

Aloe vera L. as Green Corrosion Inhibitor for Mild Steel in 5.0 M Hydrochloric Acid Solution

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Received: 9 June 2017; Accepted: 28 July 2017; Published online: 31 January 2018; AJC-18726

The leaf gel of *Aloe vera* L. was examined for its anti-corrosion properties for mild steel in 5.0 M hydrochloric acid as corroding solution by using different techniques like weight loss, gasometric, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. *Aloe vera* L. extract is selected for this study in view of its rich source of organic molecules. The percentage corrosion inhibition efficiency (PCIE) is found to increase with increase in concentration of *Aloe vera* L. *i.e.* from 0.1 to 4.0 g/L. Electrochemical experiments confirms that *Aloe vera* L. acts as a mixed-type green corrosion inhibitor. The activation parameters obtained from corrosion experiments showed that the inhibitor is adsorbed by both physisorption and chemisorption method. Scanning electron microscopy (SEM) and trinocular inverted metallurgical research microscopy study confirms the physisorption adsorption of *Aloe vera* L. in 5 M HCl solution for mild steel.

Keywords: Electrochemical impedance spectroscopy, SEM, Green corrosion inhibitor, Corrosion, Mild steel, Aloe vera L.

INTRODUCTION

Corrosion of metal and their alloys is a major problem in industries that's why corrosion protection methods are technically and economically important. Different class of corrosion inhibitors provides corrosion protection to different metals but commercially available corrosion inhibitors available in the market are mostly toxic in nature but green corrosion inhibitors are biodegradable and non-toxic, inexpensive, readily available and are reusable [1-4]. This area of research is of much importance because in addition to being environmental friendly and ecologically acceptable, plant products are inexpensive, readily available and renewable source of materials [5,6]. Recently different researchers have reported [7-9] the use of plants parts or their products like extracted organic compounds from the leaves, flowers, seeds, roots and fruits as green corrosion inhibitors. For example, Sethuraman and Raja [10] have reported the extract of black pepper as green corrosion inhibitor for mild steel in 1.0 M acid media. Similarly, Okafor et al. [11] reported the inhibitive effect of leaves, seeds and a combination of leaves and seeds extracts of Phyllanthus amarusas green corrosion inhibitor or mild steel in hydrochloric acid and sulphuric acid medium. Abdel-Gaber et al. [12] studied the inhibitive effect of lupine (Lupinus albus L.) extract on the corrosion of steel in aqueous solution of 1 M H₂SO₄ and 1 M HCl. Orubite and Oforka [13] studied the inhibition of corrosion of mild steel in HCl solutions by extract of the leaves

of *Nypa fruticans* Wurmb. Eddy *et al.* [14] studied the inhibitive and adsorption properties of ethanol extract of *Verninia amygdalina* for the corrosion of mild steel.

Aloe vera L. belongs to Asphodelaceae family and is cultivated for its agricultural and medicinal use. The flesh of leaf of Aloe vera L. has been reported to be used in the treatment of different ailments [15]. However, literature survey reveals that less study has been carried out on the inhibitive effects of leaf gel of Aloe vera L. on corrosion of mild steel in 5.0 M HCl medium [16]. In continuation to our studies [17,18], the present study aims to gain some insight into the corrosion of mild steel in 5.0 HCl in the presence of Aloe vera L. as a green corrosion inhibitor. The pulp (jelly) of *Aloe vera* L. plant in 5 M hydrochloric acid as a corrosive medium was tested by weight loss, gasometric, potentiodynamic polarization and electrochemical impedance techniques. SEM and trinocular invert metallurgical research microscopy techniques were also carried out to study the surface morphologies of corroded and uncorroded samples.

EXPERIMENTAL

Preparation of *Aloe vera* **L.:** Analytical reagents-grade HCl (Sigma Aldrich, percentage purity 99.999 %, 37.0wt %) was used for preparing corrosive medium. The fresh leaves of *Aloe vera* L. were cut from the plant and washed with double distilled water and then they are peeled to extract gel. Gel was collected in grinder and then grinded in mixer. Some warm double distilled water was added during grinding in order to form uniform paste which was used as such in different amount in 5 M HCl.

Weight loss method: Mild steel specimens having percent composition of C (0.17), Si (0.18), Mn (0.53), P (0.044), S (0.057), Cr (0.14), Ni (0.09), Mo (0.02), Cu (0.06), V (less than 0.01) and remaining Fe (chemical analysis: % by weight by equipment, IS:228) were used. Rectangular specimens with dimension 1.5 cm \times 3.0 cm \times 0.1 cm were used in weight loss experiments. The specimens were polished successively using emery papers of 100, 200, 320, 400, 600 and 1000 grade. The polished surface were degreased with acetone and washed with distilled water before the experiment. The corrosion rate (CR) and percentage corrosion inhibition efficiency (PCIE) were calculated [16] by using eqns. 1 and 2:

Corrosion rate (mpy) =
$$\frac{534 \times W}{DAT}$$
 (1)

where, W = weight loss in mg, D = density of mild steel in g/cm³, A = area of mild steel coupon in sq. inch, T = exposure time of mild steel coupons in corroding media in hours.

Corrosion inhibition efficiency (%) =
$$\frac{CR_o - CR}{CR_o} \times 100$$
 (2)

where, CR_o = weight loss of mild steel in absence of inhibitor and CR = weight loss of mild steel in presence of inhibitor.

Electrochemical polarization measurements: All the electrochemical polarization experiments were performed on an electrochemical workstation (PGSTAT 128N) Metrohm Autolab. Ltd., Netherland. The working electrode (mild steel coupons itself act as working electrode) was kept into the corroding solution (acidic solution) for 1.0 to 2.0 h to attain the equilibrium potential also known as OCP. Electrochemical polarization experiments were carried out under a constant temperature of 298.16 K. Electrochemical polarization experiments were carried out under a constant temperature of 0.01 (V/s). The corrosion rate and PCIE were calculated from the polarization experiments using the following eqns. 3 and 4, respectively [19]:

Corrosion rate (mpy) =
$$\frac{0.1288 \times I_{Corr} \times Eq.Wt}{D}$$
 (3)

where, Eq. Wt. = gram equivalent weight of mild steel, D = density of mild steel in g/cm^3 , I_{Corr} = corrosion current density in mA/cm².

$$PCIE = \frac{CR_{(Blank)} - CR_{(Inhibitor)}}{CR_{(Blank)}} \times 100$$
(4)

where, $CR_{(Blank)}$ = corrosion rate in blank sample and $CR_{(Inhibitor)}$ = corrosion rate in presence of green corrosion inhibitor.

Electrochemical impedance measurements: Electrochemical impedance measurements (EIM) were carried out using PGSTAT 128 N MetrohmAutolab. Ltd., electrochemical workstation at a constant temperature of 298.16 K and the electrochemical response of the system was observed to a.c. excitation, with a frequency ranging from 10 000 to 1.0 Hz and peak to peak a.c. amplitude of 0.05 V with quiet time of 2 s was done. The percentage corrosion inhibition efficiency (PCIE) from electrochemical impedance measurements (EIM) was calculated using eqn. 5 [20].

$$PCIE = \frac{Rct_{(Inhibitor)} - Rct_{(Blank)}}{Rct_{(Inhibitor)}} \times 100$$
(5)

where, $Rct_{(Inhibitor)}$ and $Rct_{(Blank)}$ are the values of charge transfer resistance in presence and in absence of inhibitor.

Gasometric technique: Gasometric technique is specially designed in the laboratory to measure amount of gas evolved during the corrosion experiments. It is based on the principle that the rate of corrosion reaction in corroding media is directly proportional to the evolution of gas during the cathodic reduction reaction. Volume of gas evolved is noted with respect to time and rate of evolution of gas is determined from the slope of volume of gas evolved *versus* time graph. Magnitude of surface coverage by green corrosion inhibitor and PCIE were determined with the help of rate of evolution of gas in the presence and absence of *Aloe vera* L.

Surface analysis: The mild steel coupons were examined by scanning electron microscope (SEM) model JEOL JSM 6150 and trinocular inverted metallurgical research microscopy technique for their surface study after weight loss experiments in absence and presence of *Aloe vera* L in 5 M HCl solutions at 298.16 K.

RESULTS AND DISCUSSION

Weight loss method: The weight loss, corrosion rate and PCIE at different concentrations of *Aloe vera* L. at 298.16 K temperature is shown in Table-1. From Table-1, it is clear that PCIE of *Aloe vera* L. increases with increase in concentration (0.1 to 4.0 g/L) of green corrosion inhibitor *i.e. Aloe vera* L. shows maximum 97.81 % PCIE at a concentration of 4.0 g/L. It also shows very good corrosion inhibition efficiency *i.e.* 51.78 % even at low concentration of 0.1 g/L.

TABLE-1					
WEIGHT LOSS, CORROSION RATE AND PERCENTAGE					
CORROSION INHIBITION EFFICIENCY (PCIE) OF Aloe vera L.					
AT DIFFERENT CONCENTRATION BY WEIGHT LOSS					
TECHNIQUE AT 298.16 K IN 5.0 M HCl SOLUTION					
Concentration	Weight loss (g)	Corrosion rate	PCIF		
(g/L)	Weight 1035 (g)	(mpy)	TCIL		
Blank	0.0507	664.231	-		
4.0	0.0011	14.5265	97.81		
2.0	0.0029	38.4758	94.21		
1.0	0.0042	55.5543	91.64		
0.5	0.0057	75.7737	88.59		
0.1	0.0244	320.239	51.78		

Potentiodynamic polarization measurement: Table-2 shows potentiodynamic polarization data like i_{corr} , corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_c and β_a) and PCIE for mild steel in 5 M hydrochloric acid as corroding medium with and without *Aloe vera* L. at 298.16 K.

It is observed from Table-2 that the addition of *Aloe vera* L. to corroding medium increases both anodic and cathodic over-potentials and decreases the value of i_{Corr} . It is also observed from Table-2 that the change in slopes of β_c and β_a in such a direction that adsorption of *Aloe vera* L. modifies the mechanism of anodic metal dissolution (oxidation) as well

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Conc. (g/L)	OCP	I_{corr} (µA/cm ²)	$\beta_{\rm a}$	β _c	Rp	CR (mpy)	PCIE
Blank	-0.528	4.48	5.935	7.637	3.66×10^{5}	1.7279	-
4.0	-0.755	0.78	0.508	1.380	7.75×10^{4}	0.3008	82.59
2.0	-0.560	1.12	2.330	1.504	2.58×10^{4}	0.4319	75.00
1.0	-0.523	1.23	2.899	1.589	1.25×10^{5}	0.4744	72.54
0.5	-0.518	1.36	3.462	6.771	2.63×10^{5}	0.7174	54.48
0.1	-0.502	2.21	2.592	1.847	1.22×10^{5}	0.8523	50.67

as cathodic H_2 gas evolution. Both cathodic and anodic reactions are inhibited to the same extent which proves that *Aloe vera* L. as a mixed type of green corrosion inhibitor and the rate of inhibition increases with the concentration of inhibitor. It is clear from the Table-2 that value of corrosion potential increases in presence of *Aloe vera* L.

Gasometric measurements: Table-3 shows amount of gas evolved in mL, surface coverage (θ) by the green corrosion inhibitor and PCIE of *Aloe vera* L. at five different concentrations by Gasometric method at a constant temperature of 298.16 K in 5.0 M hydrochloric acid as a corroding medium. It is clear from Table-3 that the value of RVh drops with increase in concentration of *Aloe vera* L. It is also clear from Table-3 that PCIE of *Aloe vera* L. increases with increase in concentration *i.e.* 0.1 to 4.0 g/L.

TABLE-3 AMOUNT OF GAS EVOLVED (mL), SURFACE COVERAGE (θ) AND PERCENTAGE CORROSION INHIBITION EFFICIENCY (PCIE) OF <i>Aloe vera</i> L. AT DIFFERENT CONCENTRATIONS BY GASOMETRIC METHOD AT 298.16 K IN 5.0 M HCI SOLUTION				
Concentration (g/L)	RVh	Surface coverage (θ)	PCIE	
Blank	1.0787	-	-	
4.0	0.1869	0.8267	82.67	
2.0	0.2741	0.7459	74.59	
1.0	0.3392	0.6856	68.56	
0.5	0.3423	0.6826	68.26	
0.1	0.3703	0.6567	65.67	

EIS measurements: For complete characterization of electrode/electrolyte interface and in order to study surface processes, EIS measurements were carried out at equilibrium potential in a broad frequency range at a constant temperature of 298.16 K. Fig. 1 shows Nyquist plots for MS electrode/ electrolyte interface immersed in5.0 M Hydrochloric acid as a corroding medium at 298.16 K with and without *Aloe vera* L. at five different concentrations at the open circuit potential. It is observed from Nyquist plots that the zone of the semicircle increases with the increase in concentration of inhibitor, indicating an increase in corrosion resistance due to adsorption of passive film of inhibitor molecule over the surface of mild steel.

The value of electrode/electrolyte double layer interface capacitance (C_{dl}) was calculated at the frequency, f_{max} using eqn. 6:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{CT}}$$
(6)





where, f_{max} is defined as frequency at which the imaginary component of the double layer impedance is maximum.

The electrochemical impedance data shown in Table-4 indicates that the values of both R_{CT} and PCIE are found to increase with increase in concentration of green corrosion inhibitor, while the values of C_{dl} are found to decrease with increase in concentration of *Aloe vera* L. This decrease in C_{dl} values with increase in concentration of inhibitor may be due to decrease in the dielectric constant or an increase in the thickness of the electric double layer, which further confirms that the inhibitor molecules act by adsorption mechanism at MS/acid double layer interface.

TABLE-4
IMPEDANCE SPECTROSCOPIC DATA LIKE DOUBLE LAYER
CAPACITANCE, C _{dl} , CHARGE TRANSFER RESISTANCE, R _{cl} ,
PCIE FOR MILD STEEL SAMPLES IN 5.0 M HCI SOLUTION
WITH AND WITHOUT Aloe vera L. AS GREEN CORROSION
INHIBITOR AT 298.16 K
WITH AND WITHOUT Aloe vera L. AS GREEN CORROSION INHIBITOR AT 298.16 K

Conc. (g/L)	$Cdl (\times 10^{-3} F cm^2)$	Rct (ω cm ²)	PCIE (%)
0.0	208	8.76	-
4.0	23.67	35.24	75.14
2.0	44.11	27.86	68.55
1.0	67.54	19.21	54.39
0.5	87.24	17.43	45.13
0.1	104.23	11.24	22.06

Metallurgical research microscopy technique: Fig. 2 show trinocular inverted metullurgical research microscopy micrographs of different mild steel coupons in presence and absence of *Aloe vera* L. as green corrosion inhibitor at five different concentrations. It is also clear from Fig. 2 that surface of mild steel coupons becomes more and more smother with



Fig. 2. Trinocular inverted metullurgical research micrographs of mild steel samples with and without Aloe vera L. as green corrosion inhibitor at different concentrations increase in concentration of Aloe vera L. Cracks and pits are noticeable in blank mild steel coupons but there are no cracks or pits are visible in mild steel coupons treated with 4.0, 2.0, 1.0 and 0.5 g/L of Aloe vera L. However, slight uniform type of corrosion was observed in mild steel coupons treated with 0.1 g/L of Aloe vera L.

Aloe vera L. (0.5 g/L)

Table-5 shows the coating thickness, percentage porosity and pits pore length of mild steel coupons in presence and in absence of green corrosion inhibitor. It is found that coating thickness of film adsorbed over the surface of mild steel increases with increase in concentration of green corrosion inhibitor. It is also observed from Table-5 that the values of percentage porosity decrease with increase in concentration of Aloe vera L.

Scanning electron microscopy studies: Fig. 3 shows SEM image of mild steel coupons after exposure to corroding medium (3.0 h) in 5 M hydrochloric acid medium in presence and absence of 4.0, 2.0 and 0.1 g/L of Aloe vera L. It is clear from the SEM image that surface of mild steel coupons is not smooth in absence of green corrosion inhibitor and a smooth surface was observed in presence of green corrosion inhibitor. This proves that the Aloe vera L. acts as good green corrosion

Aloe vera L. (0.1 g/L)

Name of sample	Coating thickness (µ)	Porosity (%)	Pore length (μ)
Blank	48.764	77.27	577.397
			645.23
Aloe vera 4.0 g/L	679.136	14.37	68.320
			40.255
Aloe vera 2.0 g/L	527.910	22.29	67.247
			63.158
Aloe vera 1.0 g/L	342.233	27.46	67.092
			64.245
Aloe vera 0.5 g/L	296.969	29.43	60.583
			60.125
Aloe vera 0.2 g/L	162.547	41.57	65.155
			59.137
Aloe vera 0.1 g/L	130.457	77.28	98.324
			61.940

inhibitor and slows down the corrosion rate of mild steel through physical adsorption of inhibitor molecules on mild steel surface.



Blank 500 magnification (5.0 M HCl)

Blank 100 magnification (5.0 M HCl)



Aloe vera 4.0 g/L

Aloe vera 1.0 g/L

Aloe vera 0.1 g/L

Fig. 3. SEM images of mild steel samples with and without green corrosion inhibitors at different concentrations

Conclusion

The corrosion characteristics of Aloe vera L. as green corrosion inhibitor was investigated on mild steel in 5 M HCl solution as corroding medium. It is observed that percentage corrosion inhibition efficiency (PCIE) increases with increase in concentration of the green corrosion inhibitor. Potentiodynamic polarization measurement shows that Aloe vera L. acts as a mixed type green corrosion inhibitor. EIS measurement revealed that charge transfer resistance increases with increase in concentration of Aloe vera L. indicating that the inhibition increases with increase in concentrations of green corrosion inhibitor. SEM studies confirmed that the corrosion protection provided to mild steel is due to adsorption of the inhibitor molecule over the surface. Metallurgical research microscopy image revealed that coating thickness increases and percentage porosity decreases with increase in concentration of Aloe vera L. More than 97 % corrosion inhibition efficiency was observed for mild steel by 4.0 g/L of Aloe vera L. in 5.0 M HCl solution at room temperature.

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