ISSN-1996-918X

Pak. J. Anal. Environ. Chem. Vol. 23, No. 1 (2022) 70 – 78

Cross Mark

http://doi.org/10.21743/pjaec/2021.06.07

Effect of Aloe Vera Extract as Green Corrosion Inhibitor on Medium Carbon Steel in Sulphuric Acid Environment

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Received 14 September 2021, Revised 20 December 2021, Accepted 22 December 2021

Abstract

Medium carbon steel is widely consumed by various industrial sectors due to its attractive set of mechanical properties and low cost, but it experiences deterioration when exposed to a corrosive environment. In the present study, Aloe Vera plant extract was studied as a green corrosion inhibitor for medium carbon steel in an acidic medium. The presence of inhibitive compounds in Aloe Vera plant extract was determined by FTIR. Moreover, the inhibition efficiency was determined through gravimetric analysis and electrochemical analysis. The results show that the Aloe Vera plant extract provided inhibition efficiency of more than 90% in both gravimetric and electrochemical analyses. Furthermore, the shift in polarization curves depicts that this plant extract is a mixed type inhibitor acting as an anodic and cathodic inhibitor. Overall, Aloe Vera plant extract provides excellent corrosion inhibition to medium carbon steel in the H_2SO_4 environment and can be used as a green corrosion inhibitor for mitigating internal corrosion of pipelines and storage tanks.

Keywords: Aloe vera, H_2SO_4 environment, Internal corrosion, Medium carbon steel, Eco-Friendly Inhibitor

Introduction

Medium carbon steel is commonly known as mild steel. Due to its availability in the market with low price and good mechanical properties like strength, ductility, and malleability [1]. It has been used in almost every industrial sector. But the main problem with medium carbon steel is its susceptibility towards corrosion, especially in acidic mediums [2]. Different industrial sectors such as manufacturing, automobile, chemical processing, oil, and gas use medium carbon steel extensively in their operations. Furthermore, in these industries almost in all, an acidic environment is present in various operations, as a result, such materials like medium carbon steel tend to be prone to corrosion [3]. It is obvious that when medium carbon steel comes in contact with the acidic medium, it experiences degradation and deterioration by corrosion. In industrial operations, corrosion leads to serious consequences, including leakage of hazardous fluids from containers and pipelines. Which causes product contamination and catastrophic incidents, which ultimately becomes the reason behind the shutdown of the plants and huge loss of economy [4].

In 2002, the USA, civil administration, and National Association of Corrosion

Engineers (NACE) collectively researched corrosion cost, and they estimated that around $276 billion are being spent on over corrosion prevention techniques every year in the USA, which is almost 3.1 per cent of the US gross domestic product (GDP) [5]. Thereby, it can be said that corrosion affects different areas of life directly or indirectly. For suppose sudden failure of giant oil and gas pipelines or collapse of industrial operations results in the release of toxic substances and raises serious technical and environmental concerns. Statistically, corrosion has a significant impact on the economy, therefore it is necessary to mitigate corrosion by adopting suitable prevention techniques [6]. Corrosion is broadly categorized as internal and external corrosion. Particularly, internal corrosion is observed in pipelines and storage tanks and controlled by injecting corrosion inhibitors. Because corrosion inhibitors provide better inhibition action, that's why they are far better and more effective than other prevention techniques when it comes to the internal protection of pipelines [7].

Conventionally, synthetic inhibitors are used by industries. Since, the last few decades, researchers have greatly emphasized introducing green (natural) inhibitors due to the adverse effects of synthetic compounds on workers and the environment. Natural extracts are found to be friendly with nature while performing anticorrosive actions. Meanwhile, the green inhibitors occur naturally, are readily available, biodegradable in nature, cost-effective, and do not have any momentous effect on health and the environment [8]. So, for the corrosion inhibition of various metals, multiple green inhibitors have been studied in different environmental conditions. Like Gum Arabic, Oil palm frond, Henna extract, and Aloe Vera plant extract are studied in different environments for different metals. And to support such type of eco-friendly inhibitors environmental legislation have also preferred the use of green inhibitors in the industrial sector [9]. Furthermore, Aloe Vera extract as a green inhibitor has been studied by many researchers in recent times, such as Abiola and James studied Aloe Vera in 2 M HCl for Zinc in which the efficiency of Aloe Vera was increasing as concentration was increasing [10]. Singh et al. studied the corrosion inhibition of Aloe Vera extract on mild steel in 1 M HCl medium and observed that its efficiency was 90% at 200 ppm concentration [11], likewise these researchers Mehdipour et al. also studied Aloe Vera for stainless steel in 1 M H_2SO_4 in which electrochemical study showed that as the concentration increased the effectiveness of inhibitor also increased [12].

Meanwhile, the efficiency of the inhibitor can be observed by its adsorption behaviour because adsorption is the key property of any inhibitor. It tends to protect metal through adsorbing mechanism, which acts as a barrier between the metal and the environment [13]. Moreover, it is reported that the adsorption effect of green corrosion inhibitor is a function of the presence of some functional groups, which includes such as (a) Anthraquinone, (b) P-Coumaric acid, (c) Caffeic acid, (d) Ferulic acid, which is shown in Fig.1 [14].

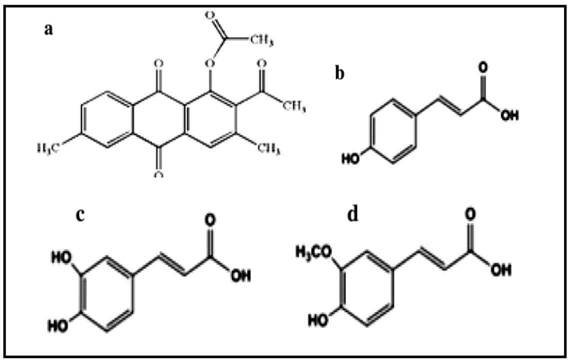

Figure 1. **Phenolic Compound structures: (a) Anthraquinone (b) P-Coumaric acid, (c) Caffeic acid, (d) Ferulic acid**

In the present study, the inhibition efficiency of Aloe Vera plant extract is determined in an acidic environment for medium carbon steel. It is reported that Aloe Vera contains several free anthraquinones and phenolic compounds, which offer good adsorption characteristics on metallic surfaces [15]. Moreover, the Aloe Vera plant extract possesses such aromatic structures and aliphatic compounds within which the presence of electron-rich oxygen, pi-electrons, and double bonds are significant, and which can easily form bonds with the ions of the metal surface in order to create a barrier between the metal and acidic environment [16].

Materials and Methods

Preparation of Aloe Vera Extract

The fresh succulent Aloe Vera plant was taken from the garden of Metallurgy & Materials Engineering Department, MUET, Jamshoro, Pakistan. The colourless extract of clean-fleshy Aloe Vera was collected into a beaker at 25°C room temperature by peeling it off with a knife and pressing it with hand. Furthermore, the obtained pulpy extract of Aloe Vera was filtered to get a more clean and pure extract. Fourier transform infrared spectroscopy (Model: Perkin Elmer Spectrum) was used to confirm the presence of phenolic compounds in the Aloe Vera plant extract.

Environment Preparation

Sulphuric Acid (H_2SO_4) of analytical grade (98.5% pure) was used to prepare the 1 M solution in deionized water. Then the Aloe Vera plant extract was used as an inhibitor at various concentrations (200 ppm, 400 ppm, 600 ppm, and 800 ppm).

Coupons Preparation

Medium carbon steel coupons used for experimental work were cut from a round bar with 1x1 inch as per the reported size of coupons [17]. Table 1 shows the chemical composition of medium carbon steel and for test spark spectrometer (Model: Bruker Q2 ION) were used. Furthermore, Initially, coupons were ground with the emery papers and polished using alumina paste to remove rust and dust from the metallic surface. After that, coupons were rinsed with deionized water and acetone ($(CH_3)_2CO$) to remove the dirt or grease from the surface of the coupons.

Table 1. **Chemical composition of medium carbon steel (wt.%).**

Elements	Phosphorus (P)	Manganese (Mn)	Silicon (Si)	Iron (Fe)	Sulphur (S)	Carbon (C)
Composition	0.0020	0.581	0.488	98.7	0.0030	0.387

Gravimetric Analysis

Gravimetric Analysis (Weight loss measurements) was performed at room temperature 25°C [18]. The coupons were pre-cleaned and weighed by using a weight balance machine(Shimadzu balance, model AY62), then placed into the 100 mL beakers containing 1 M H_2SO_4 and various concentrations of inhibitor 200 ppm, 40 ppm, 600 ppm, 800 ppm. The test was performed in an open atmosphere. Weight loss of coupons was determined after an immersion time of 24 h, 48 h, and 72 h. The weight loss of the coupons was calculated by the difference between Initial weight (Wi) and Final weight (Wf) using equation (1) [19].

$$\Delta W = W_i - W_f \quad (1)$$

Corrosion rates (CR) were determined using weight loss data in given equation (2) [20].

$$CR = \frac{\Delta W}{At} \quad (2)$$

Whereas ΔW is the weight loss of coupon in mg, A indicates the surface area of the specimen, and t determines the time of each experiment in hours.

From the obtained corrosion rate at different concentrations of inhibitor, the inhibition efficiency (IE) of the inhibitor was determined by using equation (3) [21].

$$IE(\%) = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \times 100 \quad (3)$$

CR_{blank} (absence of inhibitor) and CR_{inh} (presence of inhibitor) represent the corrosion rates.

Electrochemical Analysis

The electrochemical analysis was carried out using VersaSTAT4 Potentiostat using corrosion kit, which contained 300 mL of respective test solution. Three electrode setup was used containing saturated calomel electrode (SCE), medium carbon steel coupon, and Platinum mesh electrode as reference electrode, working electrode, and auxiliary-electrode, respectively. The analysis was conducted at room temperature 25°C. For each test, samples were properly ground using emery papers of various sizes, i.e., 400, 600, 800, 1000, and 1200–polished and cleaned with acetone. Potentiodynamic Polarization was performed in ranges from -0.4V to +0.4V at open circuit potential with a scan rate of 1 mV sec^{-1}. An Electrochemical Impedance Spectroscopy (EIS) study was performed in the frequency range from 100000 Hz to 0.004 Hz [22].

Results and Discussion

Fourier Transform Infrared Spectroscopy (FTIR)

Fig. 2 depicts the results of the FTIR spectrum of Aloe Vera extract between transmittance and wavelength. Ranges from 500 cm^{-1} to 4000 cm^{-1} were obtained. Peaks in the graph represent the evidence of phenolic compounds in Aloe Vera plant extract, the peaks at 572.8 cm^{-1}, 1251 cm^{-1}, and 1402 cm^{-1} correspond to Phenolic-OH, C=C bond, -COC. Furthermore, the presence of -NO2 group and weak bonds justifies the absorption bands at 1865 cm^{-1} 2351 cm^{-1} and 3451 cm^{-1}. And the polymeric compounds indicate the presence of C-H bonding in the extract [23].

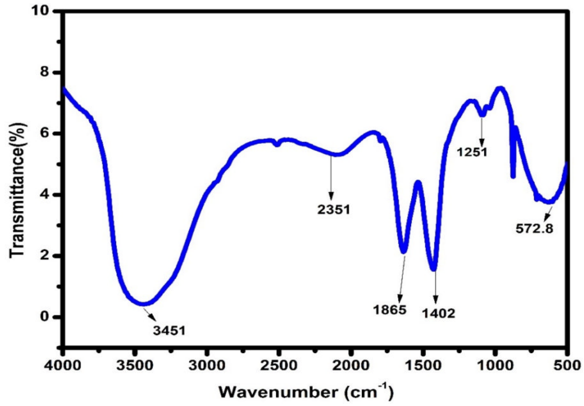

Figure 2. **FTIR of Aloe Vera plant extract**

Gravimetric Analysis

Weight loss analysis was carried out to study the effect of Aloe Vera plant extract as an eco-friendly corrosion inhibitor in a 1M H_2SO_4 environment on medium carbon steel. The test was conducted at room temperature 25°C. Samples were immersed in test solution at various concentrations of Aloe Vera plant extract 0 ppm, 200 ppm, 400 ppm, 600 ppm and 800 ppm for 24 h, 48 h, and 72 h. Weight loss measurement at different concentrations and immersion times were calculated using Eq: 01, 02, and 03. Table 2 shows the results of weight loss, corrosion rate (CR), and obtained inhibition efficiency values (IE%). The obtained data shows that weight loss of medium carbon steel samples significantly decreases with an increase in inhibitor concentration at different exposure times, as shown in Fig. 3.

Table 2 indicates the IE% of Aloe Vera plant extract as a function of adsorption inhibitor – as the concentration of inhibitor is increasing results the substantial increase in surface adsorption of anthraquinone molecules which increase inhibition efficiency of Aloe Vera plant extract. Moreover, the maximum efficacy was obtained at 800 ppm, approximately 97%, 96%, and 92% for 24 h, 48 h, and 72 h exposure times, respectively. It is reported that inhibitors are adsorbed on the metallic surface and provide a barrier between the metal and the environment [24].

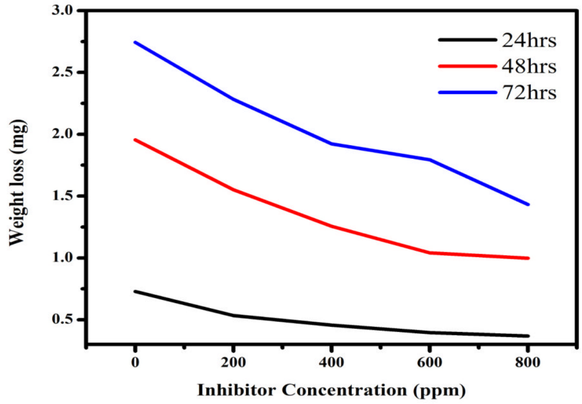

Figure 3. **Results of weight loss of medium carbon steel at various concentrations of Aloe Vera plant extract in 1M H_2SO_4**

Potentiodynamic polarization (Tafel Curves)

Electrochemical polarization measurements were conducted on medium carbon steel in 1 M H_2SO_4 solution with and without the addition of a green inhibitor. Five concentrations of 0 ppm, 200 ppm, 400 ppm, 600 ppm, and 800 ppm were added in the corrosive solution, and the obtained Tafel curves are depicted in Fig. 4. Moreover, Table 3 presents the computed Potentiodynamic parameters in the presence and absence of inhibitors. It can be observed from Fig. 4 that the addition of Aloe Vera plant extract changes the anodic (β_a) and cathodic (β_c) slopes by reducing anodic dissolution and slowing down the hydrogen evolution process, respectively. It is cited that the classification of corrosion inhibitors as cathodic, anodic, and mixed type is based on the variations observed in polarization Tafel curves after the addition of inhibitor in it [25]. However, the considerable change in Tafel curves (anodic and cathodic region) after the addition of green inhibitor specifies that Aloe Vera plant extract is a mixed-type inhibitor. It is reported that the addition of natural inhibitors slowdowns the anodic and cathodic reactions through adsorbing on active sites as a result, corrosion reactions are retarded [26]. Furthermore, the addition of inhibitor offers better surface coverage to the metallic surface in an acidic environment and shifts the corrosion behaviour towards a more inhibition region [27].

Table 2. **Gravimetric data of Aloe Vera plant extract at various concentrations.**

Time (h)	Inhibitor Concentration (ppm)	Weight Loss (g)	Corrosion Rate (mpy)	Inhibition Efficiency (IE%)	Surface Coverage (Θ)
24	0	0.7289	164.9128	-	-
	200	0. 5340	119.7312	36.34	0.3634
	400	0.4571	103.9177 90.3637	59.38	0.5938
	600	0.3962	83.5859	83.77	0.8377
	800	0.3687		97.69	0.9769
48	0	1.9544	220.2603	-	-
	200	1.5517	175.0787	25.95	0.2595
	400	1.2567	142.3220	87.81	0.8781
	600	1.0406	117.4721	93.39	0.9339
	800	0.9987	112.9540	95.96	0.9596
72	0	2.7439	206.3293	-	-
	200	2.2831	171.6901	20.18	0.2018
	400	1.9217	144.5811	42.73	0.4273
	600	1.7933	134.7918	62.04	0.6204
	800	1.4327	107.6828	91.51	0.9151

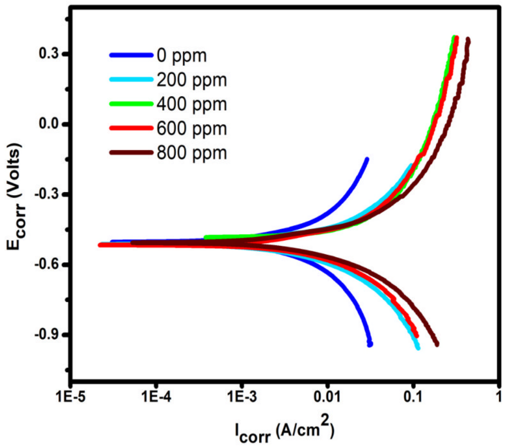

Figure 4. **Tafel plot of Aloe Vera plant extract at different concentrations on medium carbon steel in 1M H_2SO_4**

Results also show that corrosion current density (j_{corr}) values are continuously decreasing with increasing the inhibitor concentration. It confirms that increased corrosion inhibitor concentration hindered the corrosion reaction by developing a resistive layer of adsorbed molecules. In fact, a gradual decrease in corrosion rate is the function of inhibitor concentration, as the inhibitor concentration increases the corrosion rate decreases [28].

Table 3. **Electrochemical polarization parameters of Aloe Vera plant extract at various concentrations on medium carbon steel in 1M H_2SO_4.**

Inhibitor Conc. (ppm)	E_{corr} (mv)	I_{corr} (µA)	β_a (mV)	β_c (mV)	j_{corr} (µA/cm^2)	Corrosion rate (mm/yr)
0	-491.31	7.24	309.7	261.1	14.49	3.75×10^{-05}
200	-516.08	3.84	200.8	188.5	7.68	1.98×10^{-05}
400	-509.26	3.26	155.0	171.5	6.52	1.68×10^{-05}
600	-508.59	2.97	150.3	168.4	5.95	1.54×10^{-05}
800	-507.76	2.79	82.3	89.1	5.58	1.44×10^{-05}

Electrochemical Impedance Spectroscopy (EIS)

The EIS study was conducted to understand the effect of inhibitor concentration on the impedance behaviour of steel in a 1 M H_2SO_4 environment. Semi-circles in Fig. 5 show impedance change in the presence and absence of inhibitor. These results were also fitted by using the equivalent circuit (EC), and the extracted data is displayed in Table. 4. The lower values of double-layer capacitance (C_{dl}) and higher values of charge transfer resistance (R_{ct}) justified that inhibitor creates a strong protective barrier to resist the corrosion reaction by adsorbing on the metallic surface [29].

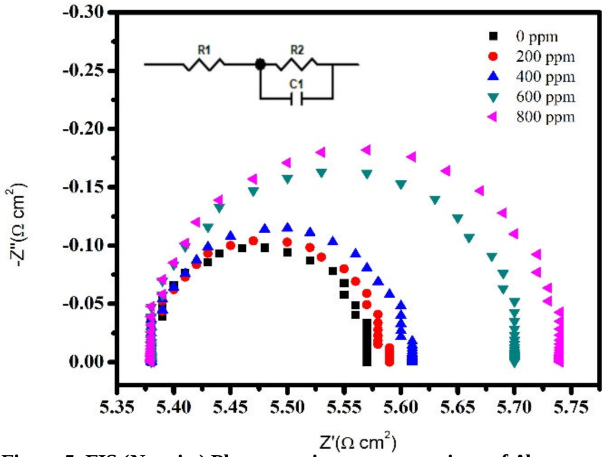

Figure 5. **EIS (Nyquist) Plots at various concentrations of Aloe Vera plant extract on medium carbon steel in 1M H_2SO_4**

Table 4. **EIS parameters at various concentrations of Aloe Vera plant extract on medium carbon steel in 1M H_2SO_4.**

Inhibitor Concentration (ppm)	Double-layer Capacitance C_{dl}(µF)	Charge Transfer Resistance R_{ct} (Ω)
0	2.2507	2.777
200	3.0576	2.926
400	2.8853	3.125
600	3.2327	4.878
800	4.6641	5.377

Adsorption Isotherm

An adsorption study was carried out to understand the interaction of inhibitor molecules with medium carbon steel substrate during corrosion test. Various methods (weight loss, EIS, and Potentiodynamic Polarization) can be adapted to calculate the degree of surface coverage (θ) for adsorption. Because surface coverage (θ) helps to evaluate the isotherms. In this study, surface coverage (θ) is determined from weight loss data shown in Table 2 and fitted to Temkin, Langmuir, Frumkin, Flory-Huggins, Bockris-Swinkels, and Dhar-Flory-Huggins model [30]. But the best fit was observed with the Langmuir model, then it was considered for the present research. This model illustrates the interaction between the metal surface and inhibitor molecules. Langmuir adsorption model is expressed in given equation (4):

$$\frac{C_{inh}}{\theta} = \frac{1}{k_{ads}} + C_{ink} \tag{4}$$

Where (C_{inh}) is the concentration of the inhibitor (Aloe Vera plant extract), (θ) is the surface coverage, and (K_{ads}) is the adsorption equilibrium constant. The graph between inhibitor concentration (C_{inh}) versus (C/θ) showed a straight line as shown in Fig. 6. This confirms that the Langmuir model is reliable to explain the interaction between inhibitor molecules and medium carbon steel surface in 1M H_2SO_4 solution.

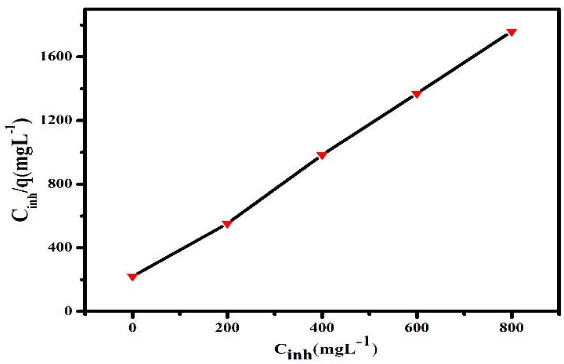

***Figure 6.* Langmuir adsorption isotherm of Aloe Vera plant extract on medium carbon steel**

Conclusion

The results conclude that Aloe Vera plant extract can be used commercially as a green corrosion inhibitor to prevent medium carbon steel from H_2SO_4 attack. It is eco-friendly and readily available at a low cost. Both gravimetric and electrochemical analysis validate its corrosion inhibition performance in an acidic medium. The maximum inhibition efficiency of 97% was achieved by gravimetric analysis for 24 h immersion time. Whereas the effectiveness of inhibitor was also confirmed from Nyquist plots. The study also reveals that Aloe Vera plant extract acts as a mixed-type inhibitor that follows the chemical and physical adsorption on medium carbon steel surface followed by the Langmuir adsorption isotherm model.

Acknowledgment

The authors acknowledge the Department of Metallurgy and Materials Engineering and Chemical Engineering, Mehran University of Engineering and Technology Jamshoro, Pakistan, for providing lab facilities and space for conducting necessary experiment work.

Conflict of Interests

There are no conflicts of interest to disclose.

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