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Corrosion inhibition and statistical data of low carbon steel in HCl media by admixed organic compounds

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Abstract. Corrosion inhibition of carbon steels with organic compounds exhibiting effective corrosion inhibition is an on-going research. The corrosion inhibition of low carbon steel in 1M HCl solution by the combined admixture of vanillin and benzonitrile (VBN), and salvia officinalis with lavendulan officinalis (SLV) was studied by weight loss method. Results obtained show that VBN and SLV performed effectively with maximum inhibition efficiency 91.03% at 1.5% VBN concentration and 97.89% at 5% SLV concentration. The inhibition efficiency of VBN increased with concentration but decreased with exposure time compared to the values obtained for SLV which showed non-dependence on concentration and exposure time after 1% SLV concentration. Correlation plots of inhibition efficiency versus inhibitor concentration show VBN to be more concentration dependent in performance. Calculated data for standard deviation shows the degree of variation from mean values for both compounds is significant at low inhibitor concentration due to time dependence action. Statistical analysis through ANOVA shows inhibitor concentration overwhelmingly influences the inhibition performance of the despite even though exposure time is statistically relevant to minimal degree.

Keywords: corrosion; inhibitor; steel; acid

1. Introduction

Corrosion degradation and its effect on carbon steels in industrial operating conditions has severe economic and financial consequence on the application of the steel in petrochemical and refinery operations, automobile radiator, energy transmission, desalination plants, energy generation and transmission and mining and extraction activities [1-5]. One of the most corrosive environments encountered in industry are acid solutions. The solutions are utilized in chemical process industries, fertilizer production, agricultural operations, mining and extraction processes for the removal of impurities, rust and scales such as oil-well acidizing, industrial acid cleaning, acid-descaling and acid pickling [6-8]. More important is the prevalence of corrosive anions of acids (Cl$^-$, SO$_4^{2-}$, NO$_3^-$ etc.) in non-acidic conditions due to other factors [9]. Chemical compounds (corrosion inhibitors) have been extensively used to hinder the corrosion of carbon steels and in most cases increase the number of conditions where they can be applied and their lifespan [10, 11]. Inhibitors of earlier origin were very toxic such as chromates, arsenics, phosphates, nitrites etc. before the gradual shift to organic chemical compounds [12]. These compounds, though not as toxic as the compounds earlier mentioned are also not sustainable due to environmental and disposal concerns [13]. Hence, green chemical compounds which are biodegradable, environmentally sustainable and user friendly have been the focus of research [14, 15]. Synergistic effect of chemical compounds is one of the most important methods in corrosion

inhibitor development which to a large extent serves as the basis for most of the modern corrosion inhibiting admixtures [16-18]. This manuscript studies the corrosion inhibition of low carbon steel in 1M HCl solution by the combined admixture of vanillin and benzonitrile, and salvia officinalis with lavendulan officinalis.

2. Experimental methods

Vanillin and benzonitrile (VBN) at ratio 1:1 was formulated in volumetric concentrations of 0%, 0.25, 0.5%, 0.75%, 1%, 1.25% and 1.5% respectively while salvia officinalis with lavendulan officinalis (SLV) at ratio 1:1 was formulated in volumetric concentrations of 0%, 1%, 2%, 3%, 4% and 5%. The volumetric concentration for both inhibitor admixtures was prepared per 200ml of 1M HCl solution. Low carbon steel (LCS) rods were cut and sectioned into 7 test samples each for the experimental study. LCS have a mean configuration of 0.7 cm radius and 0.7 cm length. The cylindrical surface ends of the steel were partially smoothened with silicon carbide abrasive papers of 80, 120 and 220 grits. Weighed specimens of the steel were individually immersed in 200ml of the HCl solution at specific concentrations of VBN and SLV inhibitor compounds for 240 h. LCS samples were weighed at 24 h interval using Ohaus analytical weighing balance. Tabulated data values of LCS corrosion at specific VBN and SLV concentrations in the acid media are shown in Tables 1 and 2. Corrosion rate was computed from the equation below;

$$R = \left[\frac{87.6W}{DAT}\right] \tag{1}$$

W represents weight loss (g), D represents density (g/cm^2), A represents area (cm^2), and T is the time of exposure in hours. W is calculated from the difference between the initial weight of the steel (maintained for 240 h) and every final weight was recorded at 24 h interval. Tables 3 and 4 shows the data of inhibition efficiency (IE) which were computed from the formula below;

$$IE = \left[\frac{W_1 - W_2}{W_1}\right] * 100 \tag{2}$$

W_1 and W_2 indicates weight-loss of the control (0% inhibitor concentration) and inhibited LCS in the acid solution with respect to exposure time.

Statistical computation
Binary-factor mono level experimental ANOVA test (F - test) was employed to evaluate the statistical influence of the inhibitor concentrations and inspection time on the inhibition performance of the inhibitor compound on LCS in 1 M HCl solution. The evaluation was done at confidence level of 95% (i.e. a significance level of $\alpha = 0.05$) analogous to the following equations. The addition of squares between columns (exposure time) was gotten from the equations below;

$$SS_c = \frac{\sum T_c^2}{nr} - \frac{T^2}{N} \tag{3}$$

Addition of squares between rows (inhibitor concentration)

$$SS_r = \frac{\sum T_r^2}{nc} - \frac{T^2}{N} \tag{4}$$

Total addition of squares

$$SS_{Total} = \sum x^2 - \frac{T^2}{N}$$

3. Results and discussion

Weight loss measurement
The corrosion rate values for VBN and SLV (Tables 1 and 2) varies significantly between the non-inhibited (0% inhibitor concentration) LCS samples and the inhibited LCS samples at specific inhibitor concentration. The non-inhibited LCS was exposed to the deteriorating effect of Cl$^-$ anions in the acid electrolyte causing accelerated degradation of the steel. The presence of the chemical inhibitors drastically reduced the rate of corrosion as earlier mentioned. However, Table 1 depict visible reduction in corrosion rate values at specific inhibitor concentration varies proportionally with VBN concentration

and despite the drastic decrease in concentration when compared to the non-inhibited LCS samples, the corrosion rate of the inhibited LCS samples increases with exposure time. Quite the contrary was observed in Table 2 for the following reasons; 1) variation of corrosion rates values of the inhibited steel is not proportional to SLV concentration and 2) the corrosion rate values of SLV inhibited LCS decreased with exposure time. Observation of Table 3 confirms the earlier assertion of inhibition efficiency of VBN being proportional to concentration as the inhibition efficiency values at 240 h of exposure shows. The inhibition efficiency of SLV was relatively higher than VBN at 240 h of exposure and tends to be non-dependent on concentration after 1% SLV concentration. Fig. 1(a) and (b) shows the plot of VBN and SLV inhibition efficiency at highest and lowest concentration versus exposure time while Fig. 2(a) and (b) shows the plot VBN and SLV concentration at 240 h of exposure versus concentration. The plots in Fig. 1(a) and (b) depict the wide difference in inhibition efficiency of the compounds with respect to concentration. At the lowest concentration, the inhibition efficiency of VBN and SLV compounds significantly decreased from onset of the exposure hours. This shows low molecular concentration of VBN and SLV are insufficient to counteract the electrochemical behaviour of Cl- anions in the acid solution. At highest inhibitor concentration, VBN and SLV compounds prove to be effective. However, plot configuration shows VBN attained relative stability at 48 h while SLV attained stability at 72 h. The plot of VBN and SLV inhibition efficiency [Fig. 2(a) and (b)] versus concentration at 240 h of exposure shows the inhibition performance of VBN varies strongly with concentration with correlation coefficient of 0.8107 compared to the corresponding value for SLV at 0.5237. The plot and coefficient value shows SLV is more reliable for corrosion inhibition as relative stability was attained at 2% concentration.

Table 1. Data on corrosion rate of LCS from 1M HCl/VBN (0% - 1.5%) solution

SLV Conc. (%) ⟍ Exp. Time (h)	0% VBN	0.25% VBN	0.5% VBN	0.75% VBN	1% VBN	1.25% VBN	1.5% VBN
24	0.0035	0.0010	0.0003	0.0001	0.0002	0.0002	0.0003
48	0.0055	0.0017	0.0007	0.0005	0.0003	0.0004	0.0003
72	0.0069	0.0021	0.0012	0.0008	0.0005	0.0004	0.0003
96	0.0079	0.0024	0.0016	0.0010	0.0006	0.0005	0.0004
120	0.0092	0.0030	0.0019	0.0013	0.0007	0.0006	0.0005
144	0.0091	0.0031	0.0021	0.0013	0.0007	0.0006	0.0005
168	0.0087	0.0035	0.0021	0.0014	0.0008	0.0007	0.0006
192	0.0078	0.0034	0.0019	0.0013	0.0009	0.0007	0.0007
216	0.0091	0.0044	0.0024	0.0016	0.0010	0.0008	0.0008
240	0.0089	0.0044	0.0025	0.0017	0.0010	0.0009	0.0008

Table 2. Data on corrosion rate of LCS from 1M HCl/SLV (0% - 6%) solution

SLV Conc. (%) ⟍ Exp. Time (h)	0% SLV	1% SLV	2% SLV	3% SLV	4% SLV	5% SLV	6% SLV
24	0.987	0.164	0.082	0.164	0.041	0.082	0.082
48	1.089	0.144	0.062	0.097	0.037	0.072	0.062
72	1.316	0.206	0.055	0.069	0.027	0.055	0.042
96	1.429	0.206	0.051	0.053	0.025	0.050	0.040
120	1.472	0.238	0.058	0.049	0.024	0.041	0.034
144	1.466	0.267	0.055	0.042	0.027	0.036	0.029

168	1.451	0.294	0.059	0.038	0.029	0.032	0.027
192	1.465	0.324	0.072	0.046	0.026	0.041	0.031
216	1.439	0.347	0.078	0.042	0.027	0.041	0.032
240	1.365	0.411	0.082	0.047	0.029	0.041	0.033

Table 3. Data on inhibition efficiency of VBN in 1M HCl

VBN Conc. (%) / Exp. Time (h)	0.25% VBN	0.5% VBN	0.75% VBN	1% VBN	1.25% VBN	1.5% VBN
24	71.99	90.97	95.83	94.68	93.52	92.13
48	69.55	86.84	90.47	93.79	93.57	95.05
72	70.05	82.46	88.66	93.37	93.60	95.64
96	69.20	80.10	87.87	92.40	93.73	95.09
120	66.93	79.33	86.16	92.29	93.93	94.90
144	65.90	76.46	86.02	91.82	93.59	94.30
168	59.61	76.07	84.08	90.46	92.35	92.96
192	55.96	75.29	83.45	88.19	90.37	90.95
216	52.14	74.05	82.85	89.59	91.03	91.60
240	50.65	72.25	81.51	88.68	90.33	91.06

Table 4. Data on inhibition efficiency of SLV in 1M HCl

| SLV Conc. (%) / Exp. Time (h)	1% SLV	2% SLV	3% SLV	4% SLV	5% SLV	6% SLV
24	83.33	91.67	83.33	95.83	91.67	91.67
48	86.79	94.34	91.13	96.60	93.40	94.34
72	84.38	95.83	94.79	97.92	95.83	96.77
96	85.61	96.40	96.26	98.27	96.47	97.19
120	83.80	96.09	96.70	98.38	97.21	97.71
144	81.78	96.26	97.15	98.13	97.57	97.99
168	79.76	95.95	97.37	97.98	97.77	98.14
192	77.89	95.09	96.84	98.21	97.19	97.89
216	75.87	94.60	97.05	98.10	97.14	97.78
240	69.88	93.98	96.57	97.89	96.99	97.59
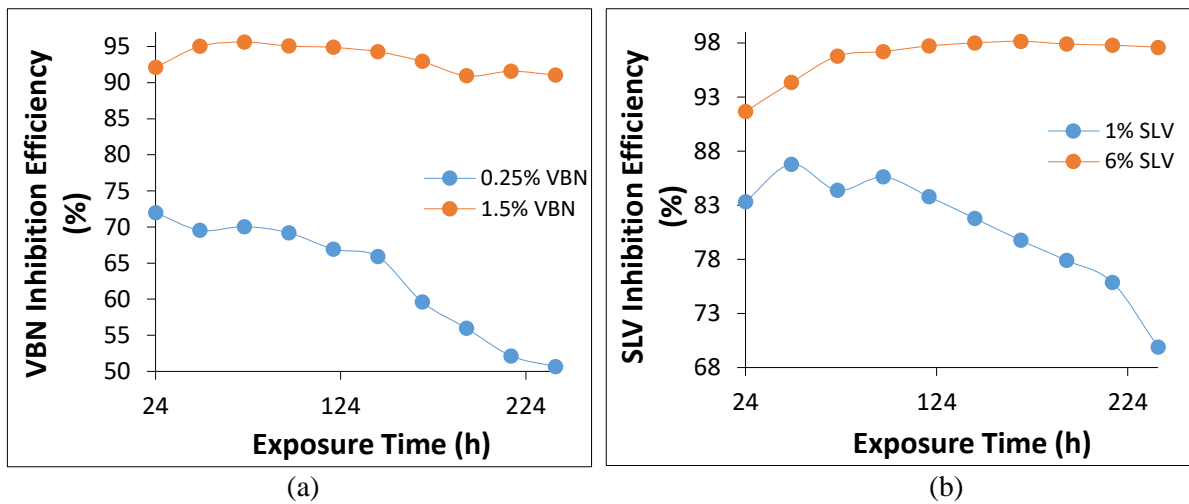
Figure 1. Plot of (a) VBN inhibition efficiency and (b) SLV inhibition efficiency versus exposure time at highest and lowest concentration
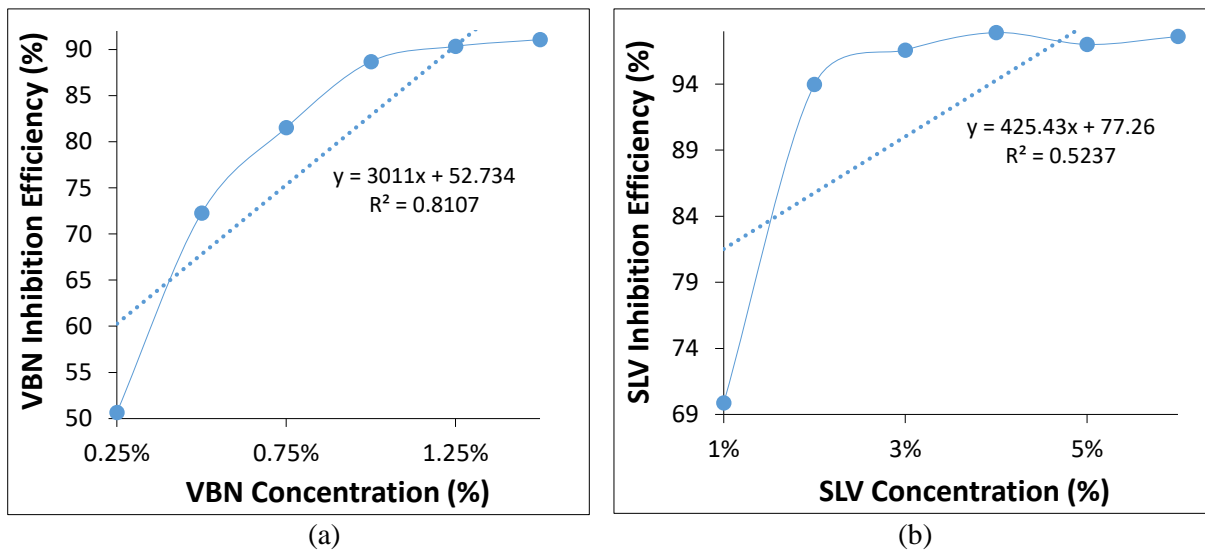

Figure 2. Plot of (a) VBN inhibition efficiency versus VBN concentration and (b) SLV inhibition efficiency versus SLV concentration

4. Statistical evaluation

Table 5 shows the mean, standard deviation and margin of error for the inhibition efficiency values of VBN and SLV. The mean values for SLV compound are generally higher than the values obtained for VBN with respect to concentration. The standard deviation for both compounds decreases generally with concentration. The highest value was obtained at lowest VBN and SLV concentration due to the wide variation of inhibition efficiency values according to exposure time at the particular concentration. This is due to the relatively weak molecular and adsorption properties of the inhibitor compounds resulting in inconsistent corrosion inhibition performance over time. At higher VBN and SLV concentration the standard deviation decreases as the inhibition performance of the compounds becomes more stable with respect to time. The margin of error for VBN and SLV shows 87% and 98% of VBN and SLV inhibition data are above 70% inhibition efficiency at margin of error of $\pm9\%$ and $\pm3\%$.

Table 5. Statistical data for the mean, standard deviation and margin of error for VBN and SLV inhibition efficiency values

VBN						
VBN Conc.	0.25%	0.5%	0.75%	1%	1.25%	1.5%
Standard Deviation	7.94	5.92	4.25	2.21	1.47	1.83
Mean	63.198	79.38	86.69	91.53	92.60	93.37
Proportion of data above 70% Inhibition Efficiency	87%	**Margin of Error**	$\pm$9%			
SLV						
SLV Conc.	1%	2%	3%	4%	5%	6%
Standard Deviation	5.18	1.46	4.41	0.83	2.01	2.09
Mean	80.91	95.02	94.72	97.73	96.12	96.71
Proportion of data above 70% Inhibition Efficiency	98%	**Margin of Error**	$\pm$3%			

Analysis of variance (ANOVA) was used to evaluate the statistical importance of VBN and SLV concentration and exposure time (independent variables) on the inhibition performance of both compounds on LCS in 1 M HCl solution. Table 6 shows the ANOVA data for VBN and SLV inhibition performance on LCS. The statistical relevance factor which depict the statistical significance (%) of the independent variables on VBN and SLV inhibition performance shows VBN and SLV concentration are the statistical relevant variables responsible for their inhibition performance. The mean square ratio is the statistical significance value which must be greater than the threshold significance factor for the statistical relevance factor to be relevant. The values are higher than theoretical significance factor, hence both inhibitor concentration and exposure time are statistically relevant despite the overwhelming influence of inhibitor concentration.

Table 6. ANOVA data for statistical influence of VBN and SLV concentration and exposure time on their inhibition performance on LCS in HCl solution

VBN						
Source of Variation	**Sum of Squares**	**Degree of Freedom**	**Mean Square**	**Mean Square Ratio (F)**	**Theoretical Significance Factor**	**Statistical Relevance Factor, F (%)**
VBN Conc.	6784.19	5	1356.84	147.81	2.42	85.63
Exposure Time	725.57	9	80.62	8.78	2.1	9.16
Residual	413.10	45	9.18			
Total	7922.85	59				
SLV						
Source of Variation	**Sum of Squares**	**Degree of Freedom**	**Mean Square**	**Mean Square Ratio (F)**	**Theoretical Significance Factor**	**Statistical Relevance Factor, F (%)**
SLV Conc.	1973.97	5	394.79	48.89	2.42	79.24
Exposure Time	153.88	9	17.10	2.12	2.1	6.18
Residual	363.41	45	8.08			
Total	2491.25	59				

5. Summary

The combined admixture of vanillin and benzonitrile, and salvia officinalis with lavendulan officinalis effectively inhibited the corrosion of low carbon steel in dilute hydrochloric acid at at concentration studied. Comparative plots show admixture of salvia officinalis with lavendulan officinalis attains relative stability in performance with respect to concentration compared to its counterpart. Standard deviation data shows significant variation from mean values occurred at low concentration resulting in limited inhibition performance compared to higher inhibitor concentration. Analysis of variance shows exposure time and inhibitor concentration are statistically relevant on influence on the inhibition performance of the inhibitors.

Acknowledgement

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