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Studying optimum conditions to reduce low carbon steel corrosion in cooling towers system of Al-Daura refinery

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The behaviour of corrosion of low carbon steel in makeup and recirculating water of cooling towers installed in AL-Daura Refinery was studied in the absence and presence of different concentrations of the commercial ku-2050 inhibitor (25 to 2000 ppm) at different pH values (7-8.5) and for different periods of immersion (1 day to 6 weeks) using Weight Loss method under static conditions (velocity=0). Factorial and Taguchi methods were applied to analyse the data by the software Minitab 2021. The analyses aimed at obtaining mathematical expressions to show the correlation of the corrosion rate with the working parameters. Monte Carlo Simulation technique was used to evaluate the effects of random events facing the corrosion process. Sensitivity analysis was utilized to see how corrosion rate variates by the variation in the working parameters in mathematical expression. The inhibitor efficiency results showed the direct increase with increasing in conc. of ku-2050 up to 500 ppm in makeup water while in recirculating water this increase continued up to 800 ppm of ku-2050 inhibitor.

KEYWORDS

Cooling towers; corrosion; weight loss method; factorial; Taguchi; Monte Carlo simulation; sensitivity analysis.

Introduction

Cooling towers are considered one of the most important pieces of equipment in the industry. It faces many problems like corrosion, scaling or scaling & clogging (especially biofilm formation) [1,2,3]. The scale is formed from water-soluble minerals deposited on heat transfer surfaces or in water pipes. Adding acid, lowering the pH of the water or adding a scale inhibitor can be done to reduce scale problems [2,4]. Two basic techniques are used to protect against corrosion in cooling towers: Using chemical corrosion inhibitors and increasing the pH of the water. Biocides, scale inhibitors should be added to prevent corrosion and Microbiological Influenced Corrosion, MIC, deposition [4,5,6]. Statistical analysis is fundamental for all branches of science and engineering, as well as in the field of corrosion [7,8]. Experiment design, DOE, is a statistical and mathematical method design for systematically performing experiments and analyzing data efficiently, in order to optimize accuracy and derive results [9,10]. The most popular DOE models are the Factorial and Taguchi methods. They make it possible to optimize the results and to study the main effects of the independent variables and their interactions with the dependent variable [11,12,13]. Monte Carlo simulation is a model used to predict the probabilities of different outcomes when random variables are involved. It is used to assess the impact of fluctuations on the dependent variable in the system [14].

This study aimed to investigate the optimal conditions to minimize the corrosion rate of low carbon steels in cooling towers under static conditions in the presence of commercial corrosion inhibitor ku-2050 and different immersion times at different values of pH then simulate the obtained models to evaluate random events on the rate of corrosion and its variation according to the change of working parameters.

Experimental

Mass loss is one of low cost, easy, and most widely recognized strategies to explore the corrosion rate. Many researchers have used immersion tests followed by a weight loss method to calculate the corrosion rate. Mass loss procedure is given in ASTM G31 standard and the general procedure to clean and prepare the material samples is given in ASTM G1 [15-18].

Corrosive Media

Twenty liters of each of makeup water and recirculating water (basin water) were sampled from CTS present in AL-Daura Refinery /Middle Refineries Company (MRC).

Additives

500 ml sample of Kurita 2050(ku-2050) commercial corrosion inhibitor was used in AL-Daura Refinery / MRC.

Metals

Strip low carbon steel coupons with the surface area of about 20 cm^2 for each coupon were applied. Table 1 demonstrates some properties of makeup and recirculating water samples.

TABLE 1 Some properties of makeup and recirculating water

Property	Makeup water	Recirculating water
pH	7.3	7.6
Conductivity µs/cm	1137	1936
Cl^- ppm	90.5	177.4
M.Alkalinity ppm	173.85	155.55

Method

Coupon preparation

Each coupon was polished, ground using emery papers (220.320.400.600) then washed with tap water, distilled water, dried by clean tissue, rinsed with acetone for several seconds, dried and put in desiccator. Then the coupon was weighed to nearest 0.1 mg (w1) by using analytical balance to measure the weight loss.

Immersion test

After weighing, the prepared coupons were immersed in makeup water samples in the absence and presence of different concentrations of (ku-2050) (25, 50, 75,100, 300, 500, 700, 800, 900, 1000, 1500, 2000) ppm at different periods ranging from 1 day to 6 weeks at different pH values (7-8.5) under static conditions (velocity=0) and at room temperature. Figure 1 shows weight loss method.

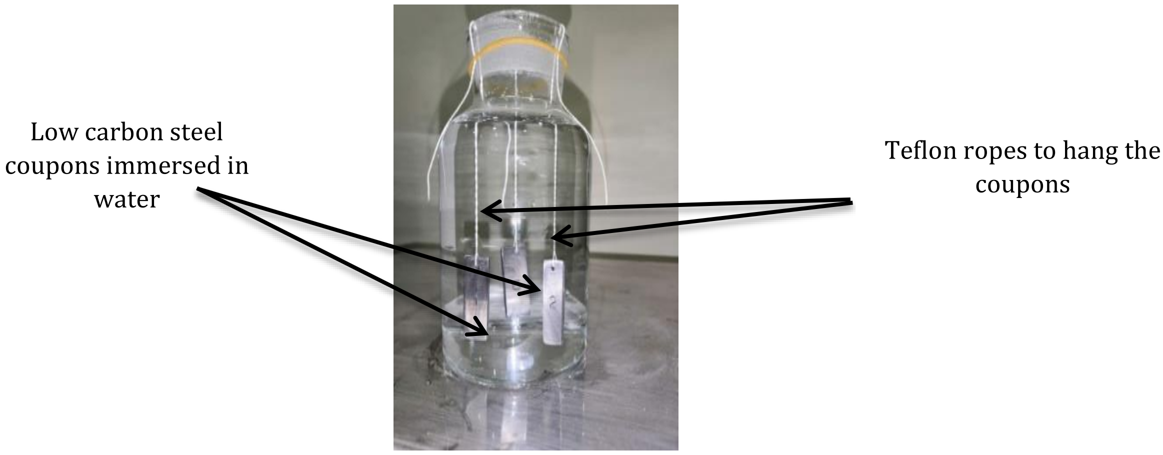

FIGURE 1 Weight loss method

Corrosion rate estimation

Corrosion rate calculations from weight loss data was performed according to Eq.1 in (mpy) units:

$$\text{Corrosion Rate (CR)}=\frac{3.45\times10^{6}\times\Delta w}{t\times d\times A} \qquad (1)$$

Where Δw is difference between weights of coupon before and after immersion test, t is time (period of immersion), d is density of low carbon steel, 7.86, g/cm^3 and A is surface area of coupon, cm^2.

Results and discussion

Experimental design & Analysis (DOE models)

First factorial Model

A two-levels two-factor 2^2 (with replication) factorial design was used to determine the effect of time (period of immersion) (weeks) and conc. of ku-2050 (ppm) on the CR in mpy unit of low carbon steel in makeup water. The low and high levels of the factors mentioned are shown in Table 2, where (-1,+1) are low and high levels for each factor.

TABLE 2 Factors and levels used in 2^2 factorial design

Factors	Low level	High level
Time (weeks)	2 (-1)	4 (+1)
Ku-2050 conc.(ppm)	25 (-1)	100(+1)

Table 3 represents the design matrix for 2^2 (with replication) with CR values measured in mpy units for each experiment. Table 3 demonstrates the design matrix for 2^2 (with replication) with CR values of low carbon steel in makeup water.

TABLE 3 Design matrix for 2^2 (with replication) with CR values of low carbon steel in makeup water

Design matrix combination	Time (weeks) X_1	Ku-2050 conc.(ppm) X_2	CR (mpy)
1	2	100	0.84443
2	2	100	0.88986
3	4	100	1.02036
4	4	25	1.26511
5	4	25	1.29916
6	2	25	0.86383
7	4	100	1.11618
8	2	25	0.93792

By analyzing factorial design in Minitab software 2021, multivariable equation were obtained with correlation coefficient R^2= 0.9603:

$$CR= 0.4708+ 0.2206\ X_1+0.00195\ X_2- 0.0012\ X_1\ X_2 \quad (2)$$

The complete Analysis of Variance (ANOVA) for the corrosion of low carbon steel in makeup water for periods of immersion (2, 4) weeks using ku-2050 inhibitor (25, 100) ppm under static conditions is shown in Table 4.

TABLE 4 Two-way ANOVA for CR (mpy) versus time (weeks), conc.(ppm)

Effect	DF	SS	MS	F	P-value
Time (weeks)	1	0.169589	0.169589	75.82	0.001
Conc. (ppm)	1	0.030651	0.030651	13.7	0.021
Interaction	1	0.016223	0.016223	7.25	0.054
Error	4	0.008947	0.002237		
total	7	0.225410			

DF denotes the degree of freedom, SS is the sum of squares, and MS signifies mean of squares.

From Table 4, p value for the (time and conc.) is <0.05 but for their interaction, it is > 0.05, meaning that the two variables are more significant than their interaction (more influence on CR than their interaction). Interaction plot between the means of CR values and conc. of ku-2050 at two levels of time are depicted in Figure 2.

From Figure 2, it is clear that the lines are less non parallel, which means that less effect can be noticed by the interaction between Ku-2050 conc. and time on the response CR.

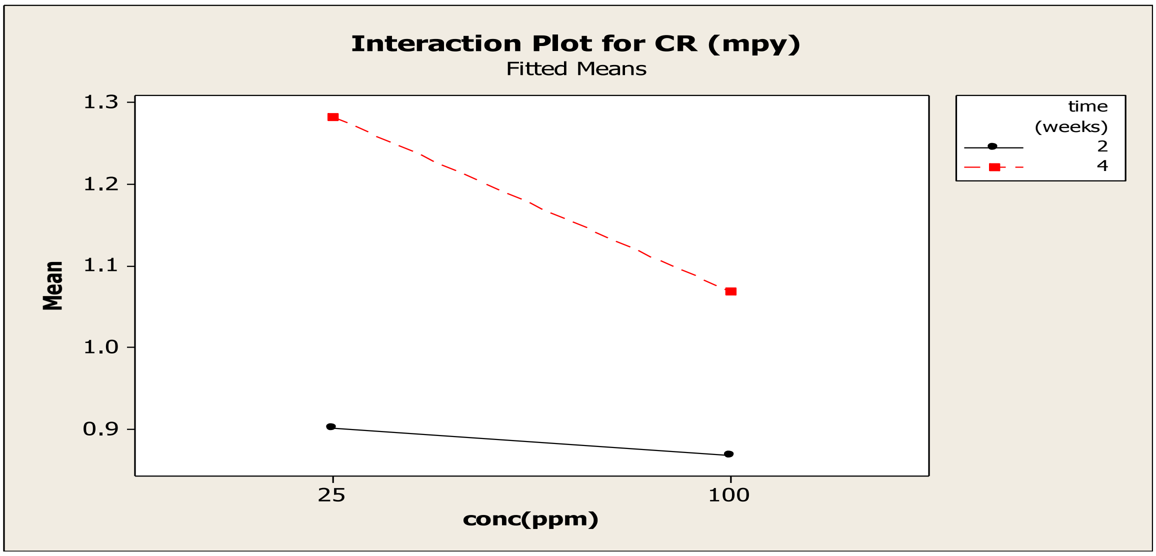

FIGURE 2 Interaction plot for Eq. 2

The two residual plots that are explained in the right part of Figure 3 show a fairly random pattern. The random patterns in Eq. 2 provide a decent fit to the data. At the left of Figure 3, Normal Probability (NP) and Histogram (Hist.) plots can be observed, which are a more specialized types of plots that can be used to see how data fits the norm, or skews from the norm. NP and Hist. plot demonstrate that the data are normally distributed.

An optimization plot was drawn by a Minitab response optimizer tool as shown in Figure 4. It is illustrated that the lowest corrosion rate of 0.8671 mpy could be obtained at 100 ppm of ku-2050 inhibitor and 2 weeks immersion period.

Contour plots, sometimes called level plots, are a way to show a three-dimensional surface on a two-dimensional. They have two predictor variables XY on the y axis response variable z as contours. It is shown from the contour plot in Figure 5 that CR is < 0.9 mpy at 2 weeks and 100 ppm of ku-2050, while at 4 weeks and 25 ppm of ku-2050, CR is >1.2 mpy.

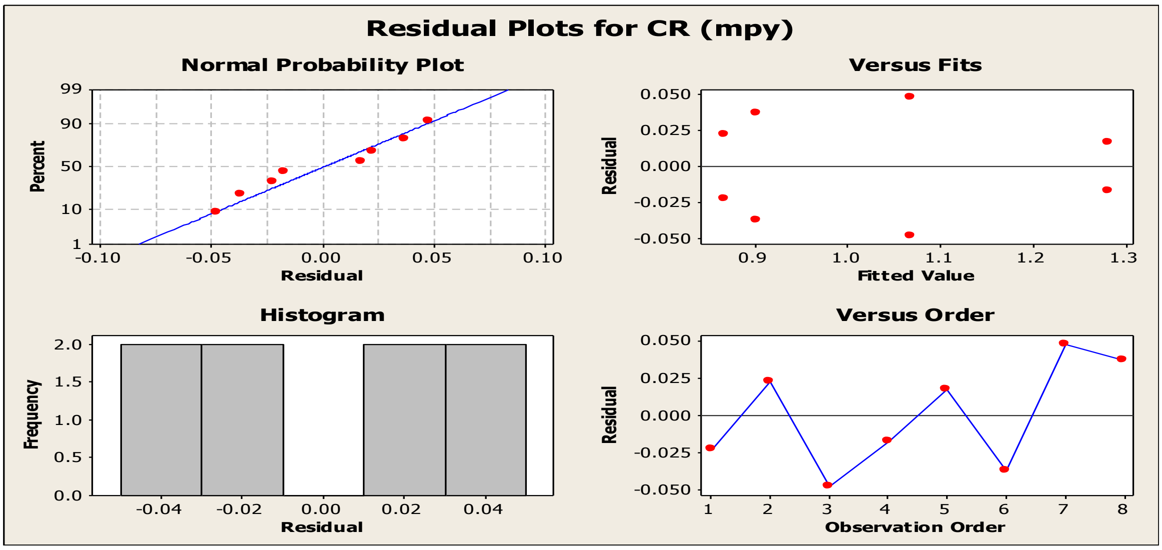

FIGURE 3 Residual plots for the Eq.2

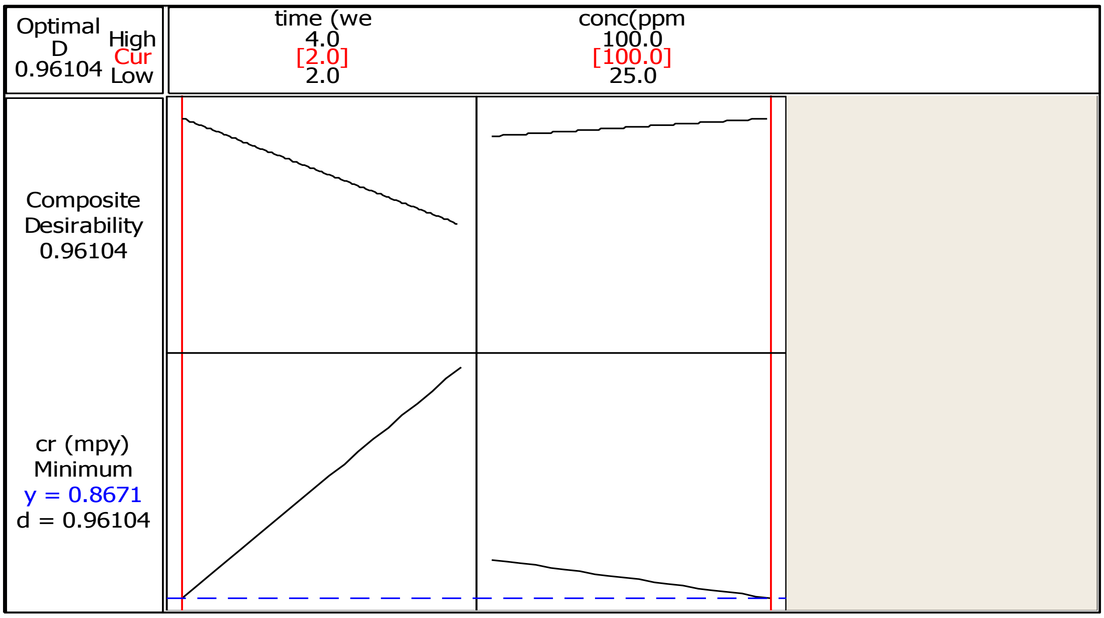

FIGURE 4 An optimization plot for Eq.2

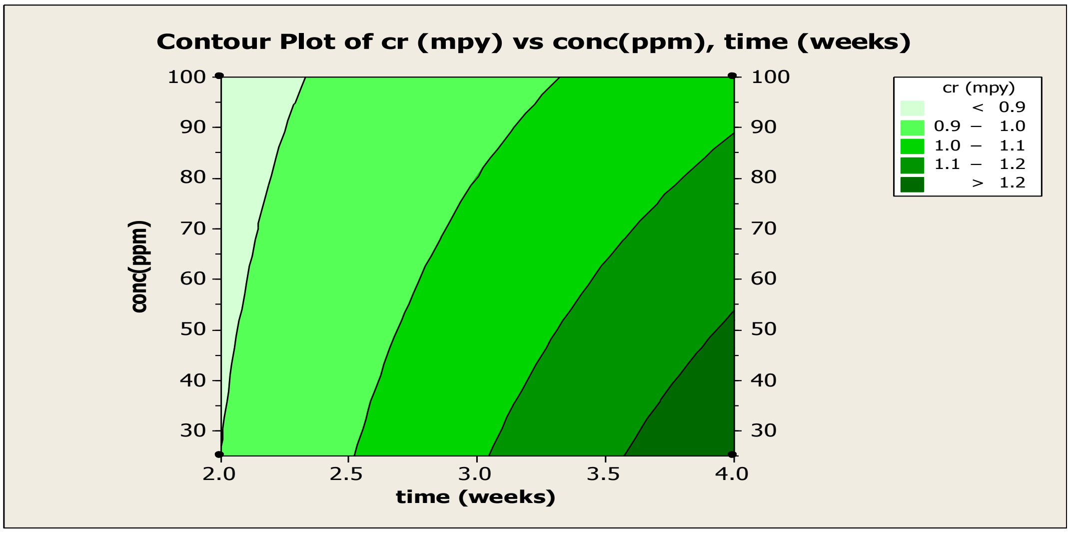

FIGURE 5 Contour plot for Eq.2

Second factorial model

The low and high levels of the factors mentioned are shown in Table 5.

Table 6 represents the design matrix for 2^2(with replication) with CR values that were measured in mpy units for each experiment.

TABLE 5 Factors and levels used in 2^2 factorial design

Factors	Low level	High level
pH	7 (-1)	8.5 (+1)
Ku-2050 conc. (ppm)	0 (-1)	100(+1)

TABLE 6 Design matrix for 2^2 (with replication) with CR values for each experiment

Design Matrix combination	pH X_1	Ku-2050 conc. (ppm) X_2	CR (mpy)
1	8.5	0	1.43068
2	8.5	100	2.01643
3	7.0	100	2.05030
4	7.0	100	1.93074
5	7.0	0	1.46852
6	8.5	100	1.87570
7	7.0	0	1.58962
8	8.5	0	1.29912

An equation was obtained with correlation coefficient of R^2=0.945 as follows:

$$CR=2.29521-0.109448\ X_1-0.000972\ X_2+0.000798\ X_1 X_2 \quad (3)$$

From ANOVA results in Table 7, p value for conc. of ku-2050 is <0.05 but for pH and its interaction with conc. is > 0.05, meaning that the conc. of ku-2050 is more significant than pH and their interaction (conc. of ku-2050 effects on CR significantly). Figure 6 depicts the interaction plot for Eq. 3.

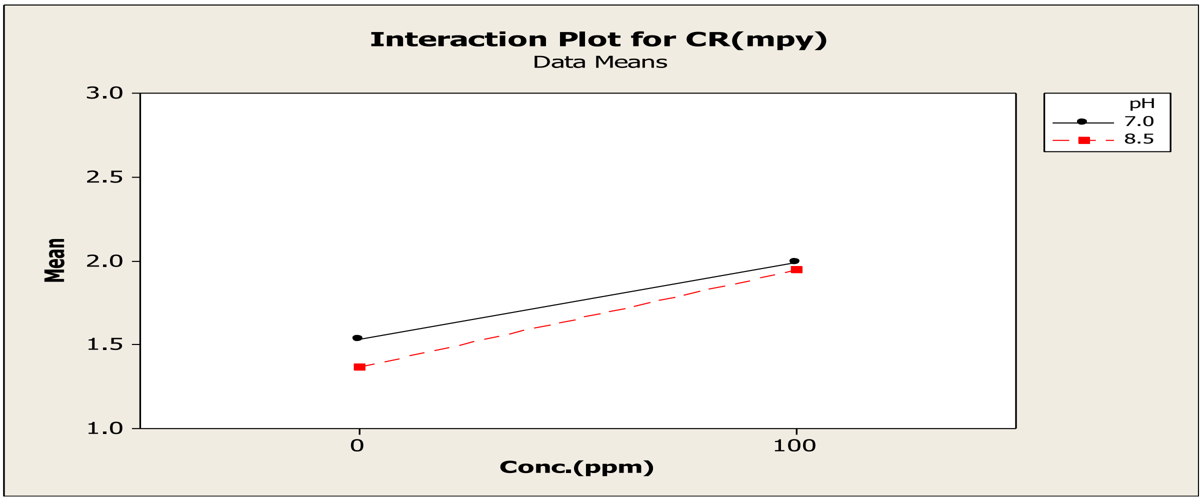

FIGURE 6 An Interaction plot for Eq.3

Taguchi models

In Taguchi design, a standard orthogonal array, L9, was designed by Minitab software 2021 including two factors (time & ku-2050 conc.) with 3 levels for each factor as shown in Tables 7and 8.

Table 9 demonstrates the responses (CR values in mpy units) for each mentioned experiment in Table 8.

TABLE 7 Factors and their levels used in Taguchi experiments design

Levels	Time (weeks)	Conc. of ku-2050 (ppm)
1	2	25
2	4	50
3	6	100

TABLE 8 Taguchi L9 orthogonal array to evaluate CR of low carbon steel immersed in makeup water

No. of experiments	Time (weeks)	Conc. of ku-2050 (ppm)
1	2	25
2	2	50
3	2	100
4	4	25
5	4	50
6	4	100
7	6	25
8	6	50
9	6	100

TABLE 9 Taguchi L9 orthogonal array with CR values in mpy units for low carbon steel immersed in makeup water

No. of experiments	Time weeks X_1	Conc. of Ku-2050 ppm X_2	CR_1 mpy	CR_2 mpy
1	2	25	0.864	0.938
2	2	50	0.791	0.829
3	2	100	0.844	0.889
4	4	25	1.265	1.299
5	4	50	1.136	1.0425
6	4	100	1.02	1.1161
7	6	25	1.33	1.579
8	6	50	1.283	1.393
9	6	100	1.195	1.207

The measurement of performance in Taguchi design is called signal to noise, S/N ratio. There are mainly three different types of S/N ratio that are applicable in the most situations: Larger is better (LTB), smaller is better (STB), and nominal is better (NTB). In this study, the quality to optimize is the corrosion rate. The used type of S/N ratio is smaller better (STB). Eq.(4) is used to calculate the ratio [12].

$$(\frac{S}{N})_{STB} = -10\log[\frac{1}{n}\sum_{i=1}^{n} y_i^2] \quad (4)$$

Regarding analyzing Taguchi design, Table 10 clarifies the effect of each of the studied factors on the CR_1 and CR_2. These outputs are shown in Figure 7. From Figure 7, it can be noted that the time has negative influence on the corrosion rate while, the conc. Of ku-2050 has a positive influence on it. Based on the recordings, time has the largest effect on the CR of low carbon steel in makeup water as shown in Figure 8.

TABLE 10 Response for S/N Ratio for CR_1& CR_2

Level	Time(weeks)	conc.(ppm)
1	1.3180	-1.5162
2	-1.1649	-0.4910
3	-2.4739	-0.3136
Delta	3.7919	1.2026
Rank	1	2

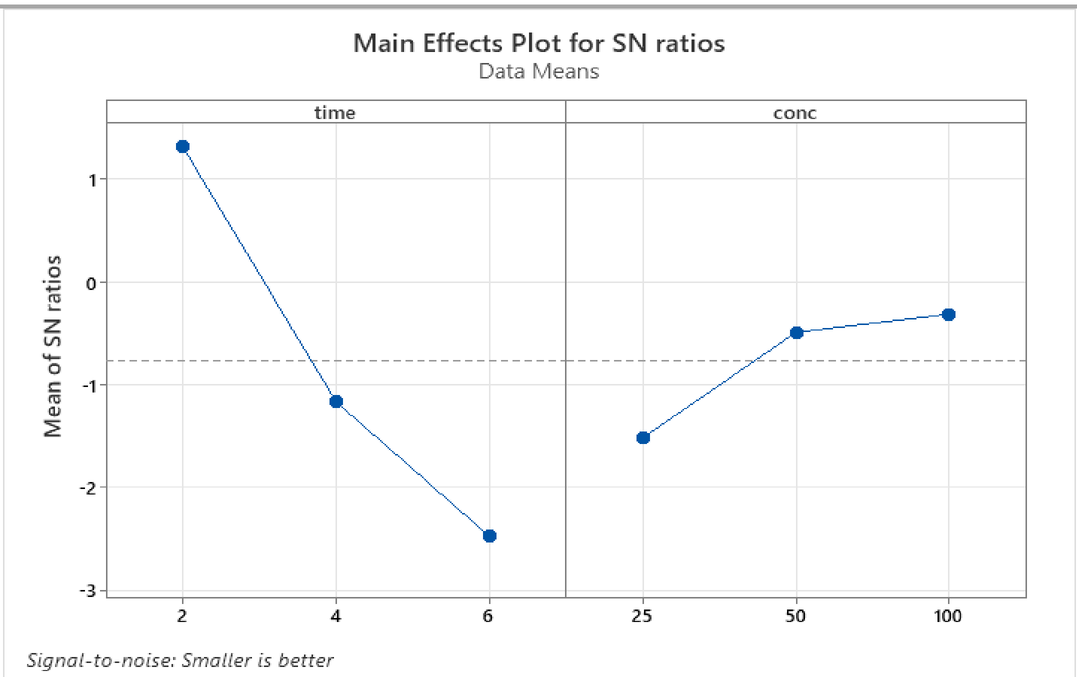

FIGURE 7 Main effects of the S/N ratio on CR_1 & CR_2

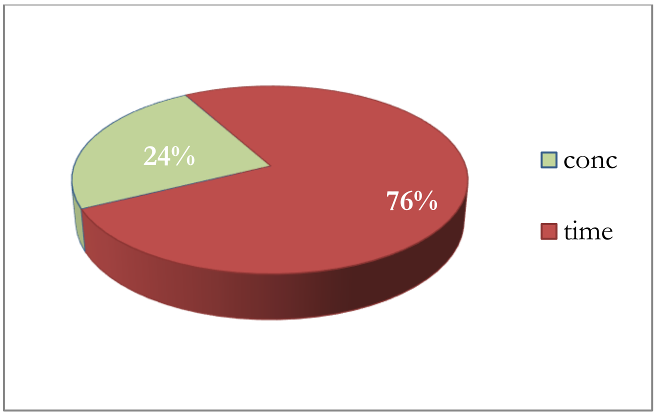

FIGURE 8 Influence of the studied parameters on CR of low carbon steel in makeup water obtained from S/N ratio

Tables 11 and 12 show the ANOVA results for the S/N ratio and the mean respectively. It is also clear from those tables that the time has an effect larger than the conc. of ku-2050.

TABLE 11 ANOVA results for S/N ratios of Corrosion Rate

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Time	2	22.2568	22.2568	11.1284	52.64	0.001
Conc.	2	2.5289	2.5289	1.2644	5.98	0.063
Residual Error	4	0.8457	0.8457	0.2114		
Total	8	25.6313				
Model Summary						
S	R-Sq	R-Sq(adj)				
0.4598	96.70 %	93.40%				

TABLE 12 ANOVA for Means of Corrosion Rate

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Time	2	0.33936	0.33936	0.169679	39.11	0.002
Conc.	2	0.04676	0.04676	0.023379	5.39	0.073
Residual Error	4	0.01736	0.01736	0.004339		
Total	8	0.40347				
Model Summary						
S	R-Sq	R-Sq(adj)				
0.0659	95.70%	91.40%				

The ANOVA analysis is shown in Figure 9, which should be explained. In this figure, there are four sub-figures. For the NP plot, it is noticed that it follows a straight line. The Hist. plot represents the normal distribution of the results about mean of zero, and since the values of skewness and kurtosis are within the range (2-(-2)), this confirms normal univariate distribution. The residual versus fit plot shows that the residuals are randomly distributed about zero-line. The residual versus order plot also confirms a random pattern around zero-line.

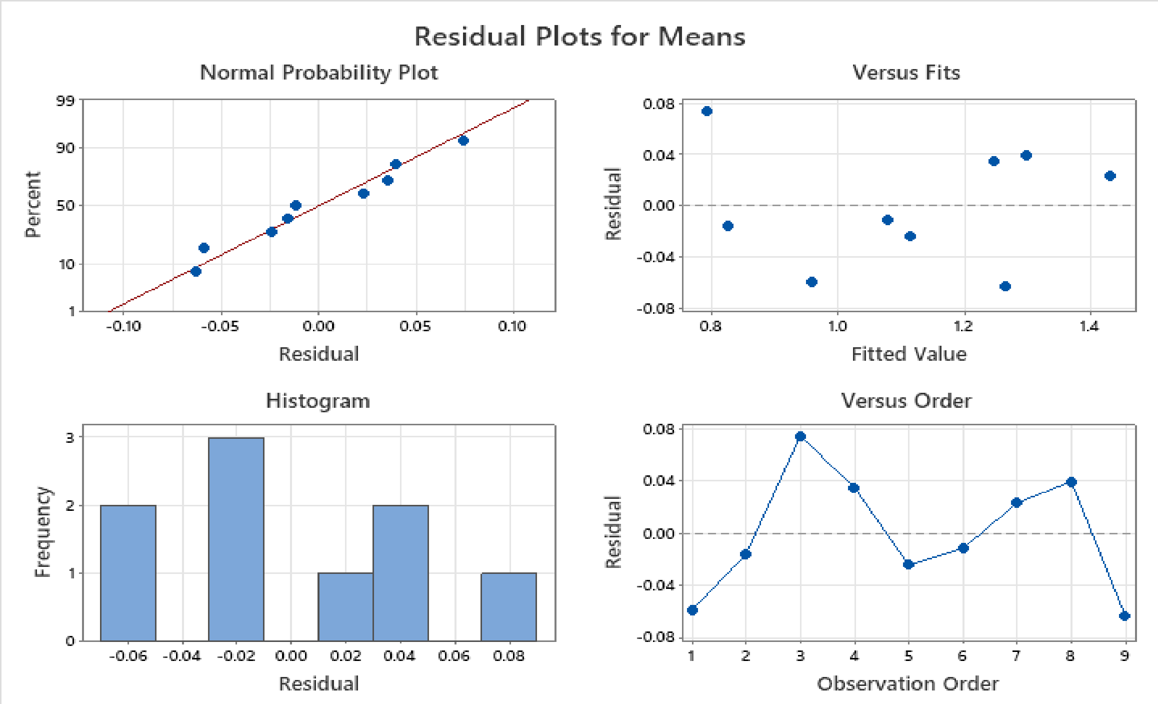

FIGURE 9 Residual plots of ANOVA analysis for Taguchi method

By using the correlation analysis for Taguchi design in Minitab software 2021, the best multiple regressions that fit the responses (CR of low carbon steel immersed in makeup water) versus the effective parameters (time & Conc. of ku-2050) were obtained for the highestR^2 with p-value < 0.05, as shown in the following Equations:

CR_1=0.445+ 0.2872 X_1- 0.001663 X_2- 0.0223 X_1^2 R^2=0.948 (5)

CR_2=0.808+ 0.1912 X_1- 0.00995 X_2+0.000093 X_2^2-0.001103 X_1 X_2 R^2=0.984 (6)

It was recorded that the above statistical models can predict the CR of low carbon steel in makeup water with high level of trust depending on the correlation obtained coefficients (R^2), and this indicates that the relation between CR and variables is strongly significant. The minimum corrosion rates for the above founded regressions Eq.5 and Eq.6 were obtained by using the minitab-2021 optimization tool. Table 13 shows the results at optimum levels from both experiments, application of designed equations, and % error between the both.

TABLE 13 Optimal run levels and comparison between the results

	Run 1 for CR_1	Run 2 for CR_2
Time(weeks)	2	2
Conc. Of Ku-2050(ppm)	25	50
Exp. Result	0.8638	0.8296
Result from Eqns.	0.8888	0.8162
% Error	2.8	1.64

The contour plots for CR $_1$ & CR_2 vs. time (weeks) and Conc.(ppm) are shown in Figures 10 and 11. It is illustrated from these figures that CR_1 was at the minimum levels when the conc. of ku-2050 increased from (46 to 78) ppm for approximately 2 weeks of immersion, while CR_2 was at the minimum levels when the conc. of ku-2050 increased from (32 to 100) ppm for (2 to 3) weeks of immersion.

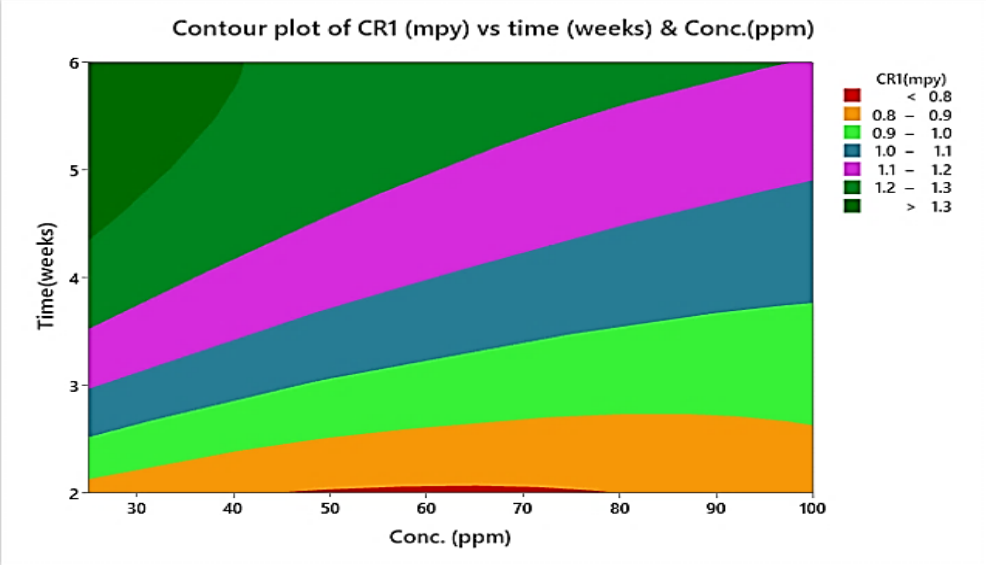

FIGURE 10 Contour plot of CR_1 vs time and conc. of ku-2050

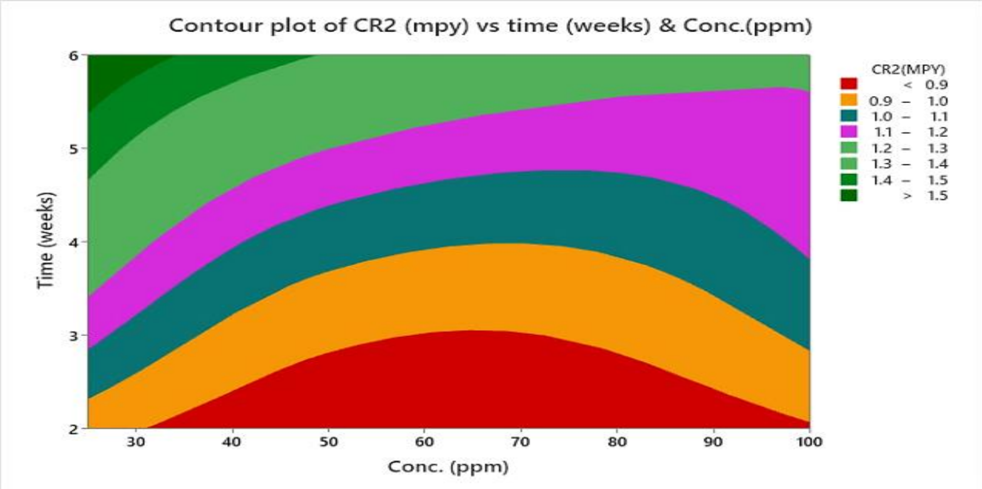

FIGURE 11 Contour plot of CR_2 vs. time and conc. of ku-2050

Monte Carlo simulation results

Monte Carlo Simulation was executed using Risk Simulator Tools in Microsoft Excel, through which 1000 random values were generated for inputs (time, conc. of ku-2050 & pH) and applied in the mentioned above DOE models. Table 14 demonstrates the Monte Carlo results for the above DOE models. Figure 12 illustrates Forecast Normal distribution obtained by Monte Carlo Simulation.

TABLE 14 Monte Carlo simulation results for the DOE models

DOE Models	Mean	Median	St.Dev.	Probability 75%	Probability 25%	Error precision	Skewness	Kurtosis
Eq.2	1.756	1.167	0.1343	1.2637	1.0751	0.0071	0.3956	-0.2608
Eq.3	1.7716	1.776	0.1152	1.8693	1.6703	0.004	-0.0974	-1.1346
Eq.5	1.1206	1.1331	0.0970	1.0565	1.1935	0.0054	-0.4943	-0.2319
Eq.6	1.0805	1.0662	0.1181	1.1442	0.9992	0.0068	0.6560	0.7031

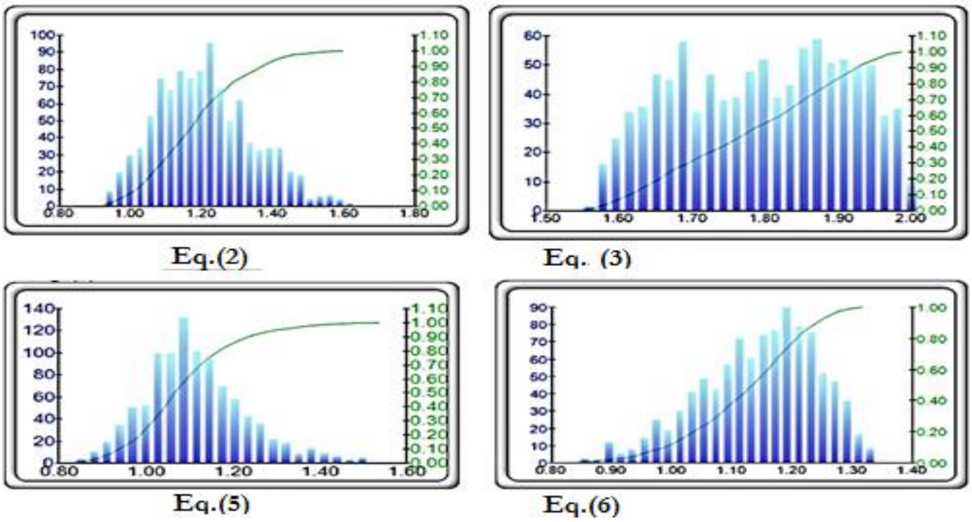

FIGURE 12 Forecast Normal distribution (for the DOE models) produced by Monte Carlo Simulation

From Table 14, it is noticed that the skewness and kurtosis have acceptable values which are included in the range of (2-(-2)) and this means the decent normal distribution for the four DOE models as shown in Figure 12.

Sensitivity analysis results

Based on Monte Carlo Simulation, it is easy to make a sensitivity analysis by the same simulator tools in Microsoft Excel. Figure 13 demonstrates the sensitivity analysis results.

FIGURE 13 Sensitivity analysis charts for each DOE model

In Figure 13, positive correlations are shown in green while negative correlations are shown in red. This means that there is a positive correlation between (time, pH) and corrosion rate, while there is a negative correlation between conc. of inhibitor and corrosion rate. Also, it is noticed from the same figure that the highest percentage variation in corrosion rate is caused by the variation in time and pH more than conc. of ku-2050.

Inhibitor efficiency

The efficiency of ku-2050 inhibitor was evaluated in the presence of different concentrations (25, 50, 100, 300, 500,700, 800, 900, 1000, 1500 & 2000) ppm, at constant conditions (room temperature, pH=7.3 & 1day period of immersion) on the corrosion rate of low carbon steel in makeup and recirculating water. Figures 14 and 15 demonstrate the efficiency of the ku-2050 inhibitor at the mentioned conditions.

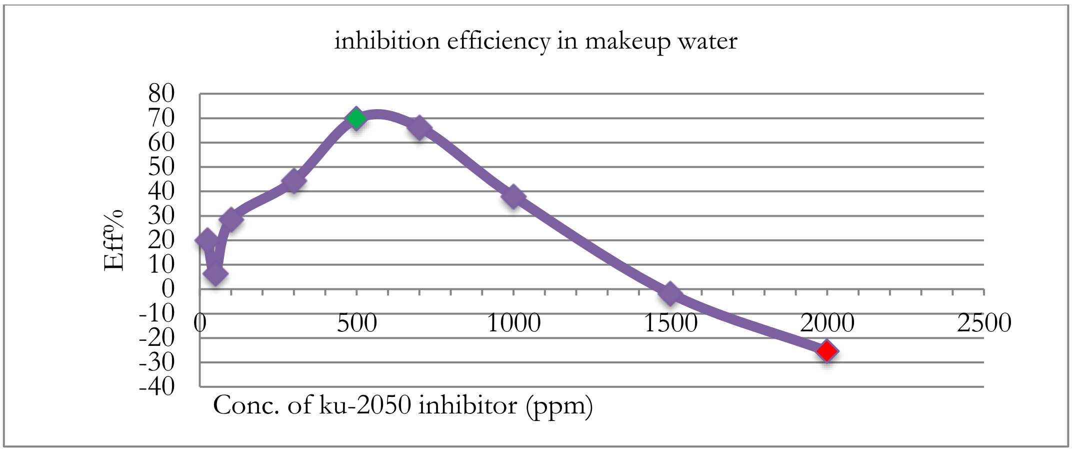

FIGURE 14 The efficiency of ku-2050 inhibitor in makeup water at room temperature and 1day period of immersion

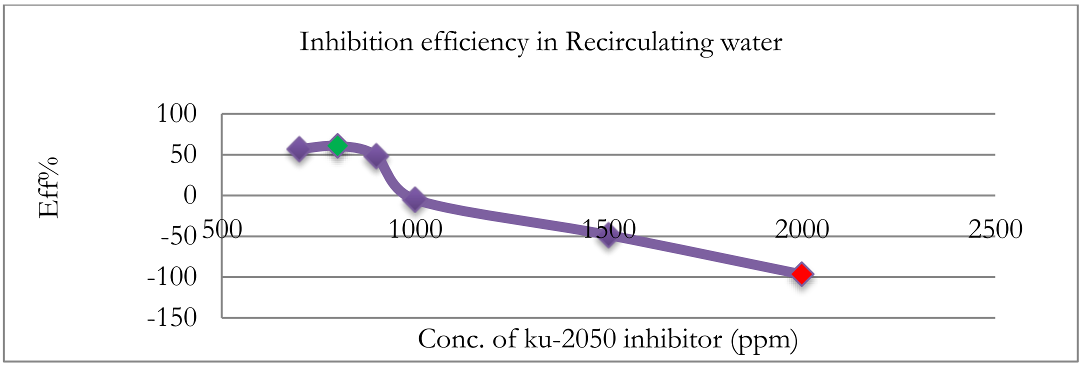

FIGURE 15 The efficiency of ku-2050 inhibitor in Recirculating water at room temperature and 1day period of immersion

From the above figures, it is illustrated that the highest eff.% is 69.7~ 70 % at 500 ppm of ku-2050 inhibitor in makeup water while in recirculating water the highest eff.% is 60.6 ~61% at 800 ppm of ku-2050 inhibitor. Above these concentrations, the eff.% demonstrated a direct decrease up to 2000 ppm of ku-2050 inhibitor.

Conclusion

It was found that Factorial and Taguchi designs prepare a useful methodology for the setup and optimization of CR of low carbon steel in makeup water with the minimum number of trials. The DOE models proved the strong relation between CR of low carbon steel and independent parameters (time, pH, conc. of ku-2050). Contour plot offers a useful method to know under which ranges we can work to have the desired CR in the situation of fixing one of the working parameters. Monte Carlo Simulation technique demonstrated the agreement of DOE models with random fluctuations in the input variables through the decent normal distribution for the results. Sensitivity analysis proved that the highest percentage of variation in CR is caused by the variation in time and pH more than the conc. of ku-2050 inhibitor.

Acknowledgments

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