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Original Article

Application of polyvinylpyrrolidone-iodine complex as corrosion inhibitor for carbon steel using an experimental design method

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ABSTRACT

Corrosion processes are responsible for numerous losses, especially in the industrial sector. Inhibitors are commonly used to prevent corrosion in acidic medium. The aim of this study was to apply an experimental design to optimize the influencing parameters such as inhibitor concentration, temperature and immersion time on the corrosion inhibition of polyvinylpyrrolidone-iodine (PVP-I) complexes on carbon steel using the weight loss technique (WL). The parameters of the corrosion protection process were optimized and predictive mathematical models were developed using the Response Surface Methodology (RSM) using the Central Composite Design (CCD). It was also found that the data predicted by the regression analysis had a good agreement with the data obtained from the experiments, with the values R^2 = 0.999 and Adj. R^2 = 0.997 for the inhibitory effect. The best efficiencies for experiments that were not performed were determined by experimental design (DOE).

1. Introduction

Carbon steels are used for various applications, such as construction materials, especially in the petroleum, oil and gas industries. Corrosion phenomena have become particularly important due to their applicability in acidic media, which is increasing especially in cleaning, descaling, pickling and oil well acidizing processes [1, 2]. Therefore, protective measures should be taken to reduce the corrosion rate in acids by using chemical and other agents. Among the various methods, the use of inhibitors is the most common and economical [3, 4]. A corrosion inhibitor is a chemical compound that, when added in small amounts to an environment, minimizes or prevents corrosion [5]. The effectiveness of inhibition depends on various factors such as the corrosive medium, temperature, pH, duration of immersion, composition of the metal, and the concentration and chemical nature of the inhibitor [6, 7]. The study of corrosion processes and their inhibition by organic compounds is a very large area of research [8]. Corrosion inhibition by organic compounds is mainly due to chemical, physical or mixed adsorption resulting from the interaction of the inhibitor with the metal surface [9, 10]. The use of polymers as corrosion inhibitors has recently attracted much attention due to their ability to form complexes with metal ions on the electrode surface.

Polyvinylpyrrolidone (PVP) together with iodine (I2) forms a complex called polyvinylpyrrolidone-iodine complex (PVP-I). This is used for its antiseptic properties in various products such as ointments, liquid soaps,

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surgical scrubs and pessaries or as an antibacterial and antimicrobial agent in medical devices [11, 12]. This complex is commonly known by the trade names Pyodine, Cipladine, Wokadine or Betadine surface. Most of the research work in the field of corrosion control has focused on the mechanism of corrosion, type and design of inhibitor, nature of materials, energy residues, high cost of maintenance, damage and repair etc. Many researchers in the field of corrosion inhibition have used design of experiments software and techniques to optimize the parameters of the corrosion inhibition process and predict their responses [13-16]. Design of experiments (DoE) has been widely used in statistical optimization of analytical approaches due to its advantages, such as reduction in the number of experiments, resulting in significantly reduced laboratory time and reagent consumption, faster implementation, and higher cost efficiency than the traditional single experiment [17-18]. Response Surface Methodology (RSM) is statistical and mathematical Design Experimental software that is widely used for optimization purposes. This study aims to optimize the inhibition effect of polyvinylpyrrolidone-iodine complex as a suitable corrosion inhibitor for carbon steel in $HClO_4$ and to establish mathematical models to predict the inhibition effect in the acidic medium.

2. Materials and Methods

2.1. Material preparation

The sample of carbon steel with a chemical composition of Mn: 0.68%, C: 0.37%, Cu: 0.16%, Cr: 0.077%, Ni: 0.059%, Si: 0.023%, S: 0.016%, Ti: 0.011%, Co: 0.009% and the remaining portion was Fe. The carbon steel samples were first polished with emery paper and then washed with distilled water. They were cleaned again with acetone and finally dried with a hot air blower. The solution of 1 M $HClO_4$ was prepared by diluting perchloric acid (70 - 72%, Sigma-Aldrich) with distilled water. The inhibitor was prepared (Sigma Aldrich) in molar concentrations and was varied from 5×10^{-5} to 5×10^{-3} M, per 50 cm^3 in solution of one molar of perchloric acid, at 293 – 333 K maintained in a thermostat water bath.

2.2. Weight loss measurements

The weight loss of carbon steel samples before and after immersion were calculated by using an analytical balance. All experiments are in triplicates and illustrated data are mean values of obtained results.

The following equations were used to calculate the weight loss (ΔW), the corrosion rate (CR) and the inhibition efficiencies (IE) [19, 20]:

$$\Delta W = w_1 - w_2 \quad (1)$$

$$CR = \Delta W/(A \times t) \quad (2)$$

$$IE = 100 \times (CR' - CR)/CR' \quad (3)$$

where w_1 and w_2 are the sample mass (mg) before and after immersion in the test solution, respectively. A is the total area of the specimen (cm^2), t is the exposure time (h), CR′ and CR are the corrosion rates (mg cm^{-2} h^{-1}) of carbon steel samples in the absence and presence of inhibitor, respectively.

2.3. Experimental design

Design of Experiment (DoE) is a method used on a very large scale to study experiments in industrial processes. DoE is a statistical technique that was applied simultaneously to determine the influence of multiple variables. In this study, the parameters affecting the corrosion inhibition of carbon steel in perchloric acid were investigated, including temperature, immersion time and concentration of inhibitor. The matrix for the three variables was varied in 3 levels (-1, 0 and +1). A low level and a high level should be defined for each factor; the low level of all factors is coded -1 and the high level is coded +1. The mean is then the average of the two values and is coded as 0. The experimental range and values of the independent variables for corrosion inhibition of carbon steel are given in Table 1

Table 1. Experimental range and level of independent variables for inhibition of corrosion of carbon steel by PVPI.

Independent Variables		Levels		
		−1	0	+1
X_1	Inhibitor Concentration (M)	5.0×10^{-5}	2.5×10^{-3}	5.0×10^{-3}
X_2	Temperature (K)	298	313	333
X_3	Time of immersion (h)	1	2	3

3. Results and Discussion

3.1. Optimization of inhibition efficiency using RSM

RSM was used to model the inhibitory effect and optimised using the CCD tool from MODDE Design of Experiments Software (DOE). A quadratic design model was used in the analysis. Temperature, immersion time and inhibitor concentration were set as independent variables, while inhibition efficiency was set as a response variable. A total of 17 experimental runs were performed to obtain the responses of the dependent variables shown in the experimental design (Table 2). The polynomial equation describing the process in terms of the factors given is expressed below as equation (1)

$$IE(\%) = 90{,}2503 + 3{,}966x_1 - 6{,}34101x_2 + 3{,}218x_3 - 1{,}7955x_1^2 + 2{,}16952x_2^2 - 7{,}4155x_3^2 + 1{,}37375x_1x_2 + 0{,}103753x_1x_3 - 0{,}143749x_2x_3 \quad (1)$$

where x_1, x_2 and x_3 are inhibitor concentration, temperature and time of exposure, respectively.

The equation calculated the parameters as the combination of second order (x_1^2, x_2^2, x_3^2), first-order (in terms of x_1, x_2, x_3), 3 interlinked effects (x_1x_2, x_1x_3, x_2x_3) with a constant, according to Eq. (1).

In general, the negative sign represents the antagonistic effect of the factors and the positive sign represents the synergistic effect of the factors.

Table 2. Actual design layout.

		Factor			Response
Exp No	Run Order	X_1 (mol/L)	X_2 (K)	X_3 (h)	IE (%)
1	2	5×10^{-5}	298	1	83.79
2	9	5×10^{-3}	298	1	88.68
3	7	5×10^{-5}	333	1	68.53
4	10	5×10^{-3}	333	1	78.95
5	6	5×10^{-5}	298	3	90.37
6	4	5×10^{-3}	298	3	95.71
7	1	5×10^{-5}	333	3	74.57
8	11	5×10^{-3}	333	3	85.37
9	15	5×10^{-5}	313	2	84.20
10	16	5×10^{-3}	313	2	92.41
11	14	2.5×10^{-3}	298	2	98.41
12	12	2.5×10^{-3}	333	2	86.13
13	8	2.5×10^{-3}	313	1	79.63
14	13	2.5×10^{-3}	313	3	85.74
15	17	2.5×10^{-3}	313	2	90.45
16	5	2.5×10^{-3}	313	2	91.03
17	3	2.5×10^{-3}	313	2	89.87

3.2. Statistical test and analysis of models

The statistical parameters obtained from ANOVA are shown in Table 3. The reliability of the analysis with 95 percent confidence level. The coefficient of determination (R^2) indicates how well the model fits. In this case, R^2 (0.999) indicates that only 0.1% of the total variations are not explained by the model. Consequently, the value of Adj. R^2 (0.997) confirms that the model is also highly significant, indicating good agreement between predicted and experimental efficiency of PVP-I. The predicted R^2 also agrees well with the fitted R^2. The Q2 value is a measure of how well the model will perform for future predictions.

Table 3. Coefficients of factors, interaction and probability values of approximate polynomials for response variables in the experimental design.

	IE (%)
R^2	0.999
Adj. R^2	0.997
Q2	0.994
R.S.D	0.437
Conf. level	0.95

From Table 3, the Q2 obtained is greater than 0.9 indicated the using an excellent model in this study. Q2 should be more than 0.1 for a significant model, and more than 0.5 for a good model. Moreover, for Q2 is higher to 0.9 the model is excellent [15, 21]. The difference between R^2 and Q2 should also be smaller than 0.3 for a good model. The residual standard deviation (RSD) for the model was 0.437. The small value of RSD indicates good model that gives near value between predicted and actual values for the responses.

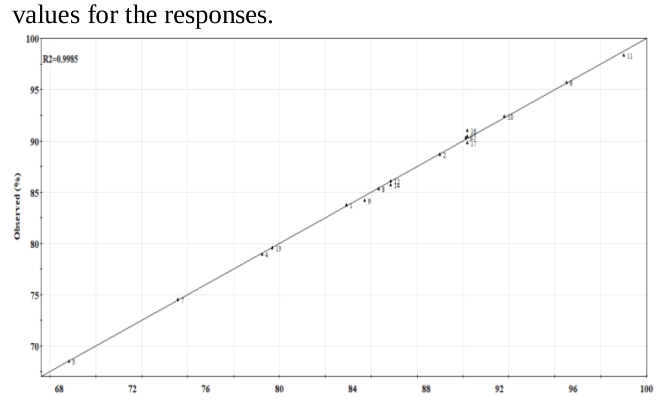

Fig 1. Diagnostic representation of predicted versus observed inhibition efficiency.

As can be seen in Figure 1, there was a linear trend in the diagnostic plots of predicted inhibition efficiency versus actual inhibition efficiency. These trends indicate that the design model is suitable to predict the inhibition efficiency of the polyvinylpyrrolidone-iodine complex. It also showed that the chosen model was suitable for predicting the response variables for the experimental data.

3. 3. Contour plot

The interactive effects of process variables on inhibition efficiency (%) were investigated by constructing a contour plot as a function of two independent variables (temperature and inhibitor concentration) for 2 hs of immersion. The contour plot for inhibition efficiency is shown in Figure 2. The figure shows that the inhibition efficiency decreases with increasing temperature for a given inhibitor concentration. This could be due to the fact that there is a physical adsorption of the inhibitor on the surface of the carbon steel [12, 22].

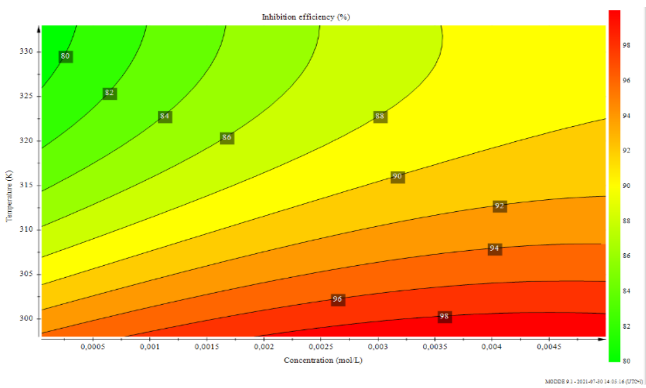

Fig 2. Contour plot showing the effects of concentration and temperature on the corrosion inhibition efficiency of PVP-I.

3. 4. Main Effects

The diagram is the additional output we obtained from the regression analysis. Figure 4 shows the effects of each of the parameters examined. A fundamental effect occurs when different degrees of a factor affect the response in unexpected ways. The efficiency of corrosion inhibition increased with an increase in PVP-I concentration.

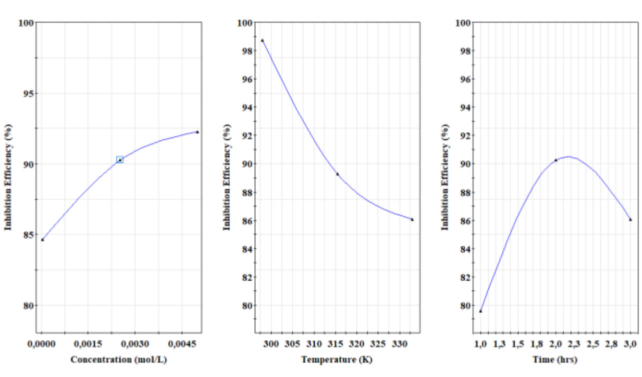

Fig 3. Main graph plot for inhibition efficiency

The increase in surface coverage improves the availability/adsorption of the active inhibitor components on the corroding metal surface [23]. According to Fig. 3, among the levels of factors considered, the maximum inhibition efficiency was observed with 5×10^{-3} mol/L concentration of PVP-I and a temperature of 298 K and at an immersion time of two hours.

3.5. Predicted optimal levels

The optimum values of the selected variables such as temperature, inhibitor concentration and exposure time were obtained by solving equation (1). The optimal values of the input variables for a maximum inhibition efficiency of 99.95% are listed in Table 4.

Table 4. Optimal values of process parameters for maximum efficiency.

Parameters	**Optimum values**
Inhibition efficiency (%)	99.95
Inhibitor Concentration (mol/L)	3.97×10^{-3}
Temperature (K)	293.50
Time of immersion (hrs)	2

The final objective of corrosion control is to increase the inhibition efficiency and decrease the corrosion rate. The results are shown in Table 4.

3.6. Mechanism of inhibition

In general, the action of an inhibitor is based on the adsorption mechanism. The adsorption of the inhibitor on the metal surface occurs either by physisorption or by chemisorption adsorption. The process of adsorption can be considered as an exchange effect between the inhibitor in the solution phase Org_{sol} and the water molecules on the metal surface H_2O_{ads} to obtain the polymer compounds adsorbed on the steel surface Org_{ads} and thus an increased inhibition effect due to the following equation:

$$Org_{Sol} + x\,H_2O_{ads} \leftrightarrow Org_{ads} + x\,H_2O$$

where x is the size ratio and simply indicates the number of adsorbed water molecules replaced by a single inhibitor molecule.

4. Conclusion

The work investigated the inhibition of carbon steel in perchloric acid using polyvinylpyrrolidone iodine complex under different independent variables of inhibitor concentration, temperature and time. With the help of experimental design, it was possible to study the effects of the variables on the inhibition effect. A full factorial design using the CCF model of RSM was successfully employed for the experimental design and analysis (17 experiments). This technique could also provide more information for understanding each application, from laboratory scale to industrial processes. The optimal inhibitory concentration, temperature and time were 3.97×10^{-3} mol/L, 293.50 K and 2 hours, respectively.

Conflict of Interest

The authors declare that they have no conflict of interest.

References

1. Abd El-Maksoud SA, Fouda A. Some pyridine derivatives as corrosion inhibitors for carbon steel in acidic medium. *Materials Chemistry and Physics*. 2005, 93:84-90
2. Attar T, Benchadli A, Choukchou-Braham E. Corrosion inhibition of carbon steel in perchloric acid by potassium iodide. *Int J Adv Chem.* 2019, 7: 35–41
3. Ikumapayi CM, Adeniji AA, Idehen EO, Barnabas AA. Combating chloride ions in reinforced concrete using $K_2Cr_2O_7$ as corrosion inhibitor. *Alg. J. Eng. Tech.* 2020, 3: 064-068
4. Evrim B, Ahmet C, Birgu Y. Inhibitory effect of Gentiana olivEIri extracts on the corrosion of mild steel in 0.5 M HCl: Electrochemical and phytochemical evaluation. *Arabian Journal of Chemistry.* 2019, 12:4303–4319.
5. Attar T, Benchadli A, Messaoudi B, Benhadria N, Choukchou-Braham E. Experimental and Theoretical Studies of Eosin Y Dye as Corrosion Inhibitors for Carbon Steel in Perchloric Acid Solution. *Chem React Eng Catal*. 2020, 15:454–464.
6. Bouraoui MM, Chettouh S, Chouchane T, Khellaf N. Inhibition Efficiency of cinnamon oil as a green corrosion inhibitor. *Journal of Bio and Tribo-Corrosion*. 2019, 5: 1–9
7. Attar T, Larabi L, Harek Y. Corrosion inhibition of cold rolled steel in 0.5 M H_2SO_4 by potassium iodide. *Der Pharma Chemica*. 2014, 6:181–186.
8. Husaini M, Usman B, Ibrahim MB. Study of corrosion inhibition performance of Glutaraldehyde on Aluminium in nitric acid solution. *Alg. J. Eng. Tech*. 2020: 2:003-010.
9. Ostapenko GI, Gloukhov PA, Bunev AS. Document investigation of 2-cyclohexenylcycl-ohexanone as steel corrosion inhibitor and surfactant in hydrochloric acid. *Corros. Sci.* 2014, 82: 265-270.
10. Popova A, Christov M, Vasilev A. Mono- and dicationic benzothiazolic quaternary ammonium bromides as mild steel corrosion inhibitors. Part III: influence of the temperature on the inhibition process. *Corros. Sci.* 2015, 94: 70-78.
11. Jones DS, Djokic J, Gorman SP. The resistance of polyvinylpyrro-lidone-iodine-poly(caprolactone) blends to adherence of Escherichia coli. *Biomaterials*. 2005, 26; 2013–2020.
12. Benchadli A, Attar T, Messaoudi B, Choukchou-Braham E. Polyvinylpyrrolidone as a corrosion inhibitor for carbon steel in a perchloric acid solution: effect of structural size. *Hungarian Journal of Industry and Chemistry*. 2021, 49: 59–69.
13. Femiana Gapsari WS, Soenoko R, Suprapto A. Minimization of corrosion rate using response surface methodology. *Eng Rev.* 2018, 38:115–9.
14. Prabhua PR, Deepa P, Padmalatha R. Analysis of Garcinia indica Choisy extract as eco-friendly corrosion inhibitor for aluminum in phosphoric acid using the design of experiment. *Journal of Materials Research and Technology.* 2020, 9: 3622-3631.
15. Attar T, Benchadli A, Mellal T, Dali Youcef B and Choukchou-Braham E. Use of Experimental Designs to Evaluate the Influence of Methyl Green Dye as a Corrosion Inhibitor for Carbon Steel in Perchloric Acid. *M J Chem.* 2021, 23: 60-69.
16. Nwose SA, Edoziuno FO, Osuji SO. Statistical analysis and Response Surface Modelling of the compressive strength inhibition of crude oil in concrete test cubes. *Alg. J. Eng. Tech.* 2021, 4:99-107.
17. Afzalkhah M, Masoum S, Behpour M, Naeimi H, Reisi-Vanani A. Experimental and Theoretical Investigation of Inhibition Efficiency of 2-(2-Hydroxyphenyl)- benzothiazole Using Impedance Spectroscopy, Experimental Design, and Quantum Chemical Calculations. *Ind. Eng. Chem. Res.* 2017, 56: 9035– 9044.
18. Maher AA, Al-Shamkhani T. Use of experimental designs to evaluate the influence of Ziziphus Leaves extracts as a corrosion inhibitor for mild steel in (3.5M) NaCl. *Int J Appl Eng Res Dev.* 2018, 13:7416–23.
19. Attar T, Nouali F, Kibou Z, Benchadli A, Messaoudi B. Corrosion inhibition, adsorption and thermodynamic properties of 2-aminopyridine derivatives on the corrosion of carbon steel in sulfuric acid solution. *J. Chem. Sci*. 2021, 133: 1-10.
20. Benchadli A, Attar T, Choukchou-Braham E. Corrosion inhibition of carbon steel (XC 38) in hydrochloric acid by potassium iodide. *Journal of Advanced Research in Science and Technology*. 2018, 5: 834–844.
21. Gao XL, Dai K, Wang Z, Wang TT, He JB, Dai K. Establishing quantitative structure tribo-ability relationship model using Bayesian regularization neural network. *Friction*. 2016, 4: 105–115.
22. Eddy NO, Odoemelam SA, Odiongenyi AO. Inhibitive, adsorption and synergistic studies on ethanol extract of Gnetum africana as green corrosion inhibitor for mild steel in H2SO4. *Green. Chem. Lett. Rev.* 2009, 2: 111–119.
23. Benchadli A, Attar T, Choukchou-Braham E. Inhibition of Carbon Steel Corrosion in Perchloric Acid Solution by Povidone Iodine. *Phys. Chem. Res.* 2019, 7: 837–848.

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