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ORIGINAL ARTICLE

Corrosion Mitigation of low Carbon Steel in Hydrochloric acid Medium by *Tagetes erecta* Stem Extract

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ABSTRACT

*The corrosion inhibitive effect of Tagetes erecta stem (TES) extract on the corrosion of mild steel in hydrochloric acid medium was studied using chemical and electrochemical studies. The maximum inhibition efficiency of **97%** was obtained at **0.3%V/V** concentration of the extract at room temperature. Potentiodynamic polarization study reveals that the extract controls both anodic as well as cathodic reactions. Double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) values were derived from Nyquist plots. A mechanism of adsorption of the stem components on the surface of the metal was proposed for the inhibition behavior on the basis of FTIR study.*
Key words: *1. mild steel, 2. Potentiodynamic polarization, 3. FTIR, 4. Corrosion rate, 5. Inhibition efficiency, 6. Adsorption isotherm.*

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INTRODUCTION

Mild steel is used as a structural material for reaction vessels, pipes, tank etc. which are known to corrode invariably in contact with various solvents and acids. It is necessary to adopt appropriate means and ways to reduce the losses due to corrosion, from the view point of nation's economy and financial implications of corrosion hazard (1). In order to prevent or minimize corrosion, inhibitors are used especially in industries.

Corrosion inhibitors can be defined as those compounds that when added in suitable amounts cause lowering in the corrosion rate of the metal without significantly changing the concentration of any other corrosive agent (2). It is generally assumed that inhibition in acid media by chemical compounds added to the electrolyte is to be attributed to the adsorption of the additive, (ion or neutral polar molecule), on the metal-solution interface. It can then retard the cathodic and/or anodic reactions, thus, reducing the corrosion rate.

A number of organic and inorganic compounds represent this type of inhibition. It provides the protection for metal surfaces by molecular adsorption into the metal surface and forming a barrier film to decrease the corrosion rate. (3-10). Because of the toxic nature and /or high cost of some chemicals currently in use as inhibitors, it is necessary to develop environmentally acceptable and inexpensive ones. Natural products can be considered as a good source for this purpose. The different parts of some plants such as Azadirachta Indica (11), Colocasia esculenta(12), Murraya Koenigh (13), Rauvolfia Serpentina (14), Hybiseus Syriacus Linn (15), Foeniculum Vulgare (16), Citrus aurantiifolia (17) have been found to be good corrosion inhibitors for many metals and alloys.

As a contribution to the current interest on environmentally friendly corrosion inhibitors, the present study investigates the inhibiting effect of acid extract of *Tagetes erecta* (ie., Stem of African marigold – AMS) stem on mild steel in hydrochloric acid medium by chemical and electrochemical methods. The inhibitor active components were investigated using FT- IR.

MATERIAL AND METHODS

Preparation of specimen:

Mild steel specimens of dimension 1×5×1cm were cut from a sheet of commercial cold rolled mild steel and mechanically polished to a mirror finish, degreased with acetone and then rinsed with distilled water, dried, stored in desiccators and used for the weight loss studies.

Preparation of extract:

The Botanical name of African marigold is Tagetes erecta, belongs to compositae family. The stem of African marigold (AMS) was collected shade dried, crushed and powdered. From this powder, 25g was taken in a RB flask, refluxed with 500ml of acid for 3h and kept it overnight. The next day, it was filtered and made up to 500ml in a standard flask with the same acid. This solution was stored as stock solution and used for further studies.

Chemical study – Mass loss:

Weighed test pieces were separately and fully immersed for different periods (1h, 3h, 5h, 7h, 12h and 24h) in each of the beaker containing the hydrochloric acid without and with the inhibitor (0.001,0.005,0.01,0.05,0.1,0.2 and 0.3%V/V). Each of the test specimens were

The corrosion rate and inhibition efficiency is being calculated using the formula,

$$C.R = 534 \times W/DAT \quad \text{------------------ (1)}$$

Where, C.R-corrosion rate (mpy), W-weight loss in mg, A-area of the specimen in square inches, D-density in g/cm^3 and T-Time of exposure in hours

$$I.E\ (\%) = \frac{C.R - C.R\ (inh)}{C.R} \times 100 \quad (2)$$

Where C.R – is the corrosion rate without inhibitor, C.R (inh) – is the corrosion rate with inhibitor.

Electrochemical Studies:

Potentiodynamic polarization and impedance measurements were carried out using an electrochemical instrument (model SOLATRON -1280B). A platinum foil was used as an auxiliary electrode, a saturated calomel electrode was used as reference electrode and mild steel was used as the working electrode. All the experiments were carried out at room temperature (30° $\pm$ 2° C) and a scan rate of 10mV/sec at OCP. The polarization curves were obtained after immersion of the electrode of the solution until a steady state was reached.

Surface Study – FTIR:

The specimens were immersed in blank solution and with inhibitor of highest concentration ie., 0.3%V/V for 12hours, taken out and dried. The film formed on the metal surface was carefully removed, mixed thoroughly with KBr and made into pellets. The FTIR spectra were recorded on Bruker (6400–V) spectrophotometer.

Result and discussion

Chemical study -Mass loss method:

Effect of concentration

The corrosion rate and inhibition efficiency were obtained from mass loss study at different concentrations of the extract at room temperature is given in table (1). It has been observed from the table that the corrosion rate decreased and inhibition efficiency increased with increase in extract concentrations.

Table: 1: Inhibition efficiency of mild steel in 1M HCl in the presence of extract (AMS)

Inhibitor Concentration V/V (%)	1h		3h		5h		7h		24h	
	C.R (mpy)	I.E %	C.R (mpy)	I.E %	C.R (mpy)	I.E %	C.R (mpy)	I.E %	C.R (mpy)	I.E %
Blank	192	-	248	-	515	-	1898	-	2287	-
0.001	146	24	184	26	242	53	645	66	755	67
0.005	132	31	144	42	149	71	512	73	595	74
0.010	108	44	67	73	124	76	418	78	343	85
0.050	84	56	52	79	108	79	380	80	297	87
0.100	60	69	50	80	93	82	285	85	183	92
0.200	40	79	35	86	72	86	247	87	160	93
0.300	33	83	35	86	57	89	190	90	137	94

The maximum inhibition efficiency is found to be obtained at **0.3%V/V** of concentration of extract. The increase in inhibition efficiency with increase in concentration of the extract may be due to the adsorption of active constituents present in the extract on the mild steel surface (21).

Effect of immersion time

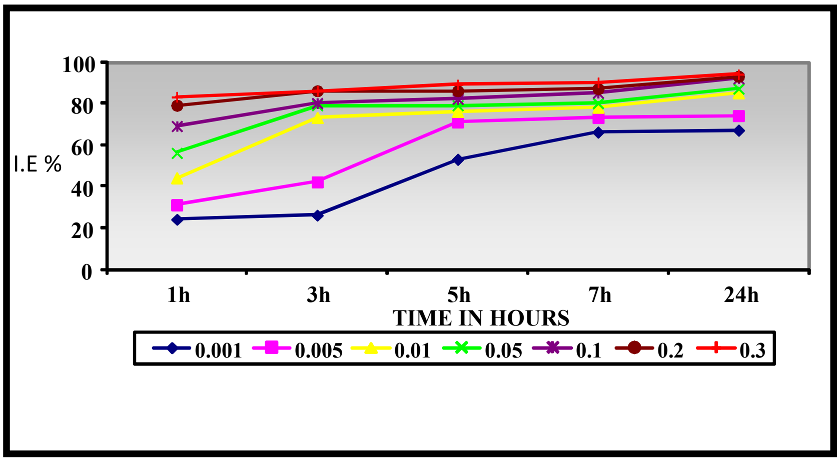


Fig. 1 Effect of immersion time on the dissolution of mild steel in HCl in the presence of extract

From the **Fig.1,** it is clear that the inhibition efficiency of the extract increased with increase in immersion time. The increased inhibition efficiency with exposure time may be attributed to the increase in the surface coverage by the adsorption of phytochemical constituents of the plant extracts (22). It may also be due to the stability of the inhibitor in the 1M HCl leading to strong adsorption of the components present in the extracts. The maximum period of immersion to get the maximum inhibition is **24h** for 0.3%V/V concentration of the extract.

Electrochemical studies:

Potentiodynamic polarization measurement:

A Potentiodynamic anodic and cathodic polarization scan was carried out at room temperature. The various electrochemical parameters calculated from the Tafel plot is given in **Table 2** and the plot is shown in **Fig.2**.

Table: 2: Electrochemical parameters for mild steel in 1M HCl in presence of AMS 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 (Ωcm^2)	I.E (%)
Blank	509	6.47	215	178	-	3.86	-
0.001	509	4.11	147	133	36.47	4.10	5.85
0.005	506	3.70	152	121	42.81	4.59	15.90
0.01	513	3.40	143	125	47.45	4.70	17.87
0.05	506	3.23	188	132	50.07	4.93	21.70
0.1	506	2.36	133	109	63.52	5.89	34.46
0.2	498	1.32	141	99	79.60	7.76	50.25
0.3	499	1.09	138	104	83.15	9.89	60.97

The lower corrosion current density (I_{corr}) values in the presence of extract without causing significant changes in corrosion potential (E_{corr}) suggests that it is mixed type inhibitor (23).

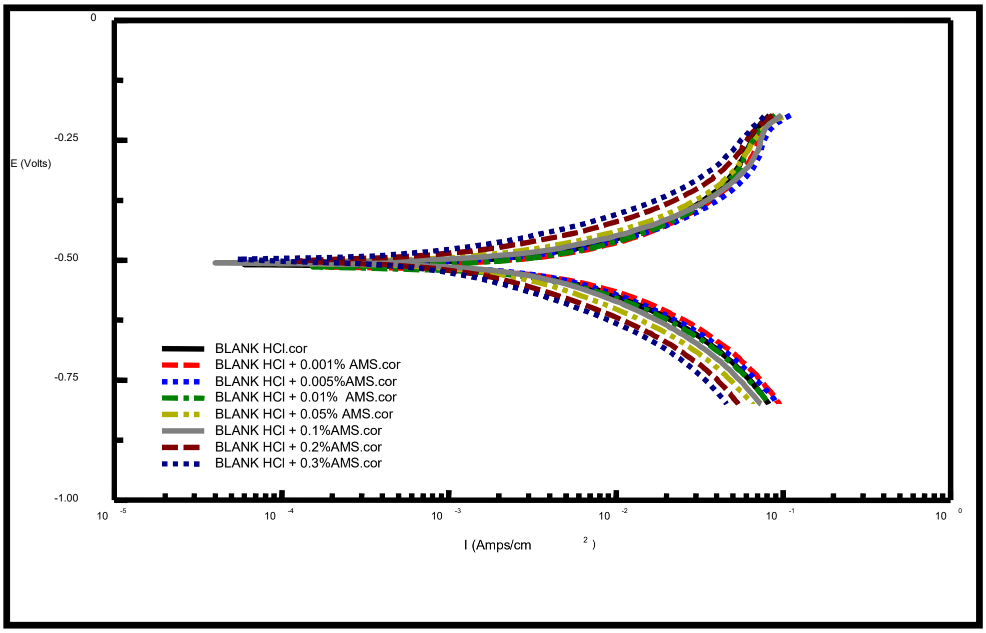


Fig. 2 Potentiodynamic polarization of mild steel in 1M HCl in presence of AMS extract

The changes in values of cathodic Tafel slope b_c with inhibitor concentrations from 178 to 99 mV dec^{-1} and the anodic Tafel slope b_a from 215 to138 mV dec^{-1} indicates that the influence of extract both on the kinetics of hydrogen evolution and reduction of the metal dissolution along with hydrogen evolution.

Impedance measurement

The corrosion behaviour of mild steel in 1M HCl in the absence and presence of extracts was investigated by the electrochemical impedance spectroscopy at room temperature (30ºC).

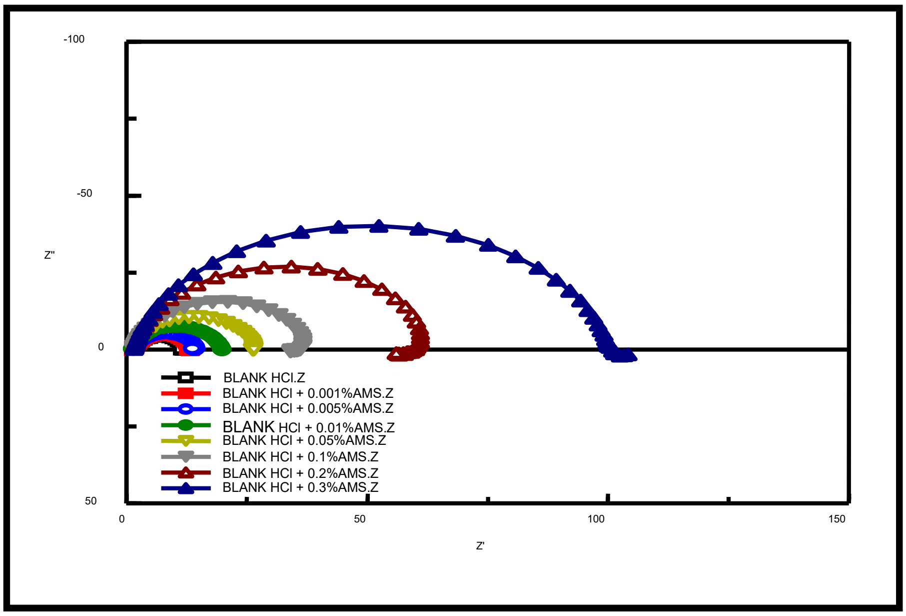


Fig. 3 Nyquist Plot of mild steel in 1M HCl

Nyquist plots of mild steel in 1M HCl containing various concentrations of extract AMS is given in figure (3) and the characteristic parameters associated to the impedance diagrams like charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) and calculated values of I.E (%) from the R_{ct} values are given in **Table 3.**

It can be seen from the **Fig.3**, the Nyquist plot contains depressed semicircles with centers under the real axis, whose size increases with the extracts concentration, indicating charge transfer process is mainly controlling the corrosion of mild steel. Such behavior is characteristic of solid electrodes and is often referred to as frequency dispersion. This has been attributed to roughness and other in-homogeneities of the solid surface (24).

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

Inhibitor concentration V/V (%)	1M HCl		
	R_{ct} (Ω cm^2)	C_{dl} (μF/cm^2)	I.E (%)
Blank	10.67	251.44	-
0.001	11.80	169.68	9.57
0.005	12.73	167.48	16.18
0.01	18.61	163.60	42.66
0.05	25.00	139.15	57.32
0.1	34.25	125.11	68.85
0.2	57.32	96.04	81.38
0.3	99.58	95.02	89.28

From the Table 3, it is observed that the R_{ct} values increases with increasing concentrations of the extracts. On the other hand, the value of C_{dl} decreases with an increase in the inhibitor concentration. This situation is due to an increase in the surface coverage by the inhibitor, which led to an increase in the inhibition efficiency. The decrease in the C_{dl} and the corresponding increase in R_{ct}, suggested that the extract molecules function by adsorption at the metal/solution interface. Thus the change in C_{dl} value is caused by the gradual replacement of water molecules by the adsorption of the organic molecules on the metal surface, decreasing the extent of metal dissolution.

Surface Study -FTIR spectra

The FTIR spectra of the film formed on the surface of mild steel in the HCl solution containing the AMS extract is given in **Fig.4**.

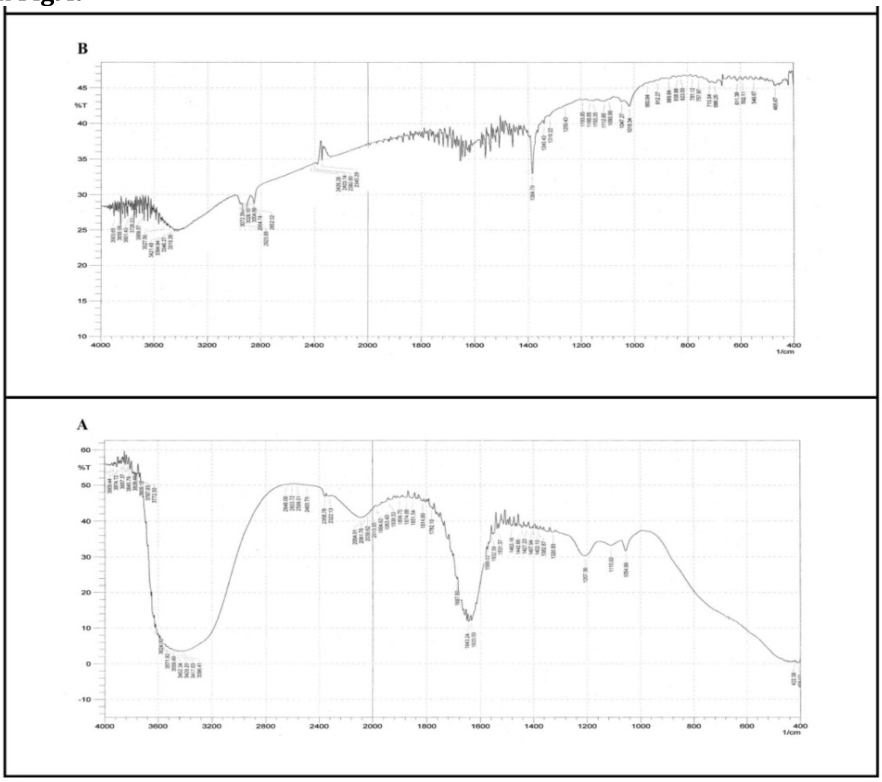


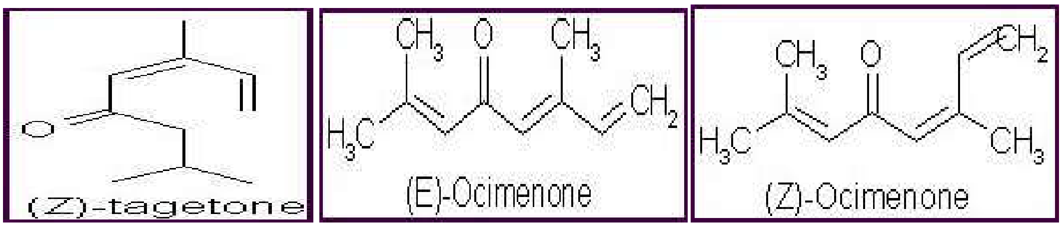
Fig. 4 FTIR spectra of AMS extract

A. **Pure AMS extract**
B. **HCl + 0.3% AMS extract (after 24h exposure)**

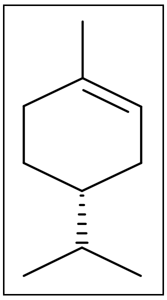
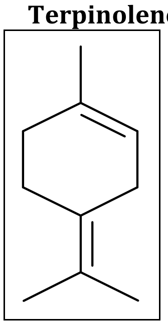
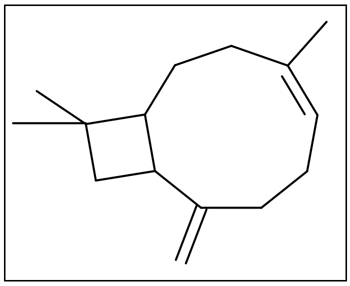
The broad band at about 3500cm^{-1} is assigned to the presence of intermolecular hydrogen bond, stretching mode of an O-H and /or N-H. Monosubstituted alkenes, that is, vinyl group and simple open chain, secondary amides, absorb near 1640cm^{-1}. The C-O stretching vibrations produce a band in the 1260-1000cm^{-1} (25). Therefore, it is evident that the extracted organic compounds are stable in 1M HCl medium. Further, the presence of these organic compounds was identified by the various phytochemical constituents screening tests. Variation in the FTIR spectra of the film formed on the metal surface in acid in the presence of extracts (0.3% V/V), may be due to the strong physical adsorption of the constituents present in the extract leading to chemisorptions.

Mechanism of corrosion inhibition:

Inhibition of corrosion of mild steel in acid medium by extract may be explained on the basis of adsorption. The stems of *Tagetes erecta* L. were analyzed by a combination of GC and GC/MS (26). Thirty three components were identified. The main characterized constituents were β–caryophyllene (8.5%), terpinolene (18.4%), and (E)–ocimenone (12.6%), (Z) β-ocimene (10.4%), piperitenone (10.4%), (Z)-ocimenone (5.5%) and limonene (6.2%).



Limonene **Terpinolene** **β– caryophyllene -iso**

The constituents present in the extract inhibit corrosion by controlling both the anodic and cathodic reactions. In acidic solutions, the components may exist as protonated species. These protonated species adsorb on the cathodic sites of mild steel and decrease the evolution of hydrogen. The adsorption on anodic sites may occur through π-electrons and lone pair of electrons of oxygen atom which may decrease anodic dissolution of mild steel.

CONCLUSION

The conclusions of the above study are

- The plant extracts AMS acts as a good inhibitor in HCl acid medium.
- The inhibition efficiency of the extract increases with increase in extract concentration and period of immersion.
- Potentiodynamic polarization study shows that it control 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.
- FTIR study confirms the adsorption of the components present in the flower extract of African marigold on the mild steel through π-electrons and lone pair of electrons present in the oxygen atom.

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