Portugaliae Electrochimica Acta 2009, 27(5), 579-589

DOI: 10.4152/pea.200905579

PORTUGALIAE ELECTROCHIMICA ACTA
ISSN 1647-1571

Ethanol Extract of *Phyllanthus Amarus* as a Green Inhibitor for the Corrosion of Mild Steel in H_2SO_4

N. O. Eddy *

Department of Chemistry Ahmadu Bello University, Zaria, Kaduna State, Nigeria

Received 23 February 2009; accepted 23 October 2009

Abstract

Inhibitive and adsorption properties of ethanol extract of Phyllanthus amarus for the corrosion of mild steel in H_2SO_4 were investigated using gravimetric, thermometric and gasometric methods. Ethanol extract of Phyllanthus amarus leaves is a good adsorption inhibitor for the corrosion of mild steel in H_2SO_4. Thermodynamic consideration indicates that the adsorption of the extract is exothermic and spontaneous. Also, the adsorption characteristic of the inhibitor is consistent with the assumptions of Langmuir adsorption isotherm. From the results and findings of the study, a physical adsorption mechanism is proposed for the adsorption of ethanol extract of *Phyllanthus amarus* on mild steel surface. The inhibition potentials of ethanol extract of *Phyllanthus amarus* leaves are enhanced by its phytochemical constituents.

Keywords: corrosion, inhibition, *Phyllanthus amarus*.

Introduction

Mild steel is widely used in the manufacturing of installations for the petroleum and other industries. During industrial processes such as acid pickling, etching, acid cleaning and acid descaling, mild steel is often made to come in contact with aggressive solutions (such as acidic, basic and salt solutions) [1-2]. Consequently, the metal is prone to corrosion attack. The extent of corrosion of the metal depends on the concentration of the aggressive medium (acid, base or salt), operating temperature, period of contact and the presence or absence of inhibitors [3-4]. Due to the viability of mild steel, its high cost of production and installations, most industries have adopted several steps aimed at prolonging the life span of this valuable metal. However, one of the most practical and preferred method is the use of inhibitors [5-8]. Most efficient corrosion inhibitors are organic compounds containing electronegative functional groups and π-electrons

* Corresponding author. E-mail address: nabukeddy@yahoo.com

in triple or conjugated double bonds. For these compounds, the presence of heteroatoms (such as sulphur, phosphorus, nitrogen and oxygen) and aromatic rings in their structures facilitates the adsorption of the inhibitor on the metal surface [9].

In spite of the wide range of organic inhibitors that have been synthesized and used as corrosion inhibitors, there is increasing concern about the toxicity of most corrosion inhibitors in industry because the toxic effects do not only affect living organisms but also poison the environment. According to Eddy and Ebenso [10], 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 mild steel in acidic and alkaline environments has been reported by some research groups [11-14]. However, the use of ethanol extract of *Phyllanthus amarus* as an inhibitor has not been reported elsewhere. Therefore the objective of the present study is aimed at investigating inhibitive and adsorption properties of ethanol extract of *phyllanthus amarus* leaves for the corrosion of mild steel in H_2SO_4.

Phyllanthus amarus is a common annual weed. The plant grows up to about 1.5 ft tall and has small yellow flowers. When the plants are picked, the feathery leaves fold in, completely closing themselves. *Phyllanthus amarus* (Chanca piedra) is used extensively in Chinese and Ayurvedic medicine throughout the centuries for the regulation of the functioning of the liver, kidney and gall bladder [15]. In recent times the leaves of this plant have been successfully used for numerous medicinal applications including internal use, for among others, jaundice, gonorrhea, frequent menstruation, diabetes and topical use as a poultice for skin ulcers, sores, swelling, and itchiness [15]. There is ongoing research on the possibilities of using *Phyllanthus amarus* as a natural medicine for antibacterial/antiviral applications and in the remediation of heavy metal polluted soil [15].

Experimental

Materials preparation

Mild steel of composition (wt%) (as determined by quantiometric method) Mn(0.6), P(0.36), C(0.15), S(0.07) and Fe(98.79) was used for the study. The sheet was mechanically press-cut to form different coupons, each of dimensions, 5 x 4 x 0.11 cm. Each coupon was degreased by washing with ethanol. The washed sample was rinsed with acetone, removed and allowed to dry in the air before use. All reagents used for the study were analar grade and double distilled water was used for their preparation.

Extraction of plants

Samples of *Phylanthus amarus* obtained from the Akwa Ibom State Polytechnic botanical garden were dried, ground and soaked in a solution of ethanol for 48 hours. After 48 hours, the samples were cooled and filtered. The filtrate was subjected to evaporation (in order to leave the sample free of the ethanol) using a rotary evaporator. The stock solution of the extract so obtained was used in preparing different concentrations of the test solutions by dissolving 0.1, 0.2, 0.3, 0.4 and 0.5 g of the extract in 1L solution of 2.5 M H_2SO_4 and 0.1 M H_2SO_4 for use in gasometric/thermometric and gravimetric analysis, respectively.

Gasometric method

Hydrogen evolution measurements were carried out at 303 and 333 K using a gasometer designed for this purpose [10]. From the volume of hydrogen gas evolved per minute, corrosion rate (CR) inhibition efficiency (%I) and degree of surface coverage (θ) were calculated using equations 1, 2 and 3, respectively.

$$\%\mathrm{I} = \left(1 - \frac{V^1_{Ht}}{V^o_{Ht}}\right) x\, 100 \qquad (1)$$

$$\mathrm{CR\ (cm^3/min)} = (\mathrm{V^0_{Ht}} - \mathrm{V'_{Ht}})/\mathrm{t} \qquad (2)$$

$$\theta = \%\mathrm{I}/100 \qquad (3)$$

where $V_{Ht}I$ is the volume of hydrogen gas at time t for inhibited solution and Vo_{Ht} is the volume of hydrogen gas evolved at time t for uninhibited solution.

Thermometric method

Thermometric analysis was carried out according to the method described by Eddy and Ebenso [10]. From the rise in temperature per minute, the reaction number (RN) and inhibition efficiency were calculated using equations 4 and 5.

$$RN\left({}^oC\ \ \mathrm{min}^{-1}\right) = \frac{T_m - T_i}{t} \qquad (4)$$

$$\%I = \frac{RN_{aq} - RN_{wi}}{RN_{aq}} x100 \qquad (5)$$

where RN_{aq} is the reaction number in the absence of inhibitors (blank solution) and RN_{wi} is the reaction number of 2.5 M H_2SO_4 containing the studied inhibitors.

Gravimetric analysis

In gravimetric experiment, a previously weighed mild steel coupon was completely immersed in 250 mL of the test solution in an open beaker. The beaker was inserted into a water bath maintained at a temperature of 30 °C. After every 24 hours, each sample was withdrawn from the test solution, washed in a solution containing 50 % of NaOH and 100 g/L of zinc dust. The washed sample was dried with acetone before re-weighing. The difference in weight for a period of 168 hours was taken as total weight loss. From the weight loss results, the inhibition efficiency (%I) of the inhibitor, corrosion rate (CR) and degree of surface coverage were calculated using equations 6, 7 and 8

$$\%I = (1 - W_1/W_2) \times 100 \quad (6)$$

$$CR\ (gh^{-1}cm^2) = (W_1 - W_2)/At \quad (7)$$

$$\theta = 1 - W_1/W_2 \quad (8)$$

where W_1 and W_2 are the weight losses (in grams) for mild steel in the presence and absence of inhibitor in H_2SO_4 solution, respectively, θ is the degree of surface coverage of the inhibitor, A is the area of the specimen (in cm^2) and t is the period of immersion (in hours).

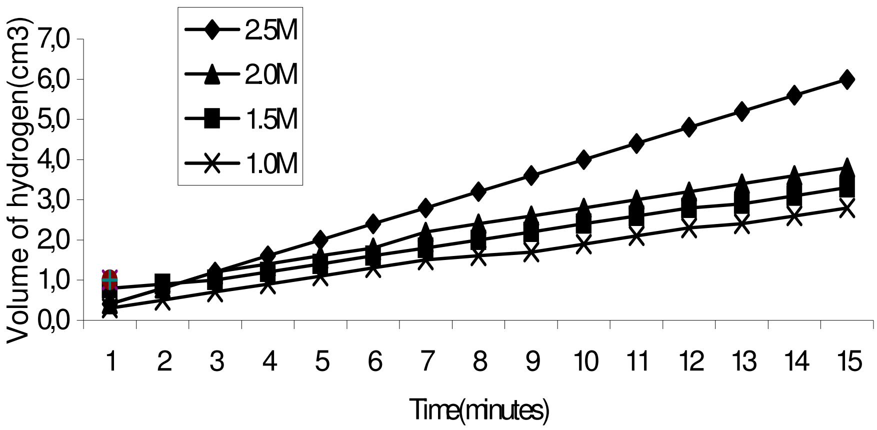

Figure 1. Variation of hydrogen gas evolved with time for the corrosion of mild steel at various concentrations of tetraoxosulphate (VI) at 303 K.

Results and discussions

Effect of ethanol extract of *Phyllanthus amarus*

Fig. 1 shows the variation of the volume of hydrogen gas evolved with time for the corrosion of mild steel in various concentrations of H_2SO_4. From Fig. 1, it is evident that the rate of corrosion of mild steel in H_2SO_4 increases with increasing concentration of H_2SO_4. Fig. 2 represents the variation of volume of hydrogen gas evolved with time for the corrosion of mild steel in H_2SO_4 containing various concentrations of ethanol extract of *Phyllanthus amarus* at 303 and 333 K. From Figs. 1 and 2, it is evident that the volume of hydrogen gas evolved increases with increase in temperature and with increasing period of contact, but decreases with increase in the concentration of ethanol extract of *Phyllanthus amarus*. These findings indicate that ethanol extract of *phyllanthus amarus* inhibited the corrosion of mild steel in H_2SO_4 and that the inhibition efficiency of the extract increases with increase in its concentration but decreases with increasing temperature and period of contact.

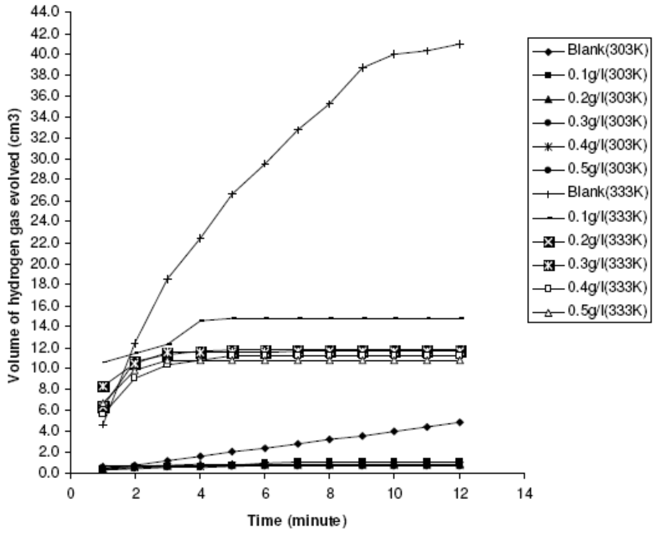

Figure 2. Variation of volume of hydrogen gas evolved with time for the corrosion of mild steel in tetraoxosulphate (VI) acid in the absence and presence of ethanol extract of *Phyllantus amarus* at 303 and 333 K.

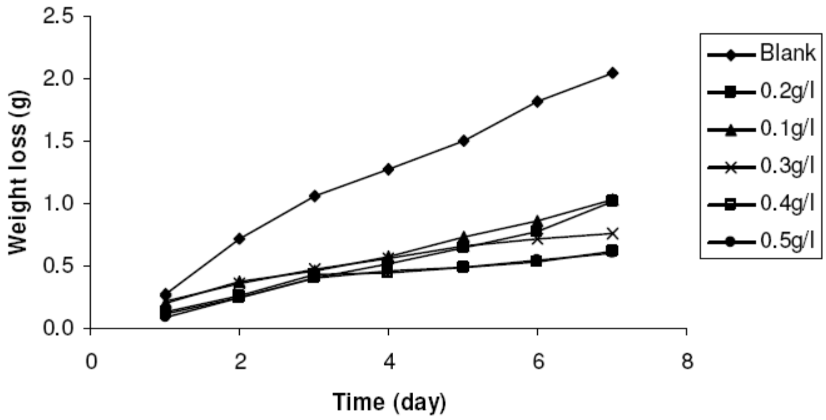

Figure 3. Variation of weight loss with time for the corrosion of mild steel in H_2SO_4 containing various concentrations of *Phyllantus amarus*.

Fig. 3 shows the variation of weight loss with time for the corrosion of mild steel in 0.1 M H_2SO_4 containing various concentrations of ethanol extract of *Phyllanthus amarus* at 303 K. Fig. 3 also reveals that the rate of corrosion of mild steel in H_2SO_4 increases with increase in the period of contact, but decreases with increasing concentration of ethanol extract of *Phyllanthus amarus*, confirming that ethanol extract of *Phyllanthus amarus* is an adsorption inhibitor for the corrosion of mild steel in H_2SO_4.

Values of corrosion rates of mild steel in various media and inhibition efficiencies of ethanol extract of *Phyllanthus amarus* for the corrosion of mild steel in H_2SO_4 are presented in Table 1. The results obtained indicate that the corrosion rates of mild steel decrease with increase in the concentration of ethanol extract of *Phyllanthus amarus*, which also indicates that ethanol extract of *Phyllanthus amarus* is an adsorption inhibitor for the corrosion of mild steel in H_2SO_4. Also, the inhibition efficiency of ethanol *Phyllanthus amarus* decreases with increase in temperature, which implies that the adsorption of the inhibitor on mild steel surface is consistent with the mechanism of physical adsorption [10, 16].

Table 1. Corrosion rates of mild steel and inhibition efficiencies of ethanol extract of *Phyllanthus amarus* for the corrosion of mild steel in H_2SO_4.

C (g/L)	Gasometric method				Thermometric (303 K)		Weight loss (303 K)	
	CR (303 K)	%I (303 K)	CR (333 K)	%I (333 K)	CR	%I	CR	%I
0.1	0.055	85.53	0.983	68.22	0.0041	65.32	0.1295	48.69
0.2	0.005	97.37	1.192	64.22	0.0032	76.43	0.1173	53.53
0.3	0.005	98.68	1.267	66.22	0.0032	78.43	0.0779	69.16
0.4	0.005	98.68	1.267	66.22	0.0030	82.12	0.0729	71.14
0.5	0.010	98.68	1.342	73.78	0.0020	88.44	0.0693	72.55

*Unit of corrosion rate (CR) = cm^3/min, °C/min and g/cm^2/h for gasometric, thermometric and weight loss data, respectively.

Effect of temperature

The effect of temperature on the corrosion of mild steel in the absence and presence of ethanol extract of *Phyllanthus amarus* was studied using the Arrhenius equation (equation 9) as follows:

$$\log\frac{CR_2}{CR_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{9}$$

where CR_1 and CR_2 are the corrosion rates of mild steel at the temperatures T_1 and T_2, respectively, E_a is the activation energy and R is the gas constant. Values of E_a calculated from equation 9 are recorded in Table 2. Calculated values of E_a ranged from 35.10 to 67.30 KJ/mol. These values are less than the threshold value of 80 KJ/mol required for chemical adsorption, hence the adsorption of ethanol extract *Phyllanthus amarus* on mild steel supports the mechanism of physical adsorption.

Table 2. Activation energy and heat of adsorption of ethanol extract of *Phyllanthus amarus* on the surface of mild steel.

C (g/L)	Q_{ads}(KJ/mol)	E_a (KJ/mol)
0.1	-21.25	35.05
0.2	-63.49	66.55
0.3	-76.38	67.29
0.4	-76.38	67.29
0.5	-68.79	59.56

It was also observed that the activation energy for the corrosion of mild steel in the presence of ethanol extract of *Phyllanthus amarus* did not increase with increase in the concentration of the extract. This may be explained as follows. The corrosion rate of a metal (M) can be expressed according to equation 10 [17]

$$-d(M)/dt = k_1(1-\theta) + k_2\theta \qquad (10)$$

where k_1 is the rate constant for the uninhibited reaction and k_2 is the rate constant for the completely covered metal surface. In most systems, k_2 may be so small that $k_2\theta$ may be negligible. When θ is very large, the term $k_1(1-\theta)$ decreases significantly, so that it would take a very large ratio of k_1/k_2 to make the term $k_2\theta$ negligible at high surface area; therefore, the corrosion rates of many inhibited systems at high coverage may not reflect the high degree of adsorption, but rather a new expression, i.e, $k_2\theta$. In such cases, the term $k_1(1-\theta)$ will be negligible and the corrosion mechanism probably involves direct reaction between the species metal atom and the adsorbed inhibitor molecules. In the case of inhibition by ethanol extract of *Phyllanthus amarus*, values of θ were relatively large and increase with increasing concentration of the inhibitor. Therefore it is most probable that the activation energies in $k_2 = A\exp(-E_2/RT)$ will be quite different from that of the uninhibited rate constant k_1. It is also possible that the activation energy of the inhibited reaction may not vary regularly with increasing concentration of the inhibitor.

Thermodynamic and adsorption considerations

Values of the heat of adsorption of ethanol extract of *Phyllanthus amarus* on the surface of mild steel were calculated using equation 11 [18-20]

$$Q_{ads} = 2.303R[\log(\theta_2/1-\theta_2)- \log(\theta_1/1-\theta_1)] \times (T_1 \times T_2)/(T_2 - T_1) \qquad (11)$$

Calculated values of Q_{ads} are presented in Table 2. These values ranged from -21.25 to 76.38K J/mol, indicating that the adsorption of ethanol extract of *Phyllanthus amarus* on the surface of mild steel is exothermic.

The adsorption characteristics of ethanol extract of *Phyllanthus amarus* 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 behaviour of ethanol extract of *Phyllanthus amarus*. The assumptions of Langmuir adsorption isotherms can be expressed as follows [20]

$$C/\theta = 1/k + C \qquad (12)$$

where C is the concentration of the inhibitor in the bulk electrolyte, θ is the degree of surface coverage of the inhibitor and K is the adsorption equilibrium constant. Taking logarithm of equation 12 yields equation 13,

$$\log(C/\theta) = \log C - \log K \qquad (13)$$

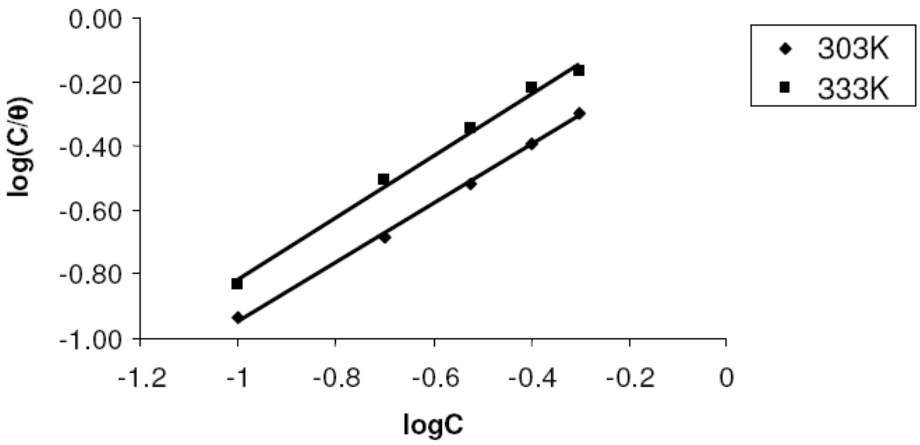

Figure 4. Langmuir isotherm for the adsorption of ethanol extract of *Phyllanthus amarus* on the surface of mild steel.

Table 3. Langmuir adsorption parameters for the adsorption of ethanol extract of *Phyllanthus amarus* on the surface of mild steel.

	Temperature (K)	logK	slope	ΔG_{ads} (KJ/mol)	R^2
Langmuir	303	0.1516	0.969	-10.97	0.9937
	333	0.0324	0.913	-10.28	0.9974

Fig. 4 shows Langmuir adsorption isotherm for the adsorption of ethanol extract of *Phyllanthus amarus* on mild steel surface. Values of adsorption parameters deduced from the isotherms are presented in Table 3. From the results obtained, it is significant to note that the R^2 values and the slopes' values of the plots are very close to unity, which indicates a strong adherence of the adsorption data to the assumptions establishing Langmuir adsorption isotherm. Also, the application of Langmuir adsorption isotherm to the adsorption of ethanol extract of *Phyllanthus amarus* on the surface of mild steel suggests that there is no interaction between the adsorbed species.

Adsorption involving organic molecule at the metal solution interface may occur in any of the following ways [21]:

(i) the electrolytic attraction between charged molecule and the charged metal,

(ii) interaction of unshared electron pairs in the molecules with the metal,

(iii) interaction of s electrons with metal, and

(iv) combination of the above.

Inhibition efficiency depends on several factors, such as the number of adsorption sites and their charge density, molecular size, heat of hydrogenation, mode of interaction with the metal surface and the formation of metallic complexes. Due to adsorption, inhibitor molecules block the reaction sites and reduce the rate of corrosion. The inhibitor molecules inhibit the corrosion of mild steel by adsorption on the mild steel-solution surface. The adsorption provides the information about the interaction around the adsorbed molecules themselves, as well as their interaction with the electrode surface. According to Bockris and

Drazic, the inhibition mechanism could be explained by Fe-$(Inh)_{ads}$ reaction intermediated as shown below [17]:

$$Fe + Inh = (Inh)_{ads} = Fe^{n+} + ne- + Inh \qquad (14)$$

The adsorbed layer combats the action of the acid solution and enhances protection of the metal surface. When there is sufficient Fe(Inh$\}_{ads}$ molecules to cover the metal surface, metal dissolution would take place at sites on the mild steel surface which are free of Fe-$(Inh)_{ads}$. With high inhibitor concentration, a compact and articulated inhibitor over layer is formed on the surface of mild steel hence the extent of chemical attack on the metal is reduced. Therefore, for adsorption inhibitors such as ethanol extract of *Phyllanthus amarus*, the inhibition efficiency increases with increase in concentration, as found in the present study.

Values of adsorption equilibrium constant determined from the slope of the Langmuir adsorption isotherms were used to calculate the free energies of adsorption of ethanol extract of *Phyllanthus amarus* on mild steel surface using equation 15 [21],

$$\Delta G_{ads}=-2.303\ RTlog(55.5K) \qquad (15)$$

where ΔG_{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 (Gads are -10.28 and -12.06 KJ/mol for adsorption at 303 and 333 K, 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 Phyllanthus amarus on mild steel surface is spontaneous and is consistent with the mechanism of physical adsorption.

***Phytochemical constituents of ethanol extract of** Phyllanthus amarus*

Inhibition efficiency of ethanol extract of *Phyllanthus amarus* is due to its phytochemical constituents. Table 4 presents the phytochemical constituents of ethanol extract of *Phyllanthus amarus*. Most of these phytochemicals are organic compounds that have center for π electron, hence the adsorption of the inhibitor on the surface of mild steel is enhanced by their presence. Eddy and Ebenso [10] stated that saponins, alkaloids, lipids and some vitamins are major constituents of plants that enhance the inhibition potentials of plant extracts. Therefore, the inhibition efficiency of ethanol extracts of *Phyllanthus amarus* is due to the formation of multi-molecular layer of adsorption between iron in mild steel and some of these phytochemicals.

Conclusion

Ethanol extract of *Phyllanthus amarus* is a good inhibitor for the corrosion of mild steel in H_2SO_4. The inhibitor is an adsorption inhibitor and the adsorption characteristic of the inhibitor is best described by Langmuir adsorption isotherm. The use of this extract as a corrosion inhibitor is therefore advocated in this work.

Table 4. Phytochemical composition of *Phyllanthus amarus.*

Phytochemicals	**Major constituents**
Liganes	Phyllanthine, hypophyllanthine, phyltetralin, nirurin, nirphylline, niranthin
Terpenes	Cymene, limonene, lupeol and lupeol acetate
Flavanoids	Quercetin, quercetrin, astragalin, rutine
Benzanoid	Methylsalicilate
Alkaloids	Norsecurinine, 4—metoxy-norsecurine
steroids	Beta-sitosterol
alcanes	Triacontanol, triacontanal
others	Vitamin c, tanines, saponins

Source: Eddy and Ekop (2007)

Acknowledgement
The author is grateful to Mrs Edikan Nnabuk Eddy for contributing to the production of this article.

References

1. N.O. Eddy, P. Ekwumemgbo and S.A. Odoemelam, *Inter. Journal of Physical Sciences*. 3(11) (2008) 1.
2. N.O. Eddy and S.A. Odoemelam, *Inter. J. of Pure and Applied Chem*. 3(4) (2008)1.
3. N.O. Eddy, S.A. Odoemelam and A.O. Odiongenyi, *J. Appl. Electrochem*. 39(6) (2009) 849 - 857.
4. N.O. Eddy, S.A. Odoemelam and N.W. Akpanudoh, *J. Chem. Technol.* 4 (2008) 1-10.
5. M. Abdallah, *Corrosion Sc*. 44 (2002) 717.
6. S. Acharya and S.N. Upadhyay, *Trans. Indian Inst. Met.* 57(3) (2004) 297.
7. E.E. Ebenso, *Mater. Chem. Phys*. 79 (2003) 58.
8. A.Y. El-Etre, M. Abdallah and Z.E. El-Tantawy, *Corrosion Science* 47(2) (2005) 385.
9. L. Anauda, R.A. Sathiyanathan, S.B. Maruthamuthu, M.C. Selvanayagam, S.B. Mohanan and N.B. Palaniswamy, *Indian J. Chem. Tech*. 12(3) (2005) 356.
10. N.O. Eddy and E.E. Ebenso, *African J. Pure Applied Chem*. 2(6) (2008) 1.
11. M.A. Bendahou, M.B.E. Benadellah and B.B. Hammouti, *Pigment and Resin Technol*. 35 (2006) 95.
12. A. Bouyanzer and B. Hammouti, *Pigment and Resin Tech*. 33 (2004) 287.
13. A. Chetounani, B. Hammouti, and M. Benkaddour,*Pigment and Resin Tech.* 33 (2004) 26.
14. E.E. Ebenso, N.O. Eddy and A.O. Odiongenyi, *Portugaliae Electrochimica Acta* 27(1) (2009) 13.
15. N.O. Eddy and A.S. Ekop, *Asian J. Chem*. 19(3) (2007) 1825.
16. A.O. Odiongenyi, S.A. Odoemelam and N.O. Eddy, *Portugaliae Electrochimica Acta* 17(1) (2009) 33.

17. *N.O. Eddy,* Inhibition of corrosion of mild steel by some antibiotics, *Ph.D Thesis, University of Calabar, (2007).*
18. S.A. Odoemelam and N.O. Eddy, *J. Surface Sci. Technol.* 24(1-2) (2008) 1.
19. E.E. Ebenso and E.E. Oguzie, *Mat. Letters* 59 (2005) 2163.
20. N.O. Eddy, S.A. Odoemelam and A.J. Mbaba, *Afri. J. Pure Applied Chem.* 2(12) (2008) 132.
21. N.O. Eddy, U.J. Ibok, E.E. Ebenso, A.E. Nemr and E.H. El Ashry, *J. Molecular Modeling*. DOI 10.1007/s00894-009-0472-7 (2009)