Data Article

Electrochemical data and analysis of the protection effect of *Citrus Sinensis* on mild steel in weak acid electrolytes

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ABSTRACT

Data on the protection effect of *Citrus Sinensis* oil extracts (CS) on mild steel in dilute H_2SO_4 and HCl solution was studied. The extract sufficiently protected the steel in both acids with respect to its concentration. CS performed more effectively in HCl compared to H_2SO_4. Inhibition performance of the extract varied significantly with exposure time. The highest inhibition efficiency of 78.47% and 85.61% was attained at the highest extract concentration in both acids. Inhibition efficiency in both acids decreased with respect to exposure time. Standard deviation showed variation of CS inhibition efficiency was significant at low concentration. Data from numerical assessment showed extract concentration is the statistically relevant factor inducing protection of the steel with statistical relevance of 89.9% and 96.39%. Data showed 58% and 86% of inhibition efficiency data in H_2SO_4 and HCl solution are above 70% inhibition value at margin of error of ±0.097 and ±0.068.

1. Rationale

Carbon steel is an Fe-C alloy containing up to a maximum of about 2.1 wt.% C content [1]. Their properties provide a unique threshold standard against which other alloy grade steels can be compared. Carbon steels represent the most versatile and important group of metallic alloys for engineering applications [2]. The recyclability, availability, ease of production, and adjustable mechanical and physical characteristics of carbon steels are the major factors responsible for their universal application globally [3]. Carbon steels are universally applied in extreme conditions, petrochemical processing, oil refining, heater tubes in power plants, exhaust train pipeline, in marine industries, nuclear power generating systems, transportation industry, chemical production plants, mining industry, construction industry, automobiles, metal processing equipment etc. due to their toughness, durability, and welding and forming properties [2]. The steels are quenchable and easily tempered for enhanced mechanical strength. The combined strength and ductility of the steel can be hardened and carburized as required. Lack of surface passivation properties in corrosive environments laden with corrosive anions such as SO_4^{2-}, Cl^- etc. is the cause of weak corrosion resistance of carbon steels because of the absence of important alloying elements [4]. This vulnerability is the main limitation of the steel for long-term applications in aqueous environments leading to corrosion failure and loss of mechanical properties. The anions are responsible for the continual breakdown and damage at short intervals. The consequences of corrosion damage are industrial plant shut down, industry downtimes, accidents, toxic leakages and component failures [5]. Chemical derivatives identified as corrosion inhibitors are currently being utilized to control degeneration of carbon steels. Corrosion inhibitor is a fluid that significantly decreases or stops the electrochemical deterioration of

metallic alloys within a corrosive environment or operating conditions [6]. Some of the high performance fluid derivatives are inorganic compounds which are costly and toxic [7]. Their application is currently under scrutiny and restriction due to their adverse effect on human health and unsustainability [8]. Corrosion inhibitors from organic sources have been established by research and field utilization to be effective but are also have varying degrees of toxicity [8]. Research on plant extracts is ongoing with promising results, though their effectiveness is limited by their short shelf life and weak adsorption [9–13]. Essential oils extracts are being tested for their corrosion inhibition properties with appreciable results thus the need for further study to establish their inhibition properties with respect to exposure time [14–22]. Data analysis of the inhibition efficiency of promising inhibitor compounds is of utmost importance to delineate the strength and possible weakness of the inhibitor analogous to exposure time and concentration of the inhibitor. This enable optimal utilization of the compounds within certain limits of applicability. This research focusses on data and statistical analysis of the inhibition performance of *Citrus Sinensis* essential oil extract on mild steel in dilute H_2SO_4 and HCl solutions

Subject area	*Chemistry*
Specific subject area	*Material Science, Corrosion*
Type of data	*Tables*
How data was acquired	*Ohaus analytical balance was used to determine the weight loss from which corrosion rate and inhibition efficiency was calculated.*
Data format	*Analyzed*
Experimental factors	*Metal samples were mechanically cut and grounded with silicon carbide abrasive paper, rinsed with distilled water and acetone and dried in a desiccator for coupon measurement*
Experimental features	*Corrosion rate and inhibition efficiency data were obtained every 24 h after immersion of the low carbon steel in 0.5 M H_2SO_4 and HCl at specific concentrations of Citrus Sinensis oil extract concentration for a total of 480 h*
Data source location	*Ota, Ogun State, Nigeria*
Data accessibility	*The data is with this article*

2. Procedure

Citrus Sinensis oil extract (CS) obtained from NOW foods USA in the synthesized form was concocted in cubic concentrates of 2%, 4%, 6%, 8% and 10% per 400 ml of 0.5 M H_2SO_4 electrolyte and HCl electrolyte separately. Mild steel (MS) rods with wt.% composition of 0.8% Mn, 0.04% P, 0.05% S, 0.16% C and 98.95% Fe from analysis with PhenomWorld electron microscope were cut into 6 test samples and polished for weight loss experimental study. Weight measured MS samples were placed in the acid electrolyte for 480 h. MS samples were measured at 24 h hiatus with Ohaus measurement device. The weight loss was determined at ambient temperature of 37 °C from the subtraction between the first weight of MS (sustained for 480 h) and subsequent weight taken at 24 h interlude for a total of 480 h. Corrosion rate of MS was determined from the equation below;

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

W illustrates weight loss (g), *D* illustrates density (g/cm^2), *A* illustrates area (cm^2), and *T* illustrates time of exposure in (h). Inhibition efficiency (η) was determined from the numerical illustration below [33];

$$\eta = \left[\frac{\omega_1 - \omega_2}{\omega_1}\right] \times 100 \tag{2}$$

ω_1 illustrates weight loss of MS from the acid solution without plant extracts while ω_2 illustrates weight loss of MS at specific CS concentrations. Corrosion rate and inhibition data obtained were tabulated and compared. Two-component unitary component experimental ANOVA test (F - test) was used to evaluate the statistical relevance of CS concentrations and observation time on CS inhibition output. The assessment was done at confidence level of 95% i.e. a significance level of $\alpha = 0.05$ with respect to the equations below. The addition of squares of columns (exposure time) was determined as follows;

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

The addition of squares among rows (plant extract concentration) was determined from Eq. (4)

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

Total computation of squares

$$SS_{Total} = \sum x^2 - \frac{T^2}{N} \tag{5}$$

3. Data, values and validation

Table 1 presents the corrosion rate output for MS in H_2SO_4 and HCl solution while Table 2 presents the corresponding data on CS inhibition efficiency for 480 h of exposure time. The corrosion rate data at 0% CS concentration in both acids significantly contrast the data at specific CS concentrations. At 24 h, the corrosion rates are 131.07 mm/y in H_2SO_4 and 79.90 mm/y in HCl. The greater corrosion rate output for MS in H_2SO_4 compared to HCl is due to the greater dissociation constant of H_2SO_4 in H_2O compared to HCl whereby it ionizes completely resulting H_3O^+ and SO_4^{2-}. H_2SO_4 being a diprotic acid releases two H atoms instead one associated with HCl being a monoprotic acid. However, the static nature of the corrosive medium causes substantial decline in corrosion rate analogous to exposure time due to gradual dilution of the acid electrolyte which weakens the release of corrosive products resulting from oxidation of the steel surface. Hence the corrosion rate of MS at 0% CS at 480 h of exposure are 15.55 mm/y and 9.04 mm/y. Addition of CS to the acid electrolyte substantially altered the mechanism of the reduction-oxidation processes causing corrosion. The corrosion rate of MS decrease significantly with respect to CS concentration in both acids. At 2% CS concentration, the corrosion rate of MS in both acids has reduced to 3.78 mm/y and 2.87 mm/y at 24 h of exposure. At 480 h, the corrosion rate has gradually increased to 14.15 mm/y and 4.48 mm/y signifying increase in gradual increase in corrosion rate with respect to exposure time. Increase in CS concentration generally results in substantial reduction in MS corrosion rate analogous to observation time. The rate of decrease is more significant in HCl solution compared to H_2SO_4. At 480 h and 10% CS concentration, the lowest corrosion rate value of 3.35 mm/y and 1.30 mm/y was obtained in H_2SO_4 and HCl solution respectively.

Observation of CS inhibition efficiency data (Table 2) in both acids provides further perspective to the inhibition performance of CS. First and foremost, inhibition efficiency decreases with exposure time, secondly inhibition efficiency appreciates with concentration and thirdly inhibition efficiency was generally higher in HCl solution compared H_2SO_4 solution. At 24 h, the inhibition efficiency values of CS inhibitor are generally above 90%. The values decreased with exposure time though the rate of decrease varies with CS concentration and acid media. The rate of decrease in inhibition efficiency were significantly high at low CS concentration in both acids. Comparison of the inhibition efficiency plots at 2% CS concentration and 10% CS concentration in both acids [Fig. 1(a) and (b)] shows the rate of decrease is more significant in H_2SO_4 than HCl as earlier mentioned. At 10% CS concentration, the rate of decrease is generally the same due to the presence of higher CS molecules in the acid solution to counteract the electrochemical action of corrosive species. At 2% CS concentration, the inhibition efficiency of CS decreased from 97.11% and 96.41% at 24 h in H_2SO_4 and HCl solution to 9.04% and 50.47% in both acids signifying higher inhibition performance in HCl solution. Effective inhibition performance occurred from 6% CS concentration in H_2SO_4 and HCl solution with values of 61.11% and 80.07% at 480 h of exposure time due to the availability of sufficient protonated molecules of CS in the acid solution. Secondly, the concentration dependent property exhibited by CS shows increase in CS concentration results in greater surface coverage of the steel. The highest inhibition value of 78.47% and 85.61% was obtained in both acids at 10% CS concentration and 480 h of exposure time.

Statistical data reflecting the mean, standard deviation and margin of error of CS inhibition efficiency values in H_2SO_4 and HCl solution are laid out in Table 3. The mean values show the average inhibition performance of CS with respect to CS concentration and observation time. The mean values in H_2SO_4 solution are smaller than the corresponding values in HCl. Secondly, the mean values in both acids appreciates with increase in CS concentration. However, the standard deviation values in H_2SO_4 are significantly greater than the values in HCl due to greater deviation of the values from mean value with respect to exposure time. The deviation values show that the variation of inhibition efficiency with exposure time was significant at lower CS concentration due to the instability of CS molecules stifling the action of the corrosive species. It also shows the performance of the inhibitor is unreliable at low concentration.
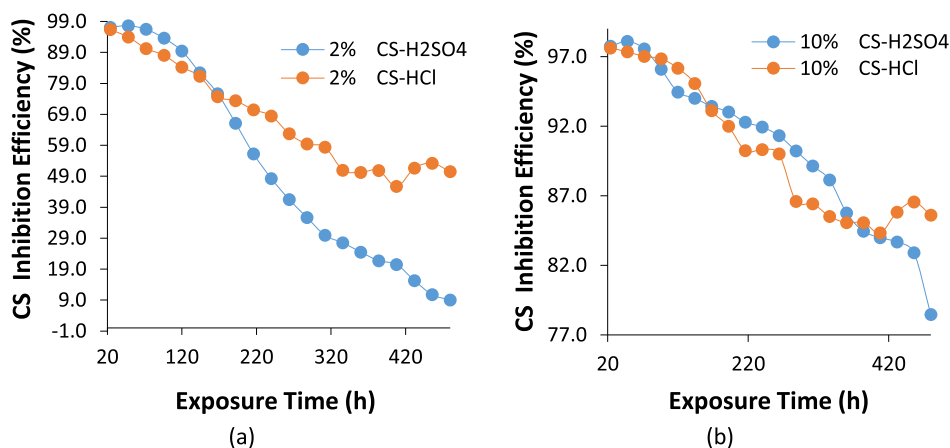
Table 1

Corrosion rate data for MS in H_2SO_4 and HCl solution at specific CS concentration for 480 h of exposure.

| CS Conc. (%)\Exp. Time (h) | H_2SO_4 (Corrosion Rate) | | | | | | HCl (Corrosion Rate) | | | | | |
	0% CS	2% CS	4% CS	6% CS	8% CS	10% CS	0% CS	2% CS	4% CS	6% CS	8% CS	10% CS
24	131.07	3.78	3.61	2.42	5.80	2.96	79.90	2.87	7.17	4.65	1.30	1.90
48	103.62	2.42	3.42	1.92	6.34	1.98	42.89	2.59	4.52	3.61	0.85	1.14
72	83.38	2.93	3.52	2.09	6.96	2.04	28.99	2.82	3.34	2.78	0.24	0.87
96	66.21	4.23	4.30	2.51	5.96	2.59	23.27	2.78	3.31	2.16	0.48	0.73
120	53.12	5.61	4.84	2.76	5.18	2.95	18.85	2.97	2.97	2.06	0.72	0.72
144	44.39	7.78	5.54	3.12	4.98	2.66	16.36	3.06	3.00	2.06	0.90	0.81
168	38.85	9.45	6.13	3.32	5.08	2.56	14.04	3.54	2.71	1.98	2.00	0.97
192	34.22	11.59	6.85	3.66	5.19	2.39	12.44	3.31	2.72	1.81	1.92	1.00
216	30.45	13.32	7.72	4.12	5.44	2.35	11.43	3.37	2.60	1.39	1.74	1.12
240	27.52	14.24	8.55	4.40	5.43	2.22	10.84	3.42	2.37	1.19	1.86	1.05
264	25.12	14.71	9.35	4.66	5.53	2.18	10.13	3.78	2.39	0.83	1.70	1.01
288	23.15	14.90	10.23	5.03	5.26	2.26	9.57	3.88	2.42	0.37	1.63	1.28
312	21.48	15.06	10.97	5.35	5.25	2.33	9.24	3.84	2.43	0.73	1.58	1.25
336	20.09	14.57	11.56	5.79	5.20	2.38	8.70	4.27	2.63	0.51	1.58	1.26
360	18.95	14.31	12.46	6.22	4.63	2.70	8.17	4.06	2.52	0.74	1.58	1.22
384	17.85	13.97	13.16	6.45	4.52	2.77	7.98	3.92	3.14	1.10	1.63	1.19
408	17.10	13.60	13.04	6.49	4.85	2.74	7.67	4.16	3.34	1.10	1.70	1.20
432	16.46	13.94	12.93	6.33	4.88	2.69	8.76	4.24	3.60	1.30	1.70	1.24
456	15.99	14.27	12.40	6.19	5.00	2.73	9.36	4.38	4.09	1.30	1.64	1.26
480	15.55	14.15	12.14	6.05	4.88	3.35	9.04	4.48	4.31	1.80	1.66	1.30

Table 2

Inhibition efficiency data for CS on MS in H_2SO_4 and HCl solution at specific CS concentration for 480 h of exposure.

CS Conc. (%)\Exp. Time (h)	H_2SO_4 (Inhibition Efficiency)					HCl (Inhibition Efficiency)				
	2% CS	4% CS	6% CS	8% CS	10% CS	2% CS	4% CS	6% CS	8% CS	10% CS
24	97.11	97.24	98.15	95.57	97.74	96.41	91.03	94.18	98.37	97.62
48	97.66	96.70	98.14	93.88	98.09	93.96	89.45	91.58	98.01	97.34
72	96.48	95.77	97.49	91.66	97.56	90.28	88.49	90.40	99.17	97.01
96	93.60	93.50	96.21	90.99	96.08	88.05	85.76	90.71	97.94	96.85
120	89.44	90.90	94.80	90.26	94.46	84.26	84.25	89.09	96.21	96.17
144	82.46	87.52	92.97	88.79	94.01	81.27	81.63	87.38	94.51	95.07
168	75.68	84.21	91.44	86.93	93.42	74.76	80.67	85.88	85.78	93.11
192	66.14	79.97	89.30	84.84	93.03	73.39	78.16	85.44	84.60	91.99
216	56.24	74.64	86.48	82.13	92.28	70.50	77.25	87.82	84.77	90.24
240	48.27	68.94	84.02	80.28	91.95	68.49	78.15	88.98	82.86	90.32
264	41.46	62.80	81.45	77.99	91.31	62.71	76.42	91.84	83.18	90.00
288	35.66	55.83	78.26	77.28	90.23	59.41	74.73	96.13	82.92	86.60
312	29.90	48.93	75.10	75.57	89.15	58.43	73.72	92.14	82.92	86.42
336	27.51	42.46	71.20	74.13	88.13	50.95	69.75	94.10	81.84	85.51
360	24.49	34.24	67.16	75.58	85.77	50.28	69.16	90.90	80.69	85.06
384	21.72	26.28	63.85	74.70	84.46	50.88	60.67	86.22	79.55	85.07
408	20.48	23.72	62.06	71.61	83.99	45.69	56.43	85.61	77.78	84.33
432	15.31	21.42	61.52	70.33	83.67	51.62	58.88	85.11	80.54	85.83
456	10.74	22.48	61.27	68.73	82.91	53.21	56.34	86.10	82.52	86.55
480	9.04	21.95	61.11	68.59	78.47	50.47	52.28	80.07	81.61	85.61

Fig. 1. Comparative plots of CS inhibition efficiency in H_2SO_4 and HCl solution (a) at 2% CS concentration and (b) at 10% CS concentration.

Table 3

Mean, standard deviation and margin of error data for CS inhibition efficiency in H_2SO_4 and HCl solution.

Acid Solution	H_2SO_4					HCl				
CS Conc. (%)	2	4	6	8	10	2	4	6	8	10
Standard Deviation	32.43	29.02	14.12	8.78	5.61	16.68	11.87	3.88	7.38	4.91
Mean	51.97	61.48	80.60	80.99	90.34	67.75	74.16	88.98	86.79	90.34
Margin of Error	±0.097	±0.068								
Proportion of Data above 70% Inhibition Efficiency	58%	86%								

The standard deviation in both acids decreased significantly as CS increases. Earlier discussion has shown that effective inhibition efficiency occurs at higher inhibitor concentration (6% CS concentration in H_2SO_4 and HCl solution), however, the standard deviation data shows performance reliability of CS over time starts at 8% CS concentration in H_2SO_4 and 6% concentration in HCl. According to Table 3, the proportion of data above 70% inhibition performance in H_2SO_4 is 58% while in HCl it is 86% at margin of error of +0.097 and +0.068.

Statistical evaluation through analysis of variance (ANOVA) was performed to assess the numerical importance of inhibitor concentration and observation time on the inhibition performance of CS compound on MS. Table 4 presents the statistical relevance factor, mean square ration and theoretical significance factor. The statistical relevance factor gives the percentage significance of the sources of variation (inhibitor concentration and exposure time) which depicts their influence on CS inhibition performance. The mean square

Table 4

ANOVA data for CS protection performance in H_2SO_4 and HCl solution.

H_2SO_4 Source of Variation	Degree of Freedom	Mean Square Ratio (F)	Theoretical Significance Factor	Statistical Relevance (%)	HCl Source of Variation	Degree of Freedom	Mean Square Ratio (F)	Theoretical Significance Factor	Statistical Relevance (%)
CS Conc.	4	94.57	2.81	89.90	CS Conc.	4	347.60	2.81	96.39
Exp. Time	10	0.25	2.05	0.59	Exp. Time	10	1.20	2.05	0.83
Residual	40				Residual	40			
Total	54				Total	54			

ratio represents the statistical value that must be greater than the theoretical significance factor for the statistical relevance value to be relevant. Inspection of Table 4 shows CS concentration is the dominant independent variable causing the inhibition performance of CS inhibition with statistical relevance value of 89.9% and 96.39% respectively. The mean square ratio for CS concentration are 94.57 and 347.6 in both acids which are higher than the theoretical significance factor. The mean square ratio for exposure time are 0.25 and 1.20 which are lesser than the theoretical significance factor thus statistically irrelevant to CS inhibition performance.

Declaration of competing interest

Authors declare no conflict of interest

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