

Corrosion Inhibitive Performance of the Waste Orange Peels (*Citrus Sinensis*) on A36 Mild Steel in 1M HCl

Ayoola Ayodeji^{1,*}, Durodola Bamidele², Fayomi Sunday^{3,4}, Agboola Oluranti¹, Alagbe Edith¹, Olagoke Oladokun¹, Nnabuko Daniel¹

¹ Chemical Engineering Department, Covenant University, KM 10, Idiroko road, Ota, Ogun State, Nigeria

² Chemistry Department, Covenant University, KM 10, Idiroko road, Ota, Ogun State, Nigeria

³ Chemical, Metallurgical and Materials Engineering Department, Tshwane University of Technology, P.M.B. X680, Pretoria, South Africa.

⁴ Department of Mechanical and Biomedical Engineering, Bells University of Technology, P.M.B 1015, Ota, Ogun State, Nigeria

*E-mail: ayodeji.ayoola@covenantuniversity.edu.ng

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This research work was carried out to investigate the corrosion inhibitive performance of the extract obtained from waste peels of orange (*citrus sinensis*) on A36 mild steel in HCl medium. A36 mild steel metal coupons were immersed in dilute hydrochloric acid solution (1M) containing different concentrations of the waste orange peels extract inhibitor (0 – 4 g/L) at different temperatures of 32^oC & 45^oC (during gravimetric tests), as well as 27^oC & 50^oC (during potentiodynamic tests). The gravimetric analysis performed revealed the highest inhibition efficiency of the extract to be 94.33% at concentration of 4 g/L and temperature of 32^oC. Also, results from this analysis revealed a spontaneous (irreversible) and physisorption mode of adsorption of the inhibitor molecules as well as the fitness of the Langmuir adsorption isotherm for the adsorption process. The phytochemical analysis carried out revealed the presence of tannins, saponins, flavonoids, terpenoids and steroids in the inhibitor. The results of the potentiodynamic polarization analysis showed that the inhibitor retarded the anodic dissolution of mild steel more than the cathodic reaction which causes hydrogen evolution via the discharge of hydrogen ions.

Keywords: Corrosion; HCl; Inhibitor; Mild steel; Waste orange peels.

1. INTRODUCTION

For reasons such as cost, ease of welding and machining, mild steel is one of the most commonly utilised variants of steel. It is used extensively in different industries such as automobile industry,

construction industry, chemical processing industry and a number of others. Although there are many benefits associated with the application of mild steel, but mild steel is highly susceptible to corrosion due to the presence of different alloying elements in their molecular forms [1]. Corrosion of mild steel in an acidic environment is a very common phenomenon in certain industrial activities involving direct or indirect combination of both the acid and mild steel. For instance, the use of hydrochloric acid (acid pickling technique) in order to remove impurities from the surface of the metal can result into steel corrosion through a side reaction process, if not properly handled with caution [2]. Hence, the corrosion inhibiting mechanisms of mild steel needs to always be put in place in order to prevent the dissolution or degradation of metals upon exposure to the acidic media.

The common technique in the inhibition of metal corrosion involves the introduction of certain chemicals, in minute quantity, to the corrosive media. These chemical substances are commonly referred to as *corrosion inhibitors*. The inhibitors stop or slow down corrosion reactions either by scavenging the corrosive environment in order to neutralize any free radical present or by blocking the active sites at the interface between the metal and the acid [3].

The commonly used corrosion inhibitors are inorganic in nature, such include sodium nitrite (NaNO_2) and hexavalent chromium. However, most of these inorganic inhibitors have toxic effects on both the environment and human health after prolong exposure [4]. And this has necessitated the search for ecofriendly inhibitors that can effectively and efficiently replace the inorganic inhibitors.

A number of research studies on the use of various plant extracts as viable corrosion inhibitors have been carried out extensively. Patel et al. [5], studied corrosion inhibition of mild steel in sulphuric acid medium using the extract of *Phyllanthus fraternus*. They observed an inverse and direct relationship for inhibition efficiency for increasing values of temperature and concentration respectively.

The corrosion inhibition effect of turmeric and ginger rhizomes for mild steel in acidic medium was investigated by Al-Fakih et al. [6]. The research work revealed an increase in inhibition efficiency as the concentration of the inhibitor increased, but insignificant effect of temperature on the inhibition efficiency was reported. Hussin et al. [7], studied the corrosion inhibition effect of *Elaeis guineensis* on mild steel in 0.5M HCl solution. In their report, inhibition efficiency decreased with increase in temperature but increased with increase in inhibition concentration. Siau and Peck (2019) investigated the inhibitive effect of the waste orange peels on mild steel subjected to HCl environment. Result revealed optimum conditions of 1:10 as the orange peel inhibitor to HCl solvent ratio, 2 hours of exposure time and 1M HCl concentration at 30°C [8].

This project aims to study the corrosion inhibitive effects and adsorption behavior of the waste orange peels inhibitor on A36 mild steel coupons in dilute acid medium (1M HCl). And the novelty of this research work is in the acid extraction of the inhibitor from the waste orange peels at the prevailing conditions.

2. MATERIALS AND METHODS

2.1 Waste orange peels Inhibitor preparation

Waste orange peels were carefully washed (in clean water) and thoroughly dried for 4 hours at temperature of 32°C. The dried peels were then cut into small pieces, approximately 3 – 7 mm in size,

to increase the surface area of the waste orange peels. Acid extraction of the inhibitor was carried out by heating a mixture of 100 g of dried peels and 300 mL of 0.01 M HCl for a period of 90 minutes at a temperature of 101°C using the reflux apparatus. The heated mixture was cooled, filtered, pressed to recover the extract solution and make-up solvent of 0.01 M HCl was then added the extract to maintain 300 mL of the total solution. The solution was then transferred back into the round-bottom flask of the reflux apparatus along with another batch of 100g dried peels. The above steps were repeated twice so as to obtain a viscous solution of the inhibitor.

The inhibitor was precipitated by adding the isopropyl alcohol in a volume ratio of 2:1; the mixture was agitated vigorously and then left to coagulate for a period of 36 hours. After which, the precipitated inhibitor was filtered out, washed with isopropyl alcohol (analytical grade), dried to constant weight at temperatures of 40°C and drying period of 7 hours and then allowed to cool at room temperature before being crushed to fine powder and then stored in air tight closed container.

2.2 Weight loss measurements

Table 1 revealed the elemental composition of A36 mild steel used. The mild steel sheet was cut into coupons having dimensions 2.2 cm x 2.5 cm x 0.1 cm and an average total surface area of 11.94 cm². They were abraded manually using emery paper. The coupons were then degreased with acetone and then air-dried. Weight loss experiments were carried out on the mild steel samples 1M HCl medium with the inhibitor concentrations of (0 – 4 g/L) at different temperatures of 32°C and 45°C. At time interval of 3 days, the weight loss of each coupon from each test setup of each group was recorded and the corresponding corrosion rate and inhibitor efficiency were determined.

Table 1. Elements and the percentage composition of A36 mild steel used

Component	Percentage (%)
Copper (Cu)	0.220
Aluminum (Al)	0.031
Nitrogen (N ₂)	0.010
Molybdenum (Mo)	0.008
Nickel (Ni)	0.090
Chromium (Cr)	0.070
Sulphur (S)	0.006
Phosphorus (P)	0.009
Manganese (Mn)	0.510
Silicon (Si)	0.220
Carbon (C)	0.240
Iron (Fe)	98.583

2.3. *Phytochemical analysis of the inhibitor*

The phytochemical analysis was done according to the approach suggested by Roghini and Vijayalakshmi [9]. The phytochemicals tested for are tannins, saponins, flavonoids, terpenoids and steroids. A table that showed the confirmatory occurrence of some of these compounds was generated.

2.3.1 *Test for Tannins*

0.5g of the dried extract was added to a test-tube and moistened with few drops of 5 wt. % ferric chloride.

2.3.2 *Test for Saponins*

To 0.5g of the dried extract in a test-tube, 4mL of distilled water was added. The mixture was then shaken for 2 minutes.

2.3.3 *Test for Flavonoids*

0.5g of the dried extract was added into a test-tube containing 3mL of 0.25M sodium hydroxide.

2.3.4 *Test for Terpenoids*

0.5g of the dried extract was added into a test-tube containing 2mL of chloroform and 3mL of concentrated sulphuric acid.

2.3.5 *Test for Steroids*

0.5g of the dried extract was added into a test-tube having 2mL of acetic anhydride and 2mL of concentrated sulphuric acid.

2.4. *Potentiodynamic measurement*

The A36 mild steel metal was cut into test coupons with dimension 1cm x 1cm x 0.1cm. The surface preparation of each of the coupons was performed using different grades of the silicon carbide emery papers (1200 grit inclusive) and then cleaned with acetone before being rinsed with distilled water. The concentrations of the treated waste orange peels inhibitor in 1M HCl solvent were varied from 0 g/L to 4 g/L and the potentiodynamic study was done at 27⁰C and 50⁰C.

The electrochemical measurements were carried out in a three electrode cell using potentiostat/galvanostat (Autolab PGSTAT 302N) connected to a computer system. The electrodes used were platinum electrode (counter electrode), Ag/AgCl (reference electrode) and A36 mild steel specimen (working electrode, W.E). Prior to potentiodynamic polarization study, the working electrode was

subjected to corrosion in order to determine its open circuit potential (OCP) as a function of time up to 2 min, in an attempt to attain a stable state of the system. The potentiodynamic measurements were carried out following cathodic to anodic direction ($E=E_{\text{corr}} \pm 250\text{mV}$) at a scan rate of 10 mV/s.

2.5. Adsorption Mechanism of the inhibitor on metal sample

Three adsorption isotherms were tested for in the determination of the adsorption isotherm suitable for the prediction of the adsorption mechanism of the inhibitor molecules on the metal samples surfaces. The three adsorption isotherms considered are Langmuir, Freundlich and Temkin adsorption isotherms. The choice of the most suitable adsorption isotherm involved the use of the linearized equations of their models, plotting their respective graphs using appropriate parameters and comparing the R^2 values obtained from the line of best fit plots for the three isotherms.

3. RESULTS AND DISCUSSION

3.1 Phytochemical analysis of the waste orange peels inhibitor

Table 2. Phytochemical compounds present in the waste orange peels inhibitor used

Phytochemical	Confirmatory Occurrence
Tannins	A dark blue or greenish black colour indicated the presence of tannins
Saponins	The ability of saponins to produce frothing in aqueous solution when shaken was used as a screening test for saponins
Steroids	A colour change from violet to dark blue or green indicated the presence of steroids
Terpenoids	The formation of a red brown colour at the interface indicated the presence of terpenoids
Flavonoids	The occurrence of a yellow colour indicated the presence of flavonoids

The phytochemical analysis showed that the phytochemicals present in the processed orange peels are tannins, saponins, steroids, terpenoids, and flavonoids, as shown in Table 2. The presence of these phytochemicals made the inhibitor performed the responsibility of an effective inhibitor, as reflected in the results obtained from the weight loss, corrosion rate and inhibitor efficiency. According to Senguttuvan, *et. al.* [10], phytochemicals are good anti-oxidants. That is, they can easily inhibit or retard the occurrence of oxidation reaction of the corrosion process [11]. This is made possible due to their ability to scavenge free radicals such as highly charged oxygen and halogens molecules [12].

3.2. Gravimetric analysis

3.2.1 Results on weight loss tests

In Figures 1–2, the effect of increase in time of exposure of mild steel to corrosion on the rate of weight loss at different concentrations and temperatures could be deduced. In general, it could be observed that the weight loss increased as the exposure time increased at a particular temperature. That

is, each metal sample suffered more corrosion as the metal exposure time increased. Also, increase in the inhibitor introduced resulted into a decrease in the weight loss recorded, at a particular temperature. Hence, the least form of weight loss was observed at inhibitor concentration of 4 g/L for each of the temperature considered. An indication that the inhibitor used was very effective in inhibiting the corrosion reactions by causing a decrease in weight loss as its concentration increased.

Comparatively, the results showed that the corrosion process is more favored by high corrosion reaction temperature. That is, the weight loss suffered by the mild steel at 32°C was lower compared to the results observed at 45°C, at the same inhibitor concentration and exposure time. This result can also be justified by the Arrhenius principle which says that reactions are generally favored by increased reaction temperature [13].

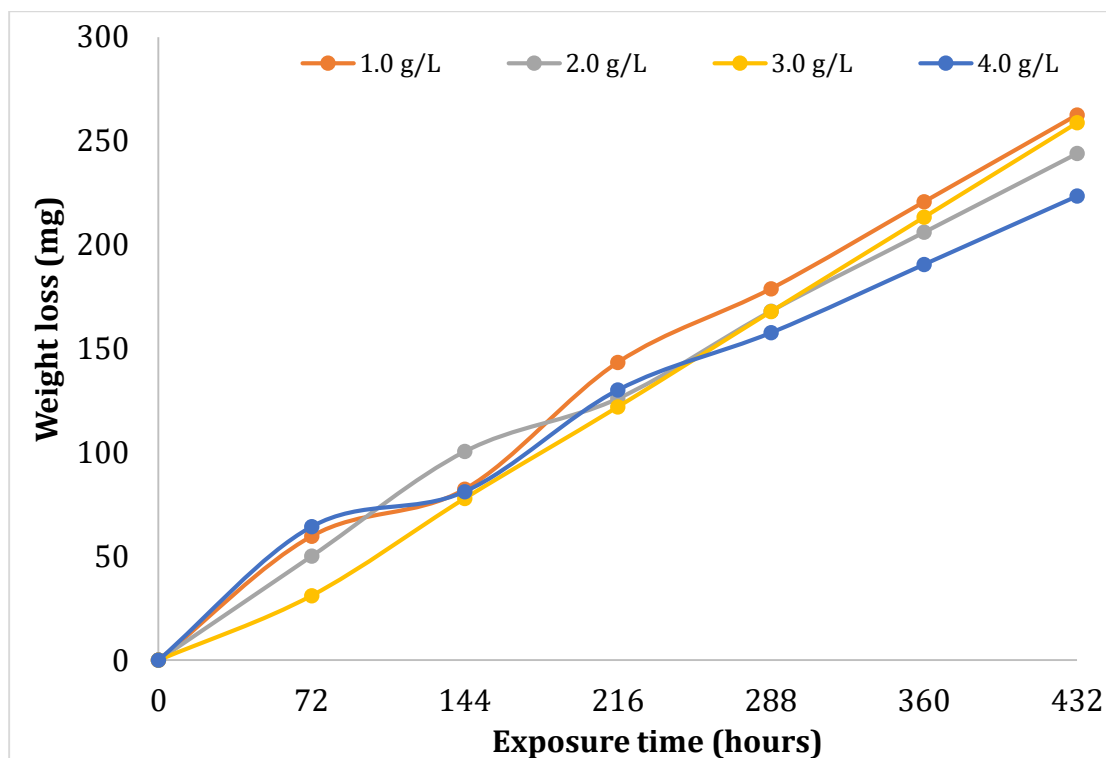


Figure 1. Weight loss and exposure time at different waste orange peels inhibitor concentrations at 32°C

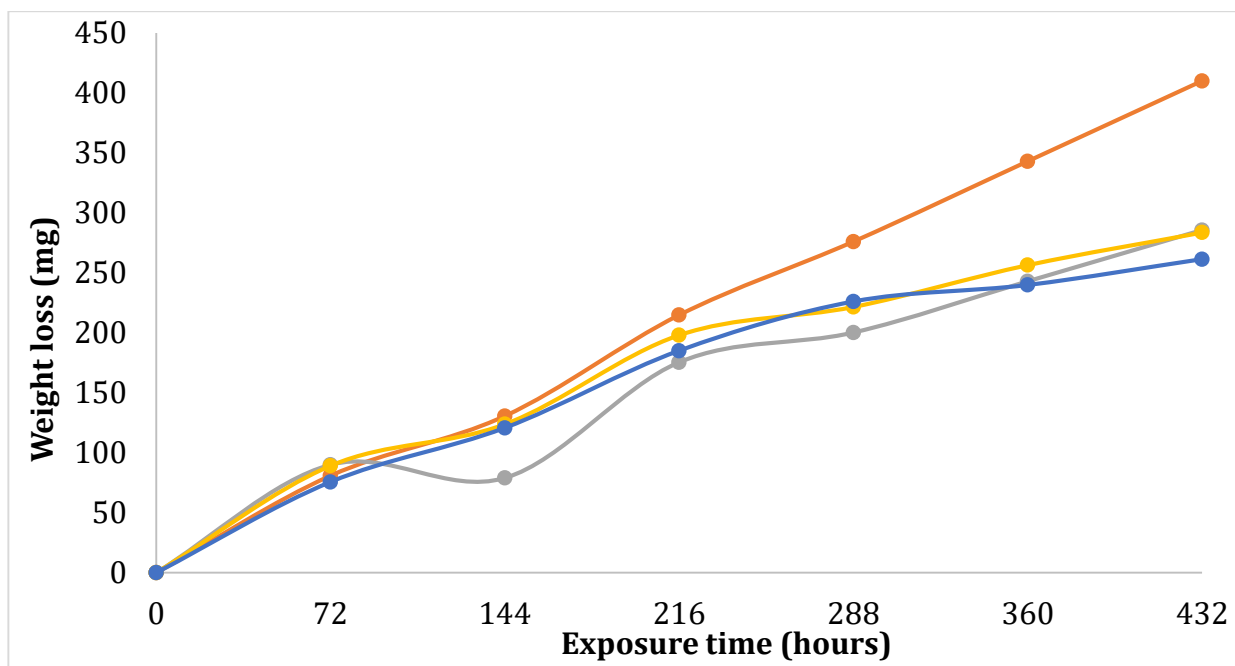


Figure 2. Weight loss and exposure time at different waste orange peels inhibitor concentrations at 45°C

3.2.2 Corrosion rate and inhibition efficiency results

Table 3. The results of the mild steel corrosion rate and inhibition efficiency at different inhibitor concentrations, after an exposure period of 432 hours (18 days).

Temperature (°C)	Concentration (g/L)	Corrosion rate, C.R. (mm/yr)	Inhibition efficiency (%)
32	0.0	8.53	0.0
	1.0	0.56	93.3
	2.0	0.52	93.8
	3.0	0.55	93.4
	4.0	0.48	94.3
45	0.0	8.65	0.0
	1.0	0.88	89.7
	2.0	0.61	92.8
	3.0	0.61	92.9
	4.0	0.56	93.5

Table 3 shows the results of the corrosion rate as well as the inhibition efficiency of the mild steel samples obtained when the samples were subjected to acidic medium corrosion process at different concentrations of the inhibitor (0 – 4 g/L) and different temperatures (of 32 and 45°C). Weight loss and inhibition efficiency of each of the samples were determined every 72 hours (3 days). In general, the

table revealed that an increase in temperature (from 32 and 45°C) resulted in an increase in corrosion rate for a particular inhibitor concentration. Also, increase in concentration of the inhibitor amounted to a decrease in corrosion rate at constant temperature. That is, an increase in temperature brought about an increase in corrosion rate thereby decreased the inhibitor efficiency. These results commensurate with the results obtained from the weight loss analysis.

Increased temperature caused an increase in corrosion process, this could be traced to the fact that reactant molecules possess higher kinetic energy at higher temperature and this caused the molecules to move and collide together at a much faster rate thereby increase the rate of oxidation (corrosion) process [13]. Also, the results revealed that increase in the inhibitor concentration brought about a decrease in corrosion rate (i.e. increased efficiency) because more molecules of the inhibitor are being adsorbed onto the surface of the metal thereby preventing the progressive bombardment or attack (reaction) of the free radicals (OH⁻ and Cl⁻ ions) on the metal active site [14].

3.2.3 Results of the adsorption model of the corrosion inhibition process

Figure 3 shows Langmuir isotherm model plot of C/θ against waste orange peels inhibitor concentration at different temperature of 32°C and 45°C. From Figure 3, it can be seen that the Langmuir isotherm plots gave R² values closer to 1. That is the mechanism of the inhibitor adsorbed on the metal surface obeys Langmuir model. The molecules of the inhibitor (adsorbate) gradually and uniformly adsorbed onto the entire surface area of the metal (adsorbent) until there exist a single layer of the inhibitor molecules after which, further adsorption stops [15]. The results of the adsorption process showed that Langmuir isotherm model plot was found to be the only suitable isotherm for the description of the adsorbed inhibitor on the metal surface.

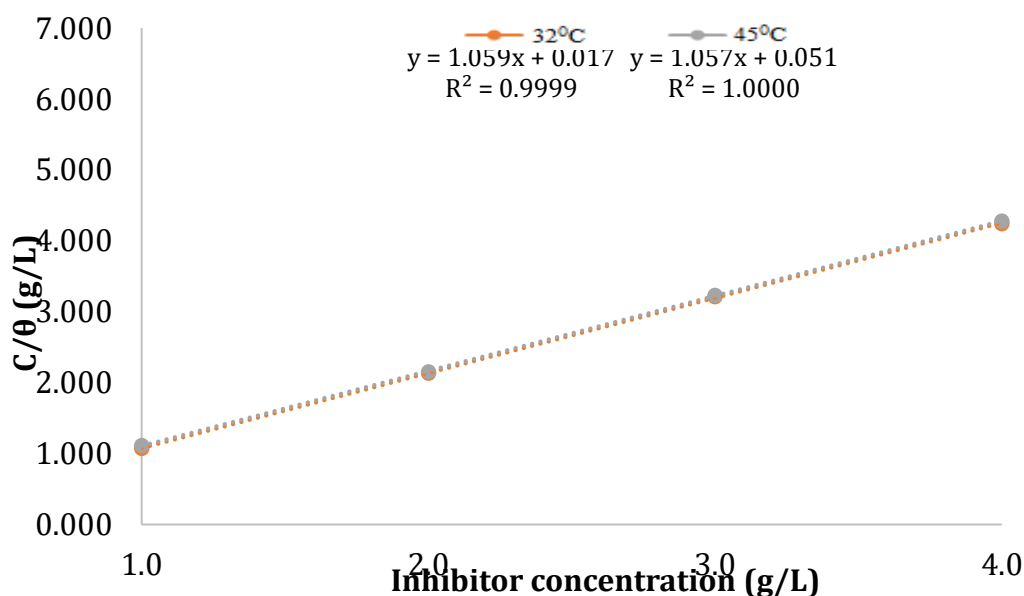


Figure 3. Plot of C/θ and waste orange peels inhibitor concentration at different temperatures (Langmuir isotherm)

3.2.4 Results on thermodynamics of the inhibition process

Having established the fact that the adsorption of the inhibitor molecules on the surface of the metal was best described by the Langmuir isotherm model, the information obtained from Langmuir model was then used to determine the thermodynamic properties of the overall inhibition process (Table 4). The data was generated using Equations 1 and 2.

$$\frac{C}{\theta} = C + \frac{1}{K_{ads}} \quad (1)$$

and the thermodynamic equation

$$\Delta G_{ads} = -RT \ln(55.5 \times K_{ads}) \quad (2)$$

where K_{ads} is the adsorption equilibrium constant, ΔG_{ads} = change in Gibbs free energy. That is, both the adsorption equilibrium constant and change in Gibbs free energy were calculated.

Table 4. Change in Gibbs free energy and adsorption equilibrium constant recorded at different temperatures (32 and 45°C) using Langmuir isotherm model

Temperature (°C)	Adsorption equilibrium constant K_{ads}	Change in Gibbs free energy ΔG_{ads} kJ/mol
32	58.82	-20
45	19.60	-18

Considering Table 4, it could be seen that change in Gibbs free energy obtained ranged from -20 kJ/mol to -18 kJ/mol. The value range was in conformity with values for physical adsorption (physisorption) process [13, 15–16]. The negative values of the Gibbs free energy revealed the spontaneous nature of the corrosion process. The physical adsorption process was characterized by an electrostatic force (van der Waals force of attraction that exists between charge molecules of the inhibitor and the electric charges present at the interface between the metal and the solution) [15–16].

3.3 Potentiodynamic polarization analysis

Analyzing Table 5, which contains the results for the potentiodynamic test carried out at 27°C, it could be seen that the corrosion rate decreased with an increase in the application of the inhibitor concentration. This indicates that the control of the anodic reaction was much greater than that of the cathodic reaction and as such, the addition of the inhibitor retarded the anodic dissolution of mild steel more than the cathodic reaction which caused hydrogen evolution via the discharge of hydrogen ions [17].

Also, it can be seen that increasing the concentration of the inhibitor from 0 g/L to 4 g/L, led to a decrease in the corrosion current density from 29.96 $\mu\text{A}/\text{cm}^2$ to 5.07 $\mu\text{A}/\text{cm}^2$ and an increase in polarization resistance from 13.15 Ω to 41.67 Ω . This suggests the formation of a protective film, via adsorption of the inhibitor molecules onto the metal surface, during the electrochemical process.

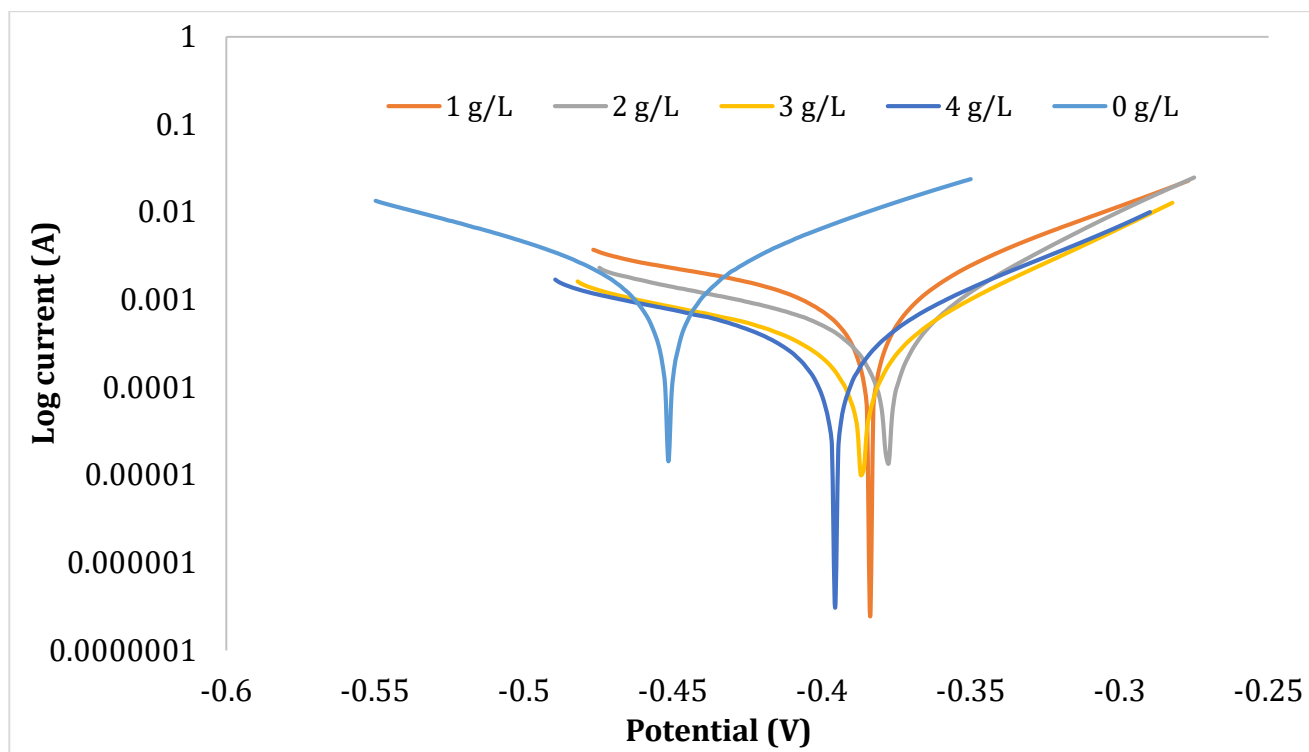


Figure 4. Potentiodynamic polarization curves for A36 mild steel in 1M HCl at different concentrations of waste orange peels inhibitor at 27°C

Table 5. Electrochemical parameters of A36 mild steel in 1M HCl at 27°C

Inhibitor Concentration (g/L)	Corrosion current density, i_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion potential, E_{corr} (mV)	Polarization resistance, R_p (Ω)	Corrosion rate, C.R (mm/year)	Inhibitor efficiency, I.E (%)
0	29.96	-451	13.15	0.34	-
1	21.70	-383	8.25	0.25	27.57
2	9.24	-377	52.57	0.10	69.16
3	6.28	-386	76.04	0.07	79.04
4	5.07	-395	41.67	0.05	83.07

Analyzing Table 6 which contains the results for the potentiodynamic test carried out at 323.15 K (50°C), increasing concentration from 0 g/L to 4 g/L, led to a decrease corrosion rate, decrease in corrosion current density (from 94.22 $\mu\text{A}/\text{cm}^2$ to 13.92 $\mu\text{A}/\text{cm}^2$) and an increase in polarization resistance (from 4.91 Ω to 41.91 Ω), with a maximum inhibition efficiency of 85.22% at inhibitor concentration of 4 g/L. These results proved that the addition of more pectin inhibitor up to 4g/L enhanced the corrosion inhibitive effects on the surface of the mild steel.

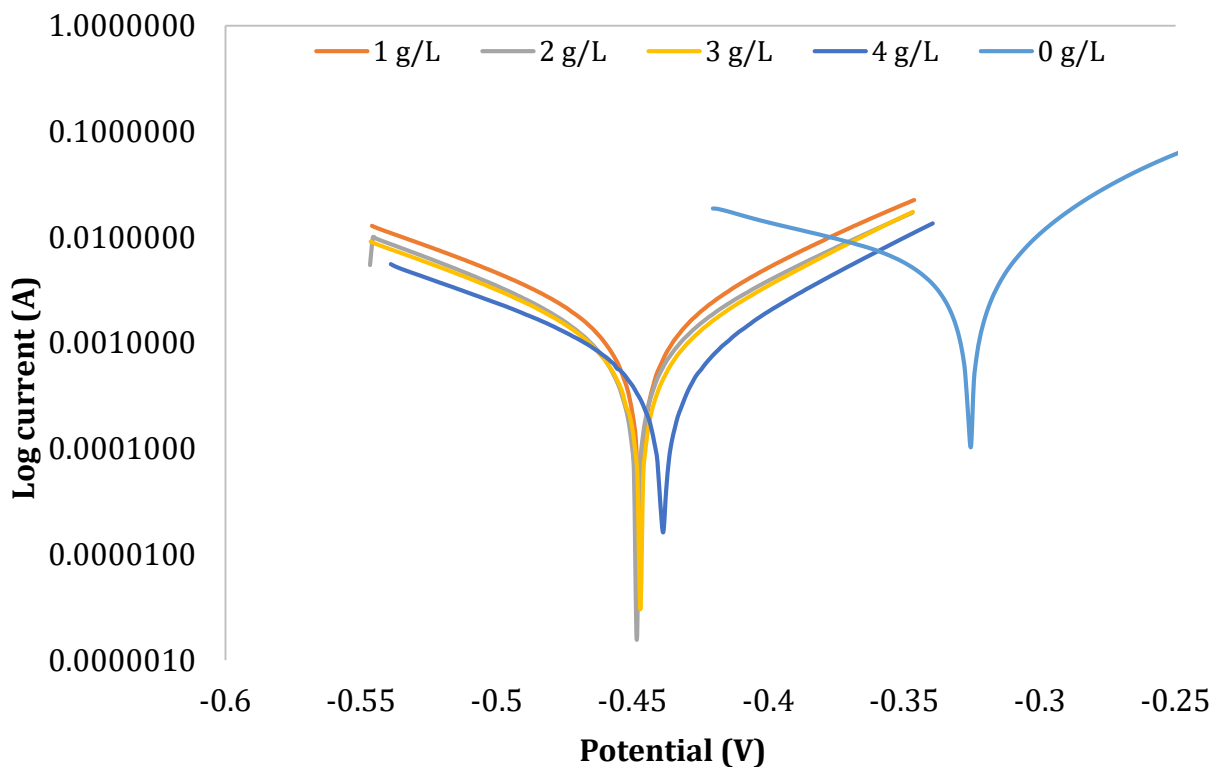


Figure 5. Potentiodynamic polarization curves for A36 mild steel in 1M HCl at different concentrations of waste orange peels inhibitor at 50°C

Table 6. Electrochemical parameters of A36 mild steel in 1M HCl at 50°C

Inhibitor Concentration (g/L)	Corrosion current density, i_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion potential, E_{corr} (mV)	Polarization resistance, R_p (Ω)	Corrosion rate, C.R (mm/year)	Inhibition efficiency, I.E (%)
0	94.22	-325	4.91	1.09	-
1	24.27	-447	19.17	0.28	74.24
2	19.95	-448	12.31	0.23	78.82
3	18.09	-447	16.45	0.21	80.80
4	13.92	-439	41.91	0.16	85.22

The effect of increase in temperature could be seen when the electrochemical parameters at 27°C were compared to that obtained at 50°C. All the parameters favoured increase in corrosion process at 50°C compared to the corrosion process at 27°C. That is, corrosion reaction was favoured at higher reaction temperature and these results were further confirmed by the results of the two potentiodynamic polarization curves (Figures 4–5).

4. CONCLUSION

From the obtained results, the following conclusions can be drawn:

- i. The phytochemicals present in the orange peel extract are tannins, saponins, steriods, terpenoids and flavonoids.
- ii. The gravimetric tests showed that the extract from the waste orange peels was an excellent corrosion inhibitor giving better inhibition results at a temperature of 32⁰C (compared to 45⁰C results) with inhibitor concentration of 4 g/L, corrosion rate of 0.4835 mm/yr and inhibitor efficiency of 94.33%.
- iii. The electrochemical potentiodynamic polarization tests showed that the waste orange peels was an excellent corrosion inhibitor giving better inhibition results at a temperature of 27⁰C (compared to the 50⁰C results) with inhibitor concentration of 4 g/L, corrosion rate of 0.0589 mm/yr and inhibitor efficiency of 83.07%.
- iv. The adsorption of the inhibitor molecules on the surface of the mild steel metal samples best follows the Langmuir adsorption isotherm.
- v. The range of values for ΔG_{ads} was from -20.528 kJ/mol to -18.497 kJ/mol. This indicated the spontaneous and physisorption nature of the adsorbed inhibitor molecules at the interface between the metal and the solution.
- vi. The tafel plots and results showed that the inhibitor acted majorly as anodic-type inhibitor in HCl solution.

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