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Study of Bitter Leaves Extract as Inhibitive Agent in HCl Medium for the Treatment of Mild Steel through Pickling

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Abstract

Bitter leaves extract as inhibitive agent in HCl medium for the treatment of mild steel through pickling was studied. Thermometric, gravimetric and potentiodynamic polarization methods were employed in the corrosion inhibition study. The bitter leaves extract was analyzed using gas chromatography-mass spectrometer. The analysis of the extract revealed the presence of C_6H_8O (96 g/mole: 2,4-Hexadienal); C_7H_{12} (96 g/mole: 3,4-Heptadiene; 1,3-Diethylallene) and $C_{10}H_{18}O_2$ (170 g/mole: 2-Decenoic acid) as the predominant chemical constituents. The activation energy for the corrosion inhibition process ranged from 39.831 to 77.533 kJ/mol, while the heat of adsorption ranged from -16.093 to -30.224 kJ/mol. These values showed that exothermic and spontaneous adsorption of the extract on the mild steel followed the mechanism of physical adsorption. Maximum inhibition efficiency of 85.4% was obtained. The extract was highly efficient in the corrosion inhibition function. The plant-based inhibitor of bitter leaves extract is a suitable additive for pickling, cleaning and descaling operations.

Keywords: Bitter leaves, treatment, mild steel, pickling.

Introduction

Mild steel is a vital metallic material used in engineering, transportation and construction industries. It has good machining properties and can be hardened by heat treatment. Besides carbon, steel contains many chemical elements which are added into iron to form steel of different kinds having various physical properties [1]. Mild steel is a medium carbon steel with carbon content of 0.2 – 0.5% [2]. It is weldable, which expands its possible applications. It is used for the production of lightly stressed machine fittings, turbine motors, railways axels, pipes and drums. Mild steel is widely used in the manufacturing of installations for chemical and allied industries. Most often processes within these industries such maintenance operations involve contact between mild steel and aggressive solution.

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Mild steel structures corrode as a result of electrochemical reaction with its environment. In most industries, maintenance operations such as pickling, cleaning and descaling are carried out to prolong the life span of the mild steel structures. But aggressive hydrochloric acid used for such operations often corrodes the mild steel structures. Considering the viability of mild steel and its high cost of production and installation, several steps are taken to prolong its life span. The synthetic chemicals commonly used as corrosion inhibitors are harmful to the environment. There is need for the corrosion inhibition using eco-friendly inhibitors of plant origin. Bitter leaves extract has been found useful in pharmaceutical applications [3, 4]. The chemical constituents of bitter leaves extract include several organic compounds with polar atoms capable of exhibiting electrochemical activity of strong adsorption onto mild steel surface.

Quantum chemical methods have been employed in determining the molecular structure as well as describing the electronic structure and reactivity. The chemical techniques apply the knowledge of the density for a complete determination of all ground state molecular properties. The basic relationship of the density functional theory of chemical reactivity is the one that links the chemical potential of density functional theory with the first derivative of the energy with respect to the number of electrons, and therefore with the negative of the electronegativity χ [5].

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(r)} = -\chi \qquad (1)$$

where μ is the chemical potential, E is the total energy, N is the number of electrons, and $v(r)$ is the external potential of the system.

For detail understanding of the chemical constituents of plant extract, sophisticated device (such as gas chromatography-mass spectrometer) is needed for the characterization of the plant extract. Gas chromatography-mass spectrometer helps in identifying the molecular compositions of the extract for the corrosion inhibition functions.

Experimental methods

Leaves of bitter leaf (*Vernonia amygdalina*) were collected from Akpugo, Enugu State, Nigeria. Sheet of mild steel with composition of P (0.02%), Mn (0.11%), Si (0.02%), S (0.02%), Cu (0.01%), C (0.23%), Ni (0.02), Cr (0.01%) and Fe (99.56 %) were cut into coupons (5 cm x 4 cm). In the extraction of the bitter leaves extract and surface preparation of the mild steel, the method used in the previous study was adopted [6]. Chemical analysis of the bitter leaves extract was carried out using gas chromatography-mass spectrometer (GCMS-QP2010 PLUS, SHIMADZU). The method used by previous authors was adopted [7, 8].

Thermometric, gravimetric and potentiodynamic polarization methods were used in the corrosion inhibition study. The method of the thermometric measurements used by previous authors was adopted with slight modification [9, 10]. The inhibitor efficiency was determined using Equation (2).

$$IE\% = \left(1 - \frac{RN_{add}}{RN_{free}}\right) * 100 \qquad (2)$$

where RN_{free} and RN_{add} are the reaction numbers for the metal dissolution in free and inhibited corrosive medium, respectively.

The potentiodynamic polarization study was carried out according to the method used by previous authors [11, 12]. For the gravimetric method, the weight loss (Δw), corrosion rate (CR), inhibition efficiency (IE) and degree of surface coverage, were determined using the standard Equations [6, 13].

Considering the corrosion rates of the metal at T_1 and T_2 as CR_1 and CR_2, the activation energy, E_a, was obtained using Equation (3) [14, 15, 16].

$$\ln\left(\frac{CR_2}{CR_1}\right) = \left(\frac{E_a}{2.303R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (3)$$

The heat of adsorption Q_{ads} ($kJmol^{-1}$) was calculated using Equation (4) [15, 17].

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] * \frac{T_2 . T_1}{T_2 - T_1} \qquad (4)$$

where R is the gas constant, θ_1 and θ_2 are the degree of surface coverage at temperatures T_1 and T_2, respectively.

Different adsorption isotherms (The Langmuir, Frumkin, Temkin and Flory-Huggins isotherms) were used to determine the mechanism of the adsorption of the extract on the metal surface [6, 15, 18, 19, 20].

The free energy of adsorption (ΔG_{ads}) was calculated according to Equation (5) [6, 15, 18].

$$\Delta G_{ads} = -2.303RTlog(55.5K) \qquad (5)$$

where R is the gas constant, T is temperature and K is the adsorption equilibrium constant.

Results and discussions

Analysis of the bitter leaves extract

In Fig. 1, the GC MS chromatogram of the bitter leaves extract shows various levels of peaks. The analysis revealed the presence of C_6H_8O (96 g/mole: 2,4-Hexadienal; Sorbaldehyde , n-Hex-2,4-dienal, Hexa-2,4-dienal; Sorbic aldehyde 1,3-Pentadiene-1-carboxaldehyde; 2,4-Hexadien-1-al; 2,4-Hexadienal; trans,trans-2,4-Hexadienal; 3-Propyleneacrolein); C_7H_{12} (96 g/mole: 3,4-Heptadiene; 1,3-Diethylallene); $C_{10}H_{18}O_2$ (170 g/mole: 2-Decenoic acid).

Other compounds present in the extract include $C_9H_{16}O_2$ (156 g/mole: 2-Nonenoic acid; trans-2-Nonenoic acid; Nonylenic acid, 2-Nonenylic acid); $C_{12}H_{14}N_2O_6$ (282g/mole: Phenol, 2-(1-methylpropyl)-4,6-dinitro-, acetate; Acetic acid, 2-(sec-butyl)-4,6-dinitrophenyl ester); $C_{12}H_{18}O$ (178 g/mole: Benzene ethanol; 2-(3-Isopropylphenyl)-1-propanol); $C_{18}H_{34}O_2$ (282 g/mole: Oleic Acid, 9-Octadecenoic acid; cis-9-Octadecenoic Acid); $C_{18}H_{34}O$ (266 g/mole: 13-Octadecenal; cis-13-Octadecenal) and $C_{16}H_{30}O$ (238g/mol: cis-9-Hexadecenal; 9-Hexadecenal).

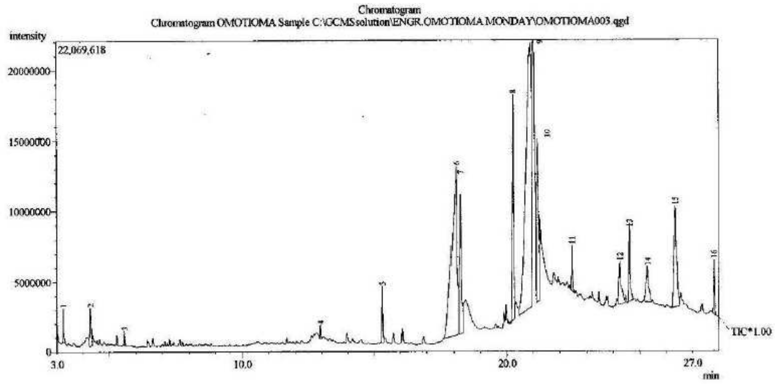

Figure 1. GC MS chromatogram of the bitter leaves extract.

Results of the thermometric method

Table 1 presents the effect of concentration on the reaction number and inhibition efficiency. The reaction number decreases with increase in concentration, while the inhibition efficiency increases with increase in concentration.

Table 1. Effects of concentration of the extracts on the IE (%) of mild steel in the media.

Medium	Inh. conc., g/L	Bitter leaves extract	
		RN	IE (%)
HCl	0.0	0.0327	
	0.2	0.0158	51.54
	0.4	0.0111	66.03
	0.6	0.0065	80.17
	0.8	0.0049	85.15
	1.0	0.0036	88.87

Results of the gravimetric method

The results of corrosion inhibition of mild steel in HCl medium with bitter leaves extract are presented in Table 2. The corrosion rate decreases with increase in concentration of the extract. This is in agreement with previous studies [6, 15]. Maximum inhibition efficiency of 85.4% was obtained. It showed that the extract of bitter leaf can be used as additive for pickling, cleaning and descaling operations. The extract is efficient for corrosion control of mild steel in the hydrochloric acid medium.

The activation energy and heat of adsorption

The activation energy and heat of adsorption are presented in Table 3. The activation energy for the corrosion inhibition process ranged from 39.831 to 77.533 kJ/mol, while the heat of adsorption ranged from -16.093 to -30.224 kJ/mol. These values showed that exothermic and spontaneous adsorption of the extract on the mild steel followed the mechanism of physical adsorption.

Table 2. Results of corrosion inhibition of mild steel in HCl with bitter leaves extract.

	0.2 g/L	0.4 g/L	0.6 g/L	0.8 g/L	1.0 g/L	0.2 g/L	0.4 g/L	0.6 g/L	0.8 g/L	1.0 g/L	0.2 g/L	0.4 g/L	0.6 g/L	0.8 g/L	1.0 g/L
T	Weight loss (g) at 303 K					Weight loss (g) at 318 K					Weight loss (g) at 333 K				
t_1	0.04	0.03	0.02	0.02	0.02	0.05	0.04	0.04	0.03	0.03	0.06	0.05	0.04	0.04	0.04
t_2	0.06	0.04	0.04	0.03	0.03	0.07	0.06	0.05	0.04	0.04	0.10	0.07	0.07	0.06	0.06
t_3	0.07	0.05	0.03	0.02	0.02	0.08	0.06	0.05	0.04	0.03	0.13	0.09	0.08	0.07	0.07
	CR (mg/cm^2hr) at 303 K					CR (mg/cm^2hr) at 318 K					CR (mg/cm^2hr) at 333 K				
t_1	0.23	0.19	0.13	0.14	0.11	0.29	0.25	0.23	0.19	0.17	0.36	0.31	0.25	0.23	0.23
t_2	0.19	0.13	0.13	0.10	0.09	0.22	0.20	0.15	0.13	0.13	0.30	0.22	0.21	0.18	0.18
t_3	0.15	0.10	0.06	0.05	0.04	0.17	0.13	0.10	0.08	0.07	0.27	0.19	0.17	0.15	0.14
	IE (%) at 303 K					IE (%) at 318 K					IE (%) at 333 K				
t_1	35.1	47.4	64.9	59.7	70.2	29.9	40.3	44.8	55.2	59.7	26.0	35.1	48.1	52.0	52.0
t_2	40	60	60	70	70	38.1	44.3	58.4	64.6	64.6	30.7	50	52.1	59.3	59.3
t_3	48.9	63.5	78.1	83.2	85.4	44.1	55.9	67.1	72.0	76.9	35	53.5	60	65	66.5

t_1, t_2, t_3 = time (t) at 8 h, 16 h and 24 h, respectively.

Table 3. Activation energy and heat of adsorption for the corrosion inhibition process.

Medium	Conc. of the plant extract (g/L)	Activation energy (kJ/mol)	Heat of adsorption, Q_{ads} (kJ/mol)
HCl	0.2	39.831	-16.093
	0.4	40.150	-11.565
	0.6	63.809	-24.221
	0.8	71.636	-27.451
	1.0	77.533	-30.224

Adsorption parameters for the corrosion inhibition process

Adsorption parameters for the corrosion inhibition of mild steel in HCl by bitter leaves extract are shown in Table 4. The values of free energy of adsorption (ΔG_{ads}) were less than the threshold value of -40 kJ/mol required for chemical adsorption. The lateral interaction term (α) gave positive values, indicating attractive behaviour of the extract on the mild steel surface. The attractive parameter value (a) is negative, which implies that repulsion exists in the adsorption layer [16]. The value of the size parameter (x) is positive. The adsorbed species of the bitter leaves extract was bulky. This is in agreement with previous works [6, 15, 21]. The values of the correlation coefficient (R^2) are close to unity (1), which implies that the Langmuir, Frumkin, Temkin and Flory-Huggins isotherms of Equations (6), (7), (8) and (9) were obeyed [15, 22].

$$log\frac{C}{\theta} = \log C - logK \quad (6)$$

$$\log\left((C) * \left(\frac{\theta}{1-\theta}\right)\right) = 2.303logK + 2\alpha\theta \quad (7)$$

$$\theta = -\frac{2.303logK}{2a} - \frac{2.303logC}{2a} \quad (8)$$

$$\log\left(\frac{\theta}{C}\right) = \log K + xlog(1-\theta) \quad (9)$$

where C is the concentration of the inhibitor, K is the adsorption equilibrium constant and θ is the degree of surface coverage.

Table 4. Adsorption parameters for the corrosion inhibition process.

Adsorption isotherm	T (K)	R^2	Log K	K	ΔG_{ads} (kJ/mol)	Isotherm property	
Langmuir	303	0.9922	-0.0496	0.8921	-10.3		
	333	0.9722	-0.1492	0.7093	-10.3		
Frumkin	303	0.9919	-1.1484	0.0711	- 3.5	α	1.9553
	333	0.9906	-1.0297	0.0934	- 4.6		1.9601
Temkim	303	0.981	1.583	38.311	-19.3	a	-2.086
	333	0.970	1.311	32.431	-20.8		-2.525
Flory-Huggins	303	0.959	0.381	3.8107	-13.5	x	0.751
	333	0.937	0.536	3.4356	-14.5		1.397

Potentiodynamic polarization curves

Potentiodynamic polarization curves for mild steel in HCl in absence and presence of bitter leaves extract are shown in Fig. 2. The extract inhibited the corrosion of the mild steel in the HCl medium, affecting both the cathodic and anodic reactions, indicating that it is a mixed type inhibitor.

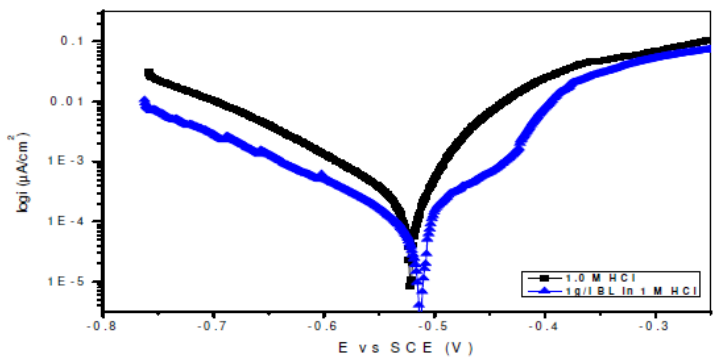

Figure 2. Potentiodynamic polarization curves for the corrosion inhibition process.

Conclusion

From the analysis of the experimental results the following conclusions can be drawn:

- The bitter leaves extract was highly efficient in the corrosion inhibition of the mild steel in HCl medium.
- It is effective for corrosion prevention of mild steel in the corrosive medium.
- The exothermic and spontaneous adsorption of the extract on the mild steel followed the mechanism of physical adsorption.
- The plant-based inhibitor of bitter leaves extract should be applied as additive for pickling, cleaning and descaling operations.

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