ANTI-CORROSIVE PROPERTIES OF *Cocos nucifera* L. WATER ON MILD STEEL CORROSION IN H_2SO_4 SOLUTION

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Abstract: The inhibitive effect of *Cocos nuciferal L.* water (CW) as green corrosion inhibitor for acid corrosion of mild steel in 0.5 M H_2SO_4 solution has been studied using chemical technique. CW shows significant inhibition as corrosion inhibitor, with 84% efficiency at the highest concentration of the inhibitor. Amongst the Langmuir, Temkin and Frumkin isotherms, the adsorption of the inhibitor molecule onto metal surface accords with Langmuir adsorption isotherm.A first-order kinetics relationship with respect to mild steel was obtained with and without the *Cocos nucifera* L. water from the kinetics treatment of the data.

Keywords: *Cocos nucifera* water, acid inhibitor, non-toxic inhibitor, mild steel

Introduction

The development and design of non- toxic corrosion inhibitors for metals in industrial environment from naturally occurring substances is central to a sustainable industrial development. Numerous inorganic and organic compounds have been reported as corrosion inhibitors for metals in different environments, but the toxic nature of some of them limits their application (Abiola *et al*., 2011a, 2011b). The bio-toxicity of inorganic inhibitors such as dichromate, chromate, nitrate and nitrite is well documented (Abiola *et al*., 2004b). Attention has been focused on the need to design and develop green corrosion inhibitors from plant products to replace toxic ones for a sustainable development.

Several plant extracts (Abiola and Oforka, 2003; Abiola and James, 2010; Abiola and Tobun, 2010; Abiola *et al*., 2016; Abullatef, 2015; Eddy and Odoemelam, 2009; Fouda *et al*., 2019; Jalajaa *et al*., 2019; Haque *et al*., 2018; Idouhli *et al*., 2019; Raja and Sethuramam, 2008; Solmaz, 2014) have been reported to inhibit the corrosion of metals in acid solutions. Their inhibitive effect has been attributed to the presence of phytochemicals in their chemical constituents and the adsorption of the phytochemicals on metal surface leads to slowing down of the electrochemical processes on the metal surface (Abiola and Oforka, 2003; Abiola and James, 2010; Abiola and Tobun, 2010; Abiola *et al*., 2016; Abullatef, 2015).

Phytochemical analysis (Abiola and Oforka, 2003; Abiola and Tobun, 2010) of the liquid endosperm of *Cocos nucifera* L. water shows that it is rich in biodegradable organic compounds.

In our previous communications (Abiola and Oforka, 2003; Abiola and Tobun, 2010), CW has been established as a green corrosion inhibitor of acid corrosion of mild steel and aluminium in HCl solution, using weight loss method. This paper reports the inhibitive effect of CW on corrosion of mild steel in 0.5 M H_2SO_4 solution using weight loss method.

Materials and Methods

Experimental

Material preparations

The mild steel test specimens of dimensions of 5 x 2 x 0.04 cm were cut from mild steel sheet of 0.04 cm in thickness and 98.8% purity. The mild steel samples were prepared, degreased and cleaned as described earlier (Abiola, 2003; Abiola *et al*., 2004b; Abiola, 2006). The H_2S0_4 was of analytical grade and 0.5 M H_2S0_4 was employed as the aggressive solution for this studied. The stock solution of CW was prepared as reported earlier (Abiola, 2003; Abiola, 2010). The stock solution of the CW was diluted with appropriate quantity of 0.5 M H_2S0_4 solution to obtain test solutions of 3 – 20% (v/v) concentrations.

Weight loss determination

The procedure for weight loss determination was as previously communicated (Abiola, 2003; Abiola *et al*., 2004a; Abiola, 2006; Abiola *et al*., 2011). Previously weighed mild steel coupons were immersed in 100 mL open beakers containing 100 mL of 0.5 M H_2S0_4 solution (blank) and then with addition of different CW concentrations to the 0.5M H_2S0_4 solution (3 – 20% v/v) at 30°C. The weight losses of the coupons were monitored after 5 h immersion period per coupon progressively for a total 25 h at 30°C. The experimental readings were recorded to the nearest 0.0001 g on a Mettler digital analytical balance. Duplicate experiments were conducted at the same time and the average weight losses were taken.

Results and Discussion

The results obtained are presented in Figs. 1 – 3 and Table 1 for different concentrations of *Cocos nucifera* L. water from weight loss measurements. The amount of material loss (mg/cm^{-2}) decreases significantly with increasing concentration of CW as presented in Fig. 1. The addition of CW resulted in noticeable reduction in the amount of material loss from the surface of the mild steel in comparison with that of control (0.5M H_2SO_4) at 30°C. As seen in Fig. 1, the weight loss decreased by a factor of 2.89, 5.08 and 6.11 over that of control at CW concentrations of 10, 15 and 20% v/v, respectively. This indicates that the additive inhibit the acid corrosion of mild steel in H_2SO_4 solutions. The values of percentage inhibition efficiency (% E) and surface coverage(θ) were determined for 5 h immersion periods from the material loss using the following equations (Abiola and Oforka, 2003; Abiola and James, 2010; Abiola and Tobun, 2010; Abiola *et al*., 2011a):

$$E\% = [w_u - w_i / w_u] \times 100 \quad (1)$$

$$\theta = E\%/100 \quad (2)$$

Where: w_u and w_i are the uninhibited and inhibited weight loss, respectively

The values of percentage inhibition efficiency at different CW concentrations are listed in Table 1. Table 1 indicates that CW acts as good corrosion inhibitor for the acid corrosion of mild steel in 0.5M H_2SO_4 solution. The % inhibition efficiency increases with increasing CW concentration and % inhibition efficiencies were relatively high in 0.5 M acid solution (84% at 20% v/v of CW concentration). The CW contains methionine, vitamin B_1, sorbitol, fructose, glucose, malic acid, ascorbic acid, gibberellin and amino acids (Abiola and James, 2010; Abiola and Tobun, 2010). The inhibition property of CW is ascribed to the presence of these organic compounds (Fig. 2) in the CW chemical constituents. As previously communicated (Abiola and Tobun, 2010), synergistic and antagonistic effects may play an important role on the inhibition efficiency of CW as an inhibitor due to the presence of several compounds in CW. Further investigation using surface analytical techniques such as XRD, SEM and EDX will lead to the characterization of the active materials in the adsorbed layer. Organic compounds having centers for pie electrons and functional groups -OR, -NR2 and/or –SR have been reported as corrosion inhibitors for metals in acid solutions (Abiola and Oforka, 2003; Abiola and James, 2010; Abiola and Tobun, 2010; Abiola *et al*., 2016).

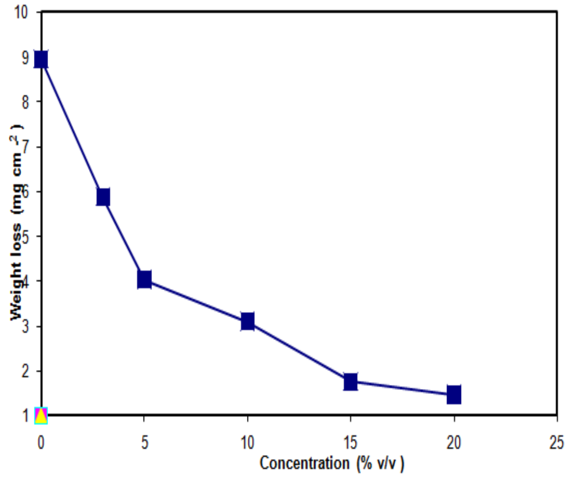

Fig. 1: Relation between material loss and *Cocos nucifera L.* water concentration on mild steel in 0.5M H_2SO_4 solution for 5 h immersion period at 30°C

Table 1: Inhibition efficiency for *Cocos nucifera L.* water on mild steel in0.5 M H_2SO_4 for 5 h immersion period at 30°C

Concentration (% v/v)	Inhibition efficiency	Surface coverage (θ)
3	34.4	0.34
5	54.9	0.55
10	65.4	0.65
15	80	0.80
20	84	0.84

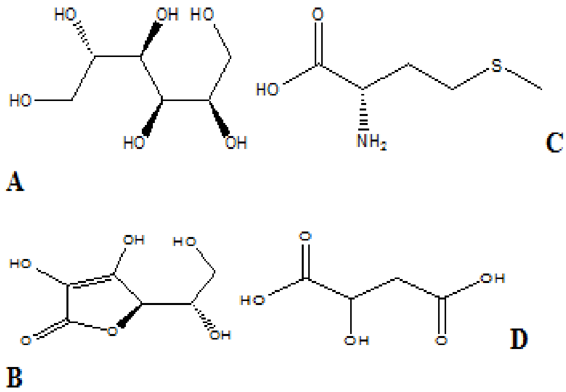

Fig. 2: Chemical structures of some compounds in *Cocos nucifera* L. water: (A) sorbitol, (B) ascorbic acid (C) methionine and (D) malic acid

The adsorption of these compounds on the metal surface reduces the surface area that is available for the attack of the aggressive ion from the acid solution. The material losses decrease with increase in CW concentration due to higher degree of surface coverage as a result of enhanced inhibitor adsorption (Fig. 1). Similar view has been expressed in our previous reports (Abiola and Oforka, 2003; Abiola and James, 2010; Abiola and Tobun, 2010; Abiola *et al*., 2011; Abiola *et al*., 2016) on inhibition of metals in acid solutions by plant extracts. Values ofθ were tested graphically for fit to different isotherms. As presented in Fig. 3, straight line is obtained when C/θ isplotted against C and the linear correlation coefficients of the fitted data is good (R^2 = 0.998).

This confirms that the inhibition is due to the adsorption of the active organic compounds onto the metal surface and the adsorption obeys the Langmuir isotherm expressed as in Equation 3 (Abiola and Oforka, 2003; Abiola and Tobun, 2010; Abiola *et al*., 2013; Abiola and Oloba-Whenu, 2015; Abiola *et al*., 2011b Abiola *et al*., 2016):

$$\frac{C}{\theta} = C + \frac{1}{K} \qquad (3)$$

Where C is the inhibitor concentration and K the equilibrium constant for the adsorption/ desorption of process of the inhibitor molecules on the metal surface.

Value of standard free energy of adsorption can be determined if the concentration of the inhibitor is known (mol L^{-1}) using Equation 4 (Abiola and Oforka, 2004; Abiola *et al*., 2011; Idouhli *et al*., 2019; Abiola and Oloba-Whenu, 2015):

$$K = \frac{1}{55.5}\exp\left(-\frac{\Delta G^0{}_{ads}}{RT}\right) \qquad (4)$$

The value of 55.5 is the molar concentration of water (mol L^{-1}) in solution. The value of $\Delta G^0{}_{ads}$ cannot be determined since the molecular weight of the inhibitor is not known because *Cocos nucifera L.* water contains several compounds.

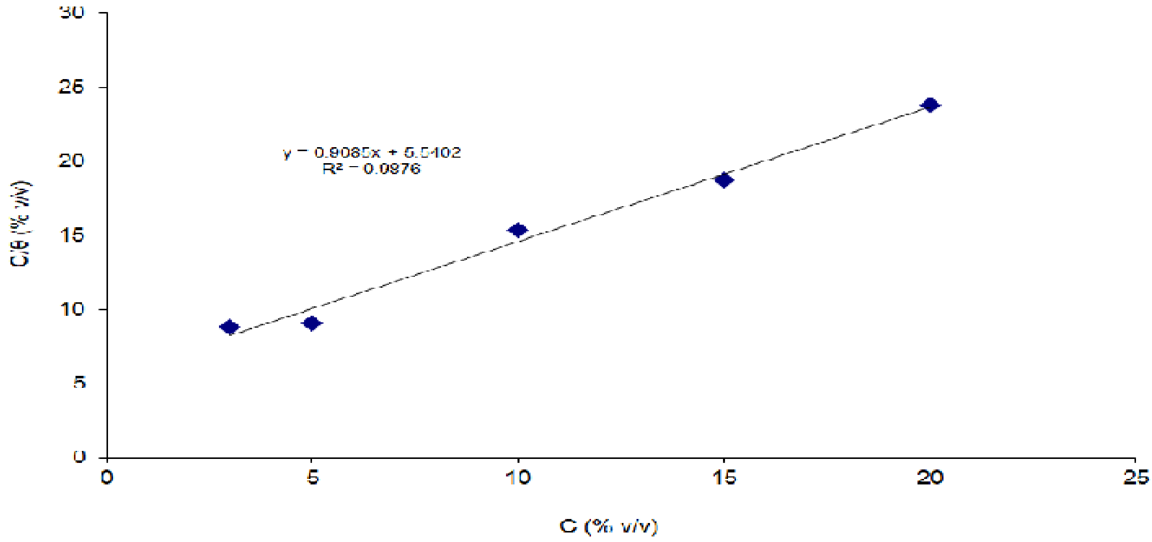

Fig. 3: Langmuir adsorption model on the mild steel surface of *Cocos nucifera L.* water in 0.5 M H_2SO_4 solution for 5 h immersion period at 30°C

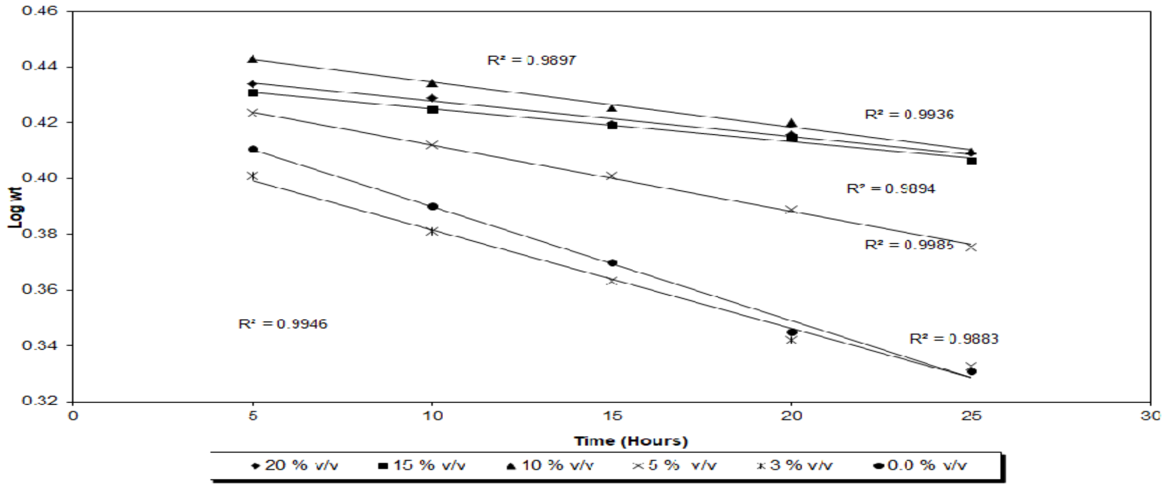

Fig. 4: Variation of log W_t for mild steel coupon with time in 0.5 H_2SO_4 solution wth and without *Cocos nucifera L.* water at 30°C

Kinetics studies of mild steel corrosion in H_2SO_4 solution in the presence Cocos nucifera L. water

The kinetics of the mild steel corrosion in 0.5 M H_2SO_4 solution and 0.5 M H_2SO_4 – inhibitor systems was studied at 30°C by fitting the corrosion data into different rate laws. Fig. 4 shows the dependence of log Wt (weight of mild steel at time t) as a function of time. As depicted in Fig. 4, the corrosion data fit the rate law for first – order reaction as expressed in equation 5 (Abiola, 2006; Abiola and James, 2010; Abiola and Otaigbe, 2008; Abiola *et al*., 2013):

$$\log [W_i - \Delta W_t] = -\frac{k}{2.303}t + \log W_i \qquad (5)$$

Where k is the first – order rate constant, W_i is the initial weight of mild steel sample , ΔW_t is the weight loss of mild steel sample at time t and the term ($W_i - \Delta W_t$) is the residual weight of mild steel sample at time t and can be designated as W_t as shown in Fig. 4.

The obtained plots are linear; confirm a first – order kinetics for the corrosion of mild steel in H_2SO_4 solution in the absence and presence of inhibitor (CW). The anodic reaction of iron in H_2S0_4 solution is;

$$Fe \rightarrow Fe^{2+} + 2e$$

And the cathodic reaction, the rate determining steps in strong acids (Abiola *et al*., 2004a; Abiola, 2006; Abiola and James, 2010; Abiola and Otaigbe, 2008; Wranglen, 1972)

$$H^{+} + e \rightarrow H_{ads}$$

Followed by

$$H_{ads} + H_{ads} \rightarrow H_2$$

Figure 4 reflects the reaction order with respect to iron. This result (Fig. 4), suggests that the adsorption of the inhibitor's molecules do not influence the anodic reaction order. As seen Fig. 4, similar plot was obtained when log Wt was plotted against time for mild steel in H_2SO_4 solution with and without CW (control). Similar results were reported on the adsorption of corrosion inhibitor on metals in HCl solution (Abiola, 2006; Abiola and James, 2010; Abiola and Otaigbe, 2008; Abiola *et al*., 2013).

Conclusion

Results obtained revealed that *C. nucifera L.* water acts as efficient corrosion inhibitor of the mild steel in acid solution. The inhibitory action of theinhibitor is ascribed to the adsorption of the phytochemicals in the plant. The adsorption of the inhibitor on the mild steel surface follows Langmuir adsorption isotherm. A first-order kinetics relationship was obtained from the kinetics treatment of the data of weight loss measurements. *Cocos nucifera L*. water can be added to acid solution as a non-toxic corrosion inhibitor for mild steel in H_2SO_4solution.

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Conflict of Interest

Authors declare that there is no conflict of interest related to this study.

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