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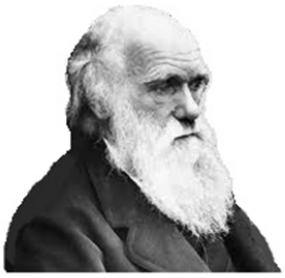

World News of Natural Sciences

An International Scientific Journal

WNOFNS 53 (2024) 17-31 EISSN 2543-5426

Gravimetric study of corrosion inhibition of mild steel in H_2SO_4 environment using watermelon (*Citrullus lanatus* (Thunb.) Matsum. & Nakai) leaf extract as inhibitor

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ABSTRACT

This work presents gravimetric study of corrosion inhibition of mild steel in H_2SO_4 environment using watermelon (*Citrullus lanatus*) leaf extract as inhibitor. The extract was characterized in terms of phytochemical status and functional groups. Its efficiency in the corrosion inhibition was optimized using response surface methodology (RSM). In the RSM, interactive effects of inhibitor concentration, temperature and time on the efficiency of the extract were monitored using central composite design of design expert software. Analysis of the results show that watermelon leaf extract successfully inhibited corrosion of mild steel in H_2SO_4 environment. Predominant functional groups of watermelon leaf include; C-H stretch (2851.4 cm^{-1}), N-H symmetric and asymmetric stretch (3267.7 cm^{-1}), C=H stretch (2195.4 cm^{-1}), =C-O-C stretch (1241.2 cm^{-1}), C=O symmetric and asymmetric stretch (17722.0 cm^{-1}), C-F (1155.5 cm^{-1}) and =C-H bend (674.0 cm^{-1}). It contains polar atoms of nitrogen and oxygen. Its major phytochemicals are alkaloids (243.14 ±0.03 mg/100g) and tannins (216.32 ±0.02 mg/100g). The extract possesses good inhibitive properties. Weight loss, corrosion rate, inhibition efficiency and degree of surface coverage were influenced by time of immersion of the mild steel, temperature and concentration. The watermelon leaf extract exhibited high inhibition efficiency. Hence, it can be used to inhibit corrosion of mild steel in H_2SO_4 solution. Quadratic equation reliably connects the inhibition efficiency with the considered factors. Optimum Inhibition efficiency of 92.96% was attained by the watermelon leaf extract.

Keywords: Gravimetric study, Corrosion inhibition, Watermelon leaf, H_2SO_4 *Citrullus lanatus*

(Received 28 November 2023; Accepted 30 December 2023; Date of Publication 04 January 2024)

1. INTRODUCTION

In general, metals (mild steel inclusive) are characterized by distinctive qualities such as lustre, conductivity, malleability and ductility. They easily form metallic connections with other metals and ionic bonds with non-metals. Large quantities of energy are required to extract metals from their ore. During the smelting and refining processes, metals store heat as potential energy. As a result, the metals are in unstable state and will eventually lose their energy by reverting to compounds that are more or less similar to their original states. In interacting with the environment, stored potential energy of the metal is released during corrosion process [1]. Corrosion is destructive and silent operating processes, which causes problems to industries. Consequences of this process are many, and the effects of these on the safety and efficient operation of equipment/structures are huge [2].

Failure of various kinds and the need for replacements of expensive metallic structures due to corrosion are of great concern. Knowing that corrosion is inevitable to eliminate, efforts are made to minimize it by adopting certain anti-corrosion procedures, which include deployment of corrosion inhibitors. Corrosion inhibition has a wide range of significance in industrial processes.

There are five primary methods of corrosion control, and they include; material selection, coatings, application of inhibitors, cathodic protection and design. Of all the mentioned methods, application of inhibitor has received favourable attention in current research works. Chemical substances such as chromates, silicates and organic amines are commonly applied as inhibitors in corrosion inhibition of metals in corrosive environment. Function of inhibitor is favoured in isolated system where the necessary concentration of inhibitor can be maintained. The mechanisms of the inhibition can be quite complex [2-5].

In the use of organic amines for corrosion inhibition, molecules of organic ammine are adsorbed on anodic and cathodic sites and suppress the corrosion current. Other inhibitors affect either the anodic or cathodic process and can also promote the formation of protective films on the metal surface. Due to environmental concerns, emphasis is shifting from use of harmful synthetic substances (such as chromates) to application of eco-friendly inhibitors (ionic liquid, plant extract, pharmaceutical drug and polymeric material) in corrosion control process. Of all the eco-friendly inhibitors, plant extract is of great research interest because it is readily available and renewable. There are several research reports on the use of plant extracts for corrosion control of metals [2, 6-9].

There is need to expand the application of plant extracts as inhibitors by including notable fruit plants (such as Watermelon) whose leaves are often discarded as wastes. Watermelon (*Citrullus lanatus*) is a flowering plant species of the *Cucurbitaceae* family. It is grown in favourable climate (from tropical to temperate regions worldwide) for its large edible fruit. Review of the literature showed that there are no available data on the application of watermelon leaf extract as corrosion inhibitor of mild steel in H_2SO_4 medium. Watermelon leaf is often discarded as waste, even when its antioxidants can be explored for various useful applications.

Thus, the aim of this study is to apply extract of watermelon leaf as inhibitor for corrosion control of mild steel in H_2SO_4 environment. Result of this work will help in developing locally sourced eco-friendly inhibitors for optimum corrosion control of mild steel. The watermelon leaf extract will be useful as inhibition additive in H_2SO_4 medium for pickling mild steel structures.

2. MATERIALS AND METHOD

2. 1. Mild steel preparations

The mild steel used for this study was cut into corrosion coupons of sizes 3×3 cm. The surface preparation of the mechanically polished specimens were carried out using different grades of emery paper and then degreased with acetone after washing with distilled water.

2. 2. Characterization of the watermelon leaf

2. 2. 1. Characterization of watermelon leaf in terms of functional groups

Fourier transform infrared (FTIR) spectrophotometer (Cary 630, Agilent Technologies USA) was employed to determine the functional groups of the watermelon leaf. FTIR spectrum was obtained in transmission mode using the Br pellet method. In the process, Fourier transform converted raw data into actual spectrum (with various peaks). Analysis of the FTIR produced peaks were carried out so as to identify the corresponding functional groups in accordance with procedure used by previous research report [10].

2. 2. 2. Phytochemical analysis of watermelon leaf

Standard methods used by previous report [11] were adopted for the phytochemical screening of the watermelon leaf. On the alkaloids screening, 1g of solvent free leaf extract was transferred in to test tube. 3 drops of dilute HCl were added, stirred and filtered. The filtrate was tested carefully with alkaloid reagents; Mayer's reagent (Cream ppt), Dragendorff's reagent (Orange-brown ppt). In the recognition of cardiac glycosides presence, 1 ml of watermelon leaf sample, 5 ml water and 2 ml glacial acetic acid were mixed in a vessel. 1 drop of $FeCl_3$ was added. Thereafter, 1ml conc. H_2SO_4 was added. There was an appearance of brown ring. For the detection of flavonoids presence, 25 ml water was added to 1g of watermelon leaf sample. It was put in an oven set at 100 °C for 15 min. 5 ml of NH_4OH was added to 2ml of the sample.

Then 1 ml conc. H_2SO_4 was added. There was an appearance of yellow colour signifying the presence of flavonoids. The presence of phenols was examined by adding 3 drops of 1% (w/v) solution of ferric chloride followed by 1% (w/v) gelatin in sodium chloride of the same concentration. The formation of a precipitate indicated the presence of phenols. For the determination of saponins presence, 1g of watermelon leaf sample was boiled in 40 ml of distilled water, and then filtered. 10 ml of the filtrate was shaken vigorously until froth formation was noticed. 3 drops of oil were added, and the mixture was shaken until emulsion of the oil was noticed. For the determination of tannins, 1g of the watermelon leaf sample was added to 25 ml of distilled water. It was then put in oven set at 100 °C for 15 min. To 1 ml of the watermelon leaf sample, 10 ml distilled water was added and then boiled. A few drops of 0.1% $FeCl_3$ were added; green colour appeared indicating the presence of tannins.

Quantitative analyses of the samples were carried out as follows:

a) **Quantitative evaluation of alkaloids in watermelon leaf**
   20 ml of 10% acetic acid in ethanol was added to the 1g of watermelon leaf sample. The mixture was shaken and allowed to settle for 4 hrs, and then filtered. The filtrate was evaporated to 1/4 of its initial volume. A drop of concentrated ammonium hydroxide was added, and the formed precipitate was filtered with the aid of filter paper. The filter

paper was left to dry in the oven at temperature of 60 °C. The filter paper was weighed after drying it to a constant weight.

$$Alkaloid = \left(\frac{w_r - w_f}{w_0}\right) \quad (1)$$

where w_r = weight of filter paper + residue, w_f = weight of filter paper, and w_0 = weight of the watermelon leaf sample.

b) Quantitative evaluation of cardiac glycosides in watermelon leaf

1g of the watermelon leaf sample was put in an oven of temperature set at 100 °C for 15 min. 1 ml of the watermelon leaf sample and 5 ml water were added to 2 ml glacial acetic acid plus 1 drop of $FeCl_3$. Then, 1 ml of conc. H_2S0_4 was added. The absorbance of the resulting solution was read at 410 nm.

c) Quantitative evaluation of flavonoids in watermelon leaf

0.5 ml of 2% $AlCl_3$ methanol solution was added to 0.05 ml watermelon leaf solution. After 1 hr at room temperature, yellow colour appeared indicating the presence of flavonoids. Flavonoids content as mg/g quereetin was then determined.

d) Quantitative evaluation of phenols in watermelon leaf

0.2% formic acid was added to 2g of the watermelon leaf sample and allowed to settle for 2 min. It was then filtered. With the aid of pipette, 2 ml of the filtrate was put into a test tube and 0.5 ml folin-ciocalteau reagent was added. It was left for 20 minutes for colour development. The absorbance at 765 nm was measured and the concentration for a standard graph was obtained, which is expressed as GAE/g (Gallic Acid Equivalent).

e) Quantitative evaluation of phytate in watermelon leaf

Ferric ammonium sulphate was added to 0.5 ml of the watermelon leaf sample in a test tube. The test tube was heated in water bath for 30 minutes. It was cooled and centrifuged. Then, 1.5 ml of 2,2-bipyridine solution was added to 1ml of the supernatant. With distilled water as blank, measurement was carried out at 519 nm.

f) Quantitative evaluation of saponins in watermelon leaf

Into 1g of watermelon leaf sample, 15 ml ethanol was added and put in a water bath with thermostat set at 55 °C for 4 hrs. It was filtered and the residue was washed twice with 20% ethanol. The watermelon leaf sample was reduced to about 5 ml in the oven. 5 ml of petroleum ether was added to the concentrated sample inside a separating funnel. The petroleum ether layer was discarded and 3 ml of butanol was added to it. It was washed with 5 ml of 5% sodium chloride, and put in the oven to evaporate to dryness. Then, the residue was weighed with electronic weighing balance.

g) Quantitative evaluation of tannins in watermelon leaf

1g of the watermelon leaf sample was extracted with 25 ml of the solvent mixture of 80:20 acetone: 10% glacial acetic acid for 5 hrs. It was filtered and the absorbance measured at 500 nm. The absorbance of the reagents blank was also measured. A standard graph with 10, 20, 30, 40, 50 mg/100g of tannic acid was drawn. Then, the concentration of tannin (taking into consideration any dilution factor) was obtained.

2. 3. Weight loss method

The weight loss (gravimetric) method used by previous research works [9, 10] was adopted in this study. The variations of weight loss were monitored periodically at various temperatures and in 1M H_2SO_4 media, in the absence and presence of various concentrations of watermelon leaf extract. 150 ml of 1M H_2SO_4 in 250 ml of beaker was used in each case. At the appropriate time, the mild steel samples were taken out, immersed in acetone, scrubbed with a bristle brush under running water, dried and reweighed. The weight loss (Δw), corrosion rate (CR), inhibition efficiency (IE) and degree of surface coverage were calculated using the Equations (2), (3), (4) and (5) respectively:

$$\Delta w = w_i - w_f \tag{2}$$

$$CR = \frac{w_i - w_f}{At} \tag{3}$$

$$IE\% = \frac{\omega_0 - \omega_1}{\omega_0} * 100 \tag{4}$$

$$\Theta = \frac{\omega_0 - \omega_1}{\omega_0} \tag{5}$$

where w_i and w_f are the initial and final weight of mild steel samples respectively; ω_1 and ω_0 are the weight loss values in presence and absence of palm fibre extract (inhibitor), respectively.

A is the total area of the mild steel sample and t is the time of immersion.

2. 3. 1. Determination of effects of corrosion control variables

Effects of corrosion control variables (inhibitor concentration, temperature and time) on weight loss, corrosion rate, inhibition efficiency) were determined.

2. 3. 2. Optimization of the inhibition efficiency

On the response surface methodology (RSM), Design Expert software was used to design the experiment. Interactive effects of inhibitor concentration, temperature and time on the inhibition efficiency were determined.

3. RESULTS AND DISCUSSION

3. 1. Characteristics of the watermelon leaf in terms of the functional groups as determined by Fourier transform infrared (FTIR) spectrophotometer

FTIR spectrum of the watermelon leaf extract is presented in Figure 1. The predominant functional groups include; C-H stretch (2851.4 cm^{-1}), N-H symmetric and asymmetric stretch (3267.7 cm^{-1}), C=H stretch (2195.4 cm^{-1}), =C-O-C stretch (1241.2 cm^{-1}), C=O symmetric and

asymmetric stretch (17722.0 cm^{-1}), C-F (1155.5 cm^{-1}) and =C-H bend (674.0 cm^{-1}). It contains heteroatoms (nitrogen and oxygen) and. double bonds. Substances of such properties have been referred to as suitable corrosion inhibitors [12, 13]. The double bonds and heteroatoms enhance inhibitive characteristics of an inhibitor.

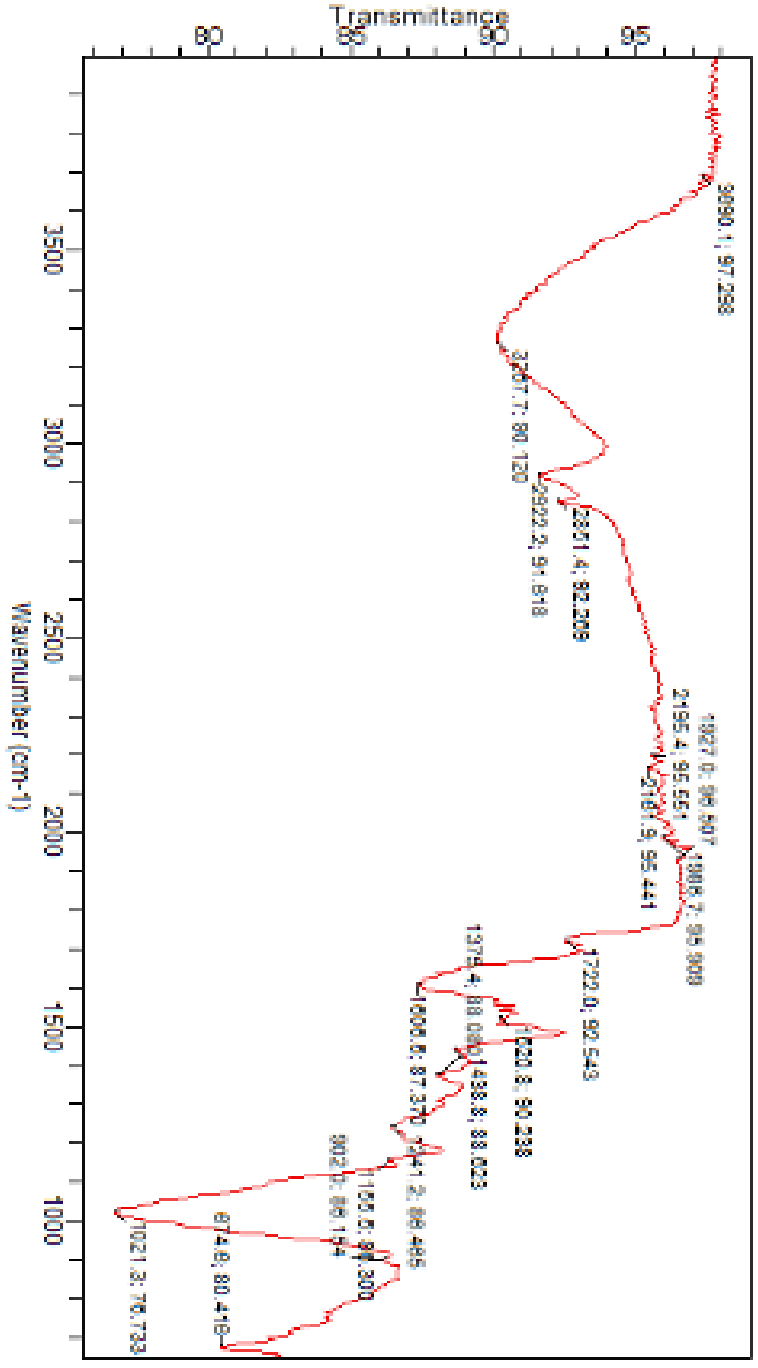

Figure 1. FTIR spectrum of the watermelon leaf extract

3. 2. Phytochemicals of the watermelon leaf extract

Result of qualitative and quantitative analyses of phytochemicals watermelon leaf extract is presented in Table 1. The qualitative information of the phytochemicals are coded with; +++ (highly concentrated), ++ (concentrated), + (in traces), and – (absent or too little to be observed qualitatively). These phytochemicals are common in plants/plant extracts [11, 14, 15]. Cardiac glycosides (6.87 ±0.01 mg/100g) appear in traces. The predominant phytochemicals of watermelon are alkaloids (243.14 ±0.03 mg/100g) and tannins 216.32 ±0.02 mg/100g) mg/100g). It shows that watermelon leaf extract has good inhibitive properties.

Table 1. Qualitative and quantitative phytochemicals of watermelon leaf extract

Phytochemicals	Qualitative results	Quantitative results
Alkaloids (mg/100g)	+++	243.14 ±0.03
Cardiac glycosides (mg/100g)	-	6.87 ±0.01
Flavonoids (mg/100g)	+	50.44 ±0.05
Phenolics (GAE/g)	+	29.50 ±0.09
Phytates (mg/100g)	++	100.36 ±0.11
Saponins (mg/100g)	+	80.15 ±0.18
Tannins (mg/100g)	+++	216.32 ±0.02

–. (too little to be observed qualitatively), + (in traces), ++ (concentrated) and +++ (highly concentrated)

3. 3. RSM results of the corrosion control process

Table 2. RSM result for mild steel in HCl medium with watermelon leaf extract

Std	Run	Factor 1 A: Inhibitor conc. g/L	Factor 2 B: Temperature K	Factor 3 C: Time hr	Response 1 Inhibition efficiency %
17	1	0.7	313	4	93.65
13	2	0.7	313	3	88.64
7	3	0.5	323	5	66.24
9	4	0.5	313	4	80.78

3	5	0.5	323	3	58.71
8	6	0.9	323	5	75.87
10	7	0.9	313	4	91.13
1	8	0.5	303	3	67.41
12	9	0.7	323	4	80.67
5	10	0.5	303	5	82.96
19	11	0.7	313	4	93.65
2	12	0.9	303	3	75.61
6	13	0.9	303	5	82.83
16	14	0.7	313	4	93.65
18	15	0.7	313	4	93.65
11	16	0.7	303	4	90.18
20	17	0.7	313	4	93.65
15	18	0.7	313	4	93.65
4	19	0.9	323	3	72.09
14	20	0.7	313	5	92.27

Table 2 presents the RSM results of the corrosion inhibition of mild steel in H_2SO_4 medium with watermelon leaf extract. Inhibition efficiency increased with increase in inhibitor concentration [16-19]. Maximum value of inhibition efficiency of the extract was recorded as 93.55% at inhibitor concentration of 0.7 g/L, temperature of 313K and time of 4hrs. This is an indication that the interactive effect of the variables on the responses is in parabolic form, which is in conformity with quadratic model [5]. Table 3 shows the fit summary response of inhibition efficiency of watermelon leaf extract Out of the four tested models (linear, 2FI, quadratic and cubic), quadratic model is suggested as the best fitted because the adjusted R^2 of is close to 1, and it is in close proximity to the predicted R^2 (0.9279).

Table 3. Fit summary response of inhibition efficiency of watermelon leaf extract

Source	Sequential p-value	Adjusted R^2	Predicted R^2	
Linear	0.2304	0.0855	-0.4120	
Two factor indicator (2FI)	0.9204	-0.0851	-4.7253	

Quadratic	< 0.0001	0.9862	0.9279	Suggested
Cubic	0.0026	0.9980	0.2149	Aliased

3. 3. 1. Mathematical model of the inhibition efficiency

Models (with regards to coded and actual factors) of inhibition efficiency of watermelon extract are shown in Equations (6) and (7) respectively. They are quadratic equations because the highest power of the variables is two. The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor [20-23]. It is useful for identifying the relative impact of the factors by comparing the factor coefficients. Negative sign denotes antagonistic influence, while the positive sign indicates synergetic influence. It means that the interactive effect of inhibitor concentration and temperature on the inhibition efficiency is of synergetic effect. Conversely, interactive effects of inhibitor concentration and time, and temperature and time on the inhibition efficiency are of antagonistic influence. The model was further examined, and the diagnostic report is presented Table 4. The statistical analyses show that the model predicted values are in close proximity to the actual (experimental) values of the inhibition efficiency.

$$\text{Inhibition Efficiency} = + 93.91 + 4.14A - 4.54B + 3.77C + 1.87AB - 1.51AC - 1.43BC - 8.36A^2 - 8.89B^2 - 3.86C^2 \quad (6)$$

$$\text{Inhibition Efficiency} = - 8659.84787 + 51.13989\ \text{Inhibitor conc.} + 55.09676\ \text{Temperature} + 84.74780\text{Time} + 0.933750\ \text{Inhibitor conc.} * \text{Temperature} - 7.55000\ \text{Inhibitor conc.} * \text{Time} - 0.143250\ \text{Temperature} * \text{Time} - 208.92045\ \text{Inhibitor conc.}^2 - 0.088868\ \text{Temperature}^2 - 3.85682\ \text{Time}^2 \quad (7)$$

Table 4. Diagnostic report of the RSM model watermelon leaf extract

Run Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residuals	Externally Studentized Residuals	Cook's Distance	Standard Order
1	93.65	93.91	-0.2647	0.118	-0.220	-0.209	0.001	17
2	88.64	86.29	2.35	0.491	2.575	4.206	0.639	13
3	66.24	66.11	0.1287	0.793	0.221	0.210	0.019	7

4	80.78	81.41	-0.6349	0.491	-0.695	-0.676	0.047	9
5	58.71	58.41	0.2957	0.793	0.508	0.488	0.099	3
6	75.87	75.11	0.7577	0.793	1.301	1.354	0.649	8
7	91.13	89.70	1.43	0.491	1.564	1.707	0.236	10
8	67.41	68.37	-0.9563	0.793	-1.642	-1.822	1.033	1
9	80.67	80.49	0.1831	0.491	0.200	0.190	0.004	12
10	82.96	81.79	1.17	0.793	2.003	2.455	1.538	5
11	93.65	93.91	-0.2647	0.118	-0.220	-0.209	0.001	19
12	75.61	75.94	-0.3273	0.793	-0.562	-0.542	0.121	2
13	82.83	83.32	-0.4943	0.793	-0.848	-0.836	0.276	6
14	93.65	93.91	-0.2647	0.118	-0.220	-0.209	0.001	16
15	93.65	93.91	-0.2647	0.118	-0.220	-0.209	0.001	18
16	90.18	89.57	0.6111	0.491	0.669	0.649	0.043	11
17	93.65	93.91	-0.2647	0.118	-0.220	-0.209	0.001	20
18	93.65	93.91	-0.2647	0.118	-0.220	-0.209	0.001	15
19	72.09	73.46	-1.37	0.793	-2.344	-3.312	2.106	4
20	92.27	93.83	-1.56	0.491	-1.706	-1.922	0.281	14

3. 3. 2. Graphical analyses of the RSM results

Graphical analyses of the RSM results are shown in Figures 2 – 5. In Figures 2, predicted versus actual inhibition efficiency of inhibitor shows linear graph. The points congregated along the line of best fit of the straight line graph. It indicates that the obtained model effectively predicted the experimental data [5, 13]. The 3-dimentional (3-D) plots of Figures 3 – 5 show the interactive effects of the considered factors on the inhibition efficiency of watermelon leaf extract. The 3-D plots revealed that the inhibition efficiency increased with increase in the inhibitor concentration and time. Conversely, increase in temperature reduces the inhibition efficiency [20-23]. They all show parabolic curves, which is in line with the generated quadratic model.. In Figures 3 - 5, optimum inhibition efficiency of the extract was displayed as 93.85 at 3.71hrs, at a temperature of 314.98K, and at inhibitor concentration of 0.76 g/L.

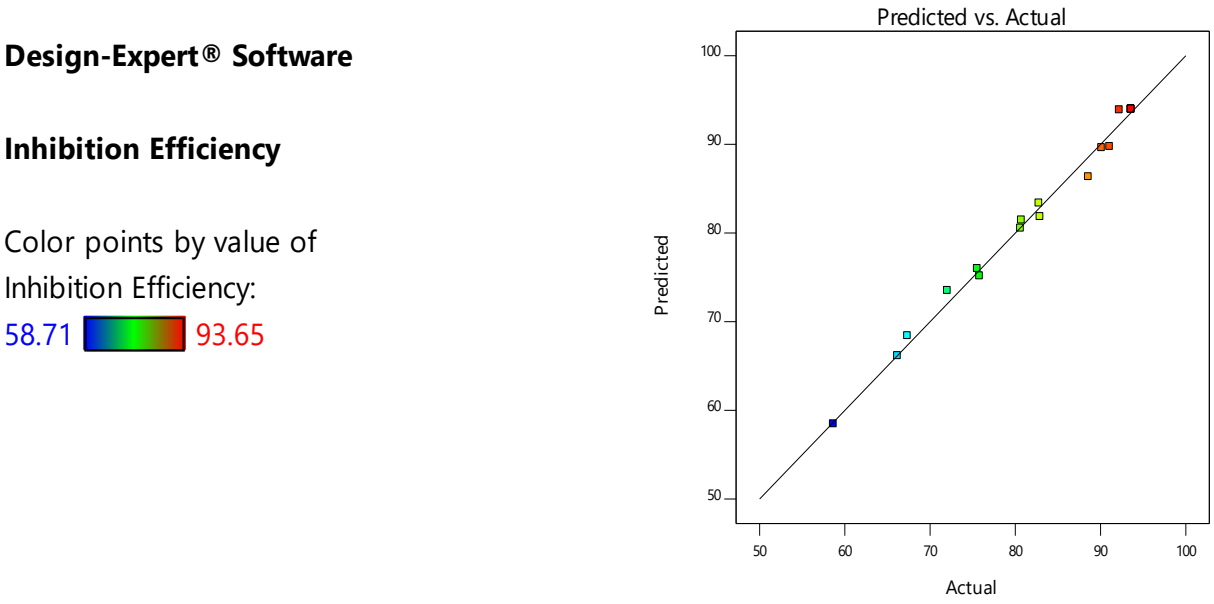

Figure 2. Predicted versus actual inhibition efficiency of watermelon leaf extract

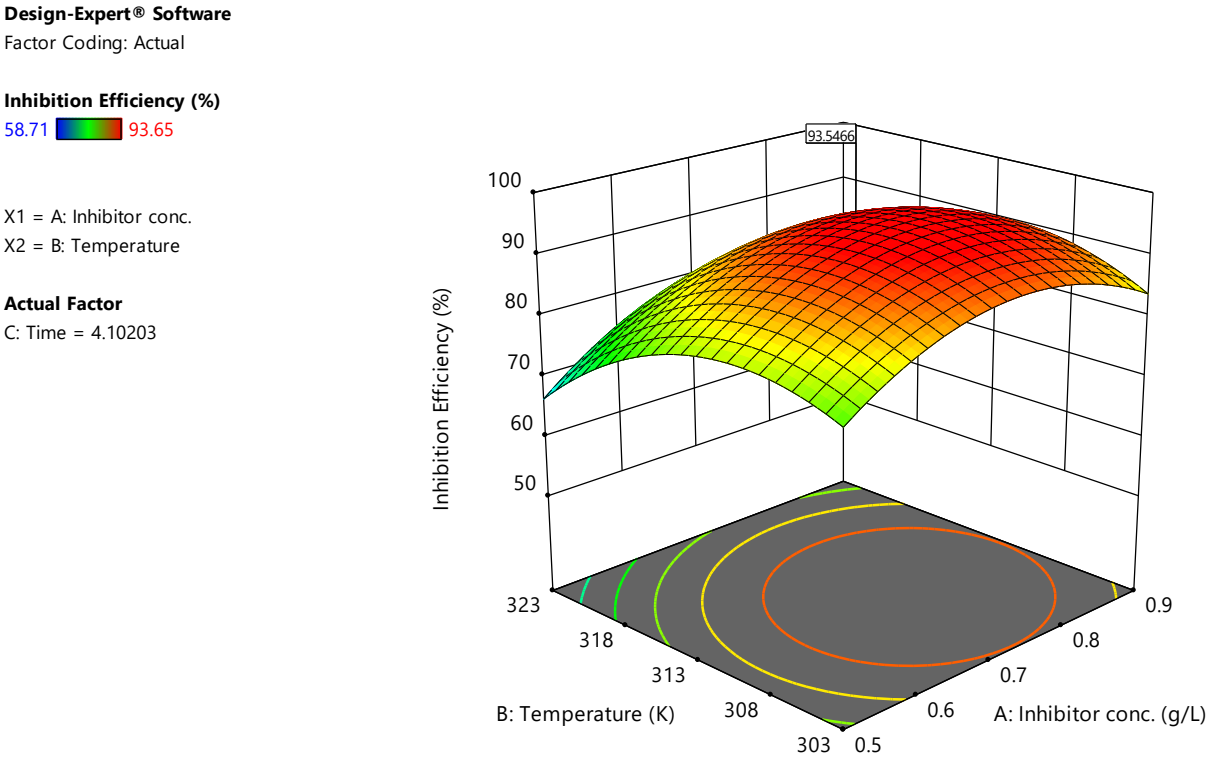

Figure 3. Effect of inhibitor conc. and temperature on inhibition efficiency of watermelon leaf extract

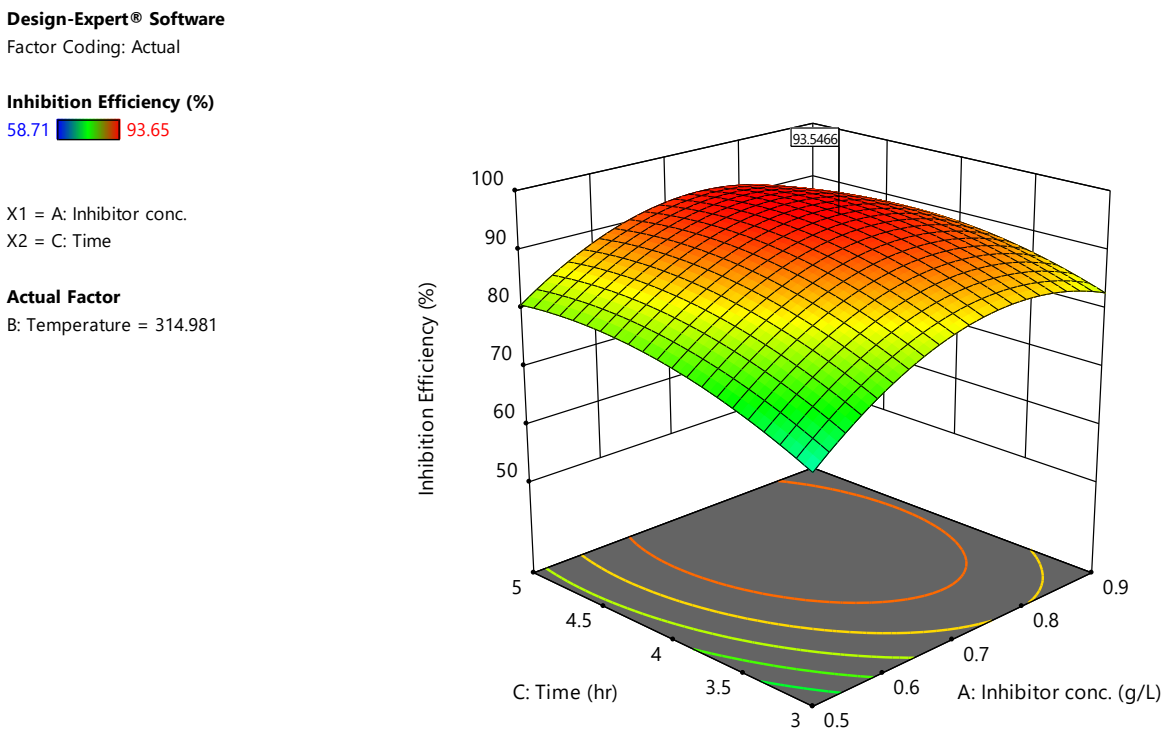

Figure 4. Effect of inhibitor conc. and time on inhibition efficiency of watermelon leaf extract

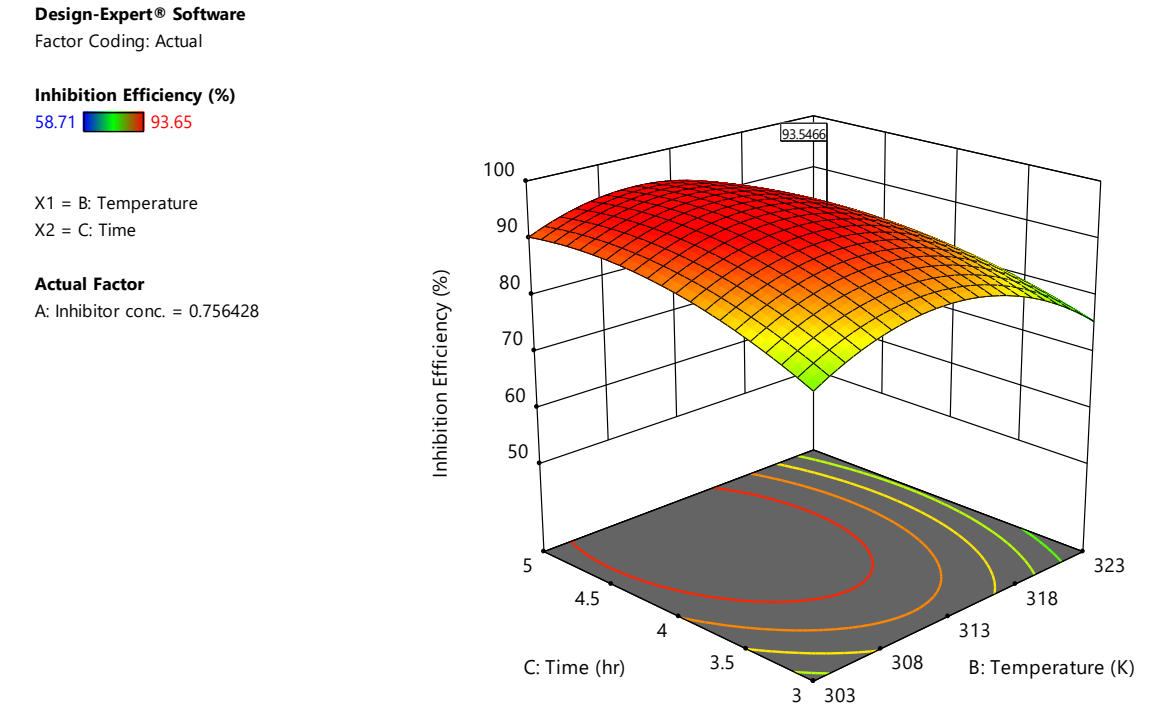

Figure 5. Effect of temperature and time on inhibition efficiency of watermelon leaf extract

3. 3. 3. Validation of the result

The RSM result was validated using percentage deviation by comparing the predicted and experimental results (Table 5). The calculated percentage deviation is less than critical value of 5%. Thus, the generated model adequately predicted the experimental result.

Table 5. Validation of the result

Inh. conc. (g/L).	Temp. (K)	Time (hr)	Predicted (Optimum) IE (%)	Exp. IE (%)	Percentage Deviation (%)
0.76	314.98	4.10	93.55	92.96	0.63

4. CONCLUSION

Watermelon leaf extract successfully inhibited corrosion of mild steel in H_2SO_4 environment. Predominant functional groups of watermelon leaf include; C-H stretch (2851.4 cm^{-1}), N-H symmetric and asymmetric stretch (3267.7 cm^{-1}), C=H stretch (2195.4 cm^{-1}), =C-O-C stretch (1241.2 cm^{-1}), C=O symmetric and asymmetric stretch (17722.0 cm^{-1}), C-F (1155.5 cm^{-1}) and =C-H bend (674.0 cm^{-1}). The watermelon leaf extract contains polar atoms of nitrogen and oxygen. Its main phytochemicals include alkaloids (243.14 ±0.03 mg/100g) and tannins (216.32 ±0.02 mg/100g). It possesses good inhibitive properties. Weight loss, corrosion rate, inhibition efficiency and degree of surface coverage were influenced by the inhibition process variables. Quadratic model sufficiently described the affiliation of inhibition efficiency with the factors of inhibitor concentration, temperature, and time. Optimum Inhibition efficiency of 92.96% was attained by the watermelon leaf extract. Watermelon leaf extract exhibited high inhibition efficiency. Hence, it should be used to inhibit corrosion of mild steel in acid solution.

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