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Adsorptive and thermodynamic properties of methanol extract of *Toona sinensis* leaves for the corrosion of mild steel in HCl medium

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ABSTRACT

The inhibition effect of Toona sinensis leaves extract (TSLE) on the corrosion of mild steel in HCl solution was studied by weight loss, Fourier Transform Infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) methods. The results show that TSLE is a good inhibitor in 1.0 M HCl, and the inhibition efficiency increases with increasing concentration of the extract and decreases with increasing temperature. Inhibitive effect was afforded by adsorption of the extract on steel surface, which was found to accord with Langmuir adsorption isotherm. Adsorption and activation parameters such as activation energy (Ea), enthalpy (ΔH), free Gibbs energy (ΔG), and entropy (ΔS)were evaluated on the corrosion and inhibition process.

Keywords: corrosion inhibition, mild steel, *Toona sinensis*, isotherm adsorption

INTRODUCTION

Mild steel is commonly used in many industrial and engineering application including construction and design due to its low cost and easy availability. However, the corrosion resistance of mild steels is poor because they rust easily, and so they should not be used in a corrosive environment unless some method of corrosion protection is used. Hydrochloric acid is the medium generally being utilized for acid pickling, industrial acid cleaning, acid descaling, and oil and gas well acidizing [1-3].

Among the several methods of corrosion control and prevention, the use of corrosion inhibitors is very popular. Most of the effective inhibitors used contain heteroatom such as O, N, S and multiple bonds in their molecules that they are adsorbed on the metal surface. Though many synthetic compounds showed a good corrosion inhibitor, most of them are highly toxic to both human being and environment. These known hazardous effects of most synthetic inhibitors are the motivation for the use of some natural products as corrosion inhibitors [4-6].

Plant extracts have become important because they are environmentally acceptable, inexpensive, readily available, and renewable sources of materials. Recently, many plant extracts have been reported to be very effective corrosion inhibitors for the protection of mild steel in acidic media [7-10].

In this study, the inhibition effect of the TSLE on the corrosion of mild steel in 1.0 M hydrochloric acid was investigated using weight loss method, FT-IR, and SEM methods. There was no literature report on the studies of corrosion inhibition effect of the above plant extracts on mild steel in hydrochloric acid medium previously.

MATERIALS AND METHODS

2.1 Preparation of mild steel specimen

Mild steel specimen having the composition (wt.%) of 0.0149 P; 0.0715 Si; 0.001 Ni; 0.141 Mn; 0.189 C; 0.019 Se;

0.0018Cr, and remaining Fe was used for all experiments. The specimens were cut mechanically into 3x2x1 cm dimension used for weight loss measurements. They were polished using emery papers, washed thoroughly with distilled water, degreased with acetone, and dried. After dried, it was weighted and a result is initial weigh (m₁), and then stored in desiccators before using for weight loss measurement.

2.2 Preparation of Toona sinensis leaves Extract.

Fresh green leaves of *Toona sinensis* were collected and air-dried and were shattered into powder. Dried leaves were crushed and ground to make powder and weighed 400 g. The powder was extracted with ± 1500 mL methanol for 3 days. The extract was filtered and the solvent was vaporized using *rotary evaporator*. From this stock solution of the extract, different concentrations of the inhibitor test solution from 0.50, 1.0,2.0, 4.0, 6.0, and 8 g/Lwere prepared for the study.

2.3 Analysis

Phytochemical analysis of TSLE was carried out according to the method described in the literature [11]. The plant extracts were screened for alkaloids, saponins, phenolics, flavonoids, coumarins, steroid, and terpenoids.

2.4 Weigh Loss Measurement

The pretreated specimens initial weight steel was immersed in 50 mL solution 1.0 M HCl in the present and absence of TSLE in various concentrations for 7 hours. Then the steel was cleaned with brush, rinsed and dried. After dried, steel was weighted and result of weighing was expressed as final weigh (m_2) .

The corrosion rate was calculated from the following equation (1)

$$CR = \frac{m_1 - m_2}{t A} \tag{1}$$

From the corrosion rate (*CR*), the surface coverage (θ) as a result of adsorption of the components of the extracts, and inhibition efficiencies (IE) of the plant extracts (%) were determined using Eqs. (2) and (3), respectively.

$$\boldsymbol{\theta} = \frac{CR_0 - CR_i}{CR_0} \tag{2}$$

$$IE(\%) = \frac{CR_0 - CR_i}{CR_0} x \, 100\% \tag{3}$$

where CR_0 and CR_i are the corrosion rates in the absence and presence of the plant extracts, respectively.

2.5 Fourier Transform Infra Red (FTIR) Analysis

Mild steel samples were immersed in 1.0 M HCl in the absent and presence of TSLE for 7 hours. After that, the samples were taken out and dried. The film formed on the samples surface was carefully removed, mixed thoroughly potassium bromide (KBr), and made as pellets. The Fourier transformed infrared (FTIR) spectra (KBr pellet) of the film formed were recorded by Fourier transforms infrared (Nicolet IS10 FT-IR, Thermo Scientific) spectrophotometer.

2.6Surface Morphology

Scan electron microscopy (SEM) was used to record surface morphology of mild steel at different concentrations of TSLE. To perform this test, mild steel specimens were immersed in 1.0 M HCl in the presence and absence of inhibitor for 7 hours at room temperature. To observe the effect of inhibitor only one concentration 6 g/L, which gives maximum efficiency, was considered and surface morphology was compared with uninhibited samples.

RESULTS AND DISCUSSION

3.1 Phytochemical Analysis of *Toona sinensis* leaves extract

The phytochemical constituents of TSLE are shown in Table 1. The result reveals that phenolic, saponin, flavonoid, triterpenoid, and steroid are present in methanol extract of TSL. This indicates that the inhibition efficiency of the extract is caused to the present of the phytochemical constituents.

Table 1/	. Phytochemical	constituents of Toona	sinensis	leaves extract
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Phytochemicals	TSLE extract
Phenolics	+
Saponins	-
Flavonoids	+
Triterpenoids	+
Steroids	+
Alkaloids	-
Coumarin	-

3.2 Weight Loss Measurement

3.2.1 Effect of extracts Concentration on corrosion rate and inhibition efficiency

Figure 1 and 2showthe effect of concentration of TSLE on corrosion rate and inhibition efficiency of steel in 1.0M HCl. It was seen that the increase of extract concentration, the decrease corrosion rate and the increase inhibition efficiency. This proposes that the decreasing of corrosion rate and increasing of inhibition efficiency was caused by adsorption of the molecules contained in extract on steel surface with formation of thin protective layer [12,13]. Increasing the inhibitor concentration increases the degree of surface coverage, θ , of the metal surface.

The inhibition efficiency increases gradually as the concentration of the extracts increases up to about 4 g/L, above which, further increase in extract concentration did not cause any significant change in the performance of the extracts which might indicate that the reaction of the inhibitors on the surface of the mild steel have reached the state of equilibrium.



Figure 1. Effect of TSLE concentration on corrosion rate of steel corrosion in 1.0 M HCl for 7 hours



Figure 2. Effect of TSLE concentration on inhibition efficiency of steel corrosion in 1.0 M HCl for 7 hours

3.2.2. Adsorption Isotherms and thermodynamic parameters

Basic information on the interaction of inhibitor on metal surface can be provided by adsorption isotherm [13]. To obtain the adsorption isotherms, the degree of surface coverage (θ) obtained from weight loss method was determined as a function of inhibitor concentration. The values of θ were then plotted to fit the most suitable model of adsorption. Several isotherms including Langmuir, Temkin, and Freundlich isotherms are used to fit the experimental data [13-16]. It is found that the adsorption of studied inhibitors on steel surface obeys the Langmuir adsorption isotherm equation:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{4}$$

where *C* is the concentration of inhibitor, K_{ads} the adsorption equilibrium constant, and θ is the surface coverage and expressed by the ratio (IE%/100). Fig. 3shows the straight lines of C/ θ versus C for inhibitors in variation of concentration of TSLE with correlation coefficients (r) are almost equal to 1. This confirms that this inhibitor obeys Langmuir adsorption isotherm at 1.0 M HCl medium. It indicates that the adsorbing TSLE species occupies typical adsorption site at the metal/solution interface.



Figure 3. Langmuir adsorption isotherm for mild steel in 1.0M HCl containing different concentrations of TSLE

The standard adsorption enthalpy (ΔH_{ads}^o) is calculated on the basis of Van't Hoff equation [17-18]:

$$\frac{d\ln K_{ads}}{dT} = \frac{\Delta H_{ads}^0}{RT^2} \tag{5}$$

where *R* is the gas constant, *T* is the absolute temperature, and K_{ads} is the adsorptive equilibrium constant. Equation (6) can be arranged as the following equation:

$$\ln K_{ads} = \frac{-\Delta H_{ads}^o}{RT} + D \tag{6}$$

Where D is integration constant. Figure 4 represents the straight line of $\ln K_{ads}$ versus 1/T and with slope of $(-\Delta H^o_{ads}/R)$, from which ΔH^o_{ads} is calculated and listed in Table 2. The negative value of ΔH^o_{ads} reflects the exothermic behaviour of the adsorption of inhibitor on mild steel, which means that decrease with raising the temperature.



Fig. 4. The relationship between ln Kads and 1/T for mild steel in 1.0 M HCl solution

 Table 2. Thermodynamic parameters for the adsorption of TSL extract in 1.0 M HCl on the mild steel surface at different temperatures (303–333 K).

T (K)	Kads	ΔG^o_{ads} (kJ/mol)	$\Delta H(kJ/mol)$	$\Delta S(J/mol)$
303	3.43	-20.51	-26.91	-21.14
313	2.02	-19.80	-26.91	-22.72
323	1.54	-19.70	-26.91	-22.33
333	1.31	-19.85	-26.91	-21.21

The standard free energy of adsorption (ΔG_{ads}^{o}) can be calculated from the K_{ads} value obtained from the above correlation [19-20]:

$$\Delta G^o_{ads} = RT ln(C_{H_20} K_{ads}) \tag{7}$$

where C_{H_2O} is the concentration of water in solution expressed in 1000 g/L. As can be seen from Table 2, the unit of K_{ads} is Lg⁻¹, which in turn implies that the unit of is gL⁻¹ with the value of approximate 1.0 x 10³.

The negative sign of ΔG^o_{ads} indicates the spontaneity of the adsorption process and stability of the adsorbed layer on the steel surface [19-20]. It is usually accepted that the values of ΔG^o_{ads} up to -20 kJ mol⁻¹ are known to be associated with electrostatic interactions between the charged molecules and charged surface (physical adsorption) while those around -40 kJ mol⁻¹ or more negative is are known to be associated with chemisorption as a result of charge sharing or transferring from organic molecules to the metal surface and form a coordinate type of metal bond) [21,22]. As could be seen from Table 2 that the values of ΔG^o_{ads} were in the order of 20 kJ mol⁻¹ and less negative, which confirmed that the adsorption of TSLE on the surface of steel was of physical adsorption nature (i.e. physisorption). With the obtained both parameters ΔG^o_{ads} and ΔH^o_{ads} , the standard adsorption entropy (ΔS^o_{ads}) can be obtained using the following thermodynamic basic equation:

$$\Delta S_{ads}^{0} = \frac{\Delta H_{ads}^{o} - \Delta G_{ads}^{o}}{T} \tag{8}$$

As for ΔS_{ads}^0 in Table 2, the sign is negative; means that the decrease in disordering takes place on going from the reactant to the adsorbed species. This can be attributed to the fact that adsorption is always accompanied by decrease in entropy [23].

3.2.3 Kinetic-thermodynamic corrosion parameters

The apparent activation energy for mild steel corrosion in the absence and presence of extract was determined from an Arrhenius equation-type plot according to the following equation [24]:

$$\ln C_R = \ln A - \frac{Ea}{RT} \tag{9}$$

Wherein E_a is the apparent activation energy, A is frequency factor, T is the absolute temperature and R is the molar gas constant. The Arrhenius plots of ln CR vs. 1/T for steel in 1.0 M HCl environment containing various concentration of inhibitor are shown in Fig. 5.

The apparent values of E_a for mild steel corrosion in the presence of *TSLE* in 1.0 M HCl are listed in the Table 3. The data shows that the activation energy (E_a) of the corrosion of mild steel in 1.0 M HCl solutions in the presence of extract is higher than that in the absence of extract. The activation energy E_a was found to be 56.27 kJmol⁻¹ for 1.0 M HCl and increases to 70.94 kJmol⁻¹ in the presence of TSLE at 0.5 % (v/v) concentration. The results indicate that the adsorbed organic matter has provided a physical barrier to the change and mass transfer, leading to reduction in corrosion rate.



Figure 5.Arrhenius plots for mild steel corrosion rate in 1.0 M HCl in the absence and presence of different concentration of TSLE Table 3. Activation parameters E_a , ΔH^* and ΔS^* of the corrosion of mild steel in 1.0 M HCl in the absence and presence of different concentrations of TSLE

TSLE concentration	Ea	∆H*	ΔS^*
(g/L)	(kJ/mol)	(kJ/mol)	(J/mol)
Blank	56.27	-53.63	-60.86
0.5	70.94	-68.30	-21.54
1	73.89	-71.25	-14.56
2	75.89	-73.25	-10.46
4	77.26	-74.62	-8.94
6	77.13	-74.49	-11.71
8	77.18	-74.54	-15.98

An alternative formulation of Arrhenius equation is the transition-state equation [22-24]

$$ln\left(\frac{CR}{T}\right) = \left[ln\left(\frac{R}{hN}\right) + \left(\frac{\Delta S^*}{R}\right)\right] - \frac{\Delta H^*}{RT}$$
(10)

where *h* is plank's constant, *N* is Avogadro's number, ΔS^* is the entropy of activation, and ΔH^* is the enthalpy of activation. A plot of $\ln C_R/T$ versus 1/T gave a straight line with a slope of $-\Delta H^*R$ and an intercept of $\ln R/hN+\Delta S^*/R$, from which the values of ΔS^* and ΔH^* were calculated and listed in Table 3.

The results presented in Table 3 show that the enthalpy of activation values were all negative for TSLE which reflects the exothermic nature of the mild steel corrosion process. Also, the entropies of activation were negative indicating that the activated complex in the rate-determining step represents an association rather than a dissociation step and that the reaction was spontaneous. These results were in good agreement with the previous study [23,24].

3.3 Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

FTIR is used to support the fact that the corrosion inhibition of steel in acid media is due to in part, at the adsorption of inhibitor molecules on the surface material. The FTIR spectrum of TSLE (Figure 6 (a)) shows a broad absorption band with maximum absorbance at 3343.11 cm⁻¹ which indicated the –OH stretching vibration. Peaks observed at 2047.22 cm⁻¹ is attributable for aliphatic and aromatic C-H stretching. A peak at 1692.17 cm⁻¹ and 1035.36 cm⁻¹ are an indicative of C=C and C-O stretching of phenolic compounds [25,26]



Figure 6.FT-IR spectra of (a). TSLE and; (b). Film formed on surface of mild steel after immersion in 1.0 M HCl and TSLE

The FTIR spectrum of the protective film formed on the surface of the mild steel after immersion in 1.0 M HCL containing TSLE is shown in Fig 6b. It is found that the –OH stretch has shifted from 3343.11 cm⁻¹ to 3186.08 cm⁻¹ and the C=C stretching frequency shifted from 1692.17 cm⁻¹ to 1623.59 cm⁻¹. These shifts or changes in the IR spectrum of the corrosion product (as opposed to the spectrum obtained for the methanol extract of *Toona sinensis*) indicate that there is interaction between mild steel and methanol extract of TSL.

3.4Scanning electron microscopy (SEM)

The SEM images were recorded to confirm the protection film formation during the corrosion process. Fig.7 shows SEM images of surface morphology of mild steel in 1.0 M HCl with and without inhibitor. Before immersing in acid mild steel sample was prepared using emery paper which created scratches on the surface and can be observed in Fig.6a. When sample was immersed in 1.0 M HCl, corrosion pits were formed on the surface due to aggressive attack of acid. A rough surface can be seen in Fig.7b, which indicates deposition of corrosion products and/or chloride ions on the surface. Presence of inhibitor retarded the corrosion rate and smooth layer was recognized due to adsorption of organic species present in the extract at most active sites (Fig.7 c). On the basis of information provided by the SEM it can be concluded that inhibitor inhibits corrosion of mild steel in acid forming a protective layer on mild steel surface.



Figure 7. SEM micrograph of mild steel (a) abraded by emery paper (b) immersed in 1.0 M HCl, and (c) immersed in 1.0 M HCl in the presence of 4 g/L extract for 7 hours

CONCLUSION

We have studied the application of TSLE extract as green corrosion inhibitor for the mild steel in 1.0 M HCl by using various methods. TSLE a good inhibitor. The inhibition efficiency increases with increased TSLE concentration, but decreases with the rise of the temperature. TSLE studied was adsorbed physically on the steel surface according to the Langmuir isotherm model. The negative values of free energy of adsorption (ΔG_{ads}) indicate that the adsorption process is spontaneous. The presence of the TSLE increases the activation energy (E_a) of the corrosion process.FTIR spectra clearly reveal that the phytochemical constituents adsorbed on the mild steel surface.

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