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Electrochemical Investigation of Coconut Oil as Green Corrosion Inhibitor for ST37 Carbon Steel Protection

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Abstract

The corrosion inhibition of ST37 Carbon Steel in 1.0 M HCl by aquatic extract of coconut has been studied as a possible source of green inhibitor using the potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The aquatic extract of coconut have many advantages over classical techniques of sample preparation of plant gums (such as drying and solvent reflux).Polarization measurements showed that the extracts act as mixed typed inhibitor but under cathodic control. The passivation layer formed on metal surface, and then inhibits the anodic dissolution of steel. The compounds that available in coconut oil provides a good protection to steel against corrosion by shifting the potential at the noble direction. The Nyquist plots showed that on increasing CW concentration, increases charge transfer resistance and decreases double layer capacitance. The Results obtained from Tafel extrapolation and EIS techniques were in good agreement. SEM studies also help to understand the changes that take place on the surfacelayer with respect to change in CW concentration.

Keywords: *Green inhibitor, Carbon steel, Passivation layer, EIS, Polarization.*

Introduction

Nowadays, studies on steel corrosion phenomena have become an industrial and academic topic, especially in acid media [1, 2]. This is because of the increasing industrial applications of acid solutions. The most important fields of applications are acid pickling, industrial cleaning, acid descaling, oil-well acidizing in oil recovery and the petrochemical processes. Aqueous solutions of acids are among the most corrosive media. So, the rate of corrosion at which metals are

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destroyed in acidic media is very high, especially when soluble corrosion products are formed. Therefore, investigating and exploring corrosion inhibitors for steel corrosion in acid solutions are not only important from an academic point of view but also for its practical applications [3-5]. Most of the reported acid corrosion inhibitors are synthetic organic compounds containing heterocyclic atoms (nitrogen, sulfur, oxygen and phosphorous), aromatic rings or triple bonds [6–8]. A corrosion inhibitor is a chemical substance employed in a very small amount that effectively reduces the corrosion rate. One strong coordination bond causes higher inhibition efficiency, consequently the inhibition increases in the series O < N < S < P [9-11].

The known hazard effects of most synthetic corrosion inhibitors are the motivation for the use of some nature products as green inhibitors. Recently, plant extracts have again become important as an environmentally acceptable, readily available and renewable source for a wide range of needed inhibitors. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost [12-17]. Among the oils of great economic interest, the coconut oil stands out for its high nutritional and pharmaceutical value [18]. Although there are few reports in the literature, some studies indicate that coconut oil has antifungal [19–21] and antioxidant activities [22, 23].

Coconut oil is an edible oil extracted from the kernel or meat of matured coconuts harvested from the coconut palm (Cocosnucifera). The coconut liquid endosperm contains several biodegradable non-toxic organic compounds and is one of the world's most versatile natural products because of its many applications [24, 25]. As a contribution to the current interest on eco-friendly, green, corrosion inhibitors, and the present study investigates the inhibiting effect of water extract of coconut (CW) on the ST37 carbon steel corrosion in 1.0 M HCl solution using the potentiodynamic polarization and EIS techniques. The inhibitory effect of the CW is ascribed to the presence of organic compounds (Fig. 1) in the CW chemical constituents. CW contains several organic compounds of high molecular weight with heteroatom in their chemical structures. These include amino acids, ascorbic acid, vitamin B1, sorbitol, fructose, glucose, malic acid, phytohormone, auxin, cytokinin, gibberellin amongst others.

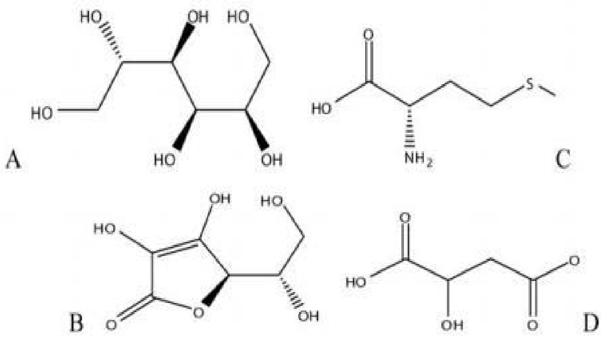

Figure 1. Chemical structures of some compounds in Cocosnucifera L. water: (A) sorbitol; (B) ascorbic acid; (C) methionine; (D) malic acid. (from Ref. [26]).

However, synergistic and antagonistic effects may play an important role on the inhibition efficiency of CW as an inhibitor because CW contains several compounds. Further investigation using surface analytical techniques (SEM, EDX and XRD) will lead to the characterization of the active materials in the adsorbed layer [26].

Experimental

Materials

A circular sheet of ST37 carbon steel 2mm in thickness and 0.7855 cm2 surface area with the following composition: C = 0.17%; Mn = 1.4%;P = 0.045%; S = 0.045%; and the balance Fe was used in the study. The working electrodes were degreased in absolute ethanol, dried in warm air and stored in moisture-free desiccators prior to use. The corrosive medium was1.0 M HCl prepared from 37% analytical grade supplied by Merck. The double distillated water was used for the preparation of allreagents. The coconut was obtained from local farmers and transported to the laboratory. 500 grams of the coconut was extracted using water for 12 h.

Electrochemical Measurements

Electrochemical measurements were carried out by using an electrochemical work station, (PGSTAT302 with GPES Manager as interface software). The electrochemical cell used was a conventional three-electrode compartment having glass cell with aplatinum counter electrode and a Saturated Calomel Electrode (SCE) coupled to a fine Luggin capillary as reference. The working electrode was made up of ST37 carbon steel. All the values of potential were with reference to the SCE.

Potentiodynamic Polarization Study

Potentiodynamic polarization measurements were carried out by scanning the electrode potential from -900 mV to -200 mV(vs. SCE) with a scan rate of 0.5 mV s^{-1}. The linear Tafel segments were chosen (approximately 50–100 mV from the corrosion potential, Ecorr, of the anodic and cathodic curves) and were extrapolated to Ecorr several times to obtain reproducible corrosion current (icorr) values. Eq. (1) shows the calculation of inhibition efficiency IE (%) from the icorr values:

$$IE(\%) = \frac{i_0 - i}{i_0} \times 100 \qquad (1)$$

Where i_0 is the corrosion current without inhibitor, i is the corrosion current density with inhibitor.

Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance measurements were performed over a frequency range of 10 KHz to 10 MHz at the stable open circuit potential with an AC wave of 10 mV (rms). The impedance results obtained are represented as Nyquist plots. IE (%) is calculated from the charge transfer resistance (Rct) values by using the following equation:

$$IE(\%) = \frac{R_{ct} - R_{ct,0}}{R_{ct}} \times 100 \qquad (2)$$

where $R_{ct,0}$ is the charge transfer resistance without inhibitor, Rctis the charge transfer resistance with inhibitor.

Results and discussion

Potentiodynamic Polarization Study

Figure 2 displays the potentiodynamic polarization curves of ST37 carbon steel in 1 M HCl medium which was obtained before and after the introduction of various doses of CW inhibitor. Various corrosion parameters viz., corrosion current (i_{corr}), corrosion potential (Ecorr) and Tafel slope values (ba and bc) derived from this figure are given in Table 1.Precise evaluation of Tafel slopes by Tafel extrapolation is often impossible, simply because an experimental polarization curve does not exhibit linear Tafel regions [27-29]. Most of the polarization curves obtained in our studies do not display the expected log/linear Tafel behavior. Bandy and Jones [29] attributed this to a number of aspects including a change in the nature of the metal surface as liberated corrosion products or impurities in the steel(e.g., Fe3C) deposit to form a non-passivating, conducting surface film [30, 31]. At both cathodic and anodic branches, since the solution is stationary, diffusion of H+ions and Fe ions will be slow, and concentration polarization can act to shorten the cathodic and anodiclinear Tafel regions.

From Table 2, it could be observed that the presence of different concentrations of green inhibitors molecules cause a decrease of the current density (icorr) when the concentration of the CWis increased.

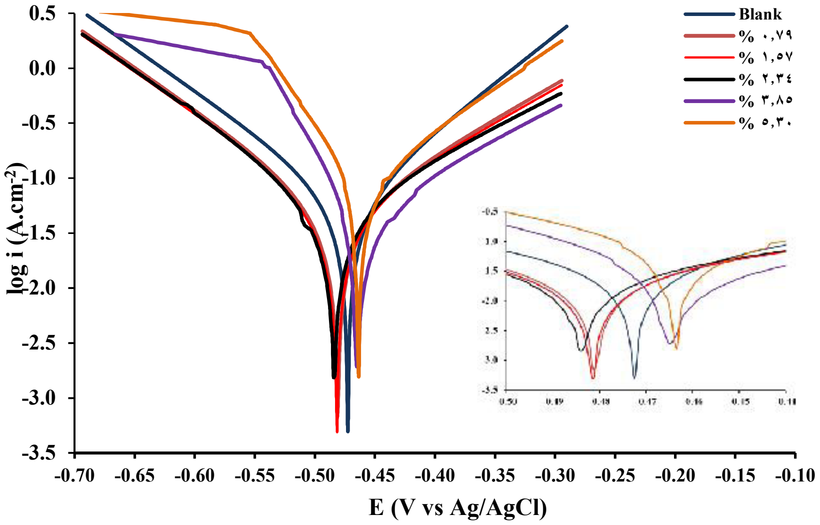

Figure 2. Tafel polarization curves for ST37 carbon steel in 1.0 M hydrochloric acid solution at different volume percent concentrations of CW.

Table 1. Electrochemical parameters obtained from potentiodynamic polarization technique for ST37 carbon steel in 1.0 M HCl in the absence and presence of CW.

V (ml)	**V/V** (%)	**E $_{Corr}$** (V vs. SCE)	**i$_{Corr}$** ($\times 10^{-5}$ A)	**b$_a$** (V dec^{-1})	**-b$_c$** (V dec^{-1})	**IE** (%)
Blank	0.00	-0.483	6.49	0.181	0.130	0.00
2	0.79	-0.481	5.29	0.161	0.131	18.49
4	1.57	-0.481	5.26	0.159	0.132	18.95
6	2.34	-0.472	5.03	0.163	0.132	22.50
10	3.85	-0.468	4.36	0.203	0.141	32.82
14	5.30	-0.466	4.27	0.211	0.144	34.21

It is also observed that addition of CW slightly shifted Ecorr values in both anodic and cathodic directions. But, analysis of both anodic (ba) and cathodic (bc) Tafel slope values indicated that anodic reaction was suppressed during the addition of green CW, which suggested that this inhibitor reduced anodic dissolution, [32] in other word, passivation layer formed on metal surface and then inhibits the anodic dissolution of steel. So dependence of activation energy of anodic dissolution on electrode potential is weakened. The maximum inhibition efficiency of 34.21% was found at 5.30% volume concentration of CW and further increase in concentration did not cause any significant change in the performance of inhibitor.

Electrochemical Impedance Spectroscopy (EIS) Study

Nyquist plots for ST37 carbon steel in aqueous media in the absence and in the presence of various concentration of the inhibitor are shown in Fig. 3.Impedance plots are semicircles both in the absence and in the presence of the CW. The diameter of the capacitive loop increased with increase in the concentration of the CW. This indicated that the impedance of the inhibited substrate increased with the inhibitor concentration. This increase in capacitive semicircles suggests that the inhibition action of these inhibitors is due to their adsorption on the metal surface without altering the corrosion mechanism. The impedance diagrams (Nyquist) obtained are depressed semicircles with the center below the real axis. This feature shows contribution from surface roughness, distribution of active sites, and adsorption of inhibitors and formation of porous layers as reported by others [33]. All the curves obtained are approximated by a single capacitive semicircle, showing that the corrosion process was mainly charge-transfer controlled [34]. The general shape of the curves is very similar for all samples; the shape is maintained throughout the whole test period, indicating that almost no change in the corrosion mechanism occurred either due to the immersion time or to the inhibitor addition [35].

A constant phase element (CPE) represents the double layer capacity. A resistance Rct represents the inhibitor's resistance to the charge transfer upon oxidation of the metal. The data obtained after the fitting procedure are shown in Table 2. The obtained IE (%) values showed similar trend with the potentiodynamic polarization results and reached maximum of above 33% at concentrations of 5.30% volume percentage. The shorter experimental duration for the impedance study in comparison with the polarization measurement may reduce the adsorption of inhibitor molecules at lower concentrations. Consequently, lessinhibitor molecules were adsorbed onto the steel surface and were not sufficient to form a time-resistant layer [36], leading to low Rct values which caused a decrease in IE (%) values at low concentrations of inhibitors.

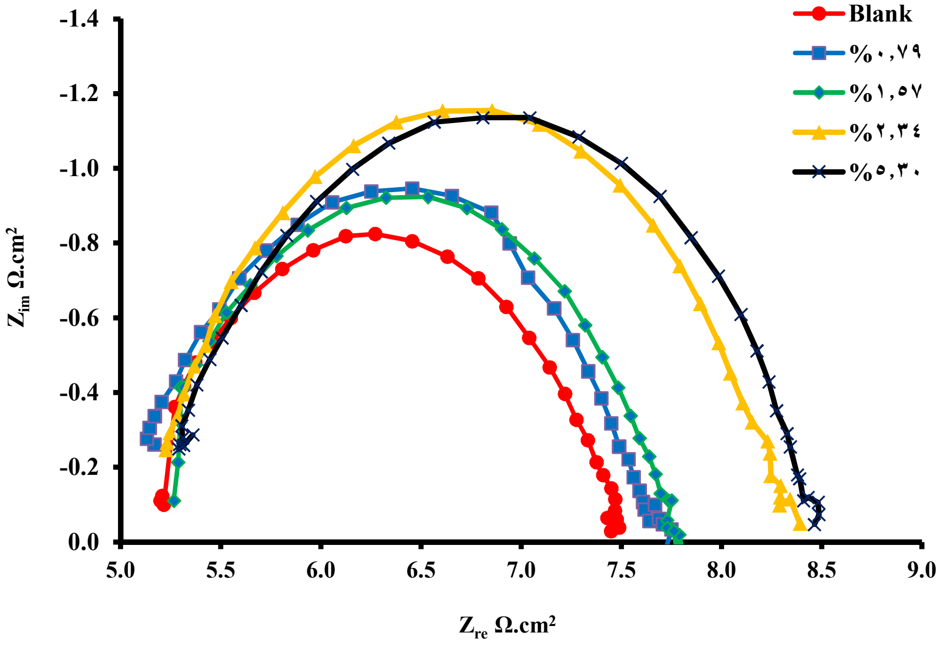

Figure 3. Nyquist plots for ST37 carbon steel in 1.0 M hydrochloric acid solution at different volume percent concentrations of CW.

Table 2. Electrochemical parameters obtained from EIS plots for ST37 carbon steel in 1.0 M HCl in the absence and presence of CW.

V (ml)	V/V (%)	R_{ct} (Ω cm^2)	IE (%)
Blank	0.00	2.23	0.00
2	0.79	2.47	9.72
4	1.57	2.58	13.57
6	2.34	3.17	29.65
14	5.30	3.35	33.43

Scanning Electron Microscopic (SEM) analysis

The SEM micrographs of the corroded and protected ST37 carbon steel are shown in the Fig.4. It is clear that the surface of the ST37 carbon steel was extremely corroded in 1.0 M HCl whereas there is a disappearance of deep cracks and protected owing to the formation of thick layer of adsorbed inhibitor on the metal.

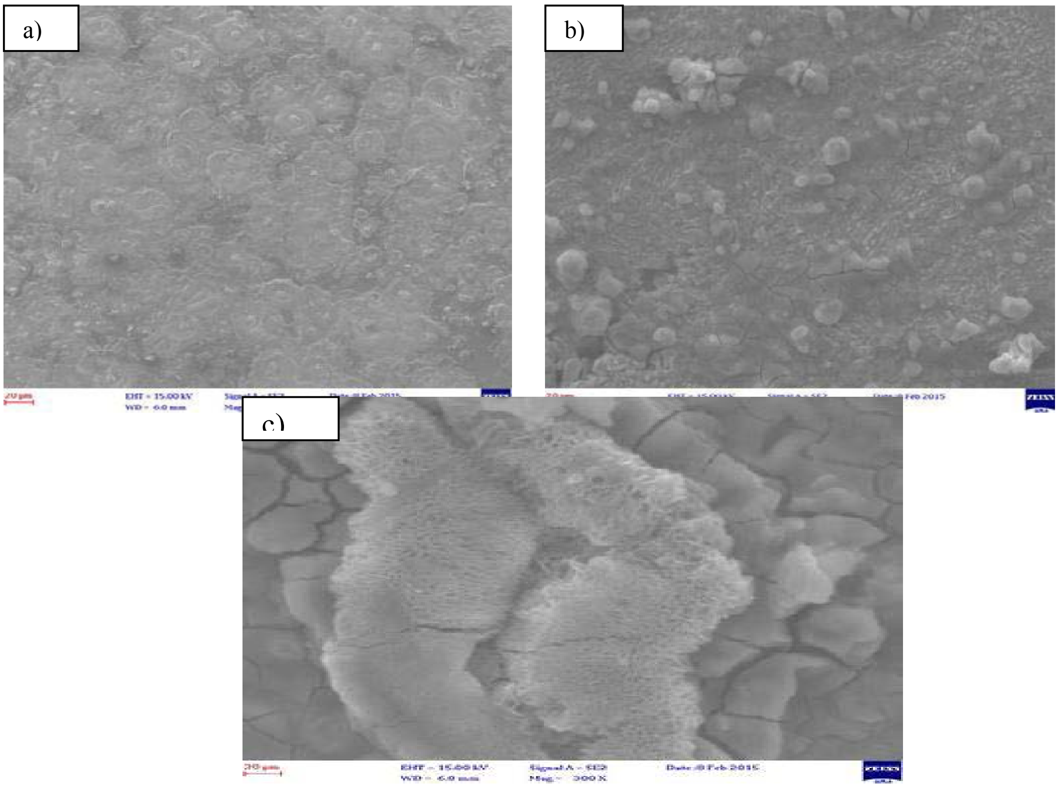

Figure 3. SEM images of ST37 carbon steel a) before immersion, b) after 3 hours of immersion in 1.0 M HCl, c) after 3 hours of immersion in 1.0 M HCland 5.30% volume concentration of CW.

Conclusion

Promising green eco-friendly water extract of coconut was successfully applied as corrosion inhibitor on the surface of ST37 carbon steel in aqueous acidic media that acts both over the anodic process of metal dissolution. Using volume percentage concentration = 5.30%, the inhibition efficiency obtained was 34%. The corrosion inhibition efficiencies, determined by AC impedance and polarization methods are in reasonable agreement. The major advantage in this paper is presented; there is lack of need to use classical techniques of sample preparation of plant gums (such as drying and solvent reflux) in corrosion inhibitor. These interesting results adapt coconut oil, as one of the natural compound, to be probably the next generation alternatives for the ordinary chemical and toxic inhibitors.

Acknowledgments

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References

[1] F. Bentiss, M. Lagrenée, M. Traisnel, *Corros*. Sci., 56, 733 (2000).

[2] R. Yıldız, A. Döner, T.Doğan, İ.Dehri,*Corros*. Sci., 82, 125 (2014).

[3] L. Wang, *Corros. Sci*., 43, 1637 (2001).

[4] L. Fragoza-Mara, O. Olivares-Xometlb, M. A. Domínguez-Aguilara, E. A. Floresa, P. Arellanes-Lozadac, F. Jiménez-Cruz, *Corros. Sci*., 61, 171 (2012).

[5] P. Morales-Gil, G. Negrón-Silva, M. Romero-Romo, C. Ángeles-Chávez, M. Palomar-Pardavé, *Electrochim. Acta*, 49, 4733 (2004).

[6] I.Jevremović, M. Singer, S.Nešić, V. Mišković-Stanković, *Corros. Sci*., 77, 265 (2013).

[7] N.M. Hashim, A.A. Rahim, H. Osman, P.B. Raja, *Chem. Eng. Commun*., 199, 751 (2012).

[8] A. Popova, M. Christov, A. Zwetanova, *Corros. Sci*., 49, 2131 (2007).

[9] X.L Cheng, H.Y Ma, S.H Chen, R Yu, X Chen, Z.M Yao, *Corros. Sci*., 41, 321 (1998).

[10] P. C. Okafor, Y. Zheng, *Corros. Sci*., 51, 850 (2009).

[11]M. Bouayed, H. Rabaa, A. Srhiri, J.-Y. Saillard, A.BenBachir, A.LeBeuze,*Corros. Sci*., 41, 501 (1998).

[12]M. B. Radovanović, M. B. Petrović, A. T. Simonović, S. M. Milić, M. M. Antonijević, Environ. *Sci. Pollut Res*., 20, 4370 (2013).

[13] S.AbdulrahmanAsipita, M. Ismail, M. ZaimiAbd Majid, Z. Abdul Majid, Ch. Abdullah, J.Mirza, *J. Cleaner Produc*., 67, 139(2014).

[14] M. M. Fares, A.K. Maayta, M. M. Al-Qudah, *Corros. Sci*.,60, 112 (2012).

[15] M. Larif, A. Elmidaoui, A. Zarrouk, H. Zarrok, R. Salghi, B. Hammouti, H. Oudda, F. Bentiss, *Res Chem. Intermed*., 39, 2663 (2013).

[16] A.Y. El-Etre, *Corros. Sci*., 45, 2485 (2003).

[17] A. Bouyanzer, B. Hammouti, L. Majidi, *Materials Letters*, 60, 2840 (2006).

[18] J. M. Al-Khayri, *Biotechnology*, 9, 477(2010).

[19] D.O. Ogbolu, A.A. Oni, O.A. Daini, A.P. Oloko, *J. Med. Food,* 10, 384 (2007).

[20] V. Agarwal, P. Lal, V. Pruthi, *J. Microbiol. Immunol. Infect.*, 43, 447 (2010).

[21] M. DebMandal, S. Mandal, *Asian Pac. J. Trop. Med.*, 4, 241 (2011).

[22] A.M. Marina, Y.B. Man, S.A. Nazimah, I. Amin, *Int. J. Food Sci. Nutr.,* 60, 114 (2009).

[23] K.G. Nevin, T. Rajamohan, *Food Chemistry*, 99, 260 (2006).

[24]J.W.H. Yong, L. Ge, Y.F. Ng, S.N., Tan, *Molecules*, 14, 5144 (2009).

[25]P. Deme, T. Azmeera, S. Kanjilal, P. Jonnalagadda, V. SaradhiUpadhyayula, *Food Anal. Methods*, 6, 1162 (2013).

[26] K. Olusegun,Y. Abiola, Tobun, *Chinese Chemical Letters*, 21, 1449 (2010).

[27] H.J. Flitt, D.P. Schweinsberg, *Corros. Sci*., 47, 2125 (2005).

[28] F.Mansfeld, Corros. Sci., 47, 3178 (2005).

[29] R. Bandy, D.A. Jones, *Corro. Sci*., 32, 126 (1976).

[30] H. Takayama, S. Tsutsumi, M. Kitajima, D. Santiarworn, B. Liawruangrath, N. Aimi,

Chem. *Pharm. Bull*., 51, 232 (2003).

[31] M. A. Amin, K.F. Khaled, S. A. Fadl-Allah, *Corros. Sci*., 52, 140 (2010).

[32] I.O.M. Bockris, B. Yang, *J. Electrochem. Soc.*, 138, 2237 (2012).

[33] G. Gunasekaran, L.R. Chauhan, *Electrochim. Acta*, 49, 4387 (2004).

[34] G. Trabanelli, C. Monticelli, V. Grassi, A. Frignani, *J. Cem. Concr. Res.,* 35, 1804 (2005).

[35] F.M. Reis, H.G. de Melo, I. Costa, *Electrochim. Acta*, 51, 1780 (2006).

[36] G. Moretti, F. Guidi, G. Grion, *Corro. Sci.,* 46, 387 (2004).