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ETHANOL EXTRACTS FROM *PIPER GUINEENSE* AS GREEN CORROSION INHIBITOR OF MILD STEEL IN SULPHURIC ACID SOLUTION

P.C. Okafor*, A.I. Ikeuba, N.E. Nya, U.J. Ekpe, V.M. Bassey

ABSTRACT
The inhibition of the corrosion of mild steel by extracts from the stem (ST), seeds (SD) and leaves (LV) of Piper guineensis was studied using gravimetric and gasometric techniques at 30 and 40°C. The results revealed that the ethanol extracts from the different part of the plant inhibited the mild steel corrosion in sulphuric acid solution. The inhibition efficiency was found to increase with increase in inhibitor concentration and decrease with increase in temperature. The inhibition efficiency followed the trend: SD>LV>ST. The activation energy in the presence of the inhibitor was greater than those for the free acid solution. Physical adsorption mechanism is proposed for the adsorption of the extracts on the metal surface. The adsorption behavior of the extracts was best approximated by Langmuir adsorption isotherm.

***Key words**: Piper guineensis; Adsorption isotherm; Corrosion inhibitor; Mild steel; Acid corrosion*

1.0 INTRODUCTION

There is increasing concern about the toxicity of most corrosion inhibitors. The toxic effect does not only affect living organisms but also poisons the environment (Eddy and Mamza, 2009). Due to the toxicity of some corrosion inhibitors, there has been increasing search for green corrosion inhibitors (Okafor *et al.*, 2012). Inhibitors in this class are those that are environmentally friendly and are obtained from natural products such as plant extracts (Znini *et al.*, 2010).

The use of plant extracts to inhibit the corrosion of metals in acidic and alkaline environment have been reported (Ekpe *et al.*, 1996; Ikeuba *et al.*, 2012, Okafor *et al*, 2003,2005,2006, 2008; Oguzie *et al.* 2010; Sarathra *et al.*, 2010). The aim of this work is to investigate the inhibitive properties of the stem, seeds and leaves of *Piper guineensis* (SD, ST and LV respectively) in sulphuric acid solution. *Piper guineensis* is a plant that belongs to the family piperacae and it is widely distributed in various parts of India, Malaysia Islands and some West African countries. In Nigeria it is commonly found in the Niger delta regions (Dodson *et al.*, 2000). The leaves and other parts are sold in almost all markets in Nigeria. These parts of *Piper guineensis* have been reported to be pharmacological importance (Daglip, 2004).

2.0 Methodology

2.1 Materials preparation

Materials used for the study were mild steel sheet of composition (wt %) Mn (0.64), P (0.06), C (0.19), S (0.05), Ni (0.09), Cr (0.08), Mo (0.02), Cu (0.27), Si (0.26) and the rest Fe (Okafor *et al.*, 2007) The sheet was mechanically pressed and cut to form different coupons, each of dimension, 5.00 x 4.00 x 0.08 cm and 1.33 x 4.00 x 0.08 cm for the weight loss and hydrogen evolution techniques respectively. Each coupon was degreased by washing with ethanol, rinsed with acetone and preserved in a desiccator. All reagents used for the study were analar grade and distilled water was used for their preparation.

2.2 Extraction of plant

The required plant parts (leaves, seeds and stem) of *Piper guineensis* were collected from Ikot Ekpene, Nigeria and identified in the Department of Biological Sciences of the University of Calabar. These were cut into small chips and dried in an N53C- Genlab oven at 50° C, grounded. 80 g of the powder was extracted continually with 250 cm^3 of absolute ethanol for 24 hrs. The solvent was then evaporated and 10 g of the jelly extract obtained was soaked in 1 L of 5 M H_2SO_4, kept for 24, filtered and stored. From this stock (10.0 g/L) solution serial dilution to concentrations of 0.5, 1.0, 2.0, 4.0 and 6.0 g/L was done.

2.3 Phytochemical screening

Phyto chemical screening was carried out on the ethanol extracts from the seeds of *Piper guineensis* following the methods described by Trease and Evans (1996). The plants were screened for alkaloids, saponins, tannins, flavonoids, polyphenols, anthranoids and anthraquinones.

2.4 Gravimetric method

In the weight loss experiment, each coupon was washed in 20% NaOH solution (containing 100 g/L of zinc dust), rinsed in deionized water, cleaned and dried in acetone. The pre-cleaned mild steel coupons were dipped in 250 mL of the respective inhibitor/blank solutions maintained at 30° C. The weight loss was determined at 2 hours interval progressively for 8 hours. The difference in weight was taken as the weight loss of mild steel. From the weight loss, the inhibition efficiency (%I) of the extract and surface coverage (CR) of mild steel were calculated using equations 1 and 2 respectively and presented in Table 1

$$\% I = \frac{R_b - R_i}{R_b} x\, 100 \qquad 1$$

$$\theta = \frac{R_b - R_i}{R_b} \qquad 2$$

R_i and R_b are the corrosion rates for the uninhibited solution and inhibited solutions respectively.

2.5 Gasometric method

Gasometric measurements were carried out at 30 and 40 ° C as described in literature (Okafor *et al.*, 2007). From the volume of hydrogen evolved per minute, inhibition efficiency (%I), and degree of surface coverage (è) were calculated using equations 1 and 2 respectively. The corrosion rates were obtained from the slope of the graph of volume of hydrogen evolved per surface area against time.

3.0 RESULTS AND DISCUSSION

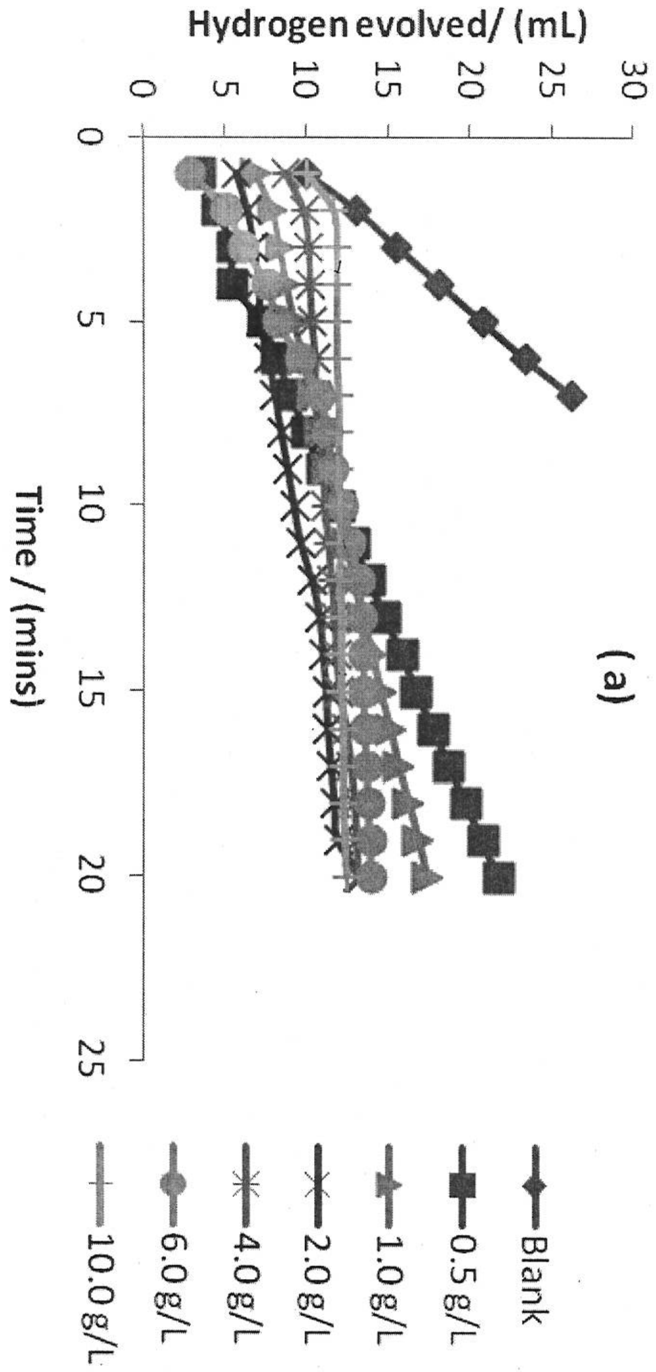
3.1 Effect of Concentration

The corrosion rate, surface coverage and inhibition efficiency for mild steel coupons in 5 M H_2SO_4 solution in the presence and absence of the parts of *Piper guineensis* using weight loss method are presented in Table 1. Table 1 clearly shows the corrosion-inhibiting ability of the extracts in acid solution becomes more pronounced with increasing inhibitor concentration. The inhibition efficiency increased with increase in the concentration of the extracts from 0.5 to 10.0 g/L. The order for the corrosion inhibitive effects is SD e" LV > ST. The plot in Fig 1 shows the hydrogen evolved in the absence and presence of the inhibitors. Fig 1 suggests that LV exerted a greater inhibiting effect than SD and ST in 5 M H_2SO_4 since the rate of hydrogen evolution is directly proportional to the corrosion rate. Fig 1 also shows a significant fall in the gradient of plot indicating a reduction in corrosion rate hence the inhibitive properties of the extracts. A sharp leveling off is observed for LV and SD at low inhibitor concentrations indicating that they are more efficient than ST at low concentrations.

TABLE 1
Corrosion rate, surface coverage and inhibition efficiency for mild steel in 5 M H_2SO_4 in the presence and absence of the stem, leave and seeds of *Piper guineensis* (ST, LV and SD respectively) using weight loss method at

Inhibitors	Conc.	Corrosion rate	θ	IE /(%)
	Blank	0.0360		
Stem (ST)	0.5 g/L	0.0169	0.5306	53.1
	1.0 g/L	0.0126	0.6500	65.0
	2.0 g/L	0.0082	0.7722	77.2
	4.0 g/L	0.0017	0.9528	95.3
	6.0 g/L	0.0004	0.9889	98.9
	10.0 g/L	0.0003	0.9917	99.2

Leave (LV)	0.5 g/L	0.0131	0.6361	63.6
	1.0 g/L	0.0139	0.6139	61.4
	2.0 g/L	0.0049	0.8639	86.4
	4.0 g/L	0.0008	0.9778	97.8
	6.0 g/L	0.0006	0.9833	98.3
	10.0 g/L	0.0005	0.9861	98.6
Seed (SD)	0.5 g/L	0.0080	0.7778	77.8
	1.0 g/L	0.0032	0.9111	91.1
	2.0 g/L	0.0028	0.9222	92.2
	4.0 g/L	0.0011	0.9694	96.9
	6.0 g/L	0.0003	0.9917	99.2
	10.0 g/L	0.0001	0.9972	99.7


Hydrogen evolved/ (mL)
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Time / (mins)
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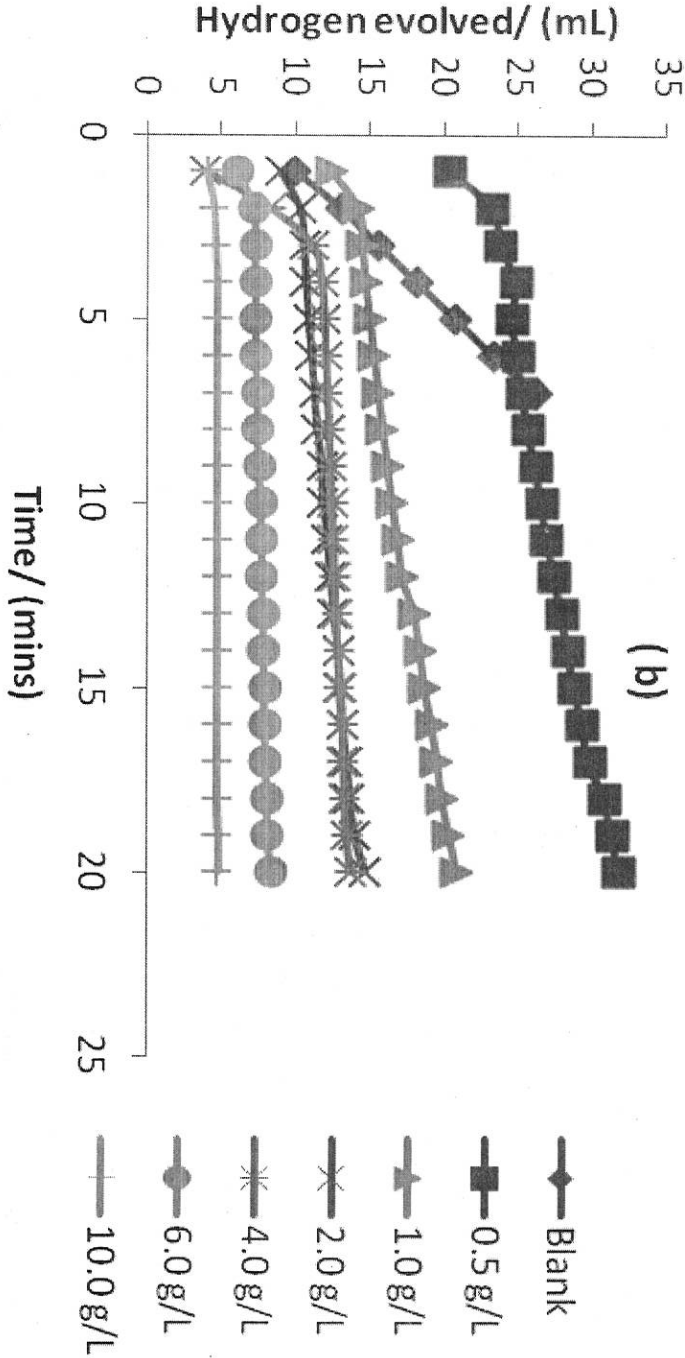
2.0 g/L
4.0 g/L
6.0 g/L
10.0 g/L


Hydrogen evolved/ (mL)
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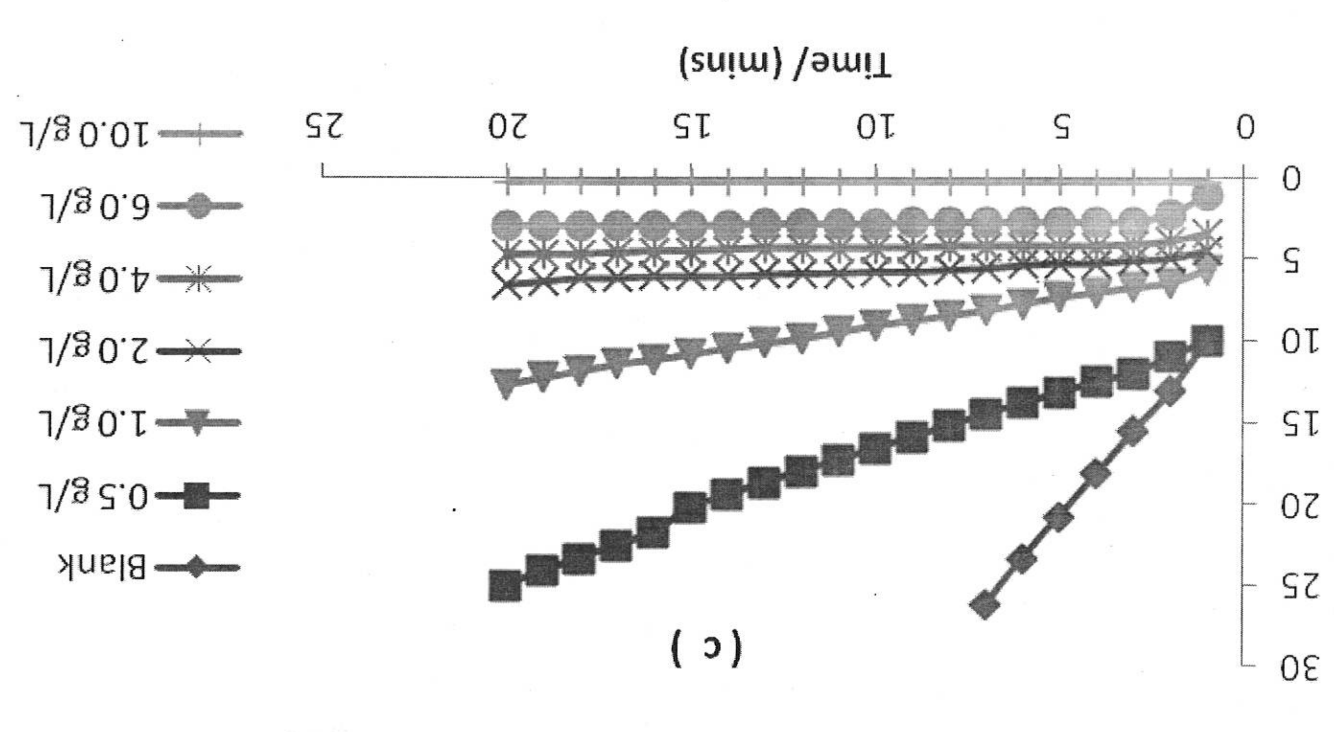


FIG. 1: Variation of volume of hydrogen evolved with time for mild steel in 5.0 M H2SO4 solution in the presence of the stem (a), seeds (b) and leaves (c) of *Piper guineensis* at 30 C.

3.2 Effect of Phytochemical Composition

The phytochemical screening of the plant part extracts are presented in Table 2. From Table 2 it can be seen that alkaloids and saponins are present in the three extracts. The stem contains a wide range of natural products but show relatively low inhibition efficiency as shown in Table 1. This suggests probable antagonism of these components. The corrosion-inhibiting effect of the extracts can be attributed to predominantly to the alkaloid and saponnins phytochemical constituents of the extracts. Alkaloids have been reported by Ikeuba *et al.* (2012) to be efficient corrosion inhibitors. *Piper guineense* have been reported to contain alkaloids, saponins and polyphenols with typical examples shown in Figs 2-5 (Lim, 2012). Fig 2 is Piperine; a typical alkaloid found in the Piper specie. It is believed that the molecules of alkaloids get adsorbed on the metal surface via the heterogeneous nitrogen atom (Ikeuba *et al.,* 2012). Solamine a saponin commonly found in the plant has abundant heterocyclic oxygen atoms as well as phenolic groups as shown in fig 3. Adsorption unto the metal surface can occur via these oxygen atoms and from the high molecular weight of the saponin the molecules are likely to be physically adsorbed on the metal. This is so because the large surface area of this molecule will favor vander waals forces of attraction. And this accounts for the relatively high inhibition efficiencies of all plant parts ; 98.4, 99.5 and 99.8 % for ST, LV and SD respectively at 30 C (Table 3). From Table 2 it is observed that polyphenols is only present in the leave extract while Flavonoids are present only in the seed extract. LV and SD have comparable inhibition efficiencies as shown in Table 3 this may be attributed to the additional phytochemicals in the extracts. The higher inhibition efficiency of SD over LV may be attributed to the heterocyclic oxygen atom (Fig. 6) present as compared to phenolic oxygen (Fig 5). This result suggests that the heterocyclic oxygen is more strongly adsorbed on the mild steel surface. Steric hindrance may come into play in the case of the polyphenol which is clustered by hydroxyl groups unlike the flavonoid which has free hetero oxygen.

TABLE 2
Phytochemical screening of the ethanol extracts fron the leaves (LV), seed (SD) and stem (ST) of *Piper guineense.*

Chemical constituents	Screening		
	LV	*SD*	*ST*
Anthranoids	-	-	+
Alkaloids	+	+	+
Saponins	+	+	+
Flavonoids	-	+	+
Tannins	-	-	+
Polyphenols	+	-	+
Antraquinones	-	-	-

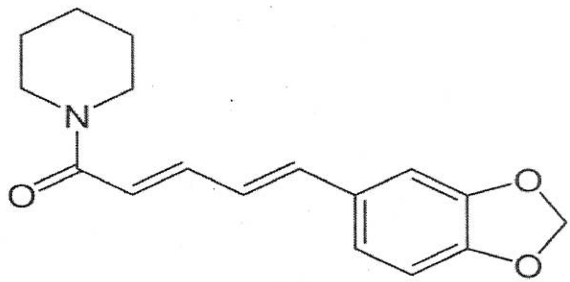


Fig 2: Piperine (An Alkaloid)

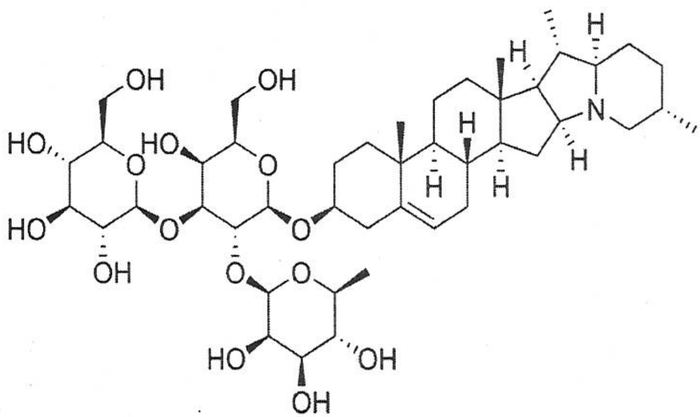


Fig 3: Solanine (A Saponin)

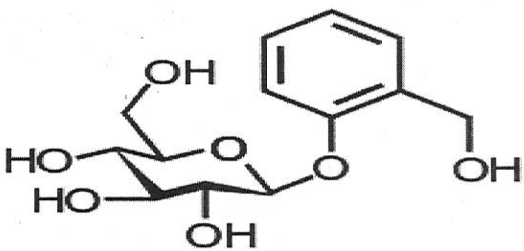


Fig 4: Phenolic glycoside (Related to aspirin polyphenol)

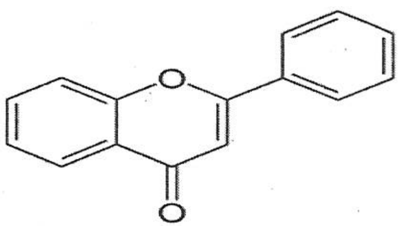


Fig 5: Flavone (A Flavonoid)

3.3 The Effect of Temperature

The rate of hydrogen evolution, inhibition efficiency and activation energy for the corrosion of mild steel in H_2SO_4 solution in the p r e s e n c e a *Piper guineensis* using hydrogen evolution technique is presented in Table 3 at 30 and 40 C.Table 3 shows the effect of temperature on the inhibitive properties of the extracts. A pronounced decrease in the inhibition efficiency is observed with increase in temperature. This suggests a physical mode of adsorption of the inhibitors on the metal surface. This result suggests that the binding force gets weak with thermal agitation as a result of increase in temperature. Arrhenius equation (equation 3) was used and the values of E_a calculated are recorded in Table 3.

$$\log \frac{R_2}{R_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad 3$$

Where R_1 and R_2 are taken to be the corrosion rates at T_1 and T_2 respectively (Okafor *et al.*, 2007). These values for the leaves and seeds are larger than the value for the blank (60.58 KJ/mol) confirming that these parts of *Piper guineense* retards the corrosion of mild steel in H_2SO_4. This may also suggest a physical mechanism for the adsorption process. Inspection of Table 3 shows that the E_a for the stem is lower than for the free solution indicating probable chemical interaction with the metal surface.

TABLE 3

Rate of hydrogen evolution, inhibition efficiency and activation energy for the corrosion of mild steel in H2SO4 solution in the presence and absence of the extracts of *Piper guineensis* using hydrogen evolution technique.

Inhibitors	Conc.	Rate of hydrogen evolution /(cm/min)		Inhibition efficiency /(%)		E_a /(KJ/mol)
		30 °C	40 °C	30 °C	40 °C	
Stem	Blank	0.2558	0.5497	-	-	60.58
	0.5 g/L	0.0781	0.2740	69.47	50.15	99.4
	1.0 g/L	0.0469	0.2345	81.67	57.34	127.46
	2.0 g/L	0.0368	0.0824	85.61	85.01	63.84
	4.0 g/L	0.0185	0.0620	92.77	88.72	95.78
	6.0 g/L	0.0142	0.0266	94.45	95.16	49.71
	10.0 g/L	0.0042	0.0081	98.36	98.53	52.01
Leave	0.5 g/L	0.0498	0.1886	80.53	65.69	105.46
	1.0 g/L	0.0347	0.1453	86.43	73.57	113.41
	2.0 g/L	0.0197	0.0893	92.30	83.75	121.32
	4.0 g/L	0.0119	0.0543	95.35	90.12	120.22
	6.0 g/L	0.0077	0.0471	96.99	91.43	143.43
	10.0 g/L	0.0014	0.0107	99.45	98.05	161.07
Seed	0.5 g/L	0.0675	0.1604	73.61	70.82	68.55
	1.0 g/L	0.0311	0.1098	87.84	80.03	99.9
	2.0 g/L	0.0078	0.0530	96.95	90.36	151.75
	4.0 g/L	0.0023	0.0138	99.10	97.49	141.9
	6.0 g/L	0.0014	0.0071	99.45	98.71	128.58
	10.0 g/L	0.0004	0.0061	99.84	98.89	215.77

3.4 Adsorption behaviour

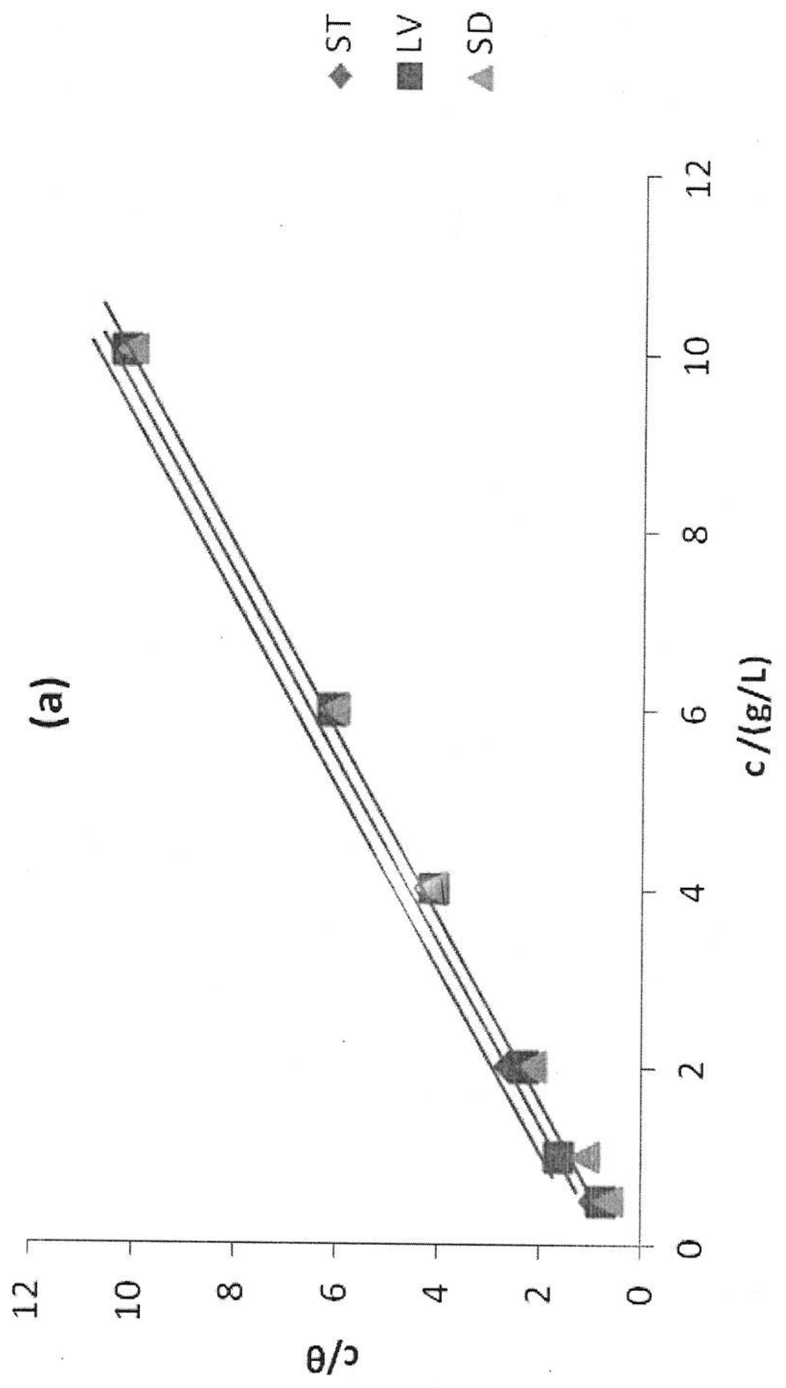
The adsorption characteristics of ethanol extracts of *Piper guineensis* were also investigated by fitting data obtained for the degree of surface coverage into different adsorption isotherms. The tests indicate that Langmuir adsorption isotherm best describes the adsorption behavior of ethanol extracts of *Piper guineense.* The assumptions of Langmuir adsorption isotherms can be expressed as follows

$$\frac{c}{\theta} = \frac{1}{K_{eq}} + c \qquad \mathbf{4}$$

where c is the concentration of the inhibitor in the solution, è is the degree of surface coverage of the inhibitor and K_{eq} is the adsorption equilibrium (Ebenso *et al.,* 2008). Fig. 3 shows Langmuir adsorption isotherm for the adsorption of ethanol extract of ST, SD and LV on mild steel surface. Values of adsorption parameters deduced from the isotherms are presented in Table 4. The linear indicates adherence to the Langmuir adsorption isotherm. The application of the isotherm to the adsorption of ethanol extract of ST, SD and LV on the surface of mild steel suggests that there is no interaction between the adsorbed species. Values of adsorption equilibrium constant determined from the slope of the Langmuir adsorption isotherms were used to calculate the adsorption free energy of ethanol extract of ST, SD and LV on mild steel surface using equation 4 (Eddy, 2009)

$$\mathrm{I}G_{ads} = \mathrm{I}RT\ln(55.5K_{eq}) \qquad \mathbf{5}$$

where $ÄG_{ads}$ is the free energy of adsorption, R is the gas constant, T is the temperature and 55.5 is the molar concentration of the acid in the solution. Calculated values of $ÄG_{ads}$ shown in Table 4 are between -11.77 and -13.28 (ST), -12.94 and -14.54 (SD), -14.39 and -15.15 (LV) respectively. The values are negative and are less than the threshold value of -40 KJ/mol required for chemical adsorption, hence the adsorption of ethanol extract of ST, SD and LV on mild steel surface is spontaneous and is consistent with the mechanism of physical adsorption.


(a)
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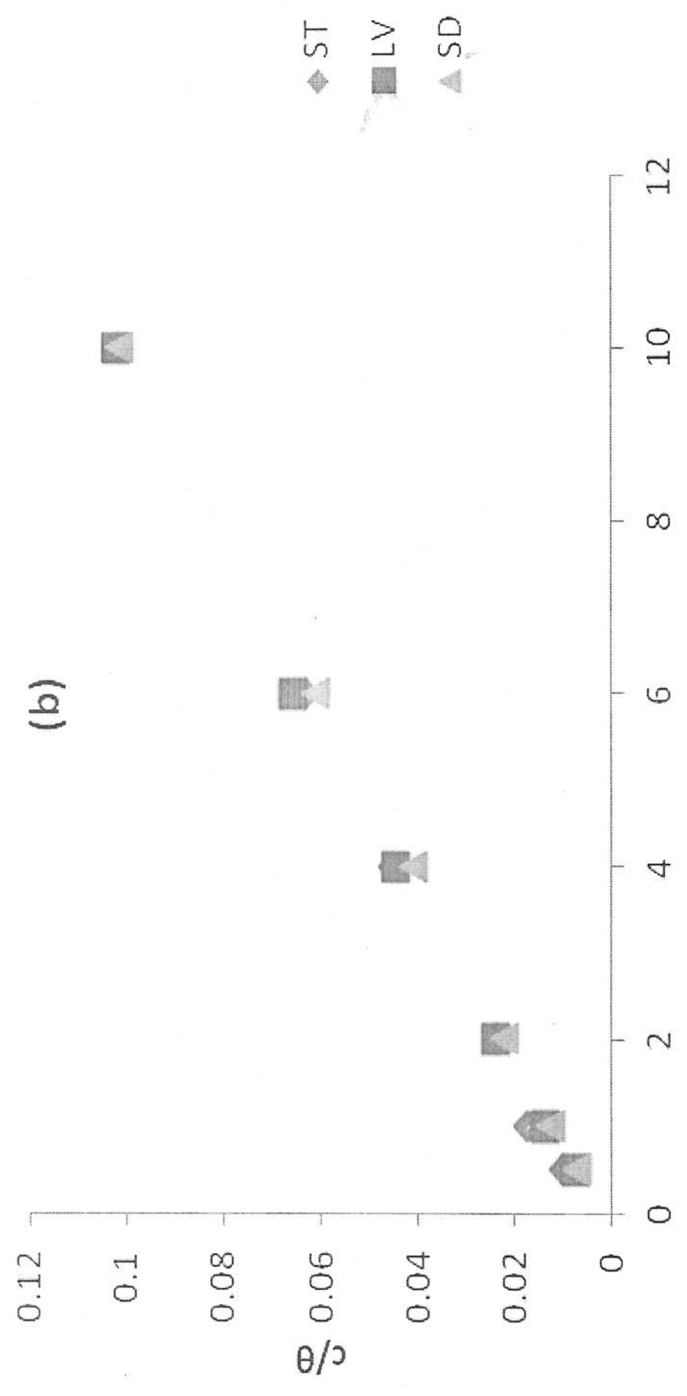

FIG 3: Langmuir isotherm for the adsorption of ethanol extract of parts of *Piper guineense* on the surface of mild steel at 30 °C (a) and 40 °C (b)

TABLE 4
Adsorption equilibrium constant and Adsorption free energy for mild steel in the presence of the inhibitors at different temperatures.

Inhibitor	Temp. (°C)	Adsorption parameters			
		Hydrogen evolution		Weight loss	
		K_{ads}	ΔG_{ads}	K_{ads}	ΔG_{ads}
ST	30	3.51	-13.28	1.78	-11.57
	40	1.6	-11.77		
SD	30	5.78	-14.54	5.47	-14.4
	40	2.6	-12.94		
LV	30	7.36	-15.15	2.27	-12.18
	40	4.55	-14.39		

4.0 CONCLUSION

Ethanol extracts of the stem, seeds and leave of *Piper guineensis* functioned as good inhibitors for the corrosion of mild steel in H_2SO_4. The inhibition efficiency for the extracts is in the order SD> LV > ST. The adsorption characteristics of the inhibitors are similar to and are best described by Langmuir adsorption isotherm. A physical adsorption mechanism is proposed for the adsorption of the extracts on the mild steel surface in sulphuric acid solution.

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