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Corrosive Inhibitive Study of Stainless Steel in Hydrochloric Acid Using Eco-Friendly *Sesmum Indicum* Oil

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ABSTRACT

The inhibitive and adsorptive properties of *Sesmum indicum* eco-friendly oil for stainless steel corrosion in hydrochloric acid was investigated using weight loss technique as well as electrochemical technique. The result has proved that the oil is excellent inhibitor for stainless steel in hydrochloric acid. The inhibition efficiency of oil for stainless steel increased with increase the amount of oil. The mechanism of the oil on the surface of stainless steel was found to be spontaneous, exothermic and physical adsorption. The experimental data fitted well to Langmuir adsorption isotherms. Obtained results were justified from the galvanostatic polarization method.

Keywords: Langmuir adsorption, Weight loss technique, *Sesmum indicum* oil, Electrochemical technique.

INTRODUCTION

Stainless steel's strength, resistance to corrosion and low maintenance make it the ideal material for a wide range of applications such as pharmaceutical industry, architecture, medical, energy, heavy industry, construction, automotive, transportation, food and catering.

Corrosion is chemical or electrochemical reaction between materials, usually a metal, and its environment that produces a deterioration of the material. The annual loss due to corrosion has been estimated for any country at about 4 percent of gross domestic product.

In stainless steel there are some amounts of chromium which can be able to forms a passive film, this passive film can protect metal from corrosive medium. Corrosion inhibitors can protect passive film from corrosive medium. Due to chloride ions pitting corrosion is occur in stainless steel which

is a great problem, face by engineers. Generally the loss of equipment is done by pitting corrosion. Many organic compounds have been studied as corrosion inhibitor for different metals [1-8]. Larger amount of organic compounds have been use as inhibitor but they are poisonous and expensive, some eco-friendly, less costly and green inhibitors are substitute of organic inhibitors [9-12]. Due to above reason in the present study eco-friendly *Sesmum indicum* oil has been tested for corrosion inhibitive property for the stainless steel metal in 0.5N hydrochloric acid.

EXPERIMENTAL

Weight loss method

Material preparation

Stainless steel coupons with major amount of iron (80%) and lesser amount of chromium (14%) with rectangular size 3×2×0.2 cm. were used for mass loss method. These coupons washed with acetone and double-distilled water, dried in electrical oven and then stored in dessicator. The same metal was used for polarization studies in which metal was coated with araldite and only 1.0 cm^2 area was opened for electrochemical study.

Solutions

0.5N HCl was prepared in AR grade chemical for mass loss and polarization study. The amount of *Sesmum indicum* in corrosive medium was of 1.0g to 6.0g in 1000ml for mass loss method and 1.0g to 5.0g in 1000ml corrosive medium for polarization studies.

CR (Corrosion rate) computation

The data of mass loss was determined using following method reported earlier [13]. Experiment was done in repeatedly in test solution. All of first the coupons of stainless steel weighted and after this all are dipped in test solutions, which containing 0.5 N HCl with absence and presence of oil by the hooks, which are made by glass. The stainless steel coupons got back from the tested solution. The coupons rubbed for clean and after this dried in electrical oven, again weight and loss of weight was evaluated. This method have been repeated for different immersion

Table 1: %IE, CR and surface covered by metal evaluated by mass loss experiment with stainless steel in hydrochloric acid (Experiment period : 1h)

Concentration of oil(gram/liter)	Loss of metal (gram)	Efficiency of inhibitor (%)	CR (mmpy)	Surface covered by inhibitor (θ)
0.00	0.0115	-	9.093	-
1.00	0.0028	75.65	2.214	0.7565
2.00	0.0025	78.28	1.97	0.7828
3.00	0.0021	81.73	1.66	0.8173
4.00	0.0018	84.34	1.56	0.8434
5.00	0.0015	86.95	1.18	0.8695
6.00	0.0012	89.56	0.94	0.8956

Table 2: %IE, CR and surface covered by metal evaluated by mass loss experiment with stainless steel in hydrochloric acid (Experiment period: 3h)

Concentration of oil(gram/liter)	Loss of metal (gram)	Efficiency of inhibitor (%)	CR (mmpy)	Surface covered by inhibitor (θ)
0.00	0.0150	-	3.95	-
1.00	0.0051	66	1.34	0.66
2.00	0.0045	70	1.18	0.70
3.00	0.0040	73	1.05	0.73
4.00	0.0036	76	0.94	0.76
5.00	0.0030	80	0.79	0.80
6.00	0.0024	84	0.63	0.84

times 1hour, 3 hours, 6 hours, 15 hours and 24 hours at room temperature (298K).

The corrosion rate (CR) was evaluated by following formula:

$$CR\ (mmpy) = \frac{87.6\ W}{dAt} \quad ...(1)$$

In above formula d = density of the coupon (gcm^{-3}), W = mass loss of metal (mg), A = area of the coupon (square inch) and t = time (hrs).

The %IE with eco-friendly *Sesmum indicum* oil calculated using the following formula:

$$\%IE = 1 - \frac{W_i}{W_0} \times 100 \quad ...(2)$$

Where W_o = Mass loss of the stainless steel specimens in the absence of *Sesmum indicum* oil and W_i = Mass loss of the stainless steel specimens in presence of *Sesmum indicum* oil.

The θ which is surface coverage was evaluated by following formula (3)

$$\text{Surface coverage } (\theta) = 1 - \frac{W_i}{W_o} \quad ...(3)$$

Electrochemical procedure

The galvanostatic polarization was done with three-electrode polarization cell. Polarization method have a working electrode which was prepared by stainless steel metal with $1cm^2$ open area, auxiliary electrode which was prepared by platinum, reference electrode which was prepared by saturated calomel electrode.

Experimental results

The inhibitor efficiency (IE %) of *Sesmum indicum* oil, degree of surface coverage (θ) by *Sesmum indicum* oil and CR (corrosion rate) with variable amount of the inhibitor in 0.5N HCl for 1hour, 3hours, 6hours, 15hours and 24hours immersion periods and different kinetic and thermodynamic parameters were evaluated by weight loss method.

Table 3 %IE, CR and surface covered by metal evaluated by mass loss experiment with stainless steel in hydrochloric acid (Experiment period: 6h)

Concentration of oil(gram/liter)	Loss of metal (gram)	Efficiency of inhibitor (%)	CR (mmpy)	Surface covered by inhibitor (θ)
0.00	0.0180	-	2.37	-
1.00	0.0071	60.55	0.93	0.6055
2.00	0.0068	62.22	0.89	0.6222
3.00	0.0064	64.44	0.84	0.6444
4.00	0.0055	69.44	0.72	0.6944
5.00	0.0047	73.88	0.61	0.7388
6.00	0.0038	78.88	0.50	0.7888

Table 4: %IE, CR and surface covered by metal evaluated by mass loss experiment with stainless steel in hydrochloric acid (Experiment period: 15h)

Concentration of oil(gram/liter)	Loss of metal (gram)	Efficiency of inhibitor (%)	CR (mmpy)	Surface covered by inhibitor (θ)
0.00	0.0225	-	1.18	-
1.00	0.0095	57.77	0.50	57.77
2.00	0.0086	61.77	0.45	61.77
3.00	0.0081	64.00	0.42	64.00
4.00	0.0073	67.55	0.38	67.55
5.00	0.0067	70.22	0.35	70.22
6.00	0.0061	72.88	0.32	72.88

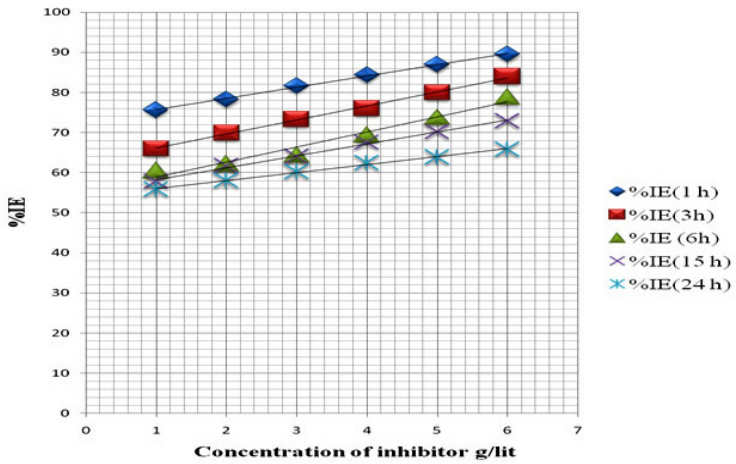

Fig. 1: Increasing of %IE with concentration of *Sesmum indicum* oil for stainless steel (immersion time periods: 1 hour, 3 hour, 6 hour, 15 hour and 24 hour) in 0.5N HCl.

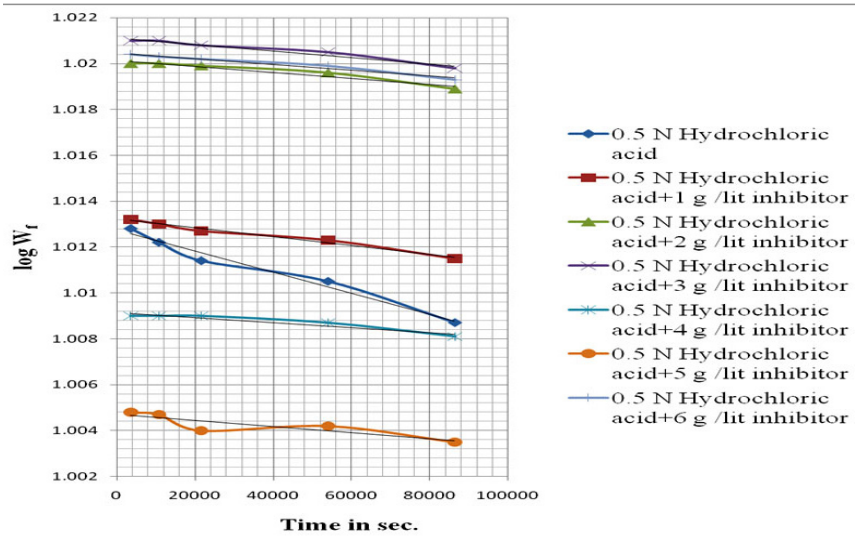

Fig.2: Chemical kinetic of stainless steel in hydrochloric acid absence and presence of oil.

Table 5: %IE, CR and surface covered by metal evaluated by mass loss experiment with stainless steel in hydrochloric acid (Experiment period: 24h)

Concentration of oil(gram/liter)	Loss of metal (gram)	Efficiency of inhibitor (%)	CR (mmpy)	Surface covered by inhibitor (θ)
0.00	0.0410	-	1.35	
1.00	0.0181	55.85	0.59	0.5585
2.00	0.0172	58.04	0.56	0.5804
3.00	0.0163	60.24	0.53	0.6024
4.00	0.0154	62.43	0.50	0.6243
5.00	0.0148	63.90	0.48	0.6390
6.00	0.0140	65.85	0.46	0.6585

Electrochemical parameters were evaluated by galvanostatic polarization method. Different parameters evaluated from mass loss procedure are presented in tables 1 to 5. In 0.5N HCl at 1g/lit of *Sesmum indicum* oil, there is 75.65% inhibition observed for immersion time 1 hour. On increasing the concentration 1 to 6 g/lit, the inhibition increases up to 89.56%. When the duration of immersion varied from 1 hour to 24 hours inhibitor efficiency decreases.

Weight loss measurements indicate that the dissolution rate decreases to significant extent due to the presence of oil especially at high concentrations. The inhibition efficiency is maximum on immersion time 1 hour at 6g/lit *Sesmum indicum.* The maximum inhibition efficiency for immersion time 24 hours at 6g/lit *Sesmum indicum* is 65.85%.The graph which is present in figure 1 shows that %IE is varies with the amount of the *Sesmum indicum* oil with variable experimental times like 1 hour, 3 hours, 6 hours, 15 hours and 24 hours.

Table 6: Kinetic parameter study of protection and destruction of stainless steel in acidic medium with and without of oil

***Sesmum indicum* oil Amount (gram/liter)**	**k(s^{-1})**	**$t_{½}$(s)**
0.00	1.15×10^{-7}	5.02×10^{6}
1.00	4.6×10^{-8}	1.50×10^{7}
2.00	2.3×10^{-8}	3.0×10^{7}
3.00	2.3×10^{-8}	3.0×10^{7}
4.00	2.3×10^{-8}	3.0×10^{7}
5.00	2.3×10^{-8}	3.0×10^{7}
6.00	2.0×10^{-8}	3.4×10^{7}

Table 7: Adsorption parameters of *Sesmum indicum* oil on the stainless steel surface in hydrochloric acid for different experimental periods

Experimental Time periods	**K_{ad}**	**Slope**	**$-\Delta G_{ads}$**	**R^2**
1 hour	2.71	1.0	25.39	0.9979
3hour	1.77	1.1	20.02	0.9943
6 hour	1.27	1.1	17.17	0.9861
15 hour	1.63	1.2	19.22	0.9964
24 hour	2.10	1.4	21.91	0.9983

Corrosion kinetics of stainless steel in hydrochloric acid with inhibitor

Figure 2 present a graph which shows log W_i (weight of stainless steel at time t) is change with time, the evaluated data putted in to the rate law for first order reaction. The plots are linear, which concluded that the reaction with stainless steel in test solution follows first order kinetic [14-15]. The rate constants measured from the figure 2 are concluded in table 6.

$$\log \frac{Wi}{\Delta Wt} = -\frac{k}{2.303} t + \log Wi \quad ...(4)$$

The half-life ($t_{1/2}$) evaluated from equation giving below.

$$(t_{½})=0.69k \quad ...(5)$$

The half life were evaluated by above formula are shows in table 6 which clearly shows that rate constant inversely proportional of half life which conclude the protection of metal by inhibitor.

Thermodynamic parameters of stainless steel in hydrochloric acid with inhibitor

The graph of C/ θ vs C presents linearity in figure 3. This conclude that adsorption of oil molecules on stainless steel metal surface follows Langmuir isotherm. According to Langmuir adsorption isotherm degree of surface coverage (θ) of stainless steel and the concentration of the inhibitor in hydrochloric acid are related to following formula (6).

$$C/\theta = 1/K_{ad} + C \quad ...(6)$$

Average values for free energy of adsorption (ΔG_{ads}), were calculated using the following equations 7.

$$\Delta G_{ads}=-RT \ln(55.5K) \quad ...(7)$$

K = equilibrium constant, R = gas constant and T = temperature. It is found that the ΔG_{ads} values for the studied compound are less than -40 kJ mol^{-1}, indicating that the *Sesmum indicum* oil are physically adsorbed on stainless steel. The less and negative value of ΔG_{ads} shows the spontaneous adsorption reaction of the oil on the stainless steel [16-18].

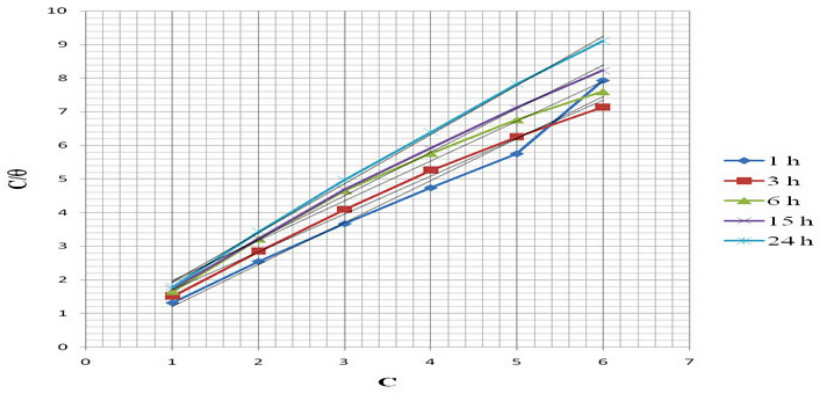

Fig. 3: Langmuir adsorption isotherm with stainless steel in hydrochloric acid with different amount of oil for different experimental time

Table 8: Electrochemical polarization parameters for stainless steel in hydrochloric acid without and with *Sesmum indicum* oil

Sesmum indicum oil Concentration (gram/liter)	$-E_{corr}$ (V)	Tafel slopes (V.dec^{-1})		I_{corr}(A.cm^{-2})	IE%
		b_c	b_a		
0.00	0.429	7.601	6.765	3.163×10^{-4}	-
1.00	0.432	4.153	8.542	1.103×10^{-4}	65.13
3.00	0.430	8.647	14.88	5.929×10^{-5}	81.25
5.00	0.443	9.504	6.506	5.207×10^{-6}	98.35

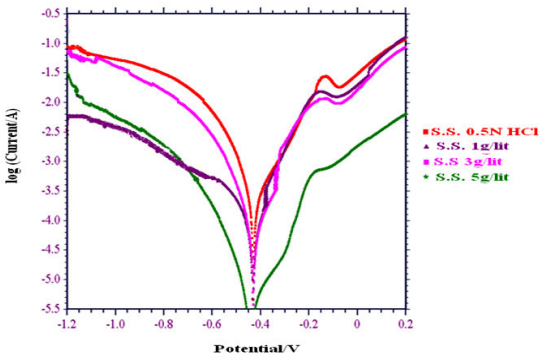

Fig. 4: Polarization curve of stainless steel in 0.5N HCl without and with of oil concentrations

Galvanostatic polarization studies

The polarization data of stainless steel working as a cathode and an anode in absence and presence of *Sesmum indicum* oil with hydrochloric acid is shown in figure 4. The electrochemical polarization parameters concluded from figure 4 like corrosion current I_{corr}, Tafel constant b_a, b_c and E_{corr} are tabulated in table 8.

A decrease in the corrosion current and increase in the cathodic and anodic Tafel slopes have been observed with the grater in the amount of oil. E_{corr} values have not significant change with the addition of inhibitor. The inhibition efficiencies determined from the values of corrosion current are found to be in comparable with those obtained from weight loss measurement. The inhibition efficiencies determined by following equation:

(Inhibitor efficiency) $IE\% = 1-(I^1_{corr} / I_{corr})\times100$ ...(8)

In the present equation I_{corr} = current densities with *Sesmum indicum* oil in 0.5N hydrochloric acid I^1_{corr} = current densities without of *Sesmum indicum* oil in hydrochloric acid. The presence of passive region in the graph as shown in figure 4 may be due to the protection layers of chromium and iron oxide formed from their respective

metals present in stainless steel. Chloride ions which are present in hydrochloric acid destroy the protective layers which are made by oil and generate pits on the stainless steel surface. $I_{critical}$ is maximum when no inhibitor was added to 0.5N HCl (uninhibited solution) the values of $I_{critical}$ decreases with increased concentration of inhibitor suggesting inhibitor is capable of reducing corrosion.

CONCLUSIONS

By the evaluated data from weight loss and polarization study the following conclusion can be explain:

1. The eco friendly *Sesmum indicum* oil was concluded as a best inhibitor for stainless steel in 0.5N hydrochloric acid.
2. Inhibition efficiency directly proportional with the amount of *Sesmum indicum* oil content up to 6g/liter to reach 89.56% in 0.5N HCl at room temperature.
3 Kinetics analyses of data showed linear variations, which confirm a first order kinetics in hydrochloric acid.
4. The above research concluded that adsorption of oil molecules on stainless steel metal surface follows Langmuir isotherm in hydrochloric acid medium.
5. The less and negative value of ΔG_{ads} shows the spontaneous adsorption reaction of the *Sesmum indicum* oil on the stainless steel surface.
6. Obtained results were justified from the galvanostatic polarization method.
7. The values E_{corr} obtained from galvanostatic polarization method are mostly constant, by this we can conclude that *Sesmum indicum* oil work as mixed type in hydrochloric acid and retard both the reaction in equal amount on anodic and cathodic ends.

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