INHIBITION EFFECT OF FLAVONOID EXTRACT OF *Euphorbia Guyoniana* ON THE CORROSION OF MILD STEEL IN H$_2$SO$_4$ MEDIUM

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ABSTRACT

The influence of flavonoids extracts of three parts of *Euphorbia Guyoniana* towards the corrosion of type API 5L X52 steel in 15% H$_2$SO$_4$ has been evaluated by weight loss method and polarization technique. The results showed that extracts are a good inhibitors for API 5L X52 steel in this medium. The corrosion inhibition efficiency increases on increasing plant extracts concentration. The inhibition is attributed to the adsorption of the surface of the metal. Potentiodynamic polarization results revealed that the studied inhibitors behave as a mixed type.

Key words: API 5L X52 steel, corrosion inhibition, sulphuric acid, *Euphorbia Guyoniana*, flavonoids extract.

1. INTRODUCTION

Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Hydrochloric and sulphuric acids are widely used in the pickling processes of metals [1]. Corrosion inhibitors are widely used in industry to prevent or to reduce the corrosion rates of metallic materials in these acid media [2,3]. A corrosion inhibition is a substance, which lowers the corrosion rate after it has been added to a given stream of interest, of corrosive conditions [4].


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Because of the toxic nature and high cost of some chemicals currently in use it is necessary to develop environmentally acceptable and less expensive inhibitors. Natural products can be considered a good source for this purpose [5]. The possible replacement of some expensive chemicals as corrosion inhibitors for metal in acid cleaning process by naturally occurring substances of plant origin has been studied by Hosary and Saleh [5]. Natural products of plant origin contain different organic compounds (e.g. alkaloids, tannins, pigments, organic and amino acids) and most are known to have inhibitive action [5,6]. Organic compounds are usually used to protect metal against corrosion as inhibitors in acidic media [7-11]. Heterocyclic compounds containing N and S atoms, such as azoles and their derivatives, have attracted much attention because of the efficient inhibition abilities to the metal [12-14]. Heteroatom, for example, N and S, usually become the active center. When metal is immersed in the inhibiting solution, N and S atoms donate lone pair electrons to the unoccupied orbits of the metal atom. strong and stable bonds are formed between the inhibitor and the metal surface during the self-assembling process [15].

Corrosion inhibition features of several substances are directly associated to adsorption phenomena, which can follow different type of isotherms such as those of Temkin, Langmuir, Freundlich and Frumkin that have been employed to ate adsorption phenomena over steel electrodes[16,17].

The adsorption of organic inhibitors at an electrode / electrolyte interface may take place through displacement of adsorbed water molecules at the inner Helmholtz plane of the electrode, likely in agreement with the following reaction scheme [17]:

$$Org_{(aq)} + nH_2O_{(ads)} \longrightarrow Org_{(ads)} + nH_2O$$
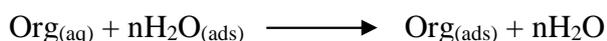
Recently, many works were devoted to study the effects of some naturally occurring substances occurring substances on the corrosion of different metals in different corrosive media [18].

In this work we have investigated the influence of flavonoids extracts of three parts of *Euphorbia guyoniana* towards the corrosion of type API 5L X52 steel in 15% H_2SO_4.

2. EXPERIMENTAL DETAILS

- **Plant description**

   Euphorbia guyoniana is an endemic Saharian plant growing in sandy and desert habitat, and belongs to the large family of Euphorbiaceae [19]. The genus *Euphorbia* is

the largest in the plant family Euphorbiaceae, comprising about 2000 known species and ranging from annuals to trees. All contain latex and have unique flower structures. A significant percentage, mostly those originating in Africa and Madagascar, are succulent [20].   Plants of this genus are known for their rich content in secondary metabolites. Indeed, numerous studies undertaken on this genus have revealed presence of triterpenes, diterpenes, macrocyclic diterpenes, steroids and aromatic compounds. Chemically, *E. guyoniana* has received little attention apart from the work done recently on the aerial parts from which two new diterpenes polyesters with jatrophane skeleton have been isolated [19].   Species of the family Euphorbiaceae are well known to be generally toxic and to show skin irritant, antitumor and tumor promoting effects [21] .

- **Preparation of plant extract**

200g of each part was subjected to petroleum ether so as to get rid of fats and waxes then the mark is percolated with methanol during 24hours for three times. The methanolic extracts are collected and concentrated under vacuum before being eluted with 100 ml of boiling water and filtrated. The filtrate is subjected again to extraction using ethyl acetate. Finally the ethyl acetate extract is separated and concentrated to be used in the inhibition tests**.**

- **Preparation of specimens**

API 5L X52 steel having percent composition of C-0.1%, Mn-0.97%, Si-0.12%,S-0.002%, Gr-0.01% and remaining Fe were used. The sample were polished with different grade emery papers, cleaned with acetone, washed with double distilled water and finally dried and kept in desiccators**.**

- **Electrolyte**

Analytical reagent-grade H_2SO_4 was used for preparing solution. Appropriate concentrations of acids were prepared by using double distilled water. The concentration of plant extract employed was varied from 200 to 1200 ppm and the electrolyte used was 200 ml**.**

- **Weight loss method**

Weight loss of rectangular steel specimens of size $1cm \times 5cm \times 2cm$ in double distilled water immersed in 200ml of electrolyte with and without the addition of different concentration of plant extract was determined after 1h.

The inhibition efficiency (I %) was determined from (1) :

$$I(\%) = \frac{W0 - W}{W0} \qquad (1)$$

Where W_0 and W are the weight losses in the corrodent (blank) and corrodent inhibitor systems.

The surface coverage   at each concentration of inhibitor was evaluated using the equation (2):

$$i = 1 - \frac{Wi}{Wb} \qquad (2)$$

Where W_b and W_i are the weight loss in corrodent and corrodent – inhibitor systems respectively at constant temperature.

- **Potentiodynamic polarization studies**

For the Potentiodynamic polarization studies, the cell used was a conventional three electrode system with platinum auxiliary electrode, saturated calomel as reference electrode and polished mild steel specimen as working electrode. The working electrode was lacquered so as to expose 1sq.cm area to contact with the solution.

The polarization curves were recorded by using computer controlled Gamry electrochemical system. The potential increased with the speed of 30 mv.min^{-1}. Experiments were carried out from -500 to -350 mv potential ranges. Before recording the polarization curves, the WE was maintained at its corrosion potential for 10 min until a steady state was obtained.

The inhibition efficiency was calculated from (3):

$$I\% = \frac{Icor - Icor(inh)}{Icor} \qquad (3)$$

Where I_{corr} and $I_{corr\ (inh)}$ are the corrosion current density values without and with inhibitor, respectively.

3. RESULTS AND DISCUSSION

- **Weight loss results**

The inhibition efficiency calculated from the mass loss measurement in 15% sulphuric acid are given in Table 1

**Table 1.** Mass loss and inhibition efficiency for the three extracts.

Inhibitor Concentration (ppm)	Mass loss (g)			Inhibitor efficiency I %		
	leaves	stems	flowers	leaves	stems	flowers
200	0.0218	0.0213	0.0202	23.81	25.65	29.32
400	0.0195	0.0192	0.0179	31.98	32.98	37.25
600	0.0165	0.0159	0.0143	42.32	44.32	49.88
800	0.0141	0.0128	0.0089	50.35	54.81	68.53
1000	0.0116	0.0088	0.0060	59.12	68.62	78.92
1200	0.0091	0.0064	0.0053	80.12	81.45	84.98

The extent of the decrease in weight loss was found to depend on the additive concentration. The inhibition efficiency increases with increasing inhibitor concentration. This behaviour may be attributed to the increase of the surface area covered by the adsorbed extract molecules
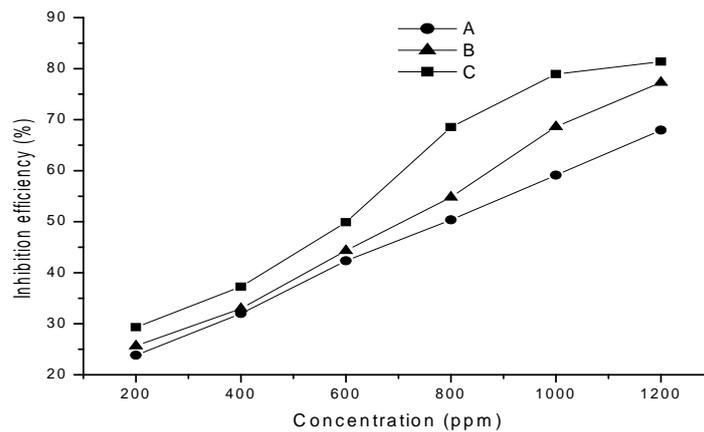
Fig.1. variation of the inhibition efficiency with plant concentrations

A: leaves extract, B: stems extract, C: flowers extract.

As shown in figure (1) inhibition efficiency increases with increasing concentration of the inhibitor up to 1200 ppm at a maximum efficiency of 80.12 % for leaves extract, 81.45 % for stems extract and 84.98 %for flowers extract.
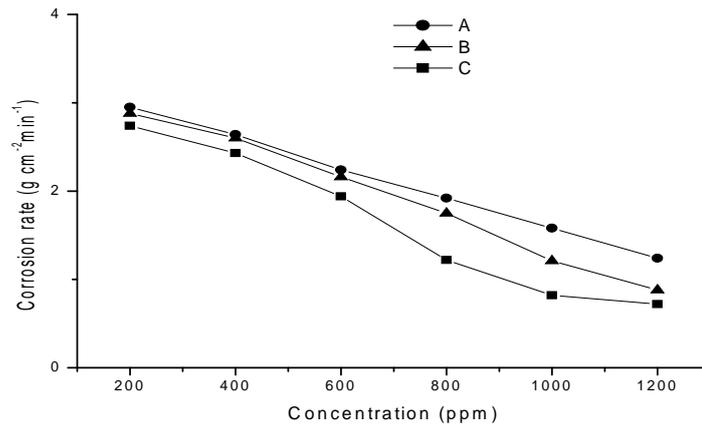
Fig.2. variation of the corrosion rate with plant concentrations A: leaves extract,

B: stems extract, C: flowers extract.

The corrosion rate decrease with increasing concentration of extracts. This confirms that the presence of the extracts in 15% H_2SO_4 solution inhibits the corrosion of mild steel and that the degree of corrosion inhibition depends on the concentration of the extract.

Table 2. Surface Coverage and Corrosion rate for mild steel in sulphuric acid solution with given inhibition concentration for the three extracts.

Concentration of inhibitor (ppm)	Surface Coverage			Corrosion (g/cm².min)		
	Leaves	**stems**	**flowers**	**Leaves**	**Stems**	**flowers**
200	0.35	0.36	0.40	2.95	2.88	2.74
400	0.42	0.43	0.46	2.64	2.60	2.43
600	0.51	0.52	0.57	2.24	2.16	1.94
800	0.58	0.62	0.73	1.92	1.75	1.22
1000	0.65	0.73	0.82	1.58	1.21	0.82
1200	0.72	0.81	0.84	1.24	0.88	0.72

The results illustrate linear decrease in corrosion rate with increasing inhibitor concentration.

- **Potentiodynamic polarization results**

Fig(3) represents the anodic and cathodic polarization curves of mild steel in 15% H_2SO_4 solution in the absence and presence of different concentrations of leaves extract. Similar curves were also obtained in stems extract and flowers extract. The other curves are not shown here because all of them have the same general feature.

Inspection of fig (3) reveals that both anodic and cathodic potentials increase slightly at the low value of applied current density. At this stage, both cathodic and anodic

reactions are established. This region of the polarization curve is known as the pre-Tafel region. As the applied anodic current is increased further, one of the two reactions becomes predominant and the variation of potential becomes higher and thus the Tafel region is obtained.

The electrochemical parameters; corrosion potential (E_{corr}), corrosion current (i_{corr}), corrosion rate (I_{corr}), anodic Tafel constant (Ba), cathodic Tafel constant (Bc) and IE were calculated and given in Table 3.
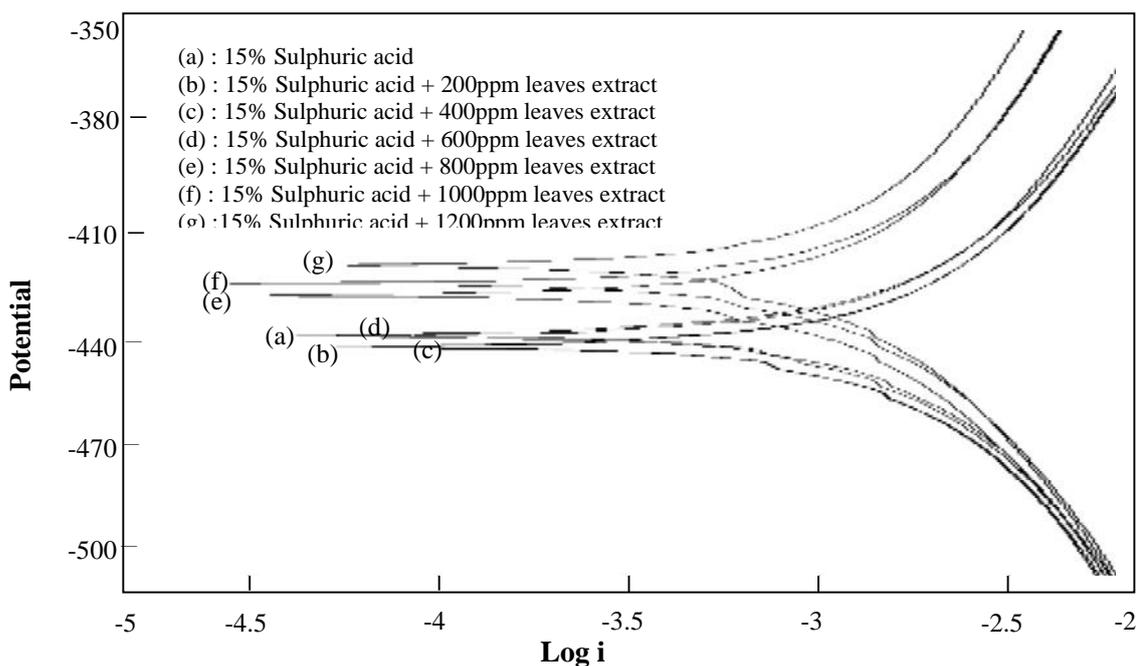
Fig.3. Polarization curves of mild steel in 15% H_2SO_4 solution devoid and containing different concentrations of leaves extract.

Table 3 reveals that the corrosion potential shifts to less negative values upon addition of the inhibitor. Nevertheless, the corrosion potential is almost independent on the inhibitor concentration.

On the other hand, the addition of leaves extract decreases markedly the corrosion current. The IE increases as the extract concentration is increased. Further inspection of Table 3 reveals also that both the anodic and cathodic Tafel constants decrease upon addition of inhibitor. This behaviour suggests that the extract inhibits the corrosion of mild steel via the adsorption of its molecules on the both anodic and cathodic sites and consequently, it acts as a mixed inhibitor.

Table 3. Electrochemical parameters for mild steel in 15% sulphuric acid containing different extracts concentrations

Extract concentration (ppm)	E_{corr} Mv	icorr mv/cm^2	a (mv/decade)	c (mv/decade)	Rate (mm/y)	% inh
Leaves extract 1- 0 ppm	-414.2	3.478	85.8	-80.9	30.71	-
2- 200 "	-412.2	1.347	51.7	-57.4	19.92	23.76
3- 400 "	-412.3	1.173	49.8	-54.7	17.77	31.96
4- 600 "	-413.8	1.017	49.1	-50.0	15.08	42.28
5- 800 "	-419.7	0.995	47.8	-49.7	13.02	50.16
6- 1000 "	-421.4	0.664	41.5	-49.2	10.71	59.01
7- 1200 "	-423.8	0.182	41.1	-47.0	8.31	67.96
Stems extract 1- 0 ppm	-414.2	3.478	85.8	-80.9	30.71	-
2- 200 "	-411.4	1.351	44.1	-45.0	19.44	25.60
3- 400 "	-411.8	1.092	40.4	-41.6	17.64	32.46
4- 600 "	-413.0	1.091	36.1	-37.4	14.62	44.04
5- 800 "	-413.4	0.499	34.6	-32.6	11.82	54.73
6- 1000 "	-413.5	0.116	33.4	-31.5	8.22	68.51
7- 1200 "	-413.4	0.062	31.9	-30.7	5.99	77.04
Flowers extract 1- 0 ppm	-414.2	3.478	85.8	-80.9	30.71	-
2- 200 "	-412.0	1.0868	33.4	-32.5	18.51	29.16
3- 400 "	-412.4	1.0066	31.3	-30.6	16.42	37.13
4- 600 "	-412.7	1.0028	31.0	-30.1	13.12	49.78
5- 800 "	-412.9	0.1324	31.0	-29.5	8.24	68.46
6- 1000 "	-417.2	0.0494	28.4	-27.4	5.48	78.99
7- 1200 "	-413.0	0.0486	24.6	-24.2	4.87	81.34

4. CONCLUSION

-The rate of corrosion of mild steel in H_2SO_4 is a function of the concentration of the flavonoid extract.

-The inhibition increased with increased additive concentration.

-The flavonoid extracts of three parts of *Euphorbia guyoniana* are a corrosion inhibitor for mild steel in H_2SO_4 solution and can be used to replace toxic chemicals.

-The plant extracts leaves, stems and flowers can be used as excellent corrosion inhibitors for mild steel in acidic medium.

-The performance of this extract as corrosion inhibitor is better in flowers extract than in leaves and stems extracts.

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