J. Mater. Environ. Sci. 7 (9) (2016) 3118-3124
ISSN : 2028-2508
CODEN: JMESC

UAE Scrophularia Arguta (Malisah) Extract as a Corrosion Inhibitor for Mild Steel in HCl Solution

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Received 04 Jun 2016, Revised 17 Jul 2016, Accepted 23 Jul 2016
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Abstract
The effect of aqueous extract of UAE Scrophularia Arguta (Malisah) on the corrosion inhibition of mild steel in 1.0 M HCl solution was investigated by weight loss experiments at temperatures ranging from 303 to 343 K. The percentage inhibition increased with the increase of the concentration of the inhibitor and decrease with the increase of temperature reaching 93.43 % with a concentration of 2.0000 g/L at 303 K. The thermodynamic parameters for the adsorption of this inhibitor on the metal surface were calculated using the Temkin adsorption isotherm. The aqueous Scrophularia Arguta leaves extract was found to be an excellent potential corrosion inhibitor.

Keywords: Carbon steel, Scrophularia Arguta, Malisah, Weight loss, Corrosion.

1. Introduction
Corrosion of metals is a serious problem in many industries. To prevent or minimize corrosion, inhibitors often are used. Organic, inorganic, or a mixture of both inhibitors can inhibit corrosion by either chemisorption on the metal surface or by reacting with metal ions and forming a barrier-type precipitates on its surface [1].
Many authors have used various synthetic organic compounds in their corrosion inhibition investigations [2-26]. Despite their good anticorrosive activity, most of synthetic compounds are of expensive and highly toxic to both environment and human beings. The safety and environmental issues of corrosion inhibitors arisen in industries has always been a global concern. The toxicity may be noticeable either during the synthesis of the compound or during its applications. Based on safety, the development of non-toxic and efficient corrosion inhibitors is considered very important and desirable.
The corrosion inhibitors of plant origin are highly preferred because they are readily available, inexpensive with an advantage of environmentally benign nature. There are many studies which report the use of leaves, bark, fruits, and vegetables of different plants as green corrosion inhibitor for metals in various aggressive media [27-42]. An excellent review of "natural products as corrosion inhibitors for metals in corrosive media" has recently been published [43].
No studies have been reported on the aqueous extract of Scrophularia Arguta (Malisah) leaves planted in UAE, as corrosion inhibitor. In our studies, mild steel was chosen since high temperature aggressive acids are widely used in industries in connection to carbon and low alloy steels.
In this work weight loss measurements are used to study the corrosion inhibition of mild steel in 1.0 M HCl solution by various concentrations of aqueous extract of Scrophularia Arguta (Malisah) leaves at different temperatures, and to calculate the thermodynamic parameters. This study aims to find a cheap and an eco-friendly natural source that can be utilized as a corrosion inhibitor for metals and alloys.

2. Experimental
2.1. Preparation of Scrophularia Arguta (Malisah)
Scrophularia Arguta (Malisah) leaves were collected from "Ras Al-Khaima" area in the United Arab Emirates, dried at room temperature, and stored in dark for later use. In this work, 2.0000 g of dry and powdered Scrophularia Arguta (Malisah) leaves were soaked in 60.0 mL deionized water at room temperature (20 ^oC) for 24 hours, and then filtered. The filtrate was added to an aqueous HCl solution to make a 1.0 L stock solution in

1.0 M HCl. From the stock solution, a series of diluted solutions in 1.0 M HCl were prepared with concentrations ranging from 2.0000 g/L to 0.0002 g/L of Scrophularia Arguta (Malisah).

2.2. *Specimen Preparation*
Rectangular specimens (1 cm x 2.3 cm x 0.3 cm) cut from a 3 mm thick mild steel sheet (IS 226 containing 0.18 % C, 0.6 % Mn, and 0.35 % Si) supplied by “Reliable Steel Traders”, Sharjah, UAE; were used. A 2-mm diameter hole was drilled close to the upper edge of the specimen, which served for hooking a glass rod for immersion purposes. Prior to each experiment, specimen was polished with 600 grade emery paper, rinsed with deionized water, degreased with acetone, dried, and finally weighed precisely on an accurate analytical balance.

2.3. *Instrumentation*
For the weight loss measurements [31, 32], a 250-mL round bottom flask fitted with a reflux condenser and long glass rod which served to hook and immerse the specimen and in turn immersed in a thermally controlled water bath was used.

2.4. *Measuring procedure*
100 mL of 1.0 M HCl solution either with or without the presence of various concentrations of aqueous Scrophularia Arguta extract were transferred in the round bottom flask which was then placed in water bath. As the required temperature was reached, the precisely weighed mild steel specimen was hooked with a glass rod and then immersed in the solution for exactly six hours. After that time, the sample was removed, rinsed with deionized water, degreased with acetone, dried, and finally weighed precisely on an accurate analytical balance. This procedure was repeated for all inhibitor concentrations ranging from 0.0002 g/L to 2.0000 g/L; and at temperatures ranging from 303 K to 343 K. These experiments were repealed for reproducibility and the average values were reported.

3. Results and discussion
Weight loss corrosion tests were carried out on the mild steel immersed in 1.0 M HCl in the absence or presence of aqueous Scrophularia Arguta extract over a period of 6 hours. Table 1 represents the corrosion rate [$mg.cm^{-2}.h^{-1}$] and the percentage efficiency for Scrophularia Arguta inhibitor with concentrations varying from 0.0002 g/L to 2.0000 g/L at 303, 313, 323, 333, and 343 K, respectively.

Table 1. The effect of concentration of the aqueous extract of Scrophularia Arguta leaves on the corrosion rate ($mg.cm^{-2}.h^{-1}$) and percentage efficiency of mild steel in 1.0 M HCl at various temperatures.

	Temperature / K									
	303		313		323		333		343	
Concentration of Inhibitor	Corr. Rate	% Efficiency	Corr. Rate	% Efficiency	Corr. Rate	% Efficiency	Corr. Rate	% Efficiency	Corr. Rate	% Efficiency
1.0 M HCl	0.3962	—	0.9426	—	2.2676	—	4.8692	—	10.030	—
1.0 M HCl + 0.0002 g/L	0.3421	13.65	0.8717	7.52	2.1292	6.11	4.6085	5.35	9.8536	1.76
1.0 M HCl + 0.0020 g/L	0.3384	14.58	0.8600	8.76	2.1195	6.53	4.5952	5.63	9.7897	2.40
1.0 M HCl + 0.0200 g/L	0.2748	30.63	0.6931	26.47	1.7805	21.48	4.0091	17.66	8.7061	13.20
1.0 M HCl + 0.2000 g/L	0.0694	82.48	0.2213	76.52	0.5897	74.00	1.4702	69.81	3.2523	67.57
1.0 M HCl + 2.0000 g/L	0.0260	93.43	0.1117	88.15	0.3534	84.42	0.8555	82.43	1.9381	80.68

The percentage efficiency was calculated according to the following equation (1):

$$\% \text{ Inhibition} = \frac{W_{Uninh.} - W_{Inh.}}{W_{Uninh.}} \times 100 \quad (1)$$

ISSN : 2028-2508
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Where: $W_{Uninh.}$ = Corrosion rate without inhibitor; and

$W_{Inh.}$ = Corrosion rate with inhibitor.

The corrosion rate of the mild steel in 1.0 M HCl as a function of various concentrations of aqueous extract of Scrophularia Arguta leaves at temperatures between 303 and 343 K are shown in Figures 1 and 2. The plots of corrosion rates versus the inhibitor concentration followed the same trend at the various temperatures; and at all concentrations the corrosion rate increased with the increase of temperature. The corrosion rate has slightly decreased when the inhibitor concentration changed from 0.0002 g/L to 0.0020 g/L, followed by slight decrease at 0.0200 g/L. Sharp decrease in corrosion rate was noticed at concentration of 0.2000 g/L, and this sharpness increased with the increase of temperature. Finally, a very small decrease in corrosion rate occurred at 2.0000 g/L.

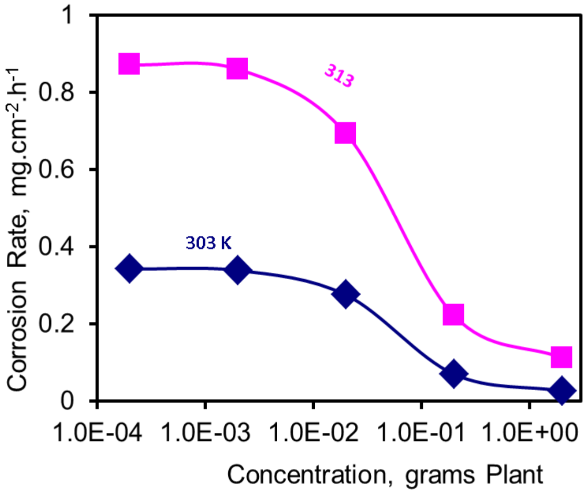

Figure 1. Effect of concentration of the aqueous extract of Scrophularia Arguta leaves on the corrosion rate ($mg.cm^{-2}.h^{-1}$) of mild steel in 1.0 M HCl at various temperatures. ◆ 303 K ■ 313 K

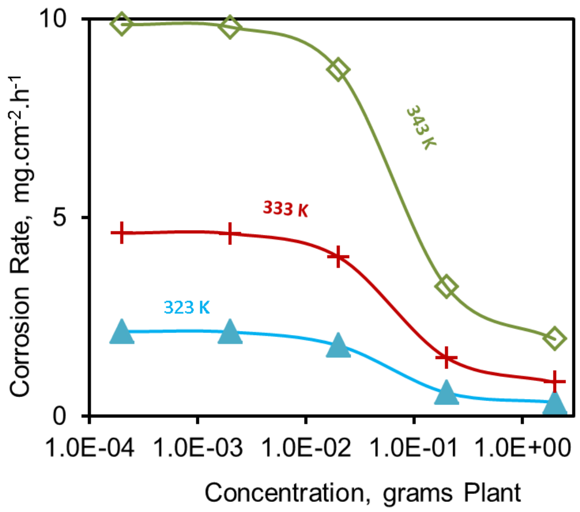

Figure 2. Effect of concentration of the aqueous extract of Scrophularia Arguta leaves on the corrosion rate ($mg.cm^{-2}.h^{-1}$) of mild steel in 1.0 M HCl at various temperatures. ▲ 323 K ✚ 333 K ◇ 343 K

The plots of the percentage inhibition as a function of the concentration of the aqueous extract of Scrophularia Arguta leaves at temperatures ranging from 303 K to 343 K are shown in Figure 3. The inhibition was more effective at low temperatures than at higher ones, reaching 93.43 % with 2.0000 g/L concentration at 303 K.

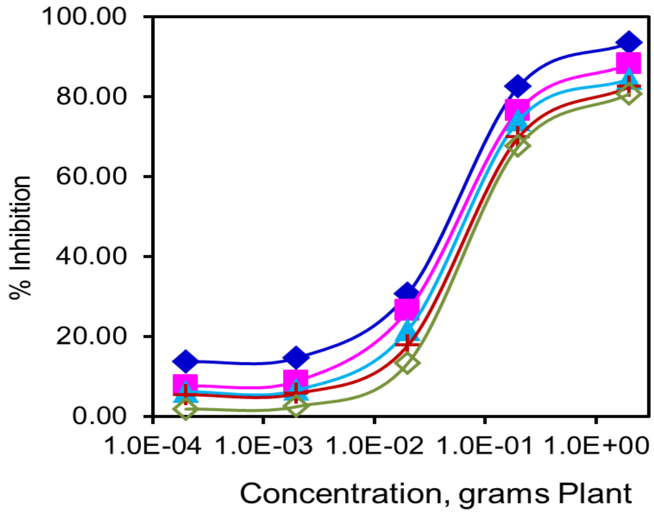

Figure 3. Effect of concentration of the aqueous extract of Scrophularia Arguta leaves on the percent inhibition of mild steel in 1.0 M HCl at various temperatures. ◆ 303 K ■ 313 K ▲ 323 K ✚ 333 K ◇ 343 K

Table 2 shows the values of natural logarithms of the rate of corrosion (ln Rate of corrosion) and the values of the reciprocal of the corresponding temperature in K^{-1} (1/T) in accordance to Arrhenius equation (2).

Table 2. The data obtained from the weight loss measurements for Arrhenius Equation: (1/T) against Ln Corrosion Rate.

	Ln Corrosion Rate ($mg.cm^{-2}.h^{-1}$)					
$(1/T)x10^3 K^{-1}$	**1.0 M HCl**	**1.0 M HCl + 0.0002 g/L**	**1.0 M HCl + 0.0020 g/L**	**1.0 M HCl + 0.0200 g/L**	**1.0 M HCl + 0.2000 g/L**	**1.0 M HCl + 2.000 g/L**
3.30	-0.9259	-1.0726	-1.0835	-1.2916	-2.6675	-3.6490
3.19	-0.0591	-0.1373	-0.1508	-0.3666	-1.5083	-2.1917
3.10	0.8187	0.7557	0.7512	0.5769	-0.5282	-1.0401
3.00	1.5829	1.5279	1.5250	1.3886	0.3854	-0.1561
2.92	2.3056	2.2878	2.2813	2.1640	1.1794	0.6617

$$\ln rate = -\frac{E_a}{RT} + const. \qquad (2)$$

Where: E_a = activation energy [$kcal.mol^{-1}$], R = gas constant [$kcal.mol^{-1}$],
T = absolute temperature [K], and const. = constant

The Arrhenius plots of the corrosion of carbon steel in 1.0 M HCl solution, (ln corrosion rate as a function of 1/T) with or without the presence of the aqueous extract of Scrophularia Arguta leaves at concentrations ranging from 0.0002 g/L to 2.0000 g/L are shown in **Figure 4**.

The slope ($-\frac{E_a}{R}$) of each line was determined from this Figure and used to calculate the activation energy (Table 3) according to equation 2, with R = $1.987x10^{-3}$ $kcal.mol^{-1}$.

It is clearly noticed that as the concentration of the extract increases, the activation energy for the corrosion of mild steel in 1.0 M HCl has increased with the increase of the concentration of the inhibitor (16.94 $kcal.mol^{-1}$ in 1.0 M HCl without inhibitor to 22.35 $kcal.mol^{-1}$ with 2.0000 g/L aqueous extract of Scrophularia Arguta leaves in 1.0 M HCl), (Table 3). The values of the surface coverage (θ = % Inhibition / 100) of various concentrations of the aqueous Scrophularia Arguta leaves extract (from 0.0002 g/L to 2.0000 g/L) on mild steel surface at various temperatures are encapsulated in Table 4.

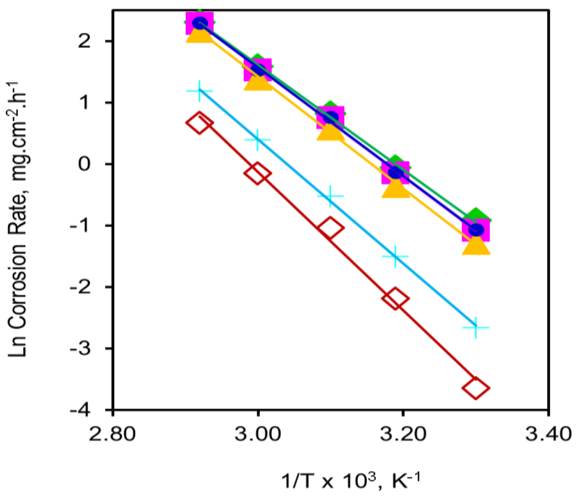

Figure 4. Effect of temperature on the corrosion rate of mild steel in 1.0 M HCl solution with and without the presence of various concentrations of the aqueous extract of Scrophularia Arguta leaves.
◆ 1.0M HCl ■ 0.0002 g/L● 0.002 g/L▲ 0.020 g/L✚ 0.2 g/L ◇ 2.00 g/L

Table 3. The activation energy (E_a) for the corrosion of mild steel in 1.0 M HCl with and without the aqueous extract of Scrophularia Arguta leaves at various concentrations.

System	1.0 M HCl	1.0 M HCl + 2.0000 g/L	1.0 M HCl + 0.2000 g/L	1.0 M HCl + 0.0200 g/L	1.0 M HCl + 0.0020 g/L	1.0 M HCl + 0.0002 g/L
Activation Energy, E_a, (kcal.mol^{-1})	16.94	22.35	20.07	18.11	17.57	17.53

Table 4. The effect of concentration of the aqueous extract of Scrophularia Arguta leaves on surface coverage for mild steel in 1.0 M HCl at various temperatures.

	Temperature / K				
	303	**313**	**323**	**333**	**343**
Concentration of Inhibitor	**Surface Coverage θ**	**Surface Coverage θ**	**Surface Coverage θ**	**Surface Coverage θ**	**Surface Coverage θ**
1.0 M HCl + 0.0002 g/L extract	0.13646	0.07517	0.06106	0.05354	0.01759
1.0 M HCl + 0.0020 g/L extract	0.14582	0.08758	0.06531	0.05627	0.02395
1.0 M HCl + 0.0200 g/L extract	0.30628	0.26468	0.21481	0.17663	0.13199
1.0 M HCl + 0.2000 g/L extract	0.82476	0.76523	0.73995	0.69806	0.67574
1.0 M HCl + 2.0000 g/L extract	0.93433	0.88147	0.84415	0.82431	0.80677

These values were extracted from the corresponding percentage efficiency values reported earlier in Table 1. Figure 5 shows the plot of the values of surface coverage, θ, against the natural logarithm of the concentration of Scrophularia Arguta leaves aqueous extract; ln C, for mild steel at various temperatures.
After examining these data and adjusting them to different theoretical adsorption isotherms, it was concluded that the inhibitor was adsorbed on the mild steel surface according to Temkin Adsorption Isotherm:

$$-2a\,\theta = \ln K\,C \quad (3)$$

Where: a = molecular interaction constant, θ = degree of coverage, K = equilibrium constant for the adsorption reaction, and C = concentration of the inhibitor.

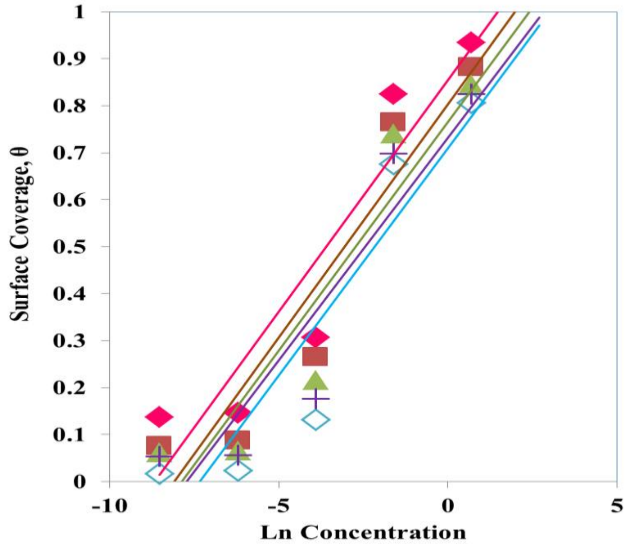

Figure 5. Effect of concentration of the aqueous extract of Scrophularia Arguta leaves on the surface coverage of mild steel in 1.0 M HCl at various temperatures.◆ 303 K■ 313 K ▲ 323 K✚ 333 K◇ 343 K

The activation energy (E_a) (Table 3) for the corrosion of mild steel in the presence of the aqueous extract of Scrophularia Arguta leaves at all concentrations (0.0002 g/L to 2.0000 g/L) were higher compared to the activation energy in the absence of the extract (22.35 kcal.mol^{-1} with 2.0000 g/L extract in 1.0 M HCl compared with 16.94 kcal.mol^{-1} in 1.0 M HCl without the extract). This could be attributed to the fact that higher values of E_a in the presence of inhibitor compared to its absence are generally consistent with a physisorption, while unchanged or lower values of E_a in inhibited solution suggest charge sharing or transfer from the organic inhibitor to the metal surface to form coordinate covalent bonds (chemisorption).
The increase in the activation energies for the corrosion is attributed to an increase in the adsorption of the inhibitor on the metal surface; and subsequently, an increase in the percent inhibition and a decrease in the corrosion rate. At higher temperatures, greater exposed area of the metal surface to the acid will occur resulting in a decrease in both activation energy and percent inhibition.

Conclusions

The aqueous Scrophularia Arguta leaves extract was found to be a highly efficient inhibitor for mild steel in 1.0 M HCl solution, reaching about 93 % at 2.0000 g/L and 303 K, a concentration considered to be very moderate. Even at one tenth of this concentration (0.2000 g/L), an inhibition of about 88 % was obtained at the same temperature (303 K).
The corrosion inhibition of the mild steel in 1.0 M HCl was directly proportional to the concentration of the Scrophularia Arguta extract. This inhibition increased as the concentration of the Scrophularia Arguta extract increased.
The percentage of inhibition in the presence of this inhibitor decreased with the increase of temperature, indicating that physical adsorption was the predominant inhibition mechanism because the quantity of adsorbed inhibitor decreases with increasing the temperature.
The aqueous Scrophularia Arguta leaves extract is an excellent, green, eco-friendly, and very cheap corrosion inhibitor for mild steel in 1.0 M HCl solution, and therefore it could be applied to replace toxic and highly cost chemicals.

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ISSN : 2028-2508
CODEN: JMESC

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(2016) ; http://www.jmaterenvironsci.com/