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Study of Green and Eco Friendly Corrosion Inhibitor to Protect the Iron in Acidic Environment

Anurag Sharma^{*1}, Anil Kumar Varshney², Sarita Varshney²

¹Swami Keshvanand Institute of Technology Management and Gramothan, Jaipur, Rajasthan, India. ²Department of Chemistry, University of Rajasthan, Jaipur, Rajasthan, India. ***Corresponding author's E-mail:** anuragsharma20oct@yahoo.co.in

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ABSTRACT

Literature reveals that numbers of organic compounds are known to be applicable as corrosion inhibitors for metal in acidic environments. Such compounds typically contain nitrogen, oxygen or sulphur in a conjugated system and function via adsorption of the molecules on the metal surface, creating a barrier to corrosion attack. But, unfortunately they have the unwanted destructive effect on environment, aquatic and animal life and expensive as well. Therefore, plants, natural product extracts, natural oils have been posed to achieve the target of employing as a cheap, environmentally acceptable, abundant source, readily available and effective molecules having very high inhibition efficiency and low or zero environmental impact. The inhibitory action of green and eco-friendly *sesmum indicum* oil on the corrosion of iron in 0.5 N hydrochloric acid was studied using gravimetric and galvanostatic polarization techniques. The corrosion rates of iron in the HCl acid solution containing *sesmum indicum* oil were measured as a function of the inhibitor concentration. The inhibitor efficiency depends on the concentration of the *sesmum indicum* oil. Adsorption of *sesmum indicum* oil on iron surface was found to obey the Langmuir adsorption isotherm. The phenomenon of physical adsorption has been proposed on the basis of obtained thermodynamic parameters. Results from this study showed that *sesmum indicum* oil was an attractive alternative to prevent corrosion as it shows the great inhibition efficiency.

Keywords: Corrosion, Gravimetric technique, Sesmum indicum, Galvanostatic polarization.

INTRODUCTION

he appearance of corrosion is an interface problem between a metal and gaseous leading to a destruction of metallic materials. This phenomenon took today a considerable importance in view of the increasing use of different metals in modern life. It is a very common in industries used the acids such as acid pickling, industrial cleaning. The search for new and efficient corrosion inhibitors has become a necessity to protect metallic materials against corrosion. The considerable efforts have been made to find suitable compound of organic origin to be used as corrosion inhibitors in various corrosive media, to either stop or delay to the maximum attack of a metal. On account of the known hazardous effects of most synthetic organic inhibitors and the need to develop cheep, non-toxic and environmentally benign processes, the efforts have been made by several researchers to focus on the use of natural products as corrosion inhibitor. $^{1\cdot8}$ Some of the natural oils are also found to be the good corrosion inhibitor like natural Artemisia oil on steel and Jojoba oil on aluminium.⁹⁻¹⁰ It has also been found that substances containing polar functions with nitrogen, sulphur and oxygen in conjugated system exhibit good corrosion inhibiting property.¹¹ The oil of Sesmum indicum is rich in manganese, copper and also contains vitamin B₁ (thiamine) and vitamin E (tocopherol). They contains lignans such as sesamol, sesamin and sesamolin. The percentage composition of fatty acid is 44%, stearic acid 4.2%, palmitic acid 9% and arachidic acid 0.7%.¹² The presence of sesamol, sesamin and sesamoline in Sesmum *indicum* oil worked as inhibitor in 0.5N HCl solution. Thermodynamic, electrochemical and adsorption parameters for iron in absence and presence of the inhibitor were evaluated and interpreted.

In view of the above, it was spurred us to study the effects of *Sesmum indicum* oil on corrosion of iron in 0.5N HCl solution by using gravimetric method and galvanostatic polarization method.

METHODOLOGY

Materials

The experiments were performed with iron coupons of the 99.5% pure iron.

Solutions

The test solutions used were made of AR grade HCl. Appropriate concentration (0.5N) of acid was prepared using de-ionized water in the absence and presence of various concentrations of *Sesmum indicum* oil. The employed concentration range of *sesmum indicum* was of 1g to 6g in 1000ml of 0.5N hydrochloric acid.

Corrosion Rates Measurements

The non-electrochemical technique of weight loss was done in order to determine the corrosion rate and percentage of inhibition.

This physical measurement will provides direct result on how the corrosive environments affect the test samples and also to give the average corrosion rate during the experiment.



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In each experiment, the test specimen's size $3 \times 2 \times 0.2$ cm were became smooth with a series of emery paper from different grades.

Then, the specimens were washed several times with deionized water, dried and stored in a desiccator. After weighing accurately, these were suspended with the help of glass hooks in 50 ml beakers containing 50 ml of 0.5 N HCl in absence and presence of a certain concentration of *sesmum indicum*.

After 300 minutes, the specimens were taken out, washed with water, dried in oven and reweighed accurately. Each reported value was a mean of the duplicate experiments results for each case.

The difference between the weight at a given time and the initial weight of the coupons was taken as the weight loss which was used to calculate the corrosion rate given by:

Where W is the weight loss in mg, ρ is the density of the specimen (gcm⁻³), A the area of the specimen in square inch and *t* the exposure time (hrs).

The inhibition efficiency of *Sesmum indicum* acting as inhibitor in 0.5 N HCl was calculated using the following expression:

$$\text{%IE} = (1 - (W_i / W_0) \times 100)$$
 (2)

Where W_o and W_i are the weight loss of the iron coupons in the absence and presence of inhibitors respectively in HCl at the room temperature. The degree of surface coverage (θ) was calculated from equation (3).

$$\theta = 1 - (W_i / W_0) \tag{3}$$

Electrochemical Polarization Method

In this method potentiostat connected to a cell with three electrodes. The working electrode iron metal with the surface area of 1 cm^2 . A saturated calomel electrode (SCE) was used as a reference.

All potentials were given with reference to this electrode. The counter electrode was a platinum plate of surface area of 1 cm^2 .

For polarization curves, the working electrode was immersed in a test solution without and with different concentrations of oil during 60 min until a steady state opens circuit potential (ocp) was obtained.

RESULTS AND DISCUSSION

Gravimetric Measurements

The loss of weight of iron coupons due to their immersion in solutions of 0.5 N HCl containing different concentrations of *sesmum indicum* was measured.

It was found that the addition of *sesmum indicum* lowers the weight loss of the iron than its value in the free acid solution. The result indicates that the *sesmum indicum* oil acts as effective inhibitor for iron corrosion in hydrochloric acid solution.

The inhibitive action of oil could be attributed to the adsorption of their molecules on the iron Surface. Hydrocarbon chains were oriented towards aqueous solution. These hydrocarbon chains being hydrophobic in nature repel the corrosion anions away from the metal surface thus forming a barrier between the metal and the corrosive environment.

The inhibition efficiencies (IE %), Corrosion rate (mmpy) and surface coverage (θ) of different concentrations of the *Sesmum indicum* oil are given in (Table 1) and inhibitor efficiencies (IE %) with concentration of oil shown in (Figure 1).

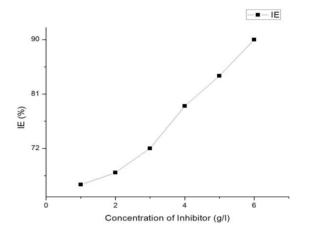


Figure 1: Variation of inhibition efficiency of iron with concentration of inhibitor in 0.5 N HCl solutions (immersion time: 5h)

Thermodynamic and Adsorption Consideration

The spontaneous corrosion of iron in acidic solutions can be represented by the anodic dissolution reaction

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

Accompanied by the corresponding cathodic reaction

$$2H^+ + 2e^- \rightarrow H_2$$

Experimental data obtained for degree of surface coverage (θ) were applied for different adsorption isotherm equations including Langmuir, El-Awady, Frumkin, Freundlich, Bockris-Swinkel, Temkin and Florry - Huggins. The results revealed that the isotherms that best described the adsorption characteristics of *sesmum indicum* oil on iron surface are Langmuir adsorption. According to Langmuir adsorption isotherm degree of surface coverage (θ) and the concentration of the inhibitor in the bulk electrolyte are related to following equation (4).

$$C/\Theta = 1/K_{ad} + C$$
 (4)

Where C is the inhibitor concentration in the bulk of solution, K_{ad} is the equilibrium constant of adsorption of *Sesmum indicum* oil on iron surface.



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From equation 4, a plot of C vs C/ θ in figure 2 produces a straight line.

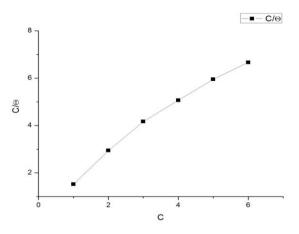


Figure 2: Langmuir adsorption isotherm of the inhibitor *sesmum indicum* oil (immersion time -5h)

The free energy of adsorption of iron is related to the equilibrium constant of adsorption according to equation (5).

$$G_{ads} = -2.303 RT \log (55.5 K_{ad})$$
 (5)

Where R is the gas constant and T is the temperature.

Results presented in the (Tables 2) indicate that the values of G_{ads} are negative in all cases. The negative values indicate a spontaneous adsorption of the inhibitor molecules. The low values of G_{ads} also suggest that the inhibitor (*Sesmum indicum*) is physically adsorbed on the surface of the metal.¹³⁻¹⁸

Polarization Method

Anodic and cathodic polarized potentials were measured in the absence and presence of *sesmum indicum*. Figure 3 shows the anodic and cathodic polarization curves for *sesmum indicum* in 0.5N HCl in the presence and absence of inhibitors at different concentration. Electrochemical parameters such as the corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (b_a and b_c), corrosion current density (i_{corr}), %IE are given in (Table 3). It is evident from figure 3 that anodic and cathodic curves both are polarized. The adsorptions of the inhibitor molecules on the metallic surface blocks the active sites and thus retard corrosion.

The inhibition efficiency was calculated using the relation:

$$IE\% = \frac{I_{corr}}{I_{corr}} \times 100$$
 (6)

Where I_{corr} and I_{corr}^1 are corrosion current densities in the presence and absence of *sesmum indicum* oil. E_{corr} values do not show any signification change suggesting *sesmum indicum* oil is mixed type inhibitor. The results obtained from the polarization technique were in good agreement with those obtained from the weight-loss method with a small variation.

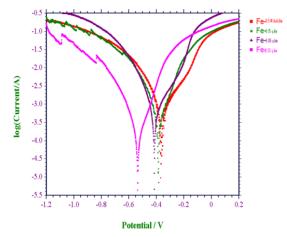


Figure 3: Cathodic and anodic polarization curve of iron in 0.5N HCl at different concentration of *Sesmum indicum* oil

Table 1: Inhibitor efficiency (%IE), corrosion rate and surface coverage (at room temperature) obtained from gravimetric method for iron in 0.5N HCI (Immersion time: 5h)

Concentration of Inhibitor (g/lit)	ΔW (g)	% IE	Corrosion Rate (mmpy)	Surface Coverage (θ)
-	0.0210	-	21.54	-
1	0.0072	66	7.38	0.66
2	0.0068	68	6.97	0.68
3	0.0060	72	6.15	0.72
4	0.0045	79	4.61	0.79
5	0.0035	84	3.59	0.84
6	0.0023	90	2.35	0.90



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Table 2: Langmuir adsorption parameter for the adsorption of sesmum indicum oil on the surface of iron.

Temperature (k)	K _{ad}	Slope	-ΔG _{ads}	R ²
298	1.22	1.019	10.44	0.9799

Table 3: Electrochemical polarization parameters: corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (b_a and b_c), corrosion current density (i_{corr}), %IE using iron in 0.5N HCl with and without *sesmum indicum* oil.

Inhibitor	F (\)	Tafel slopes (V.dec ⁻¹)		() am ⁻²)	IE%
Concentration (g/lit)	-E _{corr} (V)	b _c	b _a	I _{corr} (A.cm ⁻²)	IE 70
0.0	0.369	6.354	5.508	8.258×10 ⁻⁴	-
1.0	0.416	8.140	6.027	7.347×10 ⁻⁴	11.03
3.0	0.386	7.529	10.65	4.235×10 ⁻⁴	48.72
5.0	0.535	8.071	11.93	1.502×10 ⁻⁴	81.81

CONCLUSION

The work presented in this paper is a contribution to study the possibilities to use of a new type of corrosion inhibitors called green inhibitors.

The following conclusions can be drawn from the results:

- Sesmum indicum oil is excellent inhibitor for corrosion of iron in hydrochloric acid showing 90% efficiency at 6g/l concentration. The results obtained from mass loss and galvanostatic polarization methods are good agreement at room temperature.
- 2. Percentage inhibitor efficiency increased with increase the amount of *Sesmum indicum* oil.
- 3. The square correlation coefficient (R²) was used to choose the adsorption isotherm that fits experimental data. The oil of *Sesmum indicum* adsorption of the oil on the iron surface in 0.5 N HCl follows the Langmuir adsorption isotherms.
- 4. The negative value of free energy $(-\Delta G_{ads})$ shows that inhibition by *Sesmum indicum* oil on the iron surface is spontaneous.
- 5. The values of E_{corr} (by the galvanostatic polarization) are almost constant indicating that the inhibitor behavior as a mixed type in nature in 0.5N HCl blocking both anodic and cathodic reaction to equal extent.

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Corresponding Author's Biography: Dr. Anurag Sharma				
/ERS	Dr. Anurag Sharma is doctorate from Rajasthan University under the supervision of Dr. Sarita Varshney Associate Professor University of Rajasthan, Jaipur. He is working as Assistant Professor in Swami Keshvanand Institute of Technology, Management & Gramothan, Jaipur, Rajasthan. He is having 10 year teaching and research experience.			

