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Corrosion Inhibition and Adsorption Behaviour of Extracts from *Piper guineensis* on Mild Steel Corrosion in Acid Media

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The inhibitive action of acid extracts from *Piper guineensis* (PG) on mild steel corrosion in HCl and H_2SO_4 solutions was investigated by gravimetric and gasometric techniques at 30 °C and 60 °C. The results show PG to be a good inhibitor in both acid solutions. PG exhibited better inhibition efficiency (*IE*) in HCl than in H_2SO_4 solution and is attributed to the stronger adsorption of Cl^- on the metal surface enabling better synergism between Cl^- and the protonated inhibitor for improved protection. *IE* increased with temperature for PG extract in HCl solutions and decreased with temperature for PG extract in H_2SO_4 solutions. The mechanism of adsorption proposed for PG extract is chemisorption in HCl and physisorption in H_2SO_4 solutions. The adsorption of PG obeys Langmuir isotherm at low temperature.

Keywords: Mild steel; *Piper guineensis* extract; Weight loss; Hydrogen evolution; Corrosion inhibition; Adsorption

1. INTRODUCTION

Corrosion inhibition of mild steel using extract from plant sources have been widely studied in different media [1-10]. The main thrust in this line of research has been the demand by the oil and gas industry for inexpensive, “green” or “eco-friendly” and non-toxic materials which will meet the requirements for sustainable development of the processes and operations. Acids mainly HCl and H_2SO_4 are used in oil and gas well acidization, acid pickling of iron and steel and for general cleaning and processing in chemical and allied industries [11]. The aggressive nature of these acid solutions necessitates the use of inhibitors to reduce the corrosive damage on metals and alloys. Low-cost, environmental and practical benefits of plant extracts make them the preferred choice for corrosion protection.

The inhibitive action of plant extracts has been attributed to the presence of complex organic molecules such as alkaloids, tannins, nitrogen bases, proteins, carbohydrates and hydrolysis products [4, 9]. These phytochemical constituents function through adsorption on the metal/corrodent interface. The main adsorption sites in these organic compounds are nitrogen, sulphur or oxygen atoms present in these compounds [12-14]. In addition, the availability of a π electron system present in triple or conjugated double bonds or aromatic rings in the molecular structures of these compounds play a vital role in their adsorption and formation of co-ordinate bond with the metal surface [15].

Piper guineensis commonly referred to as West African pepper or Ashanti pepper is a spice (dried fruit and leaves) and belongs to the family *Piperaceae*. It grows as climbing vines and is native to the tropical regions of Central and West Africa . Aside from the culinary uses of *Piper guineensis*, it is utilised for medicinal, agricultural and aquacultural purposes. The use of phytochemicals from extracts of *Piper guineensis* has been applied in the treatment of sickle cell diseases [16]. Its seeds in combination with *Pterocapus osum* stem, *Eugenia caryophyllum* fruit and *Sorghum bicolour* leaves were reported to possess anti-sickling properties [17]. Extracts of *Piper guineensis* possess some level of antibacterial activities against *E. coli* and *S. aureus* with therapeutic benefits [18]. The leaves have been used in the treatment of bronchitis, cough, intestinal diseases and rheumatism [19]. It has also shown potential as a fungicide and pesticide in the control of mold fungus and maize weevil (*Sitophilus zeamaise*) in stored maize seeds [20, 21] and in the control of monogenean parasites of goldfish [22]. This versatile plant has equally found application in corrosion inhibition studies reported by Ebenso et al. [23] where ethanol extracts of *Piper guineensis* leaves showed corrosion inhibition in mild steel immersed in H_2SO_4 solution. In another report, ethanol extract of the plant was used to study its corrosion inhibiting effect on low-carbon steel in HCl and H_2SO_4 solutions in addition to determining the biocidal effect of the plant extract obtained from both aqueous and non-aqueous solvents on corrosion-associated sulfate-reducing bacteria [24].

In view of our continued interest on the application of plant extracts for metal corrosion control, we report herein investigation into the adsorption and corrosion inhibitive behaviour of acid extract of *Piper guineensis* on mild steel in HCl and H_2SO_4 solutions using weight loss and gasometric techniques. The influence of temperature on the adsorption behaviour of the extract on mild steel surface and the mechanism of adsorption is discussed. The comparison of inhibition performance in HCl and H_2SO_4 solutions is also discussed and the effect of the acid anions in understanding the inhibition behaviour of PG in these two acid systems is highlighted.

2. EXPERIMENTAL

2.1. Materials

Mild steel specimens used for the study were of composition (wt. %); C (0.19), Si (0.26), Mn (0.64), P (0.06), Ni (0.09), Cr (0.08), Cu (0.27) and the balance Fe. The specimens were of dimension

(4.0 × 5.0 × 0.08) cm and (1.8 × 5 × 0.08) cm for weight loss and gasometric measurements respectively. Prior to measurements, the mild steel specimens were mechanically ground with a series of SiC paper up to 600 grit size, degreased in absolute ethanol and dried in acetone.

2.2. Acid extraction and preparation of inhibitor solutions

Piper guineensis (PG) leaves were obtained from a local market in Calabar, Nigeria and were authenticated at the Herbarium of the University of Calabar. The leaves were oven dried below 40 °C and ground into powder. 4.0 g of the powder was digested for 24 h in separate 1 litre solutions of 1 M HCl and 1 M H_2SO_4 solutions for weight loss measurements and 4.0 g in separate 1 litre 5 M HCl and 5 M H_2SO_4 solutions for hydrogen evolution measurements. After 24 h, the solutions were filtered and the resulting solutions stored as the stock solutions (4.0 g L^{-1}). The stock solutions of the plant extract were used to prepare different concentrations of inhibitor (PG) solutions ranging from (0.1 - 4.0) g L^{-1}.

2.3. Phytochemical screening

Phytochemical screening was carried out on extracts derived from HCl and H_2SO_4 acid digestion of the leaves of *Piper guineensis* using chemical tests described by Harbone [25] and Trease and Evans [26]. The compounds tested for included alkaloids, saponins, flavonoids, polyphenols, anthraquinones, cardiac glycosides and tannins.

2.4. Weight loss and Gasometric measurements

These measurements were carried out on the mild steel specimens following procedures previously described [27]. In weight loss measurements, the specimens were pre-weighed and suspended in 250 ml of the test solutions (1 M HCl and 1 M H_2SO_4) with and without different concentrations of the plant extract with the help of glass hooks and rods at 30 ± 1 °C. The specimens were retrieved at 24 h intervals, carefully washed in 20% NaOH solution containing 200 g L^{-1} of zinc dust, rinsed in distilled water, air dried after dipping in acetone and re-weighed [27, 28]. The procedure was repeated for upwards of 7 days. The weight loss was determined as the difference in weight of the mild steel specimens before and after immersion in different test solutions.

The evolution of hydrogen gas from the cathodic reaction of mild steel corroding in aqueous media is proportional to the corrosion rate [29]. The measurements were performed at temperatures of 30 ± 1 °C and 60 ± 1 °C in test solutions of 5 M HCl and 5 M H_2SO_4 with and without different concentrations of PG extract. The volume of hydrogen gas evolved from the reaction vessel was monitored by the volume changes in the level of the paraffin oil in the burette at one minute interval. The rate of evolution of hydrogen gas R_H, (ml cm^{-2} min^{-1}) was determined from the slope of the graph of volume of gas evolved per surface area (ml cm^{-2}) against immersion time (min). The inhibition efficiency *IE*, was determined using;

$$IE = \frac{R_{\mathrm{Ho}} - R_{\mathrm{Hi}}}{R_{\mathrm{Ho}}} \times 100 \qquad (1)$$

where R_{Ho} and R_{Hi} are the rates of hydrogen evolution per surface area in the absence and presence of the inhibitor molecules respectively. Weight loss and hydrogen evolution tests were run more than twice and the data showed good reproducibility. The data presented are therefore an average of at least two measurements.

3. RESULTS AND DISCUSSION

3.1. Weight loss data

Figure 1a and 1b show the variation of weight loss per surface area with time of mild steel in uninhibited and inhibited 1 M HCl and 1 M H_2SO_4 solutions respectively at 30 °C. The weight loss per surface area was observed to increase with increase in immersion time and decrease with increase in the concentration of the inhibitors in both acid systems. The plots also show a higher rate of weight loss per surface area obtained for specimens tested in PG-H_2SO_4 solutions compared with specimens tested in PG-HCl solutions. Table 1 records this observation in numerical values of corrosion rate (mg cm^{-2} h^{-1}) obtained from the slopes of the plots as well as *IE*, determined using Eq. 1, where R_{Ho} and R_{Hi} are replaced by R_o and R_i and represent the corrosion rates in the absence and presence of the inhibiting molecules respectively. The inhibition efficiency increases with increasing inhibitor concentration for both inhibitor-acid systems. The results show that PG effectively restrains the acid corrosion of mild steel in the two acid environments and that increased adsorption and consequently an increasing surface coverage of the inhibitor molecules on the metal surface may occur with increasing inhibitor concentration. A significant 10.5-fold increase in the inhibition efficiency was observed for PG in H_2SO_4 solutions between 0.1 g L^{-1} and 4.0g L^{-1} concentration compared with a 1.3-fold increase over the same concentration range for PG in HCl solutions. *IE* values obtained at maximum inhibitor concentration studied were about 93% and 77% in 1M HCl and 1 M H_2SO_4 solutions respectively.

The results for PG-H_2SO_4 system show similar trend of increasing inhibition efficiency with increasing inhibitor concentrations reported by Ebenso and co-workers [23] for PG on mild steel in 2.5 M H_2SO_4 solution. The inhibition efficiency results obtained from gravimetric measurements by Oguzie and co-workers [24] show higher inhibition performance of PG on low-carbon steel in 0.5 M H_2SO_4 than in 1 M HCl solutions which is contrary to our results. Our test solutions have H^+ ion concentration for H_2SO_4 twice as much as HCl and its effect in facilitating the corrosion process will be more than a 1:1 ratio of H^+ ion concentration as in 1 M HCl and 0.5 M H_2SO_4 solutions. Together with competition for adsorption of inhibitor molecules, the inhibition performance of PG in H_2SO_4 may be affected.

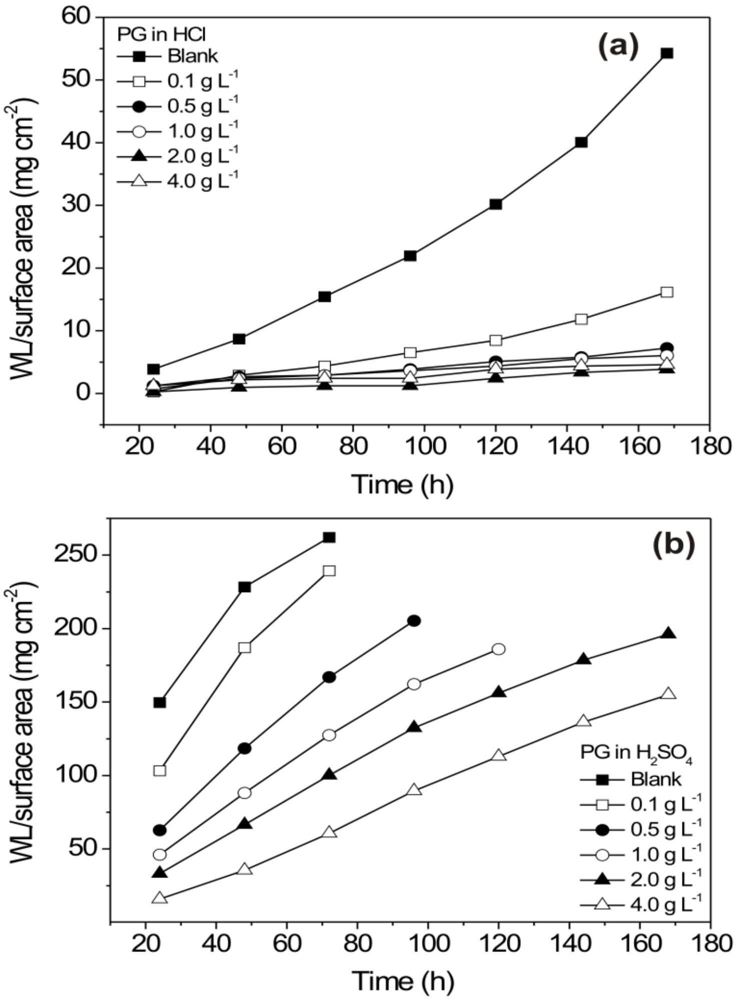

Figure 1. Variation of weight loss per surface area with time for mild steel in (a) 1 M HCl and (b) 1 M H_2SO_4 solutions containing PG at 30 °C.

Table 1. Corrosion rate and inhibition efficiency values for mild steel in 1 M HCl and 1 M H_2SO_4 solutions in the absence and presence of PG (from weight loss measurements).

System	Corrosion rate (mg cm^{-2} hr^{-1})	Inhibition efficiency (%)
1 M HCl (Blank)	0.340	--
0.1 gL^{-1} PG + 1 M HCl	0.104	69.51
0.5 gL^{-1} PG + 1 M HCl	0.040	88.40
1.0 gL^{-1} PG + 1 M HCl	0.035	89.66
2.0 gL^{-1} PG + 1 M HCl	0.025	92.62
4.0 gL^{-1} PG + 1 M HCl	0.024	93.04
1 M H_2SO_4 (Blank)	3.604	--
0.1 gL^{-1} PG + 1 M H_2SO_4	3.341	7.28
0.5 gL^{-1} PG + 1 M H_2SO_4	2.320	35.63
1.0 gL^{-1} PG + 1 M H_2SO_4	1.768	50.95
2.0 gL^{-1} PG + 1 M H_2SO_4	1.391	61.41
4.0 gL^{-1} PG + 1 M H_2SO_4	0.839	76.73

3.2. Gasometric data

The volume of hydrogen gas evolved from cathodic sites on the corroding mild steel surface immersed in PG-HCl and PG-H_2SO_4 solutions was measured with time at different inhibitor concentrations and at 30 °C and 60 °C. A higher corrodent concentration than that used in weight loss measurements is employed in the gasometric technique as such concentrations give reasonably measureable values.

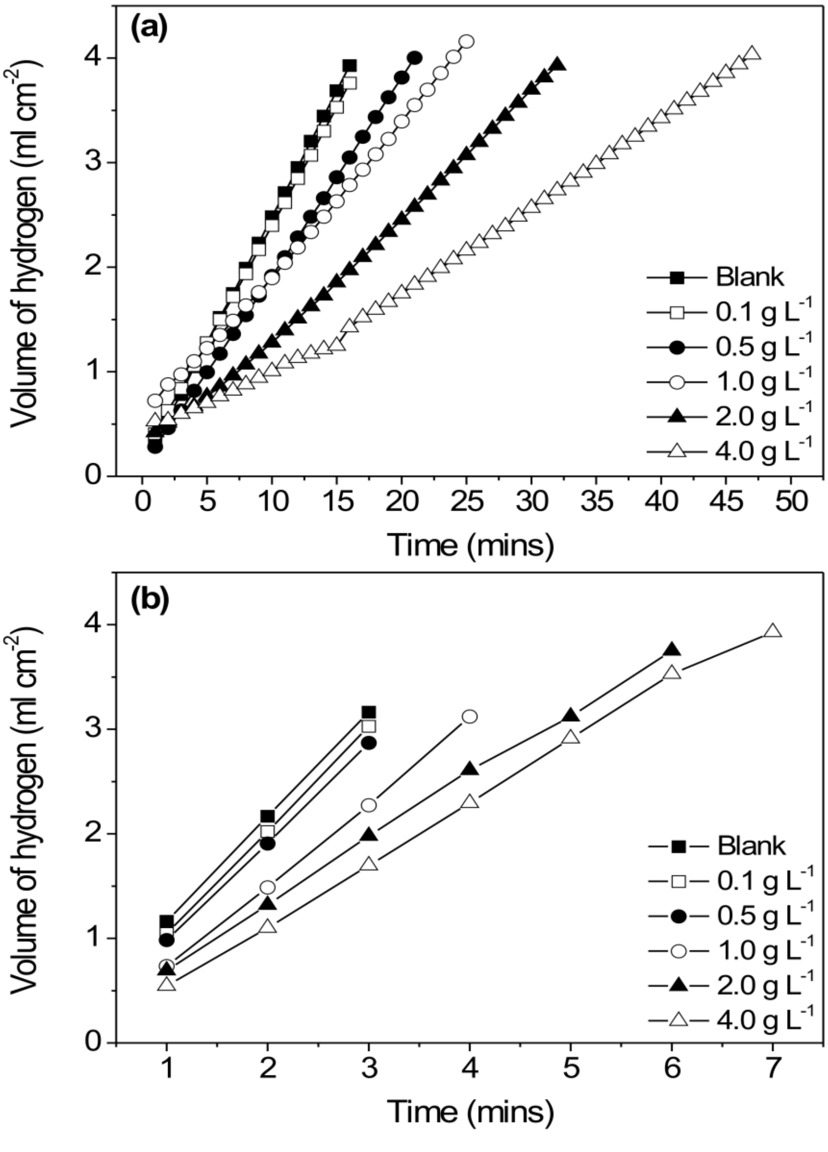

Figure 2. Variation of hydrogen evolved per surface area with time for mild steel in 5 M H_2SO_4 solutions containing PG at (a) 30 °C and (b) 60 °C.

The plot of hydrogen volume per unit area with immersion time for mild steel corrosion in 5 M H_2SO_4 solution containing PG is shown in Figure 2a and 2b for tests carried out at 30 °C and 60 °C respectively. The results show an increasing volume of hydrogen gas with time and a decreasing rate of hydrogen evolution per surface as the concentration of PG extract increases in the acid solution at both temperatures studied. A similar result was obtained for mild steel corrosion in 5 M HCl solution containing PG (data not shown). The observed trend is consistent with data from weight loss measurements and can be ascribed to adsorption of inhibitor molecules on metal surface and increasing surface coverage as the concentration of PG in the acid solution increases. The resultant effect is the reduction in corrosion occurring on the metal surface as inhibitor molecules act as a barrier separating the metal surface from the medium [30, 31]. Table 2 shows the trend of the rate of hydrogen evolution with inhibitor concentration. It also shows an increasing rate of hydrogen evolution as the temperature of the inhibitor-corrodent solution increases from 30 °C to 60 °C in both acid environments.

3.3. Effect of PG extracts concentration and temperature on inhibition efficiency

Figure 3 shows the change in the inhibition efficiency with inhibitor concentration for both acid systems and at the two temperatures studied. The inhibition efficiency of PG in HCl and H_2SO_4 solutions increases with inhibitor concentration at both 30 °C and 60 °C. A relatively small increase in the inhibition efficiency is observed with rise in temperature to 60 °C for mild steel corrosion in PG-HCl solutions, whereas the inhibition efficiency decreases as the temperature increases to 60 °C for PG in H_2SO_4 solution.

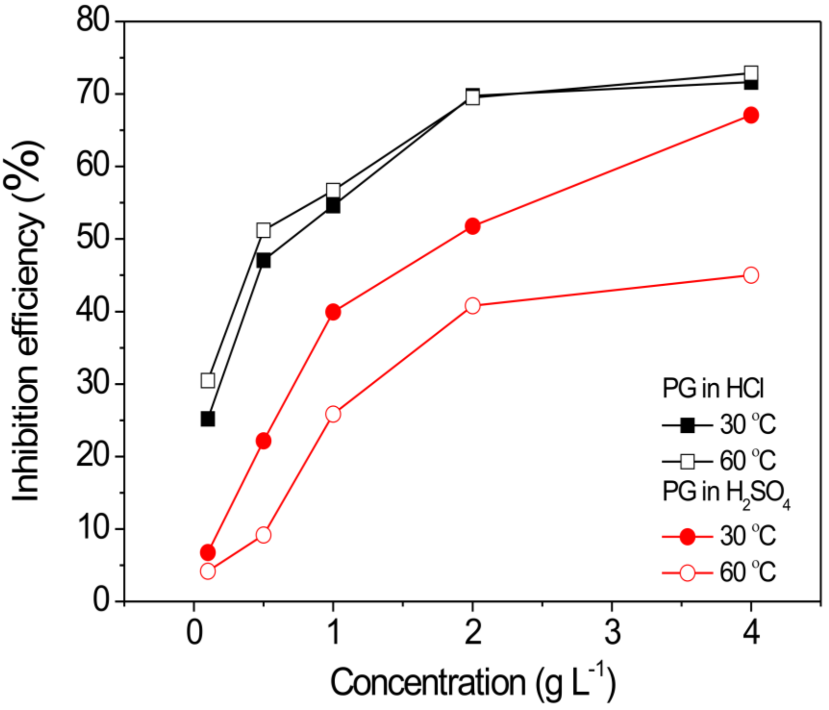

Figure 3. Variation of inhibition efficiency with extract concentration for mild steel in 5 M HCl and 5 M H_2SO_4 solutions containing PG at 30 °C and 60 °C.

The results show that PG is more effective in HCl solutions and agrees with the data obtained from weight loss measurement. It can be inferred from the dependence of *IE* with temperature that the mode of adsorption of PG in HCl solution is by chemical adsorption, whereas it is by physical adsorption for PG in H_2SO_4 solution.

PG adsorption decreases with increasing HCl and H_2SO_4 concentrations as seen by the decreasing inhibition efficiency values at 30 °C (Table 1 and Table 2). The ionic strength of solutions influences dissociation and solubility of adsorbed species and invariably the amount adsorbed, the adsorption layer thickness, expansion coefficient of the adsorbed species and the surface charge density [32]. The observed decrease in the PG adsorption may results from changes in dissociation degree of the functional groups on the inhibitor molecules and the specific conformation of the molecular structures at high acid concentrations [32].

Table 2. Kinetic and activation parameters for mild steel in 5 M HCl and 5 M H_2SO_4 solutions in the absence and presence of PG (from hydrogen evolution measurements).

System	Rate of hydrogen evolution		Inhibition efficiency		Activation energy, E_a	Heat of Adsorption, Q_{ads}
	(ml cm^{-2} min^{-1})		(%)		(kJmol^{-1})	(kJmol^{-1})
	30°C	60°C	30°C	60°C		
Blank	0.011	0.172			77.52	
0.1 gL^{-1} PG + 5 M HCl	0.008	0.119	25.21	30.49	75.47	7.36
0.5 gL^{-1} PG + 5 M HCl	0.006	0.084	47.06	51.22	75.24	4.66
1.0 gL^{-1} PG + 5 M HCl	0.005	0.074	54.62	56.71	76.19	2.36
2.0 gL^{-1} PG + 5 M HCl	0.003	0.052	69.75	69.51	77.76	-0.31
4.0 gL^{-1} PG + 5 M HCl	0.003	0.047	71.63	72.87	76.27	1.72
Blank	0.240	1.050			41.29	
0.1 gL^{-1} PG + 5 M H_2SO_4	0.224	1.006	6.75	4.19	42.05	-14.11
0.5 gL^{-1} PG + 5 M H_2SO_4	0.187	0.953	22.14	9.18	45.60	-28.93
1.0 gL^{-1} PG + 5 M H_2SO_4	0.144	0.779	39.93	25.85	47.18	-18.05
2.0 gL^{-1} PG + 5 M H_2SO_4	0.116	0.622	51.76	40.80	47.02	-12.39
4.0 gL^{-1} PG + 5 M H_2SO_4	0.079	0.577	67.09	45.04	55.64	-25.50

3.4. Adsorption and thermodynamic considerations

The inhibitive action of organic components in plant extracts is attributed to their adsorption on the metal surface. The adsorbed layer acts as a barrier for mass and charge transfer leading to a reduction in the rate of corrosion of the metal. The fraction of the surface covered by the adsorbed molecules θ, is an indication of the effectiveness of the adsorbed species and is directly proportional to the inhibition efficiency. Thus, θ is calculated using the expression, $\theta = IE/100$ [33]. Adsorption isotherms that describe the behaviour of adsorbed species examine the variation of θ with concentration of the organic species. The obtained θ values were applied to different adsorption isotherm equations and the Langmuir adsorption isotherm fitted best. The Langmuir adsorption isotherm is given as;

$$\frac{c}{\theta} = \frac{1}{K} + c \tag{2}$$

where c is the inhibitor concentration, K the equilibrium constant and θ as earlier defined above. Figure 4 shows Langmuir adsorption isotherm plots for PG in HCl and H_2SO_4 solutions at 30 ºC and 60 ºC. The inset is a graph of Langmuir plots for data obtained from weight loss measurements. The plots are near linear with an exception for PG in H_2SO_4 at 60 ºC.

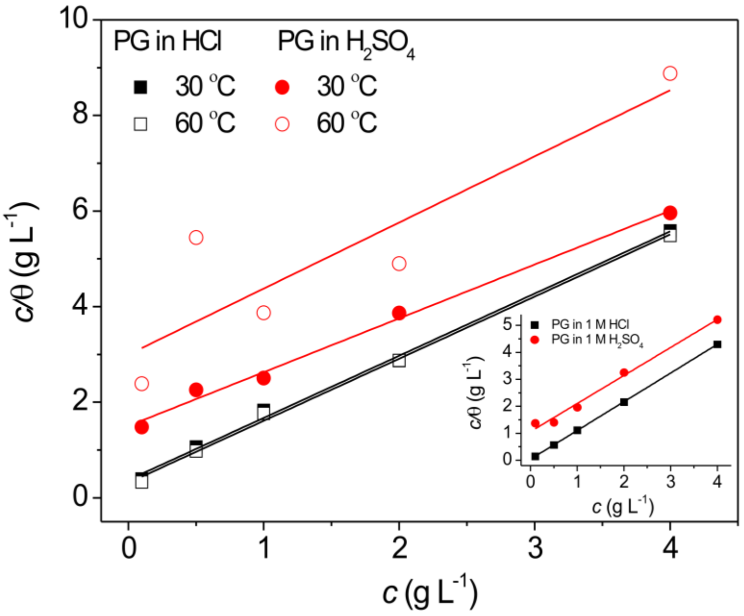

Figure 4. Langmuir adsorption isotherms for PG on mild steel in 5 M HCl and 5 M H_2SO_4 solutions at 30 °C and 60 °C (data from gasometric measurements). Inset: Langmuir isotherm plots using data from weight loss measurements.

The values of K obtained from the intercept of the isotherm plots, the slope and the corresponding R^2 values for the linear fits of the plots are presented in Table 3. A slight deviation of the slope from unity was observed in some cases. The deviation suggests interactions between adsorbed molecules on the metal surface as well as changes in the adsorption heat with increase in surface coverage [34]. A modified Langmuir isotherm (Eq. 3) that considers the above factors was proposed by Villamil et al. [35] and reported elsewhere [36, 37] and is given as;

$$\frac{c}{\theta} = \frac{n}{K} + nc \tag{3}$$

where c, θ and K are as earlier defined and n, a numerical value representing the slope in the Langmuir plot. It is known that K describes the adsorption strength of an inhibitor onto the metal surface. The value of K is seen to increase as the temperature rises from 30 °C to 60 °C in PG-HCl/metal system suggesting that the inhibitors are chemically adsorbed on the surface of the mild steel. The opposite trend is observed for PG-H_2SO_4/metal system indicative of physical adsorption of the inhibitor molecules on the metal surface. The adsorption characteristic of PG on the mild steel surface at 60 °C in H_2SO_4 solutions clearly shows a departure from a Type I adsorption isotherm and assuming more a Type V adsorption isotherm (Figure 5). The surface energy conditions of the metal can be said to change with rise in temperature making the adsorption to shift towards a multilayer coverage at low inhibitor concentration. As the inhibitor concentration increases, a flat region appears indicative of monolayer coverage.

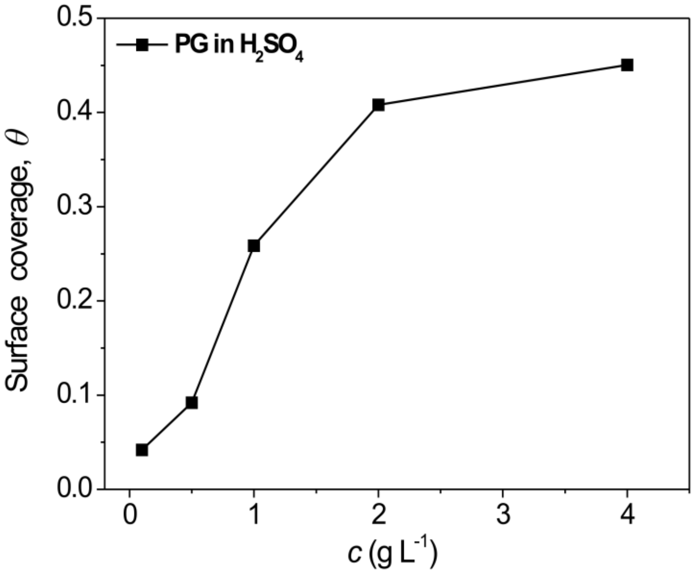

Figure 5. Type V adsorption isotherm depicting the adsorption characteristic of PG on mild steel surface in H_2SO_4 solutions at 60 °C.

The equilibrium constant of adsorption *K*, obtained from the intercept of the Langmuir plots is related to the free energy of adsorption $\Delta G^{\circ}_{\text{ads}}$ as;

$$\Delta G^{\circ}_{\text{ads}} = -2.303RT\log(55.5K) \tag{4}$$

where the value 55.5 is the molar concentration of water in solution, *R* is the universal gas constant, and T is the absolute temperature. Values of $\Delta G^{\circ}_{\text{ads}}$ calculated using Eq. 4 are presented in Table 3. The mean value of $\Delta G^{\circ}_{\text{ads}}$ for PG-HCl system is -15.62 kJ mol^{-1}, while that for PG-H_2SO_4 system is -9.48 kJ mol^{-1}. The negative values obtained indicate that the inhibitor adsorption on mild steel surface is spontaneous. Typical values of $\Delta G^{\circ}_{\text{ads}}$ up to -20 kJ mol^{-1} are consistent with the electrostatic interaction between the charged molecules and the charged metal surface (physical adsorption), while values about -40 kJ mol^{-1} or more negative are characteristic of chemical adsorption which involves charge sharing or transfer from the inhibitor molecules to the metal surface resulting in a coordinate type bond [38, 39]. Though the absolute values calculated for both inhibitor-acid systems reflect physical adsorption for the inhibitor molecules, it cannot be conclusive as other parameters namely the activation energy E_a and the heat of adsorption Q_{ads} all point to chemisorption and physisorption mechanisms for PG-HCl and PG-H_2SO_4 systems respectively. Furthermore, ΔG^o_{ads} values for PG-HCl system are relatively higher than those of PG-H_2SO_4 system.

Table 3. Adsorption parameters of PG on mild steel in 5 M HCl and 5 M H_2SO_4 solutions.

Inhibitor solution	Temperature (°C)	Equilibrium constant, K	ΔG^o_{ads} (kJmol^{-1})	Slope	Coefficient of determination, R^2
PG in 5 M HCl	30 °C	3.50	-13.28	1.30	0.99
PG in 5 M HCl	60 °C	4.17	-15.08	1.30	0.99
PG in 5 M H_2SO_4	30 °C	0.75	-9.39	1.13	0.99
PG in 5 M H_2SO_4	60 °C	0.46	-8.98	1.38	0.73
PG in 1 M HCl[1]	30 °C	27.93	-18.51	1.06	0.99
PG in 1 M H_2SO_4[1]	30 °C	0.98	-10.07	1.04	0.99

1 - data obtained from weight loss measurements

The values of the activation energy E_a (kJ mol^{-1}), shown in Table 2 were calculated using the Arrhenius equation of the form;

$$\log \frac{R_{H2}}{R_{H1}} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{5}$$

where R_{H1} and R_{H2} are the corrosion rates at temperatures T_1 and T_2 respectively. The data shows that E_a values in PG-HCl solutions are lower than those in free acid solution indicative of a chemical adsorption mechanism. For PG in H_2SO_4 solutions, E_a values are higher than those in the free acid solution indicating that the inhibitor molecules lower the inhibition efficiency at higher temperatures [40, 41], reflective of a physical type adsorption mechanism. The heat of adsorption Q_{ads} (kJ mol^{-1}), was determined using the expression;

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \left(\frac{T_1 \times T_2}{T_2 - T_1}\right) \tag{6}$$

where θ_1 and θ_2 represent the degree of surface coverage at temperatures T_1 and T_2 respectively. The calculated Q_{ads} values for PG-HCl system generally show positive values whereas they are negative in all cases for PG-H_2SO_4 system (Table 2). The positive Q_{ads} values (endothermic adsorption process) indicate enhanced adsorption and consequently increasing inhibition efficiency with rise in temperature consistent with chemical adsorption process. Negative Q_{ads} values indicate an exothermic adsorption process. The exothermic process implies either physical or chemical adsorption and is distinguished by considering the absolute values of the heat of adsorption. Energy values typically lower than 40 kJ mol^{-1} is suggestive of physical adsorption [42]. The absolute values of the heat of adsorption are lower than 40 kJ mol^{-1} which further affirms physical adsorption of PG on the surface of the metal in PG-H_2SO_4 system.

3.5. Mechanism of inhibition

Phytochemical analysis carried out reveal the presence of polyphenols cardiac glycosides and tannins. Flavonoids , alkaloids and saponins have also been reported in other literature [23, 24, 43]. The possible reason for the absence of these compounds in our test could be due to the very little amount and/or non-extraction of these compounds using aqueous solutions of HCl and H_2SO_4 such that they are below the analytical detection limit. The organic compounds in PG contain O and N atoms in functional groups such as O-H, N-H, C=O and C-O as well as O-heterocyclic rings in their molecular structures. These properties satisfy the characteristics of corrosion inhibitors; hence it is fitting to say that these compounds are responsible for the observed inhibition of mild steel corrosion in the inhibitor-acid solutions.

The inhibitive action requires knowledge of the inhibitor at the electrode-solution interface. In acid solution, the chemical compounds of PG may become protonated. The surface charge of steel in both HCl and H_2SO_4 solutions is known to be positive [44]. There is the likelihood of the acid anions of Cl^- and SO_4^{2-} to be specifically adsorbed creating excess negative charge towards the solution. This favours the adsorption by electrostatic interactions of the protonated inhibitor molecules on the negatively charged metal surface. This can be regarded as synergism existing between the acid anions and the protonated inhibitor molecule. PG exhibited better inhibition behaviour in HCl than in H_2SO_4 solutions, suggesting that the nature of the ions in the acidic solutions may play a role in the adsorption of the inhibitor. Cl^- ions are known to adsorb strongly than SO_4^{2-} ions [45]. Here the concentration of the acid anions is the same (5 M), so any possible influence on adsorption from concentration differences is minimised. It can be adduce that the reason for the higher inhibition performance in HCl than in H_2SO_4 is as a result of an increased protective effect of PG in the Cl^- containing solution due to the stronger adsorption of Cl^- ions to the metal surface and the subsequent electrostatic influence on the inhibitor adsorption. In addition, the reduced contact of SO_4^{2-} with the adsorbed protonated cations may result in a lower adsorption [46]. The adsorption of the protonated molecules in PG can also occur on the mild steel surface by direct interaction of the lone pairs of electrons on O and N with the vacant d-orbitals of Fe [45, 47]. These lone pairs of electrons could also form metal inhibitor complexes with Fe^{2+} ions formed from the anodic dissolution of steel. These complexes may adsorb onto the steel surface through van der Waals force, providing more protection against corrosion.

4. CONCLUSIONS

The extracts from the leaves of PG using aqueous solutions of HCl and H_2SO_4 show reasonably good inhibition efficiencies on the corrosion of mild steel in both HCl and H_2SO_4 solutions. Inhibition efficiency increases with increase in inhibitor concentration in both PG-HCl and PG-H_2SO_4 systems. *IE* increases with rise in temperature for PG-HCl system but decreases with increase in temperature for PG-H_2SO_4 system. The adsorption of PG on mild steel surface from HCl obeys the Langmuir adsorption isotherm at both temperatures studied whereas its adsorption from H_2SO_4 solution is consistent with Langmuir adsorption isotherm at 30 ºC. Chemical adsorption is proposed for the adsorption of PG from HCl while physical adsorption is proposed for PG from H_2SO_4. The adsorption of PG onto mild steel surface is more effective in HCl than H_2SO_4 solutions and is attributed to the enhanced adsorption of Cl^- ions promoting an increased adsorption of protonated inhibitor molecules.

References

1. A. Ostovari, S. M. Hoseinieh, M. Peikari, S. R. Shadizadeh, S. J. Hashemi, *Corros. Sci.* 51 (2009) 1935.
2. U. J. Ekpe, E. E. Ebenso, U. J. Ibok, *J. West Afr. Sci. Assoc.* 37 (1994) 13.
3. P. C. Okafor, E. E. Ebenso, *Pigment. Resin Technol.* 36 (2007) 134 .
4. P. C. Okafor, M. E. Ikpi, I. E. Uwah, E. E. Ebenso, U. J. Ekpe, S. A. Umoren, *Corros. Sci*. 50 (2008) 2310.
5. E.E. Oguzie, *Corros. Sci.* 50 (2008) 2993.
6. A.K. Satapathy, G. Gunasekaran, S.C. Sahoo, K. Amit, R.V. Rodrigues, *Corros. Sci.* 51 (2009) 2848.
7. G. Gunasekaran, L.R. Chauhan, *Electrochim. Acta* 49 (2006) 4387.
8. S. A. Umoren, I. B. Obot, E. E. Ebenso, P. C. Okafor, O. Ogbobe, E. E. Oguzie, *Anti-Corros. Method Mater.* 53 (2006) 277.
9. P. C. Okafor, E. E. Ebenso, U. J. Ekpe, *Int. J. Electrochem. Sci*. 5 (2010) 978.
10. M. A. Quraishi, A. Singh, V. K. Singh, D. K. Yadav, A. K. Singh, *Mater. Chem. Phys*. 122 (2010) 114.
11. L. Garverick (Ed.), Corrosion in the petrochemical industry, ASM International, Ohio, 1994.
12. S. N. Raicheva, B. V. Aleksiev, E. I. Sokolova, *Corros. Sci.* 34 (1993) 343.
13. A. El-Sayed, *J. Appl. Electrochem.* 27 (1997) 193.
14. X. L. Cheng, H. Y. Ma, S. H. Chen, R. Yu, X. Chen, Z. M. Yao, *Corros. Sci.* 41 (1998) 321.
15. B. M. Praveen, T. V. Venkatesha, *Int. J. Electrochem. Sci*. 4 (2009) 267.
16. C. Wambebe, H. Khamofu, J. A. Momoh, M. Ekpeyong, B. S. Audu, O. S. Njoku, E. A. Bamgboye, R. N. Nasipuri, O. O. Kunle, J. I. Okogun, M. N. Enwerem, J. G. Audam, K. S. Gamaniel, O. O. Obodozie, B. Samuel, G. Fojule, O. Ogunyale, *Phytomed.* 8 (2001) 252
17. E. W. Iyamu, E. A. Turner, T. Asakura, *Br. J. Haematol*. 118 (2002) 337.
18. O. C. Nwinyi, N. S. Chinedu, O. O. Ajani, C. O. Ikpo, K. O. Ogunniran, *Afr. J. Food Sci.* 3 (2009) 022.
19. M. A. Sumathykutty, J. M. Rao, K. P. Padmakumari, C. S. Narayanan, *Flavours fragr. J*. 14 (1999) 279.
20. M. O. Onuh, D. K. Madukwe, O. S. Nwosu, *Sci. World J.* 3 (2008) 21.
21. P. G. Udofia, P. J. Udoudoh, A. A. Okon, M. I. Ekanem, *Adv. Nat. Appl. Sci*. 2 (2008) 43.
22. A. P. Ekanem, M. Wang, J. E Simon, A. I Obiekeze, F. Morah, *Phytother. Res.* 18 (2004) 793.
23. E. E. Ebenso, N. O. Eddy, A. O. Odiongenyi, *Afr. J. Pure Appl. Chem.* 2 (2008) 107.
24. E. E. Oguzie, C. E. Ogukwe, J. N. Ogbulie, F. C. Nwanebu, C. B. Adindu, I. O. Udeze, K. L. Oguzie, F. C. Eze, *J. Mater. Sci.* 47 (2012) 3592.
25. J. B. Harbone, Phytochemical Methods: A Guide to Modern Techniques of Plant Analysis, Chapman and Hill, London, 1973.

26. G. E. Trease, W. C. Evans, A Textbook of Pharmacology, Baillier Tidally, London, 1996.
27. U. J. Ekpe, U. J. Ibok, B. I. Ita, O. E. Offiong, E. E. Ebenso, *Mater. Chem. Phys.* 11 (1995) 87.
28. [28] B. I. Ita, O. E. Offiong, *Mater. Chem. Phys*. 48 (1997) 164.
29. P. C. Okafor, U. J. Ekpe, E. E. Ebenso, E. M. Umoren, K. E. Leizou, *Bull. Electrochem.* 21 (2005) 347.
30. S. S. Rehim, O. A. Hazzazi, M. A. Amin, K. F. Khaled, *Corros. Sci.* 50 (2008) 2258.
31. M. Abdallah, E. A. Helal, A. S. Fouda, *Corros. Sci.* 48 (2006) 1639.
32. S. Chibowski, E. O. Mazur, J. Patkowski, *Mater. Chem. Phys.* 93 (2005) 262.
33. A. Y. El-Etre, *J. Colloid Interface Sci.* 314 (2007) 578.
34. E.E. Oguzie, G.N. Onuoha, A.I. Onuchukwu, *Mater. Chem. Phys*. 89 (2005) 305.
35. R. F. V. Villamil, P. Corio, J. C. Rubin, S. M. L. Agostinho, *J. Electroanal. Chem.* 472 (1999) 112.
36. E. E. Oguzie, *Portugaliae Electrochim. Acta* 26 (2008) 303.
37. I. B. Obot, N. O. Obi-Egbedi, *Corros. Sci.* 52 (2010) 198.
38. F. M. Donahue, K. Nobe, *J. Electrochem. Soc.* 112 (1965) 886.
39. E. Khamis, F. Bellucci, R. M. Latanision, E. S. H. El-Ashry, *Corros.* 47 (1991) 677.
40. F. Bentiss, M. Traisnel, M. Lagrenee, *Corros. Sci.* 42 (2000) 127.
41. M. G. Hosseini, M. Ehteshamzadeh, T. Shahrabi, *Electrochem. Acta* 52 (2007) 3680.
42. M. Hosseini, S. F. L. Mertens, M. Ghorbani, M. R. Arshadi, *Mater. Chem. Phys.* 78 (2003) 800.
43. I. T. Gbadamosi, J. O. Moody, A. M. Lawal, *J. Appl. Biosci.* 44 (2011) 2967.
44. S. Deng, X. Li, *Corros. Sci.* 55 (2012) 407.
45. N. Hackerman, E. S. Snavely, J. S. Payne, *J. Electrochem. Soc.* 113 (1966) 677.
46. F. Bentiss, M. Traisnel, N. Chaibi, B. Mernari, H. Vezin, M. Lagrenée, *Corros. Sci.* 44 (2002) 2271.
47. T. Murakawa, S. Nagaura, N. Hackerman, *Corros. Sci*. 7 (1967) 79.