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Research Article

Inhibitive Effect of *Zygophyllum album* Extract on the Sulfuric Acid Corrosion of Mild Steel Grade Api 5l x52

Namoussa Tedjani Yahia*, Ouahrani Mohammed Ridha, Laouini Salah Eddine

laboratory of Valorization and Technology of Saharian resources, faculty of technology, Echahid Hamma Lakhdar University, PB 789,39000 El-Oued, Algeria

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ABSTRACT

Application of inhibitors to prevent corrosion is a widely accepted form of protection as it is one of the easily available methods. In recent years the usage of natural products as corrosion inhibitors is gaining momentum due to environmental considerations. Extract of *Zygophyllum-album* was investigated as corrosion inhibitor of mild steel in 1 M H_2SO_4 using conventional weight loss, electrochemical polarizations, electrochemical impedance spectroscopy and scanning electron microscopic studie. The weight loss results showed that the extract of *Zygophyllum-album* is excellent corrosion inhibitor. Electrochemical polarizations data revealed the mixed mode of inhibition. The results of electrochemical impedance spectroscopy shows that the change in the mpedance parameters, charge transfer resistance and double layer capacitance, with the change in concentration of the extract is due to the adsorption of active molecules leading to the formation of a protective layer on the surface of mild steel. Scanning electron microscopic studies provided the confirmatory evidence of improved surface condition, due to the adsorption, for the corrosion protection.

Keywords: Acid corrosion inhibitor, *Zygophyllum album*, Mild steel, Electrochemical impedance spectroscopy, Electrochemical polarization.

INTRODUCTION

Mild steel finds application in many industries due to its easy availability, ease of fabrication, low cost and good tensile strength besides various other desirable properties. It suffers from severe corrosion when it comes in contact with acid solutions during acid cleaning, transportation of acid, de-scaling, storage of acids and other chemical processes. The heavy loss of metal because of its contact with acids can be minimized largely extent by the use of corrosion inhibitors. Inorganic compounds like chromates, phosphates, molybdates and a variety of organic compounds containing heteroatom like nitrogen, sulfur and oxygen are being investigated as corrosion inhibitors[1-6]. As most of the natural products are nontoxic, biodegradable and readily available in plenty, in various parts-seeds, fruits, leaves, flowers etc, have been used as corrosion inhibitors[7]. Organic compounds have become widely accepted as effective corrosion inhibitors. Most of the organic inhibitors containing nitrogen, oxygen, sulfur atoms, and multiple bonds in their molecules facilitate adsorption on the metal surface[8-11]. Although many synthetic compounds showed good anticorrosive properties, most of them are highly toxic to both human being and environment[12].The known hazardous effect of most synthetic organic inhibitors and restrictive environmental regulations have now made researchers to focus on the need to develop cheap, non-toxic and environmental friendly inhibitors likes natural products as corrosion inhibitors[13]. The natural product extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost and biodegradable in nature. This area of research is of much importance because in addition to being environmentally friendly and ecologically acceptable. Plant products are inexpensive, readily available and renewable source of materials[14-18]. The use of these natural products such as extracted compounds from the leaves, flowers, seeds and roots as corrosion inhibitors have been widely reported by several authors[19-23]. The aim of the present work is to find a naturally occurring, cheap and environmentally safe substance that could be used as corrosion inhibitors for carbon steel in acidic medium. In this present work, the *Zygophyllum album* extracts were tested as green corrosion inhibitors using various electrochemical techniques. In addition, surface examination was tested using scanning electron microscopy (SEM).

MATERIALS AND METHODS

About 20 g of dried and powdered leaves of *Zygophyllum album* was refluxed with 1M H_2SO_4 for about 5 h and was kept overnight to extract the basic components. The solution was filtered off and the filtrate was diluted with the appropriate quantities of the 1 M H_2SO_4 to obtain the desired concentrations. The aggressive acid solutions used were made of AR grade of H_2SO_4 and diluted with double distilled water. The concentration range of the powdered leaves taken was varied from 200 to 2000 ppm in 1 M H_2SO_4.

*Author for Correspondence

Figure 1: *Zygophyllum album*

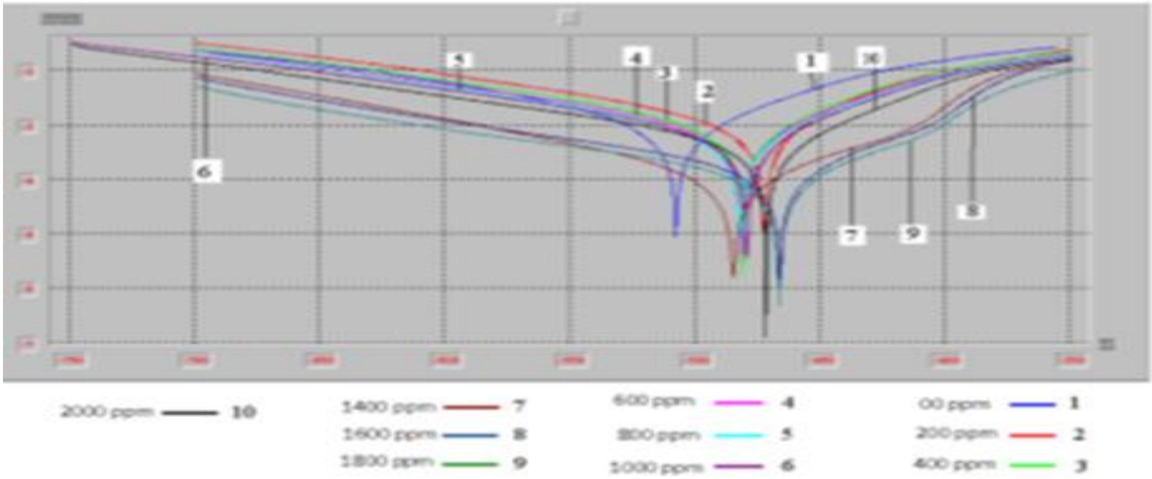

Figure 2: Tafel plots showing effect of *Zygophyllum-album* extracts on corrosion of MS in H_2SO_4 medium.

Table 1: Inhibition Efficiency of MS in 1 M H_2SO_4 at different concentrations of Zygophyllumalbum extract.

C ppm	m_1 (g)	m_2 (g)	Δm (g)	S (sm^2)	V.10^5g/cm^2.min)	V (mm/an)	IE %
200	25.1679	25.1483	0.0196	14.5796	2.2062	15.0980	37.13
400	24.9209	24.1897	0.0173	14.4592	1.8442	13.4372	44.04
600	24.7406	24.7259	0.0147	14.4062	1.5039	11.4598	52.28
800	24.2123	24.0210	0.0102	14.3403	0.8443	7.9882	66.73
1000	24.1449	24.1387	0.0062	14.1148	0.7321	4.9332	79.95
1200	24.6092	24.6056	0.0036	14.3178	0.4196	6.8238	88.66
1400	21.6072	21.6062	0.001	16.9629	0.1286	0.8340	96.69
1600	21.3683	21.3672	0.0011	12.9558	0.1415	0.9535	96.04
1800	21.3466	21.3451	0.0015	12.9488	0.3861	1.2142	94.60
2000	21.3176	21.3155	0.0021	12.9587	0.2701	1.8200	92.45

Table 2: Effect of Zygophyllum album extract on corrosion of MS in 1M H_2SO_4 solution studied by Tafel polarization method

C (ppm)	E_{corr} (mv/ECS)	Ba (mv)	Bc(mv)	I_{corr} (μA/cm^2)	IE %
200	-473.6	84.4	-169.6	1.2961	37.069
400	-482.5	88.1	-166.2	1.1466	44.33
600	- 483.2	88.00	-169.0	0.9800	52.43
800	- 483.4	77.1	-138.9	0.6885	66.567
1000	-480.8	63.00	-105.70	0.4453	78.00
1400	- 486.20	67.9	-74.9	0.0711	96.54
1600	- 468.20	67.90	-109.60	0.0817	96.03
1800	- 467.60	61.20	-99.40	0.0367	95.30
2000	- 473.3	54.60	-95.70	0.2870	86.06

Specimen preparation

Mild steel (API 5L grade X52) of the composition (MS) containing Mn (0.90-1.6), Ni (0.015 ≤), Nb (0.04 ≤), Al (0.06 ≤), Ti (0.05 ≤), Si (0.10 - 0.50), C (0.16≤), P (0.03 ≤), S (0.025 ≤), CE (0.043 ≤), (V + Nb+ Ti) (0.10 ≤), (V + Nb + P) (0.07 ≤), were used for the electrochemical polarizations and impedance measurements. Weight-loss experiments were carried out with steel of dimensions 5.0 cm x 3cm x 0.2cm abraded with fine 4000 grade emery paper, rinsed with acetone, specimens were hanging by nylon fibers which were introduced through a hole of 0.5 mm in diameter. Exposed to the aggressive solution during 2 h. After a total exposition time of 2 h, drilled in one end of the specimen. Were taken out, washed with distilled water, degreased with acetone, dried and weighed accurately. Tests were performed at room temperature 25 °C. Corrosion rates, in terms of weight loss measurements, ΔW, were calculated as follows:

$\Delta W = (m_1 - m_2)\, A$ (1)

were **m_1** is the mass of the specimen before corrosion, **m_2** the mass of the specimen after corrosion, and **A** the exposed area of the specimen. For the weight loss tests, inhibitor efficiency, IE, was calculated as follows:

$IE = 100\, (\Delta W_1 - \Delta W_2)/\Delta W_1$ (2)

where ΔW_1 is the weight loss without inhibitor, and ΔW_2 the weight loss with inhibitor. Specimens were removed, rinsed in water and in acetone, dried in warm air and stored in desiccators. Specimens were weighed in an analytical balance with a precision of 10^{-4} g.

Electrochemical and impedance measurements

The electrochemical techniques employed included potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) measurements. In all the experiments, carbon steel electrode was allowed to reach stable open circuit potential value, E_{corr}. Each polarization curve was recorded three times at constant sweep rate of 10 mV S^{-1} at the interval from -700 to - 350 mV in respect to the E_{corr} value. Measurements were obtained by using a conventional three electrodes glass cell with two graphite electrodes symmetrically situated, and a saturated calomel electrode (SCE) as a reference electrode with a Lugging capillary bridge. Corrosion current density values, i_{corr}, were obtained by using Tafel extrapolation. Inhibitor efficiency, IE, was calculated as follows:

$IE = 100\, (I_{corr1} - I_{corr2})/I_{corr1}$ (3)

where I_{corr1} is the corrosion current density value without inhibitor, and I_{corr2} the corrosion current density value with inhibitor. EIS tests were carried out three times at E_{corr} by using a signal with amplitude of 10 mV in a frequency interval of 100 mHz - 100 KHz. An ACM potentiostat, controlled by a desk top computer was used for the polarization curves, whereas for the EIS measurements, a

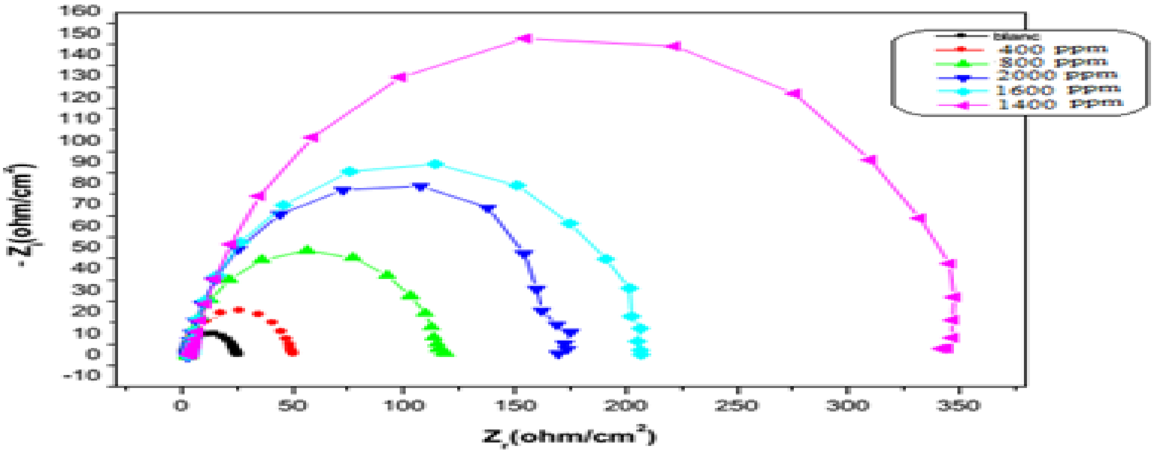

Figure 3: Nyquist plots showing effect of Zygophyllum album extracts on corrosion of MS in H_2SO_4 medium.

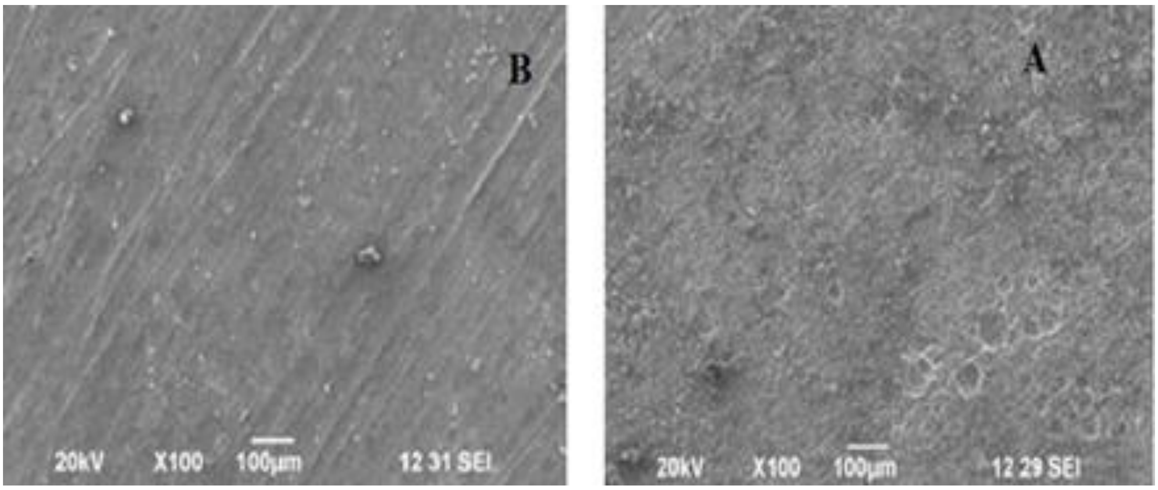

Figure 4: SEM images of MS in 1 M H_2SO_4 media (a) and (b) with *Zygophyllum album* extract (1400 ppm).

model VoltaLab 80 (PGZ402 & Volta Master 4) was used. Surface analysis of corroded specimens was carried out by a Scanning Electronic Microscope (SEM).

RESULTS AND DISCUSSION

Weight loss method

Based on the weight loss measurements, the corrosion rates (W) and the values of inhibition efficiency (IE%) for various concentrations *Zygophyllum album* extract after 2 h of immersion at 25 ºC obtained are given in (Table 1). From the table, it is clear that the value of IE% increases with the increase in the concentration reaching a maximum value of 96.69 % at the highest concentration of 1400 ppm, suggesting that the number of molecules adsorbed were increased over the MS surface, blocking the active sites of acid attack and thereby protecting the metal from corrosion.

Electrochemical polarizations method

The potentiodynamic polarization data are shown in the Tafel plots for MS in 1 M H_2SO_4 with the addition of various concentrations of the additive (Figure 1). The corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic and cathodic Tafel slopes (Ba and Bc) were derived from these curves and are given in Table 2. The values of inhibition efficiency (IE %) are calculated and tabulated (Table 2). From the Table, it observed that the I_{corr} values gradually decreased with gradual increase in the concentration of additive up to 1400 ppm leading to 96.54% of IE. Further, there was anodic shift of the E_{corr} value of -0.5 V (blank) to -0.48 V at 1400 ppm indicating that the Zygophyllum-album extracts acted as an cathodic inhibitor for MS in 1 M H_2SO_4 which was supported by the gradual and significant decrease of anodic Tafel slope, Bc is -169.6mV / decade of blank to -74.9mV/ decade at 1400 ppm. It could be derived from a decrease that the rate of cathodic dissolution was much retarded in comparison to that of anodic hydrogen evolution. There was decrease of only 16.5 mV/ decade in the corresponding values of anodic Tafel slopes. This means that the extract must have acted predominantly by blocking anodic sites, and cathodic sites to some extent, and the extract contained the active molecules, which behaved as mixed-type of the acid corrosion inhibitors.

Electrochemical impedance spectroscopy method The corrosion behavior of MS in 1 M H_2SO_4, in absence and the presence of various concentrations of *Zygophyllum-album* extract were also investigated by EIS technique. The resultant Nyquist plots are shown in (Figure 2). The existence of a single semicircle in each plot shows that there was only single charge transfer process during the anodic dissolution of MS and remained unaffected in the presence of inhibitive molecules of the extract added in the acid. The charge transfer resistance (Rct) and the interfacial double layer (Cdl) values are derived from these curves and it is found that Rct values increase with increase in the inhibitor concentration while Cdl values decrease which results in maximum IE (96.54%) at high concentration. This indicated that the inhibitive molecules of the extracts have been adsorbed on the MS surface and decreased the roughness of the MS surface.

Scanning electron microscopic method

The SEM photograph in Figure 3(a) has shown that the surface of MS was extremely damaged in the absence of the extract while Figure 3(b) has clearly shown the formation of a film by the active Zygophyllum-album constituents on the MS surface which was responsible for the corrosion inhibition. The inhibition properties of *Zygophyllum-album* must be due to the presence of nitrogenous compounds or tannins in the extract of leaves. However, tannins are complex astringent aromatic acidic glycosides found in various plants and their presence can be ruled out as they are made up of the polyphenols and their acidic and heterocyclic derivatives because such constituents would not have been extracted in the acid.

CONCLUSIONS

The active molecules present in the extract of F. exasperate have effectively inhibited corrosion of mild steel in 1 M H2SO4 at 25º C by forming a protective barrier layer. The inhibition efficiency of the extract increased gradually with increase in its concentration. Polarization measurements have shown that the extract of *Zygophyllum-album* has acted as a mixed- inhibitor, retarding predominantly cathodic dissolution of steel in 1 M H_2SO_4. The results of the weight loss, electrochemical polarization and AC impedance spectroscopy were all in very good agreement to support the above conclusions. Photographs by SEM have clearly shown the formation of the protective film on the surface of mild steel. The acid extract of *Zygophyllum-album* can be considered as a source of relatively cheap, eco-friendly and effective acid corrosion inhibitors.

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