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Corrosion inhibition of A36 mild steel in 0.5 M acid medium using waste citrus limonum peels

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ABSTRACT

Research effort is being intensified on the establishment of organic substances that can actively perform the role of metal inhibition. Investigation on corrosion inhibition of A36 mild steel in 0.5 M H_2SO_4 medium using waste citrus limonum peels as inhibitor was carried out. Gravimetric tests (weight loss, corrosion rate and inhibition efficiency) involving the variation of citrus limonum peels inhibitor concentration (0–4 w/v%), corrosion time (0–12 h) and reaction temperature (28 °C and 45 °C) were conducted. Langmuir and Freundlich adsorption isotherms were considered in the establishment of the adsorption behavior of citrus limonum peels inhibitor on A36 mild steel surface. The thermodynamic parameters (adsorption equilibrium constant k_{ads}, change in Gibbs free energy ΔG_{ads}, change in heat of adsorption ΔH_{ads} and entropy change ΔS_{ads}) of the adsorbed inhibitor on mild steel surface were determined. The results of the study showed that 0.4 w/v% citrus limonum concentration gave highest inhibition efficiency of 94% and 92% on A36 mild steel at 28 °C and 45 °C respectively. And the surface adsorption of citrus limonum inhibitor on A36 mild steel was described by both the Langmuir and Freundlich adsorption isotherms. The negative values of ΔS, ΔG_{ads}, ΔH_{ads} indicated that the inhibitor adsorption is exothermic and spontaneous (physical adsorption). SEM/EDX analysis showed that inhibitor adsorption of citrus limonum was better at 28 °C compare to 45 °C, by giving a more evenly distributed particles at 0.4 w/v% inhibitor concentration.

1. Introduction

Due to its wide range of applications, mild steel is one of the most extensively used metals in metallurgical, food processing, electricity, chemicals, and building industries. It exhibits high mechanical strength, strong resiliency and toughness, and its high demand contributes to its production (manufacturing) in large quantity [1,2]. It is a commodity that is readily available and cost effective. Hence, finding lasting solutions to the deterioration of mild steel due to its susceptibility to corrosion demands a serious attention. A lot of efforts have been made in addressing the problem of the mild steel corrosion.

The use of corrosion inhibitor is one of the effective ways of controlling mild steel corrosion. A corrosion inhibitor is a chemical substance which, when introduced in little quantity to metal surface or corrosive environment of the metal, slows down the corrosion rate of such metal [3,4]. Basically, corrosion inhibitors can be grouped into two: organic and inorganic inhibitors depending on their chemical compositions [4–6].

Recent studies have shown that the use of organic corrosion inhibitors in combating metal corrosion is an effective and sustainable way of ensuring adequate provision of the environmentally friendly inhibitor. That is, organic corrosion inhibitors are not hazardous to the environment [5–8].

Organic inhibitors in corrosive environment retard the corrosion of metal in such environment through the formation of adsorption layer(s) on the metal surface, resulting in the blockage of active sites of the anode and cathode of the metal thereby causing high protection of metal against dissolution [9–11]. And the adsorption of these inhibitors on metal surface is made possible through the present of the hetero atoms, such as O, H, N and S that prevent the anodic dissolution of the metals [9,12,13]. The chemical constituents and the inhibitive nature of the organic corrosion inhibitors are responsible for the classification of these inhibitors as anodic, cathodic, or both (mixed typed) inhibitors [14,15]. These chemical compounds, which are heterocyclic in nature, are good

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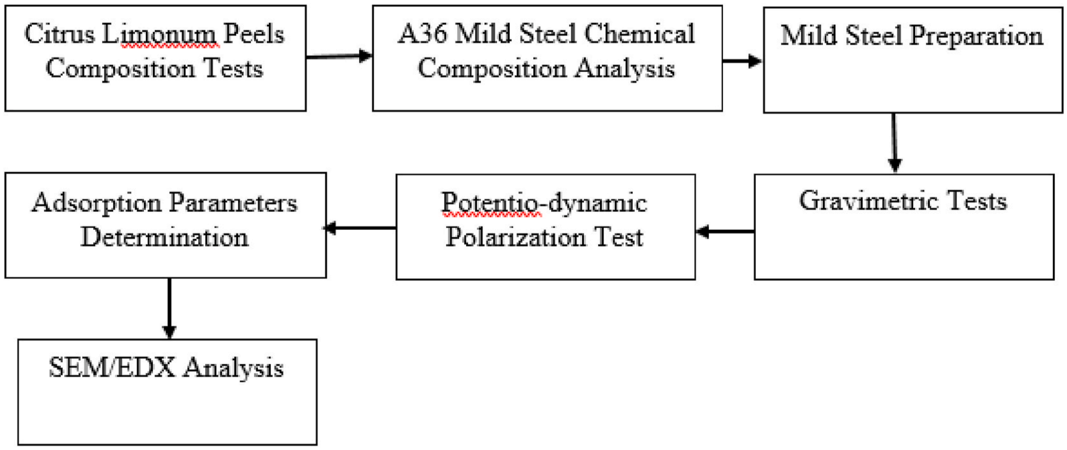

Fig. 1. Block-flow diagram of the experimental setup.

Table 1
A36 mild steel composition.

Element	% Composition
C	0.25
Si	0.28
Mn	1.03
Fe	98.0
S	0.05
P	0.40
Cu	0.20

Table 2
Phytochemical analysis of the inhibitor.

Parameter	Inference
Alkaloids	**
Tannins	***
Saponins	*
Steroids	*

Highly present = ***, Moderately present = **, Slightly present = *.

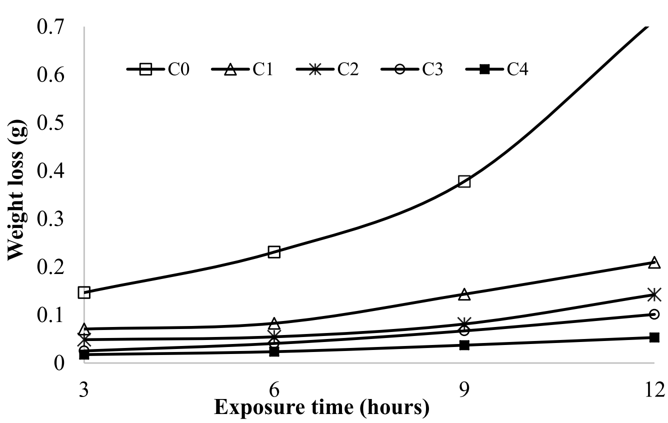

Fig. 2. Weight loss against contact time at 28 °C.

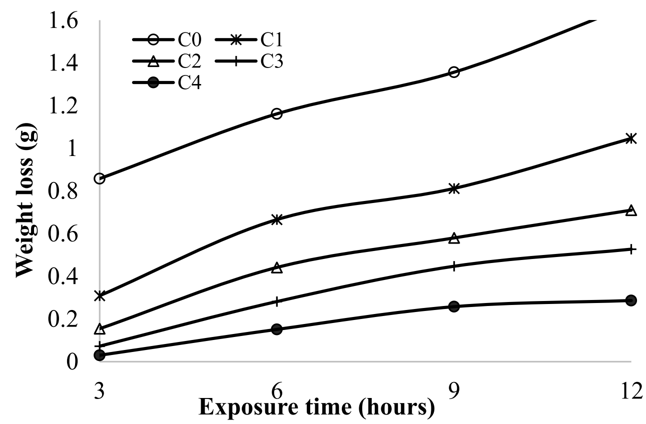

Fig. 3. Weight loss against contact time at 45 °C.

Table 3
Corrosion rate obtained from different inhibitor concentrations at 28 °C.

Concentration (%w/v)		Corrosion rate (mm/yr)			
		3 h	6 h	9 h	12 h
C0	0.0	41.52	34.01	40.45	46.68
C1	0.1	22.48	11.71	14.67	17.36
C2	0.2	15.55	7.71	8.31	10.47
C3	0.3	7.382	6.43	6.31	9.15
C4	0.4	5.37	3.62	3.79	2.24

Table 4
Corrosion rate obtained from different inhibitor concentration at 45 °C.

Concentration (%w/v)		Corrosion Rate (mm/yr)			
		3 h	6 h	9 h	12 h
C0	0.0	274.51	171.08	144.68	113.68
C1	0.1	102.72	102.13	83.02	83.16
C2	0.2	54.55	62.56	54.77	50.21
C3	0.3	22.34	43.21	45.72	37.13
C4	0.4	10.06	24.26	31.57	21.97

antioxidants. They can be obtained from the waste parts of some plants (such as orange and mango peels) and they include alkaloids, steroids, tannins and flavonoids [16–19].

Study on the use of citrus peels as inhibitor in 1.0 M corrosive media of mild steel have been extensively carried out by many researchers. Najem et al. [20] obtained 90.3% inhibitor efficiency from the use of citrus peels inhibitor concentration of 900 ppm for mild steel in 1 M HCl medium, by considering both the experimental and theoretical approaches. The novelty of this study is in the consideration of waste citrus limonum peels as inhibitor for A36 mild steel in 0.5 M H_2SO_4 medium.

The spontaneous nature of the inhibitor adsorption on metal surface is a function of the values of certain thermodynamic parameters (change

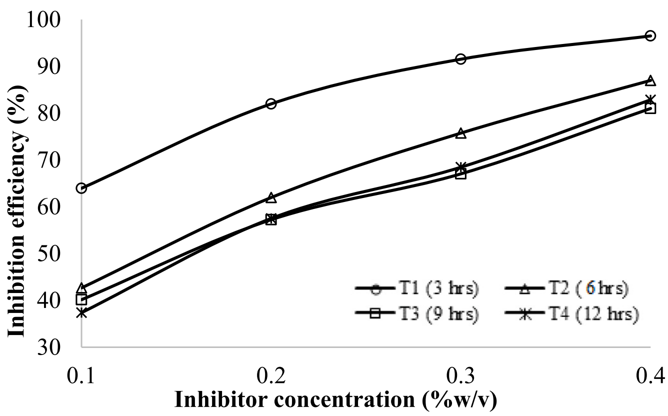

Fig. 4. Inhibition efficiency against inhibitor concentration at 28 °C.

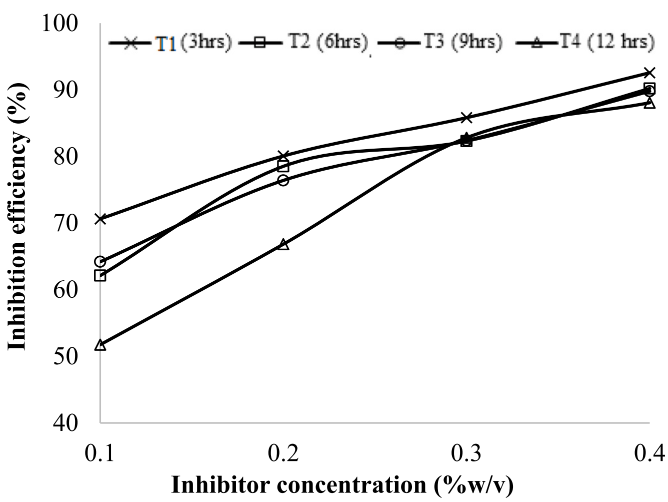

Fig. 5. Inhibition efficiency against inhibitor concentration at 45 °C.

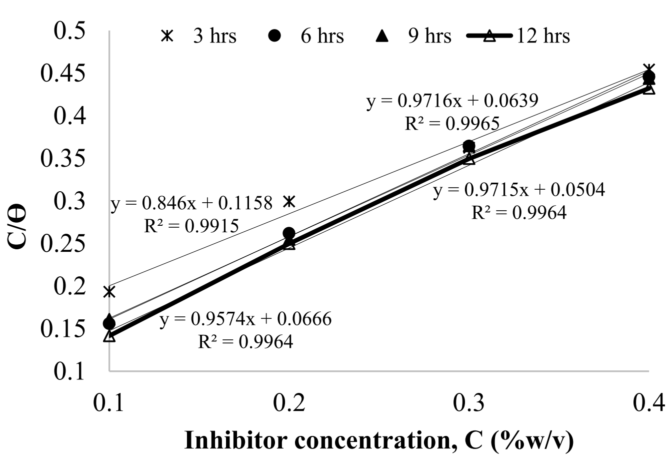

Fig. 6. Langmuir plots of the adsorbed inhibitor on mild steel in 0.5 M H_2SO_4 at 28 °C.

in Gibbs free energy, ΔG_{ads}, and adsorption equilibrium constant, K_{ads}). At high inhibitor adsorption rate, ΔG_{ads} is negative, resulting into spontaneous adsorption process. The inhibitor adsorption on mild steel surface can also be explained in terms of adsorption isotherms (such as Langmuir, Temkin and Freundlich adsorption isotherms). In their study, Manimegalai and Manjula [21] reported that the adsorption of Sargassum swartzii on mild steel in aqueous medium obeys Langmuir,

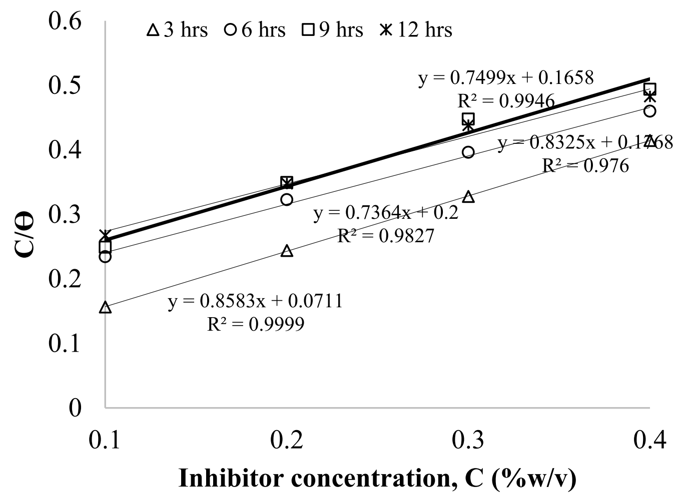

Fig. 7. Langmuir plots of the adsorbed inhibitor on mild steel in 0.5 M H_2SO_4 at 45 °C.

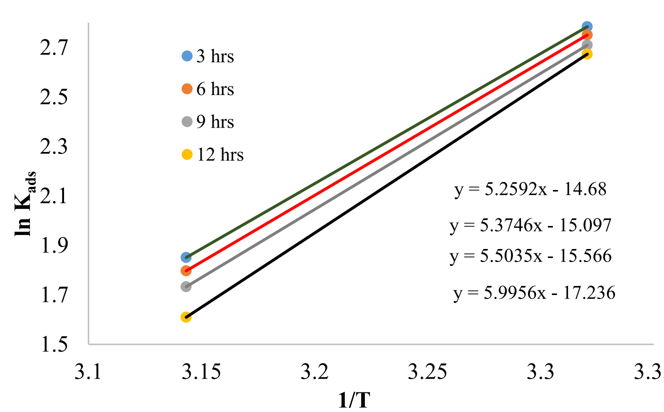

Fig. 8. ln K against 1/T for the Langmuir adsorption of the inhibitor on mild steel.

Table 5
Langmuir adsorption parameters for the adsorption of the inhibitor on mild steel.

Temperature	Time	R^2	k_{ads}	ln k_{ads}	ΔG_{ads} (kJ/mol)
28 °C (301.15 K)	3 hrs	0.9915	16.18	2.78	−17.02
	6 hrs	0.9965	15.64	2.75	−16.94
	9 hrs	0.9964	15.01	2.70	−16.83
	12 hrs	0.9964	14.84	2.67	−12.51
45 °C (318.15 K)	3 hrs	0.9999	6.36	1.85	−15.52
	6 hrs	0.9946	6.03	1.79	−15.37
	9 hrs	0.9760	5.65	1.73	−15.20
	12 hrs	0.9827	5.00	1.60	−14.88

Temkin and Freundlich adsorption isotherms. In this study, the appropriate adsorption isotherm(s) of the waste citrus limonum peels inhibitor for the corrosion inhibition process would be established.

Hence, the aim of this research work is to establish the corrosion inhibition performance of waste citrus limonum peels (as inhibitor) and to establish the appropriate adsorption isotherms for the corrosion inhibition process of A36 mild steel in 0.5 M H_2SO_4.

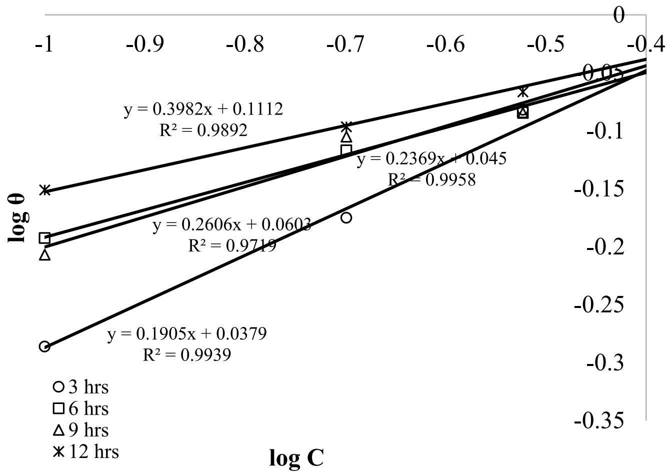

Fig. 9. Freundlich plots of the adsorbed inhibitor on mild steel surface at 28 °C.

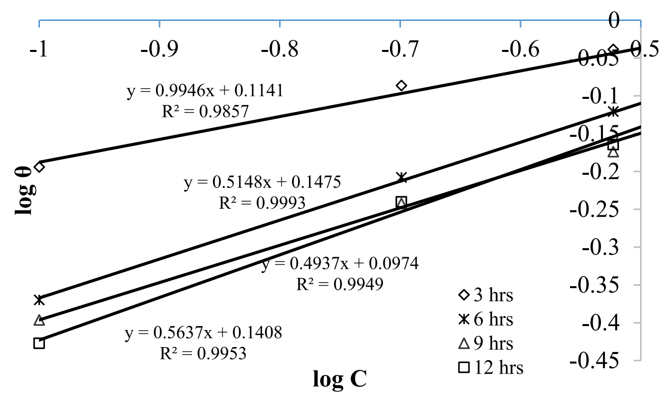

Fig. 10. Freundlich plots of the adsorbed inhibitor on mild steel surface at 45 °C.

Table 6
Thermodynamic parameters for inhibitor adsorption.

Exposure time (hrs)	ΔH_{ads} (kJ mol^{-1})	ΔS_{ads} (J mol^{-1} K^{-1})
3	−43.72	−122.05
6	−44.68	−125.52
9	−45.75	−129.42
12	−49.85	−143.30

2. Methodology

2.1. Materials, reagents and equipment

The materials utilised during the course of this research work include A36 mild steel, waste citrus limonum peels (inhibitor), emery papers (150, 320, 600 and 800 grades). The reagents include 0.1 M HCl (98%, Pharma. Tech, Mayer's reagent (99%, Quali-Tech), $FeCl_3$ (99%, Anron Chemicals Co.), Chloroform (98%, Spectrum Chemicals), 0.5 M H_2SO_4 (98%, Palvi Power Tech Ltd.). And the equipment used include XRF spectrometer and JEOL JSM 7600 F field emission scanning electron microscope. The block flow diagram of the experimental setup is shown in Fig. 1.

2.2. Mild steel samples preparation

A36 mild steel was cut into small pieces with each sample having a dimension of 2.5 cm by 2.5 cm. To ensure a smooth surface free of impurity, each sample was abraded using emery papers of different grades (150, 320, 600, 800) and then washed with acetone and distilled water before being dried. The samples were then covered with dustin powder to prevent metal samples corrosion before being used.

2.3. Preparation of citrus limonum peels inhibitor

Waste citrus limonum peels were severally rinsed in water and then sun dried for days before being oven dried for 4 h at 105 °C. The dried sample was grounded into fine particle size of ≤60 μm and the sample was then kept in an air tight container. The concentration of the inhibitor used was determined using Equation (1) [14].

$$\text{Inhibitor concentration} \quad = \frac{\text{weight of inhibitor}}{\text{100ml of solution}} * 100 \tag{1}$$

2.4. Phytochemical analysis of citrus limonum peels inhibitor

2.4.1. Test for alkaloids

0.5 g aqueous extract was mixed with 4 ml of 1% dilute hydrochloric acid. Before being filtered, it was boiled. 1 mL of the filtrate was mixed with Mayer's reagent. Turbidity or precipitation indicated the presence of alkaloids.

2.4.2. Test for tannins

3 g of the inhibitor was mixed with 6 mL distilled water and a few drops of 10% $FeCl_3$ solution was added to the mixture. A blue green colour showed that tannins were present.

2.4.3. Test for saponins

10 ml distilled water was added to 2.5 mL ethanolic extract and shaken for several minutes. Frothing and appearance of honeycomb showed that saponins are present.

2.4.4. Test for steroids

3 ml chloroform was added to 0.5 ml extract. After that, the solution was filtered, and a small amount of concentrated Sulphuric acid was added. A reddish brown colour ring with slight green fluorescence indicated the presence of steroids.

2.5. Gravimetric tests on mild steel samples

Gravimetric test involved both the weight loss and corrosion rate determinations, both at 28 °C and 45 °C. The prepared mild steel samples were subjected to weight loss in 100 ml of 0.5 M H_2SO_4, at varied concentration of the inhibitor (0–0.4 %w/v). Change in weight of the samples were noted for a period of 12 h (in every 3 h) in order to determine the rate of corrosion and inhibition efficiency. The weight loss of each of the samples was determined and the corrosion rate was calculated using Equation (2). And the Inhibition efficiency (IE) was calculated using Equation (3) [16].

$$CR = \frac{K \times \Delta m}{D \times S \times t} \tag{2}$$

$$IE(\%) = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100 \tag{3}$$

where Δm is weight loss in g, t is the immersion time in hours, K is a constant (8.76 × 10^4), D is density of the metal in gcm^{-3}, S is the total surface area of the mild steel, W_{corr} is weight loss of sample with inhibitor and W'_{corr} is the weight loss of sample without inhibitor.

2.6. Adsorption isotherms

Langmuir and Freundlich adsorption isotherms (Equations (4) and (5)) were considered in the establishment of the adsorption behavior of

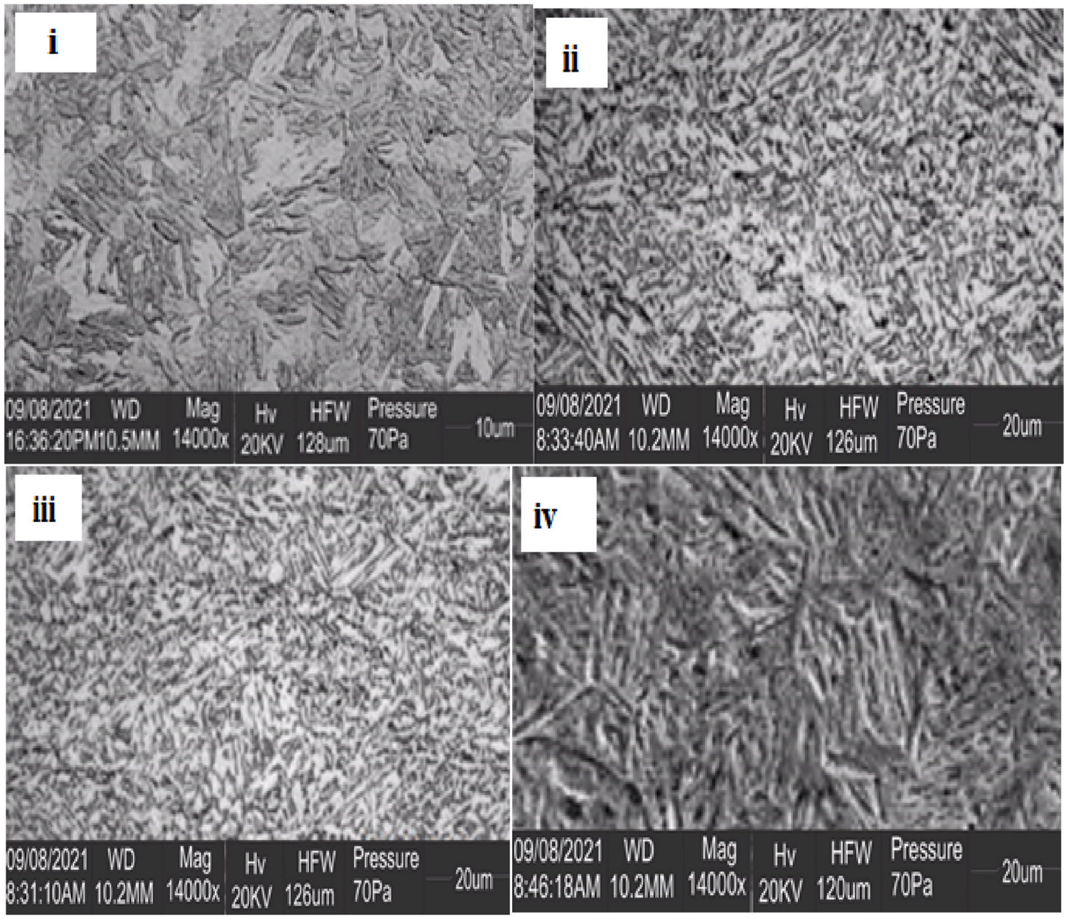

Fig. 11. SEM analysis of A36 mild steel surface at 28 °C (i) 0 w/v% (ii) 0.2 w/v% (iii) 0.3 w/v% (iv) 0.4 w/v%.

citrus limonum peels inhibitor on A36 mild steel surface [16].

$$\frac{C_{(inh)}}{\theta} = \frac{1}{K_{(ads)}} + C_{(inh)} \quad (4)$$

$$\log \theta = \frac{1}{n} \log C_{inh} + \log K_{(asd)} \quad (5)$$

where K_{ads} is equilibrium constant for adsorption process, θ is the inhibitor coverage, and $C_{(inh)}$ is the inhibitor concentration. And the K_{ads} obtained was used in the determination of the change in Gibbs free energy (ΔG_{ads}) of the adsorption process, using Equation (6) [16].

$$\Delta G_{ads} = -RTln(55.5k_{ads)} \quad (6)$$

where R is the universal gas constant and T is absolute temperature.

Change in enthalpy (ΔH_{ads}) and entropy change (ΔS_{ads}) of the inhibition adsorption process were obtained from the slope and intercept of a plot of ln K_{ads} vs 1/T using Equation (7) [16].

$$\ln k_{ads} = \left(\frac{-\Delta H^{\circ}{}_{ads}}{RT}\right) + \left(\frac{\Delta S^{\circ}{}_{ads}}{R}\right) \quad (7)$$

2.7. Surface (SEM) analysis of the samples

The surface structures of A36 mild steel samples (before and after corrosion) were examined by means of a JEOL JSM 7600 F field emission scanning electron microscope equipped with energy dispersive spectroscopy.

3. Results and discussion

3.1. A36 mild steel composition

Table 1 shows the chemical composition of A36, as revealed by XRF analysis. The iron content was 98%, manganese content of 1.03%, carbon content was found to be 0.25% and the other elements noticed, in minute quantities, are as shown in Table 1. The wide areas of application of A36 mild steel is due to the high content of iron which made the material susceptible to corrosion process.

3.2. Results of the phytochemical tests

The results of the phytochemical tests carried out on citrus limonum peels inhibitor is as shown in Table 2. The four phytochemicals identified in the citrus limonum peels inhibitor are active anti-oxidants which could slow down the oxidation reaction of the corrosion process [14].

3.3. wt loss results

The loss in weight of mild steel in corrosive environment of 0.5 M H_2SO_4 (with and without concentrations of citrus limonum peels for 3 h, 6 h, 9 h and 12 h) was determined at 28 °C and 45 °C. Figs. 2 and 3 show the plot of weight loss with exposure time for mild steel in the acidic medium both at 28 °C and 45 °C respectively. Considering the two figures, an increase in mild steel weight loss was noticed, as the exposure time increased. That is, the trends showed that the mild steel continuously suffered corrosion with time. It was also observed that the weight loss increased with increased corrosion temperature. That is, the weight

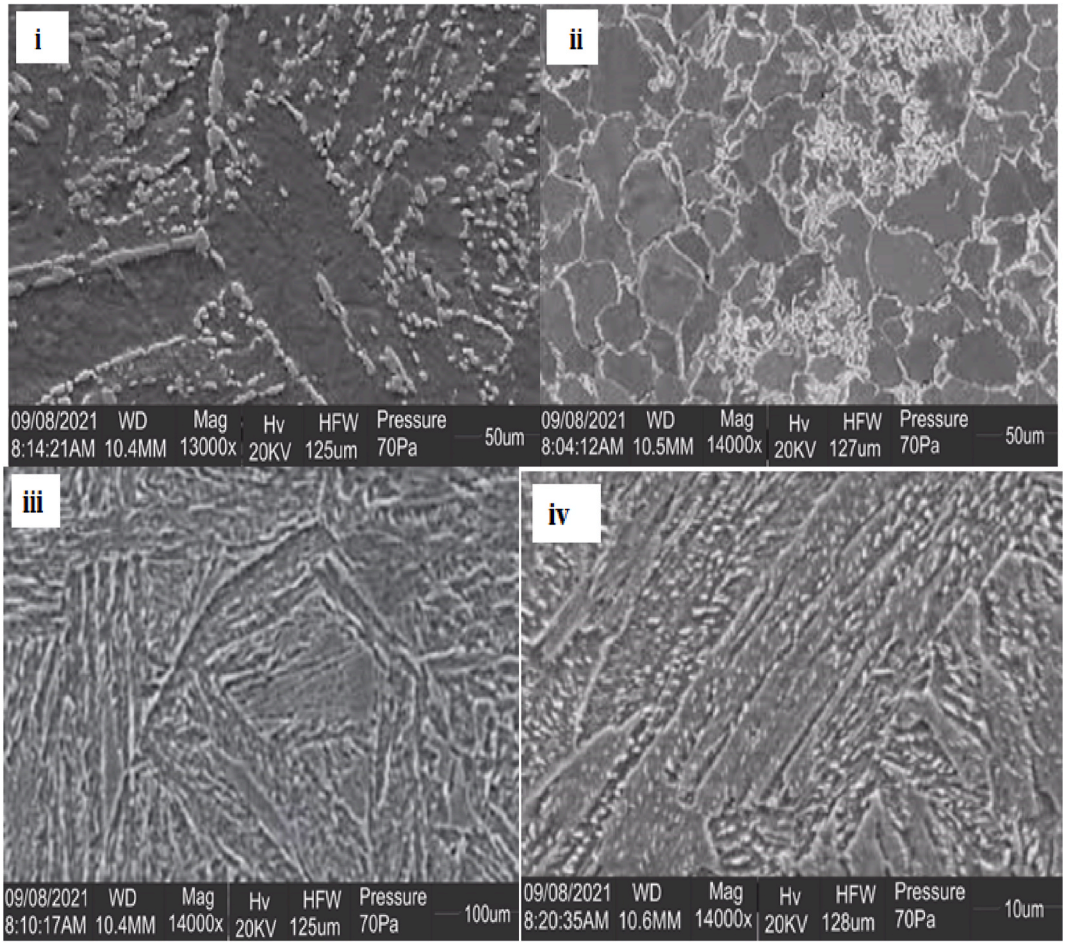

Fig. 12. SEM analysis of A36 mild steel surface at 45 °C (i) 0 w/v% (ii) 0.2 w/v% (iii) 0.3 w/v% (iv) 0.4 w/v%.

loss experienced by mild steel was higher at 45 °C compared to the result obtained at 28 °C, at any specified inhibitor concentration. This result corroborates the findings of [4] that says that corrosion process increases with increased corrosion temperature, as justified by the Arrhenius equation (Equation (8)).

$$k = k_0 e^{-\left(\frac{E}{RT}\right)} \quad (8)$$

where k is kinetic reaction rate, k_0 is rate constant, E is activation energy, R is universal gas constant and T is absolute temperature.

It could also be observed from Figs. 2 and 3 that the weight loss increased drastically when no inhibitor was considered, but the loss reduced with an increase in the concentration of citrus limonum inhibitor, for any of the corrosion temperature or exposure time considered. That is, A36 mild steel suffered the least weight loss at the highest inhibitor concentration but experienced serious corrosion when no inhibitor was considered. This proved that citrus limonum is an effective corrosion inhibitor, especially at 0.4 %w/v inhibitor concentration.

Tables 3 and 4 showed the corrosion rate obtained from the different inhibitor concentrations at 28 °C and 45 °C respectively. The corrosion rate results depicted a similar trend with the weight loss results. Comparatively, corrosion rate increased with increased temperature but decreased with increased inhibitor concentration. This is because, the increased quantity of the phytochemicals in the inhibitor reduced the corrosion process on A36 mild steel surface [4,14].

3.4. *Citrus limonum peel inhibitor efficiency*

Figs. 4 and 5 show the effects of variation in the inhibitor concentration on inhibition efficiency at 28 °C and 45 °C respectively. In general, inhibition efficiency increased with reduced temperature and reduced mild steel exposure time, while the efficiency increased with increased inhibitor concentration for both temperatures. Hence, highest inhibition efficiency of 94% was obtained at 28 °C, 3 h exposure time and 0.4 %w/v inhibitor concentration. But for 45 °C corrosion temperature, the highest inhibition efficiency recorded was 92% at 3 h exposure time and 0.4% w/v inhibitor concentration. The potency of 0.4 % w/v of citrus limonum as active inhibitor can be explained in terms of the increased quantity of the four phytochemicals identified that acted as antioxidants by impeding the oxidation behaviour of the corrosion process.

3.5. *Inhibition adsorption performance*

Figs. 6–8 show Langmuir plots of the adsorbed inhibitor on A36 mild steel surface at 28 °C and 45 °C respectively. Table 5 revealed Langmuir adsorption parameters obtained (adsorption constant, k_{ads}, and change in Gibbs free energy, ΔG_{ads}) from the adsorption of the inhibitor on mild steel. The fitness of the Langmuir isotherm (Equation (4)) in the prediction of the adsorption behavior of the inhibitor was justified by the approximate values of one (1) obtained for each of the coefficient of determination (R^2), as shown in Figs. 6–7 and Table 5. And higher values of the adsorption constant (k_{ads}) obtained at 28 °C implied that the inhibitor was firmly adsorbed at this temperature compared to the results

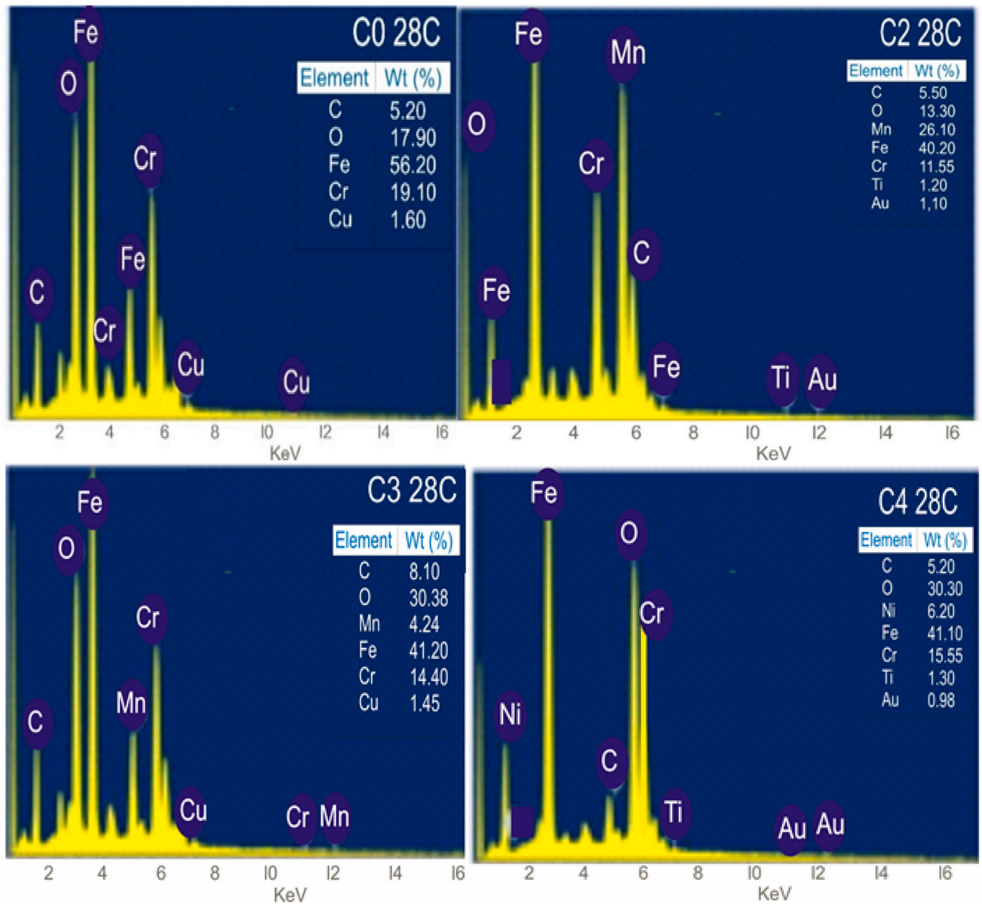

Fig. 13. EDX analysis of A36 mild steel surface at 28 °C (i) 0 w/v% (ii) 0.2 w/v% (iii) 0.3 w/v% (iv) 0.4 w/v%.

obtained at 45 °C. While the negative values of the change in Gibbs free energy, which are within −20 and 0 kJ/mol, indicated that the adsorption process involved was a physical adsorption process [22,23].

Figs. 9 and 10 show Freundlich plots of the adsorbed inhibitor on mild steel surface at 28 °C and 45 °C respectively. The fitness of the Freundlich isotherm (Equation (5)) in the prediction of the adsorption behavior of the inhibitor was justified by the approximate values of one (1) obtained for each of the coefficient of determination (R^2), at the two corrosion temperature considered.

3.6. Thermodynamic parameters for the adsorption of the inhibitor on mild steel corrosion

Table 6 shows the values of the thermodynamic parameters obtained (ΔH_{ads} and ΔS_{ads}) from the adsorption of the inhibitor on the mild steel. Change in heat of adsorption (ΔH_{ads}) is the heat released during the inhibitor adsorption process. That is, the molecules of the inhibitor are released from the solution to the surface of the metal thereby resulting in the release of energy of adsorption, an exothermic reaction. And the more the energy released the better the adsorption of the inhibitor on the surface. The effect of entropy change (ΔS_{ads}, the degree of the disorderliness of the molecules during adsorption) as indicated by the values obtained, was similar to that recorded for ΔH_{ads}. These implied that the least corrosion rate, as well as the most promising effective metal surface coating, occurred at corrosion exposure time of 3 h.

3.7. SEM/EDX results of the mild steel surfaces

Figs. 11 and 12 revealed SEM analysis of the mild steel surface (at varied inhibitor concentrations) for 28 °C and 45 °C corrosion reaction temperatures respectively. At 28 °C corrosion reaction temperature, the distribution of the inhibitor on the surfaces become more compact (with lesser gaps) as the inhibitor concentration increased from 0 to 4 w/v%, thereby causing a more uniform inhibitor distribution on metal surfaces. That is, increase in citrus limonum inhibitor concentration reduced the corrosion rate on the metal surfaces. And this finding supports the results obtained from the gravimetric tests. Similar trend of results was observed at 45 °C reaction temperature, However, more gaps were notice on the metal surface at 45 °C. This is an indication that the corrosion resistance of the inhibitor was better at 28 °C compare to the results at 45 °C.

Figs. 13 and 14 showed the Energy-Dispersive X ray (EDX) analysis of the elements existing on surface of the metal samples at 28 °C and 45 °C temperature respectively. The results obtained could be analyzed in terms of the oxygen content, a good element that accounts for the present of organic compounds in the inhibitor. EDX analysis showed that the oxygen content increased with an increase in inhibitor concentration for a particular temperature. That is, increase in inhibitor concentration increased the spread of the inhibitor on metal surface, as reflected by the oxygen content. Thereby resulting in better coating performance, as justified by the SEM analysis.

Also, the EDX results revealed that the oxygen contents decreased with increase in reaction temperature (at any specified inhibitor concentration). Thereby supporting the fact that coating performance of the inhibitor was preferred at reaction temperature of 28 °C.

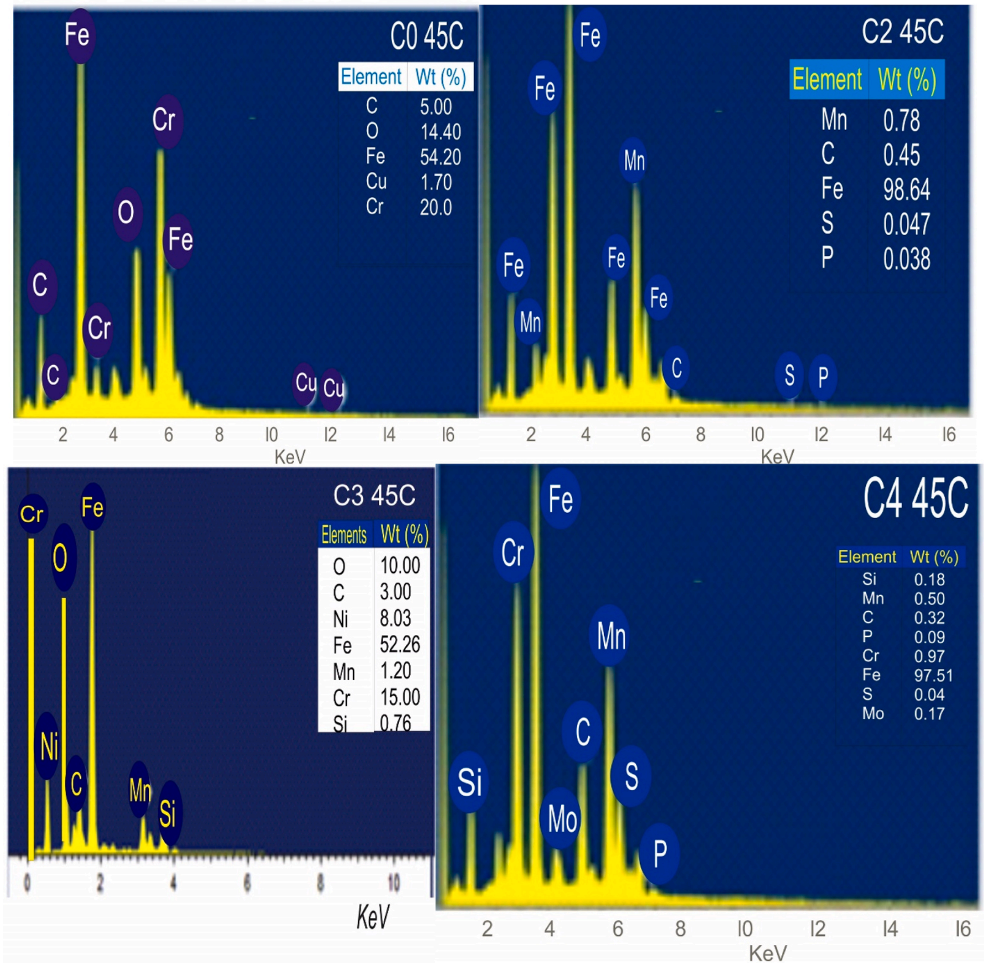

Fig. 14. EDX analysis of A36 mild steel surface at 45 °C (i) 0 w/v% (ii) 0.2 w/v% (iii) 0.3 w/v% (iv) 0.4 w/v%.

4. Conclusion

The following conclusion can be made from this research work:

i. Citrus limonum peel was found to be a good corrosion inhibitor for A36 mild steel in 0.5 M H_2SO_4 medium.
ii. 0.4 w/v% citrus limonum concentration gave highest inhibition efficiency of 94% and 92% on A36 mild steel at 28 °C and 45 °C respectively.
iii. The surface adsorption of citrus limonum inhibitor on the surface of A36 mild steel could be described by both the Langmuir and Freundlich adsorption isotherms.
iv. The thermodynamic properties (ΔS, ΔG_{ads}, ΔH_{ads}) with negative values indicated that the inhibitor adsorption is both exothermic and spontaneous (physical adsorption).
v. SEM/EDX analysis showed that inhibitor adsorption of citrus limonum was better at 28 °C compare to 45 °C, by giving a more evenly distributed particles at 0.4 w/v% inhibitor concentration.

Credit author statement

Ayoola A.A: Conceptualization, Investigation, Resources, Methodology, Project administration, Supervision, Roles/Writing – original draft. **Babalola R. Validation**, Visualization, Writing – review & editing. **Durodola B.M**. Project administration, Supervision, Validation; Visualization. **Alagbe E.E**. Supervision, Writing – review & editing. **Agboola O**. Supervision, Writing – review & editing. **Adegbile E.O**. Investigation, Formal analysis, Resources, Methodology, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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