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The Effect of Temperature and Inhibitor on Corrosion of Carbon Steel in Acid Solution under Static Study

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Abstract

The effect of temperature on corrosion rate of carbon steel was evaluated by weight loss analysis. The carbon steel specimens immersion in 1M HCl at different temperature (30, 40, 50 and 60) ºC with and with inhibitor concertation for 4 hr. The result of these investigations indicate that the corrosion rate increased between (0.12 – 0.439) mg/cm^2.hr and the inhibitor efficiency decreased by (83.98 -76.01) % with increase of temperature at 6 mg/L. Mathematical and statistical techniques with factorial design were obtained through design-expert software. Statistical analysis of variance (ANOVA) is applied to establish the correlations between the predicted and experimental results by various statistical parameters; ANOVA also enables measurement of the effects of variables and their interaction. The empirical model demonstrated that the inhibitor is highly effective on the IE. Suggested models were highly accurate for both CR and IE responses.

Keywords: Temperature Effect, Inhibitor efficiency, ANOVA, Corrosion rate, Empirical model.

INTRODUCTION

In most chemical reactions, an increase in temperature is accompanied by an increase in reaction rate due to the increase of kinetic energy. Where the reaction rate doubles for each 10 °C rise in temperature, therefore it is important to take into consideration the influence of temperature when analyzing why metals fail [1].Inhibitors are substances when added to the specific environment, reduce the CR of the metal that in touch with this environment. To be unable to use some of the common protection processes like coating to diminishing the CR in devices of some systems such as cooling towers or heating and cooling systems, where these systems are closed, so use of corrosion inhibitor is more economical to limit the corrosion of these systems [2, 3]. The importance of study the corrosion depends on three main factors: safety, economic and conservation [4]. **O.R.M. Khalifa et al.,** [5]searched the impact of adding ethylamine, Ethylenediamine and butanediamide inhibitors to 3 M Nitric acid solution of copper had a corrosion. By anticipated processes including WL, PPC. The product of these processes showed that the protection efficiency increases with decreasing temperature. **Zarrouk et al**, [6] considered copper corrosion in his studies in a solution of 2 M HNO_3 when researcher use 3-amino–1, 2, 4-triazole (ATA) inhibitor through utilizing the three corrosion techniques WL, PPC, EIS. Author noticed that the inhibitor performance declined when the temperature boost. In another word, CR increased with increasing temperature in uninhibited and inhibited solutions while the IE% decreased with temperature. **V. Manivannan and N. Chithralekha,** [7] studied the effect of temperature and inhibition the 3-phosphonopropionic acid (3-PPA) on the corrosion of mild steel in groundwater was investigated by WL and PPC experiments at ranging from 30 °C to 60 °C. It has been observed that the corrosion current density increased with rise temperature both in uninhibited and inhibited solutions. 3-PPA have inhibiting properties at all the studied temperatures and the values of IE decreases with temperature increase. In this paper, the effect of temperature on the corrosion rate of carbon steel in 1 M hydrochloric acid at (30, 40, 50, and 60) °C in the presence of a commercially available inhibitor formulation has been examined.Statistical analysis of variance (ANOVA) is applied to establish the correlations between the predicted and experimental results by various statistical parameters. It also enables measurement of the effects of variables and their interaction, which is depicted by a two-dimensional contour and three-dimensional response surfaces.

MATERIALS AND METHODS

Materials

Carbon steel tube rod with a chemical composition (wt.%) as follows: 0.26% C, 0.24% Si, 0.56% Mn, 0.022% S, 0.015% P and Fe as balance. The corrosion inhibitor used is a chemical compound processed by Baker Hughes Company, Houston, USA. Hydrochloric acid (Central Drug House Ltd., India), Raw water.

Experimental procedure

Before each test, carbon steel was cut into small discs of the dimensions (1.48 cm outside diameter, 1.27 cm inside diameter and 2 cm length). Moreover, each sample was polished with emery papers, washed with tap water followed by distilled water then dried with air dryer. Finally weighted with a sensitive digital balance that is calibrated with standard samples (10 mg).The results of the experiments are the mean of two parts: static and dynamic studies

Corrosion under static conditions

After weighing the samples precisely, the samples were submerged in 100 ml of the acidic solution (1 M HCl) with and without inhibitor. After a specific interval of time (2, 4 and 6 hours), each sample was gotten out of the acidic solution, washed with distilled water, dried and weighted. Later the experiment was repeated at specified temperatures (30, 40, 50, and 60 °C) using a water bath (Fanem/ Model 102/6-R).

Design of experiments

Design-Expert is a piece of software designed to help with the design and interpretation of multi-factor experiments [8]. The empirical model is deduced via standardised (coded) dimensionless variables. The coded independent variables (x_i) are calculated by a linear equation from their respective variation limits, $X_i = (X_i - X_i°)/\Delta X$, where X_i is an experimental value of the i^{th} variable and $X_i°$ is the centre of the experimental range [9]. The results are obtained randomly to reduce the effect of unexplainable variance in the predicted response caused by unrelated variables. The predicted response (Y) for a quadratic model is described:

$$Y = b_0 + \sum_{i=1}^{n} bi\, X_i + \sum_{i=1}^{n} bii\, X_i^2 + \sum_{i=1}^{n-1}\sum_{j=i-1}^{n} bij\, x_i\, x_j \quad (1)$$

Where n is the number of experiments and b_o, b_i, b_{ij}, and b_{ii} are the regressions for the constant.

In addition, ANOVA is used to establish the correlation between the predicted and experimental results by various statistical parameters [10]. The terms of the model are tested by Fisher's exact test (F-value) and significance probability (P-value) within a 95% confidence level [11]. ANOVA was performed using the software package Design-Expert, Version 7.1.4 (Stat-Ease Inc., Minneapolis, USA).

RESULTS AND DISCUSSION

Influence of temperature

The effect of temperature was being studied on two factors CR and IE. The results were summarized in the Table (1) below.

Table 1: Corrosion parameters for carbon steel in acidic solution for four hrs. immersion.

Temperature (˚C)	Inhibitor (mg/L)	CR (mg/cm^2.hr)	IE%	Ɵ
30	0	0.856	0.00	0.00
	2	0.214	75.00	0.75
	4	0.156	81.77	0.817
	6	0.12	83.98	0.839
40	0	0.917	0	0
	2	0.301	67.17	0.672
	4	0.245	73.04	0.73
	6	0.172	81.72	0.817
50	0	1.48	0.00	0.00
	2	0.499	66.68	0.667
	4	0.448	69.67	0.696
	6	0.321	78.31	0.783
60	0	1.83	0.00	0.00
	2	0.651	64.4	0.644
	4	0.583	67.81	0.678
	6	0.439	76.01	0.76

Generally, CR increases with temperature, rising linearly as shown in Fig.1. The effect of higher temperatures is to speed up a chemical reaction, and to reduce oxygen solubility, which allows the cathodic reaction to occur. In addition, the viscosity of water decreases with increases in temperature; this leads to increased diffusion, which will allow increased transport of reactants (dissolved oxygen or other electrons acceptors) and product (Fe^{+2} species) on the metal surface. It can be seen that the effect of temperature on CR_o is three times that on CR_i, due to the presence of an inhibitor which isolates the metal from the solution.

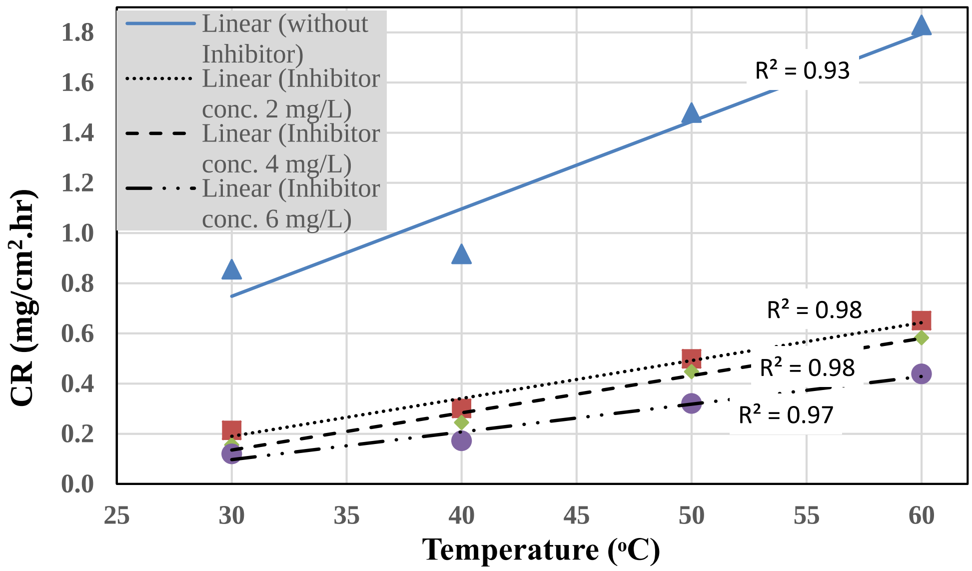

Figure 1: Effect of temperature on CR at different IC for four hrs. immersion.

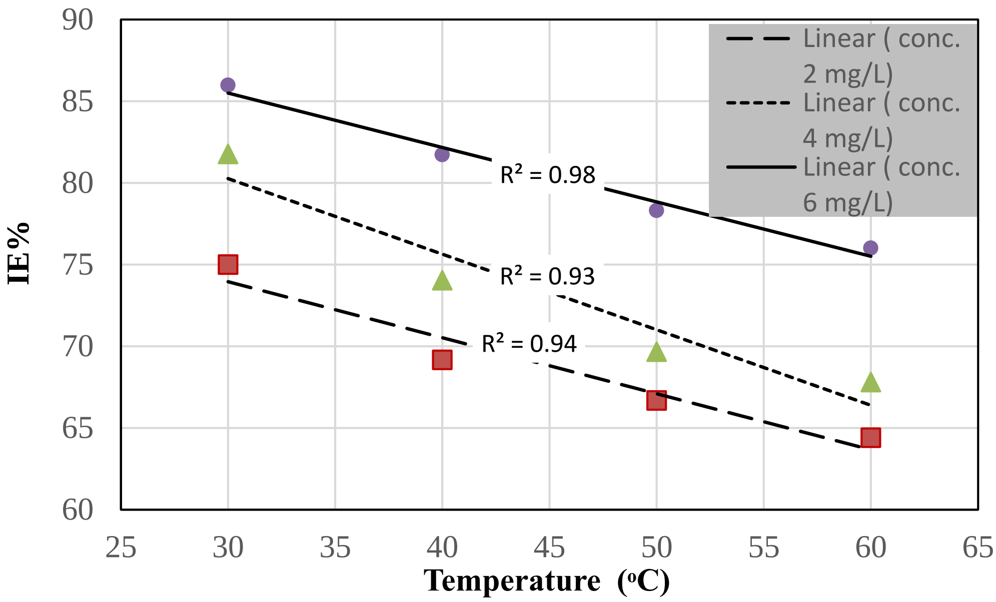

Figure 2: Effect of temperature on IE% at different IC for four hrs. immersion.

In addition, temperature has a negative effect on the IE%, by about 10%. This increment of increase in temperature leads to an increase of the dynamic energy for the inhibitor molecules. This raises the rate of their collision with each other. This is turn impedes and slows the formation of the protective film of inhibitors on the metal surface. The increase in temperature causes the strength of the adsorption molecules on the metal surface.

D. Ben Hmamon et al, used steel corrosion in 1 M HCl. The consequence of these techniques presented that with increase in temperature at rang 25-55 °C, which IE% lowering from 82.2 to 59.0%. The surface coverage (θ) reduce from 0.822 to 0.590 when the temperature expand [12]. In the same solution, I.A. Zaafarany, is also investigated that mild steel corrosion at 30–60 ºC. Author noticed that the same result in our study about the effect of temperature on CR and IE% [13].

Influence of inhibitor concentration (IC)

As shown in the (Fig.3), the CR was the highest without inhibitor solution, and then it starts decrease gradually when the inhibitor being added until become stable at the end of experiment. However, IE raises about 12% with increase of IC (2 mg/L – 6 mg/L) by linearly relationship (Fig.4). The IC rise leads to both the adsorption and surface coverage rise, therefore this growing lead to reduce the CR.

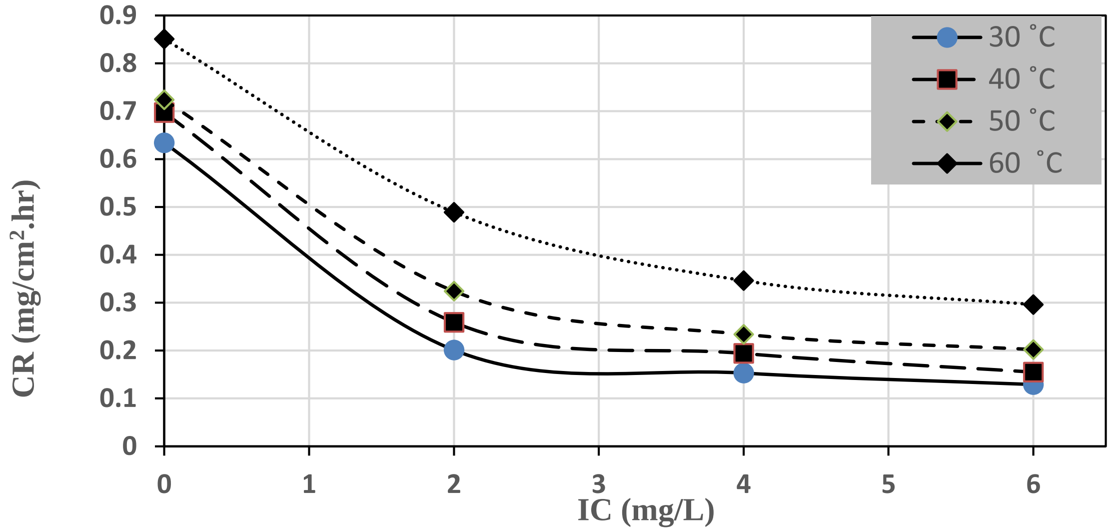

Figure 3: Effect of IC on CR for four hours immersion under static conditions.

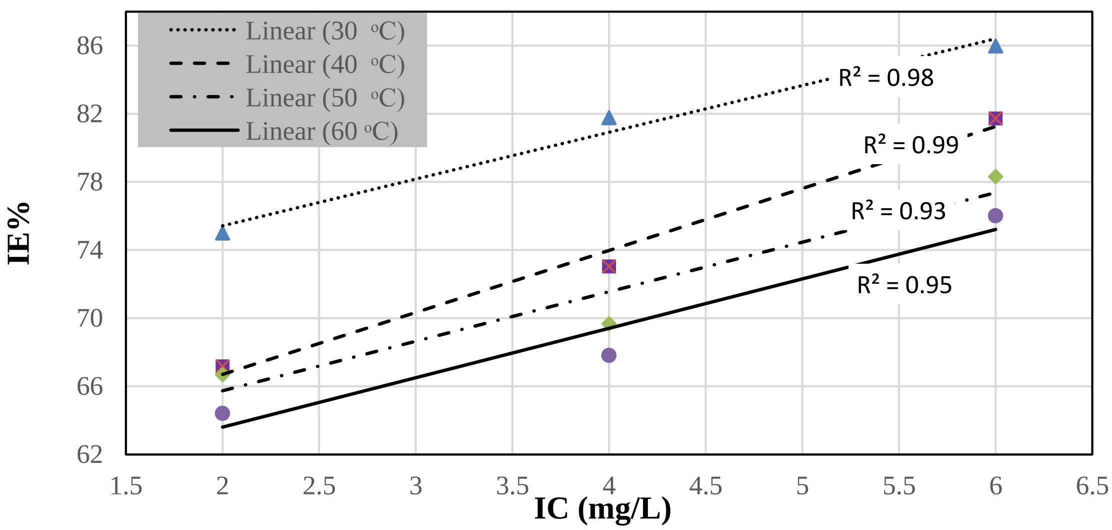

Figure 4: Effect of IC on IE% for four hrs. immersion.

Dina Raheem, studied the effect of highest corrosion inhibitors in cooling system on carbon steel specimens at different concentrations (20, 40, 60, 80 ppm). The corrosion IE was 98.1% at 80 ppm [14]. The result indicate that the CR decreases with corrosion ICs as in this study.

Factorial design study

The experimental points, in coded and actual values, and the response values are presented in Table 2. After variable identification, Design-Expert software suggests a model based on a higher-order polynomial where the additional terms are significant, and the model is not biased. The software fitted the CR and IE responses through many models. A cubic model for CR and IE responses were suggested. Quadratic models were selected for both responses for the sake of comparison. Consequently, the software recalculated the statistical ANOVA data for the responses.

Table 2: Experimental design points and the response values (CR and IE).

	Run	Factor A **Temp. (°C)**	Factor B **IC (mg/L)**	**CR ($mg/cm^2.hr$)**		**IE%**	
				Exp.Value	Pred.Value	Exp.Value	Pred.Value
1	14	30	0	0.856	0.81	0.00	0.75
2	7	30	2	0.214	0.23	75.00	74.31
3	8	30	4	0.156	0.031	81.77	80.52
4	13	30	6	0.120	0.21	83.98	85.14
5	11	40	0	0.917	1.05	0.00	-1.16
6	2	40	2	0.301	0.40	67.17	68.85
7	12	40	4	0.245	0.13	73.04	74.06
8	3	40	6	0.172	0.23	81.72	80.18
9	1	50	0	1.480	1.35	0.00	-0.30
10	10	50	2	0.499	0.62	66.68	66.25
11	15	50	4	0.448	0.28	69.67	70.51
12	6	50	6	0.321	0.32	78.31	78.19
13	9	60	0	1.830	1.70	0.00	0.68
14	16	60	2	0.651	0.91	64.40	63.83
15	5	60	4	0.583	0.49	67.81	67.20
16	4	60	6	0.439	0.46	76.01	76.51

Development of regression models

The multiple regression analysis for developing statistical relationships between independent variables (T and IC) and the responses variable is correlated in Eqs. (2) and (3). The quadratic model is represented as follows:

$$CR = 0.20 + 0.23\,T - 0.12\,IC + 0.066\,T^2 + 0.19\,IC^2 - 0.11\,T \times IC \quad (2)$$

$$IE = 81.96 - 4.64\,T + 9.13\,IC + 1.74\,T^2 - 15.35\,IC^2 - 1.42\,T \times IC \quad (3)$$

Verification of models

Fig. (5) Shows the predicted versus the experimental CR values. The fairly close plots indicate that the models developed were successful in capturing the correlation. Various parameters indicate the quality of fit, such as the correlation coefficient (R^2), standard deviation SD, predicted residual error sum of squares (PRESS) as tabulated in Table (3). R^2 reflects the proportion of total variation in the predicted response by estimating the ratio of the regression sum of squares (SS) to the total sum of squares. The R^2 values for the models in Equations (2) and (3) are 0.937 and 0.945, respectively, which reflect high precision because these values are close to one.

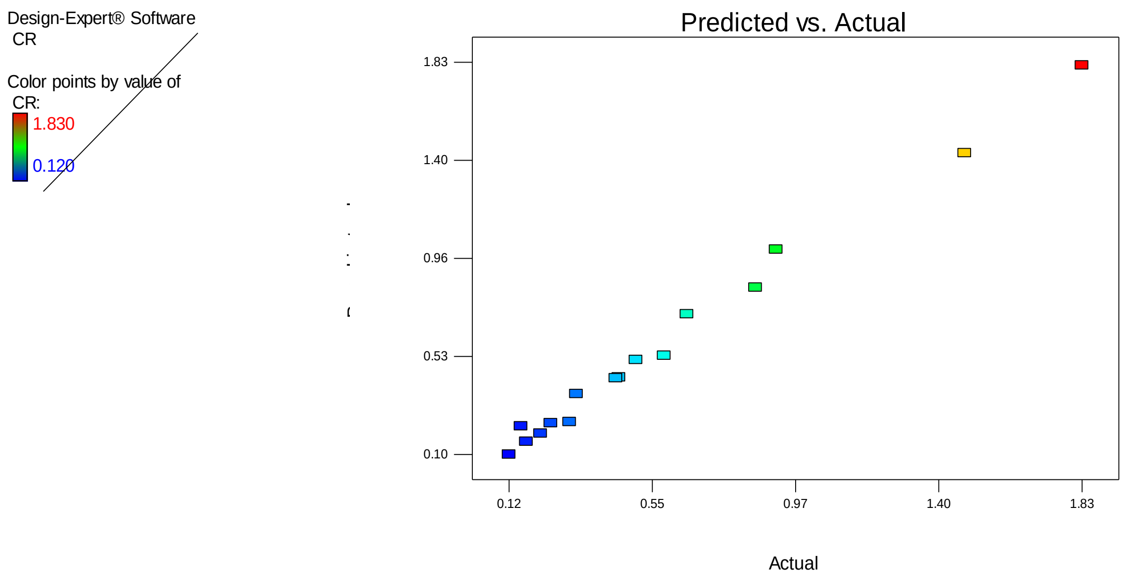

Figure 5: The discrepancy between the actual and predicted values of the CR.

Table 3: Statistical Parameters obtained by ANOVA for (a) CR and (b) IE% models.

	CR	IE
SD.	0.08	0.05
Mean	0.38	0.25
PRESS	0.58	0.36
R^2	0.9373	0.9459
R^2_{Adj}	0.9059	0.9188
R^2_{Pred}	0.8371	0.8769
Adeq Precision	18.278	14.789

Table 4: Statistical analysis of variance of the responses (a) CR and (b) IE.

Source	Sum of Squares	df	Mean Square	F-Value	P-value Prob > F	State
(a) CR Model						
Model	*3.34*	*5*	*0.67*	*29.90*	*< 0.0001*	
T-Temperature	*0.39*	*1*	*0.39*	*17.66*	*0.0018*	
IC-Inhibitor	*0.12*	*1*	*0.12*	*5.57*	*0.0399*	
T × IC	*0.13*	*1*	*0.13*	*5.74*	*0.0375*	
T^2	*0.014*	*1*	*0.014*	*0.61*	*0.4536*	***b***
IC^2	*0.58*	*1*	*0.58*	*25.84*	*0.0005*	
Residual	0.22	*10*	*0.022*			
Total	*3.56*	*15*				

(b) IE Model

Model	*15920.01*	*5*	*3184.00*	*34.95*	*< 0.0001*	
T-Temperature	*159.76*	*1*	*159.76*	*1.75*	*0.2149*	
IC-Inhibitor	*741.36*	*1*	*741.36*	*8.14*	*0.0172*	***a***
T×IC	*22.52*	*1*	*22.52*	*0.25*	*0.6297*	
T^2	*9.58*	*1*	*9.58*	*0.11*	*0.7524*	
IC^2	*3767.50*	*1*	*3767.50*	*41.36*	*< 0.0001*	
Residual	*910.90*	*10*	*91.09*			
Total	16830.91	*15*				

a: insignificant term, ***b*** : insignificant term.

i. Corrosion rate

A-three-dimensional graph of quadratic predicted model of the CR response, the CR increase when the temperature increase and the IC decrease (Fig (6)).

Temperature factor has positive effects on the response and IC with negative effect as in Equation (2). Both factors were significant on the response, but T which has more significant influence than IC. The interaction between both factors were more significant with negative effect on response indicates that increasing the levels of both variables is an inefficient method to increase CR as shown in Fig. (7) and Equation (2). The effects of the quadratic terms were represented show the $(IC)^2$ was significant, indicating linearity change of the levels with positive influence. However the effect of the quadratic temperature T^2 was insignificant, as reflected by F-values of 0.61 for CR that indicate non-linearity between Factorial Design points were also insignificant.

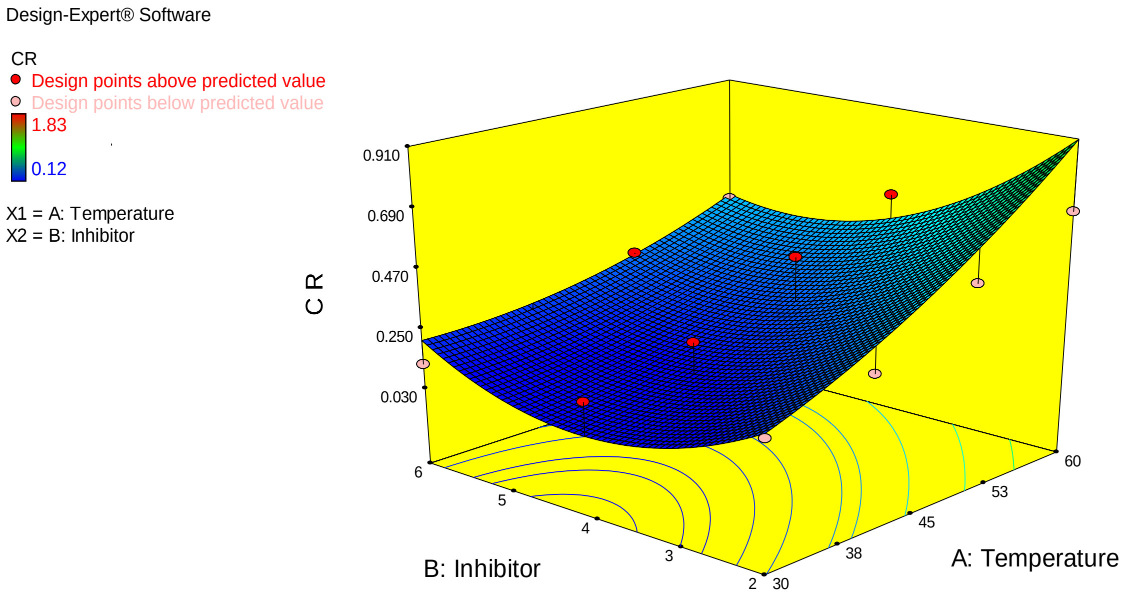

Figure 6: The effect of both temperature and inhibitor on CR .

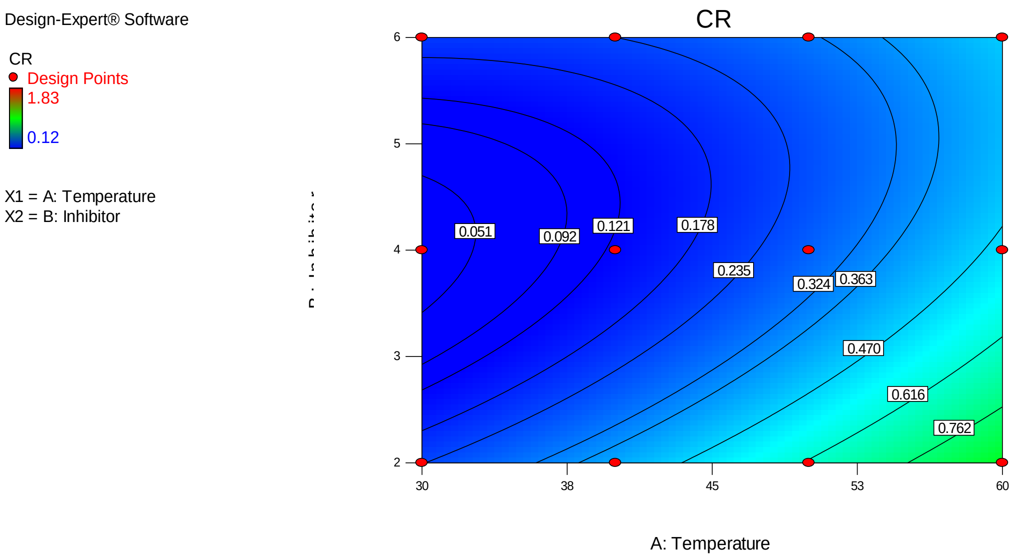

Figure 7: The relationship between temperature and IC on CR.

ii. Inhibitor efficiency

A-three-dimensional graph of quadratic predicted model (Fig. (8)), the IE increase when the temperature decrease and the IC increase due to the fact Temperature factor have a negative effect on the response and IC with positive effect as in Equation 3, and IC is more significant on IE. The effect of the quadratic term T^2 was insignificant, indicating nonlinearity change of the levels with positive influence. However the effect of the quadratic $(IC)^2$ was significant and linearity with negative influence.

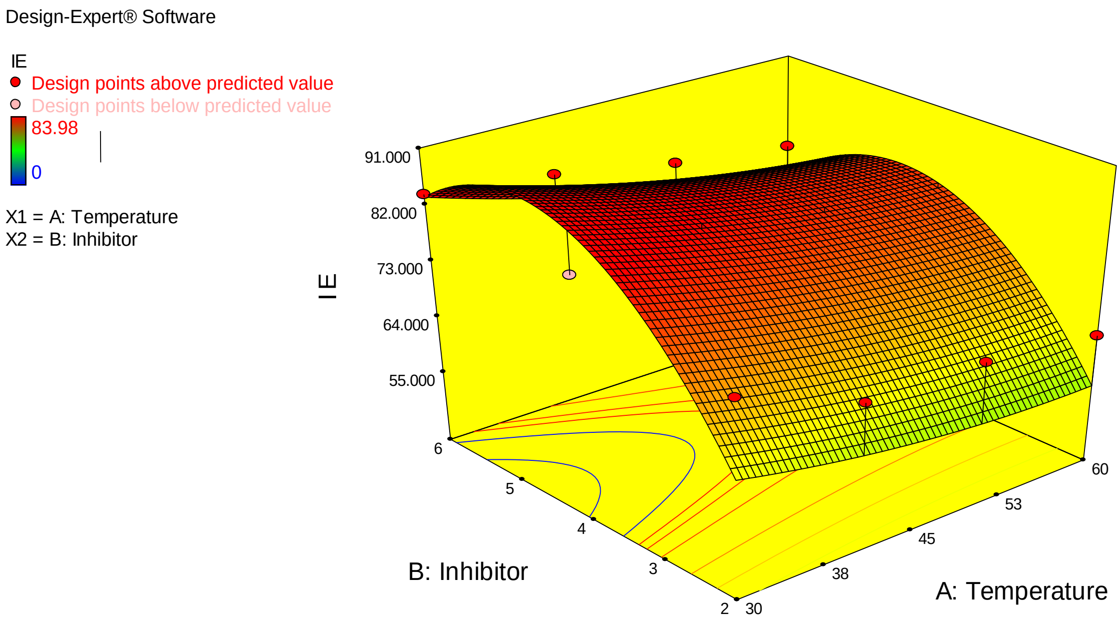

Figure 8: The effect of both temperature and inhibitor on IE.

3.4 Optimisation by response surface modelling

The last main aim of this study was to find the optimum parameters of the process to minimize the CR from the developed mathematical model equations. The experimental conditions with highest desirability are selected with the help of software. The optimum conditions for getting the lowest CR (0.105) and the highest IE% (87.6%) at static conditions is when the temperature value equal to 32 °C and the IC is 5 mg/L, (Fig. (9)).

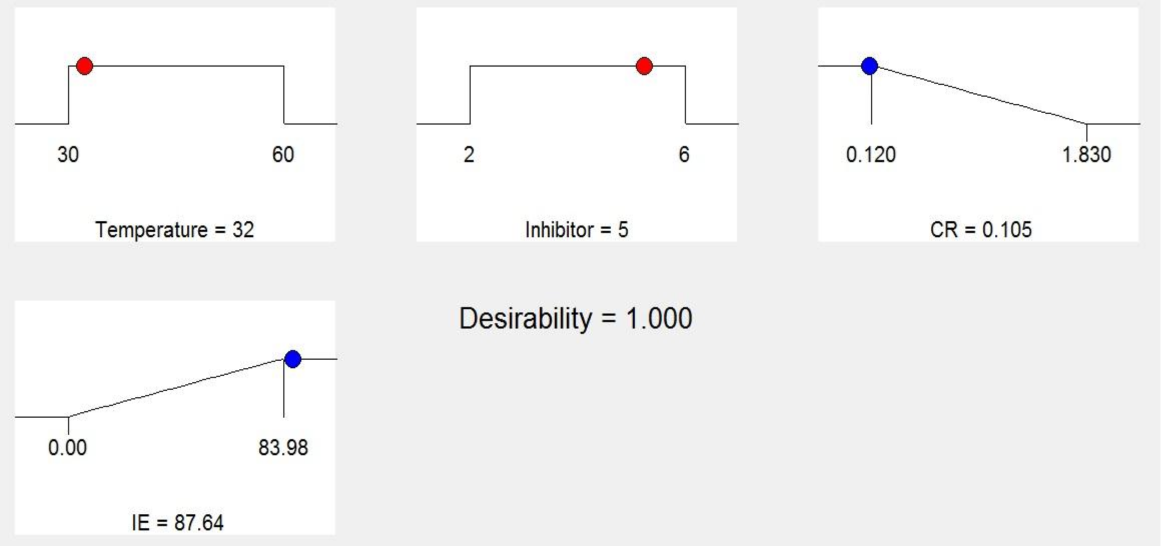

Figure 9: Optimization by response surface modeling

CONCLUSION

In view of the forgoing, lots of conclusions can be extracted from the experimental and theoretical results as follows:

a) Increase in temperature leads to increased CR and reduced IE.
b) A linearly relationship of IE raises about 12% with increase of IC (2 mg/L – 6 mg/L).
c) The proposed quadratic models coincide well with the experimental results.
d) The results of a statistical analysis of variance (ANOVA) presented that the inhibitor is highly effective on the IE.
e) The empirical model of the quadratic terms shows that the IC^2 was significant.
f) In static condition, the optimum conditions for getting the lowest CR (0.105 mg/cm^2.hr) and the highest IE (87%) were at 32 °C and 5 mg/L.

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