS AND METHODS

Preparation of *Theobroma Cacao* dry bean extracts (CDBE)

Locally grown *Theobroma cocoa* bean sample was collected from agriculture fields. It was cleaned for dirt and dried under sunlight for 20 days and then powdered using a crusher. About 50g of the powder was then extracted with 500mL of solvent methanol as a solvent using Soxhlet extraction apparatus for about 8 hours. The extract was then filtered through Whatman no 1 filter paper and brown coloured liquid *Cocoa Dry bean Extract* (CDBE) was obtained. The extract was stored in amber coloured bottle.

Fourier Transform - Infrared (FT-IR) Spectroscopic characterization

Perkin Elmer - Spectrum RX-IFTIR was used to detect the presence of different functional groups in the extract sample CDBE. The spectrum was recorded using 10 mg of liquid sample with a resolution of 1 cm^{-1} and scan range of 4000 cm^{-1} to 250 cm^{-1} .

Gas chromatography-Mass Spectroscopic (GC-MS) characterization

The chemical constituents present in the CDBE sample were determined using GC-MS technique. The spectrum for CDBE was recorded using Thermo Scientific TSQ 8000 Gas Chromatograph - Mass Spectrometer. 10 mg of sample in liquid form was subjected to GC-MS with run time 22.79 min and injection volume $10.00\mu\text{l}$ with 6701 scans from Low Mass (m/z) 50 to High Mass (m/z):700. Obtained data were compared with m/z values available in National Institute of Standards and Technology (NIST) and the most likely to be present constituents are listed.

Thermo-Gravimetric Analysis

Thermal stability of the CDBE sample was examined using TGA- DSC technique. The spectrum was recorded using instrument SDT Q600 V20.9 Build 20. The extract was evaporated in the presence of methanol and the residue obtained was in gel form. About 6-10mg of

residue sample was subjected to thermal decomposition in Alumina pan using Nitrogen gas.

Preparation of metal samples for gravimetric studies

Mild steel IS-2062 with composition (in wt %) 0.18% C, 0.6% Mn, 0.05% S, 0.04% P, 0.1% Si and the remainder 99.03 % Fe [24] was selected for the corrosion study. The metal sample was cut into apparent size with dimensions 1X 0.5 X 0.07 inch was used for weight loss measurement. Before the use, the test material was well cleaned and polished with different emery papers ranging from 80 to 2000 grade, cleaned with acetone, washed with double distilled water and dried well.

Preparation of corrosion medium

Corrosive medium of 1 M HCl was prepared by diluting analytical grade HCl using double distilled water.

Weight loss measurements

Mild steel specimen was weighed accurately and was suspended in 50mL of corrosion medium without and with different volumes (Viz., 5, 10, 20, 30 and 35 mL) of CDBE at 303K. The studies were also carried out at different temperatures i.e., 308, 313, 318 and 323K. After specified time, viz., 5 hours for HCl, the mild steel sample was taken out from the solution, washed with double distilled water, wiped with clean tissue paper, dried and weighed accurately. The weight loss was evaluated (W). The rate of corrosion (CR) of mild steel was determined using Equation (1) [25].

$$CR = \frac{534W}{ATD} \quad (1)$$

where CR is the corrosion rate of mild steel in mils penetration/year (mpy), W is the weight loss of mild steel in mg, A is the area of mild steel sample in square inches (1*0.5), T is the time of exposure in 5 hours and D is the density of mild steel in grams/cubic centimeter (7.75). The inhibition efficiency was calculated using Equation (2) [25].

$$Inhibition\ efficiency = \frac{W_2 - W_1}{W_2} * 100 \quad (2)$$

where W_1 and W_2 are weight loss of mild steel samples in the presence and absence of the inhibitor, respectively.

Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization method

EIS study was carried out using mild steel rods with approximately 1cm² circular area exposed to corrosive environment. Rest of the sample area was covered with acrylic repair material. Before the use, the test materials were well cleaned and polished with different emery papers ranging from 80 to 2000 grade. They were applied with machine polish using alumina water and then washed thoroughly with water, cleaned with acetone,

washed with double distilled water, and dried well for further study.

Electrochemical measurements were recorded using a GillAc Potentiostat CH 1480 analyser at 303 K by taking mild steel as working electrode. Saturated calomel was connected as reference electrode, and platinum electrode as auxiliary electrode. All AC impedance measurements were taken using an AC signal with amplitude of 10mV at OCP in the frequency range from 0.01 Hz to 1,00,000Hz to get Nyquist plots. The *potentiodynamic polarization* studies were carried out and potential-current curves (Tafel plots) were recorded by polarizing the specimen to -250 mV to +250 mV against OCP at scan rate of 1mV/s.

Scanning Electron Microscopy (SEM)

Surface morphology of the samples was examined by Scanning Electron Microscopy. The mild steel samples were polished, well washed with acetone and distilled water. The samples were then exposed for corrosive environment for a time period of 5 hours in the absence and presence of optimum concentration of the CDBE inhibitor in 1M HCl at 30⁰C and the surface images were recorded immediately after the corrosion tests.

RESULTS AND DISCUSSIONS

Identification of functional groups in CDBE by FT-IR

FTIR spectrometer collects high spectral resolution data over a wide spectral range. FT-IR analysis gave information about the presence of different functional groups in the extract prepared. A broad peak at 3334cm⁻¹ shows the presence of O-H group. Also a sharp peak shown at 1649cm⁻¹ corresponds to the presence of C=C stretch for cis alkenes, peaks at 1282 cm⁻¹ for the presence of C-O stretch from carboxylic acid. C-O stretch from esters is also found at the range from 1300-1000cm⁻¹. The FT-IR spectrum of CDBE is shown in Figure 3. Details about the probable functional groups that may exist in CDBE with the corresponding wave numbers are listed in Table 1.

Identification of chemical constituents in CDBE by GC-MS

The GC-MS spectrum of CDBE is shown in Figure 4. The extract showed the presence of a sharp peak at 15.32min with 71.90% peak area. The graph of CDBE obtained for retention time 15.32 minute and the GC-MS graph for cis-13-octadecanoic acid from the PubChem library (NIST Number 333585) are shown in Figures 5(a) and 5(b), respectively. The comparison confirms the presence of cis-13-octadecanoic acid as major compound and the structure of the compound is shown in Figure 6. The 7 constituents identified in CDBE are listed in Table 2.

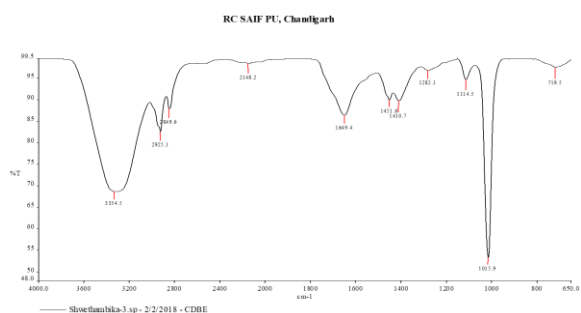


Figure 3. FT-IR Spectrum of dry *Theobroma cocoa* bean extract

TABLE 1. The list of functional groups and their stretching frequencies on FT-IR analysis for CDBE

Wave Numbers (cm ⁻¹)	Corresponding identified functional group in CDBE
3334	Stretching vibration of -OH groups [3400-3200]
2929,2849	C-H stretch for sp ³ hybridized carbon [3000-2840]
2148	C-H in plane bending of olefins[2200-2040]
1649	C=C stretch for cis alkenes [1650]
1451	C=C stretch, aromatic HC chromophore [1500-1450]
1410	=C-H bending for substituted alkenes [1420-1410]
1282	C-O stretch from carboxylic acid [1320-1210]
1114	C-H in and out of plane deformations
1015	C-O stretch from esters [1300-1000]
719.5	C-H out of plane bending [685-715]

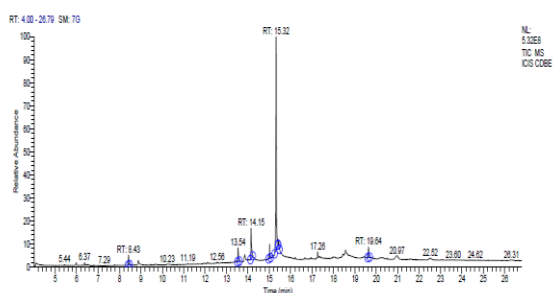


Figure 4. The GC-MS spectrum of CDBE

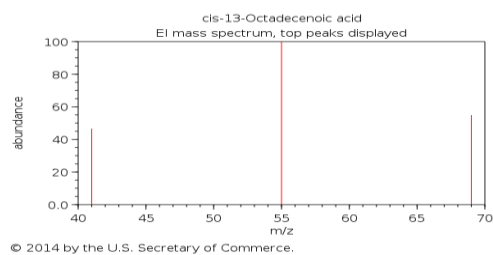
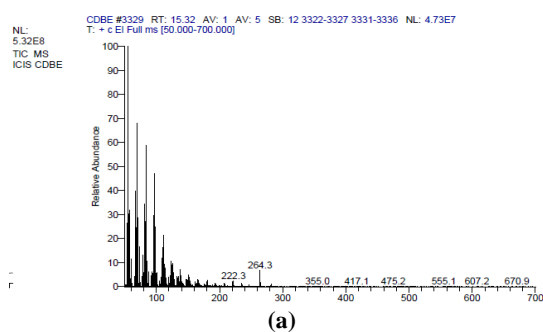


Figure 5. (a) GC-MS graph for CDBE at Rt=15.32 min, (b) GC-MS spectrum of cis-13 -octadecanoic acid.



Figure 6. Cis-13-octadecanoic acid

TABLE 2. The following compounds were identified with their molecular formula and molecular mass recorded in CDBE

Sl. No	Chemical constituents identified using m/z values of GC-MS	Retention Time (Rt)	Molecular Formula from literature	Molecular Mass
1	Ethanone, 1-(3,4-dimethylphenyl)-	8.43	C ₁₀ H ₁₂ O	148
2	1 H-purine-2,6-dione,3,7, dihydro-1,3,7-timethyl (caffeine)	13.54	C ₈ H ₁₀ N ₄ O ₂	194
3	Hexadecanoic acid (Palmitic acid)	14.15	C ₁₆ H ₃₂ O ₂	256
4	Methyl (Z)-octadec-9-enoate (Methyl oleate)	15.02	C ₁₉ H ₃₆ O ₂	296
5	Cis-13-octadecanoic acid	15.32	C ₁₈ H ₃₄ O ₂	282
6	Cis-9-Octadecenoic acid (Oleic acid)	15.43	C ₁₈ H ₃₄ O ₂	282
7	13-Docosamide	19.64	C ₂₂ H ₄₃ NO	337

Thermo gravimetric Analysis of CDBE

From the analysis of CDBE using TGA-DSC technique, the obtained graph gave information about the thermal decomposition of chemical constituents that may be present by showing the different peaks corresponding for their melting point. This gave a proof for the chemicals present in the CDBE which were identified through GC-MS. The graph obtained is shown in Figure 7. The study of the graph showed mainly the presence of 4 peaks region at different temperatures namely Region 1: 25-

100°C, Region 2: 150-375°C, Region 3: 450-650°C and Region 4: 650-700°C. The Region 1: 25-100°C accounts to the loss of moisture and volatile contents of CDBE. Also comparing the TGA data with GCMS data, the most likely to be present compounds, which have undergone thermal decomposition in those peaks region, present in the extract were identified and are listed in Table 3. The last stable state in the graph (horizontal region) i.e., Region 4: 650-700°C represents the presence of metals present in the extract [26].

Correlation of the spectral data from FT-IR and GC-MS with TGA-DTA studies

When the CDBE sample was subjected to GC-MS, different compounds have been eluted with different retention time and molecular formula. As literature study propose some structure for the chemical constituents identified with a given molecular weight and molecular

formula, functional groups present in the compound was identified. The FT-IR study results confirmed the presence of those functional groups. This made us to get a clear idea about the compounds present in the extract even though there are several compounds for a given Retention time. TGA- DTA analysis supported the presence of those chemicals showing thermal decomposition at various temperatures, corresponding to their melting and boiling points. All these helped us in proposing structure of most likely compound present in the extract.

Weight loss studies

To examine the inhibition efficiency of CDBE on mild steel surface in 1M HCl, weight loss measurements were carried out at 303K. The data obtained are summarized in Table 4. It can be seen from the data that inhibition efficiency of CDBE increases with the increase in % volume.

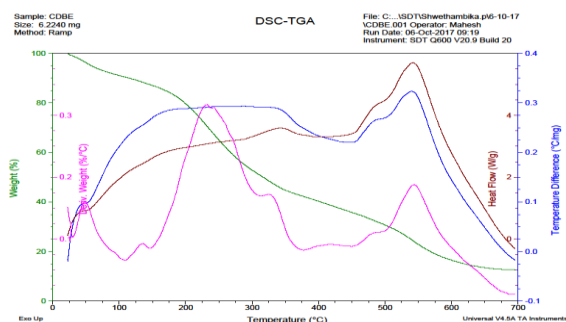


Figure 7. TGA-DSC graph of CDBE

TABLE 3. The following compounds were listed as per the thermal decomposition response of CDBE

Sl. No	Decomposition Regions	Chemical constituents identified	Melting Point (°C)	Boiling Point (°C)
1	25-100°C	Palmitic acid	61.8	-
		13-Docosenamide	75-80	-
		Cis-13-octadecanoic acid	26.5-27	-
2	150-375°C	Methyl oleate	-	218.5
		Caffeine	238	-
		Ethahanone, 1-(3,4-dimethylphenyl)-	-	243
		Oliec acid	-	286
		Palmitic acid	-	351.5
3	450-650°C	1 H-purine-2,6-dione,3,7, dihydro-1,3,7-timethyl (caffeine)	-	416±37
		13-Docosenamide	-	474±14

Effect of temperature

To study the effect of temperature on inhibitor efficiency, weight loss measurements were carried out at different temperatures viz., 308, 313, 318 and 323K. The various data obtained during the weight loss are tabulated in Table 4. The variation of corrosion rate with % volume at different temperatures is shown in Figure 8. Figure 9 shows the variation of inhibition efficiency with % volume at different temperatures. From the Figure 10 it is clear that, with the increase in temperature of reaction medium, the corrosion rate of the mild steel shows a considerable increase indicating there is decrease of inhibition efficiency of CDBE. This might have been caused due to desorption of some adsorbed molecules of CDBE from the surface of the mild steel. This causes the metal to expose greater surface area of to acid environment leading to more rate of corrosion [28-30]. It can be seen from the Figure 9 that with increase in concentration of inhibitor there is increase in the inhibition efficiency value up to 60% volume of CDBE and there afterwards it remained almost constant.

The apparent activation energy of metal corrosion in acid media can be calculated from the Arrhenius equation shown as Equation (3) [25].

$$\ln(\text{Corrosion rate}) = \ln A - \frac{Ea^0}{RT} \quad (3)$$

where Ea^0 is the apparent activation energy for the corrosion of mild steel, R is the universal gas constant, A is Arrhenius pre exponential factor and T is the absolute temperature. The plot of $\ln(\text{Corrosion Rate})$ vs. $1000/T$ is shown in Figure 10 and the values of Ea^0 obtained from the slope of the plot. The obtained values are tabulated in Table 5. It is observed that, Ea^0 values for the mild steel in HCl medium is 36.76kJmol^{-1} and that with the optimum volume of CDBE is 94.70kJmol^{-1} showing the decrease in corrosion rate.

TABLE 4. Variation of Corrosion rate of mild steel in 1M HCl and inhibition efficiency of CDBE with temperature range 303K-323K

Temperature	% Volume of CDBE	Weight loss (g)	Corrosion Rate (mpy)	Inhibition Efficiency (%)
303K	0	0.0208	565.97	
	10	0.0090	246.42	56.45
	20	0.0050	136.05	75.96
	40	0.0035	95.24	83.17
	60	0.0024	65.30	88.46
	70	0.0024	65.30	88.46
308K	0	0.0310	848.92	
	10	0.0145	397.07	53.22
	20	0.0095	260.15	69.35
	40	0.0079	216.33	74.51
	60	0.0046	125.96	85.16
	70	0.0047	128.70	84.83
313K	0	0.0373	1021.44	
	10	0.0205	561.38	49.28
	20	0.0161	440.89	56.74
	40	0.0135	369.69	63.81
	60	0.0090	246.46	75.77
	70	0.0090	246.46	75.77
318K	0	0.0461	1248.00	
	10	0.0254	691.13	44.90
	20	0.0234	656.66	49.24
	40	0.0215	584.10	53.36
	60	0.0165	448.96	64.20
	70	0.0166	454.58	63.99
323K	0	0.0535	1465.07	
	10	0.0345	944.76	35.51
	20	0.0324	887.26	39.43
	40	0.0297	813.32	44.48
	60	0.0245	670.92	54.20
	70	0.0245	670.92	54.20

Also with the increase in % volume of CDBE, the E_a^0 values show an increase, which can be due to the adsorption of the inhibitor on the mild steel surface thus forming a barrier at metal-solution interface which limits the contact of metal with corrosive medium [28]. Ekanem et al. [28] explained that the increase in activation energy can be due to an appreciable decrease in the adsorption of the inhibitor on the mild steel surface with increase in temperature, exposing greater area of metal to the acid

environment and so causing a corresponding increase in corrosion rate.

An alternative form of Arrhenius equation is the transition state equation as Equation (4) [29]:

$$Corrosion\ rate\ (CR) = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a^0}{R}\right) \exp\left(-\frac{\Delta H_a^0}{RT}\right) \quad (4)$$

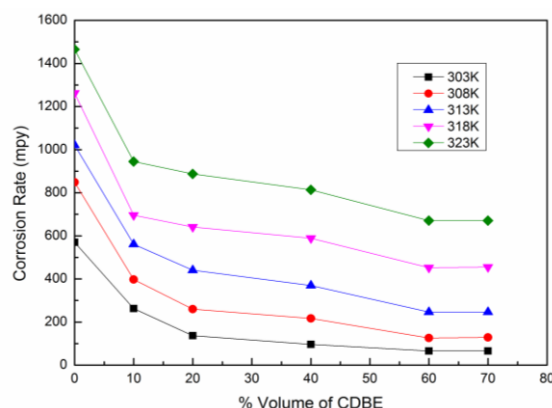


Figure 8. Variation of Corrosion rate of mild steel in 1M HCl with temperature

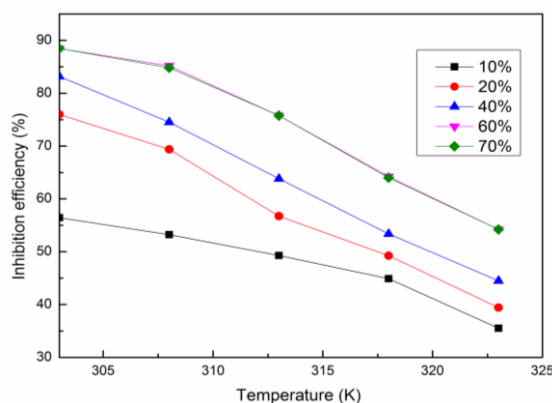


Figure 9. Variation of inhibition efficiency of CDBE for corrosion of mild steel in 1M HCl with temperature

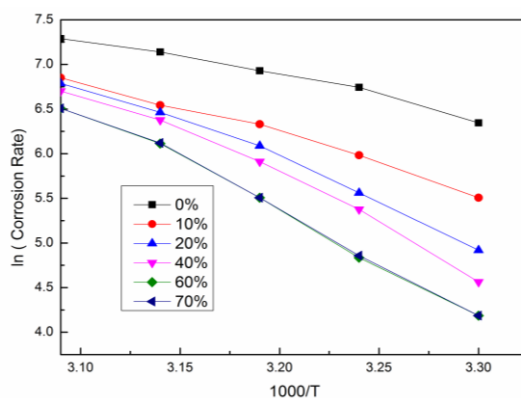


Figure 10. Variation of ln(Corrosion rate) with 1000/T

where, h is the Plank's constant, N is the Avogadro's number, ΔS_a° is the entropy of activation, and ΔH_a° is the enthalpy of activation. A plot of $\ln(CR/T)$ vs. $1/T$ gave a straight line as shown in Figure 11 with a slope of $(-\Delta H_a^\circ/R)$ and an intercept of $[\ln(R/Nh) + (\Delta S_a^\circ/R)]$, from which the values of ΔH_a° and ΔS_a° were calculated and listed in Table 5. The values of ΔH_a° obtained are positive both in the presence and absence of the inhibitor shows that, the metal dissolution process is endothermic type for the corrosion of mild steel in HCl medium. It is also shown that with the increase in the % volume of the CDBE inhibitor there is increase in ΔS_a° values. This increase in entropy from uninhibited corrosion medium to inhibited corrosion medium suggesting that there is an increase in the randomness occurred while moving from reactants state to the activated complex state [28, 29].

Electrochemical Impedance Spectroscopic measurements (EIS)

The data obtained from EIS can be plotted as impedance spectra which are also known as Nyquist plots. This plot contain depressed semicircle with centre under real axis. The Nyquist plots of mild steel in 1M HCl containing

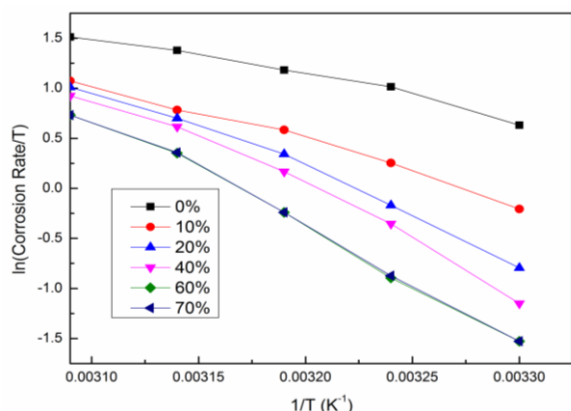


Figure 11. Variation of $\ln(\text{Corrosion rate}/T)$ with $1/T$

TABLE 5. Values of activation parameters for mild steel in 1M HCl in the absence and presence of different concentrations of the CDBE inhibitor

% Volume of CDBE	Energy of activation E_a (kJmol ⁻¹)	Arrhenius Factor (A*10 ⁹)	Enthalpy ΔH_a° (kJmol ⁻¹)	Entropy ΔS_a° (Jmol ⁻¹ /K)
0	36.76	1.32	34.21	-78.82
10	52.12	2.51*10 ²	49.57	-35.25
20	74.41	9.91*10 ⁵	71.87	33.67
40	84.72	4.43*10 ⁷	82.23	65.18
60	94.70	1.42*10 ⁹	92.21	94.11
70	94.53	1.33*10 ⁹	91.97	93.45

various % volumes of the CDBE inhibitor at 30°C is shown in Figure 12. The impedance of the solution with inhibitor has increased with the increase in the concentration of the inhibitor. It is observed that the size of the semicircle increases with the concentration of CDBE inhibitor. This indicates that the charge transfer process is the main controlling factor for the corrosion of mild steel in acidic medium [29-31]. The experimental result of EIS measurements for the corrosion of mild steel in 1M HCl in the absence and presence of inhibitor is given in Table 6.

It can be observed from the Nyquist plot data that resistance due to charge transfer (R_{ct}) value increased with increase in the concentration of the CDBE inhibitor. It is also shown that values of the capacitance of the interface (C_{dl}) showed a decrease, with increase in concentration of CDBE inhibitor, which is probably due to the decrease in local dielectric constant and/or increase in thickness of the electrical double layer. This suggests that the CDBE inhibitor acts via adsorption mechanism at the metal-solution interface. The decrease in the C_{dl} values is expected to be due to the adsorption of the CDBE inhibitor molecules on to the surface of mild steel which there by slowly replaces the water molecules, and so decreases the extent of metal dissolution in acidic medium [32].

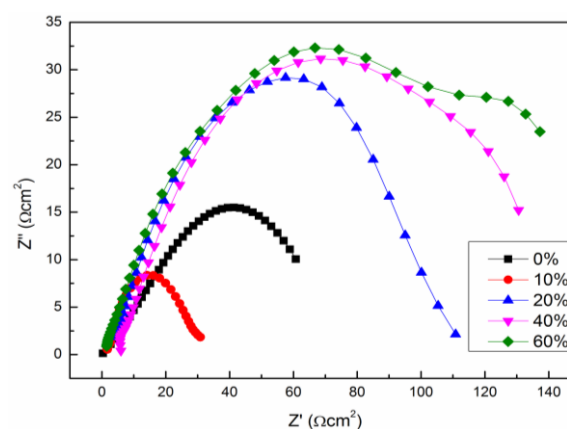


Figure 12. Nyquist plots for mild steel in 1M HCl solution at 30°C containing various concentrations of CDBE inhibitor

TABLE 6. AC impedance data of mild steel in 1M HCl solution at 30°C for various concentrations of CDBE inhibitor

% Volume of CDBE	R_{CT}	C_{dl} (μF)	Inhibition Efficiency (%)
0	29	143	
10	81	131	64.17
20	103	104	71.70
40	159	93	81.59
60	194	76	84.90

The inhibition efficiency of the CDBE inhibitor is given by Equation (5) [33]:

$$\text{Inhibition efficiency (\%)} = \left[\frac{R_{ct}(\text{inh}) - R_{ct}}{R_{ct}(\text{inh})} \right] * 100 \quad (5)$$

where R_{ct} is resistance due to charge transfer without inhibitor, and $R_{ct}(\text{inh})$ is resistance due to charge transfer with inhibitor.

C_{dl} value is obtained from the Equation (6) [33]:

$$C_{dl} = \frac{1}{R_{ct} * \omega_{max}} \quad (6)$$

where, $\omega_{max} = 2 * 3.14 * f_{max}$; f_{max} is the frequency at the top of the semicircle (where $-Z''$ is maximum).

Potentiodynamic Polarisation measurements

Potentiodynamic Polarization curves for mild steel in 1M hydrochloric acid without and with addition of different concentration of the CDBE inhibitor are shown in Figure 13. The values of electrochemical parameters, such as corrosion current densities (i_{corr}), Tafel anodic slopes (β_a), Tafel cathodic slopes (β_c), Corrosion rate, inhibition efficiency (%IE) and corrosion potential (E_{corr}) calculated are listed in Table 7. The inhibition efficiency is given by Equation (7) [32, 33]:

$$\text{Inhibition efficiency (\%)} = \left[1 - \left(\frac{i'_{corr}}{i_{corr}} \right) \right] * 100 \quad (7)$$

where, i'_{corr} and i_{corr} are the corrosion currents in the presence and absence of the CDBE inhibitor respectively.

From the electrochemical parameter values it is clear that, corrosion current density decreased with increase in CDBE concentration. This indicates an increase in the inhibition efficiency with the increase in % volume of the CDBE inhibitor. The i_{corr} obtained by weight loss method shows an agreement with the values obtained by Tafel extrapolation plots. Also the present study E_{corr} values show a shift of 12 mV shows that CDBE acts as mixed type inhibitor. Both anodic and cathodic slopes are also showing a decrease in their values confirming that, CDBE could be classified as a mixed type inhibitor. Further amongst β_a and β_c , since β_c shows a much decrease in its values, inhibitor can be expected to be more predominantly acted as cathodic type, inhibiting reduction reactions at the metal surface [33].

Scanning Electron Microscopy (SEM)

The surface morphological changes of mild steel sample in 1M HCl medium in the absence and presence of CDBE inhibitor yielded good results confirming the action of CDBE as a potent inhibitor. The SEM images are shown in Figure 14. The images shows the formation of more pits and cavities on the surface of mild steel in the absence of inhibitor compared to that of its presence. This confirms that the CDBE inhibitor markedly decreases the surface corrosion of mild steel by covering the surface with adsorbed inhibitor molecules [34].

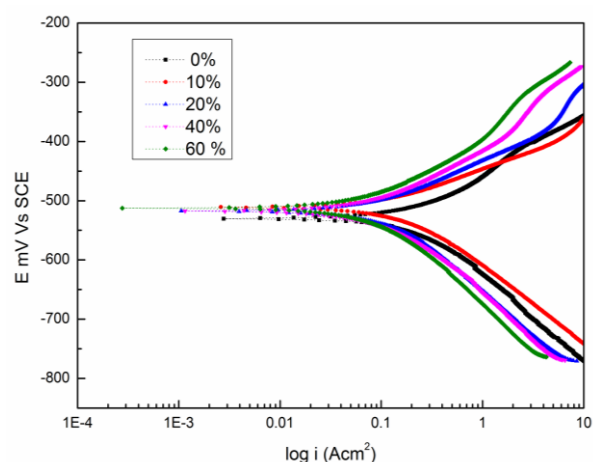
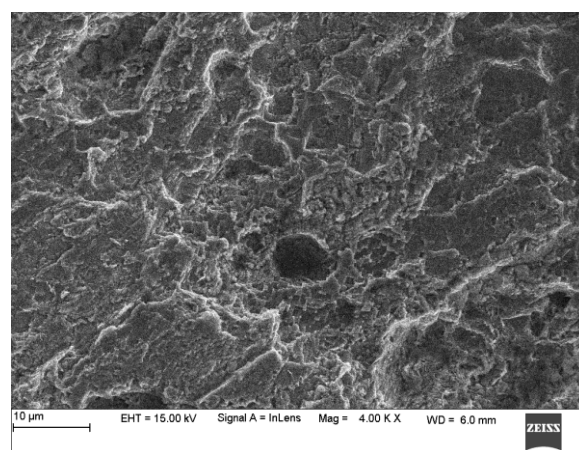
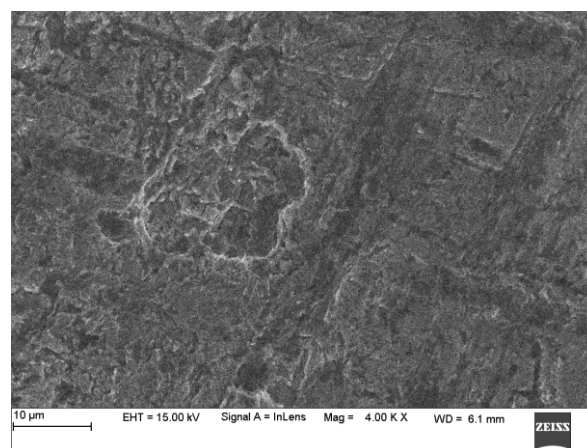


Figure 13. Potentiodynamic polarisation curves of mild steel in 1M HCl solution at 30°C containing various concentrations of CDBE inhibitor



(a)



(b)

Figure 14. SEM images of surface of mild steel after immersion for 5 hours at 30°C in (a) 1M HCl (b) 1M HCl+60% CDBE inhibitor

TABLE 7. Electrochemical parameter for mild steel in 1M HCl medium in the absence and presence of CDBE at 303K

%Volume of the inhibitor	i_{corr} (mA/cm ²)	β_a (mV)	β_c (mV)	Corrosion rate (mils/yr)	%IE	E_{corr} (mV)	i_{corr} (mA/cm ²) (Weight loss method)
0	1.1497	119.08	149.15	524.61		-529.60	565.97
10	0.5775	73.98	84.62	263.53	49.76	-510.62	246.42
20	0.3852	64.93	81.92	175.67	66.48	-516.68	136.05
40	0.2108	62.29	76.75	100.01	81.65	-518.08	95.24
60	0.1761	60.26	63.25	78.697	84.67	-517.06	65.30

CONCLUSIONS

The spectroscopic characterization reveals the presence of most likely to be present chemical constituents in CDBE showing the different functional groups and the substituent groups that involve in adsorption. Results obtained from the experimental data of weight loss, *Potentiodynamic polarization* and impedance spectroscopic studies for the corrosion behaviour of mild steel in the hydrochloric acid medium shows that CDBE acts as good inhibitor. It is clear that with the increase in the CDBE inhibitor concentration, more inhibition efficiency was exhibited. The inhibition efficiency decreased with increase in temperature in the studied temperature range indicating that adsorption of the inhibitor on to the surface of metal sample is more predominantly physisorption type. Polarization studies suggested that the CDBE hindered both oxidation and reduction, so acted as mixed type of inhibitor, with dominating cathodic type of inhibition.

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REFERENCES

- Tiwari, B.K., Brunton, N.P. and Brennan, C. eds., 2013. Handbook of plant food phytochemicals: sources, stability and extraction. John Wiley & Sons.
- John. R. Dyer, 1989. Applications of Absorption Spectroscopy of Organic Compounds, Prentice Hall of India.
- Pretsch, E., Buehlmann, P., Affolter, C., Pretsch, E., Buehlmann, P. and Affolter, C., 2000. Structure determination of organic compounds. Berlin: Springer-Verlag.
- Wang, J. and Zhang, Z., 1994. Analytical chemistry. VCH, New York.
- Willard, H.H., Merritt, L. and Dean, J.A., 1988. Instrumental methods of analysis. In Instrumental methods of analysis. Wadsworth.
- Fifield, F.W., 2000. Principles and practice of analytical chemistry. Blackwell science ltd.
- Perez, N., 2004. Electrochemistry and corrosion science (Vol. 412). Boston: Kluwer Academic Publishers.
- Ahmad, Z., 2006. Principles of corrosion engineering and corrosion control. Elsevier.
- McCafferty, E., 2010. Introduction to corrosion science. Springer Science & Business Media.
- Hasson, D., Shemer, H. and Sher, A., 2011. State of the art of friendly "green" scale control inhibitors: a review article. *Industrial & Engineering Chemistry Research*, 50(12), pp.7601-7607.
- Raghavendra, N. and Bhat, J.I., 2016. Green approach to inhibition of corrosion of aluminum in 0.5 M HCl medium by tender arecanut seed extract: insight from gravimetric and electrochemical studies. *Research on Chemical Intermediates*, 42(7), pp.6351-6372.
- M'hiri, N., Veys-Renaux, D., Rocca, E., Ioannou, I., Boudhrioua, N.M. and Ghoul, M., 2016. Corrosion inhibition of carbon steel in acidic medium by orange peel extract and its main antioxidant compounds. *Corrosion Science*, 102, pp.55-62.
- Njoku, V.O., Oguzie, E.E., Obi, C. and Ayuk, A.A., 2014. *Baphia nitida* leaves extract as a green corrosion inhibitor for the corrosion of mild steel in acidic media. *Advances in Chemistry*, 2014, pp.1-11.
- Kumar, K.P., Pillai, M.S. and Thusnavis, G.R., 2010. Pericarp of the fruit of *Garcinia Mangostana* as corrosion inhibitor for mild steel in hydrochloric acid medium. *Portugaliae Electrochimica Acta*, 28(6), pp.373-383.
- A Negm, N., A Yousef, M. and M Tawfik, S., 2013. Impact of synthesized and natural compounds in corrosion inhibition of carbon steel and aluminium in acidic media. *Recent Patents on Corrosion Science*, 3(1), pp.58-68.
- Singh, A., Ebenso, E.E. and Quraisi, M.A., 2012. Corrosion inhibition of carbon steel in HCl solution by some plant extracts. *International Journal of corrosion*, 2012, pp.1-20.
- Gerengi, H. and Sahin, H.I., 2011. *Schinopsis lorentzii* extract as a green corrosion inhibitor for low carbon steel in 1 M HCl solution. *Industrial & Engineering Chemistry Research*, 51(2), pp.780-787.
- Othman, A., Ismail, A., Ghani, N.A. and Adenan, I., 2007. Antioxidant capacity and phenolic content of cocoa beans. *Food chemistry*, 100(4), pp.1523-1530.
- Proestos, C., Zoumpoulakis, P. and Sinanoglou, V.J., 2018. Isolation and Characterization of Phenolic Compounds From Selected Foods of Plant Origin Using Modern Spectroscopic

- Approaches. In *Studies in Natural Products Chemistry* (Vol. 57), Elsevier, pp. 203-220.
20. Yetri, Y. and Jamarun, N., 2015. Corrosion inhibitor of mild steel by polar extract of theobroma cacao peels in hydrochloric acid solution. *Asian Journal of Chemistry*, 27(3), pp.876-881.
 21. Chaithra, P., Hemashree, K. and Bhat, J.I., 2016. An Investigation on the Attack of Dye Species on Freshly Synthesized and Characterized Activated Carbon from Cocoa Pod. *Iranica Journal of Energy and Environment*, 7(4), pp.350-358.
 22. Sermakkani M. And V. Thangapandian P.G., 2012. Gc-ms analysis of *cassia italica* leaf methanol extract. *Asian Journal of Pharmaceutical and Clinical Research*. 5(2) pp.90-94.
 23. Rao, V. and Johns, J., 2008. Thermal behavior of chitosan/natural rubber latex blends TG and DSC analysis. *Journal of Thermal Analysis and Calorimetry*, 92(3), pp.801-806.
 24. Bhat, J.I. and Alva, V.D., 2011. Meclizine hydrochloride as a potential non-toxic corrosion inhibitor for mild steel in hydrochloric acid medium. *Archives of Applied Science Research*, 3, pp.343-356.
 25. Bhat, J.I. and Alva, V., 2009. Corrosion inhibition of aluminium by 2-chloronicotinic acid in HCl medium. *Indian Journal of Chemical Technology*, 16(3), pp.228-233.
 26. Hemashree, K. and Bhat, J.I., 2017. Synthesis, characterization and adsorption behavior of coconut leaf carbon. *Research on Chemical Intermediates*, 43(8), pp.4369-4386.
 27. Ating, E.I., Umoren, S.A., Udousoro, I.I., Ebenso, E.E. and Udoh, A.P., 2010. Leaves extract of *Ananas sativum* as green corrosion inhibitor for aluminium in hydrochloric acid solutions. *Green Chemistry Letters and Reviews*, 3(2), pp.61-68.
 28. Ekanem, U.F., Umoren, S.A., Udousoro, I.I. and Udoh, A.P., 2010. Inhibition of mild steel corrosion in HCl using pineapple leaves (*Ananas comosus* L.) extract. *Journal of materials science*, 45(20), pp.5558-5566.
 29. Oguzie, E.E., Njoku, V.O., Enenebeaku, C.K., Akalezi, C.O. and Obi, C., 2008. Effect of hexamethylpararosaniline chloride (crystal violet) on mild steel corrosion in acidic media. *Corrosion Science*, 50(12), pp.3480-3486.
 30. Hamdy, A.S., El-Shenawy, E. and El-Bitar, T., 2006. Electrochemical impedance spectroscopy study of the corrosion behavior of some niobium bearing stainless steels in 3.5% NaCl. *International Journal of Electrochemical Science*, 1(4), pp.171-180.
 31. Ashassi-Sorkhabi, H. and Es'haghi, M., 2009. Corrosion inhibition of mild steel in hydrochloric acid by betanin as a green inhibitor. *Journal of Solid State Electrochemistry*, 13(8), pp.1297-1301.
 32. Döner, A., Solmaz, R., Özcan, M. and Kardaş, G., 2011. Experimental and theoretical studies of thiazoles as corrosion inhibitors for mild steel in sulphuric acid solution. *Corrosion Science*, 53(9), pp.2902-2913.
 33. Bentiss, F., Traisnel, M. and Lagrenee, M., 2000. The substituted 1, 3, 4-oxadiazoles: a new class of corrosion inhibitors of mild steel in acidic media. *Corrosion science*, 42(1), pp.127-146.
 34. Mistry, B.M., Patel, N.S., Patel, M.J. and Jauhari, S., 2011. Corrosion inhibition performance of 1, 3, 5-triazinyl urea derivatives as a corrosion inhibitor for mild steel in 1 N HCL. *Research on Chemical Intermediates*, 37(6), pp.659-671.

Persian Abstract

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چکیده

در عصاره لوبیایی خشک کاکائو کوبانو (CDBE) با استفاده از روش استخراج سوکسله تهیه و برای ترکیبات شیمیایی آن با استفاده از طیف سنجی مادون قرمز فوریه تبدیل شده (FT-IR)، کروماتوگرافی گازی-طیف سنجی جرمی (GC-MS) و همچنین با استفاده از ترموگرامتریک تجزیه و تحلیل شد. تکنیک های اندازه گیری کالری سنجی (TGA-DSC)، تجزیه و تحلیل FT-IR اطلاعاتی را در مورد بیشتر گروههای عملکردی موجود در عصاره ارائه داد. تجزیه و تحلیل GC-MS عصاره حضور ۰۷ ماده شیمیایی مهم با اسید سی-۱۳-اکتادکانوفیک اسید به عنوان مؤلفه اصلی را نشان داد. مطالعه TGA-DSC ایده در مورد مراحل مختلف تجزیه حرارتی از ترکیبات شیمیایی موجود در عصاره ارائه داد. سپس CDBE به دلیل توانایی آن در مهار ضریب خوردگی فولاد خفیف در محلول ۱.۰ میلی لیتر هیدروکلراید با استفاده از روش های کاهش وزن، قطبش پتانسیودینامیکی و طیف سنجی امپدانس الکتروشیمیایی (EIS) مورد آزمایش قرار گرفت. آزمایش های کاهش وزن خاصیت ضد خوردگی آن را بر روی فولاد خفیف نشان دادند که با افزایش غلظت CDBE مهار کننده افزایش یافته و با افزایش دمای محیط خورنده کاهش می یابد. نتایج EIS میزان جذب عناصر آلی موجود در عصاره را نشان داد. مطالعات قطبش پتانسیودینامیکی نشان داد که CDBE به عنوان یک مهار کننده نوع مخلوط عمل می کند. مطالعات مورفولوژیکی سطح فولاد خفیف توسط میکروسکوپ الکترونی روبشی (SEM) انجام شد. مقادیر بازده مهار به دست آمده توسط اندازه گیری های الکتروشیمیایی با اندازه گیری های کاهش وزن سازگار بوده و از این رو می توان CDBE را به عنوان یک مهار کننده قوی در جهت خوردگی فولاد خفیف در شرایط اسیدی پیشنهاد کرد.
