

Some Natural Additives as Corrosion Inhibitors for Zinc in Acetic Acid Media

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Abstract

The inhibition effect of some plant extracts, namely *Vulgaris Thymus* (VT), *Cuminum Cyminum*, (CC), *Hibiscus Subdariffa* (HS), *Feungreek* Seeds(FS) on the corrosion of zinc in 2M CH₃COOH solution has been investigated using weight loss, pH measurement and electrochemical measurements. The percentage inhibition efficiency was found to increase with increasing concentration of inhibitor and with decreasing temperature. The adsorption of these inhibitors on the zinc surface obeys Langmuir isotherm. Some activated thermodynamic parameters were calculated. The variation of the open circuit potential of zinc electrode with time in 2M CH₃COOH shows that E_{corr} is shifted with time in the cathodic direction, *i.e.* to more negative values before return to the positive direction attainment quaisteady states. But the addition of these extract, the potential is shifted initially to more positive values then returned to negative values with time by increasing concentration of the additive extracts is recorded in comparison with blank.

Keywords: Corrosion; Inhibitors; Acidic medium; *Vulgaris Thymus*; *Cuminum cyminum*; *Hibiscus subdariffa*; *Fenugreek* seeds.

Introduction

Zinc is an industrially important metal which is corroded by many agents mainly the acids.^[1] Due to its increasing use, the study of the corrosion inhibition is of paramount importance.^[1] The dissolution behavior of zinc in acidic and slightly neutral media is known to be inhibited by nitrogen and sulfur-containing organic compounds. Such compounds contain electron- donating groups that decrease the corrosion rate by increasing the hydrogen over voltages on the surface of metals.^[2] Studies of the effect of organic additives on the corrosion rate of zinc have been the subject of many investigators.^[3-4] Several investigations have been reported using economic plant extracts.^[5] El-Etre *et al.* investigate some naturally occurring substances as corrosion inhibitors for different metals in various environments.^[6-7]

Plant extracts have drawn the attention in the field of corrosion inhibition for many decades. As natural products, they are a source of non-toxic, eco-friendly, readily available and renewable inhibitors for preventing metal corrosion.^[1-6] According

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to literatures, many efforts are being made to find the suitable plant species to produce inhibitors and then clarify the inhibition mechanism.^[1-6]

Some promising plant extracts have already been studied in the corrosion inhibition of metals (e.g., steel, aluminum, zinc and nickel) in various environments, in acid and alkaline media.^[1-6] Inhibitive effect of plant extracts is mainly attributed to the adsorption of organic substances on the metal surface blocking the active sites or even forming a protective barrier film.

Natural inhibitors for the alkaline corrosion of zinc like the extract of Lawsonia^[3] and Hibiscus subdariffa^[7] which exhibit inhibitive properties to some extent.

Vulgaris Thymus belongs to the Lamiaceae family, which its oil is composed of aromatic compounds and is known to western Mediterranean region^[8,9]. It is used for seasoning fish, poultry, soups, vegetables and flavoring liqueur, in herbal teas prepared for colds and flues, as well.^[8,9] *Cuminum Cyminum* (Cumin) is flowering plants in the Apiaceous family. Its fruits have a distinctive bitter flavor, strong and warm aroma due to their abundant essential oil content^[10-12]. *Hibiscus Subdariffa* (karkade) belongs to the Malvaceae family. Its used in various foods and medicines.^[10-12] It consists of proteins, glucides, organic acids (citric, malic, and traces of tartaric acid), 16 reducing sugars, non-nitrogenous substances and cellulose.^[10-12]

Feungreek plant is native to the area of the eastern Mediterranean to central Asia and much cultivated in India, Pakistan and China.^[13] Fenugreek is also employed as a herbal medicine in many parts of the world. However, numerous studies have found that fenugreek seeds and leaves can lower blood glucose and cholesterol levels and also have an anti-diabetic effect.^[11,13] Fenugreek is commonly eaten food and regarded as safe.^[14] Fenugreek leaves are rich with the following organic substances, ascorbic acid, beta-carotene, xanthophylls, choline and methionine. As noticed, these substances are O-, N-, and/or S-containing organic compounds.^[13-14]

The aim of the present work is to test aqueous extracts of *Vulgaris Thymus* leaves (VT), *Cuminum Cyminum*, Cumin (CC), *Hibiscus Subdariffa* petals (karkade) (HS), and *Feungreek* Seeds(FS) as inhibitors for the zinc metal in acetic acid solutions.

Experimental

Materials

Zinc specimens were prepared from pure zinc sheets supplied by BDH Lab., (England). *Vulgaris Thymus* leaves, *Cuminum Cyminum* (Cumin), *Hibiscus Subdariffa* petals (karkade) and Feungreek Seeds were purchased from local market. Acetic acid was obtained from Fluka (Buchs, Switzerland) and was used as received. The other materials were used as grade reagent products. Deionized, double distilled water was used

Preparation of Specimens

The specimens were polished successively using emery paper from 220 to 1200 grades. Then, the specimen was washed several times with deionized water and acetone, dried, and weighed accurately.

Preparation of extracts

Stock solution of the inhibitor extract was prepared by boiling 10g of dried, grounded seeds or leaves of the natural products in 1L of deionized water for 15 minutes. The extract was left to night, filtered and diluted to 1L by deionized water. The freshly prepared extract was aged in a refrigerator for two months which gives almost the same results.

Preparation of Solutions

Aqueous aggressive solution of (2M) of acetic acid was prepared. The employed of different concentration range of extracts was of 10-50 (v/v %).

Weight loss method

Weight loss of rectangular pure zinc specimens of size 50 x 10 x 0.5 mm were immersed in 100 ml of electrolyte with and without the addition of different concentration of plant extract was determined after 6 hours (short time term). The specimen was taken out, washed, dried and weighed accurately. Then the tests were repeated 120 hours (long time term) at the 25 ±0.5°C using air thermostat.

The percentage inhibition efficiency (% IE) was calculated using equation (1),^[15]

$$IE(\%) = \frac{w_1 - w_2}{w_1} \times 100 \quad (1)$$

Where w_1 and w_2 are weight losses of zinc in absence and presence of inhibitors

pH measurements:

The pH of solutions were measured before and after corrosion process to the nearest 0.01 pH unit. The change in the values of pH of solutions was taken as a measure of corrosion process using a microprocessor combined pH-meter and Temperature Probe, HM-40V (Japan),.

Electrochemical measurements

Electrochemical measurements were proceeded in the electrolytic cell shown in figure 1. The cell was made of Pyrex glass with the dimensions indicated. B is a ground B-24 glass joint, which served for mounting the test electrode and fixing it inside the cell in such a manner that the electrode faces the auxiliary electrode. The counter electrode, was a large platinized Pt sheet 2 × 2 cm². M₁ is a small side compartment to support the reference electrode, L, M₂ is another compartment to hold a second electrode, X, when needed. S is a two-way stopcock to release the gas. Trap, T, containing some of the solution under investigation served as a gas outlet. 100 mL of electrolyte was used for each electrochemical measurement.

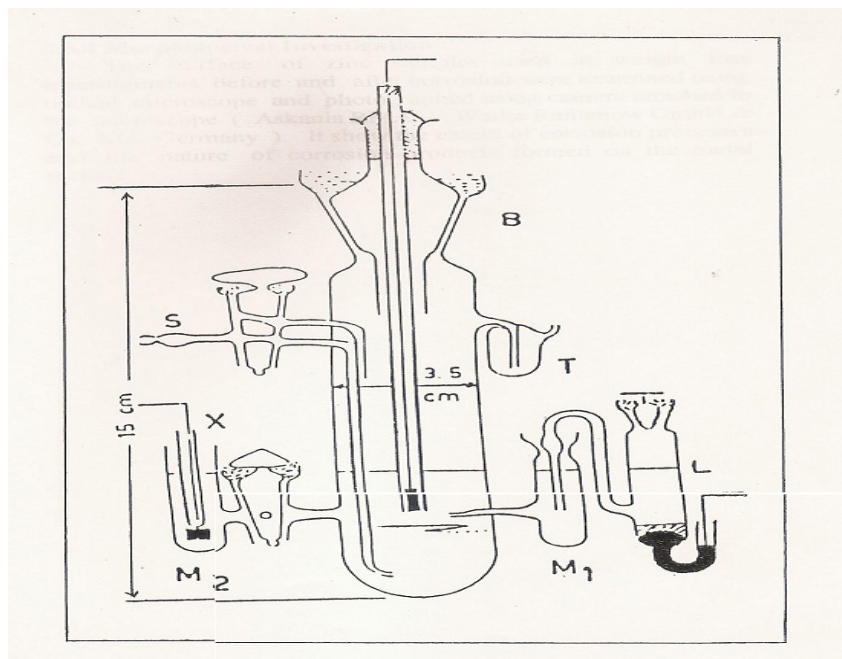


Figure 1: The Cell

All potentials of the zinc electrode under open-circuit conditions were measured versus saturated calomel electrode, SCE, ($E = 0.242 \text{ V vs. NHE}$ (hydrogen electrode) at $25^\circ\text{C} \pm 1^\circ\text{C}$), and referred to that electrode. The current is less than the potential of the zinc electrodes in naturally aerated solutions and under unstirred conditions were followed with time until a quasi-steady corrosion potentials were reached. Potentials were recorded with the aid of a voltmeter (digital multimeter). The inhibition efficiency ($IE\%$) was calculated using the following equation:^[12]

$$IE\% = \frac{I - I_i}{I} \times 100 \quad (2)$$

Where I and I_i are the corrosion rates in free and inhibited solution respectively.

Results and Discussion

Weight loss measurements

Figure 2 shows the weight loss- time curves for zinc in $2 \text{ M CH}_3\text{COOH}$ solution in absence and presence of different concentrations of compound (CC) as an example. Similar curves were also obtained for other three compounds, VT, HS and FS (not shown) but tabulated in table (1) either in short or long time. Inspection of this figure and table (1) reveal that, the curves are characterized by gradual rise in weight loss with time. The curves indicate that, the weight loss of zinc depends on the concentration of additive extracts.

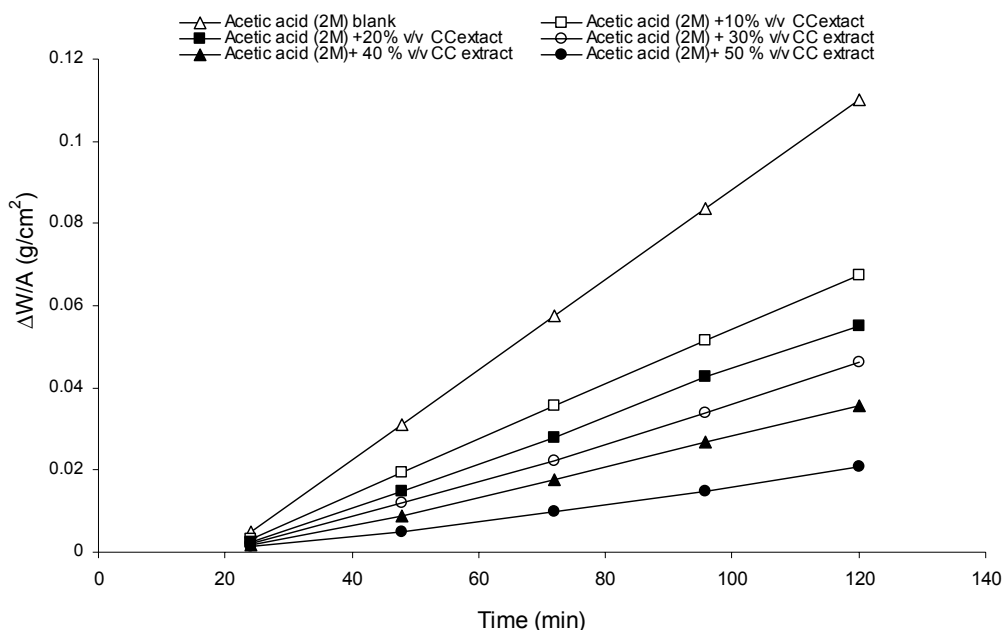


Figure 2: Variation of ΔWt loss of Zn in (2M) acetic acid in presence and absent of different (v/v%) of CC as an inhibitor at 25°C.

The calculated values of inhibition efficiencies obtained from weight loss are listed in table (2). It is obvious that the IE decreases with the increase in the inhibitor concentration, whereas decreases in the following order:

$$HS > CC > VT > FS$$

The decrease may be due to the adsorption of extracts on the surface of Zn and covered all active sites and by time the increase of extracts have no role to retard the corrosion the increase have been shown.

A good efficiency is observed at constant concentration of plant extracts as following, %IE of HS =92.3% at 120 hrs at 10% (v/v) , % IE of CC =78.0 % at 120 hrs at 40% (v/v), and %IE of FS = 73.7% at 120 hrs at 10% (V/V).The most efficient inhibitor are HS and CC extracts in 2.0 M CH_3COOH solutions. The inhibition efficiency has similar arrange like the previous order

Two main constituents of different aqueous extracts, namely the organic acids and the coloring materials were effective in retarding the dissolution of zinc metal. But the activity of the coloring portion which mainly obtained from pigments due to the presence of azo groups, that may have effected inhibition through nitrogen bond on metal surface with the formation of extracts- Zn^{2+} complex on the surface was considerably higher than of the organic acids was considerably higher than of the organic acids ,like HS extract which acts as an efficient inhibitor of the dissolution of Zn. The effect HS extract as example plays as corrosion restrainer on the dissolution of Zn in acid solutions, which was also established by the weight loss. The extent of dissolution results, as shown previously, agree with these curves which were determined by the thermometric method. Similar to this trend, HS extract containing a small amount of citric and malice, may exerts a retarding effect on the dissolution of Zn.^[12]

Table 1: Variation of weight loss of Zn with time in 2 M acetic acid in presence and absence of different concentrations (v/v %) of natural products extracts (TV, CC, HS and FS)

TIME. (HR)	W / A (MG/HR)																				
	VT				FS				CC				HS								
	10%	20%	30%	40%	50%	10%	20%	30%	40%	50%	10%	20%	30%	40%	50%	10%	20%	30%	40%	50%	
1.00	3.8 ⁴	1.6 ⁴	1.4 ⁴	0.7 ⁴	0.5 ⁴	1.0 ⁵	1.2 ⁴	1.1 ⁴	0.9 ⁴	0.7 ⁴	8.6 ⁵	3.2 ⁴	2.9 ⁴	2.6 ⁴	1.7 ⁴	1.6 ³	1.4 ³	1.3 ³	1.4 ³	1.6 ³	1.6 ³
2.00	5.8 ⁴	1.8 ⁴	1.6 ⁴	1.2 ⁴	0.9 ⁴	5.2 ⁵	2.0 ⁴	1.8 ⁴	1.2 ⁴	1.1 ⁴	0.7 ⁴	4.7 ⁴	4.3 ⁴	4.0 ⁴	3.0 ⁴	2.2 ³	1.9 ³	1.8 ³	1.9 ³	2.2 ³	2.2 ³
3.00	7.8 ⁴	2.0 ⁴	1.8 ⁴	1.5 ⁴	1.3 ⁴	7.5 ⁵	2.8 ⁴	2.4 ⁴	1.8 ⁴	1.7 ⁴	1.1 ⁴	6.1 ⁴	5.7 ⁴	5.4 ⁴	4.9 ⁴	4.4 ⁴	2.6 ³	2.3 ³	2.4 ³	2.6 ³	2.6 ³
4.00	9.9 ⁴	2.3 ⁴	2.1 ⁴	1.8 ⁴	1.6 ⁴	1.1 ⁴	3.5 ⁴	2.9 ⁴	2.3 ⁴	2.0 ⁴	1.5 ⁴	7.3 ⁴	7.0 ⁴	6.6 ⁴	6.2 ⁴	5.7 ⁴	3.2 ³	2.9 ³	2.7 ³	2.9 ³	3.2 ³
5.00	1.3 ³	2.6 ⁴	2.4 ⁴	2.2 ⁴	1.9 ⁴	1.3 ⁴	4.3 ⁴	3.8 ⁴	2.9 ⁴	2.5 ⁴	2.0 ⁴	8.4 ⁴	8.1 ⁴	7.8 ⁴	7.5 ⁴	6.8 ⁴	3.6 ³	3.3 ³	3.1 ³	3.3 ³	3.6 ³
6.00	3.2 ³	2.9 ⁴	2.7 ⁴	2.4 ⁴	2.2 ⁴	1.4 ⁴	5.2 ⁴	4.5 ⁴	6.7 ⁴	4.4 ⁴	3.3 ⁴	9.4 ⁴	9.1 ⁴	8.9 ⁴	8.6 ⁴	8.0 ⁴	4.2 ³	3.7 ³	3.5 ³	3.7 ³	4.2 ³
24.0	5.1 ³	1.1 ³	8.1 ⁴	7.4 ⁴	6.4 ⁴	4.6 ⁴	2.2 ³	9.3 ⁴	1.2 ³	0.7 ³	6.8 ⁴	3.2 ³	2.5 ³	2.1 ³	1.7 ³	1.5 ³	7.0 ³	2.2 ³	3.6 ³	2.2 ³	7.0 ⁴
48.0	3.1 ²	2.1 ³	1.6 ³	1.5 ³	1.3 ³	9.1 ⁴	2.9 ³	2.6 ³	2.6 ³	1.2 ³	9.7 ⁴	1.2 ²	1.0 ²	6.7 ³	5.8 ³	3.5 ³	2.8 ²	5.6 ³	8.0 ³	5.6 ³	2.8 ³
72.0	5.8 ²	3.2 ³	2.4 ³	2.3 ³	1.9 ³	1.4 ³	1.2 ²	7.5 ³	4.1 ³	2.3 ³	1.0 ³	2.7 ²	2.5 ²	1.6 ²	1.4 ²	7.3 ³	4.6 ²	9.4 ³	1.3 ²	9.4 ³	4.6 ³
96.0	8.4 ²	4.2 ³	3.2 ³	3.0 ³	2.6 ³	1.8 ³	1.6 ²	1.0 ²	5.5 ³	3.5 ³	2.4 ³	4.7 ²	4.5 ²	3.0 ²	2.9 ²	1.4 ²	7.0 ²	1.4 ²	1.8 ²	1.4 ²	7.0 ³
120	0.11	5.2 ³	4.1 ³	3.8 ³	3.2 ³	2.2 ³	2.1 ²	1.3 ²	6.2 ³	5.0 ³	3.2 ³	6.8 ²	6.9 ²	4.6 ²	4.7 ²	2.2 ²	9.6 ²	3.9 ²	2.4 ²	1.9 ²	9.6 ³

Table 2. IE and θ of different concentrations of natural products extracts for zinc corrosion in 2M CH₃COOH solutions as obtained from weight loss measurements during short and long time terms.

EXTRACT CONC. V/V %	IE %							θ							C / θ							
	VT	CC	HS	FS	VT	CC	HS	VT	CC	HS	FS	VT	CC	HS	VT	CC	HS	VT	CC	HS	FS	
10	59.6	95.5	24.8	77.4	68.5	92.3	60.5	73.7	60.5	73.7	60.5	73.7	60.5	73.7	60.5	73.7	60.5	73.7	60.5	73.7	60.5	73.7
20	37.7	50.5	28.3	71.4	70.6	89.3	60.4	69.0	60.4	69.0	60.4	69.0	60.4	69.0	60.4	69.0	60.4	69.0	60.4	69.0	60.4	69.0
30	53.4	76.0	34.7	68.3	68.5	83.2	60.0	67.5	60.0	67.5	60.0	67.5	60.0	67.5	60.0	67.5	60.0	67.5	60.0	67.5	60.0	67.5
40	47.0	62.6	54.5	78.0	72.0	82.8	58.6	65.0	58.6	65.0	58.6	65.0	58.6	65.0	58.6	65.0	58.6	65.0	58.6	65.0	58.6	65.0
50	52.9	62.9	48.1	62.3	62.7	68.3	46.6	51.4	46.6	51.4	46.6	51.4	46.6	51.4	46.6	51.4	46.6	51.4	46.6	51.4	46.6	51.4

IE % of 2M CH₃COOH (blank) at 6 hr equal 46.7, at 12 hr equal 78.2

Also, organic inhibitors affect the kinetics of metal corrosion by retarding the rate of either or both of the anodic and cathodic reactions. A given inhibitor functions by means of a specific mechanism, depending on the type, composition of metal and corroding material, inhibitor structure and concentration as well as temperature.^[12-15]

The effect of extracts as corrosion inhibition on the dissolution of Zn in acetic acid solutions was established by the loss in weight method. This is well demonstrated by the results obtained from variety of different experimental techniques. Thus for example, the additives reduce the reaction numbers of the Zn metal in the thermometric corrosion test.^[12,15,17] The effect depends on the surface of metal and the aggressive medium. Generally these results of corrosion of zinc in 2M CH₃COOH solution in presence of different plants extracts, suggest that the plants extracts could serve as effective corrosion inhibitors

Variation of pH measurements.

Figure 3 shows pH difference - time curves for zinc in 2 M CH₃COOH solution in presence and absence of different concentrations of compound (VT) as an example. Similar curves were also obtained for other three compounds, CC, HS and FS (not shown) but tabulated in table 3 in both short and long time. The variations also are linear and the pH of all extracts were lower than the acid. This trend may be due to the constituent of the plants extracts under investigation which contain different organic substances such as ascorbic acid, amino acids, citric acid and malic acid which lower the pH difference than the acid.

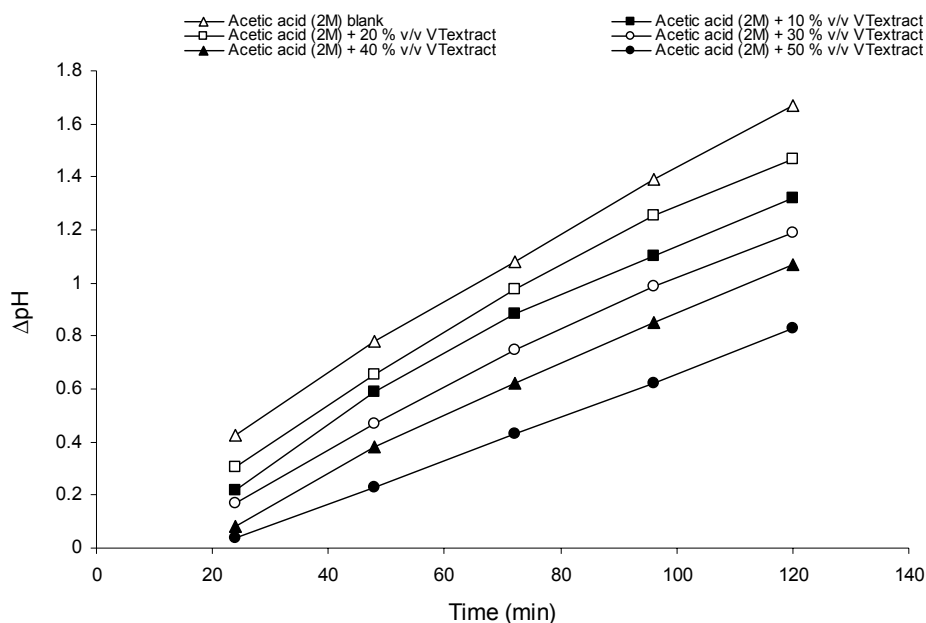


Figure 3: Variation of Δ pH of Zinc with time in 2M acetic acid in absence and presence of different (v/v%) VT extracts as inhibitor at 25°C.

Table 3. Variation of ΔpH of Zn with time in 2 M acetic acid in presence and absence of different concentrations (v/v %) of natural products extracts (thymus, cumin, hibiscus, fenugreek)

TIME. (HR)	ΔPH																			
	FS					HS					CC					VT				
	10%	20%	30%	40%	50%	10%	20%	30%	40%	50%	10%	20%	30%	40%	50%	10%	20%	30%	40%	50%
24.0	0.23	0.30	0.18	0.110	0.110	0.380	0.304	0.228	0.167	0.11	0.160	0.15	0.111	0.069	0.020	0.215	0.160	0.145	0.086	0.072
48.0	0.80	0.77	0.61	0.450	0.450	0.650	0.560	0.460	0.395	0.30	0.416	0.37	0.284	0.225	0.160	0.459	0.395	0.307	0.245	0.184
72.0	1.09	1.04	0.91	0.754	0.710	0.920	0.840	0.730	0.64	0.51	0.640	0.56	0.462	0.400	0.320	0.680	0.600	0.524	0.424	0.330
96.0	1.29	1.25	1.06	1.020	0.940	1.147	1.071	0.940	0.84	0.71	0.832	0.75	0.658	0.600	0.475	0.880	0.809	0.711	0.582	0.467
120	1.39	1.38	1.21	1.220	1.130	1.337	1.253	1.139	1.056	0.87	1.030	0.93	0.84	0.779	0.640	1.040	0.969	0.869	0.760	0.560

Adsorption isotherm

The value of degree of the surface coverage θ which represents the part of the metal surface covered by inhibitor molecules were evaluated at different concentrations of the inhibitors in 2M CH_3COOH using the following equation(3).^[12,15-17]

$$\theta = 1 - \left(\frac{\text{wt.loss}_{inh}}{\text{wt.loss}_{unhib}} \right) \quad (3)$$

The values of R_{corr} , $IE\%$ and θ at different plant extracts concentrations are listed in table (2). The data in this table, revealed that as the plant extract concentrations increases, the corrosion rate decreases while the efficiency percent and surface coverage increases. This behavior may be attributed to the increased of the surface coverage θ , which referred to the increase of the number of adsorbed molecules at the Zn metal surface.

Attempts were made to fit θ values to various adsorption isotherms. The Langmuir adsorption isotherm fits the experimental data. A plot of $\log \theta / 1 + \theta$ against $\log C$ for all concentrations of inhibitors as shown in figure 4. Approximately a straight line in all cases was obtained. This suggests that the adsorption of different plant extracts on the zinc surface follow Langmuir adsorption isotherm. These results may confirm the assumption that, these compounds are adsorbed on the metal surface through the protonated (N,S,O) atoms or via the lone pair of electrons of (N,S,O) atoms. The extent of inhibition is directly related to the performance of adsorption layer which is a sensitive function of the molecular structure.^[12,15]

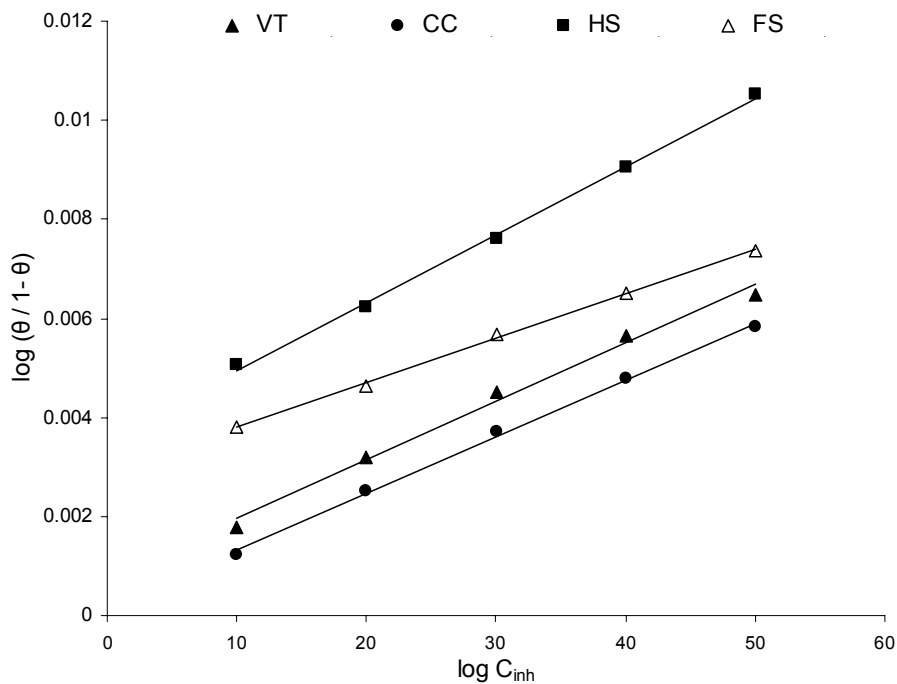


Figure 4: Plot of $\log(\theta / 1 - \theta)$ vs. $\log C_{inh}$ in (2M) acetic acid in presence of different concentrations of plant extracts at 25°C to verify Langmuir adsorption isotherm

Also the degree of surface coverage is increased with the increase in the concentration of inhibitors. This behavior may be attributed to the physical adsorption of organic matter on the zinc surface.

Discussing the corrosion inhibition by surface-active organic compounds various factors are taken into consideration including, number and types of adsorbing groups and their electron structure. Most of extracts under our investigation contain different organic substances which exhibit corrosion inhibiting capabilities such as ascorbic acid, amino acids, flavonoids, pigments and β -carotene.^[18] thus, it is difficult to assign the observed inhibiting effect to a particular constituent of the extracts.

The different values of θ for different concentrations of inhibitor C and C/ θ are presented in table 2 .In general, C/ θ increases with increasing C . In figure 5, The correlation between C/ θ vs. C was plotted, the value of K and the energy of adsorption (ΔG_{ad}^*) can be determined according to equations 4,5.^[19]

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (4)$$

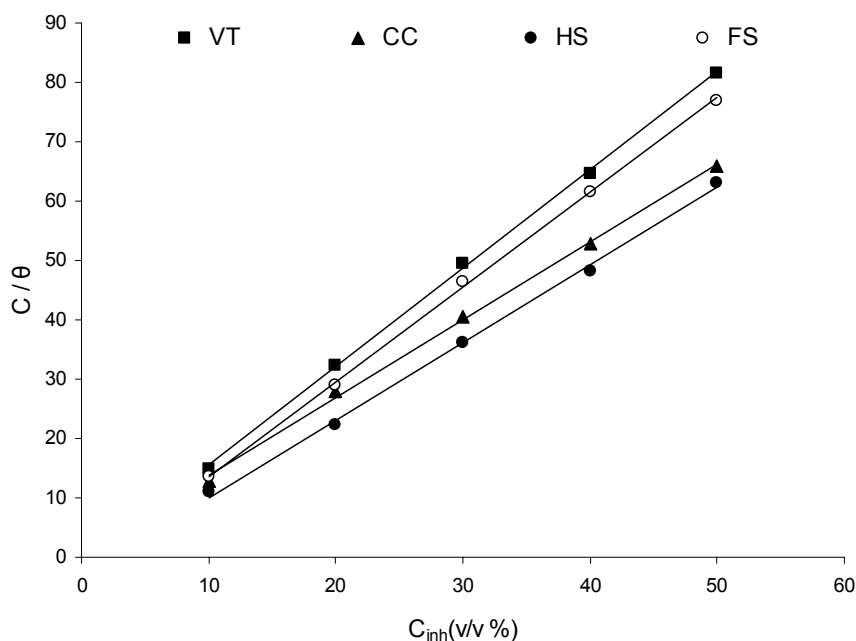


Figure 5: Plot of (C / θ) vs. C_{inh} in 2M acetic acid in presence of different concentrations of plant extracts at 25°C

The value C is the extract concentration and K the adsorption equilibrium constant, which can be evaluated from the intercepts of the plots, is related to the standard free energy of the adsorption, ΔG_{ad}^* by^[19]

$$\ln k = \ln \frac{1}{55.5} - \frac{\Delta G_{ads}^*}{RT} \quad (5)$$

The values of K and ΔG^* are 1.11 and -9.52 kJ/ mol for CC ; 0.79 and -10.3 kJ/ mol for VT ; 0.4 and -11.99 kJ/ mol for HS ; 0.87 and -10kJ/ mol for FS .These values indicate the physical adsorption of mole of the extracts from solution at the zinc metal surface. The negative sign of the free energy of adsorption indicates that the adsorption of the inhibitor at the zinc surface is a spontaneous process

Effect of temperature

The variation in temperature of the system is measured as a function of time. The reaction number (RN) is defined according to equation 6 :^[20]

$$RN = \frac{T_m - T_i}{t} , \text{ } ^\circ\text{C min}^{-1} \tag{6}$$

Where T_m and T_i are the maximum and initial temperature ± 0.5 $^\circ\text{C}$, respectively and t is the time in minutes elapsed to reach T_m . IE is calculated as the percent reduction in the RN as shown un equation 7:

$$IE\% = \frac{RN_f - RN_i}{RN_f} \times 100 \tag{7}$$

Where (RN_f) and (RN_i) are the RN of zinc dissolution in absence and in presence of inhibitor, respectively. Table (4) shows the different values of RN during short time term 6 hrs ,and long time term 24 hrs for the different inhibitors. From table 4, IE% is arranged in respectively order as in especially in long time:

$$HS > CC > VT > FS$$

This arrangement agrees with the arrangement in weight loss that was discussed before. The presence of different plants extracts, suggests that the plants extracts could serve as effective corrosion inhibitors

Table 4. Values of reaction number (RN) during short (ST) and long time (LT) and the calculated percent reduction (IE %)

TIME, MIN		REACTION NUMBER (RN) ($^\circ\text{C MIN}^{-1}$)							
		FS		HS		CC		VT	
ST	LT	ST	LT	ST	LT	ST	LT	ST	LT
60	1440	19.9	20.3	26.1	25.9	20.3	19.4	18.2	20.4
120	2880	20.8	20.8	26.1	27.5	19.9	20.2	19.3	20.5
180	4320	21.3	21.3	26.2	27.5	20.1	19.6	19.5	20.6
240	5760	21.5	21.6	26.2	24.4	19.8	19.7	19.8	20.8
300	7200	21.4	21.2	26.2	24.3	19.7	19.8	19.9	21.1
360	-	21.3	-	26.2	-	19.2	-	20.0	-
IE%		72.0	72.7	73.4	83.1	86.3	82.6	71.0	65.1

Figure 6 represents the change of temperature due to the corrosion reaction of zinc in solutions of 2M CH_3COOH in presence of different concentrations of natural product extract (FS) as an example Similar curves were also obtained for other three compounds, VT, CC, HS, (not shown). An interesting behavior could be observed in the figure where the temperature of the 2M corroding systems increases with time

higher than the acid curve alone in order $CC < HS < VT < FS$. The extent of increase and decrease in temperature value and the corresponding time depend on the solution composition. Thus, the temperature raising is the smallest within a shortest time in case of absence of inhibitors. On the other hand, both the temperature depression and its corresponding time increase with increasing inhibitor concentration. In most cases long time shows quasteady states which may due to the extracts molecules that fully cover the surface by time.

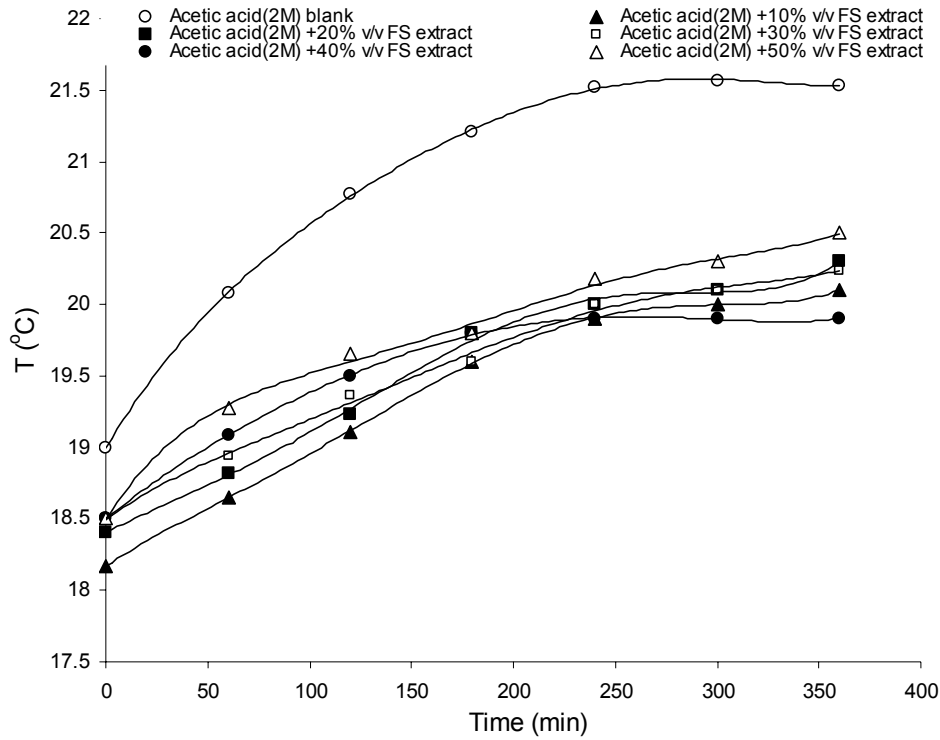


Figure 6: Thermometric curves of Zn metal in 2.0M CH_3COOH solution in absence and presence of different concentrations of FS extract at 25°C

The apparent activation energies (E_a^*) for the corrosion process in absence and presence of plant extracts were evaluated from Arrhenius equation 8:^[20,21]

$$\log R_{\text{corr}} = \log A - \frac{E_a^*}{2.303RT} \quad (8)$$

Where R_{corr} is the corrosion rate ($\text{gcm}^{-2}\text{min}^{-1}$), A is the frequency factor and (E_a^*) is the apparent activation energy, R is universal gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$).

The value of corrosion rate R_{corr} was calculated from the following equation(9):

$$R_{\text{corr}} (\text{mgcm}^{-2} \text{min}^{-1}) = \frac{W_1 - W_2}{At} \quad (9)$$

Where W_1 and W_2 are the mass of the specimen before and after corrosion, A is the total area of the specimen and t is the corrosion time.

The plots of logarithm of corrosion rate of Zn metal obtained from weight loss measurements versus the reciprocal of absolute temperature ranges ($10\text{-}60^\circ\text{C}$), gives

straight lines with slope of $E_a^*/2.303 R$, Thermodynamic parameters of Zn metal corrosion in both acidic media in absence and presence of plant extracts under test are given can be calculated using Eyring transition state equation (10).^[20-22]

$$R_{corr} = \frac{RT}{Nh} e^{\Delta S^*/R} e^{-\Delta H^*/RT} \quad (10)$$

Where h is plank's constant, N is Avogadro's number, and ΔS^* and ΔH^* are the activation entropy and enthalpy respectively. The values of E_a^* , ΔH^* and ΔS^* where calculated and listed in Table (5).

Table 5: The values of activation parameters E_a^* , ΔH^* , and ΔS^* for Zn metal in CH_3COOH media in the absence and presence (50%v/v) of different plant extracts.

PLANT EXTRACTS	E_a^* (KJ MOL ⁻¹)	ΔH^* (KJ MOL ⁻¹)	ΔS^* (KJ MOL ⁻¹ K ⁻¹)
blank	18.21	9.893	-0.464
VT	19.22	7.460	-0.460
CC	17.81	9.659	-0.475
HS	16.36	8.952	-0.467
FS	16.25	8.968	-0.461

Analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies in absence and presence of the plant extracts give some insight into the possible mechanism of inhibitor adsorption. A decrease in inhibition efficiency with rise in temperature is analogous to the increase in corrosion activation energy in the presence and absence of the inhibitor. This is frequently interpreted as being suggestive of an adsorption film of physical (electrostatic) nature. The reverse effect, corresponding to an increase in inhibition efficiency with rise in temperature and lower activation energy in the presence of inhibitor, suggests a chemisorption's mechanism.^[23,24] Data in table (5) reveal that E_a^* rises in the presence of the plant extracts in acidic media. These results depend on the nature of acetic acid and the constituents of the natural additives. So it is suggested that the corrosion inhibition of VT, CC, HS and FS occurred through physical adsorption. Also the higher ΔH^* values indicate that the degree of surface coverage is decreased with rise in temperature, supporting the proposed physisorption mechanism. The negative entropy of activation ΔS^* in the absence and presence the plant extracts, means that the increase in ordering are somewhere accompanied the dissolution process. The sequence of adsorption of these inhibitors on Zn metal surface according to ΔH^* and ΔS^* values could be arranged in the following order;

$$VT < HS < FS < CC$$

$$VT < FS < HS < CC$$

The values of ΔH^* and ΔS^* reveal that the values of free energy of adsorption ΔG_{ad}^o are negative for all system, suggesting that the adsorption processes are spontaneous. The affinity of adsorption is higher in acidic solutions for zinc.

Open circuit potential measurements;

The variation of the open circuit potential of zinc electrode with time in 2M acetic acid solution in absence and presence of different concentration (v/v%) of extracts at 25°C was followed until attainment of a steady state.

As shown in figure 7, the curve for zinc in absence of extract shows that the potential of the electrode changes towards more negative values than the starting potential. It indicates that E_{corr} shifts with time in the cathodic direction, i.e. to more negative values before returning to the positive direction and attaining a steady state. This indicates a simultaneous occurrence of a cathodic and anodic processes at the electrode surface and it would appear reasonable therefore to characterize the potential observed as being a mixed one.

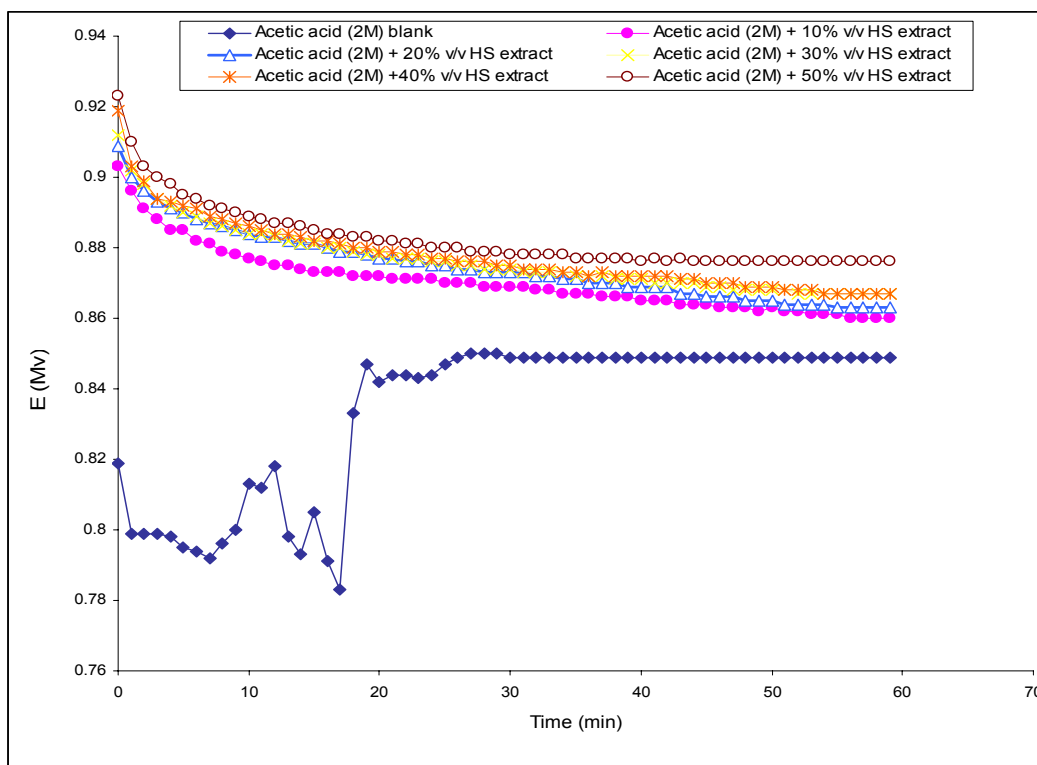


Figure 7: Potential-time plot for Zn in 2M CH_3COOH solution in absence and presence of different concentrations of HS extracts at 25°C

The other curves also represent the variation of the open circuit potential of Zn with time in 2M CH_3COOH in presence of different concentrations of VT as example at 25°C. Two features can be distinguished from the shape of the obtained curves. Firstly, a shift of the electrode potential towards more negative values by increasing concentration of the additive extracts is recorded compared to the blank. Secondly, the initial potential is moved to more positive values then returned to negative values with time. This indicates that the anodic processes are more predominant over the cathodic ones; hence, the dissolution is less than the rate of the complex formation. From the results of additives extracts, metal dissolution was inhibited to a comparative degree. The inhibition action of leaves, seeds and petals of the plants which were investigated

has been attributed to its composition. It may be reasonable to suggest that corrosion inhibition by additives may be due to bulky N-,O- and S- containing organic compounds which contain polar groups. For the extracts used, these may have inhibition through nitrogen bond on metal surface with the formation of extracts-Zn²⁺ complex on the surface of the metal. Similar curves were also obtained for the other three compounds, CC, HS, FS.

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