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Influence of *Tagetes erecta* –leaves extract on the corrosion inhibition of mildsteel in HCL medium

R.Subha[1,*] and R.Saratha[2]

[1]Department of Chemistry, Sri Sakthi Institute of Technology, Coimbatore -62.

[2]Department of Chemistry, Avinashilingam Institute for Home science and Higher education for Women, Coimbatore-43.

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ABSTRACT

The inhibitive action of *Tagetes erecta*-leaves (TEL) extract on mild steel in 1M HCl has been studied using weight loss, electrochemical polarization and AC impedance measurements and The extract shows a very good inhibition in the hydrochloric acid medium and inhibition efficiency of the extract was found to vary with the extract concentration and immersion time. The maximum inhibition efficiency of 96% was obtained at 0.3%v/v concentration of the extract at 24h immersion time at room temperature. The potentiodynamic polarization data showed that the extract is of mixed type. EIS measurements showed that the dissolution process occurs under activation control. The protective film formed on the surface of mild steel by the adsorption of phytochemical constituents present in the extract was confirmed by SEM studies

Introduction

The use of inhibitors is one of the best methods of protecting metals against corrosion. Most corrosion inhibitors are organic compounds having hetero atoms in their aromatic or long carbon chain (1-5). Before the 1960s inorganic inhibitors such as zinc, chromate, polyphosphate and nitrite were used as inhibitors (6-10). However, disposal of inhibitors has become unacceptable, due to environmental hazards. Most of the natural products are non-toxic, biodegradable and readily available in plenty. Various parts of plants such as seeds, fruits, leaves, flowers have been used as corrosion inhibitors (11-20).

Plant scientists have already established the active constituents present in most of the plant materials. The active constituents form protective film on metal surface by coordinating with metal ions through O, S or N atoms of the functional groups present in the active constituents. When the active constituents are extracted with acids /or organic solvents/ or with water, usually a mixture of several compounds is obtained.

Green inhibitors are cost effective compared to that of organic inhibitors and preparation of the inhibitor involves consumption of chemicals with reactions being carried over prolonged period. Hence in the present work, TEL extract was used as an inhibitor and evaluated for its corrosion inhibition performance by weight loss, potentiodynamic polarization, impedance studies and a probable mechanism of inhibition was also proposed.

Experimental Procedure

Preparation of extract:

The leaves of *Tagetes erecta* was collected from in and around Coimbatore district, Tamilnadu. The leaves were shade dried, crushed and powdered. From this powder, 25g was taken in a RB flask, refluxed with 500ml of 1M HCl for 3h and kept overnight. The next day, it was filtered and made up to 500ml in a standard flask with the same acid. From this stock solution, solutions of different concentration of the extract were prepared.

Weight loss studies:

Weight loss measurements were performed on the mild steel samples with rectangular form of size 5cm×1cm. The specimens were mechanically polished to a mirror finish, degreased with acetone and then rinsed with distilled water, dried, stored in desiccators. The test pieces were fully immersed for different periods (1h, 3h, 5h, 7h and 12h) in each of the beaker containing 100ml of hydrochloric acid without and with the inhibitor (0.01,0.03,0.05,0.07,0.09,0.1,0.3 and 0.5%V/V). Each of the test specimens were removed, neutralized with sodium bicarbonate, rinsed with water, dried and re-weighed. The corrosion rate and inhibition efficiency were calculated using the equations;

$$C.R = \frac{534 \times W \times 1000}{DAT}$$

where C.R is the corrosion rate in mpy
W is the weight loss of the substance in grams
D is the density of mild steel in g/cm^3
A is the area of the specimen in square inches
T is the time of immersion in hours

$$I.E\,(\%) = \frac{C.R - C.R\,(inh)}{C.R} \times 100$$

Where C.R – is the corrosion rate without inhibitor
C.R (inh) – is the corrosion rate with inhibitor.
Potentiodynamic polarization measurements:

Potentiodynamic polarization and impedance measurements were carried out using an electrochemical instrument (mod SOLATRON -1280B). A platinum electrode was used as the auxilliary electrode, a saturated calomel electrode was used as

Tele:
E-mail addresses: subhablj@yahoo.com

the reference electrode and mild steel was used as the working electrode. All the experiments were carried out at room temperature (30° $\pm$ 2° C) at a scan rate of 10mV/sec at OCP.

Result and discussion

Weight loss method:

Effect of extract concentration:

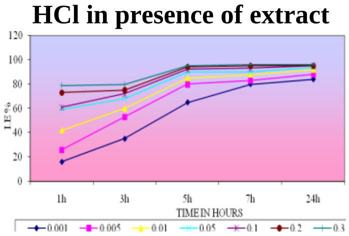
The inhibition efficiency was obtained from weight loss studies at different concentration of the extract at room temperature, and is given in table (1). It is clear from the table that the additions of inhibitor increased the inhibition efficiency in acid medium. The maximum inhibition efficiency (96%) is found at 0.3%V/V of concentration of extract.

Effect of immersion time

The figure (1) shows that inhibition efficiency of the extract increased with increasing immersion time from 1 to 24h. The increase in inhibition efficiency upto 24h reflects the strong adsorption of constituents present in the extract on the mild steel surface, resulting in a more protective layer formation at mild steel/hydrochloric acid interface. Even though there is increase in inhibition efficiency upto 24hours, there is no much difference between in inhibition efficiency at 7h and 24h. Hence, the optimum time for maximum inhibition efficiency (96%) is obtained at 7h immersion time.

Figure-1

Effect of immersion on the dissolution of mild steel in 1M HCl in presence of extract

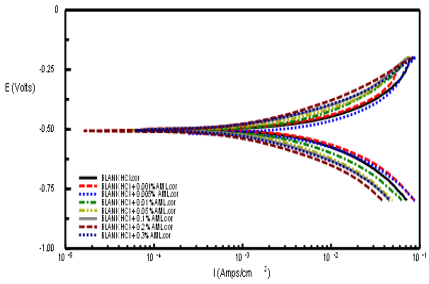


Potentiodynamic polarization measurement:

The polarization behavior of mild steel in 1M HCl in absence and presence of inhibitor is shown in figure 2. Electrochemical parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), Tafel constants (b_a and b_c) and percentage inhibition efficiency (%IE) calculated from Tafel plots are given in table 2.

Figure: 2

Potentiodynamic polarization of mild steel in 1MHCl in the presence of extract



It is observed from table 2 that Tafel slope constants b_a and b_c varies equally on the both sides indicates that it controls both anodic dissolution reaction as well as cathodic hydrogen evolution reaction. The lower corrosion current density (I_{corr}) values in the presence of extract without causing any significant changes in corrosion potential (E_{corr}) suggests that it is mixed type inhibitor. Increase in linear polarization resistance in the presence of inhibitor shows that the extract adsorbs on the metal surface by blocking the active sites of the steel surface without affecting the mechanism of corrosion reaction.

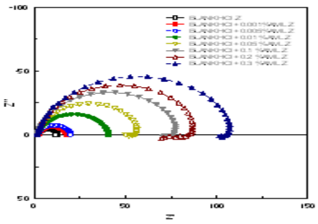
Impedance measurements

Nyquist plot is shown in figure-3 and the corresponding values are given in the table-3. From the figure-3, the impedance spectra are characterized by slightly depressed one capacitive loop. Deviations from the ideal semicircles can be attributed to the inhomogenities of the surface as well as due to mass transport process.

It is clear from the table-3; the increase in polarization resistance and the decrease of double layer capacitance were attributed to the enhanced adsorption of the inhibitor molecule on the metal surface. The decrease in C_{dl}, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer suggest that the studied extract function by adsorption at the metal-solution interface.

Figure: 3

Nyquist Plot of mild steel in 1MHCl in the presence of extract

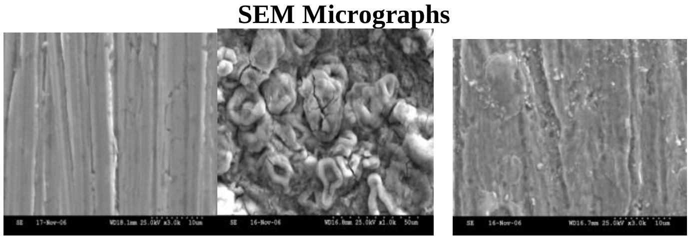


Surface Study

The polished specimen and the test specimens that are immersed in the blank (1M HCl) and in the presence of extract for 24h were observed under a scanning electron microscope. These SEM micrographs are given in picture-1(a, b &c). Picture-1a, shows the polished mild steel surface which is associated with polishing scratches. It is clear from the picture -1b, the surface of the mild steel was heavily corroded (many cracks) in 1M HCl. Picture-1c, clearly indicates that the surface of the mild steel gets protected by the adsorbed inhibitor which is firmly attached to the surface.

Picture-1

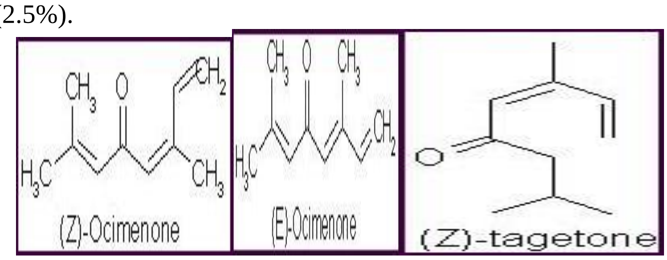
SEM Micrographs



a.Polished mild steel surface b. Mild steel in 1M HCl c. Mild steel in TE-L extract

Mechanism of corrosion inhibition:

Inhibition of corrosion of mild steel in acid medium by extract may be explained on the basis of adsorption. The flowers of *Tagetes erecta* L. were analyzed by a combination of GC and GC/MS. Thirty four components were identified (21-25). The main characterized constituents were β-caryophyllene (35.2%), terpinolene (6.3%), and (E)-ocimenone (9.8%), (Z) β-ocimene (13.7%), piperitenone (2.6%), Tagetone (6.2%) and limonene (2.5%).



The high performance of TE-L extract could also be due to large size of constituent's molecule which covers wide areas on the metal surface and thus retarding the corrosion. The main constituents of the leaves extract contain functional groups such as C=O, C=C and C-H, which meets the general consideration of typical corrosion inhibitors. The non-bonded electrons of heteroatom get protonated and thereby they get adsorbed on the negatively charged metal surface. Due to electrostatic interaction, the protonated constituent's molecules are adsorbed on the metal surface (strong physisorption) and high inhibition is expected.

Conclusion:

Tagetes erecta- leaves act as a good inhibitor in 1M HCl acid medium. The inhibition efficiency of the extract increases with increase in extract concentration and immersion time. The maximum inhibition efficiency (96%) is obtained at 0.3%V/V of extract at 7h immersion period. Potentiodynamic polarization study shows that it controls both the cathodic and anodic sites of the metal surface, thus acts as a mixed type inhibitor. Electrochemical impedance spectroscopy shows that R_{ct} values increases, while C_{dl} values decreases in the presence of extract. SEM study indicates that the surface of the mild steel gets protected by the adsorption of the components presents in the leave extract of *Tagetes erecta* on the mild steel through π-electrons and lone pair of electrons present in the oxygen atom.

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Table-1 Inhibition efficiency of MS in 1M HCl in the presence of extract-TE-L

Inhibitor Concentration V/V (%)	Inhibition efficiency %				
	1h	3h	5h	7h	24h
0.001	16	35	40	80	84
0.005	26	53	80	83	88
0.010	42	60	85	88	92
0.050	59	68	90	90	94
0.100	61	72	92	93	95
0.200	73	75	94	95	95
0.300	79	80	95	96	96

Table: 2 Electrochemical parameters for mild steel in 1M HCl in the presence of extract

Inhibitor concentration V/V (%)	$-E_{corr}$ mV	I_{corr} µA cm^{-2}	b_a mV/dec	b_c mV/dec	I.E (%)	R_p (Ω cm^2)	I.E (%)
Blank	502	5.83	223	169	-	6.08	-
0.001	498	5.15	183	164	11.66	7.27	15.27
0.005	514	4.96	174	148	14.92	7.58	24.67
0.01	505	2.76	166	148	52.65	11.78	48.39
0.05	502	1.56	150	116	73.24	17.59	65.43
0.1	502	1.22	142	116	79.07	23.23	73.83
0.2	506	0.89	137	121	84.73	25.98	76.59
0.3	500	0.82	122	100	85.93	31.13	80.47

Table: 3 Impedance parameters for the corrosion of mild steel in 1MHCl

Inhibitor concentration V/V (%)	R_{ct} (Ω cm^2)	C_{dl} (µF/cm^2)	I.E (%)
Blank	10.98	252.87	-
0.001	15.99	185.68	31.33
0.005	18.23	165.95	39.77
0.01	38.63	109.00	71.57
0.05	52.53	90.34	79.09
0.1	73.67	90.12	85.09
0.2	79.71	88.36	86.22
0.3	104.17	79.23	89.46