

RESEARCH ARTICLE

Investigating the effect of aloe-vera extract on the corrosion inhibition of medium carbon steel in seawater

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Abstract

Corrosion is said to be a function of the material and the environment. If that is the case, it is possible that corrosion inhibitor efficiency could also be a function of the material and the environment. Aloe vera extract has been used as an inhibitor in different environments and materials, this work however focuses on the effect of aloe vera extract on 0.39%C steel in seawater. Aloe vera extracts of 1%, 2%, 3%, and 4% concentrations were obtained from 2kg of aloe vera plant and added to the corrosive media. They were exposed for a period of 1008th hours. Samples were retrieved from the environment at an interval of 168th hours. The gravimetric and the potentiodynamic method was used for the analysis. To better understand the mode of the inhibitor absorption, the experimental data were fitted into the Langmuir, Temkin, and Freundlich isotherm. The results from the gravimetric study show that there was an increase in the inhibitor efficiency as the concentration of the extracts increased but decreased with prolonged exposure time. The extract was found to be more effective in seawater at 4% concentration with 85% inhibitor efficiency at the 168th hour. The potentiodynamic results also affirmed that the sample with 4% aloe vera addition had the highest efficiency with about 97%. The graph showed a shift at both the anodic and cathodic slopes, but the inhibitor was observed to act more as an anodic inhibitor. The values obtained from the absorption isotherm show that the aloe vera molecules were weakly bonded to the substrate suggesting physisorption. The absorption pattern was found to be more fitted to the Freundlich and Temkin isotherm. The result, therefore, shows that aloe vera can act as an inhibitor to 0.39%C steel in seawater.

1. Introduction

Corrosion is a natural and unavoidable process. Considering the adverse effect that arises as a result of corrosion, there is a constant need to study corrosion and how it can be controlled so that metals can perform their required tasks. For most parts, corrosion is a gradual and unspectacular process when compared to other natural processes like earthquakes, tornadoes, floods, and volcanic eruptions [1].

For years, reports have been done on the corrosion of carbon steel and its alloys in seawater [2]. The use of inhibitors has been discovered to be one of the most effective methods of corrosion protection especially in a hostile environment like seawater [3]. Synthetic compounds show good corrosion inhibition ability. They, however, possess toxic substances. The adverse effect of synthetic inhibitors has generated the need for research to be done on finding alternative natural occurring, inexpensive, environmentally friendly, and renewable sources of materials [4, 5]. Plants have been found to possess compounds with some of them having complex molecular structures with varied chemical, biological and physical properties [6]. Plant extracts are regarded as a very rich source of naturally synthesized chemical compounds that can be extracted by using simple procedures which are inexpensive and environmentally friendly.

Several plant extracts apart from aloe vera extract have been used as inhibitors. Curcumin, for instance, was used as an inhibitor for α -brass in 2M nitric acid solutions [7]. Research conducted on the twigs, stems, and leaves of tobacco shows that

they can effectively protect steel and aluminum in strong pickling acids and saline solutions [8]. Yang et al also investigated the effectiveness of garlic as an inhibitor of mild steel in acidic media [9]. Aqueous extracts of eucalyptus leaves were found to protect mild steel and copper in IM of HCl solution from corrosion [10].

Aloe vera, commonly known as *barbadensis miller* is a juicy plant species of the genus aloe. It belongs to Asphodelaceae (Liliaceae) family. It is a shrubby or arborescent, perennial, xerophytic, succulent, pea-green color plant. There are numerous organic components present in aloe vera. Studies have shown that, apart from aloe vera's nutritional component, it contains polysaccharides, steroids, a polygol, organic acids, and essential elements, such as nitrogen, tannins, and antibiotics. The tannin from aloe vera has been revealed to be adsorbed on the surface of metals, blocking the active sites on the surface, and thereby reducing the rate at which corrosion occurs on the metal. [11].

The inhibitive performance reported in most of these plant extracts including aloe vera is a result of a surface specie possessed by most of these plant extracts which helps in the creation of film over the metallic surface. This creates a barrier between the environment and the metal which prevents corrosion from taking place. The chemical buildup of most of the extracted compounds is a long-chain hydrocarbon in molecules that bear polar groups which mostly contain heteroatoms like nitrogen, oxygen, or sulfur [12].

Some of the work done on aloe vera include the work done by Sribharathy et al, [13]. They studied the corrosion inhibition of mild steel in seawater using an aqueous extract of aloe vera. Al-Asadi [14] also worked on aloe vera extract in a 1%w NaCl environment and found out that aloe vera was a very efficient inhibitor for mild steel and that it can replace inhibitors that contain toxic chemicals. The effect of acid extract of aloe vera was also carried out by Ndibe et al [15], as an inhibitor for corrosion of mild steel in acidic media. Most of this research on aloe vera as an inhibitor was done in different environments and materials. The few that made use of seawater as the environment worked majorly on mild steel. It has been shown that the corrosion properties of carbon steel vary with chemical composition. This is a result of the unique difference in the microstructure. Research shows that the carbide phase becomes the cathode while the ferrite phase the anode [2,16]. It is therefore possible that the effect of a particular inhibitor on various compositions of carbon steel could also vary. This work focuses on the effect of aloe vera extract on 0.39%C steel (medium carbon steel) in seawater in order to characterize the effect aloe vera as an inhibitor, has on this particular steel.

2. Materials and Methods

2.1 Material Preparation

Steel samples used for this study were obtained from the Warri refining and petrochemical company (WRPC) workshop, a subsidiary of Nigeria National Petroleum Company. (NNPC). Each sample, which was 5mm in thickness, was cut into a rectangular coupon size of 25mm x 30mm. These coupons were washed with distilled water, degreased in absolute ethanol, and dried (ASTM 1990). The samples were then weighed with a digital compact scale. For easy suspension in a corrosive media, a 4mm hole was drilled into each sample. The composition of the medium carbon steel used in the experiment is shown in Table 1. The composition of the medium carbon steel was carried out by using an X-ray Fluorescence spark spectrometer analyzer (NCS labspark 700B) at the quality control laboratory of a universal steel company in Lagos Nigeria.

Table 1. Chemical composition of 0.39%C medium carbon steel

Elements	% Composition
C	0.39
Si	0.20
Mn	0.68
P	0.02
S	0.03
Cr	0.94
Mo	0.84
Ni	0.19
Cu	0.09
Fe	96.62

2.2 Plant extract Preparation

About 2kg of fresh aloe vera leaves were used for this experiment. Aloe schweinfurthii Baker with herbarium number FPI 2175 was used for the experiment. The aloe vera was obtained from the Federal University of Petroleum Resources Effurun, Delta State Nigeria. The fresh aloe vera leaf was cut into an electric blender, blended, and filtered through cheesecloth. The aloe vera extract of different concentrations

(0%, 1%, 2%, 3% and 4%) were then introduced into the corrosion media.

2.3 Corrosive Media Preparation

The corrosive media used in this study is natural seawater, which was gotten from the Atlantic Ocean, near the off-shore operation base of Chevron Nigeria Limited in Warri, Delta State Nigeria. The dissolved oxygen was done immediately in the laboratory using the Winkler method [17]. The other ionic specie were analyzed by using the ion chromatographic method [18].

Table 2: Chemical analysis of water (sea water) sample used for this research

Ions species in water sample	Seawater(mg/l)
Ca ²⁺	3.53
Mg ²⁺	3.22
CO ₂	0.30
Fe ²⁺	0.0014
Cl ⁻	54.37
O ²⁻	0.55
SO ₄ ²⁻	3.00
Na ⁺	30.00
HCO ₃ ⁻	5.23
NO ₃ ⁻	0.001

2.4 Corrosion Rate Measurement

The test coupons were immersed totally in 100ml of seawater containing different concentrations of aloe vera extract at room temperature. The experiment was conducted in an aerated and unstirred solution. At every seven days intervals, specimens were retrieved, rinse in acetone, scrubbed with a bristle brush, washed, dried, reweighed and the values recorded. The inhibitor efficiency was also calculated and recorded.

The corrosion penetration rate (mm/yr) was computed by using equation 1[19, 20].

$$CPR \left(\frac{mm}{yr} \right) = \frac{KW}{\rho At} \quad (1)$$

Where;

mm/yr is millimeter penetration per year, ρ is the density of the metal in g/cm³, t is time in hours, A is the cross-sectional area in cm², W= weight loss in milligrams, K= 87.6

The inhibitor efficiency (I.E) was calculated by using equation 2 while the surface coverage was calculated using equation 3 [21].

$$I.E = \frac{W_0 - W_1}{W_1} \times 100 \quad (2)$$

$$\theta = \frac{(W_0 - W_1)}{W_0} \quad (3)$$

Where;

I.E is Inhibitor efficiency (%), θ is surface coverage, W₀ is weight loss in the absence of inhibitor, W₁ is weight loss in the presence of inhibitor

2.5 Potentiodynamic Polarization Technique

To prevent corrosion attacks on the surface, one side of each specimen with a known surface area was coated with an epoxy-insulating material. The measurements were done with Autolab

Potentiostat. The reference electrode used was silver/silver chloride and the counter electrode was platinum. The working electrode was the medium carbon steel sample. Prepared surfaces of mounted steel samples were immersed in the corrosion cell which contained 100ml of seawater, starting with blank (0% of aloe vera extract) and various concentrations of the additive added to the seawater environment. The specimens were scanned with Versastat equipment in potentiostatic mode at ± 0.5 V, and at a rate of 1.0mV/s.



Figure 1. The weight loss method.

To obtain the corrosion potential (E_{corr}) and corrosion current density (i_{corr}), the anodic and cathodic curves in the linear Tafel plot were extrapolated. The rate of corrosion (in mm/yr) was determined using equation 4. [19].

$$CR = K_1 \frac{i_{corr}}{\rho} EW \quad (4)$$

Where;

CR is corrosion rate in mm/yr, i_{corr} in μA , EW is Equivalent weight of steel (value =27.9), ρ is density (7.86) and $K_1=3.27 \times 10^{-3}$ mg/ μA cm μ yr.

Also, values for the efficiency of the inhibitor and surface coverage were determined using the equations 5 and 6 [19].

$$\eta_p(\%) = \left(\frac{i_{corr} - i_{corr(inh)}}{i_{corr}} \right) \times 100 \quad (5)$$

$$\theta = \left(\frac{i_{corr} - i_{corr(inh)}}{i_{corr}} \right) \quad (6)$$

Where;

i_{corr} is corrosion current density without inhibitor, $i_{corr(inh)}$ is corrosion current density with inhibitor and θ is surface coverage.

2.6 Adsorption Isotherm

The langmuir, frendlich and Temkin isotherms were employed in order to obtain more insight about the iteface between the 0.39%C steel surface and the inhibitor. To adjudge the model that best fit the experimental values obtained, the linear regression coefficient of determination (R^2) was used.

2.6.1 Langmuir Adsorption isotherm

This is based on the fact that the reactive groups are homogeneously distributed over the surface of the particulate and that there is no lateral interaction. The Langmuir relationship is shown in equation 7 [22].

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (7)$$

Where;

K is , the equilibrium constant of adsorption, C is the inhibitor concentration, θ is the degree of surface coverage

2.6.2. Temkin Isotherm

Temkin isotherm relationship is shown in equation 8. [22].

$$\theta = \frac{1}{f} \ln C + \frac{1}{f} \ln K \quad (8)$$

Where;

θ is the degree of surface coverage, K is the equilibrium constant of adsorption (L/g), C is the inhibitor concentration (g/l) and $1/f$ is the constant related to the heat of sorption (J/mol).

$$f = C/RT \quad (9)$$

Where;

R is gas constant (8.314J/mol), T is the temperature at 301 $^{\circ}$ F.

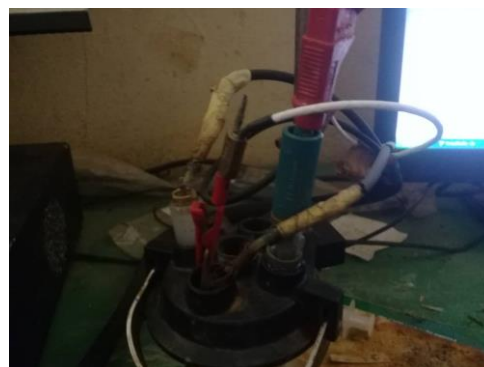


Figure 2. The Potentiodynamic polarization experimental set up.

2.7.3 Freundlich Isotherm

The Freundlich isotherm is usually used to describe the adsorption characteristics of heterogeneous surfaces. It is expressed in equation 10 as

$$\theta = KC^n \quad (10)$$

Equation 10 was further simplified to give equation 11 [22].

$$\ln \theta = \ln K + n \ln C \quad (11)$$

Where;

θ is the surface coverage, C is the inhibitor concentration (g/l) and n is a physical constant known as the Freundlich component which is the intensity of the adsorption process on the medium carbon steel surface.

The standard Gibb’s free energy of adsorption ΔG^0_{ads} (kJ/mol) at temperature 28°C was obtained from equation 12 [22].

$$\Delta G^0_{ads} = -RT \ln(55.5K) \quad (12)$$

3. Results and Discussion

3.1 Corrosion Rate and Inhibition Efficiency Results

The corrosion rate in the uninhibited sample in Figure 3 and Table 3 was found to be higher than in the uninhibited sample. The highest corrosion rate for the uninhibited sample was found to be at the 168th hour of sample exposure to seawater. After that, there was a gradual decrease in the corrosion rate. This could be a result of the corrosion product acting as a protective barrier [20]. The results from the gravimetric study show that the inhibitor efficiency increased as the concentration of extracts increased, but decreased with prolonged exposure time. The aloe vera in the inhibited samples resulted in a gradual decrease from the 168th to 336th hours of exposure. The sample with the 4% aloe vera additions had the lowest corrosion rate at the 168th hour. The reason for this could be that there is a higher degree of inhibitor adsorption at the metal/solution boundary for the 4% aloe vera addition sample as compared to others. Corrosion rate at 336th to 504th hours of exposure to seawater showed no steady pattern in the corrosion rate for the inhibited sample. According to Sriharathy et al [13], the reason for this behavior could be attributed to the Fe²⁺-mannose-6-phosphate complex that is formed on the metal surface, going into the solution and destroying the protective film. The sample with 4% inhibition of aloe vera however started maintaining a gradual decrease in the corrosion rate after the 504th hour of exposure. This could be a result of further adsorption of the aloe vera extract.

Table 3. Corrosion rate of 0.39%C steel with aloe vera additions in seawater (mm/yr)

Exposure Time (hrs)	Aloe Vera Additions				
	Blank	1%	2%	3%	4%
168	0.1759	0.0713	0.1007	0.1094	0.0265
336	0.1772	0.0663	0.0610	0.0984	0.0844
504	0.1130	0.0937	0.0639	0.0472	0.0884
672	0.0983	0.0775	0.0381	0.0407	0.0534
840	0.1098	0.0964	0.0518	0.0556	0.0491
1008	0.0880	0.0796	0.0365	0.0505	0.0281

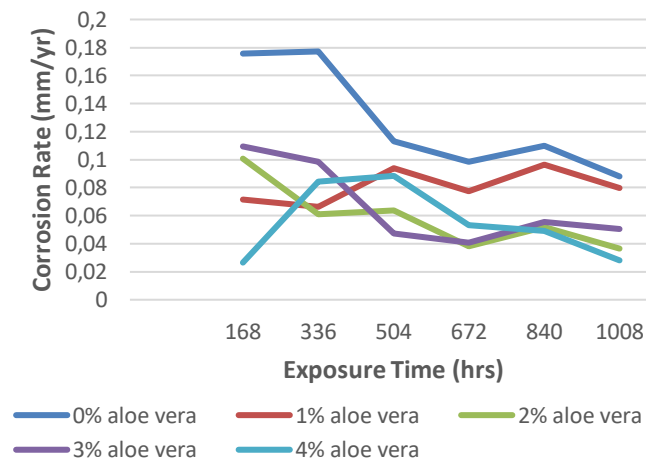


Figure 3. Corrosion rate of 0.39%C steel with aloe vera additions in seawater

Table 4. Inhibitor efficiency of 0.39%C steel with aloe vera additions in seawater (%)

Exposure Time (hrs)	Inhibitor Efficiency			
	1%	2%	3%	4%
168	59.47	42.75	37.81	84.95
336	14.12	20.98	44.47	52.37
504	17.08	43.45	58.23	21.78
672	21.16	61.24	58.60	45.72
840	12.20	52.82	49.36	55.28
1008	09.55	58.52	42.61	68.07

Figure 4 and Table 4 show that the inhibitor efficiency increased with increased inhibitor. The highest inhibitor efficiency of 85% was observed at the 168th hour of exposure for samples with 4% aloe vera additions while the lowest inhibitor efficiency of 10% was noticed at the 1008th hour for the sample with 1% of aloe vera additions.

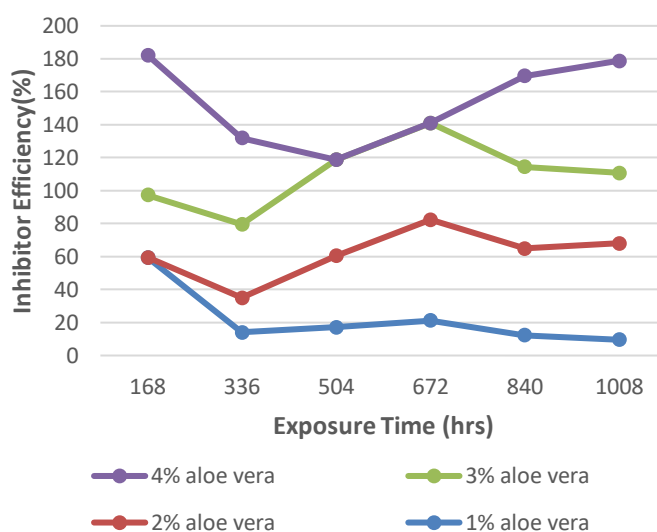


Figure 4. Inhibitor efficiency of 0.39%C steel with aloe vera additions in seawater

3.2 Potentiodynamic Polarization Result

Table 5 and Figure 5a-f show that the initial potential when 0.39%C medium carbon steel was immersed in seawater is 1996mV. With aloe vera additions, the corrosion media, the potential shifted to the less negative potential, but not in an orderly decreasing pattern. These fluctuations in potential could be a result of the competing effect between anodic and cathodic inhibiting reactions [24, 25]. The anodic and cathodic Tafel slopes were observed to shift in the presence of the inhibitor. However, from the graph, it is clear that the shift is more to the anodic side. The cathodic slope appears to fluctuate significantly and as seen in the graph it appears there is no uniform pattern in the slope. The non-uniform pattern seen in the graph could explain the high values of the cathodic slope. Though there is no uniform pattern in both slopes, the anodic slope tends to have closer values and as such, it can be inferred that the inhibitor behaves more as an anodic inhibitor. This is in agreement with the reasoning of Kumar et al and Malomo et al [24, 25] on what makes an inhibitor a mixed inhibitor. They observed that an inhibitor can be referred to as a mixed inhibitor if the cathodic and anodic slopes do not show any increase or decrease in a definable manner. There was also no clear pattern

in the corrosion density and ask such there was no uniform decrease in the corrosion rate. The result is in agreement with the gravimetric result since there appears to be no clear pattern in the corrosion rate until about the 504th hour when a steady reduction in the result was observed for the sample with a 4% addition. Both methods also confirm the fact that the sample

with 4% aloe vera addition had the lowest corrosion rate and corrosion was also observed to reduce with an increase in the inhibitor percentage. This behavior could probably be attributed to the instability of the Fe²⁺-mannose-6-phosphate complex film [13].

Table 5. Potentiodynamic Polarization values

Conc. of aloe vera (%)	E _{corr} (mV)	bc (mV dec ⁻¹)	ba (mVdec ⁻¹)	j _{corr} (μA cm ⁻²)	C.R (mm /yr)	IE (%)	Θ
0	-1996	122.52	296.95	1430	16.6	-	-
1	-750	10.55	14.22	1253	14.55	12.35	0.12
2	-722	-434.77	3.43 x10 ³³	321	3.725	77.56	0.78
3	-871	8.157	196.587	636	7.386	55.5	0.56
4	-681	59.36	694.13	42	0.4896	97.05	0.97

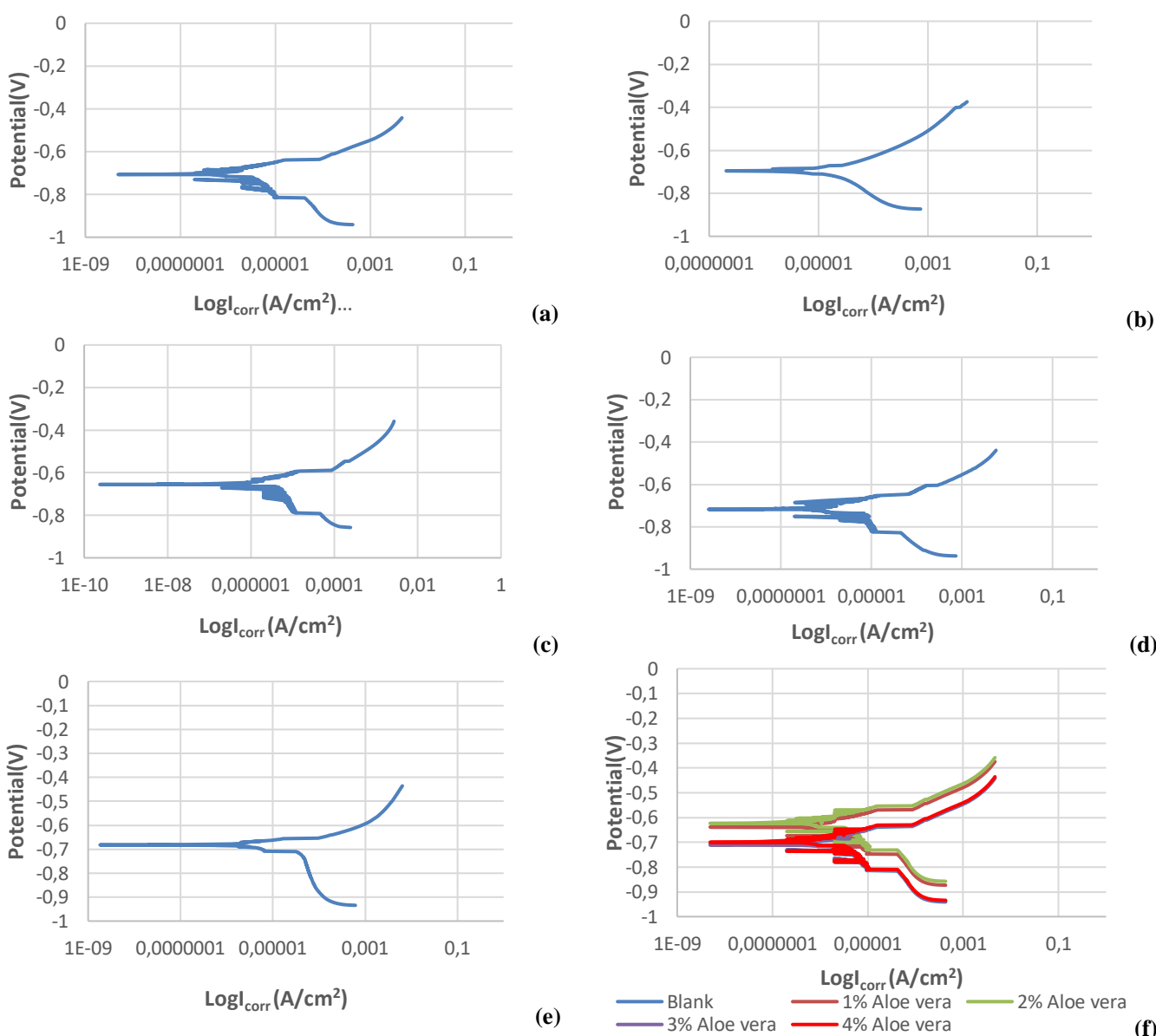


Figure 5. Tafel Plot for: (a).blank sample without inhibitor (b).1% aloe vera addition (c). 2% aloe vera addition (d) 3% aloe vera addition.(e). 4% aloe vera addition and f).A combination of blank sample without inhibitor and the samples at different aloe vera addition

3.3 Adsorption isotherm

3.3.1 Langmuir Isotherm

A plot of C/θ was used to determine if the experimental values fit the langmuir relationship. Figure 5 shows that the plot deviates from being linear as seen in the R^2 values (0.2702). The slope is close to unity showing that the molecules adsorbed do not interact with one another as they are formed in the cathodic and anodic sites of the metal and as such no chemical bonds were formed. This is further explained from the gibbs free energy value (2.51kJmol^{-1}). The positive value shows that the reaction is not spontaneous and very weak bond are formed which signifies physisorption [22, 23]. This explains the fluctuations in the corrosion density values with increase in time.

Table 6. Experimental data used in plotting the adsorption isotherm graph

θ	C(g/l)	lnC	Ln θ
0.12	20	2.995732	-2.12026
0.78	40	3.688879	-0.24846
0.56	60	4.094345	-0.57982
0.97	80	4.382027	-0.03046

3.3.2 Temkin Isotherm

A plot of θ against $\ln C$ shows that the R^2 value was 0.7469 and the constant related to the heat of sorption is 0.5257J/mol . This indicates that the heat of sorption is physical adsorption. According to [23] if the heat of sorption value is less than 1.0 kcal/mol , then physical adsorption occurs. If its value is $20\text{-}50\text{ kcal/mol}$, then chemical adsorption occurs. If the heat of sorption value is in-between ($1 - 20\text{ kcal/mol}$), then both physical and chemical adsorptions are involved in the adsorption. The physical adsorption further confirms the reason behind the fluctuations in the corrosion density values since the aloe vera molecules were weakly bonded to the substrate. The Gibbs free energy is -3.46kJ/mol which suggests physisorption [22].

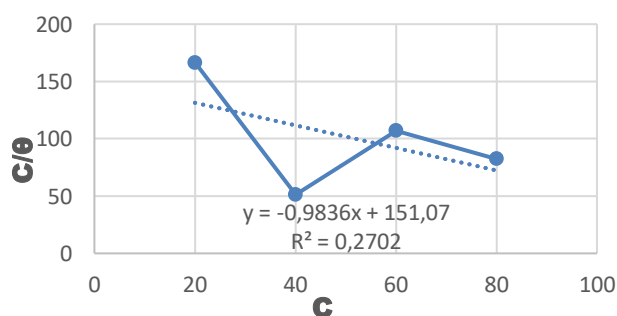


Figure 6. Langmuir Isotherm

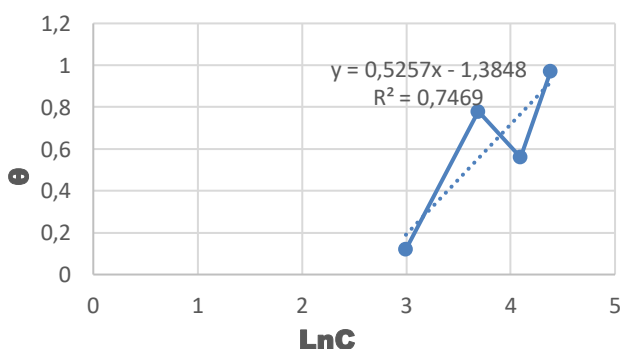


Figure 7. Temkin Isotherm

3.3.3 Freundlich Isotherm

The plot of $\ln\theta$ against $\ln C$ shows that k is 0.00238L/g , n is 1.398 and $1/n$ is 0.715 . The n and $1/n$ value indicates a normal and favorable sorption process. The Freundlich isotherm has the highest R^2 value indicating that the experimental values best fit the Freundlich isotherm [26]. The positive Gibbs free energy value (5.07kJ/mol) also signifies the mode of absorption as physisorption.

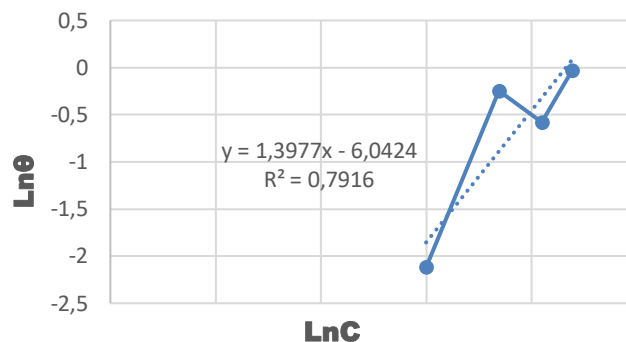


Figure 8. Freundlich Isotherm

Table 7. Absorption Isotherm parameters

Absorption Isotherm	K_{ads} (L/g)	f	n	R^2	ΔG (KJmol^{-1})
Langmuir	0.006619			0.2702	2.51
Temkin	0.071776	1.902226		0.7469	-3.46
Freundlich	0.002376		1.3977	0.7916	5.07

4. Conclusions

The result shows that aloe vera effectively inhibited the corrosion of $0.36\%C$ steel in seawater. The highest corrosion inhibition efficiency was observed in the sample with the 4% aloe vera addition at 168th hours. It had an efficiency of 85% in the gravimetric result. A similar result was also observed with the potentiometer result. The sample with the 4% aloe vera addition was also found to have the lowest current density and the lowest corrosion rate. Aloe vera was also found to behave more as an anodic inhibitor. The values obtained from the absorption isotherm show that the aloe vera molecules were weakly bonded to the substrate suggesting physisorption. The absorption pattern was found to be more fitted to the Freundlich and Temkin isotherm.

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