2016-01-15

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Investigation of *Aloe lateritia* Gel as Corrosion Inhibitor for Mild Steel in 2 M HNO$_3$ and 1 M H$_2$SO$_4$ Media

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Abstract

Corrsion inhibition of *Aloe lateritia* gel for Mild steel in 2 M HNO$_3$ and 1 M H$_2$SO$_4$ solutions was investigated by potentiodynamic polarization, Scanning electron microscopy (SEM) and Foutier transform infrared (FT-IR). Inhibition efficiency increased with the increase of the concentration of the gel. The optimal concentration of the gel gives maximum inhibition efficiency of 77.4% and 70.3% in 1 M H$_2$SO$_4$ and 2 M HNO$_3$ respectively. Polarization plots shows that, the gel works as a mixed type inhibitor altering both cathodic and anodic reaction. SEM proves the uniform and pitting corrosion at the surface of Mild steel in 1 M H$_2$SO$_4$ and 2 M HNO$_3$ respectively. Using FT-IR potential function groups from pure gel and some stretch shift was observed from corrosion product and some stretch shift from corrosion products was observed.

Keywords

Corrosion Inhibitor, Mild Steel, Potentiodynamic Polarization, Sulfuric Acid, Nitric Acid

1. Introduction

Mild steel is popular in the construction of different structures like pipelines, thermal chemical reactor and cooling system, since it is excellent in performance, highly recyclable, high life span, strength as well as more ductile [1].

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Corrosion is the catastrophic deterioration of material's properties due to electrochemical reaction caused by potential differences between the oxidant (corrosive medium) and reductant (metals). The external energy absorbed by the metal during their extraction is the driving forces to return to their stable oxidation state (ores) by corrosion, since always exist in the temporary unstable state.

Mild steel suffers from corrosion when exposed acidic medium. For this study 2 M HNO_3 and 1 M H_2SO_4 is going to be used as the corrosion medium. Nitric acid participates during corrosion by cathodic reactions:

$$H^+ + \overline{e} \leftrightarrow H \tag{1}$$

$$HNO_3 + H^- \leftrightarrow NO_2 + H_2O \tag{2}$$

$$NO_2 + \overline{e} \leftrightarrow NO_2^- \tag{3}$$

$$H^+ + NO_2^- \leftrightarrow HNO_2 \tag{4}$$

$$HNO_2 + H \leftrightarrow NO + H_2O \tag{5}$$

Interaction between nitrous acid (HNO_2) from Equation (4) and nitric acid (HNO_3) produces nitrogen dioxide (NO_2).

$$HNO_2 + HNO_3 \leftrightarrow 2NO_2 \tag{6}$$

Finally the cathodic reaction becomes autocatalytic, where NO_2 combine with ammonium (NH_3) to produce ammonium salt (NH_4NO_2) and (NH_4NO_3) which finally decomposes to give nitrogen gas (N_2 (g)) and nitrogen oxides. These products are accompanied by brown gas evolution.

$$NH_4NO_2 \leftrightarrow N_2 + 2H_2O \tag{7}$$

$$NH_4NO_3 \leftrightarrow N_2O + 2H_2O \tag{8}$$

As reported by [2].

Sulphuric acid is the most used chemicals in almost every industry like in petroleum production, fertilizer manufacture, paint production, metal pickling and extraction of non-metals [3].

Major challenge with acid like H_2SO_4 and HNO_3 they accelerate corrosion in several equipments, so there is a need to be inhibited. There are several methods has been used to control and prevent corrosion. However, use of corrosion inhibitor is more effective, especially in corrosion enhanced by acid. Inhibitor performs well due to ability to create a barrier for interaction between the materials and the medium. This is due to presence of electrons rich functional groups and atom like Oxygen (O), Sulpher (S), Nitrogen (N) and the multiple bonds in their conjugate system [4].

Synthetic corrosion inhibitors used for several years have been reported to be unfriendly to the environment; therefore, searching for green ones is inevitable. Compounds from plants recently have been recognized to be the best eco-friendly inhibitors [5]-[8].

This study intends to investigate the insight about corrosion of Mild steel in 1 M H_2SO_4 and 2 M HNO_3 in presence of *Aloe lateritia* gel. The use of *Aloe lateritia* gels as corrosion inhibitor has been hardly reported. The inhibitory effect of these naturally occurring plant gels on corrosion of Mild steel in 1M H_2SO_4 and 2 M HNO_3 was investigated by potentiodynamic polarization. Additionally, surface analysis was obtained from SEM. FT-IR was used to identify functional groups from the gels and that of corrosion products from metals which were inhibited.

Potentiodynamic polarization was used to control the electrochemical reaction of corrosion by monitoring Anodic and Cathodic reactions:

$$Fe \leftrightarrow Fe^{2+} + 2\overline{e} \tag{9}$$

$$2H + 2\overline{e} \leftrightarrow H_2 \tag{10}$$

This is useful to determine the corrosion rate, passivation especially the region where metal is active and noble. It helps to determine pitting tendency of metal during corrosion reaction. The overall reaction produces the anodic current, for uninhibited system produces more current as compared to inhibited; due to high dissolution of metal. The expression below in Equation (11) uses the current to determine the inhibition efficiency when inhibitor is used [9].

$$\% \text{ IE} = \frac{i_{corr}^{o} - i_{corr}}{i_{corr}^{o}} \times 100 \qquad (11)$$

where %IE is inhibition efficiency, i_{corr}^{o} and i_{corr} are corrosion current densities of unhibited and inhibited solutions respectively.

To determine extend of corrosion, SEM was used to monitor the level of deterioration of the metal surface. Inhibited metal expected to have a smooth surface comparatively with uninhibited; this is due to fact that inhibitor prevents interaction of the metal and the surrounding medium [10]. FT-IR was used to determine function groups of the inhibitor before and after being applied therefore, obtained corrosion product has comparable functional groups to that of inhibitor; this is along with that reported by [11].

2. Materials and Methods

2.1. Sample Preparation

2 M HNO_3 and 1 M H_2SO_4 was prepared by diluting 69% HNO_3 and 98% H_2SO_4 with distilled water as corrosive medium. Plant inhibitor *Aloe lateritia* gel was obtained from the western part of Kahama district at Wendere village, Tanzania. The gel was obtained by cutting the leaves and squeezing, then filtering through the mesh of cloth to get pure gel. About 1 kg of fresh leaves was used to obtain 2 Litters of gel. It was kept cool in a refrigerator prior to testing this is, in similar to what reported by [12]. Concentration of inhibitors: (0%, 3.2%, 6.3%, 9.1%, 11.8%, 14.3% v/v) was used at room temperature.

Mild steel with following composition was used: C—0.15, Mn—1.26, V—0.017, Si—0.035, S—0.008, Cr—0.036, Ni—0.03, Al—0.083, Cu—0.038 and the remainder is Fe. The metal was cut into 2 cm×1 cm as working electrode for electrochemical measurements. The surface of metal was pre-cleaned using silicon carbide paper; it was made to silver mirror by cleaning using diamond paste. Finally, by using acetone and distilled water in an utrasonicator bath was washed and rinsed then stored for use.

2.2. Potentiodynamic Polarization

The experiment was performed in a conversational cell with three electrodes connected to a potentiostat (PGSTAT 302N). Mild steel was used as working electrode in 2 M HNO_3 and 1 M H_2SO_4 corrosive medium. Platinum wire, saturated calomel electrode was used as a counter and reference electrodes respectively. The plots used to obtain the tafel curve were done by changing the potential from −250 to +250 mV at scan rate of 1mV·s^{-1} against open circuit potential.

2.3. SEM for Surface Morphology Analysis

The surface of Mild steel exposed to uninhibited 2 M HNO_3 and 1 M H_2SO_4 and to that containing optimal concentration of inhibitor, was examined by Field Scanning Electron Microscope (FE-SEM, Hilachi, S-4700). Before exposing to SEM the metal was cleaned thoroughly to remove the oxide layer and after 24 hours prior-o to measurement was washed using running distilled water and dried. Corrosion products were obtained by removing the oxide surface of the metal using the utrasonicator, and then were submitted for measurement.

2.4. FTIR for Functional Group Identification

The inhibitor gels and the corrosion products were subjected to Varian 660-IR for the determination of appropriate functional groups available. Few drops of *Aloe lateritia* gel and the corrosion products obtained after 24 hours of metal corrosion in optimal inhibitor were subjected to FTIR measurements.

3. Results and Discussion

3.1. Potentiodynamic Polarization

It was used to obtain polarization curves for the Mild steel in 2 M HNO_3 and 1 M H_2SO_4 with and without the addition of *Aloe lateritia* gel.

The plots from **Figure 1** and **Figure 2** reveal that Tafel plot was obeyed by anodic and cathodic reactions. The linear part of the Tafel plots were extrapolated, at the point of intersection is where corrosion potential (E_{corr})
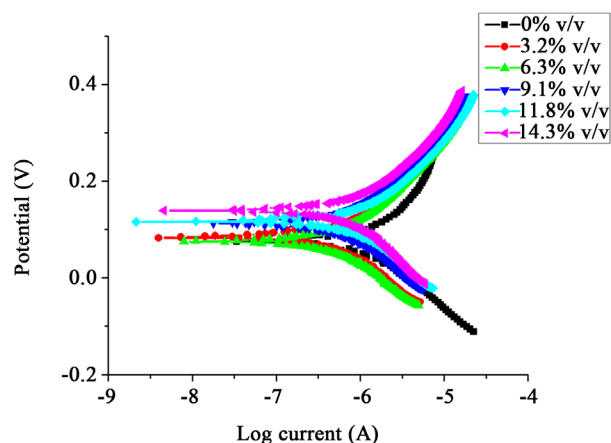
Figure 1. Polarization curves of mild steel in 2 M HNO$_3$ in presence with different concentration of *Aloe lateritia* gel.
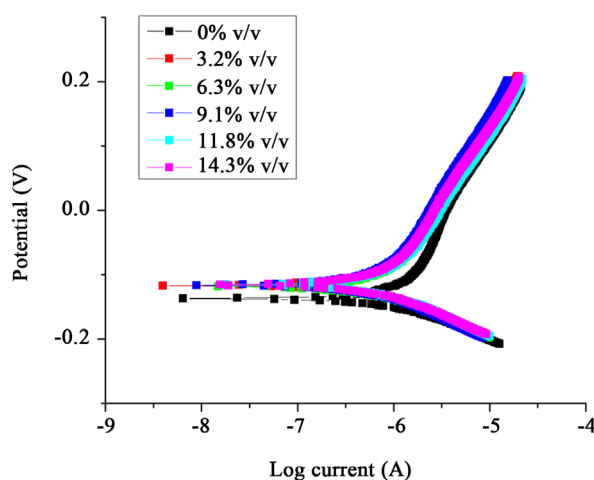

Figure 2. Polarization curves of mild steel in 1 M H$_2$SO$_4$ with different concentration of *Aloe lateritia* gels.

and corrosion current density *(i$_{corr}$)* were obtained.

Related parameters like Cathodic Tafel slope (β_c), anodic Tafel slope (β_a), corrosion current density (*i$_{corr}$*) and corrosion potential (*E$_{corr}$*) were calculated and results are tablated in **Table 1**.

An increase in the concentration of inhibitor resulted in the following:

There is equal shift for the potential toward more negative and positive relating to cathodic and anodic respectively; this indicates that reaction mechanism was the same. From **Table 1** it is observed that there is a decrease of corrosion current density (*i$_{corr}$*) contrary to inhibitor concentration. This is attributed by the ability of inhibitor to prevent interaction between metal and the corrosive medium which leads to corrosion. Although, the corrosion current density (*i$_{corr}$*) decrease as inhibitor's concentration increases; no remarkable shift of corrosion potential (*E$_{corr}$*) was observed. This is to say a mixed type inhibition for both anodic and cathodic reactions took place, the observation is associated with that reported by [13].

Inhibition efficiency (%IE) was obtained by Equation (11) when the concentration of inhibitor increased %IE increases too. From **Table 1** at 14.3% v/v of inhibitor %IE reached maximum 77.4% for 1M H$_2$SO$_4$ while for 2M HNO$_3$%IE increased with concentration of inhibitor up to 11.8%v/v which attained 70.3%, then started to decrease as concentration increased. So the inhibitor performs better with H$_2$SO$_4$ than HNO$_3$.

3.2. Surface Morphology

Mild steel was exposed to 1M H$_2$SO$_4$ and 2M HNO$_3$ medium in the absence and presence of optimal amount

Aloe lateritia gel for 24 hours at room temperature. Their morphology was determined by SEM, the results from **Figure 3(a)** and **Figure 3(c)** verifies that the steel more corroded as the surface was more rough in blank medium. However, **Figure 3(b)** and **Figure 3(d)** is for the steel which was exposed in a corrosive medium with optimal concentrations of inhibitor.

The presence of inhibitor reduced the extent of corrosion, the surface become smoother compared to the uninhibited. This reveals the performance of inhibitor by protective layer formation; which separates the interaction between the metal and corrosive medium similar behavior observed by [14]. From **Figure 3(a)** and **Figure 3(c)** the metal exposed to blank 1 M H_2SO_4 and 2 M HNO_3 displayed uniform and pitting corrosion respectively.

3.3. FT-IR Analysis

For determination of the functional groups few drops of *Aloe lateritia* gel and that of corrosion products was used. The results were displayed for FT-IR spectrum as shown in **Figure 4**.

Aloe lateritia gel and that of corrosion product was exposed to IR spectrum and the results are shown in **Figure 4(a)** and **Figure 4(b)**. The stretch for O-H which was around 3339.60 cm^{-1} was shifted to 3360.29 cm^{-1}, from 1635.49 cm^{-1} to 1641.08 cm^{-1} for C=C when the pure inhibitor gel and corrosion product respectively. The presence of stretch at 551.87 cm^{-1} indicates presence of γ-Fe_2O_3 this verifies the interaction between the inhibitor and the metal surface was also observed as shown in **Table 2** [15].

Table 1. Potentiodynamic polarization parameters for Mild steel in 2 M HNO_3 and 1 M H_2SO_4.

Acid medium	Extract concentration (%v/v)	E_{corr} (Mv/SCE)	I_{corr} (μA·cm^{-2})	β_c (mV·dec^{-1})	β_a (mV·dec^{-1})	%IE
	2 M H_2SO_4	−0.1368	3.25×10^{-06}	−1.3363	0.1252	-
	3.2	−0.1170	1.84×10^{-06}	−1.1848	0.1106	43.3
H_2SO_4	6.3	−0.1183	9.74×10^{-07}	0.2715	0.0855	70.1
	9.1	−0.1161	8.64×10^{-07}	0.2811	0.0881	73.4
	11.8	−0.1158	9.00×10^{-07}	0.2359	0.0809	72.3
	14.3	−0.1161	7.35×10^{-07}	0.0679	0.2340	77.4
	1 M HNO_3	0.0745	2.38×10^{-06}	0.3903	0.22058	-
	3.2	0.0831	8.38×10^{-07}	0.1948	0.21413	64.8
	6.3	0.0746	7.69×10^{-07}	0.1965	0.20044	67.7
HNO_3	9.1	0.1124	7.30×10^{-07}	0.1508	0.17174	69.4
	11.8	0.1156	7.09×10^{-07}	0.1201	0.11627	70.3
	14.3	0.1393	7.27×10^{-07}	0.1353	0.16888	69.5

Table 2. Different frequencies of IR spectrum of corrosion product and pure *Aloe lateritia* gel.

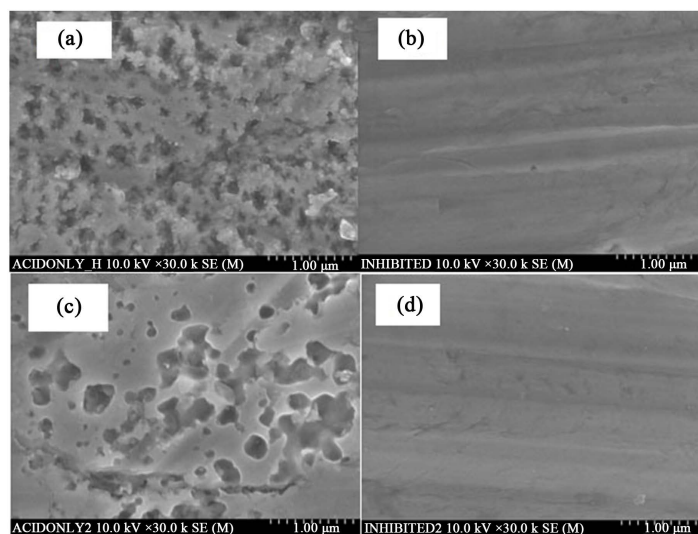| Pure extracts		Corrosion products	
Frequencies (cm^{-1})	Assignment	Frequencies (cm^{-1})	Assignment
3339.60	O-H	3360.29	O-H
1635.49	C=C	1641.08	C=C
2110.25	C≡C	1339.45	C-H rock
1275.68	C-O-C	551.87	γ-Fe_2O_3

Figure 3. SEM micrographs of mild steel surface exposed in (a) 1 M H_2SO_4 solution (b) 1 M H_2SO_4 with 14.3 (%v/v) *Aloe lateritia* gel; (c) 2 M HNO_3 solution and (d) 2 M HNO_3 with 11.8 (%v/v) *Aloe lateritia* gel at room temperature for 24 hours.
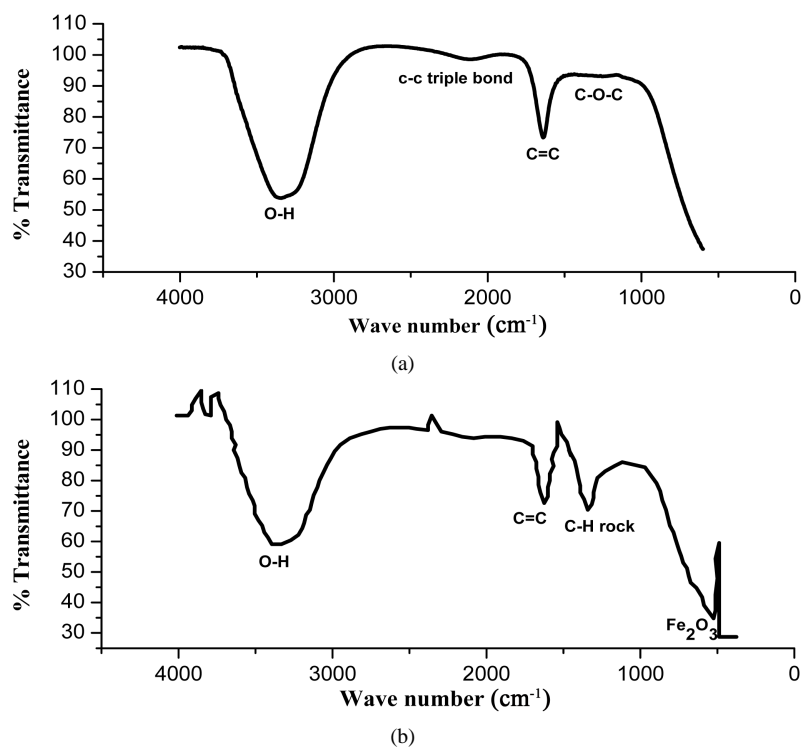

Figure 4. FT-IR spectrum for the (a) pure *Aloe lateritia* gel and (b) corrsion products respectively.

4. Conclusion

The inhibitor gel was observed to perform well on both H_2SO_4 and HNO_3 medium. Inhibition efficiencies were observed to rise with a concentration of inhibitor. Maximum efficiencies of 77.4% at 14.3% v/v for 1 M H_2SO_4 and 70.3% at 11.8% v/v for 2 M HNO_3 were noticed. Mixed type of inhibition was revealed since no remarkable shift of E_{corr}. SEM images revealed effective performance of inhibitor since inhibited metal appeared to be smoother than uninhibited. FT-IR information's proved the interaction between inhibitor and metal surfaces. Additionally the functional groups stretch shift and decrease of I_{corr} proves the film formation and lowering met-

al dissolution.

Acknowledgements

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