J. Mater. Environ. Sci. 4 (2) (2013) 217-226
ISSN : 2028-2508
CODEN: JMESCN

Inhibition of acid corrosion of mild steel by biomass extract from the *petersianthus macrocarpus* plant

Chris O. Akalezi, Conrad K. Enenebaku, Emeka E. Oguzie*
Electrochemical and Material Science Unit (EMRU), Department of Chemistry,
Federal University of Technology Owerri, PMB 1526 Owerri, Nigeria

Received 30 March 2012, Revised 26 Oct 2012, accepted 26 Oct 2012
**Corresponding author: email: oguziemeka@yahoo.com*

Abstract

Inhibitive action of *petersianthus macrocarpus* leave extract on corrosion of mild steel in 1M HCl and 0.5M H_2SO_4 solutions was studied using gravimetric, electrochemical impedance and potentiodynamic methods. The results indicated that the extracts functioned as a good inhibitor in both environments and inhibition efficiency increased with extract concentration. Temperature studies in the range 313-333K reveal increase in inhibition efficiency of the extract with rise in temperature. A mechanism of chemical adsorption on the extract components on the surface of the metal is proposed for the inhibition behavior. The adsorption characteristics of the inhibitor were found to obey Langmuir adsorption isotherm.

Keywords: Biomaterial; metals; chemical technique, electrochemical technique; adsorption; corrosion.

1. Introduction

Mild steel is widely used in most of the chemical industries for the fabrication of various reaction vessels, pipes, tanks, etc; due to its easy availability and low cost [1,2]. Acids are generally used for the removal of undesirable scales and rust in several industrial processes. Hydrochloric and sulphuric acids are extensively used in the prickling and descaling operations. The use of corrosion inhibitors is one of the most effective and economic methods to protect metal surfaces against corrosion in such aggressive media [3-5]. A number of organic compounds have been reported as effective corrosion inhibitors especially those containing nitrogen, oxygen, sulphur, phosphorus, and multiple bonds or aromatic rings in their structures [6-9]. The number of lone pairs of electron and loosely bound π-electrons in these functional groups are the key structural features that determine the inhibition efficiency [10-12].

Apart from structural aspects, there are also economic considerations since the whole subject of corrosion is about its destructive economical effects. Therefore the used inhibitor must be cost effective and also readily available. Furthermore, due to recent environmental awareness and restrictions, the inhibitor must be nontoxic and biodegradable.

Several studies have been published on the use of natural products as corrosion inhibitors in different media [11-14], and these reports provide evidence that natural products contain several compounds that satisfy the mentioned features. El-Etre [15] has studied the application of natural honey as corrosion inhibitor for copper in aqueous solution. Parikh et al. [16] studied the anticorrosion activity of onion, garlic and bitter gourd for mild steel in HCl media. Ethanolic extract of *Ricimus communis* leaves was studied for the corrosion inhibition of mild steel in acidic media by Sathyanathan et al. [17]. Aqueous extract of Hibiscus flower and *Agaricus* has been studied as corrosion inhibitors for industrial cooling system by Minhaj et al. [18].

The anticorrosion effect of *Andrographis paniculata* [19] and tea wastes [20] have been reported by Sethuraman et al. Klinskic et al. analyzed aqueous extract of *Rosmarinus officinalis* [21] as corrosion inhibitor for aluminium alloy corrosion in chloride solution. Guar gum was analyzed for its anticorrosion activity by Abdallah et al. [22]. Martinez and Stern have studied the inhibitory mechanism of Mimosa tannin with low carbon steel in H_2SO_4 media [23]. Oguzie and co-workers studied the corrosion inhibition of leaf extracts of

Occimum viridis, Telferia occidentalis, Azadirachta indica and *Hibiscus sabdariffa* [24-27] on mild steel corrosion in acidic solutions. Other than the plant extracts, pure organic compounds extracted from natural products such as ascorbic acid, succinic acid, caffeine, amino acids [28-31] are also used for inhibition of corrosion.

In the present study the inhibiting properties of aqueous extract of *Petersianthus macrocarpus* (PM) in 1 M HCl and 0.5 M H_2SO_4 were studied using weight loss, electrochemical impedance and potentiodynamic methods. PM belongs to the Lecythidaceae plant family widely distributed in the West African sub-region including Benin, Burkina Faso, Ghana, Mali and Nigeria. Phytochemical characterization tests revealed that the plant's barks of stem and trunk contain several bioactive principles such as sterols, polyterpenes, polyphenols, saponosides and alkaloids [32]. Petersaponin has been identified as the major chemical constituent of the plant. β-sitosterol, octacosanol, and ellagic acids have also been isolated [33-35].

2. Experimental

2.1 Preparation of plant extract

Stock solutions of the plant extract were prepared by boiling weighed amounts of the dried and ground leaves of PM plant under reflux for 3 hours in 1.0 M HCl and 0.5 M H_2SO_4 solutions, respectively. The resulting solutions were cooled and then filtered twice. The amount of plant material extracted into solution was obtained by comparing the weight of the dried residue with the initial weight of the dried plant material before extraction. From the respective stock solutions, inhibitor test solutions were prepared in the concentration range 50–1000 mg/L in respective corrodents. Solutions of 1.0M HCl and 0.5M H_2SO_4 solutions were prepared for the experiment using analytical grade reagents and distilled water. Working electrode was prepared from a rectangular coupon cut from a mild steel sheet with the composition (wt%) C- 0.15%, Mn-1.4%, P-0.36%, Si-0.3% and Fe balance.

2.2 Weight loss measurements

Mild steel sheets of dimensions 3.0 x 3.0 x 0.2cm were used in the weight loss experiment. Before each experiment the coupons were abraded using emery papers (grades 200-800) washed with distilled water and acetone and finally dried. The initial weight of each specimen was noted before immersion using an analytical balance. Then the specimens were immersed in aerated (200mL) of 1.0 M HCl and 0.5M H_2S0_4 solutions without and with different concentrations of the PM extract for 6 h. After the elapsed time the specimens were taken out, washed, dried and reweighed. All the experiments were performed in triplicate and average values were recorded.

2.3 Electrochemical experiment

Electrochemical experiments were performed using a VersaSTAT3 potentiostat/galvanostat from AMATEK Inc. operated with V3 studio software. The working electrode (We) was the mild steel of dimension 1.5cm x 1.5 x 0.2cm which was polished and appropriately sealed with epoxy to leave an exposed surface area of $1cm^2$. A saturated calomel electrode (SCE) and platinum foil were used as the reference and auxiliary electrodes respectively. WE were immersed in the respective corrodents for 30 min until a steady-state open circuit potential (OCP) was obtained. EIS were carried out over a frequency range of 100 kHz–10 MHz. The sinusoidal potential perturbation was 5 mV in amplitude. Tafel polarization scans were carried out by changing the electrode potential automatically from -0.25 to 0.25 mV versus OCP with a scan rate of 0.333mV/s. The data recordings and the calculation of the electrochemical parameters were performed using V3 software and interpreted with Zsimpwin software. Measurements were performed at 303K and each test was run in triplicate to verify the reproducibility and the average values reported. All potentials were referred to the SCE.

3. Results and discussion

3.1. Weight loss measurements

Weight loss measurements were carried out in 1.0 M HCl and 0.5M H_2SO_4 solutions in the absence and presence of different concentrations of PM extract. This physical measurement provides direct answer on how the corrosive environments affect the test samples and also show us the average corrosion rate during the experiment. The corrosion rates of the mild steel coupons were calculated from the weight loss data using Eq(1):

$$C_R(\text{mdd}) = \frac{\Delta w}{st} \quad (1)$$

where, Δw is mass loss (mg), s is area of specimen (dm^2) and t is the immersion time in days.
The inhibition efficiency (IE%) and surface coverage (θ) were calculated according to the following equation:

$$q = \frac{w_o - w_1}{w_o} \quad (2)$$

$$I.E\% = \frac{w_o - w_1}{w_o} x100 \quad (3)$$

where w_o and w_1 are the weight loss in absence and presence of inhibitor
Fig. 1 represents the effect of increasing the concentration of PM extract on the corrosion rate of mild steel. The results show that this plant extract inhibited the corrosion of mild steel in 1.0 M HCl and 0.5M H_2SO_4 solutions at all the concentrations studied and the extent of corrosion inhibition depends on the concentration. Increasing the concentration of the extract decreases the corrosion rate of the metal. The data also reveals higher corrosion susceptibility of the mild steel in 0.5 M H_2SO_4 solution compared to the HCl solution. The fact that the metal specimen manifests higher corrosion susceptibility in 0.5 M H_2SO_4 is evident that the acid anions influence the corrosion process in different ways. Fig. 2 represents the dependence of the inhibition efficiency IE% on concentration calculated from gravimetric data obtained at 303K (Eq.2). It is clear from the plot that the inhibition efficiency increased with increase in inhibitor concentration. This suggests that more inhibitor molecules were adsorbed on the metal surface at higher concentration, leading to higher surface coverage. The plot also shows better performance of the extract in 1 M HCl solution.

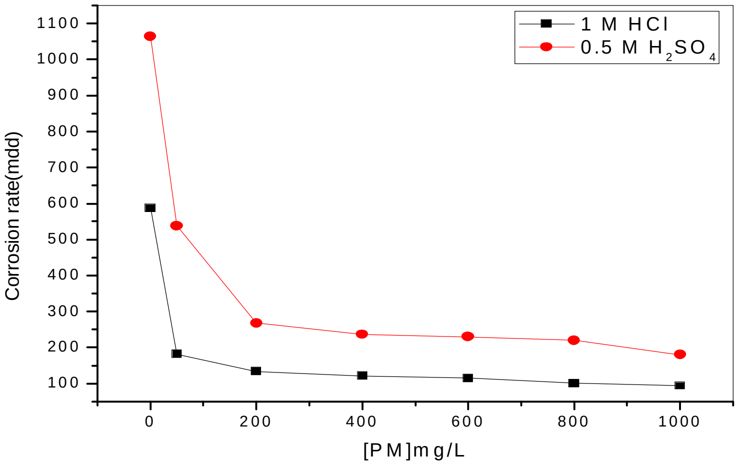


Fig. 1 Variation of corrosion rate without and with various concentrations of PM extract during mild steel corrosion in 1M HCl and 0.5M H_2SO_4 for 6h immersion period at 303K.

3.2 Electrochemical impedance spectroscopy measurements

Electrochemical impedance spectroscopy (EIS) is a well-established and powerful tool in the study of corrosion. Surface properties, electrode kinetics and mechanistic information can be obtained from the impedance diagrams [36]. Fig. 3a and b shows the Nyquist plot obtained at the open-circuit potential, while

Table 1 summarizes the impedance data extracted from EIS experiments carried out both in the absence and presence of 50mg/L and 1000mg/L concentrations of PM extract.

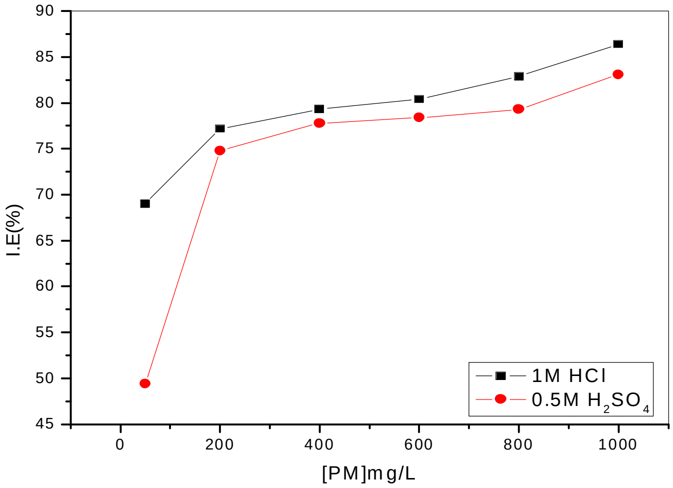


Fig. 2 Variation of inhibition efficiency with concentrations of PM extract for steel corrosion in HCl and H_2SO_4

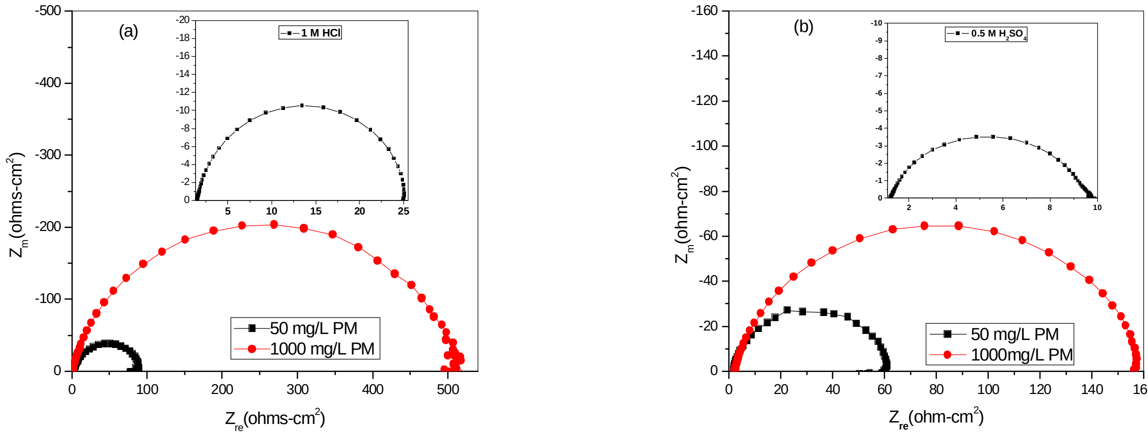


Fig.3 Electrochemical impedance spectra of mild steel without and with PM in:
(a) 1M HCl and (b) 0.5M H_2SO

It is apparent from Fig.3 that all the Nyquist plots are similar in shape and consists of a single capacitive loop, which means only one charge transfer reaction during the metal dissolution process. The impedance spectra for the Nyquist plots were analyzed by fitting to the equivalent circuit model: $R_s(C_{dl}R_{ct})$. In this equivalent circuit, R_s is the solution resistance, R_{ct} is the charge transfer resistance and C_{dl} is the double layer capacitance. The capacitance values were calculated using the equation:

$$C_{dl} = \frac{1}{2\Pi f_{\max} R_{ct}} \qquad (4)$$

where $f_{\max}$ is he frequency at which the imaginary component of impedance is maximum. The impedance diagram does not give a perfect semicircle, which has been attributed to frequency dispersion of the interfacial impedance. The percentage inhibition efficiency IE_E% was calculated using the following equation:

$$\text{IE}_\text{E}\% = \frac{R_{ct} - R_{ct}^{o}}{R_{ct}} x100 \qquad (5)$$

where R_{ct} and R_{ct}^{o} are the charge transfer resistance of mild steel in presence and absence of inhibitor respectively.

Table-1: EIS parameters for mild steel in 1.0M HCl and 0.5M H_2SO_4 in the absence and presence of 50 and 1000mg/L PM leaves extract

System	$R_s(\Omega cm^2)$	$R_{ct}(\Omega cm^2)$	$C_{dl}(\mu F cm^{-2})$	$IE_R\%$
1.0 M HCl	1.32	32.8	82.4	-
50mg/L CS	2,61	84.7	31.40	61.3
1000mg/L CS	1.32	509.6	1.06	93.5
0.5 M H_2SO_4	1.26	8.45	44.41	-
50mg/L CS	2.24	23.3	13.48	64.2
1000mg/L CS	2.25	150.6	1.61	82.9

It is clear from Table 1 that by increasing the inhibitor concentration, the C_{dl} values tend to decrease and the inhibition efficiency increases. The decrease in the C_{dl} which can result from a decrease in local dielectric constant and/ or an increase in the thickness of the electric double layer, suggested that PM extract function by adsorption at the metal/solution interface. Thus the change in C_{dl} values was caused by the gradual replacement of water molecules by the adsorption of the extract organic matter on the metal surface, decreasing the extent of metal dissolution [37]. It is apparent from the Nyquist plots that the impedance response of mild steel in the inhibited HCl and H_2SO_4 solutions changed significantly after the addition of the extract in the acid solutions and the impedance of inhibited substrate increased with increasing concentration of inhibitor in both acids. Inhibition efficiency was found to increase with inhibitor concentration in both acids.

3.3 Polarization measurements

Polarization curves for mild steel at the presence 50mg/L and 1000mg/L concentration of PM leaves extract in 1.0M HCl and 0.5M H_2SO_4 solutions are shown in Fig. 4a and b. The extrapolation of Tafel straight line allows the calculation of the corrosion current density (i_{corr}). The $IE_p(\%)$ is calculated using the following equation:

$$\text{IE}_\text{p}(\%) = \frac{i_{corr}^{o} - i_{corr}^{i}}{i_{corr}^{o}} \qquad (6)$$

where i_{corr}^{o} and i_{corr}^{i} are the corrosion current density values without and with inhibitor respectively. The values of i_{corr}, the corrosion potential (E_{corr}) and inhibition efficiency $IE_P\%$ are given in Table 2. From Fig. 4, it is obvious that the presence of the additive resulted in a marked shift in the cathodic branches in H_2SO_4 and to a lesser extent in HCl solution. This result indicates that PM extract can be classified as a cathodic inhibitor in H_2SO_4, while in HCl we have mixed inhibition. Basically, anodic polarization is the shift of anode potential to the positive (noble) direction whereas cathodic polarization is the shift of cathode potential to the negative (active) direction. In literature [38], it has been reported that if the displacement in E_{corr} is >85 mV the inhibitor can be seen as a cathodic or anodic type inhibitor and if the displacement of E_{corr} is <85 mV, the inhibitor can be seen as mixed type. In this study, the maximum displacement in E_{corr} value was up to 100 mV for PM in H_2SO_4 solution. It is illustrated from the data of Table 2 that the addition of PM extract decreases corrosion current density. Also, it can be clearly seen that the inhibition efficiency of PM extract increases with inhibitor concentration. The values differ somewhat from those obtained from gravimetric measurements due basically to factors associated with the different techniques, but the trend remains the same.

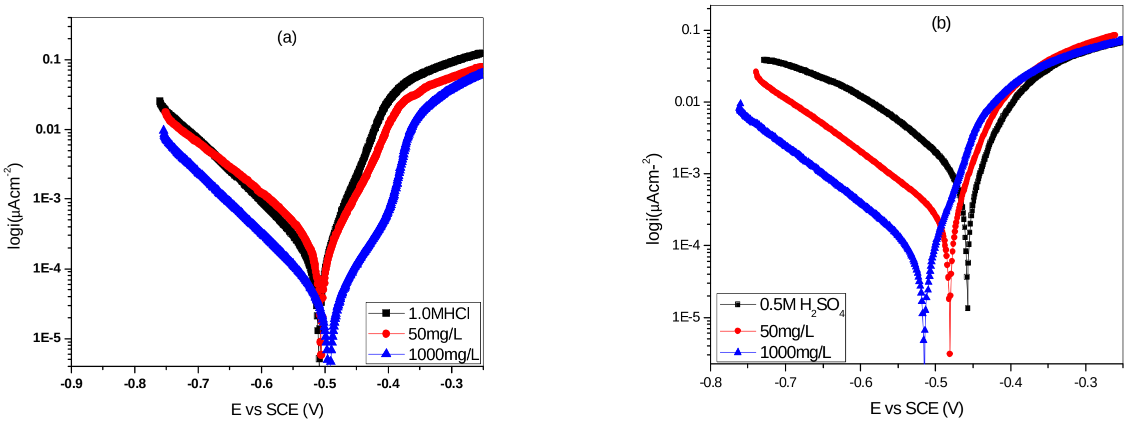


Fig.4 Potentiodynamic polarization curves of mild steel in: (a) 1 M HCl and (b) 0.5 M H_2SO_4 without and with PM.

Table-2: PDP kinetic parameters, inhibition efficiency for PM in 1.0M HCl an 0.5M H_2SO_4 without and with 50 and 1000mg/L Concentrations at 303K

System	I_{corr} (µA/cm^2)	E_{corr} (mV)	IE%
1.0M HCl	888.7	-521.6	-
50mg/L CS	313.4	-512.4	64.8
1000mg/L CS	120.2	-493.2	86.5
0.5M H_2SO_4	1534.9	-607.0	-
50mg/L	476.6	-601.0	67.6
1000mg/L	322.7	-515.2	79.0

3.4 Adsorption isotherm.

Corrosion inhibition of mild steel in acid solutions by inhibitors can be explained based on molecular adsorption. The adsorption process is influenced by the chemical structures of organic compounds, the distribution of charge in molecule, the nature and surface charge of metal and the type of aggressive media [39]. Basic information on the interaction between the inhibitors and the mild steel surface can be provided by the adsorption isotherms [40]. Totally, adsorption isotherms provide information about the interaction among the adsorbed molecules themselves and their interactions with the electrode surface [41]. In order to obtain a proper adsorption isotherm, Langmuir, Temkin, and Freundluich adsorption isotherms were tested. Langmuir adsorption isotherm, which is given by Eq. (5) [42], was found to be more suitable:

$$\frac{C}{q} = C + \frac{1}{K} \qquad (7)$$

where θ is the fraction of surface coverage, C is the inhibitor concentration, K is the equilibrium constant for the adsorption/desorption process. The relationship between C/θ and C at 303K for mild steel in 1 M HCl and 0.5 M H_2SO_4 with various concentrations of the plant extract is shown in Fig. 5 with slopes of 1.2 respectively. As can be seen by the good fit, PM extract as inhibitor obeys the Langmuir adsorption isotherm.

3.5 Effect of temperature

Analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies in the absence and presence of inhibitor gives some insights into the possible mechanism of inhibitor adsorption [43-47]. In order to evaluate the adsorption of inhibitors and to calculate thermodynamic and activation parameters of the corrosion processes of the mild steel in acidic media, the effect of temperature on the corrosion parameters was studied using the gravimetric technique. Measurement were made in the temperature range 313-333k in the absence and presence of 50mg/L and 1000mg/L concentrations during 3h immersion period. The effect of increasing temperature on the corrosion rate of the mild steel in the absence and presence of 50 and 1000mg/L concentrations in both corrodents is presented in Table 3. Inspection of the data shows that the corrosion rate of the mild steel increased with increase in temperature. The increase in corrosion rate is more pronounced for the uninhibited acid solutions. The inhibition efficiency data (Table 3) shows that the IE% increased with increasing temperature. The observed increase in IE% with increase in temperature in both media is an indication that some of the extract components become better adsorbed at higher temperature and so contribute more to the overall inhibiting effect.

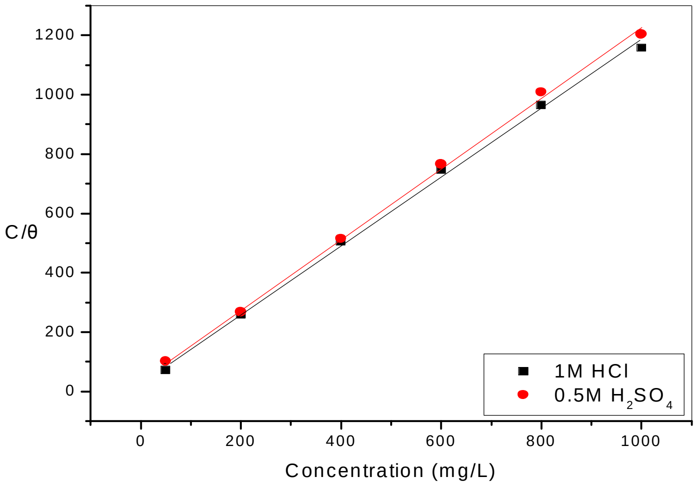


Fig.5 Langmuir adsorption isotherm plot for mild steel coupons immersed in 0.5M H_2SO_4 and 1M HCl

Table-3: Effect of temperature on the corrosion rate of mild steel with and without the addition of PM extract

System	303 K	313 K	323 K	333 K
1M HCl	Inhibition efficiency (%)			
50mg/L	67.1	71.7	76.5	92.9
1000mg/L	76.4	80.1	86.7	96.4
0.5MH_2SO_4	Inhibition efficiency (%)			
50mg/L	49.4	71.0	76.7	78.9
1000mg/L	82.4	83.1	90.3	95.8

The log of corrosion rate is a linear function with 1/T (Arrhenius equation) [48, 49]:

$$\log C_R = \frac{-E_a}{2.303RT} + A \qquad (8)$$

where E_a is the apparent effective activation energy, R is the general gas constant and A is the Arrhenius pre-exponential factor. A plot of log of corrosion rate vs. 1/T gave a straight as shown in Fig. 6 with a slope of -E_a/2.303R. The values of the activation energies are listed in Table 4. The data shows that the thermodynamic activation functions (Ea) of the corrosion in mild steel in 1 M HCl and 0.5M H_2SO_4 solution in the presence of extract are lower than those in the free acid solution indicating that extract exhibit high IE%

at elevated temperatures. An increase in inhibition efficiency with rise in temperature with analogous decrease in corrosion activation energy in the presence of inhibitor compared to its absence is frequently interpreted as being suggestive of formation of an adsorption film of chemical (molecular) nature [50, 51]. .

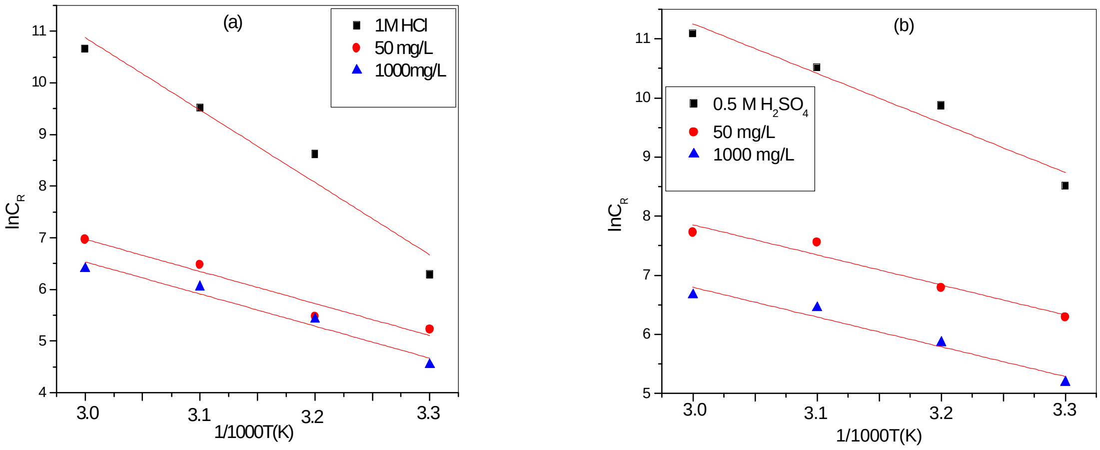


Fig.6 Arrhenius plots for mild steel corrosion in (a) 1 M HCl and (b) 0.5 M H_2SO_4 solutions without and with PM extract

An alternative formulation of Arrhenius equation is [53]:

$$C_R = \frac{RT}{Nh}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(\frac{\Delta H^*}{RT}\right) \qquad (9)$$

where h is the plank's constant, N is Avogadro's number, S^* the entropy of activation and H^* is the enthalpy of activation. A plot of $\log(C_R/T)$ vs. 1/T gave a straight line with a slope of $-H^*/2.303R$ and an intercept of $\log(R/Nh)+ S^*/2.303R$, from which the values of S^* and H^* were calculated and listed in Table 4. The positive signs of enthalpies (H^*) obtained in both systems reflects the endothermic nature of dissolution process. The shift towards negative value of entropies (S^*) in the inhibited solutions imply that the activated complex in the rate determining step represents association rather than dissociation, meaning that disordering decreases on going from reactants to the activated complex [52].

Table-4: Values of activation parameters: E_a, ΔH^*, ΔS^* for mild steel in 1 M HCl and 0.5M H_2SO_4 at 50 and 1000mg/L concentrations of PM extract.

system	E_a(kJmol^{-1})	ΔH^*(kJmol^{-1})	ΔS^*(JK^{-1}mol^{-1})
1 M HCl	116.48	113.4	163.28
50 mg dm^{-3}	52.78	40.21	-36.69
1000mg dm^{-3}	51.50	38.29	-45.76
0.5 M H_2SO_4	69.75	67.93	31.26
50 mg dm^{-3}	43.29	49.97	-60.12
1000mg dm^{-3}	41.62	48.63	-74.6

3.6 Mechanism of inhibition

The first stage in the action mechanism of inhibitor in acid media is adsorption on the metal surface. In most inhibition studies, the formation of donor–acceptor surface complexes between π-electrons of inhibitor and the vacant d-orbital of metal were postulated [53, 54].The main constituents of extract of PM are Petersaponin, β-sitosterol, and ellagic acid with the structures given in Fig.7 having a number of hydroxyl group (-OH) and aromatic rings. In the acid solution, due to protonation of hydroxyl group, the inhibitor molecules get adsorbed on the mild steel surface. As the constituent molecules contain aromatic rings (π-electrons) and electron releasing groups attached to these aromatic rings, the availability of π-electrons to get bonded to the vacant d-orbital of Fe is increased. The high performance of PM extract could also be due to large size of constituent's molecule which cover wide areas on the metal surface and thus retarding the corrosion [55, 56].

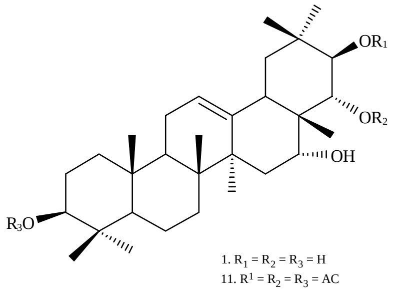
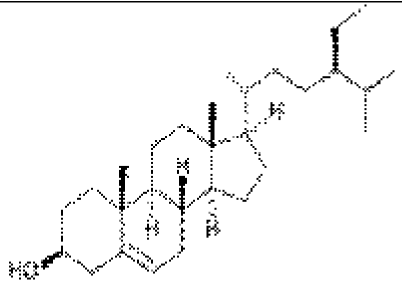
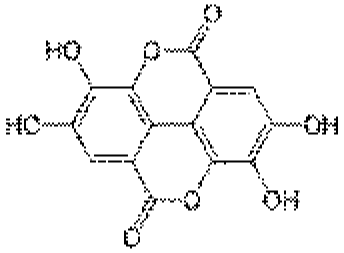
 1. Petersaponin (1) and (11)	 2. β-sitosterol	 3. ellagic acid

Fig. 7 Structures of main constituent of *Petersiantus macrocarpus* leaves extract:
(1) petersaponin (2) sitosterol and (3) ellagic acid.

Conclusions

The results obtained show that PM extract is a good corrosion inhibitor for mild steel under acidic conditions. The inhibition efficiency increased with increase in concentration and with increase in temperature up to 333k. Excellent agreement between the inhibition efficiencies calculated using different techniques was obtained. EIS data show that extract organic matter is responsible for the corrosion inhibiting effect and functioned via adsorption on the metal surface.

There is an adequate change of the apparent activation energy when compared to that in the case of uninhibited solutions. The lower activation energy of the corrosion process in the presence of the corrosion inhibitor, when compared to that in its absence demonstrated the chemisorptive nature of the adsorption.

The adsorption of PM extract on the mild steel surface was approximated by the Langmuir isotherm.

Acknowledgement

This project is supported by TWAS, the academy of Science for the developing world, under the TWAS Grants for Research units (TWAS-RGA08-00

References

1. Bentiss, F., Lagrenée, M., Traisnel, M. *Corros. Sci.* 56 (2000) 733
2. Chauhan, L.R., Gunasekaran, G. *Corros. Sci.*49 (2007) 1143
3. Satapathy, A.K., Gunasekaran, G., Sahoo, S.C., Amit, K., Rodrgues,P.V. *Corros. Sci* 51(2009) 2848
4. de Souza, F.S., A. Spinelli, A. *Corros. Sci.* 52 (2009) 1845
5. Da Rocha,J.C., Da Cumha Ponciano Gomes, Eliane D'Elia. *Corros Sci.* 52 (2010) 2341
6. Jia-Jun Fu, Su-ning Li, Ying Wang, Lin-Hua Cao, Lu-de Lu, J. *Mater. Sci* 46 (2010) 6255
7. Shukla, S.K., Singh, A.K., Ahamad, I., Quraishi,M.A. *Mater Lett.* 63 (2009) 819
8. Shukla,S.K., Quraishi, M. A. *J Appl. Electrochem* 39 (2009) 1517
9. Sinko, J. *Prog Org Coat* 42 (2001) 267
10. Bothi, P.R., Sethuraman, M.G. *Mater Lett* 62 (2008) 1602
11. Ketsetzi, A., Stathoulopoulou, A., Demadis, K.D. *Desalination* 223 (2008) 487
12. Umoren, S.A., Obot, I.B., Obi-Egbedi, N.O. *J. Mater Sci* 44 (2009) 274.
13. Hackerman, N., Hurd, R.M. Proceedings of International Congress of Metallic Corrosion, Butterworth, London, 1962, p. 166.
14. Srivasthava, K., Srivasthava, P. (1980), *Corros. Prev. Control* 27 (1980) 5

15. El-Etre, A.Y. *Corros. Sci.* 40 (1998) 1845
16. Parikh, K. S., Joshi,m K.J (2004), *Trans. SAEST* 39 (2004) 29
17. Ananda R., Louise Sathiyanathn, Maruthamuthu, S., Sevanayagam,M., Mohanan,S., Palaniswamy,N. *Ind. J. Chem. Tech.* 12 (2005) 356
18. Minhaj, A., P. Saini, A., Quarishi, M.A., Farooqi, I. H. *Corros, Prev. control* (UK) 46 (1999) 32
19. Ramesh, S. P., Vinod Kumar, K. P., Sethuraman, M. G. *Bull. Electrochem.* 17 (2001) 141
20. Sethuraman, M. G., Vadivel, P., Vinod Kumar, K. P. *J. Electrochem. Soc. Ind.* 50 (2001) 143
21. Kliskic, M., Radosevic, J., Gudic, S., Katalinic, V. *J. Appl. Electrochem.* 30 (2000) 823
22. Abdalla. M. Port. *Electrochem. Acta* 22 (2004) 161
23. Martinez, S., Stern, I. *J. Appl. Electrochem.* 31(2001) 973
24. Oguzie, E. E. *Mat. Chem. Phy.* 99 (2006) 441
25. Oguzie, E. E. *Pigment and Resin Tech.* 34 (2005) 321
26. Oguzie, E. E. *Corros. Sci.* 50 (2008) 2993
27. Oguzie, E. E. *Pigment and Resin Tech.* 35 (2005) 334
28. Gonçalves, R.S., Mello, L.D. *Corros. Sci.* 43 (2001) 457
29. Amin, M.A., El-Rehim, S.S.A., El-Sherbini, E.E.F., Bayoumy, R.S. *Electrochim. Acta* 52 (2007) 3588
30. Fallavena, T., Antonow, M., R. Gonçalves, S. *Appl. Surf. Sci.* 253 (2006) 566
31. Letícia Guerreiro da Trindade, Reinaldo Simões Gonçalves, *Corrosion Science* 51 (2009) 1578
32. N'GUESSAN Koffi, Edouard, K. K., Noël, Z. G. *Pharm. Med. Trad. Afr. (*2006), Vol. XIV, pp. 97-l16
33. Olugbade, T. A., Ogundaini, A., Birlirakis, N., Païs, M., Martin, M.T. *J. Nat Prod.* 63(5) (2000) 716
34. Ogundaini, A.O. From Green into Medicine: Taking a Lead from Nature, Inaugural Lecture Series 176 (2005), OAU Press Ile-Ife Nigeria
35. Ogundaini, A.O., Wolde-Ab Yisak , Ojewole, J. A. O. *J. of Ethnopharmacol*, **9**, (1983) 337
36. Lorenz, W. J., Manfield, F. (1981), *Corros. Sci.* 21 (1981) 647
37. Quaraishi, M. A. Singh, A., Sigh, V. K., Yadav, D. K., Sigh, A. k. *Mater. Chem Phy* 122 (2010) 114
38. Ahamad, I., Prasad, R., Quraishi, M.A. *Corros. Sci.*52 (2010) 1474
39. Maayta, A.K., Al-Rawashdeh, N.A.F. *Corros. Sci.* 46 (2004) 1129
40. Ismail K .M. *Electrochim. Acta* 52 (2007) 7811
41. Noor, E.A., Al-Moubaraki, A.H. *Mater. Chem. Phys.* 110(2008) 145
42. Abdallah, M. *Corros. Sci.* 44(2002) 717
43. Bahrami, M.J., Hosseini, S.M.A., Pilvar, P. *Corros. Sci.* 52(2010) 2793
44. Oguzie, E. E. *Corros. Sci.* 50 (2008) 2993
45. Lebrini, M., Bentiss,F., Vezin, H., Lagrenee, M. *Corros. Sci.* 48 (2006) 1279
46. Hosseini, S. M. A., Azimi, A. *Mater. Corros.* 59 (2008) 41
47. Popova, A., Sokolova, E., Raicheva,S., Christov, M. *Corros. Sci.* 45 (2003) 33
48. Rehim El-Abd, S.S., Ibrahim, M.A.M., Khalid, K. F. *Mater.Chem. Phy.*70 (2001) 269
49. Quraishi, K. F. Ambrish Singh, Vinod Kumar Singh, Dileep Kumar Yadav, Ashish Kumar Singh, *Materials Chemistry and Physics* 122 (2010) 114
50. Szauer,T., Brandt, A. *Electrochim. Acta* 26 (1981) 1253
51. Martinez, S., Stern, I. *Appl. Surf. Sci.* 199 (2002) 83
52. Bockris, J.O.M., Reddy, A.K.N. Modern Electrochemistry, vol. 2, Plenum Press, New York, 1977, p. 1267.
53. Noor, E.A., Al-Moubaraki, A.H. *Mater. Chem. Phys.* 110 (2008) 145
54. Abdallah, M. *Corros. Sci.* 44 (2002) 717
55. Martinez, S., Stagljar, I. *J. Molecular structure (Theochem)* 640 (2003) 167
56. Hong Ju, zhen-Pen Kai, Yan Li, *Corrosion Sci.,* 50 (2008) 865