INHIBITION OF ALUMINIUM CORROSION IN KOH SOLUTION USING EXTRACT OF GRAPE LEAF AS INHIBITOR

ABSTRACT

This work focused on the inhibition of aluminium corrosion in KOH solution using extract of grape leaf as inhibitor. It involved the characterization of the extract in terms of functional groups and phytochemicals. Gravimetric (weight loss) method was used for the corrosion control study. The grape leaf contains polar atoms of nitrogen and oxygen, which means that it is a suitable corrosion inhibitor. On the level of the phytochemicals, alkaloids, tannins, flavonoids and saponins are present in the leaf extract at various degrees. Corrosion inhibition of aluminium in KOH was found to be dependent on inhibitor concentration, temperature and time. Grape leaf extract displayed high level of inhibition efficiency. Optimum inhibition efficiency of grape leaf extract is 87.44%, which was obtained at inhibitor concentration of 0.79g/L, temperature of 312.57K, and time of 3.90hr. Grape leaf extract should be applied in corrosion control of Al in the alkaline solution.

Keyword: aluminium. grape leaf, corrosion inhibition, inhibita

1.0 Introduction

Corrosion has been expressed as a serious engineering problem in this modern age of technological advancement. It causes irreversible structural damage with significant economic implications (Muralisankar et al; 2017; Izadi et et al, 2017). It reduces the shelf life of steel (Akpan, 2012; Aziz et al, 2015). Negative effects of corrosion on society cannot be overemphasized. More awareness are been engendered. As products and manufacturing processes become more complex, consequences of corrosion become more costly (Solmaz, 2014; Akpan, 2012; Heydari et al, 2018). Umoren et al (2016) stated that corrosion leads to economic losses, and it is also linked to health and safety issues. As such, various corrosion control measures are being practiced, which include application of inhibitors. In many situations, better coatings and cathodic protection are aided by corrosion inhibitors.

In various engineering industries, application of corrosion inhibitor is well recognized as a proficient method of corrosion inhibition. Corrosion inhibition can be achieved through addition of chemical compounds (Raja et al., 2016). Corrosion inhibitors are chemical additives or compounds that, when introduced in small amounts to an aggressive / corrosive environment either reduce or prevent corrosion of metal surface (Muralisankar et al2017; Ramezanzadeh et al 2019). Inhibitors provide a protective barrier on the metal surface (Fernández, and Cabeza, 2019; Raja et al, 2016; Umoren et al, 2019). Majority of well-known inhibitors are organic compounds with electronegative functional groups and double or triple bonds constituents. They exhibit good inhibitive properties by electrons delivering. There is also a unique interaction between functional groups comprising heteroatoms such as nitrogen, sulphur, and oxygen that have a free lone pair of electrons and the metal surface (Omotioma and Onukwuli, 2016).

In order to improve coated surfaces and prevent corrosion, many applications, such as pickling solution and industrial water treatment systems, combine more than one corrosion inhibitor. KOH solution used for pickling operations is aggressive, and synthetic chemicals commonly used as the inhibitive additives are harmful to man and environ. As such, plant extract has been identified as corrosion inhibitor; suitable additive in pickling solution

(Ezeugo et al, 2019; Cookey et 2021). There are numerous research works on corrosion inhibition of metals in corrosive environment using plant extracts (Petchiammal and Selvaraj, 2013; Ananth et al, 2013; Sirajunnisa et al, 2014; Umoren et al, 2016; Udeh et al, 2021a). It has been established that plant extract has not been fully explored in corrosion mitigation efforts. Eco-friendly plant extracts have not been fully explored as corrosion inhibitors of aluminium. There is need to develop more of the inhibitors for corrosion inhibition process. Grape leaf is used in the cuisines of a number of cultures. The leaf is commonly rolled or stuffed with mixtures of meat and rice. It is also used in various recipes and dishes (Davidson et al, 2014). There is need to expand its applications especially in the area of corrosion control. Thus, the aim of this study is to inhibit corrosion of aluminium in KOH solution using extract of grape leaf.

2.0 Materials and Method

The materials, equipment and reagents used in this study include; grape leaf; KOH; distilled water; acetone, volumetric flasks; beakers; conical flasks; measuring cylinder; funnel; electronic weighing balance; water bath; stop watch; thermometer; retort stand; petri dish; Fourier transform infrared spectrophotometer (Cary 630, Agilent Technologies USA). Other materials used include filter paper, thread, masking tape, emery papers and aluminium. The aluminium was cut into coupons; Al (3cm x 3cm). The coupons were cleaned followed by polishing with emery paper to expose shining polished surface. To remove oily impurities, the coupons were degreased with acetone and washed with distilled water, and dried in air (before using it for the corrosion study).

2.1 Characterization of the grape 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 grape leaf. It was done in accordance with procedure used by Omotioma and Onukwuli (2016). In the process, Fourier transform converted raw data into actual spectrum (with various peaks). Analysis of the FTIR produced peaks were carried out in identifying the corresponding functional groups.

2.2 Determination of the Phytochemical Constituents of grape leaf

Standard methods used by previous research reports (Belani, and Kaur, 2018; Omotioma and Onukwuli, 2019; Haruna et al, 2019) were employed for the qualitative and quantitative determination of sample's alkaloids, cardiac glycosides, flavonoids, phenolics, phytates and saponins.

2.3 Determination of Effects of Process Variables on the Corrosion Control Process

Standard method of corrosion study reported by previous researches (Udeh et al, 2021b; Onukwuli et al, 2021; Anadebe et al, 2018; Omotioma and Onukwuli, 2016) was employed in this study. Considering one factor at a time, the gravimetric (weight loss) method was carried out at various inhibitor concentrations, temperatures and times. According to this method, weighed Al coupons was immersed in 250 ml open beakers containing 150 ml of 1 M KOH (without inhibitor). Also, Al coupons were separately immersed in 250ml open beakers containing 150 ml of 1 M KOH with various concentrations of the grape leaf extract.

Variation of weight loss was investigated at various times and temperatures, in the absence and presence of various concentrations of the inhibitor. At regular time interval, the coupons were taken out, immersed in acetone, scrubbed with a bristle brush under running water, dried and reweighed. The inhibition efficiency (IE) was calculated using Equation (1):

$$IE\% = \frac{\omega_0 - \omega_1}{\omega_0} * 100 \quad (1)$$

where ω_1 and ω_0 are the weight loss values in presence and absence of inhibitor, respectively. Effects of inhibitor concentration, temperature and time on the weight loss, corrosion rate, inhibition efficiency and degree of surface coverage were determined.

2.4 Optimization of the inhibition efficiency

On response surface methodology, Design Expert Software was used to design the experiment for the weight loss method. Inhibitor concentration, temperature and time were the independent variables while inhibition efficiency is the response. Optimum inhibition efficiency was determined in line with the procedure used by Omotioma and onukwuli (2016).

3.0 Results and Discussion

3.1 Fourier transformed infrared (FTIR) spectroscopic results of the inhibitor

The spectrum of the FTIR of the grape leaf (inhibitor) is shown in Figure 1. It shows the relationship between the transmission and wave number. It contains polar atoms of nitrogen and oxygen, which means that grape leaf is a suitable corrosion inhibitor. This observation is in agreement with the report of Omotioma and Onukwuli (2016), which stated that polar atoms are present in corrosion inhibitor. It means that guava leaf and grape leaves have suitable corrosion inhibitive capabilities.

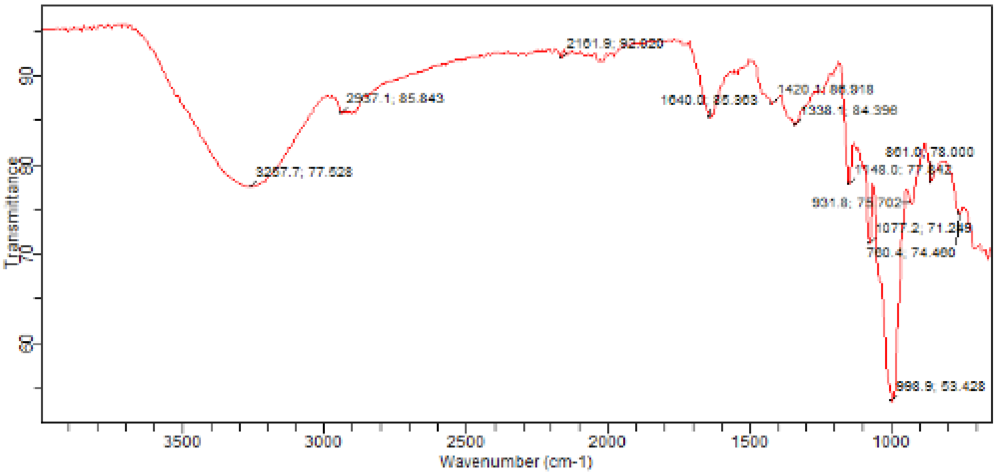

Figure 1: Spectrum of the grape leaf extract

3.2 Results of the phytochemical analysis of the inhibitors

Phytochemicals of the extract of grape leaf are presented in Tables 1. Alkaloids, cardiac glycosides, flavonoids, phenolics, phytates and saponins are present in the extract. The presence of these phytochemicals shows that the extract is potential corrosion inhibitor (Belani, and Kaur, 2018; Omotioma and Onukwuli, 2019). Alkaloids is highly concentrated in the extract; 198.05 ±0.21 mg/100g. Cardiac glycoside is the least in the extract, indicating less quantity of starch. Except phytates, the other phytochemicals (tannins, flavonoids and saponins) are concentrated in the extract.

Table 1: Phytochemical (Qualitative and Quantitative) Analysis of the grape leaf

Phytochemicals	Qualitative results	Quantitative results
Alkaloids (mg/100g)	+++	198.05 ±0.21
Cardiac glycosides (mg/100g)	-	8.06 ±0.34
Flavonoids (mg/100g)	++	152.41 ±0.02
Phenolics (GAE/g)	+	33.16 ±0.24
Phytates (mg/100g)	+	74.56 ±0.03
Saponins (mg/100g)	++	112.07 ±0.21
Tannins (mg/100g)	++	101.45 ±0.11

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

3.3 Optimization Results

Optimization results of corrosion control of Al in KOH medium with grape leaf extract are presented in Tables (2) respectively. Interactive effects of process variables on the in inhibition efficiency of the extract were revealed. Maximum inhibition efficiency of the grape leaf is 87.62%. It was obtained at inhibitor concentration of 0.8g/L, temperature of 313K and time of 4hrs. Highest value of the inhibition efficiency was obtained at the mid-points of the considered factors, which suggests parabolic behaviour of the relationship between dependent and independent variables. This observation is in agreement with the report of Udeh et al (2021b). So, the inhibition efficiency of each extract is related to the factors of inhibitor concentration, temperature and time in a quadratic equation form.

Table 2: RSM result corrosion control of Al in KOH medium with grape leaf

Std	Run	Factor 1 A: Inhibitor concentration , g/L	Factor 2 B: Temperature K	Factor 3 C: Time hr	Response 1 Inhibition efficiency %
11	1	0.8	303	4	83.84
6	2	1	303	5	76.46
7	3	0.6	323	5	59.87
10	4	1	313	4	84.79
12	5	0.8	323	4	74.29
5	6	0.6	303	5	76.64
18	7	0.8	313	4	87.62
3	8	0.6	323	3	52.44
8	9	1	323	5	69.54
1	10	0.6	303	3	60.97
9	11	0.6	313	4	74.47

2	12	1	303	3	69.28
15	13	0.8	313	4	87.62
16	14	0.8	313	4	87.62
4	15	1	323	3	65.74
17	16	0.8	313	4	87.62
20	17	0.8	313	4	87.62
19	18	0.8	313	4	87.62
13	19	0.8	313	3	82.19
14	20	0.8	313	5	85.93

3.3.1 Fit summary of the model of inhibition efficiency

Fit summaries of inhibition efficiency models of grape leaf extract are presented in Table 3. The predicted R^2 of 0.9289 is in reasonable agreement with the adjusted R^2 of 0.9873. Of the models tested (linear, 2FI, quadratic and cubic), quadratic model is the best fitted. It means that quadratic model best described the relationship between inhibition efficiency and the considered factors of the inhibition process. Mathematical models of the inhibition efficiencies in terms of coded and actual factors are presented in Equations (2) and (3) respectively. The model in terms of coded factors can be used to make predictions about the response for given levels of each factor. Coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients (Udeh et al, 2021c; Anadebe et al, 2019).

Table 3: Fit summary of the model of inhibition efficiency of grape leaf

Source	Sequential p-value	Adjusted R^2	Predicted R^2	
Linear	0.2386	0.0809	-0.4151	
2FI	0.9224	-0.0914	-4.7313	
Quadratic	< 0.0001	0.9873	0.9289	Suggested
Cubic	0.0002	0.9992	0.6931	Aliased

$$\text{Inhibition efficiency} = +87.79 + 4.14A - 4.53B + 3.78C + 1.85AB - 1.52AC - 1.45BC - 8.41A^2 - 8.97B^2 - 3.98C^2 \quad (2)$$

$$\text{Inhibition efficiency} = -8764.13439 + 96.99341\text{Inhibitor concentration} + 55.55233\text{Temperature} + 87.12343\text{Time} + 0.927500\text{Inhibitor concentration} * \text{Temperature} - 7.57500\text{Inhibitor concentration} * \text{Time} - 0.145250\text{Temperature} * \text{Time} - 210.18182\text{Inhibitor concentration}^2 - 0.089723\text{Temperature}^2 - 3.97727\text{Time}^2 \quad (3)$$

3.3.2 Graphical results of the inhibition efficiencies of grape leaf extract

Graphical results of the inhibition efficiencies of grape leaf extract are presented in Figures 2 – 5. In Figure 2, predicted versus actual values of inhibition efficiency of grape leaf extract revealed linear graph. It suggests that the RSM is fit for optimization of the inhibition efficiency. Figures 3 – 5 display parabolic curves of the relationship between inhibition efficiency and the factors of time, temperature and inhibitor concentration. The RSM result was validated using percentage deviation (comparing the predicted and experimental results), as shown in Table 4. Determined percentage deviation is less than of 5%, which shows that generated model adequately predicted the experimental result.

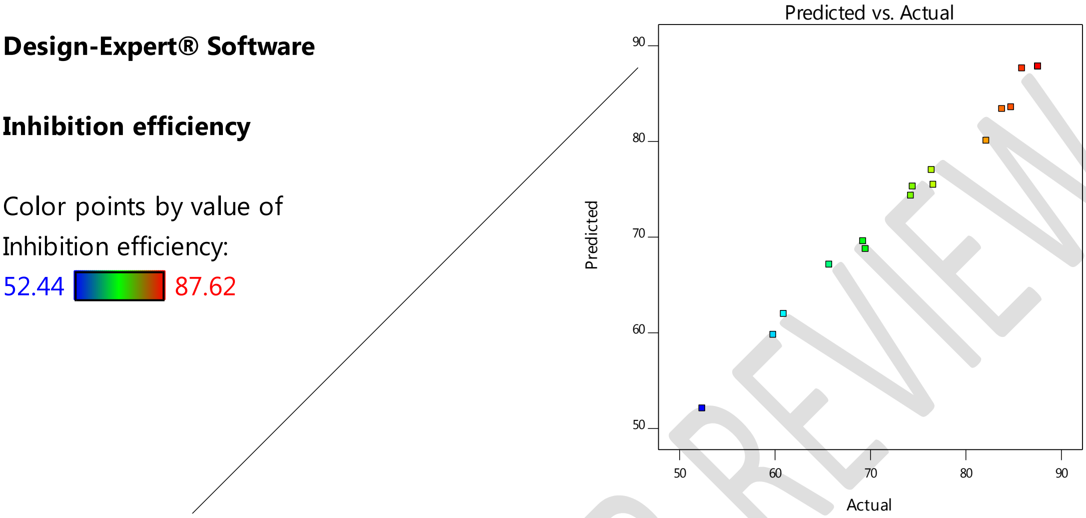

Figure 2: Predicted against actual IE of grape leaf extract

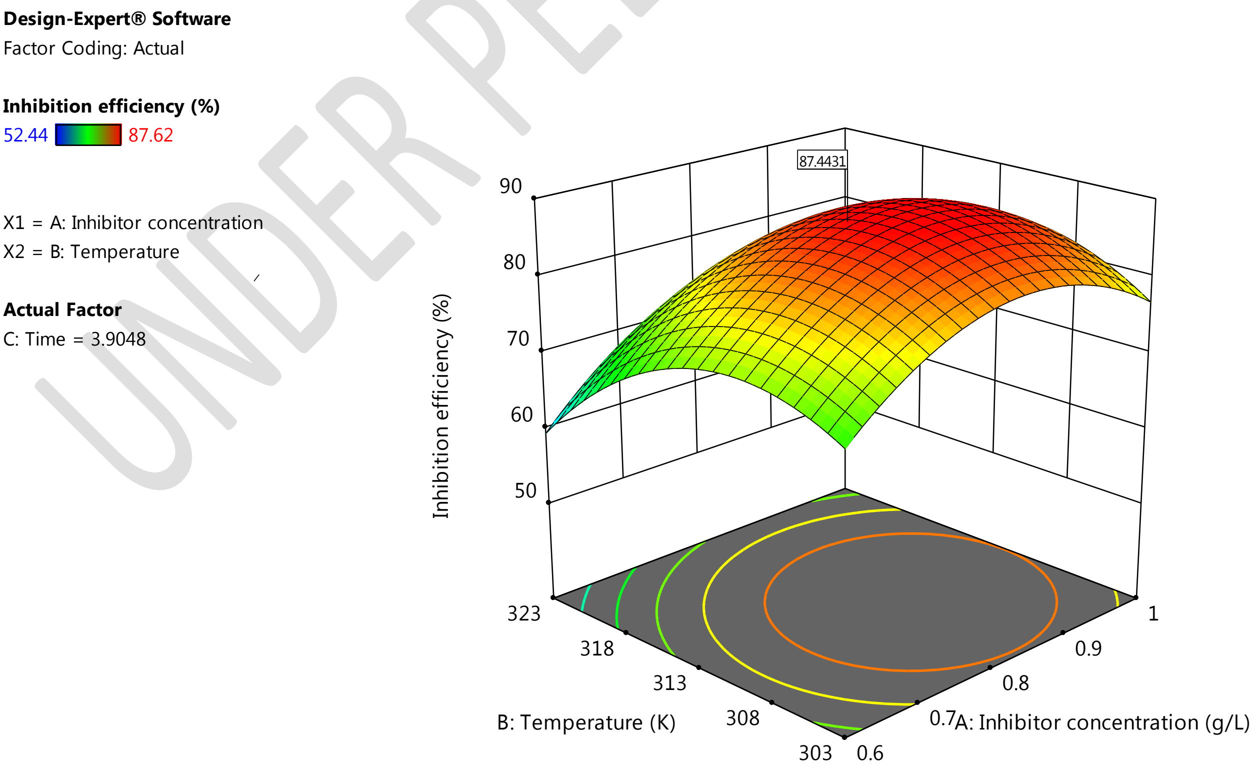

Figure 3: Interactive effect of inhibitor conc. and temperature on IE of grape leaf extract

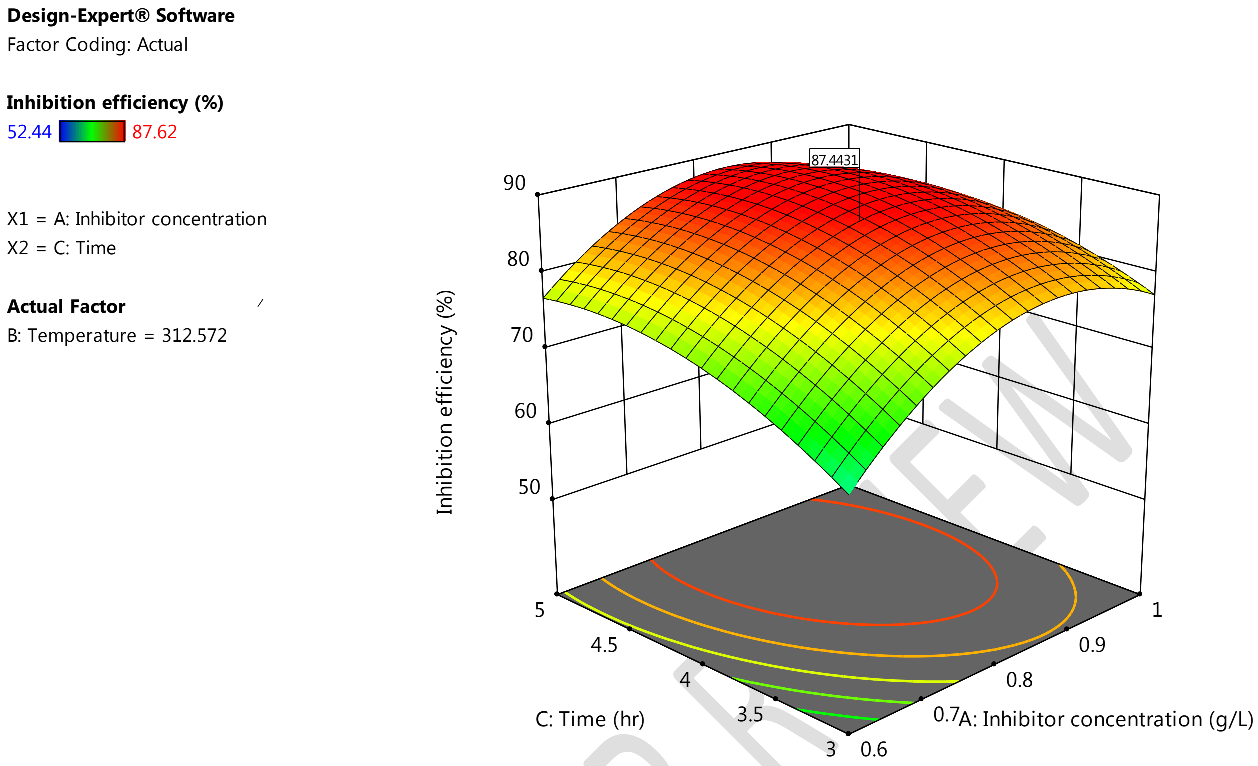

Figure 4: Interactive effect of inhibitor conc. and time on IE of grape leaf extract

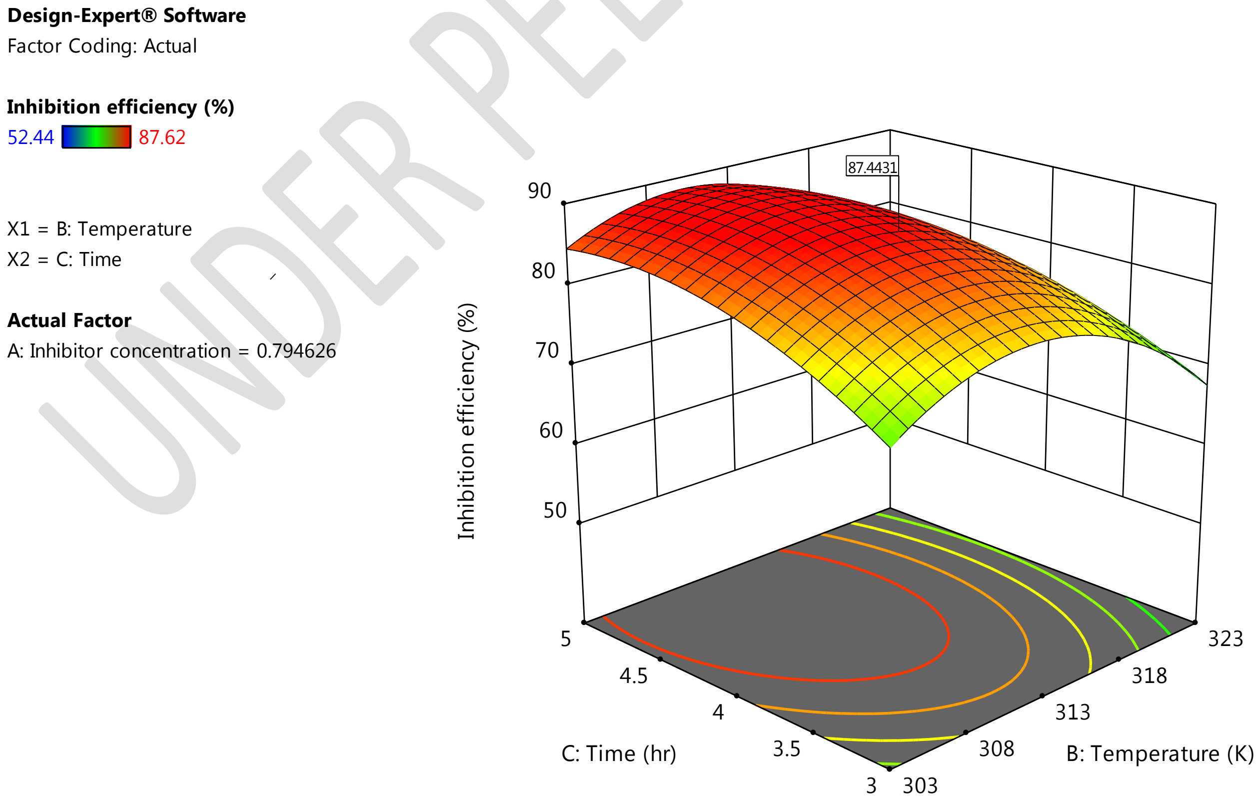

Figure 5: Interactive effect of temperature and time on IE of grape leaf extract

Table 4: Validation of the result of the RSM

Inh. conc. (g/L).	Temp. (K)	Time (hr)	Predicted IE (%)	Exp. IE (%)	Percentage Deviation (%)
0.79	312.57	3.90	87.44	87.03	0.47

Conclusion

Grape leaf contains polar atoms of nitrogen and oxygen, which means that it is a suitable corrosion inhibitor. On the level of the phytochemicals, alkaloid is highly concentrated in the extract; 198.05 ±0.21mg/100g. Tannins, flavonoids and saponins are present at concentrated level. Weight loss, corrosion rate, inhibition efficiency and degree of surface coverage were influenced by the inhibitor concentration, temperature and time. Grape exhibited high inhibition efficiency. Hence, it can be used to inhibit corrosion of Al in KOH solution. Optimum inhibition efficiency of grape leaf extract is 87.44%, which was obtained at Inhibitor concentration of 0.79g/L, temperature of 312.57K, and time of 3.90hr.

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