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Green Corrosion Inhibitor for Carbon Steel by *Marrubium astranicum* Leaves Extracts in 1 M HCl

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Abstract

The aim of this study was to investigate the effect of inhibition of *Marrubium astranicum* leaves extract on the corrosion of carbon steel in hydrochloric acid solution by using weight loss and tafel polarization methods. Inhibition was found to increase with increasing concentration of the leaves extract. The inhibition efficiency of this extract at an optimum concentration of 100 mg L^{-1} was 99.9 %. The effect of inhibitor concentration, immersion time and temperature on the corrosion behavior of carbon steel in 1 M HCl was also studied. The inhibition was assumed to occur via adsorption of the inhibitor molecules on the metal surface. The adsorption of the extract on the carbon steel surface obeys the Langmuir adsorption isotherm. The results obtained show that the leave extract of plant could serve as an effective green inhibitor of the corrosion of carbon steel in hydrochloric acid.

Keywords: *Chemical composition, Corrosion, Adsorption, Inhibition.*

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Introduction

Carbon steel, the most widely used engineering material, accounts for approximately 85%, of the annual steel production of worldwide. Despite its relatively limited corrosion resistance, it is used in large tonnages in marine applications, nuclear power and fossil fuel power plants, transportation, chemical processing, petroleum production and refining, pipelines, mining, construction and metal-processing equipment [1].

On the other hand, Acids are used for acid cleaning, descaling and pickling due to their chemical properties [2-5]. In general, the high corrosive nature of acids causes damage to the steel during pickling. Several methods were used to decrease the corrosion of metals in acidic medium. Using of inhibitors is the most economical and practical method to reduce electrochemical corrosion [6-10].

It has been reported that heterocyclic organic compounds having π bonds and containing heteroatoms such as nitrogen, oxygen, phosphorous and sulphur were reported as corrosion inhibitors by few researchers [11-16].The most of the organic inhibitors are toxic, highly expensive and environmentally unfriendly. The researchers intend to use of natural products instead of the most synthetic organic inhibitors because of their low cost and non-toxic. These natural organic compounds are either synthesized or extracted from aromatic herbs, spices and medicinal plants. The yield of these natural products as well as the corrosion inhibition abilities of the plant extracts vary widely depending on the part of the plant[17, 18]and its location[19]. It is different the effect of compounds on corrosion inhibitor of metals in every medium [20, 21].

Parikh et al. [22] studied the anticorrosion activity of onion, garlic and bitter gourd for steel in HCl media. Ethanolic extract of *Ricimus communis* leaves was studied for the corrosion inhibition of steel in acid media by Sathyanathan. Okafor et al. found that *Phyllanthus amarus* extracts can be good inhibitors for steel in acid medium [23]. Quraishi et al. studied the extract of *Murraya koenigii* leaves as corrosion inhibitor for mild steel in acid media [24].Helen et al. have investigated the anticorrosion activity of *Aquilaria Crassna* Leaves Extracts for carbon steel in acid medium [25].The inhibition effect of *Zenthoxylum alatum* plant extract on the corrosion of carbon steel in hydrochloric acid solution has been investigated by Chauhan and Gunasekaran [26].

The corrosion inhibition activity in many of these plant extracts could be due to the presence of heterocyclic constituents like alkaloids, flavonoids etc., Even the presence of tannins, cellulose and polycyclic compounds normally enhances the film formation over the metal surface, thus aiding corrosion [23].

Marrubium is a flowering plant in the family Lamiaceae, native to Europe, northern Africa, and southwestern and central Asia. It is also widely naturalized in many places, including most of North and South America. It is a perennial, herbaceous plant commonly known as “Horehound”. As a medicinal plant, it was frequently employed in folk medicine to treat a variety of ailments, exhibits antinociceptive and antispasmodic effects in different experimental models. It possesses tonic, aromatic, stimulant, expectorant, diaphoretic and diuretic properties. It is helpful for bronchial asthma and non-productive cough. It was formerly much esteemed in various uterine, visceral and hepatic affections and in phthisis. The plant is reported to possess hypoglycemic, antihypertensive, analgesic, anti-inflammatory, and many other reported biological activities. In Tunisian folk medicine, it was used as hypoglycemic, hypotensive and cardiotonic. Essential oils extracted by distillation from aromatic plants are appreciated for their bioactive efficacy as fungicides, bacteriostatics, antioxidant, and other biological activities [27-31].

Hmamou et al. studied Inhibition effects of horehound (*Marrubium astranicum*) extract with high concentration (g L^{-1}) towards C38 steel corrosion in HCl solution [32].As a contribution to the current interest on environmentally friendly corrosion inhibitors, in the present work we were studied inhibiting properties of alcoholic extract of *Marrubium astranicum* with low concentrations (mg L^{-1}) in 1 M HCl using weight loss method, and Tafel polarization method.

Experimental

Preparation of plant extract

Marrubium astranicum leaves were collected from Kiasar city (Iran). These were dried in a laboratory oven at 50^0C, and ground to powder form. Fifty gram of the powder was digested in ethanol and it was kept for 72 h, then filtered and stored.This was used to prepare solutions of different concentrations by dilution method.

Apparatus

The cylinder specimens of carbon steel with definite dimension (diameter = 1.2 cm and height = 0.1 cm) were used. The chemical composition (wt. %) of these carbon steel samples is (C: 0.072, Si: 0.666, Mn: 0.554, Al: 0.53 and Fe: balance). Carbon steel specimens were pre-treated prior to the experiment by grinding with emery paper then cleaned with double distilled water, degreased with acetone and dried.

Gravimetric analysis method performed by using the Sartorius-BL 210 S digital balance (sensitivity = ±0.1 mg).

Electrochemical experiments were carried out by a computer controlled potentiostat/galvanostat μ-Auto lab type III modular electrochemical system (Eco Chemie BV, Netherlands), driven by a general purpose electrochemical system (GPES) software (Nova). A platinum rod from Azar electrode (Urmia, Iran) as counter-electrodeand an Ag / AgCl / KCl (3 M) from Azar electrode (Urmia, Iran) as reference electrode. The working electrode was a cylindrical, carbon steel specimen inserted into the end of a plastic tube with a copper wire as electrical contact. The carbon steel electrode was mounted on the tube such that only a 1.13 cm^2 cross-section of the cylinder was exposed to the solution. Before the experiments, the working electrode was pre-treated by grinding with emery paper then cleaned with double distilled water, degreased with acetone and dried. The polarization curve measurement system performed a scan starting from -0.8 to 0.2 V vs. open-circuit potential at a scan rate of 1 mV s^{-1}.

Results and discussion

Corrosion inhibition studies

Weight loss method

In each experiment, the carbon steel specimens were rinsed in deionised water and acetone, finally dried, then kept in desiccators before their use in corrosion studies. The cleaned carbon steel specimens were weighed and suspended in hydrochloride acid at room temperature for each inhibitor concentration for the period of 3 h.

The weight loss can be calculated as the difference between the weight at the end of the given immersion test time (3 h) and the initial weight of the test specimens. The experiments were repeated thrice and the mean values of the weight loss were recorded. The corrosion rate obtained from weight loss, CR (corrosion rate) of the carbon steel in hydrochloride acid containing different concentrations of inhibitors was studied as the following Equation [24]:

$$\mathrm{CR}\ (\mathrm{mm\ year}^{-1}) = 87.6\ w/AtD \qquad (1)$$

Where *w*is the corrosion weight loss of carbon steel (mg), *A* is the area of the carbon steel specimen, the exposure time in 1 M HCl solution (*t*) and *D* is the density of carbon steel (g cm^{-3}). The percentage inhibition efficiency (IE%) and surface coverage (Θ) was determined by using the following equation:

$$\Theta = w_0 - w_i / w_0 \qquad (2)$$

$$\text{IE \%} = w_0 - w_i / w_0 \times 100 \qquad (3)$$

Where w_i and w_0 are the weight loss value in the presence and absence of inhibitor, respectively.

Effect of inhibitor concentration

The variation of inhibition efficiency with increasing in inhibitor concentrations is done. It shows that inhibition efficiency, increase as the concentration of inhibitor was changed towards the higher side. The values of IE % and CR obtained from weight loss method at different concentrations of inhibitor at 303 K are summarized in Table 1. It has been found that this extract inhibits the corrosion of carbon steel in hydrochloric acid solution, at all concentrations used in this study, i.e., 1–150 mg L^{-1}. It is evident from the Table 1 that the corrosion rate is decreased from 825.6 to 13.76 mpy with the addition of 100 mg L^{-1} of extract.

Table 1. Corrosion parameters for carbon steel in the solution of 1 M HCl in absence and presence of different concentrations of inhibitor from weight loss measurements at 303 K for 3 h.

Concentration / mg L^{-1}	**Weight loss / mg**	**CR / mpy**	**IE%**	**θ**
1	36	825.6	94.48	0.944
2	22.3	511.41	96.81	0.968
3	7.1	162.82	98.98	0.990
5	4.1	94.02	99.41	0.994
10	2.7	61.92	99.61	0.996
30	2.6	59.62	99.62	0.996
50	1	22.93	99.85	0.998
100	0.6	13.76	99.99	1
150	0.6	13.76	99.99	1

Effect of immersion time

Table 2 shows the effect of immersion time on inhibition efficiency from 1 to 12 h. It was found that the inhibition efficiency increases with increasing in an immersion time and it get to 99% after 12 hours. This showed that it takes some times for effect of the inhibitor in corrosion of carbon steel.

Table 2. Effect of immersion time for carbon steel in the solution of 1 M HCl at 303 K (concentrations of inhibitor = 100 mg L^{-1}).

Time / h	Weight loss in the absence of inhibitor / mg	Weight loss in the presence of inhibitor / mg	IE%
1	5	1.3	74
2	13.3	2.4	81.95
3	21	1	95.23
5	87	3	95.40
8	483	18	96.27
12	782	7.8	99

Effect of temperature

The influence of solution temperature on inhibition efficiency is shown in Table 3. It is observed that inhibition efficiency decreases with increase in temperature 303–333 K (concentration of inhibitor is 100 mg L^{-1}). It is clear that change in solution temperature from 303 to 333K did not cause any significant change in inhibition efficiency values from 303 to 323 K after that it shows a decreasing in inhibition efficiency. The decrease in inhibition efficiency with temperature may be attributed to desorption of the inhibitor molecules from metal surface at higher temperature [33].

Table 3. Effect of temperature for carbon steel in the solution of 1 M HCl for 3 h (concentrations of inhibitor = 100 mg L^{-1}).

Temperature /K	Weight loss in the absence of inhibitor / mg	Weight loss in the presence of inhibitor / mg	IE%
303	699	1	99.86
313	398	3	99.25
323	386	15.4	96.01
333	126	39.2	68.9

Tafel polarization

Figure1 shows the Tafel polarization curves for carbon steel in 1 M HCl with the addition of various concentrations of inhibitor. Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), and (IE %) are calculated from the Tafel plots are given in Table 4. It is clear that the I_{corr} values decrease from 1240 to 65.9 μA cm^{-2} with the addition a concentration of inhibitor. It is seen from the results that E_{corr} values is significantly shifted to more positive values in the higher concentration of inhibitor. As well, the value of the anodic current in the curve decreases with the presence of the corrosion inhibitor. These results show that it behaves as an anodic inhibitor.

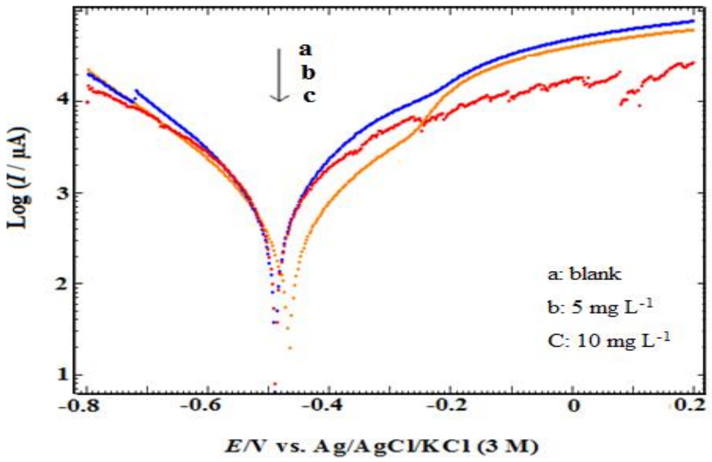

Figure 1. Tafel polarization plots of carbon steel in 1 M HCl with the addition of inhibitor (a) 0, (b) 5 and (c) 10 mg L^{-1}.

Table 4. Tafel polarization parameters for the corrosion of carbon steel in 1 M HCl in absence and presence of different concentration inhibitor.

[Inhibitor] / mg L^{-1}	$-E_{corr}$ / mV	I_{corr} /mA cm^{-2}	R_P / Ω	IE%
0	523	1240	39.89	———
5	472	909	56.69	26.7
10	476	316	105	74.5
100	327	65.9	864	94.7

Adsorption isotherm

The adsorption isotherm provides basic information on theinteraction between inhibitor and carbon steel surface. In order to evaluate the adsorption process of the synthesized inhibitors on the carbon steel surface, Langmuir, Frumkin, Temkin, adsorption isotherms were evaluated according to the following Eqs.(4)–(6) [34-36]:

Langmuir: $C_{inh}/\Theta = 1/K_{ads} + C_{inh}$ (4)

Frumkin: $\text{Log}\,\Theta = \text{Log}\,K_{ads} + n\,\text{Log}\,C_{inh}$ (5)

Temkin: $\Theta = 1/f\,\text{Ln}K_{ads} + 1/f\,\text{Ln}C_{inh}$ (6)

Where Θ is the surface coverage, K_{ads} the adsorption–desorption equilibrium constant, $C_{inh}$the inhibitor concentration, for the adsorbate interaction parameter and n is constant (0 <n<1). The obtained results were best fitted by Langmuir adsorption isotherm. The straight line ($R^2 = 1$) obtained in Fig. 2Asuggests that the adsorption of inhibitors on carbon steel in 1 M HCl solution follows Langmuir's adsorption isotherm [37,38].The equilibrium constants (K_{ads}) are correlated to the standard free energy of adsorption (G°_{ads}) of the inhibitor molecules according to Eq. (7) [39, 40]:

$$K_{ads} = 1/55.5 \exp\,[-\Delta G^0_{ads}/RT] \qquad (7)$$

From the ΔG^0_{ads}, the type of adsorption can be determined. For values closer to -20 KJ mol^{-1}, the adsorption leans towards physisorption while for values closer to -40 KJ mol^{-1}, the adsorption leans towards chemisorption. The chemisorption phenomenon indicates the occurrence of sharing of electrons or transferring of organic molecule charges with the metal surface while the physisorption phenomenon is attributed to electrostatic interactions between the charged metal and charged molecules [41]. According to the calculated value (ΔG^0_{ads}= -16.75), the adsorption mechanism of inhibitor on the carbon steel is mainly physisorption.

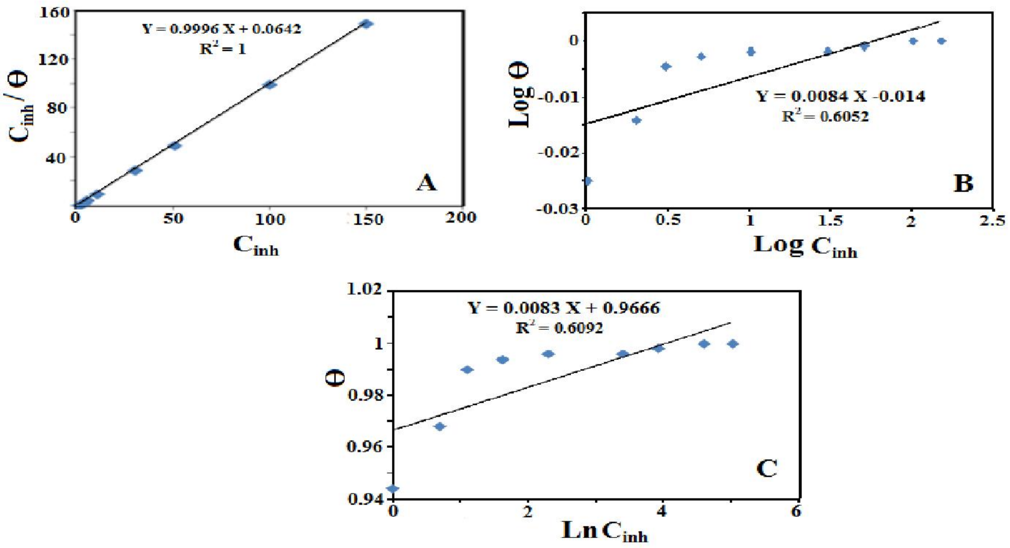

Figure 2. Plots of different adsorption isotherms: (a) Langmuir, (b) Frumkin and (c) Temkin.

Conclusion

1- The Extract of *Marrubium astranicum* leaves is an effective inhibitor for carbon steel in acidic solution and inhibition efficiency, increased with concentration of it.

2- Tafel polarization measurements show that The Extract of *Marrubium astranicum* leaves functioned as an anodic inhibitor.

3- Adsorption of inhibitor molecules (extract of *Marrubium astranicum* Leaves) on the carbon steel surface is found to obey the Langmuir adsorption isotherm.

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