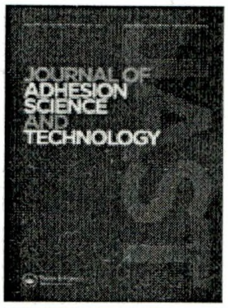

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Study of synergistic influence of L-cysteine on polyvinyl alcohol – Taguchi method: continuous electrochemical monitoring of corrosion inhibition of mild steel by poly(vinyl alcohol-cysteine)

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Parametric optimization for better synergism between polyvinyl alcohol (PVA) and L-cysteine was optimized using Taguchi design, a statistical approach. The corrosion inhibition property of poly(vinyl alcohol-cysteine) (PVAC) on mild steel corrosion was continuously monitored using electrochemical techniques such as polarization and impedance methods. Continuous monitoring of the system reveals the formation of stable film on the metal surface. Temperature effect on the inhibition properties of PVAC was studied using electrochemical measurements. Calculated kinetic and thermodynamic parameters supported the spontaneous adsorption of PVAC. Atomic force microscopic and laser profiler analysis confirmed the adsorption of PVAC on mild steel surface. Theoretical calculations using Hyperchem 7.0 proved the better corrosion mitigation properties of PVAC compared to PVA.

Keywords: mild steel; poly(vinyl alcohol-cysteine); acid inhibition; adsorption; AFM

Introduction

The current scenario of the world needs high intensified research for the alternative sources for the natural resources. As an additional support, the research has to give much attention globally toward the protection and maintenance of the outcomes. One such a problem facing losses of natural resources and economy is due to corrosion. Mild steel is an important material of choice due to low cost and easy availability. Acids are deployed in many service environments such as pickling, cleaning of boilers, de-scaling, and acidization of oil well. In order to reduce the undesirable base metal dissolution by these processes, corrosion inhibitors are usually added.[1] Research on organic corrosion inhibitors has been mainly focused on the inhibitor structure relationship with its adsorption properties and mechanism. It has been observed that the adsorption acutely depends on specific physicochemical properties of the inhibitor molecule such as functional groups, steric factors, aromacity, electron density at the donor atoms, and π-orbital character of donating electrons.[2,3] Usually, the organic compounds get adsorbed on the metal surface, block the active sites on the surface,

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and thereby reduce the corrosion attack. Recently, many corrosion inhibition works across the world are based on the polymeric compounds.[4–7]

Evolution of new polymer composites, copolymers, and graft polymers requires predetermination of the combined effect of the individual components on the desired property. To study this, it is essential to run lot of experiments in presence of the individual components and in its combined form. In practical, to optimize all the parameters and to establish the best possible conditions for better performance is a tedious process. To inter-relate all the parameters, numerous experiments have to be carried out with all possible parameter combinations, which are considered to be uneconomical and difficult. This conventional optimization procedure involve altering of one parameter at a time keeping all other parameters constant, which enables to assess the impact of the particular parameter on the process performance. This procedure is time-consuming, cumbersome, requires more experimental data-sets, and cannot provide information about the mutual interactions of the parameters.[8–11]

In this study, the above problem was solved by adopting Taguchi parametric optimization method for better corrosion inhibition performance. 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.[8,9] 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.[9–11] Tang et al. 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.[12] This method determines the optimal level of the important controllable factors based on the concept of *S/N* ratio. Taguchi experimental approach identifies the influence of individual factors, establishes the relationship between variables and operational conditions, and finally, predicts the performance at the optimum levels obtained with a few well-defined experimental sets.

The polymer was synthesized and its corrosion mitigating property was evaluated by conventional weight loss measurements.[7] Therefore, the present focus is to study the thermal properties of the polymer and to investigate its corrosion inhibition behavior continuously by means of electrochemical impedance spectroscopy, potentiodynamic polarization, and linear polarization methods. Finally, the corrosion inhibition was confirmed by the surface analytical techniques such as atomic force spectroscopy and laser profilometry.

Materials and methods

Polyvinyl alcohol (PVA) (Himedia – 140,000 g/mol; 89% hydrolyzed), L-cysteine (131.17 g/mol), oxalic acid (AR), ammonium persulfate, acetone, hydrochloric acid received from Merck were used for the studies. Mild steel of composition: 0.196 Mn, 0.106 C, 0.027 P, 0.022 Cr, 0.016 S, 0.012 Ni, 0.006 Si, 0.003 Mo, and remainder as Fe has been used as a working electrode with 1 cm^2 exposed area. MS specimens of size 1 cm × 5 cm were used for gravimetric measurements.

Four factors which affect the corrosion inhibition, namely, concentration of PVA, L-cysteine, exposure time, and temperature were selected at three different levels (Table 1) The L_9 orthogonal array of gravimetric experiments (Table 2) were conducted following ASTM G31 [13] procedure and the inhibition efficiencies were calculated using the relation:

Table 1. Experimental parameters and its different levels.

No.	Factors	Level 1 (L1)	Level 2 (L2)	Level 3 (L3)
1	F1-PVA (g)	0.0000 g	0.25 g	0.50 g
2	F2-L-cysteine (g)	0.0000 g	0.05 g	0.05 g
3	F3-time (h)	1 h	2 h	3 h
4	F4-temperature (K)	313 K	323 K	333 K

Table 2. L9 orthogonal array of experiments.

Experiments	Levels of factors				*IE* (%)	*S/N* ratios
1	1	1	1	1	00.00 ± 0.00	−119.25
2	1	2	2	2	61.10 ± 3.02	35.79
3	1	3	3	3	50.39 ± 1.52	34.02
4	2	1	2	3	37.70 ± 3.19	31.51
5	2	2	3	1	69.53 ± 1.44	36.83
6	2	3	1	2	74.12 ± 3.35	37.28
7	3	1	3	2	38.89 ± 1.76	31.70
8	3	2	1	3	61.93 ± 1.20	35.77
9	3	3	2	1	65.35 ± 1.55	36.28

$$IE_w\ (\%) = \frac{W - W_i}{W} \times 100 \tag{1}$$

where W and W_i are the weight loss in g of the uninhibited and inhibited systems, respectively.

The resulted inhibition efficiencies are analyzed for *S/N* ratios using Qualitek 4 software with larger the better characteristic relation,

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

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

The synergism parameter for PVA and L-cysteine system was calculated using the relation initially given by Aramaki and Hackermann and reported elsewhere.[14,15]

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

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

Based on Taguchi experimental results, poly(vinyl alcohol-cysteine) (PVAC) was synthesized following the procedure described in our previous communications.[16,17] The grafting characteristic parameters such as grafting percentage (%*G*), conversion percentage (%*C*), and add-on percentage (%*A*) of PVAC were calculated by the relations,[18]

$$\text{Grafting-ratio}, \quad (\%G) = \frac{W_3}{W_1} \times 100 \tag{4}$$

$$\text{Percentage-conversion}, \quad (\%C) = \frac{W_3}{W_2} \times 100 \tag{5}$$

$$\text{Add-on-percentage}, \quad (\%A) = \frac{W_1}{W_3} \times 100 \tag{6}$$

where W_1, W_2, and W_3 are the weights of PVA, L-cysteine, and graft polymer PVAC, respectively. Theoretical calculations were performed by Hyperchem 7.0 software using AM1 semi-empirical calculations.

Corrosion inhibition performance of PVAC was monitored using electrochemical frequency response analyzer Solatron Model 1280B with three-electrode conventional system consists of standard calomel electrode as reference electrode. Impedance spectroscopic measurement has been conducted with 10-mA amplitude current in frequency range of 20,000–0.1 Hz following ASTM standard procedures.[16] The potentiodynamic polarization measurements were carried out in the potential range of −1 to −0.1 V at a sweep rate of 2 mV/s (ASTM G3). Linear polarization resistance was measured in the potential range of −0.02 to +0.02 V at 0.01625 mV/s scan rate as per ASTM G3 standards. The surface coverage and inhibition efficiencies are calculated from charge transfer resistance (R_{ct}), corrosion current density (I_{corr}), and polarization resistance (R_p) values using the relations:

$$\theta_X = \frac{X^i - X^o}{X^i} \quad (\text{or}) \quad = \frac{X^o - X^i}{X^o} \tag{7}$$

$$IE_X\ \% = \frac{X^i - X^o}{X^i} \times 100 \quad (\text{or}) \quad = \frac{X^o - X^i}{X^o} \times 100 \tag{8}$$

where X^i and X^o are inhibited and uninhibited corrosion monitoring parameters. Theoretical calculations were performed by Hyperchem 7.0 software using AM1 semi-empirical calculations.

Results and discussion

Parametric optimization for better synergism between PVA and L-cysteine

Effects of factors on inhibition efficiency

The inhibition efficiencies and their *S/N* ratios of the L_9 experiments are presented in Table 2. The *S/N* ratios of the different factors at the considered levels are presented in

Table 3. Significance of the factors on the corrosion inhibition of mild steel.

	Mean *S/N* ratio			
Factors	Level 1	Level 2	Level 3	Max–Min [a]
PVA	−16.48	35.21	35.58[b]	51.68
L-cysteine	−18.68	36.13[b]	35.86	54.81
Exposure time	−15.94	34.53[b]	34.18	49.96
Temperature	−15.38	34.93[b]	33.77	50.31

[a]Significance of matching parameters = Maximum *S/N* − Minimum *S/N*.
[b]Level having highest *S/N* ratio indicating optimum levels for each factors.

Table 3. The negative *S/N* ratio of the level 1 corresponds to the uninhibited system. Individually at level stage, all the considered four factors have highest effect in level 2 (3 for PVA). The difference between the maximum and minimum *S/N* ratios (L2−L1) of the each factor indicates the relative influence of the effect. The larger the difference, the stronger will be the influence on the inhibition process. L-Cysteine individually has the stronger influence on the inhibition process followed by PVA, exposure temperature, and time. This is due to the presence of strong electron donating centers in L-cysteine which enhanced the corrosion inhibition process.

Interaction between factors

The interaction between two factors gives a better insight for the understanding of the overall process analysis. Each factor can interact with any individual factor or with all the other factors resulting in large number of interactions and are all considered in Taguchi experimental design. The different possible interactions and the estimated interaction severity index (SI) of the studied factors help to know the influence of two individual factors at various levels of the interactions (Table 4). In table, the column represents the column locations to which the interacting factors are assigned, whereas the reserved column indicates the column that should be reserved if this interaction effect has to be studied (2-L factors only). 'Optimum Levels' in Table 4 represents the factor levels desirable for the optimum conditions. If the interaction is included in the study and found significant in ANOVA, then the indicated levels must replace the factor levels indentified for the optimum conditions.

If the interaction between two factors is perpendicular, then the SI is 100% whereas for parallel interactions SI is 0%.[19] From table, it can be followed that interaction between PVA and exposure time showed highest interaction SI (51.36%) followed by exposure time and temperature with 50.15% SI. The next higher SI was observed for interaction between PVA and temperature followed by the interactions of L-cysteine with temperature and L-cysteine with time. Interaction between PVA and cysteine has the least SI of about 47.82%.

Individually, the factors 1 and 2 have high impact on inhibition efficiency, whereas factors 3 and 4 have either low or high impact depending on the inhibitor system. However, in combination, the interaction of factors 1 and 2 (PVA and L-cysteine) showed least SI. All the possible interactions showed almost equal SI on interaction with others. This is evidenced by the lower deviation in severity indexes (47 ± 5% SI) for all the possible interactions. The data indicate almost equally inclined interactions between factors on the inhibition process.

Table 4. Estimated interaction severity indexes for different factors.

No.	Interacting pairs[a]	Columns	Reserved column	Optimum level	SI (%)
1	PVA × time	1 × 3	2	[1,2]	51.36
2	Time × temperature	3 × 4	7	[1,2]	50.15
3	PVA × temperature	1 × 4	5	[2,2]	49.37
4	L-cysteine × temperature	2 × 4	6	[2,3]	48.54
5	L-cysteine × time	4 × 3	1	[1,3]	48.15
6	PVA × L-cysteine	1 × 2	3	[2,3]	47.82

[a]Order based on SI.

ANOVA calculations

The contribution of individual factors is the key for the control of the mild steel corrosion process. Taguchi method cannot judge and determine the effect of individual parameters on entire process while percentage contribution of individual parameters can be well determined using ANOVA. ANOVA can be useful for the determination of the influence of any given parameter from a series of experimental results by designing the experiments and it can be used to interpret experimental data. ANOVA calculations were performed to investigate the effect of the selected factors on the inhibition efficiencies (L_9 experiments) using Qualitek 4 software and the results are presented in Table 5.

All the factors have two degrees of freedom and the error value for the current system is zero. The variances of the four factors are found to be higher and that of error term is zero (unexplained variance). This indicated that all the considered factors are controllable and the error had no significant effect on the results. The *F*-ratios (ratio of the explained variance to the unexplained variance) of the considered factors are found to be infinity due to the zero error. Similar type of results (zero error and infinity *F*-values) was observed for the ANOVA calculations for the factors affecting the tensile strength of the polymer blend, Rajan et al. [20]. *F*-ratio is a tool to demonstrate whether the parameter has a significant effect or not. The higher *F*-values indicated the greater significance of all the four factors.

Optimum conditions for better synergism

Based on the *S*/*N* ratios, Qualitek 4 software predicted the optimum conditions and their performances in terms of contributions for achieving higher inhibition efficiency are shown in Table 6. It can be seen from table that cysteine have the significant role in controlling the corrosion process than the other selected factors. The expected result at the optimum conditions is 87.47% *IE* with the grand average performance of 17.77% from all the factors. The performance distribution of current condition along with the new improved condition is presented in Figure 1. It is evident from figure that on considering the optimum inhibition condition from the experimental design, the inhibition was increased from 69.7% to 87.47% which was about 18% increase on adopting the prescribed optimum conditions.

Among the factors studied, cysteine showed strong influence on the corrosion inhibition process though taken in minimum quantity followed by PVA. This indicated the relatively high influence of the inhibitor added to the system than the other controlling parameters like exposure time and temperature.

Table 5. ANOVA results for the *S*/*N* ratios of the inhibition efficiencies.

Factors	D.F.	Sum of sq.	Variance	*F*-ratio	Percent (%)
PVA	2	5279.24	2639.62	α	24.95
L-cysteine	2	5978.21	2989.11	α	28.26
Exposure time	2	4950.47	2475.23	α	23.40
Temperature	2	4957.55	2473.78	α	23.39
Error	0	0	0	–	–
Total	8	21,155.47	–	–	100