

Short Paper

Jackfruit (*Artocarpus heterophyllus* Lam.) and teak (*Tectona grandis* L.) leaf extracts as green corrosion inhibitors

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Abstract. The inhibition effect of water and methanol extracts (WE and ME) of raw and ripe jackfruit leaves (JL) and raw teak leaves (TL) on the corrosion of mild steel (MS) in 1M HCl was studied. Weight loss measurements and potentiodynamic polarization techniques were used to investigate the behavior of the above inhibitors. The percentage of inhibition efficiency (% IE) increased with the increasing concentration of inhibitors in 1 M HCl medium. Water extract of ripe JL was found to be the most effective inhibitor and % IE was 73 at the concentration of 400 ppm. The effectiveness of other inhibitors towards corrosion in the descending order is WE of TL, ME of ripe JL, WE of raw JL, ME of TL and ME of raw JL. With the increase of the temperature, even the adsorption of the most efficient inhibitor, WE of ripe JL, decreased and the rate of corrosion increased. According to the estimated adsorption equilibrium constant, K_{ads} and standard Gibbs free energy change, ΔG^0_{ads} , adsorption of WEs of ripe JL and TL on mild steel surface mainly observed to be by chemisorption. Potentiodynamic polarization scans have revealed the possibility of mixed type corrosion inhibition by WEs of ripe JL and TL.

Keywords. Adsorption, Langmuir isotherm, corrosion inhibitor, weight loss measurements

1 Introduction

Mild steel (MS) has versatile applications in industries and machinery due to low cost, accessibility and their excellent mechanical properties. However, corrosion of MS is an internationally accepted issue in these industries. The study of the corrosion of MS has become important particularly in acidic media because HCl and H₂SO₄ are commonly used in industrial processes such as acid descaling, acid pickling of metals, chemical cleaning, oil-well

cleaning in oil recovery and the petrochemical processes (Ostovari *et al.* 2009; Verma and Khan 2016a).

The utilization of corrosion inhibitors is often a good alternative to minimize metal corrosion and to afford a more acceptable lifetime to metals. Majority of synthetic compounds, specifically organic inhibitors are highly toxic to both human beings and the environment, though most of them behave as anticorrosive inhibitors (Raja and Sethuraman 2008; Andreani *et al.* 2016). This problem has promoted to find eco-friendly and readily available corrosion inhibitors and there is an increased interest in employing plant extracts as corrosion inhibitors for metals in acid solutions. Plants are incredibly rich sources of naturally occurring chemical compounds that are environmentally acceptable, inexpensive, readily available and renewable source of materials (Abiola and James 2010). Green organic compounds serve as effective inhibitors due to the presence of polar functional groups with S, O, or N atoms in molecules, heterocyclic compounds and π electrons. Plant extracts containing tannic acid, polyphenols, polysaccharides, alkaloids, amino acids, and vitamins have been employed as corrosion inhibitors. These compounds have known to adsorb on metal surfaces and block the active sites on the surface and reduce the corrosion rate (Verma and Khan 2016a).

Precursors of green corrosion inhibitors have been identified in *Limbarda crithmoides* essential oil, *Euphorbia falcata*, *Artemisia pallens* and Jackfruit (*Artocarpus heterophyllus* Lam.) and Teak (*Tectona grandis* L.) leaves (Andreani *et al.* 2016; Verma and Khan 2016b). In this work, water extract and methanol extract of ripe JL, raw JL and TL were investigated as potential green corrosion inhibitors for mild steel in 1M HCl medium using weight loss measurements. The effect of temperature on inhibition efficiency (IE) was also studied. The behavior of the most effective inhibitors, water extracts of ripe JL and raw TL was further investigated using potentiodynamic polarization techniques.

2 Material and Methods

Phytochemical screening was carried out for the extracts studied. Mild steel coupons of 0.04 x 3.86 x 2.12 cm³ were used for the study. Water and methanol extracts of ripe and raw jackfruit leaves (JL) and raw teak leaves (TL) were prepared. Percentage inhibition efficiencies (% IE) of all the extracts were calculated using weight loss measurements. Further experiments were carried out using water extracts (WE) of ripe JL and TL since the weight loss measurements revealed that these extracts possess higher IE than others.

2.1 Weight loss measurements

Cleaned and weighed MS plates were immersed in 1M HCl with concentrations of the extracts ranging from 0 to 450 ppm for 3 h at 298 (± 2) K. Then the MS plates were rinsed with distilled water and air-dried before measuring the final weight. Percentage inhibition efficiency, (% IE) was calculated using the following equation;

$$\% EI = 100 \left(\frac{W_u - W_i}{W_u} \right)$$

Where W_i and W_u are the inhibited and uninhibited weight losses of MS specimens respectively.

2.2 Electrochemical measurements

Polarization measurements were taken using a conventional three electrode system at 298 (± 2) K with different concentrations of the inhibitor and without the inhibitor. % IE and the potential were scanned in the range of -1.5 to 0.4 V with a scan rate of 100 mV/s. GAMRY software was used for data acquisition and analysis.

3 Results and Discussion

The phytochemical screening test indicated that the extracts contain tannins, phenolic and carbohydrate compounds. According to data of water extract (WE) of JL in 1M HCl at 300 K obtained from the weight loss measurements, % IE increased with the increasing concentration of WE of JL and it has reached a maximum of 73 % at 400 ppm. However, for TL it reached the maximum (32%) at 150 ppm.

Langmuir adsorption isotherms for WE of ripe JL on MS surface in 1M HCl at 300, 328, 348 and 363 K were plotted using weight loss measurements. The plot of 300 K is given in Figure 1.

Linear plot with high value of regression coefficient (0.99) was obtained giving evidence that the adsorption obeys Langmuir adsorption behaviour at 300 K. For all the other temperatures, linear plots were obtained, and the values of relevant regression coefficients were found to be not less than 0.90. These results revealed the formation of a monolayer of the inhibitor molecules on MS surface in 1M HCl. The values of adsorption equilibrium constants, K_{ads} , were calculated using the Langmuir isotherms and hence the standard Gibbs free energy change ΔG_{ads}° of this process was also calculated using the equation, $\Delta G_{ads}^{\circ} = -RT \ln (1000 K)$. It was found that both values decreased with increasing temperature (Table 1).

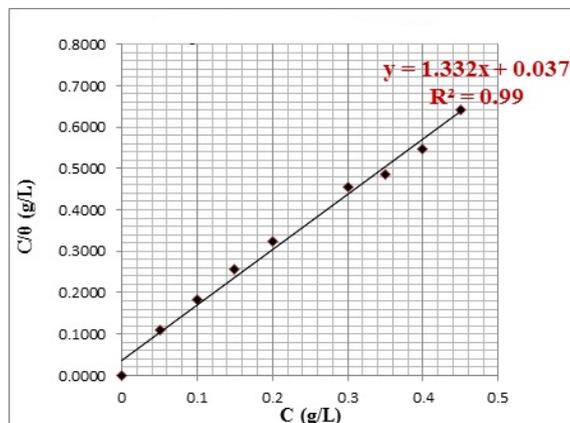


Fig. 1. Langmuir adsorption isotherm for water extract of ripe jackfruit leaves in 1M HCl at 300 K.

Langmuir adsorption isotherm for WE of TL in 1M HCl at 300 K was also indicated a good linear relationship with R^2 value of 0.98. $\Delta G_{\text{ads}}^\circ$ and K_{ads} were calculated using the graph and they are $-27.54 \text{ kJ mol}^{-1}$ and 62.5 respectively.

Table 1: Thermodynamic parameters calculated from Langmuir adsorption isotherms for adsorption of water extract of ripe jackfruit leaves.

	Temperature (K)			
	300	328	348	363
K_{ads}	27.03	4.13	1.87	0.37
$\Delta G_{\text{ads}}^\circ/(\text{kJ/mol})$	-25.45	-22.71	-21.80	-17.88

The results given in the table signify a decrease in the degree of adsorption of molecules on metal surface at elevated temperatures. In this study, it was also found that the rate of corrosion increased with increasing temperature. The decrease in % IE with temperature might be attributed to desorption of the inhibitor molecules from the surface at higher temperatures (Abiola and James 2010). Decrease in the K_{ads} values suggests that the adsorption of the inhibitors on mild steel surface is unfavorable at higher temperatures and chemisorption of the inhibitor molecules is not activated. It is generally accepted that the $\Delta G_{\text{ads}}^\circ$ values higher than 20 kJ mol^{-1} are consistent with chemisorption process. Consequently, it is indicative of adsorption process that occurs via chemisorption mechanism during the inhibition process as a result of sharing or transfer of electrons from indicator molecules to the metal

surface to form a coordinate type bond (Babatunde *et al.* 2012). Phenolic compounds present in both JL and TL might adsorb on the steel surface through the lone pairs of electrons on the oxygen atoms forming an isolating film layer. The values of the regression coefficients (R^2) of Langmuir plots confirmed the validity of this approach. However, since the ΔG_{ads} values are not significantly high, most probably chemisorption bonds between the molecules of the inhibitors and the MS surface might be relatively weak.

Using potentiodynamic polarization measurements, Tafel plots of MS in 1M HCl with various inhibitor (JL and TL) concentrations and without the inhibitor at 300 K, were obtained and plots for WE of TL are illustrated in the Figure 2.

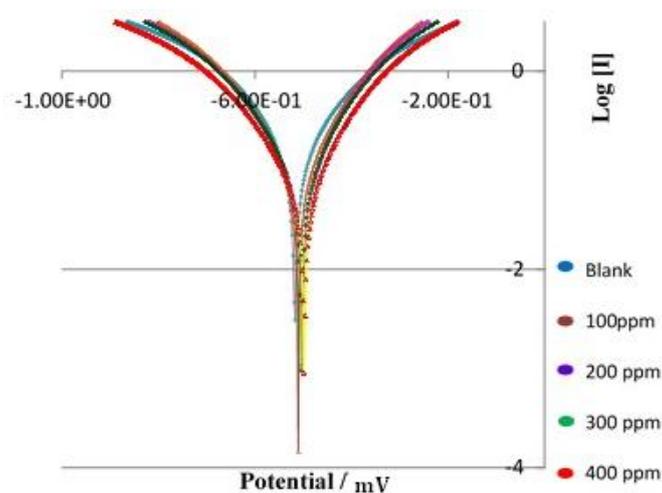


Fig. 2. Polarization curves for water extract of teak leaves in 1M HCl at 300 K.

According to the plots in the Figure 2, due to the presence of the inhibitor, both anodic and cathodic corrosion rates and corrosion current density were decreased, giving evidence that it is a mixed type inhibitor. According to Rekkab *et al.* (2012), it can be explained that if the shift of corrosion potential due to the addition of an interface inhibitor is negligible, the inhibition is most probably caused by a geometric blocking effect of the adsorbed inhibitive species on the surface of the corroding metal (Hosseini *et al.* 2003).

From the plots obtained using water extracts of ripe JL as inhibitors, both the anodic and cathodic current densities have decreased suggesting that the compounds in the extracts act as mixed type inhibitors (Hosseini *et al.* 2003; Machnikova *et al.* 2008; Rekkab *et al.* 2012; Hussin and Kassim 2010). It was also found that in the presence of the inhibitor, the E_{corr} of mild steel becomes less negative as the concentration increases and similar results have been reported by Hussin and Kassim (2010).

4 Conclusion

The inhibition efficiency of water extract (WE) of ripe jackfruit leaves (JL) increases with increasing inhibitor concentration and reaches a maximum of 73% at 400 ppm. The % IE of WE of TL increases with increasing inhibitor concentration and reaches a maximum of 32% at 150 ppm. With increasing temperature, adsorption of WE of ripe JL decreased and the rate of corrosion was increased. Both inhibitors obey the Langmuir adsorption isotherm and the inhibitors were adsorbed on the mild steel surface mainly by non-activated chemisorption. Adsorption of both extracts on mild steel surface mainly takes place by chemisorption. Potentiodynamic polarization studies revealed that the extracts contain mixed type corrosion inhibitors.

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