

## ***Vigna unguiculata* Coat Extract as Green Corrosion Inhibitor for Steel Pipeline in HCl**

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### **Authors' contributions**

*This work was carried out in collaboration among all authors. Authors AOJ and NCN designed and supervised the work. Author NKK carried the laboratory work and wrote the initial draft of the manuscript. Author NCN corrected the manuscript. All authors read and approved the final manuscript.*

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### **ABSTRACT**

The inhibitive performance of aqueous *Vigna unguiculata* coat extract on the corrosion of pipeline steel in 0.5 M HCl solution was studied by electrochemical, Gravimetric and UV-Visible spectroscopy techniques at varying temperatures. The extract was characterized using Gas Chromatography-Mass Spectrometer, GC-MS analysis. The results revealed that increase in concentration of extract yielded an increased inhibition efficiency up to 86.7% at 303 K; but showed a reversed trend at elevated temperature. The potentiodynamic polarization data indicate that aqueous *Vigna unguiculata* is a mixed type inhibitor of steel pipeline corrosion in acidic environment, while the electrochemical impedance spectroscopy result showed the extract's activity was on the solution-metal interface. Also, adsorption of aqueous *Vigna unguiculata* coat molecules on steel pipeline followed Temkin isotherm. The GC-MS results showed presence of heavy hetro-molecules. While, the adsorption of extract film deposited on the steel surface was characterized using FT-IR. The thermodynamic data strongly suggests that the mode of adsorption involved both physisorption and chemisorption.

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## 1. INTRODUCTION

The challenge posed by acid corrosion of metals is heightened by the problems of polluted environmental. Acids contribute to polluted environment because of acidic gases released into the atmosphere, also acids like Hydrochloric acid are utilized in various industrial applications for removing impurities, scales and rust [1]. Corrosion is a dangerous phenomenon due to its negative impacts. The Petroleum industry spends huge sum annually as lost revenues and maintenance cost which include corrosion prevention [2]. Other economic sectors like manufacturing, transportation, fabrication and construction are also faced with similar dilemma.

Therefore, corrosion is a global menace that requires enhanced solutions. However, one of the reliable ways of curtailing corrosion is by applying inhibitors because they appreciable minimize corrosion rate of materials [3,4]. Several literature have proposed that synthetic inhibitor has excellent inhibitive ability owing to the presence of heteroatoms like S, O and N. They inhibit corrosion by adsorption; resulting from the interaction between metal surface and molecules of the inhibitors [4-6]. Nonetheless, these inhibitors are very costly and sometimes harmful to the environment. Hence, they are banned by many countries and environmental regulators [7]. Consequently, replacing them with green inhibitors is of utmost necessity because they are affordable, pose less environmental threat and are renewable. They contain phytochemicals such as alkaloid, flavonoids, tannins, saponins etc. Previously, literature have severally reported plants and plant waste extracts as corrosion inhibitors [8-16].

In West Africa, *Vigna unguiculata* (Beans) is very common food. It is cultivated in the months of July to August mostly by local farmers in the northern parts of Nigeria. Germination occurs after 4 or 5 days and take about 2 - 4 months to mature. Beans are a legume and have around 32 species. It belongs to the plant group of leguminous. Beans possess high nutritional and health importance [17]. The bean seed coats are removed and disposed as waste in the process of making bean cakes (Akara and Moi- Moi). Bean seed coat was proposed as a source of green inhibitor because of its renewability and lessening of waste disposal challenge. This research studied the corrosion inhibiting

performance of beans coat extract (BCE) in 0.5 M HCl using electrochemical, weight loss measurement and UV visible spectroscopy techniques to further understand corrosion inhibition. The phyto-chemical composition was ascertained by Gas Chromatography-Mass spectrometer to further strengthen the attribution of phyto corrosion inhibition to phyto hetero compounds.

## 2. MATERIALS AND METHODS

### 2.1 Preparation of Aqueous Bean Coat Extract

Commercially obtained and characterized brown beans seeds were washed in flowing water and then soaked in water for 15 minutes. Thereafter, the coat was peeled out from seeds, air dried and converted to fine powder using electrical blender. The powder was sieved with a mesh size of 150  $\mu\text{m}$ . 70 g of beans coat powder was dissolved in 1 L of distilled water heated at 60°C by means of a thermostatic water bath for 1hour, 25 mins. The set was allowed to cool and settle for 24 hours. It was filtered and concentrated using rotary evaporator and thermo-stated water bath at 30°C. The test medium was prepared by serial diluents of BCE in 0.5 M HCl (0.1, 0.2, 0.3, 0.4 and 0.5 g/L).

### 2.2 Preparation of Steel Pipeline

Steel pipeline coupon (weight %) 0.47 C, 0.005 S, 0.003 P, 0.24 Si, 1.44 Mn, 0.01 Al and rest Fe [18], were polished with 200 to 1500 gritz emery paper, cleansed with ethanol, degreased in acetone and dried to a constant weight. The ready coupons were stored in an active desiccator. The initial weights were noted using electrical weight balance AS220/C/2 model.

### 2.3 Weight Loss Method

The coupons used for the weight loss measurement (3.0  $\times$  2.5  $\times$  1.0 cm), were immersed in both 0.5 M HCl with each of the serial quantities of BCE separately. After immersion period of 24 hours, the immersed coupons were taken out from both solutions, brushed and rinsed in distilled water to remove corrosion products, degreased and cleaned. The coupons were dried to a constant weight. Thereafter, the final weights were recorded. The

total weight loss (WL) was obtained from the difference between the initial and final weight. The inhibition efficiency (IE), surface coverage ( $\theta$ ) and corrosion rate ( $C_R$ ), material half life ( $t_{1/2}$ ) and corrosion rate constant (k) were obtained using the equations below.

$$WL = \Delta W_B - \Delta W_I \quad (1)$$

$$IE = \frac{\Delta W_B - \Delta W_I}{\Delta W_B} \times \frac{100}{1} \quad (2)$$

where  $\Delta W_B$  weight loss of steel pipeline in 0.5 M HCl with no BCE and  $\Delta W_I$  is weight loss of steel pipeline in test solution.

$$\Theta = \frac{IE\%}{100} \quad (3)$$

$$C_R = \frac{87.6 \times \Delta w}{DAT} \quad (4)$$

where  $\Delta w$  denotes change in weight loss, D is density of steel pipeline, A represents area in centimeter square and T is immersion time.

Half life

$$t_{1/2} = \frac{0.693}{k} \quad (5)$$

where k represents rate constant

The rate constant

$$K = \frac{2.303}{Time} \log \frac{w_1}{w_2} \quad (6)$$

where  $w_1$  is the initial weight whereas  $w_2$  means final weight.

## 2.4 Electrochemical Method

Electrochemical investigations for the corrosion of steel pipeline were carried out in both 0.5 M HCl solution with and without serial concentrations of BCE (0.1, 0.3 and 0.5 g/L), at 303 K using Princeton Applied Research Model 263A Potentiostat/Galvanostat. A conventional three electrode arrangement consisting of a counter electrode (platinum foil) and reference electrode (SCE) was used while steel pipeline coupon of size 1 cm × 1 cm functioned as working electrode. The experiment commenced immediately after the steel pipeline was allowed to corrode freely and its open circuit potential was obtained as a function of time for 1800 s. The Tafel plots were gotten by varying the electrode potential from - 0.15 to + 0.15 V with respect to OCP at a scan rate of 0.2 mV/s. The

data for corrosion density ( $I_{corr}$ ) and corrosion potential ( $E_{corr}$ ) were acquired automatically using Versa Studio software.

$$E.I\% = 100 \left[ 1 - \frac{I_{corr}^b}{I_{corr}^i} \right] \quad (7)$$

where  $I_{corr}^b$  represent corrosion density without BCE and  $I_{corr}^i$  denotes corrosion density with BCE. The electrochemical impedance spectroscopy was studied at a frequency of 10 kHz to 10 MHz by applying ac signal of 5 mV. These experiments were done in triplicate to ensure reproducibility of its data.

The corrosion inhibition efficiency was calculated using equation 8.

$$IE_{EIS} = 100 \times \frac{(R_{ctI} - R_{ctB})}{R_{ctI}} \quad (8)$$

Where  $R_{ctB}$  and  $R_{ctI}$  represent charge transfer resistance without and BCE respectively [18].

## 2.5 UV-visible Spectroscopic Analysis

Advanced microprocessor UV- visible spectrophotometer single beam model 295 was used to examine 0.5 M HCl acid solution consisting of 0.5 g/L aqueous BCE prior to and after immersing pipeline steel in solution for a period of 24 hrs.

### 2.5.1 FT-IR analysis

The FTIR analysis of BCE and surface film of steel pipeline in 0.5 M HCl solution with 0.5 g/L aqueous BCE after 24 hours immersion period was carried by using Buck scientific M530 USA FTIR.

## 2.6 Phytochemical Examination

Phytochemicals test for flavonoid, carbohydrate, steroid, phenol, triterpenoid, saponis, glycoside, tanins and alkaloids were done using previously reported procedures of several authors [19-22].

## 2.7 GC-MS Analysis

The organic matters present in the aqueous BCE was analysed using GCMS- QP2010 Plus Shimadzu Japan. It has a column size (25 m × 0.25 mm × 0.22  $\mu$ m) and column flow (1.38 mL/min). During analysis the injection mode was split less at an injection temperature of 250°C. The carrier gas (He) was carrying samples in a linear velocity (46.3 cm/sec) at a pressure of

108.0 Kpa; an initial column temperature of 80°C was constant for 1min and then rose to 200°C at 10°C/m with (4 mins) holding time and was further raised to 250°C at 10°Cm<sup>-1</sup>. Other procedure includes; ionization source 230°C and interface temperature 250°C.

### 3. RESULTS AND DISCUSSION

#### 3.1 Effect of BCE on Steel Pipeline Half-life and Corrosion Rate Constant

Table 1 Shows corrosion rate constant and material half life of steel pipeline in 0.5 M HCl solution with and without BCE at varying temperatures. In the acid solution, the corrosion rate constant and half-life of steel pipeline are 0.00185 (day<sup>-1</sup>) and 374.59 (days) respectively. A change in temperature from 303 K - 323 K caused a tremendous rise in the corrosion rate constant and sudden drop in the half- life of steel pipeline in 0.5 M HCl. However, the impact of aqueous BCE was instantly obvious because corrosion rate constant decreased from 0.00185 in 0.1 g/L to 0.00025 in 0.5 g/L BCE and then the half-life of steel pipeline increased from 374.59 – 2772 (days). This behavior may suggest that aqueous BCE can act as a good corrosion inhibitor and it may be considered as a useful tool for assessing the integrity of materials [23]. This corresponds to results reported by Hassan, et al. and Akalezi and Oguzie [23,24].

#### 3.2 Effect of BCE on Corrosion Rate and Inhibition Efficiency

Table 2 shows corrosion inhibition efficiency and corrosion rate of steel pipeline in 0.5 M HCl solution was with and without aqueous BCE. At 303 K, the corrosion rate of steel pipeline in unprotected 0.5 M HCl is 0.01349 (mmyear<sup>-1</sup>), but at higher temperature (323 k), the corrosion rate rose to 0.17029 (mmyear<sup>-1</sup>). However, the presence of aqueous BCE reduced the corrosion rate from 0.00647(mmyear<sup>-1</sup>) in 0.1 g/L to 0.00181(mmyear<sup>-1</sup>) in 0.5 g/L BCE; this decrease resulted in a significant increase in inhibition efficiency from 52.2% to 86.7%; this implies that the steel pipeline was protected by the increasing molecules of aqueous BCE [25, 26]. Although, at elevated temperatures the inhibition efficiency decreased from 86.7% at 30°C to 57.8% at 50°C. This may be due to the effect of temperature on physisorbed molecules [27], similar result has been previously reported [26].

#### 3.3 Kinetic Consideration for BCE

The activation energy for the corrosion of steel pipeline in 0.5 M HCl and solution containing serial concentration of aqueous BCE was computed using Arrhenius equation (9). The above expression reveals how corrosion rate is influenced by temperature change.

$$\text{Log } C_R = \text{Log } A - \frac{E_a}{2.303RT} \quad (9)$$

Where R represents general gas constant, E<sub>a</sub> represents apparent activation energy, T is the temperature, A denotes Arrhenius pre-exponential factor.

A straight line graph was gotten from a plot of Log CR versus ( $\frac{1}{T}$ ) as shown in Fig. 1. The resulting slope represents the E<sub>a</sub> value which can be found in Table 3.

Priya, et al. [27], [28] suggested that once inhibition efficiency decreases with increase in temperature, E<sub>a</sub> values obtained in the presence of inhibitor will be higher compared to that gotten in the absence of inhibitor; the observation is in consonance with those of Tables 2 and 3. It is interesting to note that the decrease in corrosion inhibition efficiency with increased temperature were not really significant. Table 3 reveals that the E<sub>a</sub> values of the solution containing selected concentrations of aqueous BCE are greater than that recorded in blank solution. The increase in E<sub>a</sub> values in the presence of aqueous BCE may possibly suggest that the molecules of BCE were physically adsorbed on steel pipeline [29]. This corresponds to observations reported by Mourya, et al. and Umoren, et al. [30,31].

#### 3.4 Thermodynamic Consideration of BCE

The data gotten from weight loss measurement were inputted into some adsorption isotherms such as Langmuir, Temkin and El-Awady isotherms to determine the isotherm that best describes the interaction between molecules of aqueous BCE and steel pipeline. Results reveal that temkins is the most suitable isotherm. The Temkins equation is provided in Eq. 10 [32].

$$\text{Exp } (-2a_0) = KC \quad (10)$$

Afterward, Equation (6) was reshuffled into

$$\ln \theta = \frac{1}{-2a} \ln C + \frac{1}{-2a} \ln K \quad (11)$$

Where  $\theta$  stand for the degree of surface coverage by aqueous BCE,  $(a)$  defines the molecular interaction between molecules,  $C$  means concentration of extracts,  $K$ - means equilibrium constant. The molecular interaction

(a) is divided into positive value (+a) which means there is a force of attraction that occurs between molecules of aqueous BCE and negative value (-) indicates that there is a force of repulsion between molecules [32,33].

**Table 1. The kinetic values for pipeline steel in 0.5 M HCl solution containing BCE extract**

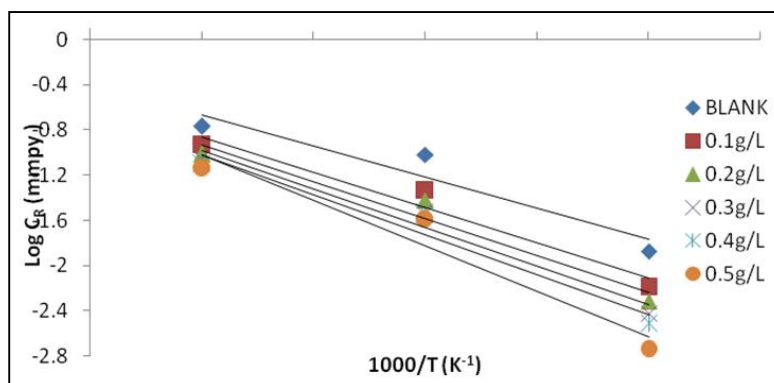
BCE (g/L)	Rate constant k (day <sup>-1</sup> )			Half-life(t <sub>1/2</sub> )(days)		
	10 <sup>-3</sup>	10 <sup>-3</sup>	10 <sup>-3</sup>			
	303K	313K	323K	303K	313K	323K
Blank	1.85	14.3	24.4	374.59	48.46	28.40
0.1	0.89	7.1	17.5	778.65	97.61	36.90
0.2	0.65	5.4	14.0	1066.15	128.33	49.50
0.3	0.52	4.4	11.5	1332.69	157.50	60.26
0.4	0.42	4.0	11.1	1650.00	173.25	62.43
0.5	0.25	3.8	10.6	2772.00	182.37	65.38

**Table 2. Corrosion rate and inhibition efficiency values obtained from weight loss measurement BCE**

Concentration	30°C		40°C		50°C	
	CRmmpy	IE <sub>WL</sub> (%)	CRmmpy	IE <sub>WL</sub> (%)	CRmmpy	IE (%)
0.5M HCl	0.01349	—	0.09546	—	0.17029	—
0.1g/L	0.00647	52.2	0.04618	51.4	0.11580	32.2
0.2g/L	0.00487	64.0	0.03788	60.2	0.09722	43.0
0.3g/L	0.00379	72.0	0.03043	68.0	0.08707	49.0
0.4g/L	0.00304	77.6	0.02787	70.6	0.07926	53.6
0.5g/L	0.00181	86.7	0.02551	73.1	0.07256	57.8

**Table 3. Activation energy values for corrosion of steel pipeline in HCl solution without and with varying concentrations of BCE**

Concentration (g/L)	E <sub>a</sub> (kJ mol <sup>-1</sup> )	R <sup>2</sup>
Blank	105.40	0.9102
0.1	119.90	0.9583
0.2	124.60	0.9564
0.3	130.30	0.9653
0.4	135.50	0.959
0.5	153.50	0.941



**Fig. 1. Arrhenius plot for corrosion of steel pipeline in 0.5 M HCl solution without and with selected concentrations of aqueous BCE**

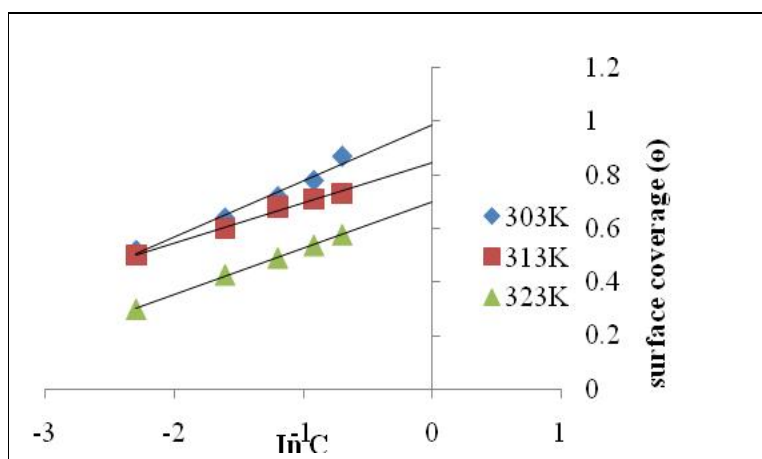


Fig. 2. Temkins adsorption isotherm for the corrosion of steel pipeline in 0.5 M HCl solution without and with selected concentration of BCE at separate temperatures

Table 4. Thermodynamic parameters for interaction of BCE molecules in HCl on steel pipeline

Temperature	A	$\ln K_{ads}$	$\Delta G_{ads}$	$\Delta H_{ads}$	$\Delta S_{ads}$	$R^2$
303K	-2.392	4.724	-22.018	-27.48	-18.03	0.977
313K	-3.362	5.677	-25.225	-27.48	-7.20	0.990
323K	-2.909	4.063	-21.697	-27.48	-17.90	0.998

Fig. 2 shows a plot of  $\theta$  against  $\ln C$ . with the slope  $\frac{1}{-2a}$  and intercept  $(\frac{1}{-2a})$ .

A linear graph with decent correlation coefficients were achieved, such results confirms that the interaction between molecules of aqueous BCE and steel pipeline best suits temkins isotherm.

The negative (a) values found in Table 4 proves that a force of repulsion transpired throughout adsorption process [33]. Furthermore, the  $K_{ads}$  values decreased from (112.61 at 303 K – 58.15 at 313 K). Perhaps, this means desorption of aqueous BCE molecules from steel surface may have occurred at increased temperature [34].

The  $K_{ads}$  data was used to acquire the values of free energy ( $\Delta G_{ads}$ ) at separate temperatures using equation (12)

$$\Delta G_{ads} = -RT \ln (55.5 K_{ads}) \quad (12)$$

The  $\Delta G_{ads}$  data is used to categorize adsorption mechanism. Once  $\Delta G_{ads}$  value is not more than -20  $\text{kJmol}^{-1}$ , it point towards physisorption mechanism, whilst chemisorption arises once the  $\Delta G_{ads}$  values are equal to or above 40  $\text{kJmol}^{-1}$  [35,36]. Table 4 shows that  $\Delta G_{ads}$  values are negative which implies that molecules of

aqueous BCE were spontaneously adsorbed on steel pipeline. In this research, the  $\Delta G_{ads}$  values are above 20  $\text{kJmol}^{-1}$ . According to Li, et al. 2012.

Alberty and Silbey [34] it implies that the adsorption of molecules of aqueous BCE on steel pipeline may involve both physisorption and chemisorption mechanism. Similar observations have been severally reported [34,37-39].

Firstly, the enthalpy ( $\Delta H_{ads}$ ) was evaluated by using Van Hoff equation 13

$$\ln K = -\frac{\Delta H_{ads}}{RT} + \text{Constant} \quad (13)$$

A plot of  $\ln k$  against  $\frac{1}{T}$  provides a straight line with a slope of  $-\frac{\Delta H_{ads}}{R}$ , the slope represents  $\Delta H_{ads}$  whereas  $\Delta S_{ads}$  values were calculated using equation (14)

$$\Delta S_{ads} = \frac{\Delta H_{ads} - \Delta G_{ads}}{T} \quad (14)$$

The calculated values of thermodynamic parameters are presented in Table 6. The  $\Delta H_{ads}$  values are negative (-27.48  $\text{kJmol}^{-1}$ ), it implies that the adsorption process is exothermic, which insinuates that at high temperature (303 K - 323 K) inhibition efficiency will decrease [34]. Martinez and Stern, 2002 [40] grouped

exothermic process into chemisorption and physisorption using the enthalpy value ( $\Delta H_{ads}$ ), physisorption dominates when the value of  $\Delta H_{ads}$  is below  $41.8 \text{ kJmol}^{-1}$  meanwhile chemisorption shifts toward  $100 \text{ kJmol}^{-1}$ . Therefore the value of  $\Delta H_{ads}$  in Table 4 indicates that the molecules of aqueous BCE were physically adsorbed on steel pipeline. Also, the  $\Delta S_{ads}$  values are negative and falls within the range of  $(-18.03 \text{ to } -17.904 \text{ kJmol}^{-1})$ . This indicates that the adsorption process is associated with a decrease in entropy; the decrease shows that aqueous molecules of BCE were orderly arranged on the steel pipeline. This trend agrees with a simple thermodynamic principle that says exothermic process must go with a decrease in entropy [41].

### 3.5 Electrochemical Impedance Studies of Aqueous BC

The equivalent electrical circuit used for obtaining the impedance data is given Fig. 5. The solution resistance ( $R_s$ ) and CPE are in series and parallel to charge transfer resistance ( $R_{ct}$ ). In this arrangement, capacitor was replaced with CPE due to the nature of electrode surface that is usually characterized with impurities and roughness. Hence,  $n$  is less than 1.

$$Z_{CPE} = Y_0^{-1} (j\omega)^{-n} \quad (15)$$

Where  $Z_{CPE}$  is referred to as impedance of CPE,  $j=(-1)^{1/2}$  represents an imaginary number,  $Y_0$  denotes CPE constant,  $\omega$  means angular frequency and  $n$  represents the nature of electrode surface (rough or smooth). Whenever  $n = 1$ , CPE denotes capacitor,  $n = 0$  represents resistance,  $n = -1$  means inductance and  $n$  equal to 0.5 denotes Warburg impedance. In order to understand the effects of aqueous BCE on the  $C_{dl}$  behavior the equation below was used [42].

$$C_{dl} = (Y_0 R_{ct}^{n-1})^{1/n} \quad (16)$$

Fig. 4 displays the Nyquist plot for corrosion of steel pipeline in 0.5 M HCl solution containing 0.1 g/L, 0.2 g/L and 0.5 g/L aqueous BCE at 303 K. From the charge transfer resistance, it can be seen that an increase in the concentration of the BCE led to a corresponding increase in the inhibition efficiency from 71.1% in 0.1 g/L to 83.3% in 0.5 g/L. These can be attributed to increased surface coverage by more BCE molecules and adsorption of its molecules on the steel pipeline [43]. It was revealed that as the concentration of aqueous BCE was changing from 0.1 g/L to 0.5 g/L, the values of  $n$  was increasing from (0.792 to 0.848). This behavior may be attributed to a reduction in the surface roughness of the steel owing to the formation of protective film by the molecules of aqueous BCE [44]. From the information in Table 6 it is evident that the  $C_{dl}$  values decrease with increasing concentration of BCE because the adsorbed molecules of aqueous BCE displaces water molecules at the metal - solution interface; thus, causing a decrease in local dielectric and or an increase in the thickness of the protective layer, thereby improving the smoothness of the steel pipeline surface [45]. The diameter of the semicircles is equivalent to the charge transfer resistance [32]. Also, the diameter of the semicircle increased with concentrations of BCE confirming that the extract possesses good corrosion inhibitive properties [46].

### 3.6 Potentiodynamic Polarization Studies for Aqueous BCE Corrosion Inhibition of Steel Pipeline in HCl

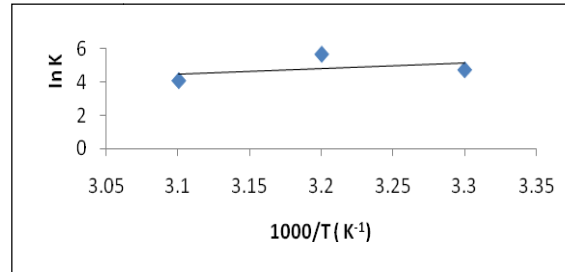
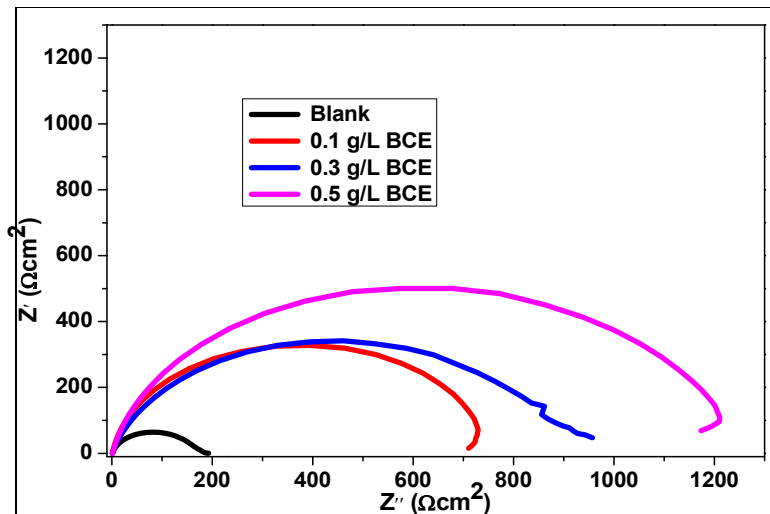
The Tafel diagram is used to describe the anodic and cathodic behavior of pipeline steel in 0.5 M HCl in the presence and absence of aqueous BCE at 303 K. The following electrochemical kinetic parameters such as corrosion potential ( $E_{corr}$ ), corrosion current density ( $I_{corr}$ ), Tafel anodic constant ( $\beta_a$ ) and Tafel cathodic

**Table 5. Nyquist plot parameters for the corrosion of pipeline steel in 0.5 M HCl solution in the absence and presence of aqueous BCE at 303 K**

Parameters	Blank	0.1 BCE	0.3 BCE	0.5 BCE
$R_s (\Omega cm^2)$	1.02	1.09	1.14	1.16
$R_{ct} (\Omega cm^2)$	192.2	665.1	939.5	1152.7
$Y_0 (\Omega^{-1} s^n cm^{-1})$	201.8	125.5	158.2	171.7
$\alpha (x10^{-3})$	877.5	883.0	885.7	892.5
Fit ( $x10^{-3}$ )	12.4	28.9	110.4	44.6
$n$	0.792	0.804	0.831	0.848
$C_{dl} (\mu F cm^{-2})$	169.9	141.8	131.4	108.6
$\epsilon_{EIS} (\%)$	-	71.1	79.5	83.3

**Table 6. PDP Parameters for aqueous BCE**

Parameters	Blank	0.1 BCE	0.3 BCE	0.5 BCE
$\beta_a$ (mV/decade)	84.4	89.7	96.2	105.1
$\beta_c$ (mV/decade)	93.7	87.4	86.8	91.5
$I_{corr}$ ( $\mu\text{Acm}^{-2}$ )	611.8	172.3	121.3	99.8
$E_{corr}$ (mV)	-529	-524	-519	-481
$\epsilon_{PDP}$ (%)	-	71.8	80.2	83.7

**Fig. 3. A plot of lnK against 1/T****Fig. 4. Nyquist plot for corrosion of pipeline steel in 0.5 M HCl solution without and with various concentration of aqueous BCE at 303 K**

constant  $\beta_c$  were evaluated using Versa Studio Software. It was noticed that an increase in concentration of aqueous BCE reduced the  $I_{corr}$  values from  $611 \mu\text{Acm}^{-2}$  to  $99.8 \mu\text{Acm}^{-2}$  suggesting that the aqueous BCE impeded the dissolution of steel pipeline in HCl solution. Perhaps, the molecules of BCE formed protective films on the surface of steel pipeline [47]. Similar observation was reported by Gopal, et al. [48]. Also changes in the concentration of BCE cause the  $E_{corr}$  values to shift toward positive direction. This may be attributed to the formation of protective layers on the surface of steel pipeline resulting from adsorption of the molecules of BCE [49].

However, the largest shift between the blank solution and that containing aqueous BCE is -48 mV and is less than 85 mV. Hence, cannot be classified as either cathodic or anodic inhibitor; this observation means aqueous BCE is mixed class inhibitor [50]. The obtained data confirms that the Tafel constants values were not significantly affected in the presence of BCE but slight alteration was noticed in  $\beta_a$  than in  $\beta_c$  suggesting that BCE is a mixed inhibitor with anodic predominance [18]. An optimum concentration of 0.5 g/L showed 83.7% inhibition performance, similar results was also estimated using weight loss and EIS technique.



### 3.7 UV Studies for Aqueous BCE Corrosion Inhibition of Steel Pipeline in HCl

UV-Visible absorption spectra for 0.5 M HCl solution containing 0.5 g/L aqueous BCE before and after pipeline steel was immersed can be found in Fig. 7. The electronic absorption spectrum of aqueous BCE shows that a peak appeared at 260 nm prior to immersion of steel. This may be due to  $\pi$ - $\pi$  and  $n$ - $\pi$  transitions. After steel was immersed, there was a bathochromic and hyperchromic shift. This can be attributed to the presence of a new compound resulting from the  $\text{Fe}^{2+}$ -BCE interaction [18,26].

### 3.8 FT-IR of BCE

The pure BCE consist of these functional groups at different wave band. The peaks at  $3509\text{ cm}^{-1}$  and  $3328\text{ cm}^{-1}$  may suggest the presence of O-H (alcohol) and carboxylic acid stretching vibration. These subsequent peaks at  $2735\text{ cm}^{-1}$ ,  $2116\text{ cm}^{-1}$ ,  $1785$  and  $1651\text{ cm}^{-1}$  are perhaps assigned to R-CHO,  $\text{C}\equiv\text{C}$ , C=O (ketone) and C=O (ester). After comparing the FT-IR

spectrum of pure BCE with FT-IR spectrum of adsorbed protective film deposited on steel pipeline after immersion in 0.5 M HCl consisting of 0.5 g/L BCE. It was noticed that new peaks surfaced some disappeared while others shifted to higher wave band. The O-H stretching vibration shifted from  $3509$  to  $3475\text{ cm}^{-1}$ ,  $3328$  to  $3364\text{ cm}^{-1}$  and also shifted  $1651$  to  $1618\text{ cm}^{-1}$  which suggest an interaction occurred between BCE and  $\text{Fe}^{2+}$ . While  $1785\text{ cm}^{-1}$  and  $1114\text{ cm}^{-1}$  to  $767\text{ cm}^{-1}$  peaks as- signed to C=O (carboxylic acid) and aliphatic C-H disappeared after adsorption on steel surface [34,51].

### 3.9 GC-MS Analysis and Phytochemical Screening of Aqueous WSE

The results obtained from GC-MS analysis are presented in Table 7 and Fig. 9, while the result of the phytochemical screening is presented in Table 8. The presence of same chemical functionalities in BCE GC-MS, phytochemical screening and FT-IR of BCE surface film on steel pipeline confirmed the mechanism of corrosion inhibition to adsorption of BCE molecules.

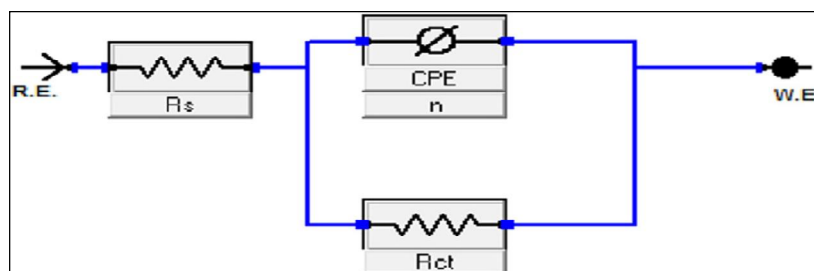


Fig. 5. Electrical equivalent circuit for corrosion of steel pipeline in HCl with and without BCE

Table 7. GC-MS identified compounds

Retention time	Peak area	Compounds	MW	MOL. formular
15.288	4.87	1- Octadecyne	250	C18H34
15.382	2.47	2-Undecanone,6,10- dimethyl	198	C13H26O
16.057	2.73	Phytol	296	C20H36O
17.974	12.10	n- Hexadecanoic acid	256	C16H32O2
19.984	1.79	11- Octadecenoic acid, methyl ester	296	C19H36O2
20.905	51.55	Oleic acid	282	C18H34O2
21.122	11.98	Octadecanoic acid	270	C18H36O2
22.456	1.12	Decane, 1- fluoro	160	C10H21F
22.728	1.43	E-2-Octadecadecen-1-ol	268	C18H36O
23.306	4.19	Eicosanoic acid	312	C20H40O2
24.275	2.60	2- Methyl-z-z-3,13-octadecadienol	280	C19H36O
24.782	2.69	Octadecanal	268	C18H36O

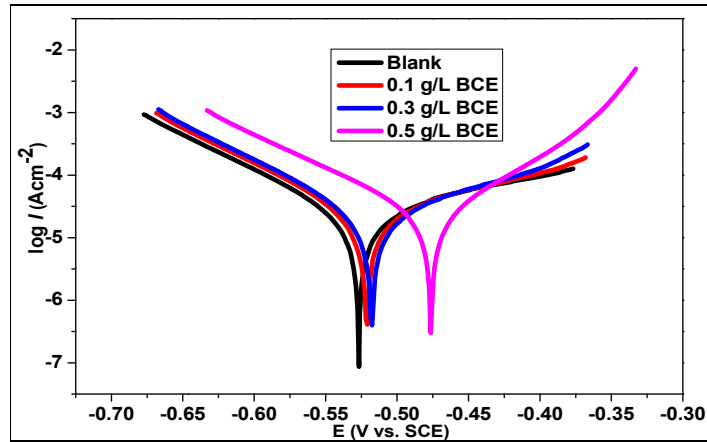


Fig. 6. Tafel plots for steel pipeline corrosion in 0.5 M HCl solution without and with concentrations of BCE

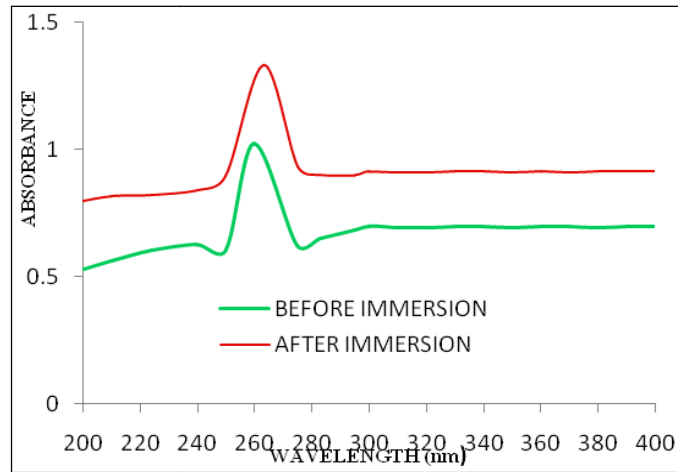


Fig. 7. UV - visible spectrum for steel pipeline corrosion in 0.5M HCl solution without and with aqueous BCE

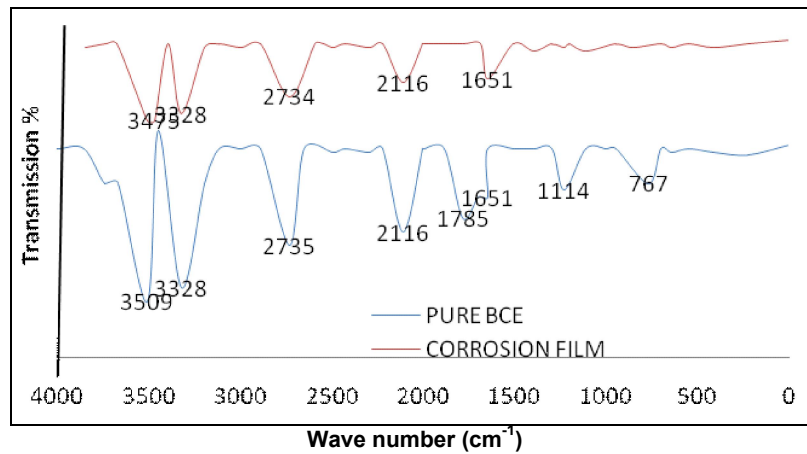


Fig. 8. FT-IR spectre of BCE and BCE surface film on steel pipeline surface in 0.5 M HCl

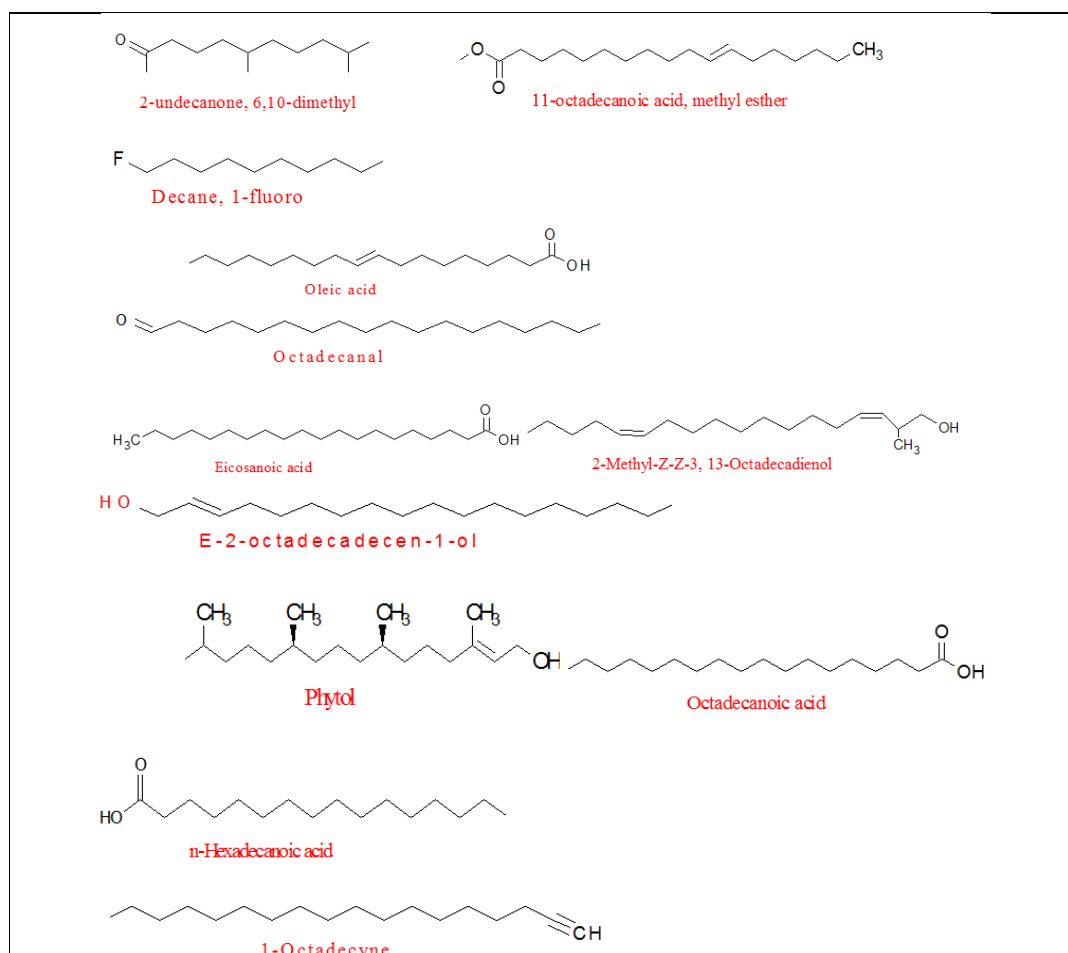


Fig. 9. Structures of GC-MS identified compounds of aqueous BCE

Table 8. Phytochemical screening of aqueous BCE

Phytochemicals screening of aqueous extract of beans coat
<b>Alkaloids</b>
(a) Dragendorff's test -
(b) Wagner test -
(c) Mayer test -
<b>Flavonoids (alkali test)</b>
Carbohydrates (Molisch test)++
Tannins -
<b>Steroids</b>
(a) Liebermann Burchard test -
(b) Salkowski test -
<b>Triterpenoids</b>
(a) Liebermann Burchard test +
(b) Chloroform test -
Cardiac glycoside (Keller Killiani test)±
Anthraquinone (Borntrager's test) -
Saponins±
Phenol -
Protein -

+++ = high, ++ = moderate, + = low, ± = negligible, - = absent

### 3.10 Adsorption Mechanism

The results gotten from FT-IR and GC-MS analysis shows that aqueous BCE contains these functional groups O-H, C=O, COOH and alkyne; these polar atoms may be responsible for adsorption on the surface of steel. The thermodynamic functions such as  $\Delta H_{ads}$ ,  $\Delta G_{ads}$  and  $\Delta S_{ads}$  suggests that the adsorption mechanism involves a mixture of chemisorption and physisorption. Also, the results obtained from tafel plots shows that aqueous BCE functioned as a mixed class inhibitor and can inhibit both cathodic and anodic reaction through the mechanism below. The hydroxyl groups are protonated in the presence of  $H^+$ , these positively charged products moves to the cathodic area of the steel and then the rate of hydrogen evolution would reduce; while the pi-electrons and lone pairs from O atom and 1-octadecyne impedes the reactions that occurs at anodic area [34]. Adsorption may also occur due to interaction between protonated molecules of BCE with negatively charge steel pipeline (physisorption) and chemisorption may take place through electron transfer between molecules of BCE and unfilled d- orbitals.

### 4. CONCLUSION

The aqueous BCE showed a good corrosion inhibition performance for acid corrosion of steel pipeline from the results obtained from the gravimetric, electrochemical and UV-Visible spectroscopy, while the FT-IR and phytochemical analysis strongly suggests the mode of corrosion inhibition is by adsorption of organic compounds in the extract. The thermodynamic calculation on the inhibition data of BCE is by physio and chemo adsorption mechanisms. The Tafel plots disclosed that aqueous BCE functioned as a mixed class inhibitor. BCE surface coverage data fitted into Temkin's adsorption isotherm.

### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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