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CORROSION INHIBITION OF A36 MILD STEEL IN ACIDIC MEDIUM USING *Citrus paradisi* Rind Inhibitor

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ABSTRACT

The effectiveness of grapefruit (*citrus paradisi* rind) peel powder as a green corrosion inhibitor on A36 mild steel in 0.5M H_2SO_4 was examined. Gravimetric tests, SEM-EDS, and adsorption isotherm techniques were used to determine the corrosion inhibition features of the inhibitor on the surface of A36 mild steel. The tests were carried out with variation in concentration of inhibitor (0–0.4 %w/v), corrosion temperature (301K and 318K), and corrosion time (3–12 hours). The findings demonstrated that *citrus paradisi* rind powder effectively inhibited the corrosion of A36 mild steel on the surface with maximum corrosion inhibition efficiency of 85% at 0.4 w/v% inhibitor concentration at 310K corrosion temperature. The SEM-EDS analysis established the presence of sulphur, nitrogen, and oxygen (organic constituents), as well as the formation of a protective coating on the mild steel surface. Langmuir adsorption isotherm was found suitable for the prediction of the adsorption of *citrus paradisi* rind inhibitor on the mild steel surface. The thermodynamic considerations (ΔH and (ΔS) indicated that the inhibition of A36 mild steel corrosion (using *citrus paradisi* rind inhibitor) was an exothermic process and the inhibitor molecules were physically adsorbed on the metal surface.

Keywords: *Citrus paradisi* Inhibitor, Corrosion, Gravimetric Test, Mild Steel.

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INTRODUCTION

The corrosion process involves the breakdown or degradation of metal owing to interactions between the metal and its corrosive environment. Many industrial operations entail the direct contact of metals with acidic solutions before production, cleaning, maintenance (etc.) can be achieved. And by so doing, such metallic materials suffer corrosion.[1-2] The extent of the negative impacts of corrosion on equipment, factories, the environment, and man is a function of the degree of corrosion suffered by the metallic materials involved. The impacts range from equipment damage or repair, plant shutdown, industrial accidents, the threat to both the environment and human lives, and in extreme cases death.[3-4] According to a study conducted by the National Association of Corrosion Engineers (NACE), worldwide corrosion costs were projected to be US$ 2.5 trillion in 2013, an amount that was calculated to be 3.4 percent of the global GDP worldwide in the same year.[5] One of the effective ways of tackling corrosion problems involves the introduction of corrosion inhibitive substances (inhibitors) that will slow down (or prevent) the corrosion interaction between metals and their corrosive environments.[6-8] Inhibitors are chemical substances, added in minute quantities to the corrosive environment, to resist the degradation of the metal in the corrosive environment.[9-11] Basically, inhibitors are categorized into organic and inorganic inhibitors. Due to the environmental concerns associated with the application of inorganic inhibitors, the research focus has been shifted to the use of organic inhibitors.[9,12-13] Organic inhibitors are not only eco-friendly but also sustainable. Examples of organic inhibitors include extracts from the waste parts of some plants such as orange peels, banana peels, moringa leaves, neem leaves, and mango barks. Studies have shown that organic inhibitors, when introduced into the corrosive environment, are adsorbed on the surface of the metals through the formation of the film (as a coat). The adsorption behaviors of these inhibitors on the metal surface can be

established through certain adsorption isotherms such as Freundlich isotherm, Langmuir isotherm, and Tempkin isotherm.[14-15] In this study, the viability of *citrus paradisi* rind (grapefruit peel) powder as a corrosion inhibitor on A36 mild steel subjected to a corrosive environment of 0.5M H_2SO_4 at corrosion temperatures of 301 and 318 K, and corrosion time of (0–12) days would be investigated.

EXPERIMENTAL

Preparation of Grapefruit Peel (*Citrus paradisi)* Inhibitor

The grapefruit peels were obtained from a local fruit selling kiosk in Ota market, Ogun State Nigeria. The peels were thoroughly washed (using clean water to completely removed all forms of impurities) and then sundried. The crisp form of the peels obtained was further dried in an oven at 105°C for 4 hours to ensure complete water removal. Fine particle size of < 600 µm obtained through the grinding of the dried peels was then stored in an airtight container to prevent the absorption of moisture. The corrosion inhibitor concentrations of (0 – 0.4) %w/v used during corrosion tests were calculated using Eqn.-1.

$$\%\,{}^{w}/_{v} = \frac{weight\ of\ solute}{100ml\ of\ solvent} * 100 \quad (1)$$

Where the solute is the corrosion inhibitor and the solvent is the acid used.

Preparation of A36 Mild Steel Samples

A36 mild steel was cut into 2.5 cm x 2.5 cm samples using tin snip (KSEIBI 142032, USA) and the samples were then polished using different grades of emery papers to remove rust and debris in order to obtain a smooth surface of each of the samples. The samples were then thoroughly rinsed in distilled water and acetone and then dried before being preserved in talcum powder before usage. The chemical composition of the A36 mild steel sample is given in Table-1.

Table-1: A36 Chemical Constituents

Element	C	Si	Mn	Cu	Mo	Al	Ni	Cr	Fe
Composition (%)	0.29	0.26	1.02	0.20	0.07	0.05	0.02	0.09	98

Phytochemical Tests on the Inhibitor

In order to ascertain the presence of certain compounds, the grapefruit peel powder was subjected to phytochemical tests. That is, alkaloids, tannins, saponins, flavonoids, and phenols were tested for.[13]

Gravimetric Tests

Gravimetric tests of the mild steel were carried out in a corrosive environment of 0.5M H_2SO_4 at different inhibitor concentrations of (0–0.4 %w/v), corrosion time of (3–12 hours), and corrosion temperatures of 301K and 318K. Five sets of experiments (at different inhibitor concentrations with a range of 0 – 0.4 w/v) were carried out at temperatures of 301 and 318 K each. Each of the samples was measured and weighed before and after the corrosion test before being immersed in a 100 ml test solution of 0.5M H_2SO_4 (at different inhibitor concentrations). At a specified corrosion time, each sample was withdrawn from the medium and carefully rinsed in both the acetone and distilled water, dried, and then reweighed. The difference in weights after and before corrosion was noted as the weight loss. Corrosion rate, CR, (mm/yr.) was calculated using Eqn.-2.

$$CR = \frac{K \times \Delta m}{D \times S \times t} \quad (2)$$

Where, Δm = weight loss in g, D = density of the metal in gcm^{-3}, S = total surface area of the specimen, t = immersion time in hours, K= 8.76. Inhibition efficiency, IE, (%) was calculated using Eqn.-3.

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

Where W_{corr} and W'_{corr} are weight loss in the absence and presence of inhibitors respectively.

Adsorption Isotherm

The appropriate adsorption isotherm that described the adsorption of the inhibitor on the metal surface was obtained by fitting the calculated surface coverage (Θ, as expressed in Eqn.-4) to each of the isotherms (Langmuir, Freundlich, and Tempkin isotherms). The Langmuir isotherm (Eqn.-5) expresses the relationship between the surface coverage (Θ) and inhibitor concentration (C).

$$\theta = \frac{W_{corr} - W'_{corr}}{W_{corr}} \quad (4)$$

$$\frac{C}{\theta} = \frac{1}{k_{ads}} + C \quad (5)$$

Where k_{ads} is the adsorption equilibrium constant. And the energy loss to the environment, the Gibbs free energy of adsorption (ΔG_{ads}) was calculated using Eqn.-6.

$$\Delta G_{ads} = -2.303RT\log(55.5k_{ads}) \quad (6)$$

Where R = universal gas constant, T = temperature in Kelvin, and k_{ads} = adsorption equilibrium constant.

Equation-7 was used in the determination of the other thermodynamic parameters such as a change in enthalpy (ΔH_{ads}) and entropy change (ΔS_{ads}) during the adsorption process by making a plot of $\log k_{ads}$ vs $^1/_T$.

$$\log k_{ads} = \frac{1}{2.303}\left(\frac{-\Delta H_{ads}}{RT}\right) + \left(\frac{\Delta S_{ads}}{R}\right) \quad (7)$$

RESULTS AND DISCUSSION

Phytochemical Analysis Result

Phytochemical analysis revealed a high level of flavonoids and the absence of tannins in the inhibitor, as indicated in Table-2.

Table-2: Phytochemical analysis of the inhibitor

Compound	Inference
Tannins	-
Alkaloids	*
Flavonoids	**
Saponins	*
Phenols	*

** = *highly present*, * = *moderately present*, - = *absent*

Weight Loss Results

The results of the weight loss suffered by A36 mild steel with and without the use of inhibitor at varying concentrations (0 – 0.4 %w/v) and varied temperatures (301 and 318 K) are shown in Figs.-1 and 4. In Fig.-1 and 2, weight loss trends increased with an increase in corrosion time from 3 to 12 hours at both 301 and 318K. But it was observed that the metal samples suffered more weight loss at a higher temperature of 318K (under the same experimental conditions). Also, high weight loss (of up to 0.43 g and 1.40 g in Figs.-1 and 2 respectively) were noticed when no inhibitor was used while insignificant weight loss change was observed with the use of the high inhibitor concentration of 0.4 %w/v in Figs.-1 and 2. Figures-3 and 4 showed the variation of weight loss with the inhibitor concentrations. That is, the lower weight loss recorded at higher inhibitor concentration revealed that *citrus paradisi* rind inhibitor was adsorbed firmly on the metal samples thereby preventing the loss of the metal surface.[3]

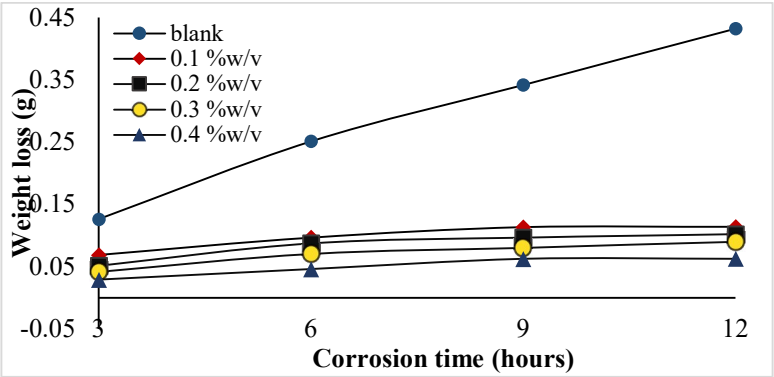

Fig.-1: Weight Loss and Corrosion Time at 301K

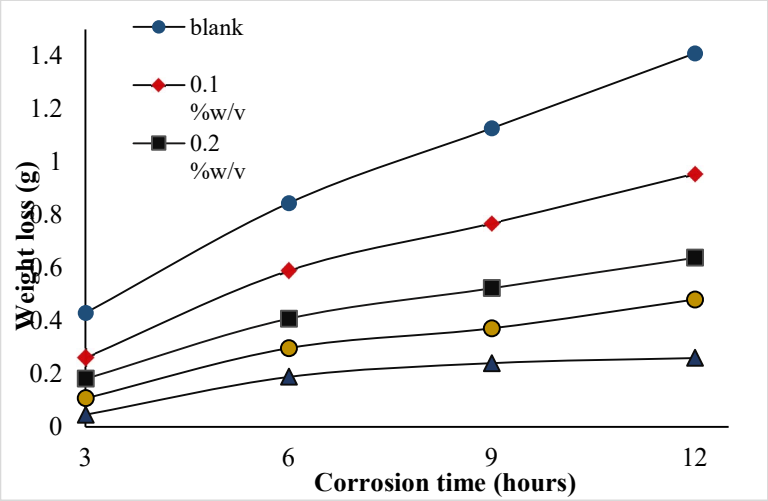

Fig.-2: Weight Loss and Corrosion Time at 318K

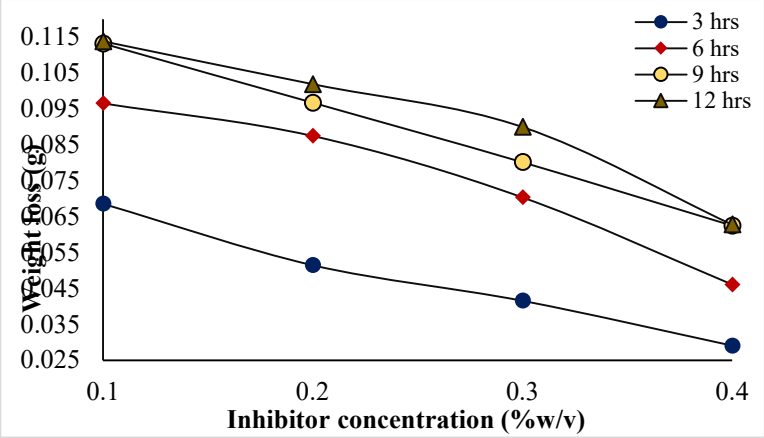

Fig.-3: Weight Loss and Inhibitor Concentration at 301K

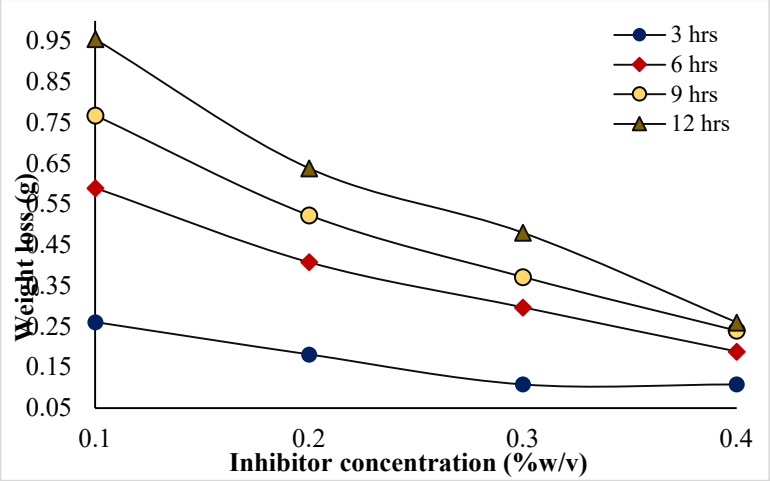

Fig.-4: Weight Loss and Inhibitor Concentration at 318K

Corrosion Rate Results

The results of the variation in corrosion time and inhibitor concentrations on corrosion rate are shown in Figs.-5 to 8. Similar to weight loss results, the highest corrosion rate of 135 mm/yr. was recorded with no inhibitor concentration at 318K (Fig.-6). While the lowest corrosion rate of 4 mm/yr. with 0.4%w/v inhibitor concentration at 301K was recorded (Figs.-5 to 7). That is, there was a general trend of reduction in corrosion rate with increased inhibitor concentration from 0 – 0.4 %w/v and at increased corrosion

temperature from 301 to 318K. An increase in corrosion temperature speed up the corrosion reaction mechanism thereby leading to an increased corrosion rate but the increased inhibitor concentration increases the amount adsorbed on the metal surface thereby reducing the corrosion rate[15]. Figs.-1 to 4 revealed a similar trend of results.

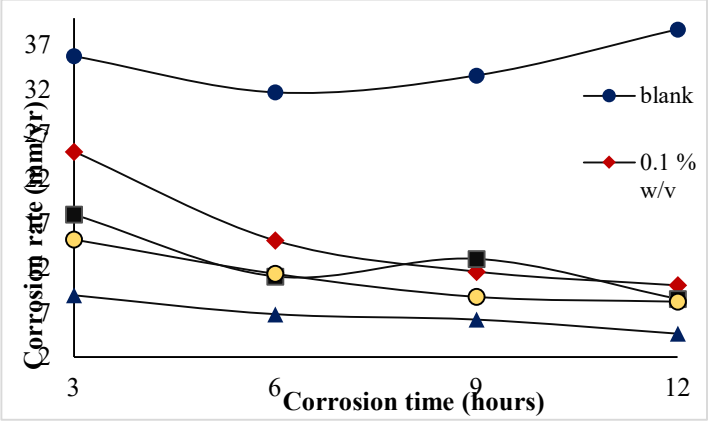

Fig.-5: Corrosion Rate and Corrosion Time at 301K

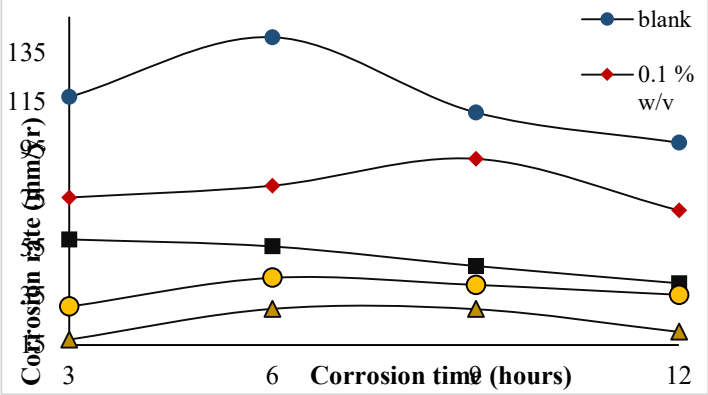

Fig.-6: Corrosion Rate and Corrosion Time at 318K

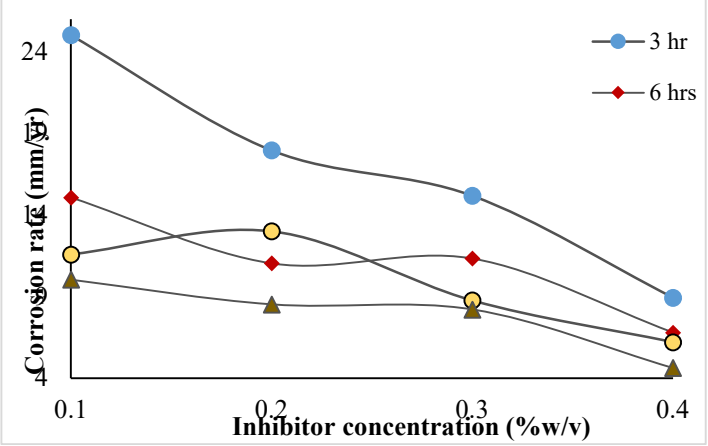

Fig.-7: Corrosion Rate and Inhibitor Concentration at 301K

Inhibition Efficiency Results

The results of the inhibition efficiency at varied *citrus paradisi rind* inhibitor concentrations (0–0.4 %w/v) both at 301 and 318 K are shown in Fig.-9 to12. The general trend revealed an increase in inhibition efficiency when there was an increase in inhibitor concentrations but a decrease in corrosion temperature. That is, the highest inhibitor efficiency of 87% was noticed at the inhibitor concentration of 0.4 %w/v, 12

hours corrosion time and 301K corrosion temperature. And the least inhibition efficiency of 20% was recorded at the concentration of 0.1 %w/v, 6 hours corrosion time, and 318K corrosion temperature.

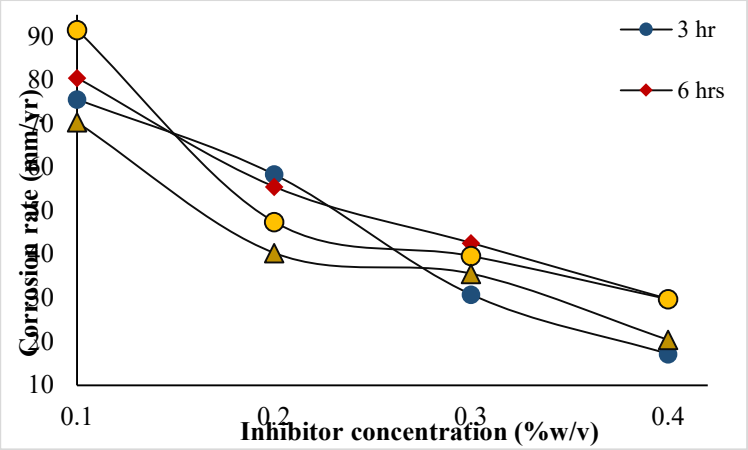

Fig.-8: Corrosion Rate and Inhibitor Concentration at 318K

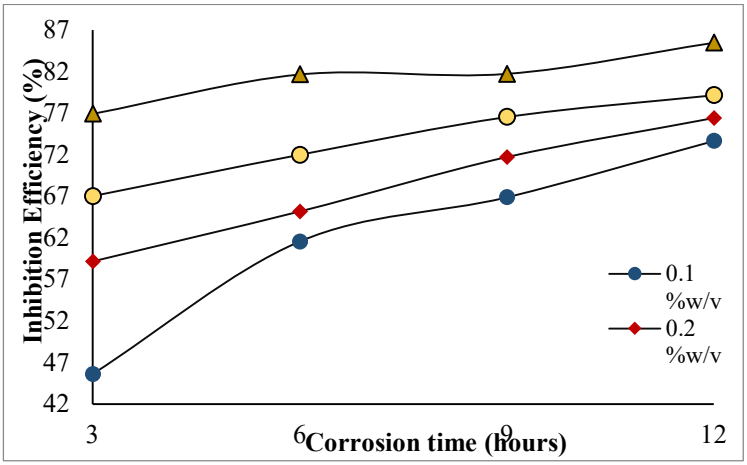

Fig.-9: Inhibition Efficiency and Corrosion Time at 301K

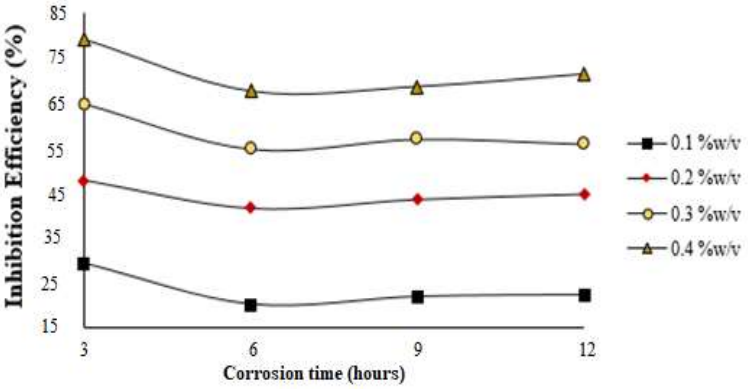

Fig.-10: Inhibition efficiency and corrosion time at 318K

SEM – EDS Analysis

The inhibitive effects of c*itrus paradisi* rind powder inhibitor on the surface of the mild steel metal samples were studied through the use of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), as shown in Figs.-13 and 14. SEM morphology revealed in Figs.-13a and 14a that the metal samples without inhibitor suffered a great degree of corrosion in each case of the two temperatures.

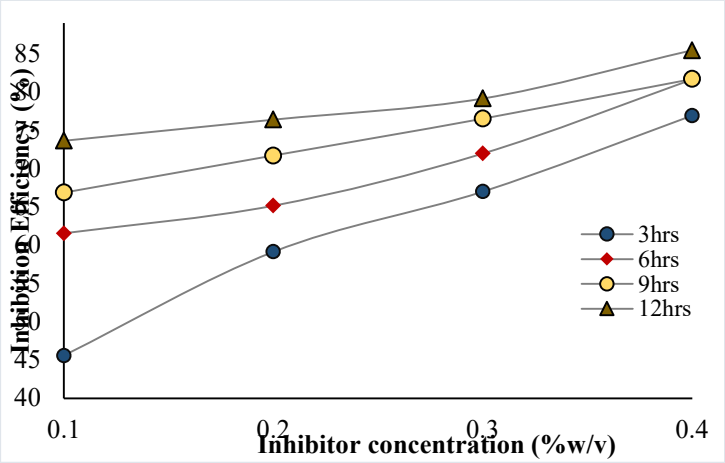

Fig.-11: Inhibition Efficiency and Inhibitor Concentration at 301K

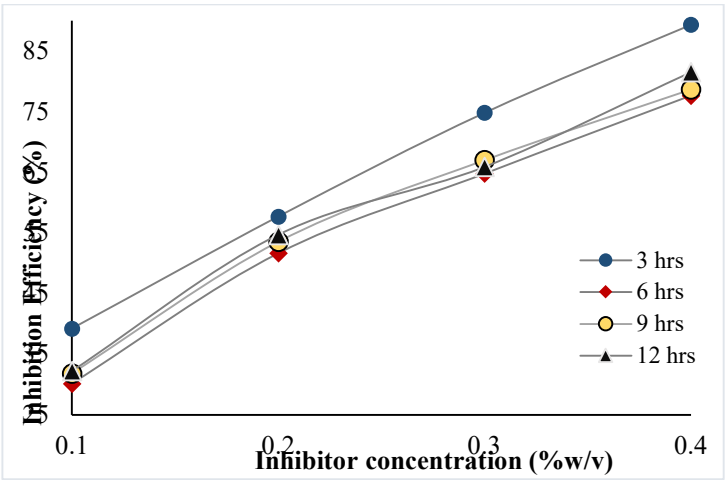

Fig.-12: Inhibition Efficiency and Inhibitor Concentration at 318K

While the least case of corrosion was noticed when the highest inhibitor concentration of 0.4 %w/v was used in each case of the two temperatures. That is, as the inhibitor concentration increased, the degree of metal corrosion decreased. This is an indication of progressive adsorption of *citrus paradisi* rind inhibitor on the metal surface thereby inhibiting corrosion reaction on the surfaces. Comparing Figs.-13a and 14a (at the same inhibitor concentration), it could be seen that increase in corrosion temperature promoted the corrosion process since the level of corrosion was more pronounced at 318K (45^0C) compared to 301K (28^0C). Also, a keen observation of Figs.-13b and 14b (energy dispersive spectroscopy of the metal surfaces) showed that the application of the corrosion inhibitor at 0.4 %w/v increased the levels of both the organic compounds and iron (for each of the corrosion temperatures considered) but decreased the inorganic constituents. This further confirmed the fact that *citrus paradisi rind* inhibitor is rich in organic compounds (such as flavonoids and alkaloids) that behave as antioxidant phytochemicals.[13,16] This correlates with findings in the literature that organic inhibitors like flavonoids, alkanoids, and phenols are good inhibitors during the corrosion of metals.[13,16]

Adsorption Isotherm Results

The results of Langmuir isotherm plots obtained at different inhibitor concentrations and corrosion temperatures were presented in Fig.-15. It could be generally observed that the plots of $^{C}/_{\theta}$ vs C yielded straight-line graphs of the increase in values of $^{C}/_{\theta}$ as the inhibitor concentration increased. The straight lines obtained gave linear correlation coefficient (R^2) values of approximately one (1).

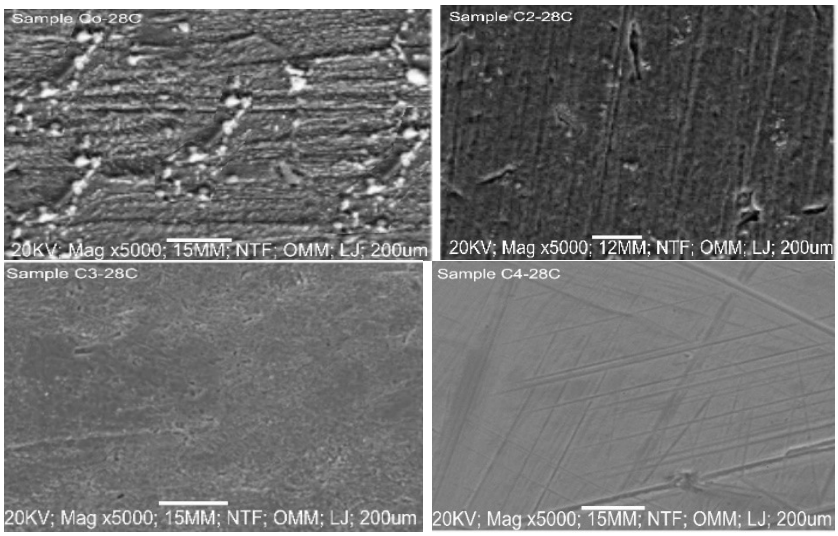

Fig.-13a: Scanning Electron Microscope Images of A36 Mild Steel in (a)0.0 %w/v (b)0.2 %w/v (c)0.3 %w/v and (d) 0.4% w/v *Citrus paradisi* Rind Inhibitor at 301K (28^0C)

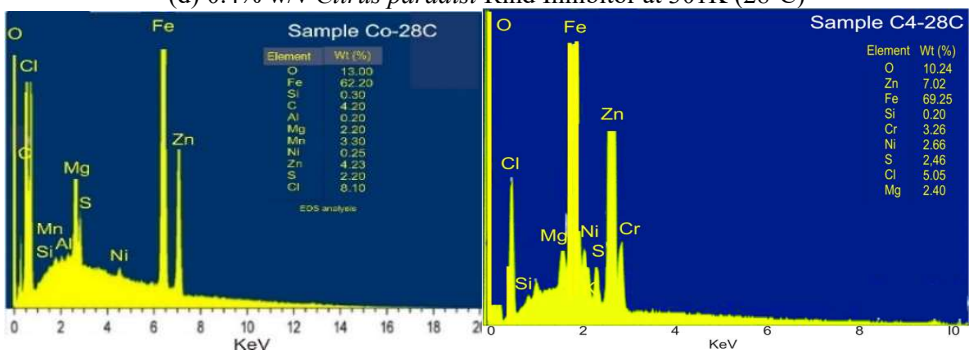

Fig.-13b: EDS Images of A36 Mild Steel in (C0) 0.0% w/v and (C4) 0.4% w/v *Citrus paradisi* Rind Inhibitor at 301K (28^0C)

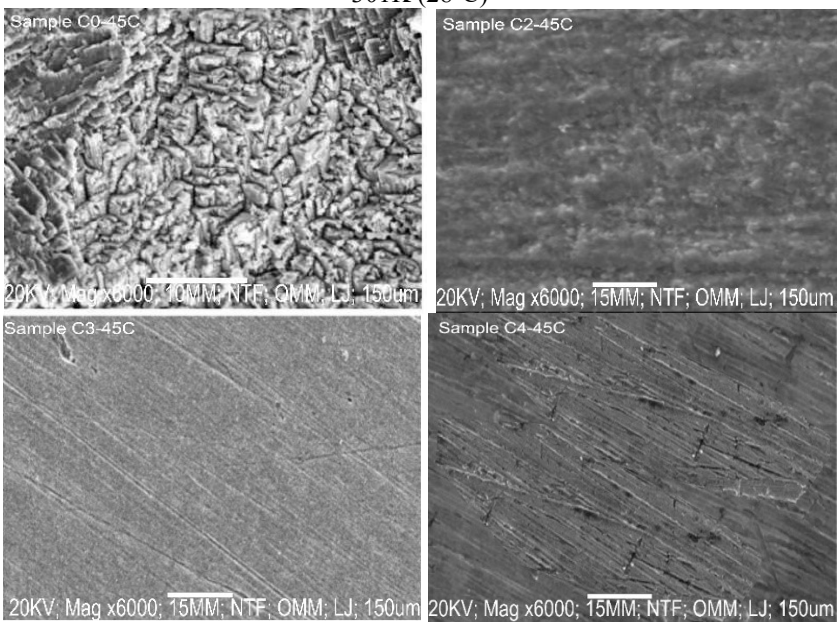

Fig.-14a: Scanning Electron Microscope Images of A36 Mild Steel in (a)0.0 %w/v (b)0.2 %w/v (c)0.3 %w/v and (d) 0.4% w/v *Citrus paradisi* Rind Inhibitor at 318K (45^0C)

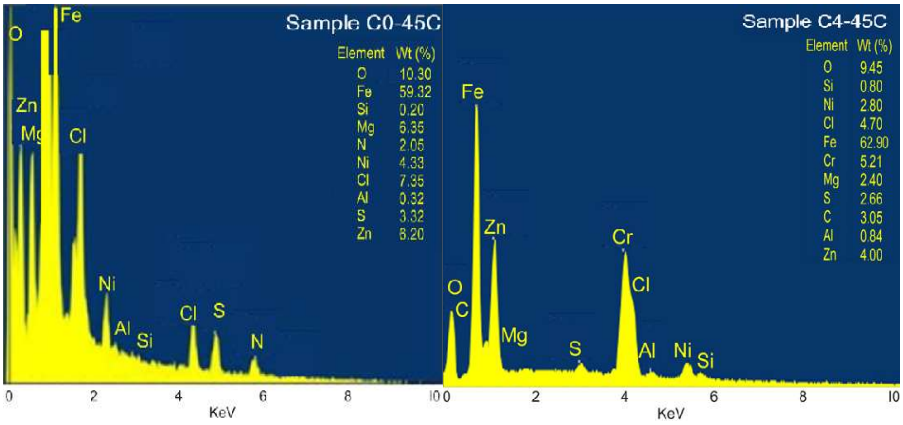

Fig.-14b: EDS Images of A36 Mild Steel in (C0) 0.0% w/v and (C4) 0.4% w/v *Citrus paradisi* Rind Inhibitor at 318K (45^{0}C)

That is, the high values of R^2 obtained in all cases indicate that the Langmuir adsorption isotherm was suitable for the accurate description of the adsorption mechanism of *citrus paradisi* rind inhibitor on the metal surface.

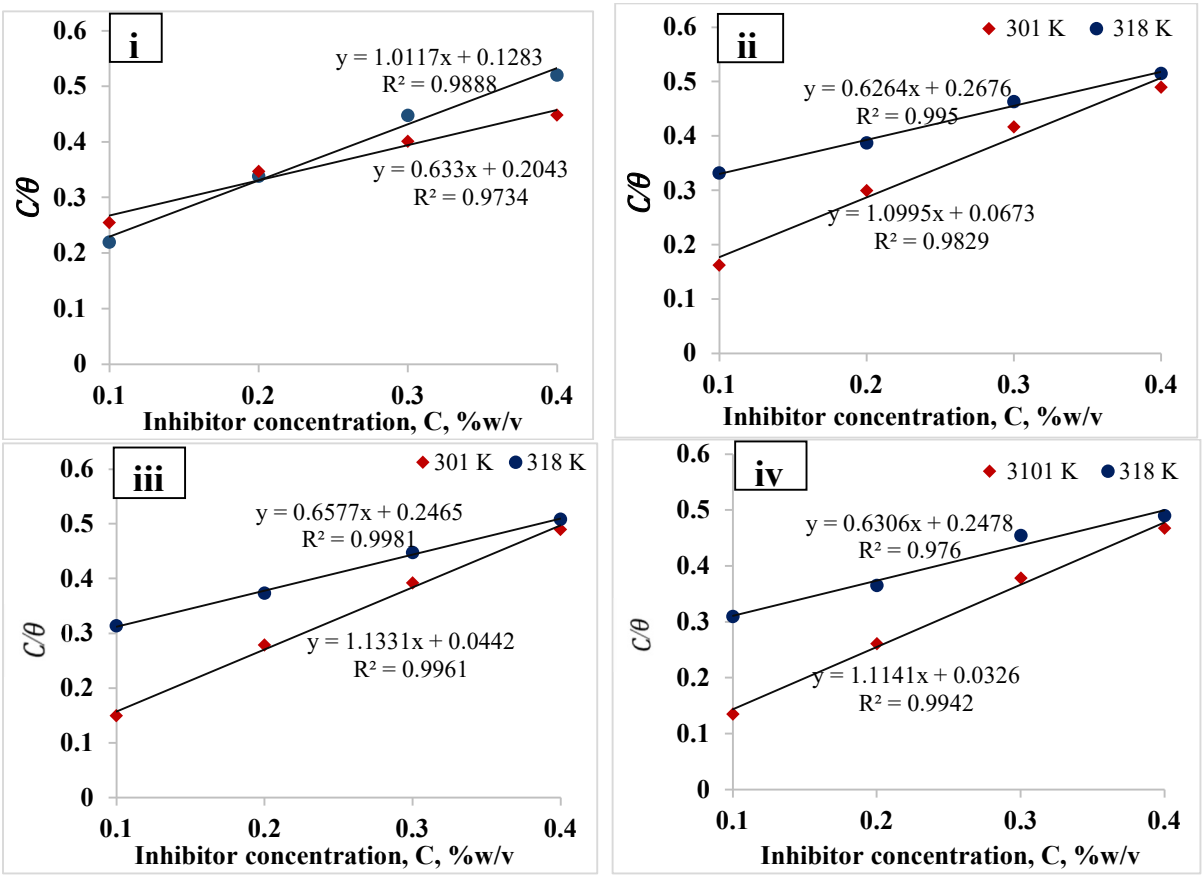

Fig.-15: Langmuir Isotherm Plots at (i) 3 hours, (ii) 6 hours, (iii) 9 hours, (iv) 12 hours

As shown in Table-3, the values of the adsorption constant (k_{ads}) obtained were positive, confirmation of good adherence to the inhibitor on metal surfaces. Higher the positive value of k_{ads}, the better the level of adherence to the inhibitor. Hence, the adsorption of the inhibitor on the metal surface at 301K was better compared to the results obtained at 318K. This can also explain the reduction in corrosion rate obtained at a lower temperature of 301K (Figs.-7 and 8). The calculated values of the other thermodynamic properties (change in enthalpy ΔH, and entropy change ΔS) were shown in Table-4. The negative values of ΔH imply

that the corrosion process of the mild steel was an exothermic reaction and the process was decreasingly exothermic with increased inhibitor concentration due to better inhibitory action at higher inhibitor concentration. The values obtained for ΔS are negative and there was an increase in negativity as the inhibitor concentration increased. These values revealed a higher level of disorderliness of the corrosion process at lower inhibitor concentrations. These thermodynamic properties (ΔH and ΔS) also corroborate the fact that *citrus paradisi* rind inhibitor performed well as a corrosion inhibitor, especially at the higher inhibitor concentration of 0.4 %w/v.

Table-3: Langmuir Adsorption Isotherm Data

Time	R^2 value		k_{ads}	
	301K	318K	301K	318K
3	0.9888	0.9734	7.79	4.89
6	0.9950	0.9829	14.86	3.74
9	0.9981	0.9961	22.62	4.06
12	0.9760	0.9942	30.67	4.03

Table-4: Thermodynamic Parameters for the Adsorbed *citrus paradisi* Rind Inhibitor on Mild Steel within the Corrosion Temperature (301 – 318K) at 12 hours Corrosion Time

Concentration (%w/v)	ΔH_{ads} (kJ mol^{-1})	ΔS_{ads} (kJ mol^{-1})
0	-26.84	-109.64
0.1	-25.49	-108.90
0.2	-11.28	-159.30
0.3	-10.25	-162.99
0.4	-7.79	-171.32

CONCLUSION

Based on the results obtained, the following conclusions can be made:

1. *Citrus paradisi* rind powder is established to be a good corrosion inhibitor for mild steel in 0.5M H_2SO_4 solution.
2. The maximum inhibition efficiency of *citrus paradisi* rind powder was found to be 85% at an inhibitor concentration of 0.4 %w/v, corrosion time of 12 hours, and corrosion temperature of 301K.
3. The SEM-EDS analysis established the presence of sulphur, nitrogen, and oxygen (organic constituents) as well as the formation of a protective coating on the mild steel surface.
4. Langmuir adsorption isotherm was found suitable for the description of the adsorption of *citrus paradisi* rind inhibitor on A34 mild steel surface.
5. Thermodynamic considerations indicated that the inhibition of A34 mild steel corrosion (using *citrus paradisi* rind inhibitor) was an exothermic process.

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