



Fenugreek leaves and lemon peel as green corrosion inhibitor for mild steel in 1M HCl medium

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Abstract

Inhibitive action of the extracts of Lemon peel (LP) and Fenugreek leaves (FL) on the corrosion of mild steel in 1M HCl has been studied using weight loss method and electrochemical methods. The non-electrochemical and electrochemical measurements showed that both extracts have good inhibition properties. The electrochemical results indicate that both extracts act as mixed inhibitor. The adsorption of lemon peel and fenugreek leaf extracts on the mild steel surface in hydrochloric acid obeys the Langmuir adsorption isotherm model and the adsorption is physical and spontaneous.

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Introduction

Mild steel has diverse applications but it suffers severe corrosion in acidic environment. Hydrochloric acid is one of the most common chemical used for derusting and descaling of mild steel. So, to avoid undesirable alloy dissolution, inhibitors are added to HCl solution^{1,2}. Generally, organic compounds of higher molecular weight with hetero atoms (having lone pair of electrons like N, S, O) are used as inhibitors in HCl medium for mild steel. Unfortunately, most of the organic and inorganic inhibitors are toxic and non-biodegradable. Due to the increasing awareness of health and environment, nowadays more emphasis is given on using natural products from plant parts as corrosion inhibitor as they are eco-friendly and inexpensive. Extracts from plant parts are organic in nature and contain proteins, polycarboxylic, polysaccharides acids, tannin, alkaloids and pigments etc. These compounds work as potential inhibitors for many metals in acidic environment³⁻⁵. The effectiveness of corrosion inhibition by *Uncaria gambir*⁶, *Strychnos nux-vomica*⁷, *Nyctanthes arbortristis*⁸, *Cordia dichotoma*⁹, *Cola acuminata* and *Nicotiana*¹⁰, *Rosmarinus officinalis* oil¹¹, *Ficus nitida*¹², *Aloe vera*¹³, *Areca catechu*¹⁴, *Ocimum sanctum* (Tulasi), *Aegle marmelos* (Vilvam) and *Solanum trilobatum* (Thuthuvalai)¹⁵, *Phyllanthus amarus*¹⁶, *Cyamopsis Tetragoloba* seed¹⁷, *Ajowan Seeds*¹⁸, *Acacia Senegal*¹⁹, *Acalypha indica* L.²⁰, *Allium Sativum*, *Juglans Regia* and *Pogostemon Cablin*²¹, *Black Pepper*²², *Spirulina*²³, *Zizyphus Spina-Christi*²⁴, *Red Peanut Skin*²⁵, *Brugmansia suaveolens* (BS) and *Cassia roxburghii* (CR)²⁶, *Henna*²⁷, *Natural Honey*²⁸ and *L-Tryptophan*²⁹ are proven to be effective for mild steel.

The aim of the present work is to show corrosion inhibitive property of fenugreek leaves and lemon peel using weight loss and electrochemical studies in 1M HCl for mild steel. Lemon peel was selected because it is a waste product and there is no meaningful use of it. Choice of fenugreek leaves was made because it is herbal medicine and generally regarded as safe.

Experimental

Materials

Preparation of the specimens

Mild steel (0.18% C; 0.001% Si; 0.99% Mn; 0.024% S; 0.0085% P; 0.034% Ni; 0.021% Cr; 0.005% Mo; 0.006 % Al; 0.062 % Cu; 0.001 % Ti; 0.004 % Nb; 0.007 % Co; 0.002 % Pb; 0.001 % V; 0.003 % Zr; balance Fe) specimens of dimension 3.00x2.54x0.25 cm were used for weight loss and electrochemical studies. Before all measurements, the specimens were polished using different grades of emery paper from 220 to 1200, washed with distilled water and degreased with acetone and later dried.

Preparation of plant extract

The fresh leaves of Fenugreek were washed under running water, shade dried, powdered and then 10g of powder was soaked in 250 mL of 1 M HCl and boiled for 4 hours. After that solution was left overnight and then filtered and made to 250 mL by 1M HCl. Lemon peel was treated in the same way.

Electrolyte

An appropriate concentration of acid (1M) was prepared by using distilled water and AR grade hydrochloric acid. The concentration range of inhibitors employed was 5 and 10 % v/v for weight loss experiments and 2-10 % v/v for electrochemical studies.

Methods

Weight loss method

Weighted steel specimens of dimension 3.00x2.54x0.25 cm were completely immersed in 100 mL of electrolyte (1M HCl) with and without different concentrations of FL and LP extracts at room temperature. To prepare different concentrations, different amounts of FL and LP extracts were added to 1M HCl accordingly in v/v ratio. Specimens were immersed for 2, 4, 8, 16, 32, 64, 96 and 120 hours. Specimens were then retrieved, washed with water, dipped into acetone, air dried and reweighed. From the weight loss data, the corrosion rates (R) were calculated from Eq. (1):

$$R \text{ (mpy)} = \frac{KW}{DAT} \quad (1)$$

where mpy is Mills per year, w is weight loss in grams, A is the specimen surface area in cm² (centimetre), T is the immersion

period in hours, D density of steel in gm/cm^3 and K is constant equal to 3.45×10^6 for mpy.

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

$$\theta = \frac{R_0 - R_i}{R_0} \quad (2)$$

$$\eta (\%) = \frac{R_0 - R_i}{R_0} \times 100 \quad (3)$$

where R_0 and R_i are the corrosion rates in the absence and presence of the plant extracts, respectively.

Electrochemical measurements

Electrochemical measurements were carried out in a conventional three electrode cylindrical cell, containing 400 mL of electrolyte at room temperature. Platinum electrode was used as a counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Working electrode was mild steel with surface area 1cm^2 . Before measurement, the working electrode was polished mechanically, washed with acetone, rinsed several times with double distilled water and dried. All tests have been performed with freshly polished electrodes. Polarization studies were conducted using computer controlled AC Gill 843 model potentiostat at a scan rate of 0.5 mV S^{-1} . Before each potentiodynamic polarization (Tafel) the electrode was allowed to corrode freely and its open circuit potential (OCP) was recorded as a function of time for 10 min. After this time a steady-state OCP, corresponding to the corrosion potential (E_{corr}) of the working electrode, was obtained. The potentiodynamic Tafel measurements were started from cathodic to the anodic direction, $E = E_{\text{corr}} \pm 350\text{ mV}$. The above procedures were repeated for every concentration of LP and FL extracts. The inhibition efficiency $\text{IE}\%$ was calculated using the following equation:

$$\text{IE} (\%) = \frac{I_{\text{corr}} - I_{\text{corr}}^*}{I_{\text{corr}}} \times 100 \quad (4)$$

where I_{corr} and I_{corr}^* are the corrosion current density without and with the inhibitor, respectively.

Results and Discussion

Weight loss experiment

The variation of the corrosion rate (in mpy) of mild steel with immersion time in 1M HCl solutions in the absence and presence of FL and LP extracts are shown in Figure 1. It also indicates that FL and LP extracts are indeed a corrosion inhibitor for mild steel in hydrochloric acid solution as there was a decrease in corrosion rate as compared to control. Values of maximum inhibition efficiencies of FL and LP extracts for the corrosion of mild steel in 1M HCl are presented in Table 1.

Table 1: Inhibition efficiency for different concentration extracts for the corrosion of mild steel in 1M HCl obtained from weight loss measurement.

Concentration of plant extract (% v/v)	Inhibition Efficiency (%)	
	FL	LP
5	87.49	85.19
10	76.87	77.38

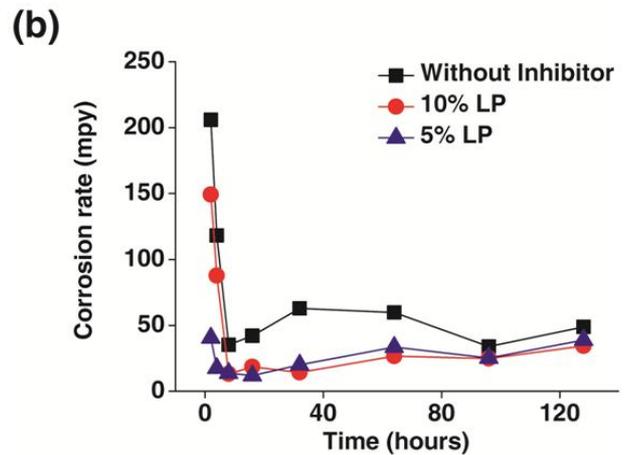
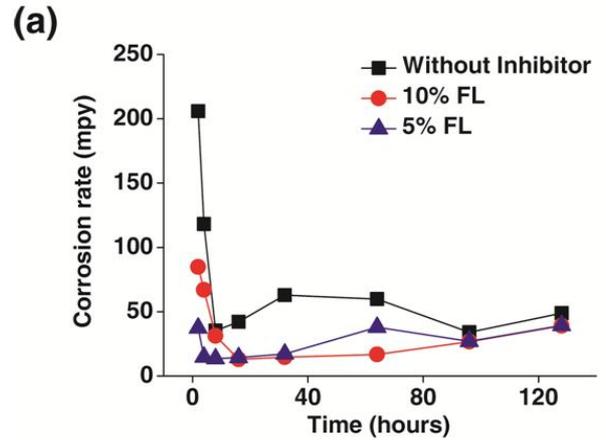


Figure 1: Variation of corrosion rate with exposure time for the mild steel specimen immersed in 1M HCl, with varied concentrations of (a) Fenugreek leaves (FL) and (b) Lemon peel (LP) extracts.

Potentiodynamic polarization

The effect of plant extracts on the anodic and cathodic polarization behaviour of mild steel in 1M HCl solution has been studied by polarization measurements and the recorded Tafel plots are shown in Figure 2. The respective kinetic parameters derived from the above plots are given in Table 2. It is illustrated from the data of Table 2 that both anodic metal dissolution of iron and cathodic hydrogen evolution reaction were inhibited after the addition of FL and LP extracts to 1M HCl solution. It is also clear that as inhibitor concentration increases inhibition efficiency increases. Addition of the inhibitors slightly shifts the E_{corr} values in the cathodic direction. The values of both anodic and cathodic Tafel constants β_a and β_c respectively are markedly changed in the presence of the FL and LP extracts. This confirms the mixed mode of inhibition of both the extracts.

Table 2: Potentiodynamic polarization parameters for mild steel in 1M HCl containing various concentrations of the FL and LP extracts.

Name of extract	Concentration Of inhibitor C (% v/v)	E_{corr} (mV)	I_{corr} (mA/cm^2)	Tafel slope (mV)		Inhibition efficiency (%)	Surface coverage θ
				β_a	β_c		
Blank	-	-525.33	4.9484	281.11	190.16	-	-
	2	-487.71	1.7031	202.16	180.69	66.58	0.6658
	5	-488.83	1.3188	182.07	148.13	73.35	0.7335
LP	10	-512.74	1.2825	214.10	159.93	74.08	0.7408
	2	-485.03	1.0770	194.31	145.82	78.24	0.7824
	5	-479.08	0.9510	149.46	185.77	80.78	0.8078
FL	10	-466.67	0.7966	171.69	157.47	83.90	0.8390

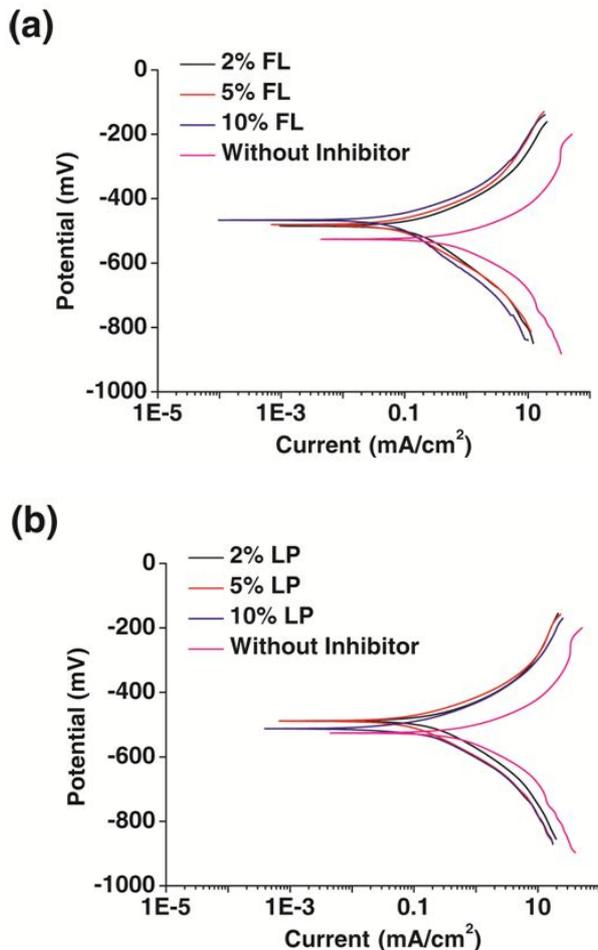


Figure 2: Potentiodynamic polarization of mild steel in 1M HCl with various concentrations of (a) Fenugreek leaves (FL) and (b) Lemon Peel (LP) extract.

Adsorption Isotherm

Primary step in the action of inhibitors in acidic solutions is generally considered to be adsorption on to the metal surface, which is usually oxide free in acidic solutions. Most organic inhibitors get adsorbed on the metal surface by displacing water molecules on the surface and forming a compact barrier³⁰.



where n is the number of water molecules displaced by the one inhibitor molecule. When equation (5) reaches to equilibrium, then diverse expression of the adsorption isotherm plots can be obtained, and thus the relation between the degree of surface coverage ($\Theta = \text{IE} (\%) / 100$) and the inhibitor concentration under test can be plotted. From Table 2, it can be concluded that Θ increases with the inhibitor concentration; this is attributed to more adsorption of inhibitor molecules onto the steel surface. From the polarization data, the surface coverage (Θ) values for different inhibitor concentrations in acidic medium have been evaluated. Then a suitable adsorption isotherm (Figure 3) was obtained using the data.

The Langmuir adsorption isotherm is applied to investigate its mechanism by the following equation:

$$C/\Theta = 1/K + C \quad \text{with } K = 1/C_{\text{H}_2\text{O}} \exp(\Delta G_{\text{ads}}/RT) \quad (6)$$

where C is the inhibitor concentration (mL L^{-1}) in the electrolyte, K ($\text{mL}^{-1} \text{L}$) is the equilibrium constant for the adsorption/desorption process, $C_{\text{H}_2\text{O}}$ is the concentration of water molecules (mL L^{-1}) at the metal/solution interface, ΔG_{ads} is the standard free energy (J mol^{-1}), R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the temperature in Kelvin.

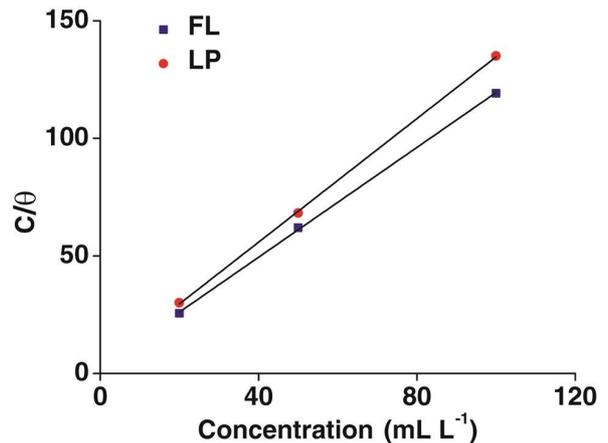


Figure 3: Langmuir adsorption plots for mild steel in 1M HCl, where C stands for concentration of inhibitor in mL L^{-1} and Θ stands for surface coverage.

The adsorption parameters from Langmuir adsorption isotherms are estimated and given in Table 3. Data indicates that the adsorption of inhibitor follows Langmuir model as the experimental data gives good curve fitting for this adsorption isotherm as the correlation coefficient (r^2) for both inhibitors were 0.9998 and also it yields a slope of almost unity³¹.

Table 3: Adsorption parameters for LP and FL extracts in 1 M HCl obtained from Langmuir adsorption isotherm

Name of extract	Slope	K (mL L^{-1})	r^2	ΔG_{ads}
LP	1.3144	0.3077	0.9998	-7.032
FL	1.1679	0.3697	0.9998	-7.486

From the intercepts of the straight lines on C/Θ -axis, K value is calculated. The value of standard free energy of adsorption (ΔG_{ads}) is determined using the equation

$$\Delta G_{\text{ads}} = -2.303RT \log(55.5K) \quad (7)$$

The stability of the adsorbed layer on the metal surface and spontaneity of the adsorption process is attributed to the negative sign of ΔG_{ads} ³². Generally, the value of ΔG_{ads} around -20 kJ mol^{-1} or more are known to be associated with physical adsorption (electrostatic interactions between charged surface and the inhibitor) while values around -40 kJ mol^{-1} or less are known to be associated with chemisorption (charge sharing or transferring from organic molecules to the metal surface and forming a coordinate type of bond). So, it can be concluded that both plant extracts adsorbed by creating an electrostatic interaction with charged mild steel surface showed physical adsorption¹.

Inhibitor Constituents

FL extract

Following organic substances are found in plenty in fenugreek leaves³³:

- Ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$),
- Beta-carotene ($\text{C}_{40}\text{H}_{56}$),

- Xanthophylls ($C_{40}H_{54}(OH)_2$),
- +
- Choline ($N(CH_3)_3C_2H_4OH$)
and
- Methionine ($HOOCCHNH_2CH_2CH_2SCH_3$)

It can be noticed that these substances are nitrogen, oxygen and/or sulphur containing organic compounds. It was earlier found that the concentration of Ascorbic acid and beta-carotene gets remarkably decreased by storage and cooking (i.e. boiling). So, these two components cannot be regarded as the cause of corrosion inhibition. Since sulphur-containing compounds are not of major importance as corrosion inhibitor additives in HCl, so both choline and methionine compounds in Fenugreek leaves can be considered as the major components for inhibition of corrosion of mild steel in HCl.

LP extract

Lemon peel contains Flavanoids, Tannins, Alkaloids, Steroids, Cardiac glycosides and Phytosterol³⁴. Earlier, it has been shown that compounds such as alkaloids may be responsible for the inhibition of corrosion in hydrochloric acid medium²⁶. In the present case the mixture of the different compounds may be responsible for the corrosion inhibitive effect.

Conclusions

1. Lemon peel and Fenugreek leaf extracts were found to be good non-toxic and safe inhibitor for mild steel corrosion in 1M HCl.
2. The electrochemical measurements showed that inhibition efficiency increased with an increase in plant extracts concentrations; however this could not be reproduced in weight loss experiments. This may be due to the nonrobust nature of the weight loss method.
3. The electrochemical results from potentiodynamic polarization indicate that the both plant extracts affected both anodic and cathodic processes, i.e., these are mixed type inhibitors.
4. The adsorption of lemon peel and fenugreek leaf extracts on the mild steel surface in hydrochloric acid obeys the Langmuir adsorption isotherm model and the adsorption is physical.
5. The negative value of free energy change of adsorption indicates that the adsorption of the inhibitors on mild steel surface was spontaneous.

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