International Year of
CHEMISTRY
2011

Portugaliae Electrochimica Acta 2011, 29(1), 9-21

DOI: 10.4152/pea.201101009

PORTUGALIAE
ELECTROCHIMICA
ACTA
ISSN 1647-1571

Corrosion Inhibition of Aqueous Extract of Cocos nucifera - Coconut Palm - Petiole Extract from Destructive Distillation for the Corrosion of Mild Steel in Acidic Medium

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Received 6 December 2009; accepted 2 February 2011

Abstract

The inhibitive effect and adsorption properties of petiole extract obtained from destructive distillation of *cocos nucifera* for the corrosion of mild steel in 0.5 M H_2SO_4 and 1 M HCl were investigated using mass loss, polarization and electrochemical impedance techniques of monitoring corrosion. The results obtained indicate that petiole extract of *cocos nucifera* behaves as good inhibitor for the corrosion of mild steel in 0.5 M H_2SO_4 and 1 M HCl. Activation energy of thermodynamic parameter was evaluated from temperature studies result. The adsorption of the inhibitor on mild steel surface was found to be spontaneous, endothermic and consistent with the assumptions of Langmuir adsorption isotherm. The electrochemical measurements reveal that the petiole extract behaved like mixed type inhibitor. Efforts are made to analyze the effectiveness of petiole extract of coconut palm in industrial processes.

Keywords: corrosion inhibition, mild steel, adsorption, *cocos nucifera* petiole, GC-MS.

Introduction

The environmental consequence of corrosion is enormous and its inhibition has been deeply investigated. It has been found that one of the best methods of protecting metals against corrosion involves the use of inhibitors, which are substances that slow down the rate of corrosion [1]. An inhibitor is usually added in small amounts in order to slow down the rate of corrosion through the mechanism of adsorption [2]. Over the years, several inhibitors have been

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synthesized or chosen from existing compounds and it has been found that the best inhibitors are those that have centre for p electron donation (usually enhanced by the presence of hetero atoms in aromatic compound), while others may be obtained from extracts of naturally occurring compounds [3]. The last class of inhibitors (green inhibitors) are significant because they are non toxic and do not contain heavy metals hence they are environmentally friendly [4]. Several studies have been carried out on the inhibition of corrosion of metals by plant extracts [5 -11]. In this direction the present study is aimed at investigating the inhibitive and adsorption properties of petiole extract obtained from destructive distillation of *cocos nucifera* for the corrosion of mild steel in 0.5 M H_2SO_4 and 1 M HCl.

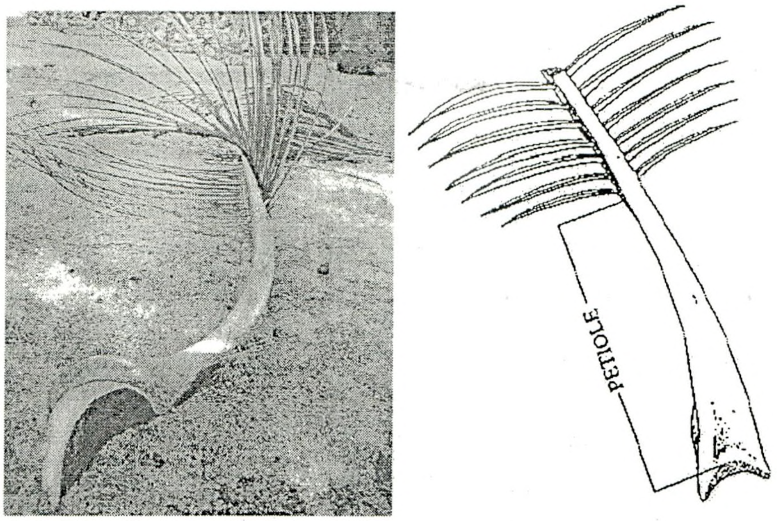
Experimental details

Materials preparation

Materials used for this study were mild steel sheet of following chemical composition in wt %: C, 0.11; Si, 0.061; Mn, 0.197; S, 0.023; P, 0.025; Ni, 0.010; Mo, 0.013; Cr, 0.037; Fe, 99.524. The sheet was mechanically pressed cut into 5 cm x 1 cm coupons with 2 mm thickness, mechanically polished, their edges were abraded with fine grade of emery papers, degreased with acetone, washed in double distilled water, dried, stored in a dessicator and used for the entire immersion studies. All reagents used for the study were analar grade and double distilled water was used for their preparation. Concentrations of H_2SO_4 and HCl used for gravimetric studies were 0.5 M and 1 M, respectively.

Preparation of cocos nucifera petiole extract

The *cocos nucifera* petiole (see Fig. 1) were collected from the tree, cleaned and chopped into small pieces, air dried and stored at room temperature prior to use. 200 g of air dried coconut palm petiole pieces were transferred to a 2000 mL round bottomed flask, directly heated in a mantle with water condenser at about 80 °C in the absence of air and without a carrier solvent (destructive distillation). The products obtained are: i) a gaseous mixture or wood gas; ii) 95 mL of the **aqueous distillate obtained which was used as inhibitor**; iii) 5 mL of a thick black liquid or wood tar which was separated from the aqueous distillate using a separating funnel; iv) 71 g of a solid residue or wood charcoal were left in a round bottle flask. Phytochemical composition of aqueous distillate of *cocos nucifera* petiole extract was analysed by Gas Chromatograph - Mass Spectrometry (GC - MS) [12]. The chromatogram of aqueous distillate is shown in Fig. 2. The phytochemical composition of aqueous destructive distillate of *cocos nucifera* petiole extract is shown in Table 1. Efforts have been taken to analyse the effectiveness of the petiole extract of coconut palm in industrial processes.



(a) (b)

Figure 1. (a) *Cocos nucifera* frond; (b) *Cocos nucifera* petiole.

Table 1. Phytochemical constituents identified in the aqueous distillate of *cocos nucifera* petiole extract by GC - MS analysis.

CHEMICAL COMPOUNDS
L-Histidine, Methyl ester, Dihydrochloride
4,4-Dimethyl-2-Cyclopenten-1-one
Ethanone, 1-(1H-Pyrrole-2-yl)
Cis-4-Hydroxy-2-Methyl-5-(1-Hydroxy-1-Isopropyl)-2-Cyclohexen-1-one
1-(2-Pyrazinyl)-1-Ethanol
2(1H)-Naphthalenone,4A,5,6,7,8,8A-Hexahydro-8A-Methyl
Phenol,3,4-Dimethoxy

Results and discussion

Chemical technique (mass-loss method)

Fig. 3 shows the weight loss (g) - time (min) curves for the corrosion of mild steel in 0.5 M H_2SO_4 and 1 M HCl in absence and presence of the coconut palm petiole extract. The concentration of the extract was varied from 0.5%v/v to 3%v/v, and the time of immersion was from 30 to 1440 minutes at 303 K. It is observed from the figure that the weight loss decreased, and therefore the corrosion inhibition strengthened, with increase in inhibitor concentration. This trend may result from the fact that adsorption and surface coverage increases with the increase in concentration. Thus the surface is efficiently separated from the medium [13]. The inhibitive effect of the extract could be attributed to the presence of some phytochemical constituents in the coconut petiole extract. These extracts contain oxygen atom and aromatic rings which are the centers of adsorption (see Table 1). Similar plots were obtained for other temperatures (313 K - 343 K).

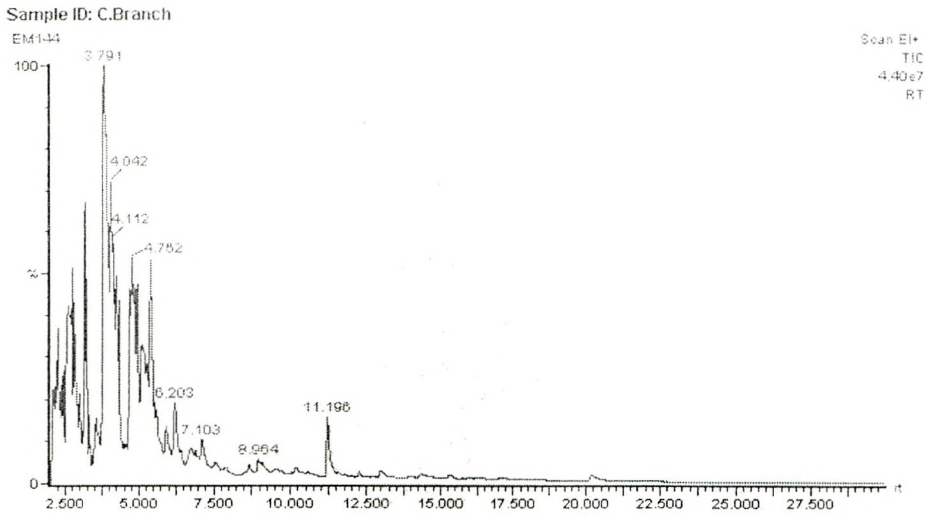
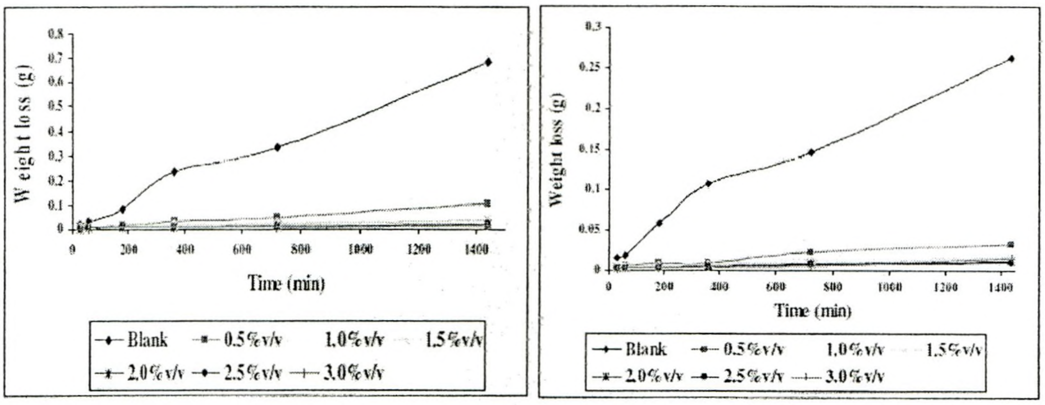


Figure 2. Total Ion Chromatogram resulting from the aqueous distillate of *cocos nucifera* petiole extract obtained by destructive distillation.

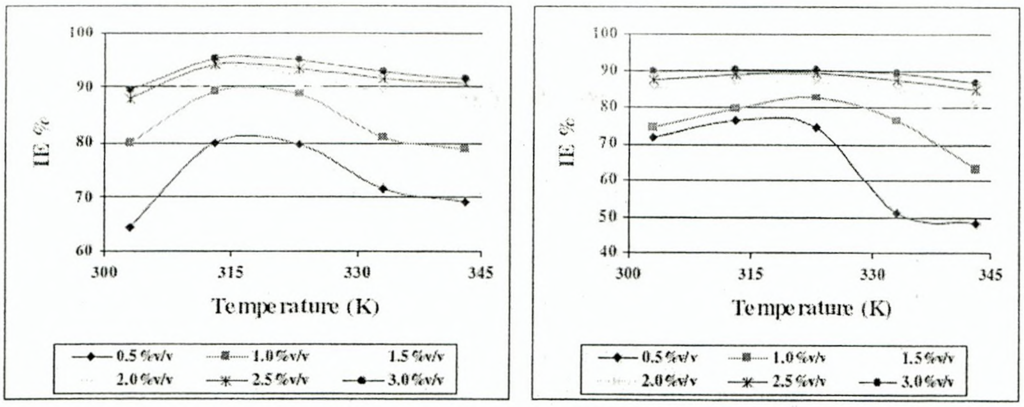


a) b)

Figure 3. Plot of weight loss (g) against time (min) for the corrosion of mild steel in **a)** 0.5 M H_2SO_4 and **b)** 1 M HCl, in absence and presence of different concentrations of the *cocos nucifera* petiole extract at 303 K.

Effect of temperature

From Fig. 4, for each temperature the corrosion rate decreased and the inhibitor efficiency increased with increase in the concentration of coconut palm petiole extract. In both the acid baths, IE increases up to 313 K and after that there is a decline in IE at 323 K. Maximum IE was found to be 95.24% and 90.35% with 3.0%v/v concentration of coconut palm petiole extract in 0.5 M H_2SO_4 and 1 M HCl. Putilova [14] explained as adsorption and desorption of inhibitor molecules continuously occur at the metal surface, and an equilibrium exists between these two processes at a particular temperature. With the increase of temperature, the equilibrium between adsorption and desorption processes is shifted leading to a higher desorption rate than adsorption until equilibrium is again established at a different value of equilibrium constant [15].



a) b)

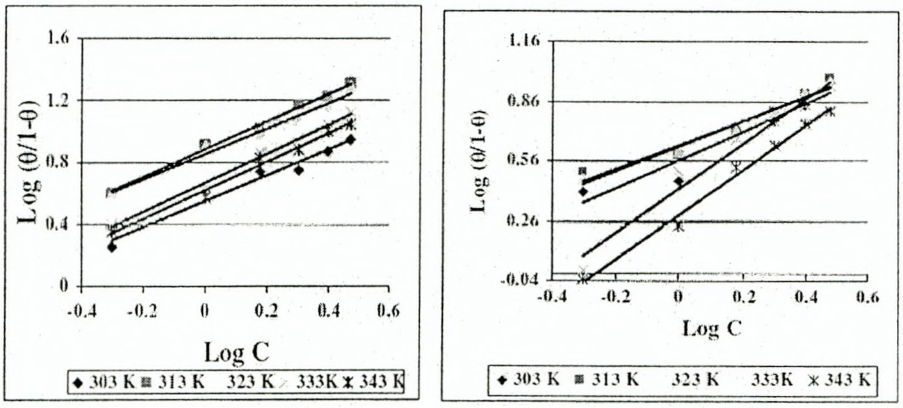
Figure 4. Variation of I.E% for different temperatures at different concentrations of coconut palm petiole extract in **a)** 0.5 M H_2SO_4 and **b)** 1 M HCl.

Adsorption isotherms

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reaction [16]. In this study, Langmuir adsorption isotherm was found to be suitable for the experimental findings. The isotherm is described by the equation:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \ (\text{with } \Delta G^{\circ}_{ads} = -RT\ln(55.5K)) \qquad (1)$$

where C is the inhibitor concentration, K_{ads} the adsorption equilibrium constant and ΔG°_{ads} the standard free energy of adsorption. The plot of log (θ/1-θ) versus log C was linear (see Fig. 5) (correlation > 0.9), the deviation of the slopes from unity can be attributed to the molecular interaction among the adsorbed inhibitor species. The fit of the experimental data to this isotherm provides evidence for the role of adsorption in the observed inhibitive effect of the coconut palm petiole extract.



a) b)

Figure 5. Langmuir adsorption isotherm for mild steel corrosion in **a)** 0.5 M H_2SO_4 and **b)** 1 M HCl in the presence of coconut palm petiole extract.

Kinetic / thermodynamic studies

The adsorption of the organic compounds can be described by two main types of interactions: physical adsorption and chemisorptions. They are influenced by the nature of the charge of the metal, the chemical structure of the inhibitor, pH, the type of the electrolyte and temperature [17]. Thus, in order to elucidate the inhibitive properties of the inhibitor and the temperature dependence on the corrosion rates, the apparent activation energy (E_a) for the corrosion process in the absence and presence of the inhibitor was evaluated from Arrhenius equation:

$$\log \mathrm{CR} = \mathrm{Log}\ \mathrm{A} - \frac{E_a}{2.303RT} \qquad (2)$$

where CR is the corrosion rate, E_a is the apparent activation energy, R is the molar gas constant, T is the absolute temperature and A is the frequency factor. Arrhenius plot for the corrosion rate of mild steel in the presence of coconut palm petiole extract is given in Fig. 6. Straight lines were obtained from the plot of Log CR versus 1/T with slope equal to $-E_a / 2.303R$.

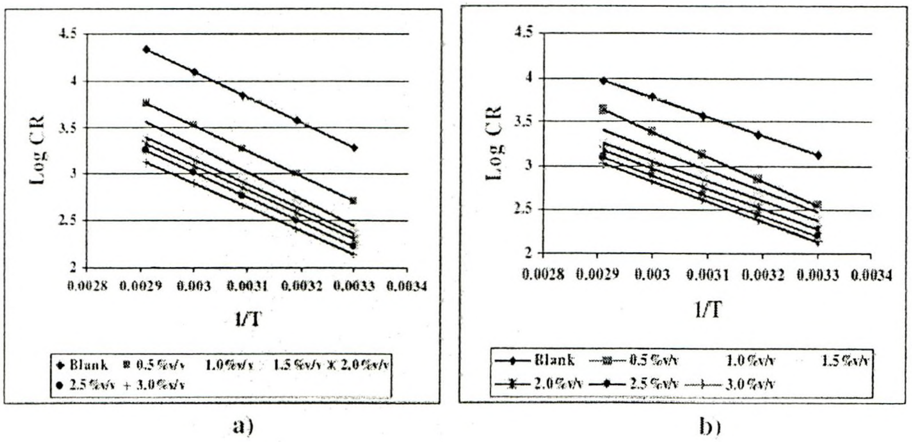


Figure 6. Arrhenius plot for mild steel corrosion in **a)** 0.5 M H_2SO_4 and **b)** 1 M HCl in the absence and presence of coconut palm petiole extract.

The estimated values of E_a for mild steel corrosion in the presence of coconut palm petiole extract in 0.5 M H_2SO_4 and 1 M HCl are listed in the Table 2. Abiiola et al. [18], Ebenso et al. [19] and Ebenso [20] reported that the values of $E_a > 80$ kJ/mol indicate chemical adsorption whereas $E_a < 80$ kJ/mol infer physical adsorption. The E_a values indicate that the process is activation controlled. In the present study, the activation energy values support the fact that the inhibitors are physically adsorbed on mild steel surface. The estimated E_a in the presence of inhibitor infer that the interaction between the metal surface and the inhibitor was found to be strong enough to reduce corrosion.

The free energy of adsorption values ΔG°_{ads}, were obtained from equation (1). The values obtained are presented in Table 2. Results obtained indicate that the values of ΔG°_{ads} are negative in all cases, indicating that the coconut palm petiole extract is strongly adsorbed on the mild steel surface [21]. The value of ΔG°_{ads} indicates that the inhibitor functions by physically adsorbing on the surface of the mild steel. Generally values of ΔG°_{ads} up to -20 $kJmol^{-1}$ are consistent with electrostatic interaction between charged molecules and a charged metal (which indicates physisorption), while those more negative than -40$kJmol^{-1}$ involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (which indicates chemisorption) [22]. Physical adsorption is a result of electrostatic attraction between charged metal surface and charged species in the bulk of the solution. Adsorption of negatively charged species can also protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions adsorbed on the metal surface [23].

Table 2. Thermodynamics and activation parameters for mild steel in presence of coconut palm petiole extract in 0.5 M H_2SO_4 and 1 M HCl.

Acid medium	Inhibitor conc. (% v/v)	Ea kJ/mol	-ΔG (kJ / mol)					ΔS kJ/mol	+ΔH kJ/mol
			303 K	313 K	323 K	333 K	343 K		
0.5 M H_2SO_4	Blank	52.00	-	-	-	-	-	-	-
	0.5	52.03	13.33	15.80	16.27	15.54	15.71	-0.0098	19.06
	1.0	55.33	13.57	15.91	16.31	15.08	15.19	-0.0339	26.75
	1.5	51.39	13.32	15.42	15.71	15.39	15.70	+0.0049	13.93
	2.0	50.31	12.65	15.58	15.51	15.02	15.22	-0.0158	20.52
	2.5	51.23	12.83	15.33	15.40	15.14	15.38	-0.0009	15.62
	3.0	49.19	12.76	15.36	15.73	15.21	15.11	-0.0128	19.56
1 M HCl	Blank	41.12	-	-	-	-	-	-	-
	0.5	54.33	14.18	15.27	15.52	13.10	13.20	-0.0861	42.54
	1.0	46.46	12.78	13.98	14.52	14.34	12.94	-0.0330	24.79
	1.5	43.80	13.22	13.55	14.05	14.22	13.73	+0.0071	11.54
	2.0	44.89	12.76	13.46	13.91	14.00	13.63	+0.0057	11.88
	2.5	44.45	12.66	13.44	13.89	13.89	13.71	+0.0080	11.08
	3.0	44.46	12.84	13.39	13.74	14.00	13.61	+0.0092	10.64

Other kinetic parameters such as enthalpy (ΔH°) and entropy (ΔS°) of activation of corrosion process may be evaluated from the effect of temperature. A plot of -ΔG°_{ads} vs. T is a straight line. Enthalpy and entropy of activation were obtained from the slope and intercept of the linear plots, respectively .The results which are presented in Table 2, show that the enthalpy of activation values are all positive for both the acid baths. The positive sign of the enthalpies reflects the endothermic nature of the mild steel dissolution process [24]. Also, the entropies of activation were positive and negative for both the acid baths, indicating that the activation complex represents both association and dissociation steps [25].

Electrochemical technique

Polarization measurement is an important research tool in the investigation of a variety of electrochemical phenomena. Such measurements permit studies of the reaction mechanism and the kinetics of corrosion phenomena on the metal deposition. All electrochemical measurements were made using a three electrode glass cell connected to a solartron 1280B potentiostat controlled by a personal computer. The software package used was corrware and zplot. The corrosion kinetic parameters such as E_{corr}, I_{corr}, Tafel constant b_a, b_c are tabulated in Table 3. A similar displacement of cathodic and anodic Tafel lines indicated that the inhibitor inhibited both the hydrogen evolution and the metal dissolution process. Thus this inhibitor acted as a mixed type inhibitor [26]. Tafel slopes of b_a and b_c for mild steel in the presence of the inhibitor change uniformly. This behavior indicated that the molecules are adsorbed on both the anodic and cathodic sites, acting as a mixed type of inhibitor (see Fig. 7). No significant change in E_{corr} values also supported the mixed behavior of the inhibitor. I_{corr} was found to decrease as the concentration of the inhibitor increases. Linear polarization resistant R_p increases with increase in concentration of petiole extract. This confirms the inhibitive action of coconut palm petiole extract on metal surface.

Table 3. Electrochemical and corrosion parameters for mild steel in the presence of coconut palm petiole extract in 0.5 M H_2SO_4 and 1 M HCl.

Acid medium	Inhibitor conc. (%v/v)	I_{corr} mA cm^{-2}	-E_{corr} V/dec	b_a mV/dec	b_c mV/dec	IE (%)
0.5 M H_2SO_4	Blank	6094	523	226.94	182.30	-
	0.5	2573	516	197.13	125.65	57.77
	1.0	1860	507	177.45	111.80	69.47
	1.5	1379	501	161.50	100.84	77.37
	2.0	589	495	157.64	74.94	90.33
	2.5	506	492	126.12	72.27	91.69
	3.0	487	489	124.14	70.90	92.00
1 M HCl	Blank	6153	508	185.49	122.29	-
	0.5	3828	507	182.48	121.11	37.78
	1.0	3077	505	156.24	114.92	49.99
	1.5	1242	498	151.30	110.71	79.81
	2.0	1182	495	150.36	104.38	80.78
	2.5	1056	491	146.24	95.04	82.83
	3.0	571	484	144.63	89.69	90.71

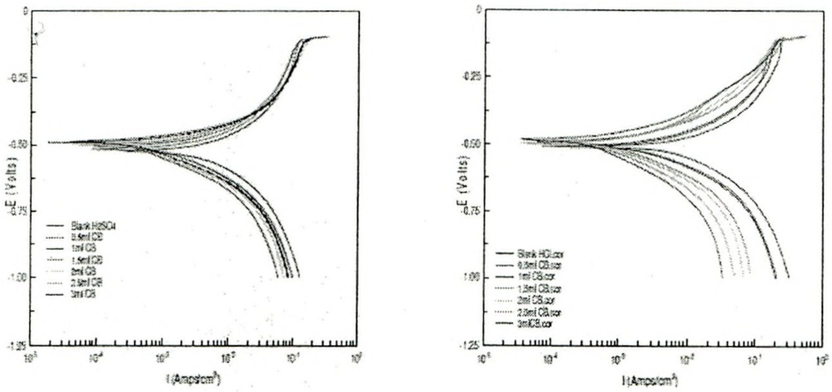
Electrochemical impedance spectroscopy (EIS)

Nyquist plots for mild steel in 0.5 M H_2SO_4 and 1 M HCl in the absence and presence of coconut palm petiole extract at various concentrations were shown in Fig. 8. The Nyquist plots show that the diameter of the capacitive loop and consequently the value of the charge transfer resistance, R_{ct}, increased with the concentration of inhibitors, which is an indication of the inhibitive action.

In all cases, the semicircle corresponds to a capacitive loop. The semicircle radii depend on the inhibitor concentration. The diameter of the capacitive loop increased with increasing inhibitor concentration. The results show that R_{ct} values increased with an increase in inhibitor concentration. Inhibition efficiency can be determined using the following relationship:

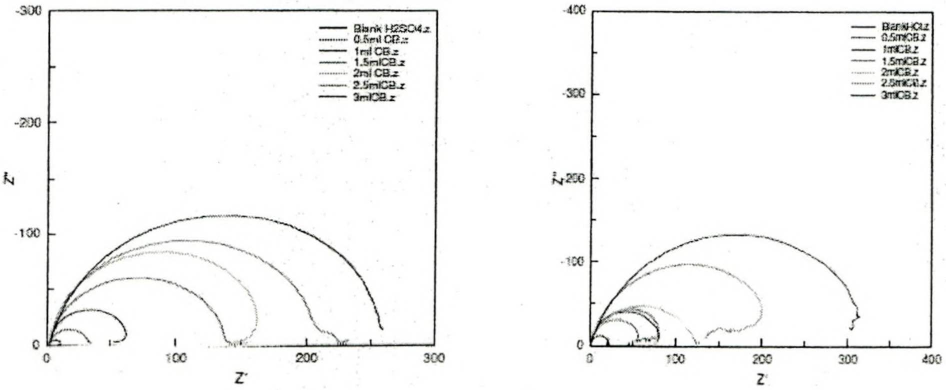
$$IE\% = [(R_{ct} - R_{ct}') / R_{ct}] \times 100 \qquad (3)$$

where R_{ct} and R_{ct}' are the polarization resistance in the presence and absence of inhibitors, respectively. The electrochemical impedance parameters derived from the Nyquist plots and the inhibitors efficiencies (IE%) are shown in the Table 4. From the results obtained, it was clear that the extract inhibits the corrosion of mild steel in both acid media.



a) b)

Figure 7. Polarization curves for mild steel in **a)** 0.5 M H_2SO_4 and **b)** 1 M HCl in the presence of coconut palm petiole extract at different concentrations.



a) b)

Figure 8. Nyquist plot of mild steel in presence of coconut palm petiole extract in **a)** 0.5 M H_2SO_4 and **b)** 1 M HCl.

Fig. 9 revealed that the results of mass loss and electrochemical measurement methods are in good agreement within the experimental error. The difference in inhibition efficiency values obtained by mass loss and electrochemical techniques can be attributed to the fact that weight loss method gives average corrosion rates, whereas the electrochemical measurement gives instantaneous corrosion rate. The difference may be expected to arise because of the difference in time required to form an adsorbed layer, which brings down corrosion.

Table 4. Impedance parameters and inhibition efficiency for mild steel in 0.5 M H_2SO_4 and 1 M HCl containing different concentrations of coconut palm petiole extract.

Acid medium	Inhibitor conc. (%v/v)	R_{ct} (ohm cm^2)	IE (%)	C_{dl} x10 $^{-4}$ Fcm^2	θ	R_p (ohm cm^2)	IE (%)
0.5 M H_2SO_4	Blank	8.92	-	1.895	-	7.25	-
	0.5	30.83	71.06	1.792	0.054	11.99	39.53
	1.0	62.78	85.79	1.680	0.113	14.87	51.24
	1.5	137.11	93.49	0.862	0.545	18.59	61.00
	2.0	170.21	94.75	0.751	0.603	23.06	68.56
	2.5	208.83	95.72	0.405	0.786	29.47	75.39
	3.0	263.96	96.62	0.335	0.823	32.46	77.66
1 M HCl	Blank	23.18	-	2.944	-	3.84	-
	0.5	83.17	72.12	1.539	0.477	7.71	50.19
	1.0	84.15	72.45	1.456	0.505	9.10	57.80
	1.5	92.70	74.99	0.826	0.719	18.72	79.48
	2.0	124.48	81.37	0.612	0.792	21.97	82.52
	2.5	213.28	89.13	0.424	0.855	27.15	85.85
	3.0	330.83	92.99	0.287	0.902	41.06	90.64

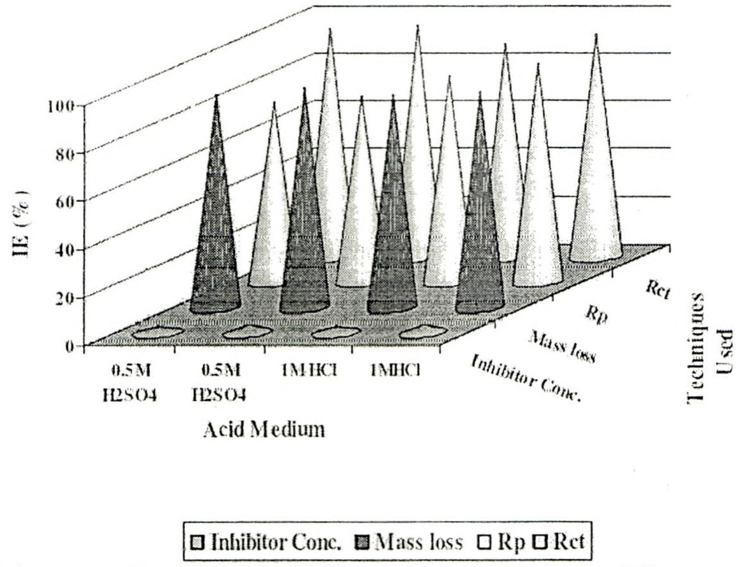


Figure 9. Comparison of inhibition efficiencies obtained from different methods.

Industrial application of coconut palm petiole extract on mild steel acid medium

There is a class of chemical inhibitors which work by removing electrons from the metal, thereby pushing the potential into a positive region where an oxide film spontaneously forms. This results in a stable, passive surface with a very low corrosion rate. Industries apply this technology in processes where the inhibitor can be conveniently added without causing environmental or health problems.

One of the categories of corrosion inhibitors are those which form a surface layer of a foreign chemical compound provided by the inhibitor itself. Many commercial inhibitors, for example, calgon, is a solution of sodium

hexametaphosphate, a condensed phosphate polymer based on the unit $(\text{-}PO_3\text{-})_n$, used as an inhibitor in potable water systems (drinking water) because it is non-toxic and widely used in large institutions such as hotels and hospitals [27].
In the present investigation, efforts are taken to test the coconut palm petiole extract as corrosion inhibitors in various industries at Coimbatore. The reports furnished from the industries reveal that the coconut palm petiole extract functions effectively as a corrosion inhibitor. Industries can utilize this type of low cost / zero cost inhibitor for these pickling processes.

Mechanism of corrosion inhibition

The isotherm depicted in Fig. 5 characterizes the spontaneous physisorption of phytochemical composition (Table 1) of coconut palm petiole extract on heterogeneous surfaces [28]. Thus, the mechanism of corrosion inhibition of mild steel in acidic solution by the phytochemical compounds of the extract can be explained on the basis of adsorption on the metal surface. This indicates that the inhibition efficiency of the extract is due to the presence of some or all of the above listed phytochemical constituents. The adsorption of the inhibitor molecules on the mild steel surface is due to the donor - acceptor interaction between π electrons of donor atoms O and aromatic rings of inhibitors and the acceptor, ie., vacant d orbital of iron surface atoms [29]. The inhibitor molecules can also be adsorbed on the metal surface in the form of negatively charged species which can interact electrostatically with positively charged metal surface, which led to increase the surface coverage and consequently protect efficiency even in the case of low inhibitor concentration. Eddy and Ebenso [30] also stated that sapponins, tannins and alkaloids are active constituents of most green inhibitors.

Conclusions

Based on the above results, the following conclusions can be drawn:

- Aqueous extract of destructive distillate of coconut palm petiole extract was found to be an efficient inhibitor for the corrosion of mild steel in 0.5 M H_2SO_4 and 1 M HCl.
- Inhibition efficiency increased with an increase in coconut palm petiole extract content up to 3%v/v to reach 95.24% in 0.5 M H_2SO_4 and 90.35% in 1 M HCl at 313 K, but decreased with rise in temperature.
- The corrosion process is inhibited by adsorption of the coconut palm petiole extract on the mild steel surface following the Langmuir adsorption isotherm. This indicates that the inhibition effect of the extract is due to adsorption of some or all the listed phytochemical constituents.
- Adsorption of aqueous extract of destructive distillate of coconut palm petiole extract on the surface of the mild steel is spontaneous and occurs by physical adsorption.
- The negative free energy $(-\Delta G^\circ_{ads})$ of adsorption indicates strong and spontaneous adsorption of the coconut palm petiole extract on the mild steel surface.

- Values of Tafel constant b_a and b_c confirm that the coconut palm petiole extract acts like mixed type inhibitor.
- Increase in R_p and R_{ct} values and decrease in I_{corr} and C_{dl} values confirm that the coconut palm petiole extract is adsorbed on the mild steel surface and inhibition process is followed by monolayer adsorption.
- The inhibition efficiencies determined by mass loss and electrochemical methods are in reasonable good agreement.
- Thus the coconut palm (*cocos nucifera*) petiole extract was proved to be an effective eco friendly and low cost inhibitor.

References

1. N.O. Eddy, S.A. Odoemelam, *Pigment Resin Tech.* 38 (2009) 111. 10.1108/03699420910940617
2. A. Bouyanzer, B. Hammouti, *Pigment Resin Tech.* 33 (2004) 287. 10.1108/03699420410560489
3. N.O. Eddy, E.E. Ebenso, *Afri. J. Pure Appl. Chem.* 2 (2008) 46.
4. E.E. Ebenso, N.O. Eddy, A.O. Odiongenyi. *Port. Electrochim. Acta* 27 (2009) 13. 10.4152/pea.200901013
5. D. Maheswari, R. Rajalakshmi, S. Subhashini, M. Viswanathan, S. Sivakamasundari, *Proceedings of Enviro.,* Coimbatore, India (2001) 534.
6. C.A. Loto, A.I. Mohammed, R.O. Loto, *Corrosion Prevention Control* 50 (2003) 107.
7. A.Y. El-Etre, *Appl. Surf. Sci.* 252 (2006) 8521. 10.1016/j.apsusc.2005.11.066
8. S. Subhashini, S. Sathyanarayana, C. Marikkannu, S. Sivakamasundari, *ISAEST VII* (2002) 146.
9. R. Rajalakshmi, S. Sathyanarayana, C. Marikkannu, S. Sivakamasundari, *ISAEST VII* (2002) 142.
10. G. Manohari, R. Rajalakshmi, Ninth Seminar Proceedings, Tamil Nadu State Council for Science and Technology, India (2001) 318.
11. A. Prithiba, S. Sathiyanarayana, R. Rajalakshmi, S. Sivakamasundari, Proceedings of 11th NCCI, Baroda, India (2003) 3.
12. M.D.J. Kawser, A.Farid Nash, *J. Oil Palm Research* 12 (2000) 86.
13. N. Al-Andis, E. Khamis, A. Al-Mayouf, H. Aboul-Enein, *Corros. Prev. Cont.* 42 (1995) 13.
14. I.N. Putilova, S.A. Balezin, V.P. Barannik, *Met. Corros. Inhibitors*, Pergamm Press, NewYork, 1960. p.31.
15. N.S. Rawat, A.K. Singh, *Bull. Electrochem.* 3 (1987) 7.
16. B.B. Damaskin, O.A. Petrii, B. Batraktov, Adsorption of organic compounds on electrodes, Plenum Press, New York, (1971).
17. M. Benabdellah, A. Aouniti, A. Dafali, B. Hammouti, M. Benkaddour, A. Yahyi, A. Ettouhami, *Appl. Surf. Sci.* 252 (2006) 8341. 10.1016/j.apsusc.2005.11.037
18. O.K. Abiiola, N.C. Oforka, *Corros. Sci. Eng.* 3 (2002) 21.

19. E.E. Ebenso, P.C. Okafor, U.J. Ekpe, *Anti-Corrosion Methods Materials* 50 (2003) 414. 10.1108/00035590310501576
20. E.E. Ebenso, *Mater. Chem. Phys.* 79 (2003) 58. 10.1016/S0254-0584(02)00446-7
21. S.A. Umoren, I.B. Obot, E.E. Ebenso, P.C. Okafor, O. Ogbobe, E.E. Oguzie, *Anti-Corrosion Methods Materials* 53 (2006) 277. 10.1108/00035590610692554
22. A.Y. El-Etre, *J. Colloid Interface Sci.* 314 (2007) 578. 10.1016/j.jcis.2007.05.077
23. S.A. Umoren, I.B. Obot, E.E. Ebenso, N.O. Obi-Egbedi, *Desalination* 247 (2009) 561. 10.1016/j.desal.2008.09.005
24. G. Quartarone, G. Moretti, A. Tassan, A. Zingales, *Werkst Korrosion* 45 (1994) 641.
25. M. Abdallah, E.A. Helal, A.S. Fouda, *Corros. Sci.* 48 (2006) 1639. 10.1016/j.corsci.2005.06.020
26. J.O'M. Bockris, O.A.J. Swinkell, *J. Electrochem. Science* 111 (1964) 736. 10.1149/1.2426222
27. Graeme Wright, "Corrosion Protection of Metals", Chemical Processes in New Zealand, 2nd Ed., NZIC (1998) p. 8J 1-10.
28. E. McCafferty, N. Hackerman, *J. Electrochem. Soc.* 119 (1972) 146. 10.1149/1.2404150
29. M. Stern, A.L. Geary, *J. Electrochem. Soc.* 104 (1957) 56. 10.1149/1.2428496
30. N.O. Eddy, E.E. Ebenso, *Afri. J. Pure Appl. Chem.* 2 (2008) 046.