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Efficacy of Salvodera Persica Fruit as Corrosion Inhibitor on Mild Steel in Hydrochloric Acid Solution

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Abstract- The inhibition actions of ethanolic extract of Salvodera persica fruit for mild steel surface in HCl has been studied by weight loss, gasometric method, and thermometric method. Inhibition efficiency was studied in different concentration of acid with different concentration of inhibitor (0.2%,0.4%,0.6%,0.8%). Inhibition efficiency was found to be increase with increase in concentration of inhibitor and acid. The adsorption of ethanolic extract of Salvodera persica fruit on to mild steel surface pursued that as indicated by Langmuir model. This study showed that this particular plant extract is an effective inhibitor in suppressing the corrosion on the surface of the metal.

Keywords- Corrosion, mild steel, isotherm, Langmuir etc.

I. INTRODUCTION

Corrosion is the destructive consequence of a chemical reaction between a metal or metal alloy and its environment. In nature, metal atoms occur in chemical compounds (ie minerals)[1]. The chemical reactions that cause corrosion release the same amount of energy needed to separate the metals from their minerals. Corrosion returns the metal to a combined state in chemical compositions that are similar or even identical to the minerals from which the metals were extracted. Thus, corrosion has been called reverse extractive metallurgy [2-4]. The interaction between metal and its environment cannot be avoided. Metals exposed to highly corrosive environments have many applications, such as the textile, dye, and fertilizer industries [5,6]. Strong acids such as HNO3, H2SO4, and HCl can break the galvanic cell and change into ions that promote corrosion [7]. Many studies have been done to observe the corrosion behavior of metals in acidic solutions, so it would be interesting to study the effects of acidic mixtures and find out the nature of metal deterioration [8].

The use of a corrosion inhibitor is one of the most well-known and useful methods of protecting materials against corrosion in the industry [9,10]. Many of the synthetic inhibitors used are inorganic salts or organic compounds with limited solubility and toxic properties. Aware of the health and environmental risks, our attention was directed to finding more suitable, non-toxic and environmentally friendly inhibitors [11,12]. In this study, Salvadora persica plant was chosen to investigate its anti-corrosion behavior of mild steel in acidic environment (HCl). The alcoholic extract of different aerial parts (fruit, leaves and stem) of this plant has been used in various concentrations as a corrosion inhibitor.

Miswak tree (Salvadora persica L., family Salvadoraceae) is an evergreen tree that grows in various regions of Africa and Asia [13-15]. The roots and stems of S. persica have been used for centuries as a natural toothbrush in many cultures where it is known as Arak, Kharijal, Miswak or Siwak. In addition, extracts of S. persica leaves, fruits and seeds have been prescribed to treat fever, colds, malaria, constipation and rheumatoid arthritis.

II. EXPERIMENTAL

1. Experimental

Rectangular specimens of mild steel of dimension 2.5 × 2.5 × 0.04 cm containing a small hole near the upper edge were used for the experiment. . Mild steel coupons were polished with emery paper, washed thoroughly with doubly distilled water, degreased with acetone and weighed.

The solution of HCl was prepared by dilution of analytical reagent grade HCl with bi-distilled water The extracts were prepared by drying the fruit part of the plant in air, then finely powdered and extracted by boiling with ethanol in the Soxhlet apparatus. The concentration range of various extracts of a plant used was 0.2 % - 0.8%.

Weight Loss Method

Each sample was suspended by a V-shaped glass hook made of a capillary tube and immersed in a beaker containing 50 mL of the hydrochloric acid solution of different concentration with and without inhibitor solution. After sufficient exposure, the sample was cleaned with running water and then dried in air and the final weight was taken. In each case, duplicate experiments were performed and average weight values were determined. From the initial and final weight the loss in weight of each specimen due to corrosion was calculated. The inhibition efficiency percentage (η%) ,degree of surface coverage (Ɵ) and corrosion rate (C.R) was calculated as follows using equation 1,2,3[16,17]-

$$\eta\% = \frac{100\,(\Delta W_o - \Delta W_i)}{\Delta W_o} \quad (1)$$

$$\theta = \frac{(\Delta W_o - \Delta W_i)}{\Delta W_o} \quad (2)$$

ΔWo= weight loss of sample without inhibitor
ΔWi = weight loss of sample with inhibitor

$$\text{Corrosion rate(C.R).} = \frac{87.6\Delta W}{ATD} \quad (3)$$

ΔW = weight loss of specimen in mg
A = surface area of specimen in cm2
T = Time of exposure in hours
D = Density of metal in g/cm3

Table 1 - Corrosion rate (CR) and percentage inhibition efficiency (η %) of salvodera persica for mild steel in HCl by weight loss method

Concentration of Inhibitor	Weight loss in mg (ΔW)	Inhibition efficiency (η %)	Surface coverage (θ)	Corrosion rate (mmpy) (C.R)	$\log\left(\frac{\theta}{1-\theta}\right)$
2 N HCl					
Uninhibited	1182			116.9484	
0.2%	130.37	88.97	0.8897	12.8989	0.9066
0.4%	107.09	90.94	0.9094	10.5956	1.0016
0.6%	101.89	91.38	0.9138	10.0811	1.0253
0.8%	97.63	91.74	0.9174	9.6596	1.0455
1 N HCl					
Uninhibited	983			36.4721	
0.2%	133.98	86.37	0.8637	4.9710	0.8018
0.4%	99.08	89.92	0.8992	3.6762	0.9503
0.6%	97.22	90.11	0.9011	3.3433	0.9596
0.8%	88.76	90.97	0.9097	3.3753	1.0032
0.5 N HCl					
Uninhibited	776			14.39	
0.2%	123.23	84.12	0.8412	2.2860	0.7240
0.4%	111.13	85.68	0.8568	2.0616	0.7769
0.6%	109.96	85.83	0.8583	2.0399	0.7823
0.8%	106.62	86.26	0.8626	1.9779	0.7962
0.1 N HCl					
Uninhibited	179			2.6565	
0.2%	98.05	45.22	0.4522	1.4551	-0.0832
0.4%	92.36	48.40	0.4840	1.3707	-0.0278
0.6%	83.24	53.50	0.5350	1.2353	0.0609
0.8%	80.96	54.77	0.5477	1.2015	0.0831

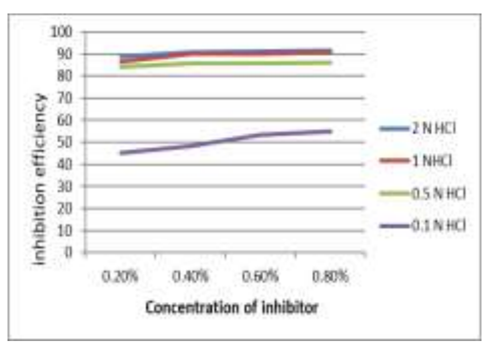

Figure 1: Variation of inhibition efficiency with concentration of inhibitor in HCl by weight loss method

Gasometric Method

To study corrosion is by monitoring the volume of hydrogen gas that has evolved (or gasometric method) with time through corrosion. Such a method is applied when the corrosion process is associated with a degaging of gas, mainly dihydrogen gas (H2) generally, it is used to investigate the corrosion of metallic materials in concentrated acidic solutions.

Table 2 -Hydrogen evolution rate(CRh) and Inhibition efficiency (η%) of salvodera persica for corrosion of mild steel in HCl solution by gasometric method

Concentration of inhibitor	Volume change (ΔV) in mL	Inhibition efficiency (η %)	Hydrogen evolution rate (CR_h)
3 N HCl			
Uninhibited	23.6		2.36
0.2	8.5	63.98	0.85
0.4	6.3	73.30	0.63
0.6	4.6	80.50	0.46
0.8	3.1	86.86	0.31
2.5 N HCl			
Uninhibited	20.4		
0.2	11.7	42.64	0.78
0.4	9.8	51.96	0.65
0.6	6.1	70.09	0.41
0.8	5.4	73.53	0.36
2 N HCl			
Uninhibited	18.0		
0.2	9.2	48.88	0.46
0.4	8.9	50.55	0.45
0.6	6.6	63.33	0.33
0.8	5.0	72.22	0.25
1 N HCl			
Uninhibited	15.5		
0.2	7.3	52.54	0.24
0.4	5.7	62.67	0.19
0.6	4.6	70.21	0.15
0.8	4.0	73.65	0.13

Metal coupon were dropped into the gasometric chamber containing 50 mL of the acid solution and inhibitor solution (0.2%, 0.4%, 0.6%,0.8%). The volume of hydrogen produced in the course of corrosion is recorded by a burette, this is due to the displacement of paraffin oil in the burette by hydrogen gas. The difference in the amount of paraffin oil present in the burette was recorded. From the volume of hydrogen gas evolved the rate of hydrogen evolution and Inhibition efficiency (IE%) was determined using equation 4 and5[18,19]

$$CR_h = \frac{V_t - V_i}{t_t - t_i} \tag{4}$$

V_t = volume of hydrogen evolved at time tt for inhibited solution

V_i = volume of hydrogen evolved at time ti for uninhibited solution

$$\%IE = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \times 100 \tag{5}$$

CRblank = corrosion rate in absence of plant extract

CRinh = corrosion rate in presence of plant extract

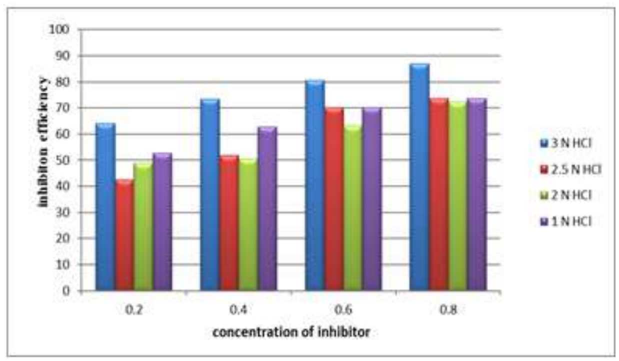

Figure 2: change in inhibition efficiency with concentration of inhibitor for mild steel in HCl by gasometric nethod

Thermometric Method

Thermometry is another destructive method to determine the corrosion behavior of metals and alloys. The development of the corrosion process is monitored with a calibrated thermometer determining the temperature changes of the corrosion system (metal or corrosion solution) as a function of time. The sample was immersed in the test solution and the initial temperature was recorded. As soon as the reaction started, the temperature first rise slowly, then rapidly and reached a maximum value before falling. The Maximum temperature was recorded. After that, the reaction number (RN) is calculated using equation 6[20]-

$$RN = \frac{T_m - T_o}{t} \qquad (6)$$

Tm = Maximum temperature
Ti = Initial temperature
t = Time
Percentage inhibition efficiencies were calculated as[21]

$$\eta\% = \frac{(RN_f - RN_I)}{RN_f} \times 100 \qquad (7)$$

RNf = reaction number of acid in abscence of inhibitor

RNI = reaction number of acid in presence of inhibitor

Table: -3 Reaction number (RN) and inhibition efficiency(η%) data of salvodera persica in HCl solution on mild steel by thermometric method

Concentration of inhibitor	Reaction number	Inhibition efficiency	Reaction number	Inhibition efficiency
	3 N HCl		2.5 N HCl	
Unhinhibited	1.0456		0.8333	
0.2	0.2050	80.39	0.2364	71.62
0.4	0.1663	84.10	0.2099	74.81
0.6	0.1393	86.76	0.1802	78.38
08	0.1384	87.59	0.1625	80.50
	2 N HC l		1 N HCl	
Unhinhibited	0.3120		0.0513	
0.2	0.1046	66.45	0.0265	48.23
0.4	0.0949	69.58	0.0248	51.64
0.6	0.0866	72.24	0.0221	56.81
08	0.0733	76.49	0.0194	62.07

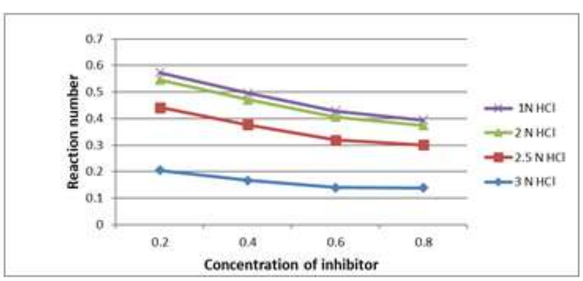

Figure 3: variation in reaction number with concentration of inhibitor for corrosion reaction of mild steel in HCl by thermometric method

III. RESULT AND DISCUSSION

The weight loss data and inhibition efficiency percentage (η%)for different concentrations of acid and inhibitor are given in Table 1. It is clear from the table inhibition efficiency increases with increasing concentration of extract in each strength of acid solution. The maximum efficiency 91.74% was obtained for 2 N HCl at 0.8% of inhibitor and minimum efficiency 54.77% was found at 0.2% of inhibitor in 0.1 N HCl.

Volume changes, percentage inhibition efficiency, hydrogen evolution rate for different concentration of HCl solution with different concentration of inhibitor are depicted in table-2. From the table it is observed that inhibition efficiency increases with increasing strength of HCl solution and it also increases with increasing concentration of extract. The maximum inhibition efficiency has been observed in highest acid concentration i.e. 3 N HCl with highest concentration of inhibitor i.e. 0.8% (86.86%) for salvodra persica fruit extract.

Table 3 shows the corresponding data of reaction number (RN) with concentration of inhibitor in 1N, 2N and 3N HCl solution. Table 3 indicates that reaction number increases with increasing strength of HCl solution as well as it decreases with increasing concentration of inhibitor in each solution. The maximum efficiency has been observed in highest acid concentration i.e. 3 N HCl acid with highest concentration of inhibitor i.e. 0.8% (87.39%) for fruit extract.

Adsorption Studies

The effectiveness of organic compounds as corrosion inhibitors can be ascribed to the adsorption of molecules of the inhibitors through their polar functions on the metal surface [22]. Adsorption isotherm provides valuable information about the interaction of adsorbed molecules with each other and also on the metal surface. The method of adsorption (physiological or chemisorptions) is determined by the electronic structure of the metal, the nature of the corrosive substance and the chemical nature of the inhibitor [23].

To understand the nature of adsorption, Surface coverage values θ evaluated from weight losss measurements were fitted into different adsorption isotherms like Langmuir adsorption isotherm, Temkin adsorption isotherm, Freundlich adsorption isotherm and best results judged by the correlation coefficient (R2) was obtained with Langmuir adsorption isotherm.

Langmuir isotherm is given by the expression [24]:

$$\frac{c}{\theta} = \frac{1}{K} + C \qquad (8)$$

The free energy of adsorption was calculated from the equilibrium constant of adsorption using the equation [25] –

$$\Delta G°ads = - RT \ln (55.5K) \qquad (9)$$

Where, K = θ/c(1-θ) (from Langmuir equation) is the equilibrium constant of adsorption

θ = Surface coverage of the inhibitor
C = Concentration of the inhibitor:

Table 4 Thermodynamic adsorption parameters for mild steel surface in HCl

Acid concentration	*Salvodera persica* fruit		
	R^2	K_{ads}	ΔG^0
2 N HCl	0.96	11.69	-16.15
1 N HCl	0.92	10.86	-15.96
0.5 N HCl	0.93	6.42	-14.65
0.1 N HCl	0.95	1.28	-10.64

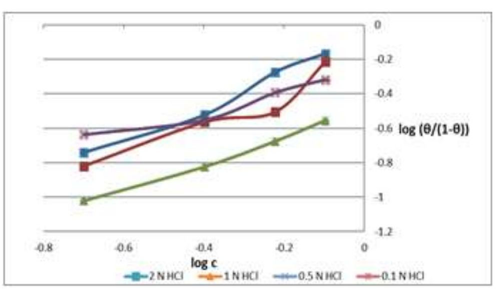

Figure 4: Langmuir isotherm for the adsorption of salvodera persica fruit extract on the mild steel surface in HCl

The negative values of ΔGads indicate that the adsorption of salvodera persica fruit on the mild steel surface is spontaneous. The value of ΔGads around − 20 kJ/mol or lower supports the electrostatic interaction (physisorption) between the adsorbent and adsorbate and −40 kJ/ mol or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of metal bond (chemisorptions). The adsorption of salvodera persica fruit on mild steel surface in HCl is physisorption.

IV. CONCLUSION

Weight loss, gasometric method and thermometric method show that Salvodera persica is a good corrosion inhibitor for mild steel in HCl solution. The maximum inhibition efficiency shown by fruit extract was 91.74% for 0.8% concentration in 2 N HCl. All method show same trend for corrosion inhibition efficiency and methods are in good agreement with each other.

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