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Corrosion Mitigating Effect of *Cyamopsis Tetragonaloba* Seed Extract on Mild Steel in Acid Medium

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Abstract: The role of seed extract of *Cyamopsis tetragonaloba* on corrosion mitigation of mild steel in 1 M HCl has been investigated by weight loss method and potentiodynamic polarization technique. Maximum inhibition efficiency of *Cyamopsis tetragonaloba* in 1 M HCl was found to be 92%. Experimental results were fitted into Langmuir and Temkin adsorption isotherm to study the process of inhibition. The potentiodynamic polarization results reveal that the seed extract behaved like mixed type inhibitor.

Keywords: Corrosion, *Cyamopsis tetragonaloba*, HCl medium, Mild steel, Inhibitor, Natural products.

Introduction

The environmental consequences of corrosion on metals are enormous and its inhibition has been deeply investigated. The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media¹. Inhibitors play an important role in controlling corrosion of metals². The use of naturally occurring substances as inhibitors for metals exposed to acid environment has continued to receive attention as replacement for synthesized organic inhibitors mainly due to its biodegradability and eco-friendliness.

Natural oil extracted from *Pennyroyal mint* was evaluated as corrosion inhibitor of steel in molar hydrochloric acid³. Extracts of different parts of *Carica papaya* (seeds, leaves, heart wood and bark) were proved as eco-friendly corrosion inhibitors⁴. Acidic extracts of *Ficus benghalensis* and sprouted seeds of *Phaseolus aureus* were also found to have excellent inhibition properties^{5,6}.

Green inhibitors displaying substantially improved environmental properties will be the inhibitors most widely used in future. Hence, the present study has been effectuated to investigate the action of seed extract of *Cyamopsis tetragonoloba* (CT) on corrosion inhibition of mild steel in hydrochloric acid medium.

Experimental

Materials and methods

Mild steel (MS) specimens of the following chemical composition in wt % - carbon 0.046, manganese 0.548, silicon 0.029 phosphorus 0.012, sulphur 0.019, chromium 0.050, molybdenum 0.015, nickel 0.013, lead 0.003 and Fe 99.265, were used for the entire study. Weight loss and electrochemical studies were carried out for assessing the efficacy of the inhibitor. For weight loss study, MS specimens of size 1 x 5 cm² were used. MS specimens with an exposed area of 1 cm² were used for electrochemical study. The specimens were mechanically polished, degreased, dried and stored in a desiccator.

Preparation of plant extract

25 g of dried and powdered seeds of CT was refluxed with 500 mL of 1 M HCl for 3 hours and kept overnight. The cooled extract was filtered and made up to 500 mL (5% extract).

Weight loss method

Pre weighed test pieces were immersed in triplicate in 100 mL of the solution containing various concentration of the inhibitor and in the absence of inhibitor for a predetermined time period. The test specimens were removed and then washed with de-ionised water, dried and reweighed.

The experiments were performed for various parameters such as:

- Concentration variation (0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6% and 0.7%)
- Different time intervals (½ h , 1 h , 3 h , 6 h , 12 h and 24 h)
- Temperature variation (303 K, 313 K, 323 K, 333 K and 343 K)

Electrochemical measurements

Potentiodynamic measurement-Tafel polarization curves were recorded using computerized Solartron model 1284. In this setup a platinum electrode, calomel electrode and MS specimens were used as auxiliary, reference and working electrodes respectively which were immersed in acidic medium in the presence and absence of different concentration of the inhibitor.

Results and Discussion

Effect of concentration

Table 1 depicts the variation of inhibition efficiency (IE) with respect to concentration of the inhibitor. It can be inferred that as the dosage of inhibitor increased, the IE was found to increase.

Table 1. Effect of concentration and time on corrosion inhibition of mild steel in CT extract in 1 M HCl

Conc of the Inhibitor, %	Inhibition Efficiency, %					
	½ hr	1 h	3 h	6 h	12 h	24 h
0.1	80.8	75.4	81.8	87.0	77.3	83.8
0.2	83.6	80.2	84.4	88.0	80.0	87.1
0.3	88.5	81.2	84.9	88.9	80.1	88.6
0.4	89.0	81.2	86.4	88.5	80.8	89.6
0.5	89.0	84.2	89.2	90.2	81.4	89.2
0.6	89.0	86.4	89.3	91.8	82.0	89.9
0.7	92.3	86.6	90.1	91.9	82.9	92.1

This behaviour can be attributed to the increase in surface area covered by the adsorbed molecules of the extract with increased concentration⁷. A maximum of 92.3% was obtained at 0.7% concentration of the extract.

Impact of immersion time

To investigate the effect of inhibition with exposure time, experiments were carried out at various time intervals. It is clear from Table 1, that, as the time of immersion increases from $\frac{1}{2}$ an hour to 6 hours, the protection efficiency increases from 92.3% (0.7% concentration at $\frac{1}{2}$ an h) to 91.9% (0.7% concentration at 6 h). After 6 hours there is a slight decline in IE to 82.90% at 12 hours and then an increase in IE at 24 h (92.1%) was observed⁸. This behaviour can be discussed on the following basis: prolonged immersion of steel in acidic solutions, allows the cathodic or hydrogen evolution kinetics to increase presumably as more cathodic or carbon containing sites are exposed by the corrosion process⁹ and increase the concentration of ferrous ion which is known for its stimulation of corrosion attack of the acid on the base metal¹⁰. It is obvious from the table that CT seed extract is a promising inhibitor in 1 M HCl at various time of immersion.

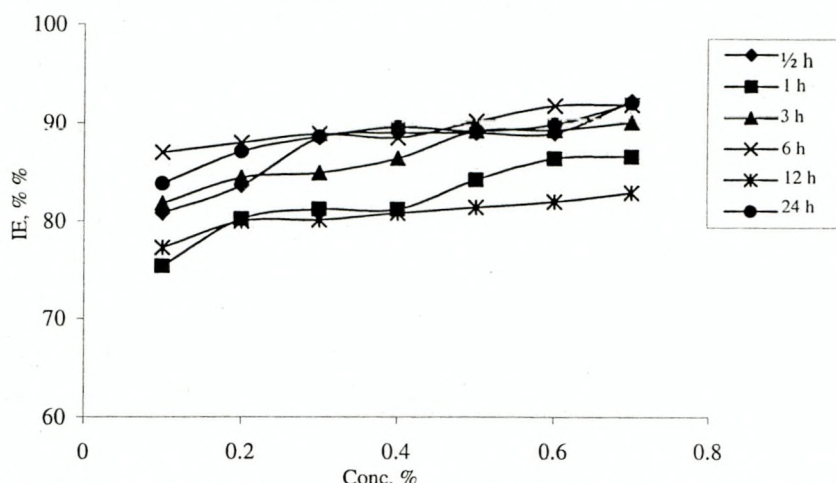


Figure 1. Effect of CT extract on corrosion inhibition of mild steel in 1 M HCl

Role of temperature

The influence of temperature on acid extracts of CT in 1 M HCl was investigated in the temperature range, 303K-343K, for $\frac{1}{2}$ an hour of immersion and the results are presented in Figure 2. Analysis of the figure indicates that, as the temperature increases from 313K to 333K, the IE also increased. The increase in IE was from 80.3% to 91.5% for 0.7% concentration of CT in 1 M HCl. Further rise in temperature (343 K) results in slight depletion of inhibitor efficiency (87.4%).

From the data, it can be inferred that the protective layer formed on MS surface, due to adsorption of plant extract, was stable up to 333 K and after that there may be desorption of plant extract at 343 K. Considering the magnitude of rise in temperature and the marginal drop in IE we can conclude that the extract worked out as a temperature resistant inhibitor in 1M HCl.

Adsorption Isotherm

The phenomenon of interaction between the metal surface and inhibitor can be better understood in terms of adsorption isotherm. The degree of surface coverage (θ) for different concentrations of inhibitors in both the acids has been evaluated from weight loss values. Data were tested graphically by fitting to various isotherms such as Langmuir and Temkin. A plot of $\log C$ vs. $\log \theta / 1 - \theta$ gave a straight line indicating that the adsorption of CT extract

on mild steel surface is by the formation of mono layer . A plot of $\log C$ vs. θ also furnishes a straight line indicating that it obeys Temkin adsorption isotherm and the behaviour of adsorption is affected by the heterogeneity of the electrode surface¹¹.

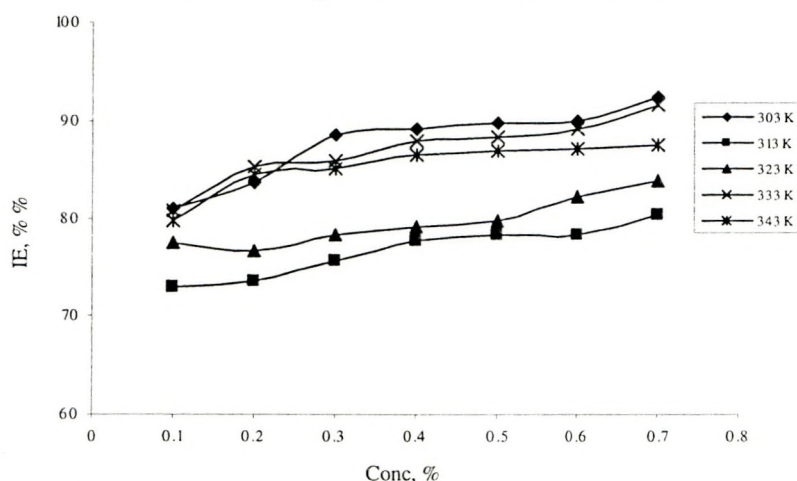


Figure 2. Effect of temperature on the corrosion inhibition of mild steel in the presence of CT extract in 1 M HCl

Electrochemical measurement-polarization studies

Polarization and impedance parameters are presented in Table 2. From the table, it can be seen that as the concentration of the CT extract increases, the value of I_{corr} decreases.

Table 2. Polarization data and IE of CT in 1M HCl

System	E_{corr} mV	$I_{\text{corr}} \times 10^{-4}$ Amp / cm^2	ba mV/ decade	bc mV/ decade	I.E, %	R_p Ohm/ cm^2	I.E, %
Blank	503	20.5	152	174	-	14.5	-
0.3% of CT	476	2.23	138	97	89	119	87.82
0.4% of CT	473	2.0	123	95	90	87	83.49
0.7% of CT	476	1.7	126	97	91	116	87.51

This indicates the inhibiting nature of the CT extract. The values of Tafel slopes "ba" and "bc" vary with increase in concentration of the CT extract. This result infers that the CT extracts function as a mixed type inhibitor. Increase in R_p values with increase in concentration of CT extract revealed that the inhibition process takes place by adsorption of the CT extract on the MS surface.

Mechanism of Inhibition

Most organic inhibitors contain at least one polar group with an atom of nitrogen or sulphur or in some cases selenium and phosphorus. The inhibiting properties of many compounds are determined by the electron density at the reaction center¹². With increase in electron density in the center, the chemisorption between the inhibitor and the metal are strengthened^{13,14}.

The plant extract CT contain the phytochemical constituents such as 3-epikatonnic acid 7-*o*-beta-(2-rhamnosyl-glucosyl) myricetin, ash, astragaln, caffeic acid, chlorogenic acid,

ellagic acid, fat, gallic acid, guaran, kaempferol-3-o-rutinoside, kaempferol-7-o-beta-D-glucoside-3-glycoside, linoleic acid, myricetin-7-o-beta-D-glucoside-3-glycoside, myristic acid, oleic acid, palmitic acid, protein, stearic acid (Ref: Duke's phyto chemical database).

The above said phytochemical constituents present in CT, having many active centers such as nitrogen and oxygen, are adsorbed on the metal surface and the effectiveness of these inhibitors on the corrosion of MS may be due to the electron densities on the active centers. The adsorption takes place through the active centers. The possible synergistic interactions between adsorbed species could also contribute to the high IE of the extract. In the current investigation the seed extract of CT was found to perform as a good inhibitor for mild steel corrosion.

Conclusion

The extract of *Cyamopsis tetragonoloba* shows significant inhibitive action of HCl induced corrosion of mild steel and the inhibitive action may be due to strong adsorption of the chemical constituents of the extract on the surface of mild steel. Weight loss method furnishes 92% IE at 0.7% concentration and electrochemical measurements could give 91% using I_{corr} values and 87% using R_p values at 0.7% concentration of extract. Experimental data are well fitted into Langmuir and Temkin adsorption isotherms. Electrochemical methods also confirm the mixed mode of inhibition. Weight loss and electrochemical methods are quite comparable.

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