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Synergistic Influence of Leucine on Polyvinyl alcohol in the Corrosion Inhibition of Mild Steel in Molar Hydrochloric Acid – Taguchi Method

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Abstract

In this paper, Taguchi method is applied to find the optimum conditions for the synergistic influence of L-leucine on polyvinyl alcohol (PVA) in the corrosion inhibition of mild steel. A L_9 orthogonal array of experiments is constructed and the resulted experimental inhibition efficiencies are adopted for the signal to noise ratio and variance analysis (ANOVA). The proposed Taguchi methodology consists of four factors viz., concentration of L-Leucine, concentration of PVA, exposure time and temperature, at three different levels which are connected in sequence wise to achieve the overall inhibition optimization. The experimental results performed with the selected factors and levels were further processed with Qualitek-4 software at bigger is better as quality character to find the optimized conditions. The experimental result at the optimized conditions are used to calculate the synergism parameter and is found be greater than one.

Keywords: Taguchi method, corrosion inhibition, polyvinyl alcohol, Leucine.

Introduction

In practical, the optimization of all the considered parameters to establish a best combination for the better performance is a tedious process. To interrelate the studied parameters, large number of experiments has to be carried out to cover all the possible parameter combinations. This process is highly uneconomical and difficult. The conventional optimization procedures involve alteration of one parameter and keep the other parameters a constant. It enables us to study the impact of particular parameters on the entire performance of the process. This procedure is time consuming, cumbersome and requires large number of experimental data sets. It is difficult to provide information about the mutual interactions of the parameters in the classical method of optimization process[1].

For this type of cases, statistical tools and experimental design help to gain more information about the optimization conditions. Taguchi dynamic approach facilitates the study of interaction of a large number of variables spanned by factors and their settings with a small number of experiments leading to considerable saving in time and cost for the process optimization[2-5]. In literature many have employed the Taguchi method as a tool to evaluate the influence of various parameters on the properties of the system under consideration[6-9]. Tang, C. *et. al.,* in 2013 have studied the inhibitive property of *Murraya koenigii* extract and *Cymbopogen citratus* extract in 0.25-1.0 M H_2SO_4 concentration using Taguchi dynamic approach[10].

Mild steel is an important material of choice due to low cost and easy availability. Hydrochloric acid is one of the most important pickling acids, which is widely used in steel and ferrous alloy industry for acid cleaning, acid descaling, oil well oxidizing and other petrochemical processes. Polyvinyl alcohol (PVA) has been reported as corrosion inhibitor for mild steel in 0.5 M H_2SO_4 by Umoren[11] but the maximum efficiency was only 30%. Amino acids[12] and its derivatives[13] were examined for their inhibition property in acidic environment but their biological importance restricts the use.

Synergism is a combined action of compounds greater in total effect than the sum of individual effects. Improved performance of inhibitors in the presence of halide ions has been observed by several investigators[14-16]. Most of the acid corrosion inhibitors are known for their specificity of action. Interestingly, the addition of other substances and the combination of inhibitors has provided multiple effects to achieve effective corrosion inhibition.

In this paper synergistic influence of L- Leucine on the corrosion inhibition performance of mild steel in 1M HCl is presented by adopting Taguchi experimental design. This approach of process optimization enables the study of influence of individual factors, establishes the relationship between variables and operational conditions, and predicts the performance at the optimum levels based on the concept of *S/N* ratio of the response values of a few well-defined experiments[17].

Material and Methods

Taguchi methodology involves four phases viz., planning of experiments (phase 1), conducting planned experiments (phase 2), analysis of experimental results (phase 3) and validation of the optimized conditions (phase 4). During the design of the experiment, the experimental factors and their different levels need to be selected in order to reduce errors, enhance inhibition efficiency and reproducibility of the results.

Design of Experiments (Phase 1): In phase 1, the various factors having critical effect on the corrosion inhibition process to be optimized are determined and their ranges are assigned. In dynamic Taguchi method, the influencing parameters are characterized into signal factor, control factor and noise factor. Signal factor is a variable which initials the process and sustain its function. Thus HCl concentration is selected as the signal factor since HCl is responsible for the corrosion process. The noise factor is a variable that known to affect the response but it is difficult to control. Fe^{2+} concentration and surface roughness are assigned as noise factors. The control factor is a variable that is expected to give impact on the response. The exposure time, temperature, PVA concentration and L-leucine concentration are selected as control factors.

Keeping the level of signal and noise factors constant, the levels of control factor is changed. The four factors (concentration of L-leucine, concentration of PVA, exposure time and temperature) having significant influences on the corrosion inhibition process are considered in the current experimental design. In the present case, the three different levels of each factor are considered which resulted in nine set of experiments represented by L9 arrays. The considered four factors at three different levels for the experimental design are depicted in tables 1 and 2. All the factors have been assigned with three levels in a layout of L9 and a total of 8 degrees of freedom (number of experiments minus one).

Weight loss Measurements (Phase 2): The average chemical composition of the MS sample as analyzed by optical emission spectrometry (Baird Spectrovac 1000 Optical Emission Spectrometer) is found to be as follows: (% by weight) Mn - 0.196, C-0.106, P-0.027, Cr-0.022, S-0.016, Ni-0.012, Si-0.006, Mo-0.003 and remainder Fe. The mechanically polished mild steel sheet is cut into strips of dimensions 1cm x 5cm x 0.15cm. The samples are degreased using soap solution and rinsed with trichloroethylene followed by rinsing with double distilled water. The samples are allowed to dry at room temperature. AR grade chemicals polyvinyl alcohol, L-leucine and hydrochloric acid and double distilled water are used for the corrosion inhibition studies. Weight loss corrosion measurements are performed for mild steel specimens for the nine experimental trials following the ASTM G31 standard procedure[18]. The weight loss results after the exposure of MS specimens is used to calculate inhibition efficiencies using the relation,

$$IE_w(\%) = \frac{W - W_i}{W} * 100 \quad (1)$$

where W and W_i are weight loss of specimens exposed to uninhibited and inhibited solutions.

Table-1
Experimental parameters and its different levels

Experimental Parameters			
Factors	**Level 1 (L1)**	**Level 2 (L2)**	**Level 3 (L3)**
F1-Conc. of PVA (g)	0.0000 g	0.2500 g	0.5000 g
F2-Conc. of L-leucine (g)	0.0000 g	0.0500 g	0.0540 g
F3-Exposure Time (h)	1 h	2 h	3 h
F4-Exposure Temperature (K)	313 K	323 K	333 K

Table-2
L9 orthogonal array of experiments

Experiments	Combinations of Factors and Levels				IE(%)
1. – C1	F1L1	F2L1	F3L1	F4L1	00.00±0.0
2. – C2	F1L1	F2L2	F3L2	F4L2	35.41±1.89
3. – C3	F1L1	F2L3	F3L3	F4L3	27.89±1.61
4. – C4	F1L2	F2L1	F3L2	F4L3	37.87±3.02
5. – C5	F1L2	F2L2	F3L3	F4L1	54.15 ±4.07
6. – C6	F1L2	F2L3	F3L1	F4L2	64.64±1.86
7. – C7	F1L3	F2L1	F3L3	F4L2	38.51 ±1.38
8. – C8	F1L3	F2L2	F3L1	F4L3	49.27±3.57
9. – C9	F1L3	F2L3	F3L2	F4L1	47.72±1.87

Analysis of Results (Phase 3): Qualitek-4 software (Nutek Inc., MI) is used for the automatic design of experiments based on Taguchi approach. Qualitek-4 software can be applied to automize L4 to L64 experimental arrays with 2 to 63 factors at their two, three or four different levels. The Qualitek-4 allows to select the desired arrays and to assign factors to the appropriate columns. The resulted experimental data are processed with Qualitek-4 software using bigger is the better quality characteristics for the determination of optimum corrosion inhibition performance. The results enable the identification of the influence of individual factors to estimate the optimum performance conditions. In Taguchi's method, the responses of the control factors ie, inhibition efficiencies are taken for S/N ratio analysis using larger the better characteristic equation,

$$S / N_i = -10 \log \left[\frac{1}{N_i} \sum_{u=1}^{N_i} \frac{1}{y_u^2} \right] \qquad (2)$$

where N_i is the number of trails for experiment number i, u is the trial number and y is the response value (IE).

Validation of Results (Phase 4): In order to validate the methodology, corrosion inhibition experiments are further performed for mild steel using the optimized conditions. The individual performances of L-leucine and PVA are also determined under the same experimental conditions. The inhibition efficiencies are used to calculate the synergism parameter (S) between PVA and L-leucine. The synergism parameter 'S' is calculated using the relation initially given by Aramaki and Hackermann and reported elsewhere[15,19].

$$S = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \qquad (3)$$

where I_{1+2} indicates the sum of individual inhibition efficiencies of halide ion and inhibitor, I'_{1+2} denotes the combined inhibition efficiency.

Results and Discussion

Main Effects of Factors: Weight loss corrosion experiments studies with the designed experimental conditions are presented in table 2, which showed significant variation in the inhibition efficiencies. The average effect of the factors along with interactions at the assigned levels on the corrosion inhibition of mild steel is shown in table 3. Individually at level stage, all the considered four factors have highest effect in level 2. The relative influence of each factor is represented by the difference between the maximum and minimum S/N rations of the levels. Thus L2–L1 in table 3 of various factors in the present system indicates the relative influence. The larger the difference, the stronger is the relative influence. Among the factors studied, PVA shows stronger influence than the other factors followed by L-leucine, exposure temperature and time. It is reported that, inhibition efficiencies of an organic compound can be increased by increasing the concentration and also by the addition of different compounds as synergistic inducers to the media[20]. The synergism of the added compound is found to mainly depend on the nature, concentration, exposure time and temperature to the stagnant solution.

Table-3
Main effects of selected factors

Factors	Level 1	Level 2	Level 3	L2-L1
Concentration of PVA	-19.80	34.12	33.03	53.91
Concentration of L-leucine	-18.68	33.14	32.88	51.81
Exposure Time	-12.41	32.01	31.74	48.42
Temperature	-17.02	32.96	31.41	49.98

Figure 1 shows the influence of each individual factor on the inhibition efficiency. Increase in concentration of factors PVA and L-leucine has resulted in increase in inhibition performance. Increase in exposure time and temperature has also resulted in higher inhibition efficiency up to level 2 and subsequent increase results in decrease in the inhibition efficiency to a minor quantity. This is due to the adsorption of the added inhibitors on the metallic surface. Moreover the impact of exposure time and temperature on the corrosion rate of the metal was reported in many literatures, which indicated both positive as well as negative trends. It is mainly depending on the nature of the adsorption process. If the adsorption proceeds via chemical process then the temperature shows some positive impact on inhibition efficiency. If the adsorption process is of physical phenomenon the inhibition efficiency decreases at higher temperatures. This is the situation in the current system.

Interactions between two factors: Understanding the various types of interactions between any two factors gives a better insight into the overall process analysis. Each factor may interact with any other factor or all of the other factors and develops the possibility of numerous interactions. Taguchi dynamic method accounts for this kind of all possible interactions and estimates their interaction severity indexes (SI). The possible interactions and their severity indexes are presented in table 4. The interaction severity index presents 100% of SI for 90 degrees angle between the lines while, 0% SI for parallel lines. In the present system all the interactions shows about 47-50% SI.

From the table it follows that exposure time and temperature interaction showed highest severity index of about 51% followed by others. All other interactions namely PVA with L-leucine, PVA with time, PVA with temperature, L-leucine with time and L-leucine with temperature show reasonably good severity index. It is evident from the results that the influence of individual factors on the corrosion mitigation has varying efficiencies, while in combination the efficiency is quite independent of individual influence. Figure 2 showed the contribution of selected factors on the corrosion mitigation at optimum performance. The figure shows the impact on the corrosion inhibition in individual cases.

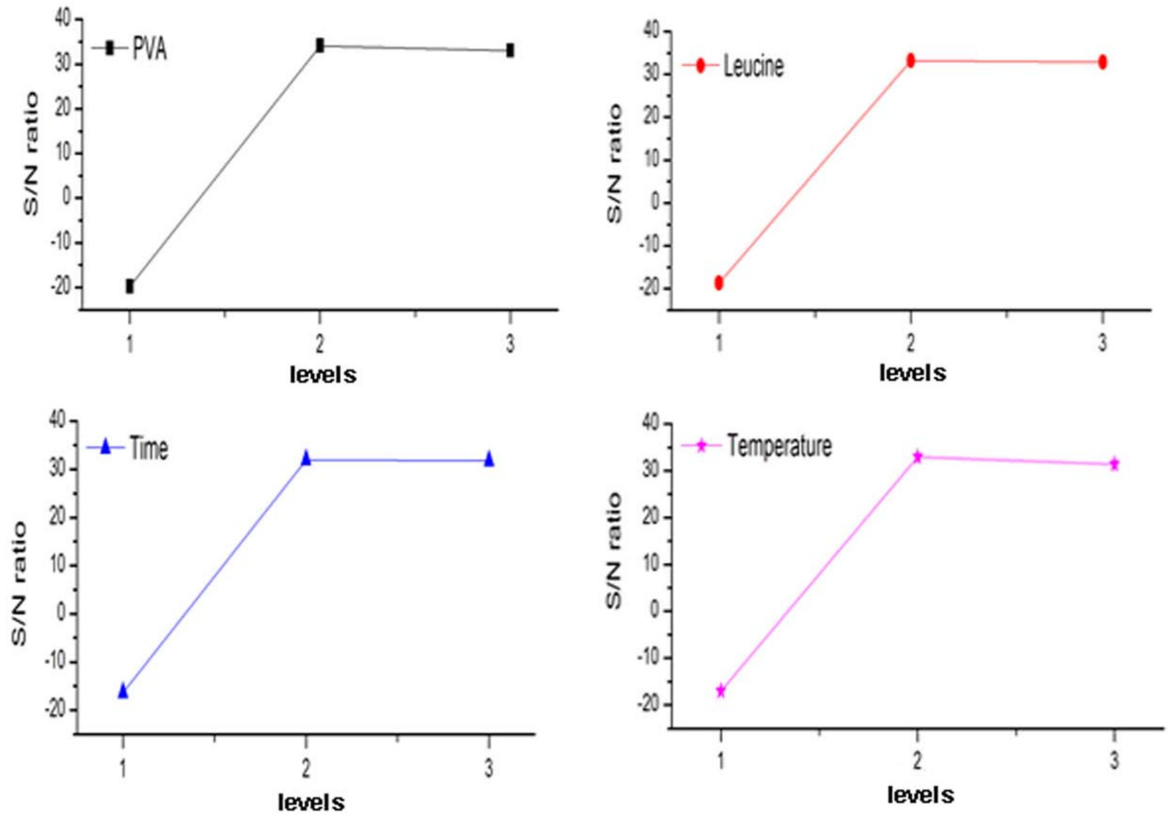

Figure-1
Main effects of factors at their different levels

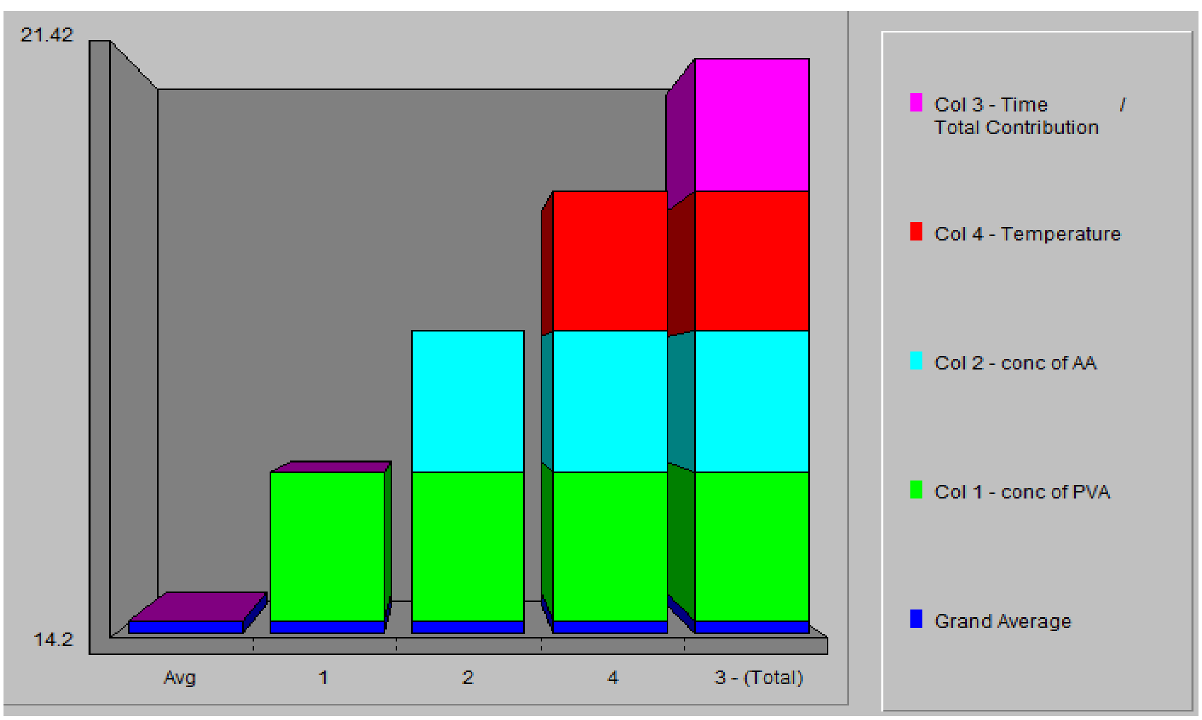

Figure-2
Optimum contribution of factors for PVA + L-leucine

Variance Analysis (ANOVA): In this approach, ANOVA is employed to analyze the experimental results to determine the contributions of different factors. The results of ANOVA calculations with the percentage contribution of the factors are shown in table 5. It can be concluded from the table that PVA is the most significant factor for the corrosion mitigation process since it constitutes almost 90% of the added additive. L-Leucine and exposure temperature are the next most important significant factors in the inhibition process. Exposure time shows least impact among the factors studied with the assigned variance of values.

The values reported as errors arise from uncontrollable factors (noises), which should be less than 50%; otherwise the results would not be reliable[21]. The error value reported in table 5 is 0%. This indicates that all the considered factors are controllable and the error had no significant effect on the results. The 0 error term made the F-values for the factors to infinity. F-ratio is a tool to demonstrate whether a parameter has a significant effect or not. Higher the F-values indicate the greater significance of the factors.

F-calculated values for concentration of PVA is infinity while the F-table value is 3.5546 at 5% confidence level and 6.00 at 1% confidence level which indicates that it has a significant effect on the corrosion inhibition process of the metal. Similar type of results (zero error and infinity F-values) is observed for the ANOVA calculations of the factors affecting the tensile strength of the polymer blend was reported by Rajan[22]. This indicated that L-leucine concentration, exposure time and temperature, are the significant factors mitigating the corrosion process.

Optimum Conditions: Optimum conditions for better performance in terms of contributions to achieve higher inhibition efficiency are shown in table 6. It can be seen from the table that PVA and L-leucine have significant role in the corrosion inhibition than the other selected factors. The results of the S/N and variance analysis clearly indicate that the level of concentration of the inhibitor increases, the S/N ratio also increases. The larger S/N ratio is observed for the PVA and L-leucine in level 2. Time and temperature are the other important factors which affect the corrosion process and hence the inhibition efficiencies. Exposure time shows the positive impact on the studied parameters. Level 2 is the optimum condition resulting in higher corrosion rate for the studied system. For the temperature level 2 yields better results.

Table-4
Various interactions and their interaction severity indexes

S. No.	Interactions	SI (%)
1	Concentration of PVA with L-leucine - [F1xF2]	47.31
2	Concentration of PVA with time - [F1xF3]	49.82
3	Concentration of PVA with temperature - [F1xF4]	47.80
4	Concentration of L-leucine with time - [F2xF3]	49.40
5	Concentration of L- leucine with temperature - [F2xF4]	49.73
6	Time with temperature - [F3xF4]	50.83

Table-5
ANOVA results for S/N ratios of inhibition efficiencies

Factors	DOF (f)	Sum of Squares (SS)	Variance (V)	F-ratio (F)	Percent P (%)
Conc. of PVA	2	5698.28	2849.14	∞	27.73
Conc. of L-Leucine	2	5343.04	2671.52	∞	26.00
Time	2	4662.65	2331.32	∞	22.69
Temperature	2	4844.93	2422.46	∞	23.58
Error	0				
Total (N=27)	8	21155.47			100%
F critical value for (2,18) is 3.55 at 5% and 6.00 at 1% confidence level					

Table-6
Optimal Conditions of the factors

Factors	Optimum Levels	Level Description	Contribution
Conc. of PVA	2	0.25 g	18.33
Conc. of L-leucine	2	0.05 g	17.35
Time	2	2 h	16.23
Exposure temperature	2	50 ^oC	17.18
Total Contributions from all factors			69.09
Average performance			15.78
Expected result at their optimum conditions			84.87

The expected result at optimum condition is 85 % with total contribution from all the factors being 69 % with grand average performance of 16 %. Based on the average effects of the factors the optimum conditions are 5:1 ratio of PVA and L-leucine. The optimum exposure time and temperature for the better performance is found to be 2 hours and 50 °C respectively. The performance distribution of current experimental conditions and the new improved conditions (optimized) is shown in figure 3. It is shown that the figure clearly reveals the increased performance of corrosion mitigation process at the optimal conditions.

Validation Experiment and Synergism Parameter: Further to validate the proposed experimental methodology, weight loss corrosion inhibition experiments are performed for mild steel specimens at the optimized conditions (table 6) which provide about 88.01% inhibition efficiency. The ratio of polyvinyl alcohol (0.25 g) and L-leucine (0.05g) in the optimum condition is 5:1. The results proved that higher inhibition efficiency is achieved with obtained optimized conditions. Experiments are also conducted at the optimized conditions by neglecting factor 1 and in other case factor 2. The experimentally observed inhibition efficiencies are presented in table 7. The results are used to evaluate the synergism parameter (S) and are provided in table 7. The S value is found to be greater than unity indicating better synergism between the PVA and L-leucine.

Table-7
Experimental results at new improved conditions

System– 2h, 50°C	IE (%)	Synergism Parameter (S)
1M HCl	0.00	1.1338
0.25 g PVA	64.24±2.04	
0.05 g L-Leucine	35.41±1.89	
0.25 g PVA + 0.05 g L-leucine	88.01±2.31	

Conclusion

System conditions and inhibitors composition optimization by a conventional method is not only cumbersome and time consuming, but also ignores the important interactions between the studied parameters. Taguchi process optimization involves the study of different variables named as factors over a specific region of interest designated as levels. The Taguchi method reveals the influence of individual factors and establishes the interactions between variables. Finally the method involves validation experiments at the obtained optimum levels and confirms the results predicted by the Qualitek-4 software. The calculated synergism parameter between PVA and L-leucine is greater than unity indicating the enhanced corrosion mitigation of mild steel.

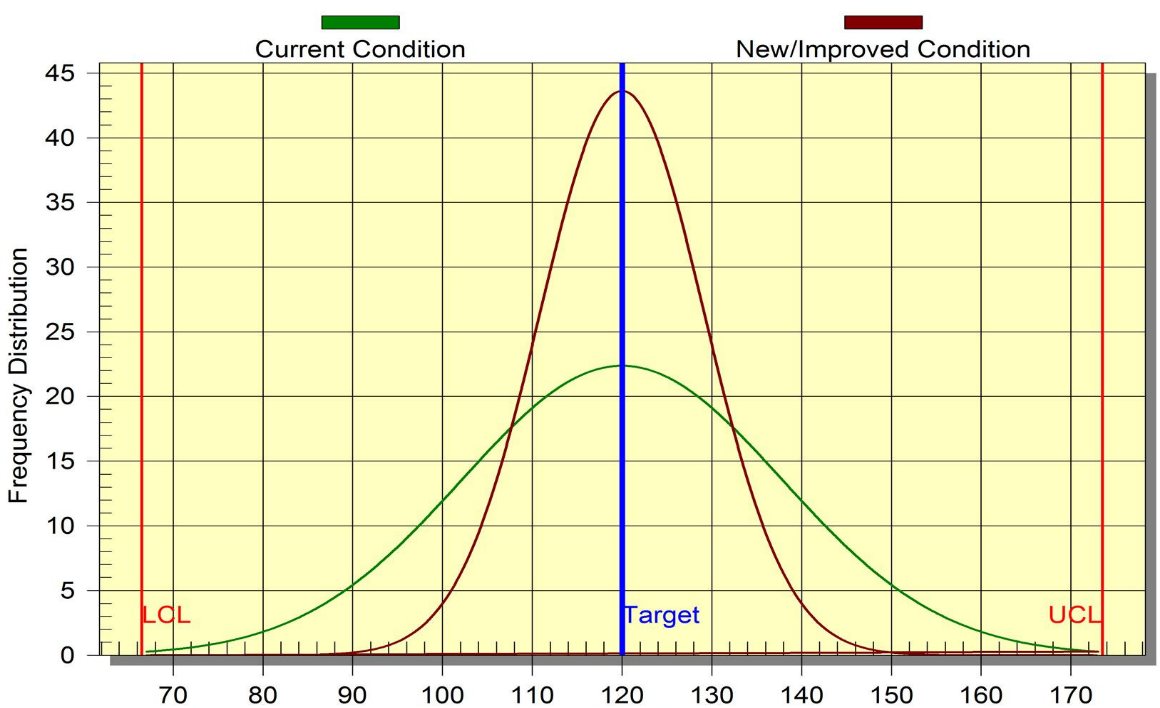

Figure-3
Performance distribution of current and improved condition

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Reference

1. Beg Q.K., Sahai V. and Gupta R., Statistical Media Optimization and Alkaline Protease Production From *Bacillus Mojaensis* in a Bioreactor, *Proc. Biochem.,* **39(2)**, 203-209 **(2003)**
2. Murthy B.R.N., Lewlyn L.R. Rodrigues and Anjaiah Devineni, *Res.J.Recent Sci.,* **1(6),** 7-15 **(2012)**
3. Park S. H. and Park, S. H., Robust Design and Analysis for Quality Engineering, *London: Chapman & Hall.,* 2-6 **(1996)**
4. Phadke M. S., Quality Engineering using Robust Design. *Prentice Hall PTR* **(1995)**
5. Tong L. I., Su C. T. and Wang, C. H., The Optimization of Multi-Response Problems in the Taguchi Method, *Int. J. Qual. Reliab. Manag.,* **14(4)**, 367-380 **(1997)**
6. Aslan E., Camuşcu N. and Birgören B., Design Optimization of Cutting Parameters when Turning Hardened AISI 4140 Steel (63 HRC) with Al_2O_3 + TiCN Mixed Ceramic Tool, *Mater. Design.,* **28(5)**, 1618-1622 **(2007)**
7. Davim J. P. and Figueira L., Machinability Evaluation in Hard Turning of Cold Work Tool Steel (D2) with Ceramic Tools Using Statistical Techniques, *Mater. Design.,* **28(4)**, 1186-1191 **(2007)**
8. Basavarajappa S., Chandramohan G. and Paulo Davim J., Application of Taguchi Techniques to Study Dry Sliding Wear Behaviour of Metal Matrix Composites, *Mater. Design.,* **28(4)**, 1393-1398 **(2007)**
9. Oktem H., Erzurumlu T. and Uzman, I., Application of Taguchi Optimization Technique in Determining Plastic Injection Molding Process Parameters for a Thin-Shell Part, *Mater. Design.,* **28(4)**, 1271-1278 **(2007)**
10. Tang C., Rohani J. M. and Yajid M. A. M., Characterization of Green Corrosion Inhibitor using Taguchi Dynamic Approach, *Int. J. Electrochem. Sci.,* **8(6)**, 7991-8004 **(2013)**
11. Umoren S. A., Ogbobe O. Ebenso E. E. and Ekpe U. J., Effect of Halide Ions on the Corrosion Inhibition of Mild Steel in Acidic Medium using Polyvinyl Alcohol, *Pigm. Resin Technol.,* **35(5)**, 284-292 **(2006)**
12. Taha A. A., Selim I. Z. and Khedr A. A., Evaluation of Some Amino Acids as Corrosion Inhibitors for Carbon Steel in Sulphuric Solutions at Different Temperature. *Egypt. J. Chem.,* **38(2)**, 141-156 **(1995)**
13. Amin M. A., Khaled K. F., Mohsen Q. and Arida H. A., A Study of the Inhibition of Iron Corrosion in HCl Solutions by Some Amino Acids, *Corros. Sci.,* **52(5)**, 1684-1695 **(2010)**
14. Bouklah M., Hammouti B., Aouniti A., Benkaddour M. and Bouyanzer A., Synergistic Effect of Iodide Ions on the Corrosion Inhibition of Steel in 0.5 MH_2O_4 by New Chalcone Derivatives, *Appl. Surf. Sci.,* **252(18)**, 6236-6242 **(2006)**
15. Obot I. B., Obi-Egbedi N. O., Umoren S. A. and Ebenso E. E., Synergistic and Antagonistic Effects of Anions and Ipomoea Invulcrata as Green Corrosion Inhibitor for Aluminium Dissolution in Acidic Medium, *Int. J. Electrochem. Sci.*, **5(7)**, 994-1007 **(2010)**
16. Bılgıç S. and Çalıskan N., The Effect of *N*-(1-toluidine) Salicylaldimine on the Corrosion of Austenitic Chromium–Nickel Steel, *Appl. Surf. Sci.,* **152(1)**, 107-114 **(1999)**
17. Tong L., Wang C. and Chen C., Dynamic Multiple Responses by Ideal Solution Analysis, *Eur. J. Oper. Res.,* **156(2)**, 433–444 **(2004)**
18. ASTM G 1–2, Volume-0.3.02, Wear and Erosion; Metal Corrosion, Annual Book of ASTM Standards, ASTM, West Conshohocken, PA, 89–95 **(1996)**
19. Çalişkan N. and Bilgiç S., Effect of Iodide Ions on the Synergistic Inhibition of the Corrosion of Manganese-14 Steel in Acidic Media, *Appl. Surf. Sci.,* **153(2-3)**, 128-133 **(2000)**
20. Fares M. M., Maayta A. K. and Al-Mustafa J. A., Synergistic Corrosion Inhibition of Aluminum by Polyethylene Glycol and Ciprofloxacin in Acidic Media, *J. Adhes. Sci. Technol.,* (ahead-of-print), 1-12 **(2013)**
21. Gönder Z. B., Kaya Y., Vergili I. and Barlas H. Optimization of Filtration Conditions for CIP Wastewater Treatment by Nanofiltration Process using Taguchi Approach, *Sep. Purif. Technol.,* **70(3)**, 265-273 **(2010)**
22. Rajan K. P., Veena N. R., Singh P. and Nando G. B. Optimization of Processing Parameters for a Polymer Blend using Taguchi Method, *Yanbu J. Eng. Sci., **1***, 59-67 **(2010)**