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Full Length Research Paper

Corrosion inhibitive properties and adsorption behaviour of ethanol extract of *Piper guinensis* as a green corrosion inhibitor for mild steel in H_2SO_4

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The corrosion inhibition of mild steel by ethanol extract of *Piper guinensis* (EEPG) has been studied using gravimetric, gasometric and thermometric methods. The results of the study reveals that the different concentrations of ethanol extract of *Piper guinensis* (EEPG) inhibit mild steel corrosion. Inhibition efficiency of the extract is found to vary with concentration, temperature and period of immersion. Values of activation energy of the inhibited corrosion reaction of mild steel are greater than the value obtained for the blank. Thermodynamic consideration reveals that adsorption of *P. guinensis* extract (EEPG) on mild steel surface is spontaneous and occurs according to Langmuir adsorption isotherm. Physical adsorption mechanism has been proposed for the adsorption of the inhibitor from the trend of the inhibition efficiency with temperature and the values of some kinetic and thermodynamic parameters obtained.

Key words: Corrosion inhibition, mild steel, Langmuir adsorption isotherm, physical adsorption, *Piper guinensis*.

INTRODUCTION

A corrosion inhibitor, when added in minute quantity, slows down the rate of corrosion of a metal or a metal alloy. Due to their industrial importance, most corrosion inhibitors have been synthesized from cheap raw materials or chosen from compounds containing hetero atoms in their aromatic or long carbon chain (Abdallah, 2004; El Ashry et al., 2006). Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. The successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment have been reported by some research groups (Abiola et al., 2007; Kliskic et al., 2000; El-Etre, 1998, 2003, 2006; Ebenso et al., 1998, 2004; Ebenso and Ekpe, 1996; Ekpe et al., 1994; Zucchi and Omar, 1985; Umoren et al., 2006a, 2008a-d; Umoren and Ebenso, 2008; Abdallah, 2004; Okafor et al., 2005, 2007, 2008; Okafor and Ebenso, 2007; El-Etre and Abdallah, 2000; Chetouani et al., 2004; Bouyanzer and Hammouti, 2000; Oguzie, 2005, 2006a, b, 2007; Oguzie et al., 2006, 2007; Bendahou et al., 2006; Sethuraman et al., 2005; Rajendran et al., 2005; Eddy and Ebenso, 2008) to mention but a few. Efforts to find naturally organic substances or biodegradable organic materials to be used as corrosion inhibitors over the years have been intensified in our research group.

Piper guineensis (African bush pepper) are climbing glabrous creeper cultivated in various parts of India, Malaya Island, Nigerian and other West African countries. There is considerable local use of this species as a condiment and it is widely found in almost all Nigerian market. The roots, fruits and leaves of this plant are widely used in the treatment of asthma, bronchitis, fever and pain in abdomen, as stimulant and in haemorrhoidal infection. The fresh fruits of *P. guineensis* are often eaten raw for their spicy taste. The fruits are also dried and are then pounded and sieved; this powder is added to tea or coffee or used for seasoning vegetables (Daglip, 2004).

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P. guineensis is a plant among the candidates with enormous potential for use as a bio insecticide; it is a member of the *Piperraceae* family (Dodson et al., 2000). It is used in small quantities for flavour in foods and medicinal purposes, the excess post harvest is usually wasted since new stock come to meet the previous season' stock. Adgeh (1989), Gbenwonyo et al. (1993) and Su and Hovart (1981) reported that amide olifinic, or alkyl isobutylamines compounds (piperine, tricostacine, peepulidin, piplartin and trichonine are responsible for the insecticidal effect of the plant product. At the rural level, pulverized seed of *P. guineensis* is extracted with cold solvents like ethanol, methylated spirit and acetone; the extracts are diluted with hot water and used in dressing the maize before storage (Udofia et al., 2008).

The present study therefore seeks to investigate the inhibitive and adsorptive characteristics of ethanol extract of *P. guinensis* (EEPG) for the corrosion of mild steel in H_2SO_4.

Experimental

Materials preparation

Materials used for the study were mild steel sheet of composition (wt %) Mn (0.6), P (0.36), C (0.15) and Si (0.03) and the rest Fe. The sheet was mechanically pressed cut to form different coupons, each of dimension, 5 x 4 x 0.11 cm. Each coupon was degreased by washing with ethanol, dried with acetone and preserved in a desiccator. All reagents used for the study were analar grade and double distilled water was used for their preparation.

Extraction of plant

Samples of *P. guinensis* were obtained from the Akwa Ibom State Botanical garden in Uyo, South east of Nigeria. Samples of the leaves of *P. guinensis* were dried, grounded and soaked in a solution of ethanol for 48 h. After 48 h, the samples were cooled and filtered. The filtrates were further subjected to evaporation at 352 K in order to leave the sample free of the ethanol. The stock solutions of the extract so obtained were used in preparing different concentrations of the extract by dissolving 0.1, 0.2, 0.3, 0.4 and 0.5 g of the extract in 1 L of 2.5 M H_2SO_4 respectively.

Gasometric method

Gasometric methods were carried out at 303 and 333 K as described in literature (Oguzie et al., 2006b; Umoren et al., 2006b, 2007). From the volume of hydrogen evolved per minute, inhibition efficiency (%I), and degree of surface coverage (θ) were calculated using equations 1 and 2 respectively.

$$\%I = 1 - \frac{V^1_{Ht}}{V^o_{Ht}} x100 \qquad (1)$$

$$\theta = 1 - \frac{V^1_{Ht}}{V^o_{Ht}} \qquad (2)$$

Where V'_{Ht} is the volume of hydrogen evolved at time t for inhibited solution and V^0_{Ht} is the volume of hydrogen evolved at time t for uninhibited solution. The volume of hydrogen gas evolved per minute was recorded until there was no evolution of gas anymore.

Thermometric method

The reaction vessel is a three-necked round bottom flask and the procedure for determining the corrosion behavior by this method has been described elsewhere by other authors and also reported by Ebenso (2003b) and Umoren et al. (2006b, 2007). The flask was well lagged to prevent heat losses. In the thermometric technique the corrodent (H_2SO_4) concentration was kept at 2.5 M. The volume of the test solution used was 100 ml. The initial temperature in all the experiments was kept at 30°C. The progress of the corrosion reaction was monitored by determining the changes in temperature with time using a calibrated thermometer (0 - 100°C) to the nearest ± 0.05°C. This method enabled the computation of the reaction number (RN). From the rise in temperature of the system per minute, the reaction number (RN) was calculated using equation 3:

$$RN\left({}^{o}C/\min\right) = \frac{T_m - T_i}{t} \qquad (3)$$

where T_m is the maximum temperature attained by the system, T_i is the initial temperature and t is the time. From the above, the inhibition efficiency (%I) of the used inhibitor was computed using equation 4:

$$\%I = \frac{RN_{aq} - RN_{wi}}{RN_{aa}} x100 \qquad (4)$$

where RN_{aq} is the reaction number of aqueous acid in the absence of *P. guinensis* (EEPG), and RN_{wi} is the reaction number of aqueous acid in the presence of *P. guinensis extract* (EEPG).

Gravimetric method

In the weight loss experiment, the pre-cleaned mild steel coupons were dipped in 200 ml of the respective inhibitor/blank solutions maintained at 303 and 333 K in a thermostated bath. The weight loss was determined by retrieving the coupons at 24 h interval progressively for 168 h (7 days). Prior to measurement, 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 difference in weight was taken as the weight loss of mild steel. From the weight loss, the inhibition efficiency (%I) of the extract and the corrosion rate (CR) of mild steel were calculated using equations 5 and 6 respectively.

$$\%I = (1 - W_2/W_1) \times 100 \qquad (5)$$

$$CR\ (gh^{-1}cm^{-2}) = \Delta W/AT \qquad (6)$$

Where W_1 and W_2 are weight loss of mild steel in the absence and presence of the inhibitor respectively. A is the area of the coupon in cm^2, T is the period of immersion in hours and $\Delta W = W_1 - W_2$.

RESULTS AND DISCUSSION

Effect of ethanol extract of *P. guinensis* (EEPG) on the corrosion of mild steel

The variation of volume of hydrogen gas evolved by

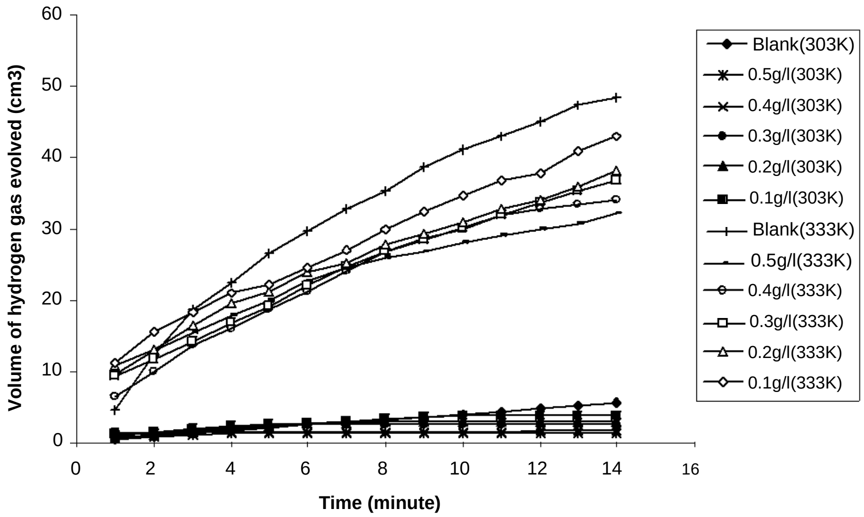

Figure 1. Variation of volume of hydrogen gas evolved with time for the corrosion of mild steel in tetraoxosulphate (VI) acid containing various concentrations of ethanol extract of *Piper guineensis* at 303 and 333K.

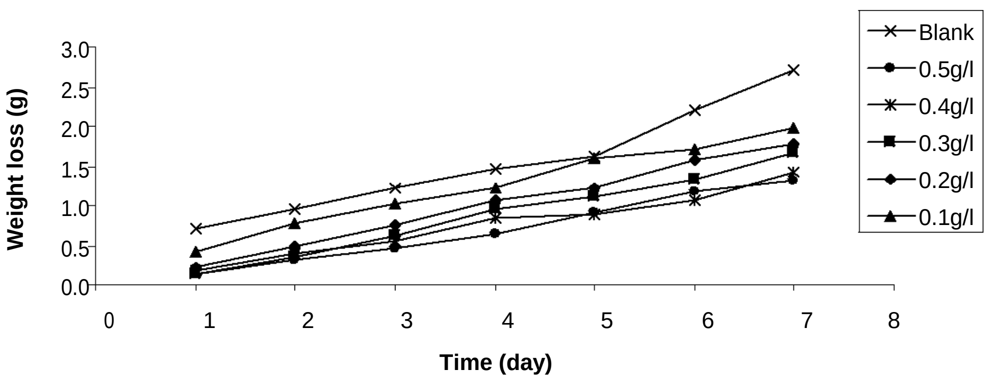

Figure 2. Variation of weight loss with time for the corrosion of mild steel in tetraoxosulphate (VI) acid containing various concentrations of ethanol extract of *Piper guinensis*

various concentrations of *P. guinensis* (EEPG) at 303 and 333 K are shown by Figure 1. From the figure, it is seen that the volume of hydrogen gas evolved increases with time and temperature but decreases as the concentration of EEPG increases indicating that the rate of corrosion of mild steel increases as the temperature and period of immersion increases and that various concentrations of EEPG retards the corrosion of mild steel in H_2SO_4. These findings were also applicable to the weight loss measurements (Figure 2).

The values of corrosion rates and reaction numbers for the corrosion of mild steel in the absence and presence of various concentrations of EEPG are recorded in Table 1. From Table 1, it is seen that the corrosion rates and reaction numbers for the corrosion reaction of mild steel in the presence of EEPG were lower than values obtained for the blank indicating that various concentrations of EEPG inhibits the corrosion of mild steel in H_2SO_4. The corrosion rate and the reaction numbers were also observed to decrease as the concentration of EEPG increases indicating that the rate of corrosion of mild steel in H_2SO_4 decreases as the concentration of EEPG increases.

Table 2 shows values of inhibition efficiency of different concentrations of EEPG obtained from weight loss, gasometric and thermometric methods. From the results, it is seen that values of inhibition efficiency of EEPG for the corrosion of mild steel increases as the concentration of the extract increases indicating that the extract act as an adsorption inhibitor. Figure 3 shows the variation of inhibition efficiency versus the different concentrations of *P. guinensis* (EEPG) at both 303 and 333 K. The significant difference between the values of inhibition efficiency of *P. guinensis* (EEPG) obtained at 303 and 333 K suggests that the mechanism of adsorption of the inhibitor on the mild steel surface is by physical adsorp-

Table 1. Values of corrosion rates (CR) and reaction numbers (RN) for the corrosion reaction of mild steel in the presence and absence of EEPG.

Concentrations of EEPG (g/l)	Gasometric method		Weight loss method		Thermometric
	CR (303K) (cm^3/min)	CR (333K) (cm^3/min)	CR(303K) x 10^{-3} ($gh^{-1}cm^{-2}$)	CR(333K) x 10^{-3} ($gh^{-1}cm^{-2}$)	RN(303K) (°C/min)
Blank	0.38	3.12	14.98	34.7	0.31
0.1	0.14	2.26	5.62	17.80	0.10
0.2	0.13	1.97	5.29	15.13	0.09
0.3	0.08	1.98	4.32	13.36	0.08
0.4	0.03	1.96	4.18	12.25	0.06
0.5	0.03	1.61	4.14	11.56	0.03

Table 2. Values of inhibition efficiency (%I) of various concentrations of EEPG for the corrosion of mild steel.

Concentrations of EEPG (g/l)	Gasometric method		Weight loss method		Thermometric method
	%I (303K)	%I (333K)	%I (303K)	333K	303K
0.1	64.47	27.46	62.12	48.72	62.33
0.2	67.11	36.61	62.87	56.41	67.34
0.3	80.26	36.84	80.71	61.54	78.67
0.4	92.11	37.07	91.46	64.74	93.45
0.5	92.11	48.51	93.76	6.67	94.00

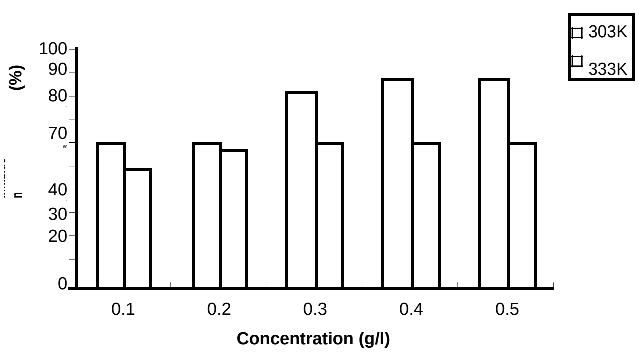

Figure 3. Variation of inhibition efficiency of ethanol extract of Piper guinensis with concentration at 303 and 333K

tion. For a physical adsorption mechanism, inhibition efficiency of an inhibitor decreases with temperature while for a chemical adsorption mechanism,values of inhibition efficiency increase with temperature (Ebenso, 2003a, b, 2004). Comparing values of the inhibition efficiencies obtained from the three methods (Table 2), it is seen that the values obtained at 303 K are comparable at all the concentrations studied.

Thermodynamics and adsorption considerations

In order to calculate the activation energy (E_a) for the corrosion reaction of mild steel in the absence and presence of various concentrations of EEPG, the Arrhenius equation was used and the values of E_a calculated are recorded in Table 3 and was found to range from 58.9481 to 71.0810 KJ/mol. These values are larger than the value for the blank (34.567 KJ/mol) confirming that EEPG retards the corrosion of mild steel in H_2SO_4.

The heat of adsorption (Q_{ads}) of EEPG on the surface of mild steel has been calculated using equation 7 (Ebenso, 2003a, b, 2004; Umoren et al., 2006a, b, 2007).

$$Q_{ads} = 2.303R\left[\log\frac{\theta_2}{1-\theta_2} - \log\frac{\theta_1}{1-\theta_1}\right] x \frac{T_1 T_2}{T_2 - T_1} kJmol^{-1} \quad (7)$$

Values of Q_{ads} calculated through equation 7 are recorded in Table 3. These values are negative and ranged from -26.4744 to -62.6459 KJ/mol indicating that the adsorption of the extract is exothermic (Ebenso, 2003a, b, 2004; Bhajiwala and Vashi, 2001).

Values of free energy of adsorption of EEPG were calculated using equation 8.

$$\Delta G_{ads} = -2.303RT \log (55.5 K) \quad (8)$$

where KC = $\theta/(1 - \theta)$. C is the concentration of the inhibitor. Calculated values of ΔG_{ads} were negative and ranged from - 5.8193 to -14.5648 KJ/mol indicating that the adsorption of the extract is spontaneous and that the mechanism of adsorption is physical adsorption (ΔG_{ads} <

Table 3. Values of thermodynamic parameters for adsorption of EEPG on the surface of mild steel.

Concentrations of EEPG (g/l)	E_a (KJ/mol)	Q_{ads} KJ/mol)	ΔG_{ads} (KJ/mol)
Blank	34.56	-	-
0.1	58.95	-32.87	-5.82
0.2	57.22	-26.47	-7.86
0.3	60.63	-40.73	-10.62
0.4	67.08	-62.65	-14.00
0.5	71.08	-52.80	-14.56

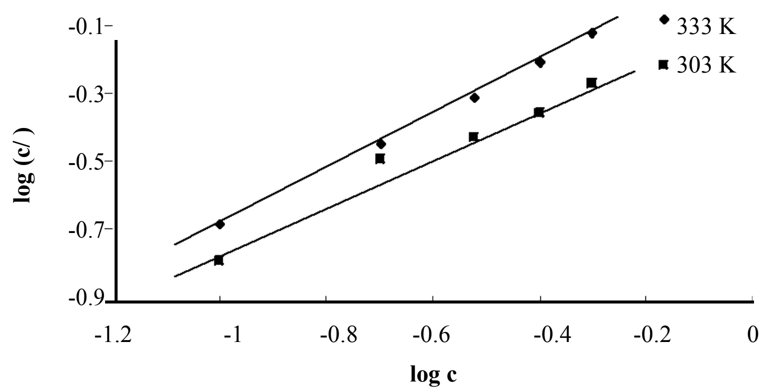

Figure 4. Langmuir isotherm for the adsorption of ethanol extract of *Piper guinensis* (EEPG) on the surface of mild steel

40 KJ/mol) (Ebenso, 2003a, b, 2004; Bhajiwala and Vashi, 2001; Bilgic and Sahin, 2001).

Adsorption isotherms are very important in determining the mechanism of corrosion reactions. The most frequently used isotherms are Langmuir, Frumkin, Hill de-Boer, Parsons, Temkin, Flory-Huggin, Freundlich, Dhar-Flory-Huggin, Kinetic/Thermodynamic model of El-Awady et al. and Bockris-Swinkels. All these isotherms are of the general form:

$$f(\theta, x)\exp(-2a\theta) = KC \qquad (9)$$

where f(θ, x) is the configurational factor which depends upon the physical model and the assumptions underlying the derivation of the isotherm, θ the surface coverage, C, the inhibitor concentration in the electrolyte, x the size factor ratio, a the molecular interaction parameter and K the equilibrium constant of the adsorption process. The degree of surface coverage ( ) was evaluated from the weight loss measurements.

In this study, Langmuir adsorption isotherm was found to be suitable for the experimental findings and has been used to describe the adsorption characteristic of this inhibitor. Assumptions of Langmuir adsorption isotherm is expressed in equation 10 below (Shockry et al., 1998);

$$C/\theta = 1/k + C \qquad (10)$$

where k is the equilibrium constant of adsorption. By plotting values of log C/θ versus log C, (Figure 4) a linear plot was obtained indicating that the adsorption of the inhibitor is consistent with the assumptions of Langmuir adsorption isotherm and the slopes obtained are close to unity. Also, the applicability of Langmuir adsorption isotherm to the adsorption of EEPG on the surface of mild steel indicates that there is no interaction between the adsorbate and adsorbent (Ashassi-Sorkhabi et al., 2004). The parameters derived from Langmuir adsorption isotherms for *P. guinensis* (EEPG) (obtained from weight loss measurements) are given in Table 4. It is seen that the Langmuir adsorption isotherm is best applicable at 303 K (R^2 = 0.9956). Table 5 shows the phytochemical constituents of EEPG. It shows presence of saponins, terpenes, tannins, flavonoids, alkaloids and cardiac glycosides. Daglip (2004) also reported the presence of piperine, pipernoaline, guineensine, alkaloids and isobutyl amide of 11-(3,4 methylenedioxyphenyl) undeca -2, 4, 10-trienoic acid. Adgeh (1989), Gbenwonyo et al. (1993) and Su and Hovart (1981) also reported that amide olifinic, or alkyl isobutylamines compounds (pipe-rine, tricostacine, peepulidin, piplartin and trichonine which are present in the plant are responsible for the insecticidal effect of the plant product. All these com-pounds combine to cause corrosion inhibition. Figures 5 and 6 show the IR spectrum of the corrosion product in the absence and presence of ethanol extract of *P. guineensis* respectively. Figure 7 shows the IR spectrum of ethanol

Table 4. Langmuir adsorption parameters and free energy of adsorption of ethanol extract of *Piper guinensis* (EEPG) on the surface of mild steel.

Langmuir	Temperature (K)	log K	slope	ΔG_{ads} (KJ/mol)	R^2
	303	0.05	0.71	-11.80	0.9956
	313	0.11	0.80	-10.41	0.9878

Table 5. Phytochemical constituents of ethanol and aqueous extracts of *Piper guineensis* (EEPG).

Phytochemical constituents	*Piper guineensis*	
	Aq	Et
Saponins	-	+++
Terpenes	+	+++
Tannins	-	++
Flavonoid	-	++
Phlobatannins	-	-
Anthraquinones	-	-
Cardiac glycoside	-	+++
Alkaloids	-	+++

**Et = ethanol extract, Aq = Aqueous extract, +++ = highly present, ++ = moderately present, - = absent or presence in negligible quantity

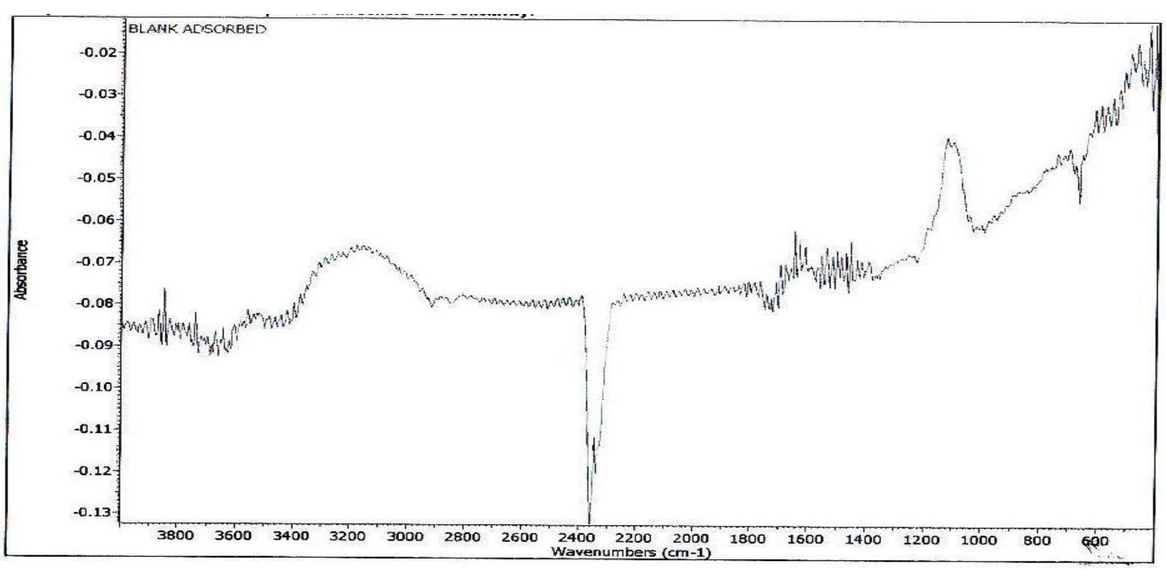

Figure 5. IR spectrum of the corrosion product of mild steel in 0.1 M H_2SO_4 (without inhibitor).

ethanol extract of *P. guineensis* adsorbed on / in combination with mild steel. From the figures, the wavelengths where adsorption occurred were deduced and are recorded in Table 6. Comparing Figures 6 and 7, it was found that the –OH stretch was shifted from 3469.22 to 3434.77 cm^{-1}, the N-H bend was slightly shifted from 1642.64 to 16131.98 and the C-O stretch was shifted from 1132.44 to 1126.50 cm^{-1} indicating that there is interaction between *P. guineensis* extract and Fe in the mild steel and that these functional groups are involved in the formation of bond with Fe in mild steel (Rajappa et al., 2008).

Conclusion

Ethanol extract of *P. guinensis* (EEPG) acted as an inhi-

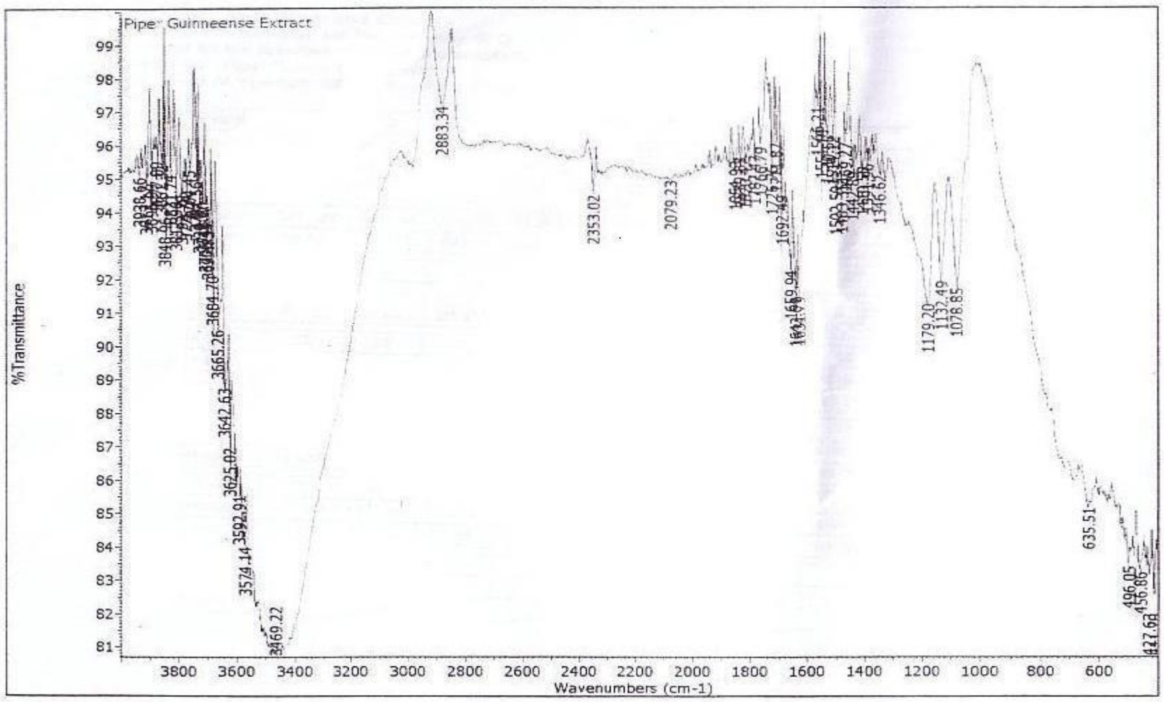

Figure 6. IR spectrum of ethanol extract of *Piper guineensis*.

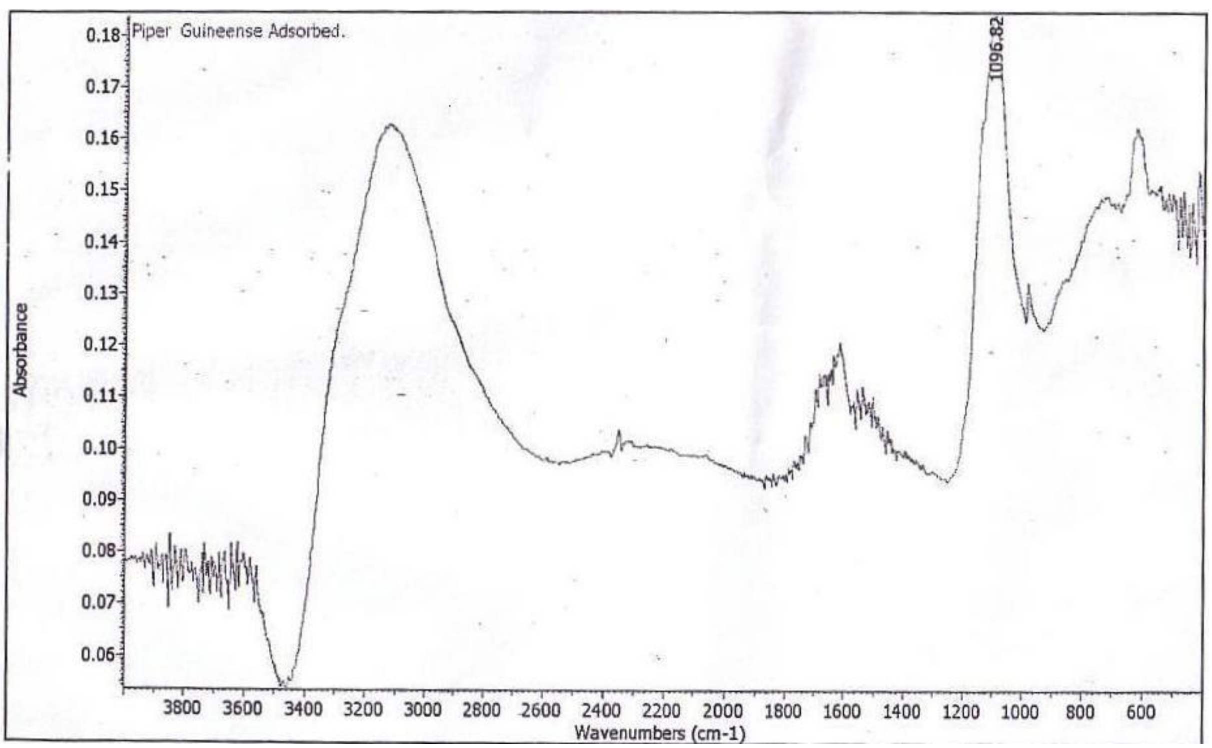

Figure 7. IR spectrum of the corrosion product in the presence of ethanol extract of *Piper guineensis*.

bitor for the corrosion of mild steel in H_2SO_4. The compound exerts its inhibitive properties by being adsorbed spontaneously on the surface of mild steel. The adsorption characteristics of the compound have been found to

Table 6. Frequencies and peaks of adsorption of IR by ethanol extract of Piper guineensis (EEPG).

Ethanol extract			**Ethanol extract**		
Frequency (cm^{-1})	**Height (cm)**	**Assignment**	**Frequency (cm^{-1})**	**Height (cm)**	**Assignment**
3592.91	85.480	O-H stretch	1566.21	97.114	C=C stretch, NO_2-assym stretch
3574.14	83.968	O-H stretch	1551.19	96.438	“
3469.22	80.690	O-H stretch	1530.58	96.268	“
2883.34	97.148	C-H stretch	1483.35	94.808	C-C stretch (in ring)
			1469.27	96.057	C-C stretch (in ring)
1854.93	95.487	C-H finger print region	1442.89	95.177	C-C stretch (in ring)
1839.33	95.589	“	1410.58	95.327	C-C stretch (in ring), -OH bend
1820.47	95.534	”	1391.96	95.415	C-H scissoring and bending
1787.47	95.654	“	1346.62	95.082	NO_2-sym stretch
1766.79	95.895	“	1179.20	91.226	C-H wag (-CH_2X)
1726.76	95.347	α,β unsaturated aldehyde, ketone	635.51	85.120	—C≡C—
1711.87	96.022	Weak overtone, aromatic	1132.49	91.908	“
1692.49	94.467	Weak overtone, aromatic	**Corrosion product in the presence of the extract**		
1659.94	92.240	C=C stretch	**Frequency (cm^{-1})**	**Height (cm)**	**Assignment**
1642.64	91.397	“	3434.77	16.512	-OH stretch
1631.79	91.455	C-H finger print region	1631.98	55.955	C=O stretch
			1126.50	92.905	C-N stretch

obey physical adsorption mechanism and follows Langmuir adsorption isotherm.

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