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Investigation of some Natural Product Extracts as Corrosion Inhibitors for Mild Steel in Acid Medium

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The inhibitive effect of extracts of tamarind seeds and jackfruit seeds, curry leaves and henna leaves on corrosion of mild steel in 1M HCl solution have been studied by weight loss, potentiodynamic polarization and impedance measurements. Results obtained from the electrochemical techniques were in good agreement with weight loss results. From the weight loss data, the values of surface coverage (θ) and corrosion rate were calculated. The inhibition efficiency (IE) increased with increasing inhibitor concentration in 1M HCl solution. In all the cases the adsorption of the natural product extracts on the mild steel surface from 1M HCl follows the Langmuir adsorption isotherm relationship. Potentiodynamic polarization studies reveal the fact that all the four natural product extracts act as mixed type inhibitors. The decrease in the inhibition efficiency follows the order:

Extracts of jackfruit seed > henna leaves > curry leaves > tamarind seed

Keywords *: natural products, corrosion inhibitors, mild steel, potentiodynamic polarization studies.*

1. Introduction

Pure synthetic chemicals are costly, toxic and their disposal create pollution problems to the environment. To overcome the above factors, it is necessary to develop environmentally acceptable and less expensive inhibitors. Natural products can be considered as a good source for this purpose. Organic compounds having heteroatoms are found to have higher basicity and higher electron density and thus worked as corrosion inhibitors.[1),2)] There are numerous naturally occurring substances like tea leaves, pomegranate juice and peels,[3),4)] quinoline based cinchona alkaloids[5)] as well as antimalarial ayurvedic powder maha sudarahana churna[6)] have been evaluated as effective acid corrosion inhibitors.

Hence in the present work, the extracts of jackfruit seeds, tamarind seeds, curry leaves and henna leaves are collected and evaluated for their corrosion inhibition performance in 1M HCl medium. Due to their bio-degradability, eco-friendliness, cost effectiveness and easy availability of these natural inhibitors, the trend of using them has become increasingly important in the recent years.

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2. Experimental details

2.1 Preparation of extracts

The jackfruit seeds, tamarind seeds, curry leaves and henna leaves were taken and cut into small pieces. These were separately dried at room temperature for five days. These were ground well into powder and soaked separately in ethanol for five days and then filtered at the end of soaking period. The excess of alcohol is removed from each of the extracts by vacuum distillation procedure. From these extracts, solutions of various concentrations of extracts were prepared using 1M HCl solution.

2.2. Material preparation

The mild steel specimens containing C-0.07%, Si-Nil, Mn - 0.34%, P- 0.008%, S- Nil and Fe- remainder and of size 4.5 cm X 2.5 cm X 0.01 cm were used for non-electrochemical studies. For electrochemical measurements, mild steel specimens of the same composition with an exposed area of 1 cm^2 were used. All test solutions were prepared from analytical grade HCl and double distilled water. The inhibitor concentrations of 0.5, 1.0, 1.5, 2.0 and 2.5% (v/v) were prepared using 1M HCl solution. The inhibitors chosen for the study are given in

Table 1. Name of the inhibitors used

S.No	Name of the Inhibitors
1	Jackfruit seed extract
2	Tamarind seed extract
3	Curry leaves extract
4	Henna leaves extract

Table 1.

2.3 Techniques used for the study

2.3.1 Weight loss method

Weight loss measurements were carried out as described earlier.[7] Mild steel specimens were immersed in 100 ml of inhibited and uninhibited solutions for 3 hours at 30°C. Inhibition efficiencies were calculated from the difference in weight loss values in the absence and presence of the natural product extracts in 1M HCl solution using the following equation

$$IE(\%) = \frac{W_0 - W_1}{W_0} \times 100 \quad (1)$$

Where W_0 and W_1 are weight loss per unit time in the absence and presence of inhibitors.

2.3.2 Potentiodynamic polarization studies

Polarization studies were carried out using an EG&G-Electrochemical analyzer (Model-6310) in a conventional three-electrode glass cell at a sweep rate of 1 mV_s^{-1}. Mild steel strips of the same composition with an exposed area of 1 cm^2 were used as the working electrode. A platinum foil of surface area 2 cm^2 was used as the auxiliary and saturated calomel electrode (SCE) as the reference. Both anodic and cathodic polarization curves were recorded in the absence and presence of different concentrations of natural product extracts. The inhibition efficiencies of the natural product extracts by polarization method were calculated using the following equation:

$$IE(\%) = \frac{I_{Corr} - I^*_{Corr}}{I_{Corr}} \times 100 \quad (2)$$

Where, I_{corr} and I^*_{corr} are corrosion current in the absence and presence of inhibitors.

2.3.3 Electrdochemical impedance studies

The electrochemical AC impedance measurements were performed using EG&G Electrochemical impedance analyzer (Model-6310).[8] A sine wave amplitude of 10mV was superimposed on the steady open circuit potential. The real part (Z') and the imaginary part (Z") were measured at various frequencies in the range of 100 kHz to 10 mHz. The percentage of inhibition efficiencies of the natural product extracts were calculated using the following equation:

$$IE(\%) = \frac{R^*_t - R_t}{R^*_t} \times 100 \quad (3)$$

Where, R_t^* and R_t are the charge transfer resistance in the presence and absence of inhibitors.

3. Results and discussion

3.1 Weight loss method

Different corrosion parameters such as corrosion rate, surface coverage (θ) and inhibition efficiency were obtained by weight loss method at different concentrations of natural product extracts are given in Table 2. It can be seen from the table that the extracts of tamarind seed, jackfruit seed, curry leaves and henna leaves inhibit the corrosion of mild steel to a greater extent in 1M HCl solution. Plot of inhibition efficiency against concentration of extracts are shown in Fig. 1. Inhibition efficiencies of all these extracts increased with increasing concentration of natural product extracts. This is due to the fact that

Table 2. Corrosion parameters obtained from weight loss measurements for mild steel in 1M HCl containing various concentrations of natural product extracts at 30°C

Name of the Inhibitors	Conc. (% v/v)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)	Surface Coverage (θ)
Jackfruit seed	Blank	30.91	-	-
	0.5	4.309	86.06	0.86
	1.0	4.240	88.45	0.88
	1.5	2.248	92.73	0.92
	2.0	2.107	94.73	0.94
	2.5	1.124	96.36	0.96
Tamarind seed	0.5	16.30	47.27	0.47
	1.0	15.18	50.90	0.50
	1.5	14.24	53.94	0.53
	2.0	12.37	60.00	0.60
	2.5	11.99	64.12	0.64
Curry leaves	0.5	8.619	72.12	0.72
	1.0	7.682	75.15	0.75
	1.5	6.558	78.79	0.78
	2.0	5.946	81.81	0.81
	2.5	5.621	84.52	0.84
Henna leaves	0.5	7.307	76.36	0.76
	1.0	6.554	78.49	0.78
	1.5	5.942	81.82	0.81
	2.0	5.632	83.03	0.83
	2.5	4.275	87.56	0.87

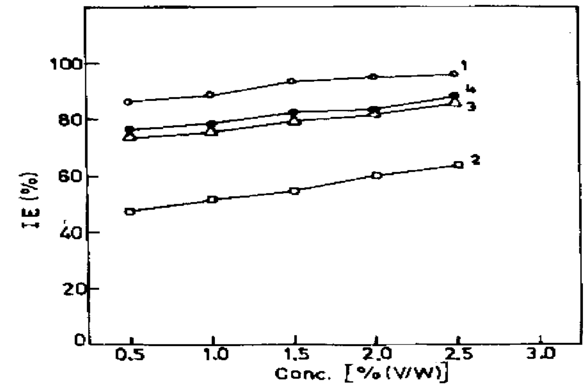

Fig. 1. Plot of inhibition efficiency with various concentrations of natural product extracts for corrosion of mild steel in 1M HCl solution
(1) Jackfruit seed extract (2) Tamarind seed extract
(3) Curry leaves extract (4) Henna leaves extract

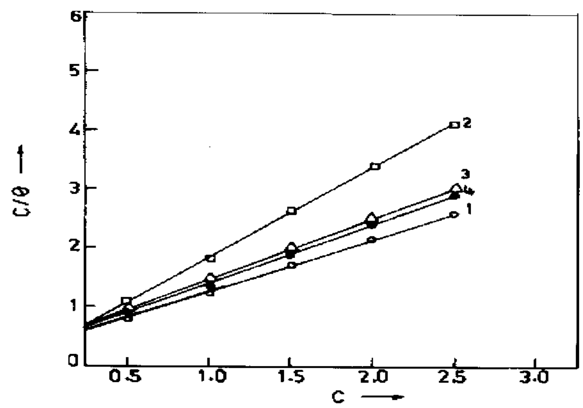

Fig. 2. Langmuir adsorption isotherm plot for the adsorption of various concentrations natural product extracts on mild steel in 1M HCl solution
(1) Jackfruit seed extract (2) Tamarind seed extract
(3) Curry leaves extract (4) Henna leaves extract

the corrosion inhibition may be due to the increase in adsorption of natural inhibitors on the metal surface.

The decrease in inhibition efficiency follows the order:

Extracts of jackfruit seed > henna leaves > curry leaves > tamarind seed.

3.2 Adsorption isotherm

The values of surface coverage (θ) for various concentrations of natural product extracts in 1M HCl solution were evaluated from weight loss measurements are given in Table 2. The data were tested graphically by fitting to various isotherms including Frumkin, Langmuir and Temkin. Langmuir adsorption isotherm was tested by plotting C/θ vs log C. A straight line was obtained by plotting C/θ vs log C (Fig. 2) suggesting that the adsorption of natural product extracts on mild steel surface in the acid solution follows Langmuir adsorption isotherm.

The observed inhibitive action of natural product extracts is due to the adsorption of its molecules on the steel surface making a barrier for charge and mass transfer between the metal and the environment. As the concentration of extract is increased, the fraction of steel surface covered by the adsorbed molecules (θ) increases leading to higher inhibition efficiency.

3.3 Potentiodynamic polarization studies

Table 3 gives various corrosion kinetic parameters such as corrosion current (I_{corr}), corrosion potentials (E_{corr}), and anodic and cathodic Tafel slopes (b_a and b_c) for all the four natural product extracts were derived from potentiodynamic polarization curves for mild steel in the absence and presence of natural product extracts and a representative polarization curve for both jackfruit seed and henna leaves is shown in Figs. 3 & 4 respectively. It can be

Table 3. Potentiodynamic polarization parameters for mild steel in 1M HCl containing various concentrations of natural product extracts at 30℃

Inhibitor Conc. (% v/v)	E_{corr} (mV)	I_{corr} (mA/cm^2)	Tafel Slope mV/decade		Inhibition Efficiency (%)
			b_a	b_c	
Blank	-472	3.57×10^{-3}	78	124	-
Jackfruit seed					
0.5	-474	5.27×10^{-4}	80	126	85.23
1.0	-472	3.75×10^{-4}	78	124	89.49
1.5	-472	1.89×10^{-4}	76	126	94.70
2.0	-474	1.13×10^{-4}	74	123	96.83
2.5	-472	0.62×10^{-4}	78	124	98.27
Tamarind seed					
0.5	-474	18.41×10^{-4}	74	126	48.43
1.0	-472	16.91×10^{-4}	76	124	52.64
1.5	-472	15.84×10^{-4}	78	124	55.62
2.0	-472	13.67×10^{-4}	74	122	61.71
2.5	-474	12.34×10^{-4}	76	124	65.45
Curry leaves					
0.5	-472	9.02×10^{-4}	76	122	74.73
1.0	-472	8.37×10^{-4}	78	124	76.56
1.5	-472	7.41×10^{-4}	78	122	79.25
2.0	-472	6.15×10^{-4}	74	124	82.77
2.5	-474	5.16×10^{-4}	76	122	85.53
Henna leaves					
0.5	-472	7.43×10^{-4}	78	126	79.19
1.0	-472	6.36×10^{-4}	74	124	82.20
1.5	-472	5.71×10^{-4}	74	122	84.00
2.0	-474	4.64×10^{-4}	76	122	87.01
2.5	-472	3.40×10^{-4}	76	124	90.47

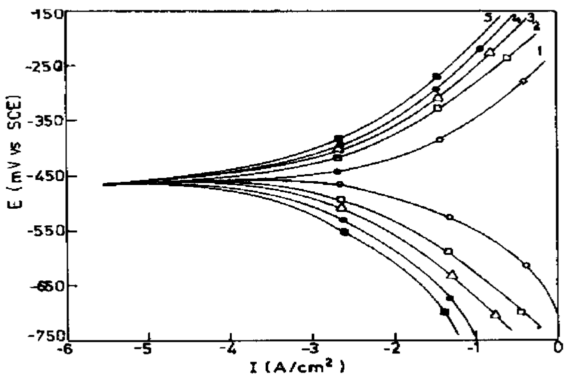

Fig. 3. Potentiodynamic polarization curves for mild steel in 1M HCl solution containing various concentrations of jackfruit seed extract
(1) Blank (2) 1.0 ml (3) 1.5 ml (4) 2.0 ml (5) 2.5 ml

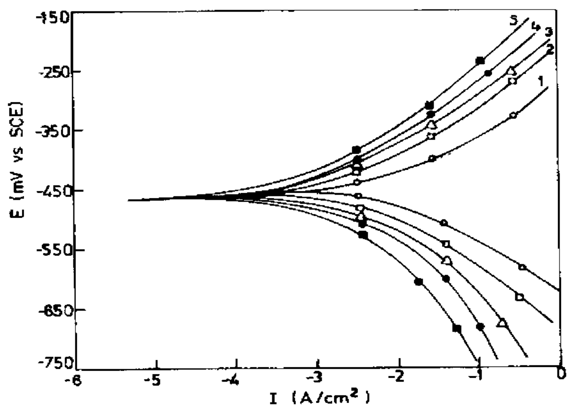

Fig. 4. Potentiodynamic polarization curves for mild steel in 1M HCl solution containing various concentrations of henna leaves extract
(1) Blank (2) 1.0 ml (3) 1.5 ml (4) 2.0 ml (5) 2.5 ml

seen from the table that the values of E_{corr} are not shifted significantly in presence of the inhibitors (natural product extracts) in addition with controlling both the anodic and the cathodic reactions by blocking the active anodic and cathodic sites of the metal surface, suggesting that all the four natural product extracts inhibited the corrosion of mild steel under mixed control. The corrosion current (I_{corr}) decreases with increase in concentrations of the natural product extracts and a maximum decrease in I_{corr} is observed at the concentration of 2.5% (v/v) in 1M HCl solution. It was found that jackfruit seed extract produced a maximum decrease in I_{corr} followed by henna leaves, curry leaves and tamarind seed extracts. This order is similar to that observed from weight loss measurements.

3.4 Impedance measurements

Table 4 gives various impedance parameters such as R_t, C_{dl} and IE obtained from Nyquist plots for mild steel in the absence and presence of natural product extracts and a representative impedance diagram for both jackfruit seed and henna leaves is shown in Figs. 5 & 6 respectively. C_{dl} values were calculated from the frequency at which the imaginary component of impedance was maximum (Z_{im}) using the relation:

Table 4. Impedance parameters for the corrosion of mild steel in 1M HCl in the absence and presence of various concentrations of natural product extracts at 30°C

Inhibitor Conc. (% v/v)	R_t (Ω cm^2)	C_{dl} (μF/cm^2)	Inhibition Efficiency (%)
Blank	7.63	283.64	-
Jackfruit seed			
0.5	47.94	178.18	84.08
1.0	61.79	164.36	87.65
1.5	85.65	135.97	91.09
2.0	131.59	120.22	94.20
2.5	316.63	108.28	97.59
Tamarind seed			
0.5	15.40	197.41	50.45
1.0	16.83	181.90	54.66
1.5	17.97	168.32	57.54
2.0	19.39	152.83	60.65
2.5	21.36	136.28	64.28
Curry leaves			
0.5	27.19	182.00	71.93
1.0	29.87	169.84	74.45
1.5	35.09	148.27	78.35
2.0	45.42	131.15	83.20
2.5	59.39	125.80	84.27
Henna leaves			
0.5	33.55	180.25	77.25
1.0	41.07	162.23	81.42
1.5	54.15	141.92	85.90
2.0	62.78	123.35	87.84
2.5	106.87	104.56	89.59

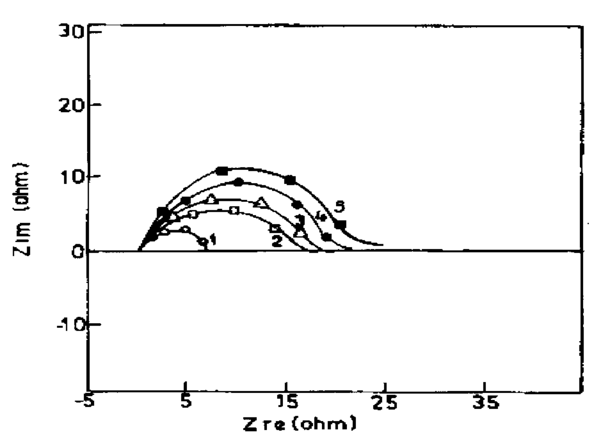

Fig. 5. Impedance diagrams for mild steel in 1M HCl solution containing various concentrations of jackfruit seed extract
(1) Blank (2) 1.0 ml (3) 1.5 ml (4) 2.0 ml (5) 2.5 ml

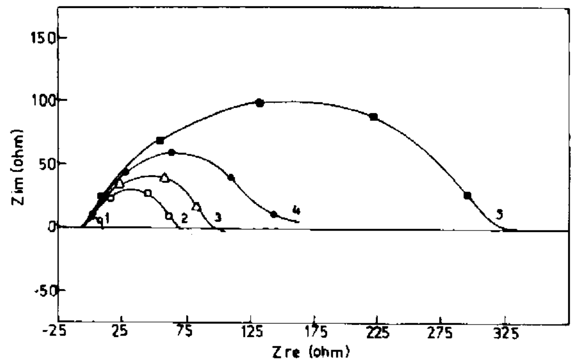

Fig. 6. Impedance diagrams for mild steel in 1M HCl solution containing various concentrations of henna leaves extract (1) Blank (2) 1.0 ml (3) 1.5 ml (4) 2.0 ml (5) 2.5 ml

$$C_{dl}=\frac{1}{2\pi f_{max}\ R_t} \quad (4)$$

The values of double layer capacitance (C_{dl}) are brought down to the maximum extent in the presence of extract of jackfruit seed followed by extracts of henna leaves, curry leaves and tamarind seed in the decreasing order. The decrease in C_{dl} can be attributed to the adsorption of these natural inhibitors on the metal surface, leading to the formation of a protective film on the metal surface.[9]

3.5 Mechanism of inhibition

The obtained results indicate that natural product extracts perform good inhibition for the corrosion of mild steel. The inhibitory effect of tamarind seed extracts is due to the presence of high tannin content. Jackfruit seed extracts contain aromatic compounds with nitrogen and oxygen atoms. It is possible that these plant based inhibitors adsorb on the metal surface through the donation of the lone pair electrons of oxygen or nitrogen or by being adsorbed on the metal surface through their Π electrons.[10]

The inhibitory effect of Henna leaves extract is due to the presence of hydroxy aromatic compounds such as tannin and lawsone. The inhibitive action of tannin was attributed to the formation of a passivating layer of tannates on the metal surface.[11] The other constituent of the henna leaves extract is lawsone which is present in a relatively higher amount. Lawsone molecule is a ligand that can chelate with various metal cations forming complex compounds. Therfore, the formatiom of insoluble complex compounds, by combination of the metal cations and the lawsone molecules adsorbed on the metal surface, is a probable interpretation of the observed inhibition of lawsone. Curry leaves extract shows inhibition efficiency due to the presence of monoterpene hydrocarbons (pinene, camphene and limonene etc.,) and nonterpenoid acyclic β-ketones.

4. Conclusion

1. The chosen four natural product extracts perform well in 1M HCl solution and inhibit the corrosion of mild steel in the following decreasing order:
   Extracts of jackfruit seed > henna leaves > curry leaves > tamarind seed.
2. The adsorption of natural inhibitors on mild steel in 1M HCl solution obeys the Langmuir adsorption isotherm.
3. Natural product extracts control both anodic and cathodic reactions by blocking the active sites of steel surface and thus the natural inhibitors are of mixed type.

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