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EXPERIMENTAL AND THEORETICAL STUDY OF INHIBITION EFFECT OF *TRIBULUS TERRESTRIS* ON CORROSION OF ALUMINIUM IN ACIDIC MEDIUM

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Abstract : The simplest and direct way to apply green chemistry in corrosion protection, is to utilize eco-friendly, non-hazardous, reproducible and efficient green corrosion inhibitors (extracts of plant materials). The corrosion inhibition efficacy of alcoholic extract of different aerial parts of plant *Tribulus terrestris* for aluminium in acid media has been studied in relation to the concentration of inhibitor by mass loss method. It has been observed that the *Tribulus terrestris* alcoholic extract acts as a good corrosion inhibitor in acidic solution and the adsorption of the extract provides a good protection against aluminium corrosion. It has been observed that the inhibition efficiency increases with inhibitor concentration. The negative sign of the free energy of adsorption indicates that the adsorption of the inhibitors on the aluminium surface was a spontaneous process and was found to be physisorption. Adsorption process follows Langmuir adsorption isotherm.

Keywords **- Corrosion, Inhibitors, *Tribulus terrestris*, Langmuir adsorption isotherm.**

1. INTRODUCTION

Corrosion of metal is a major industrial problem and many current corrosion control methods use coating and conversion layers which contain toxic and environmentally hazardous material [1]. Therefore, a great need to investigate a nontoxic replacement that is compatible with current industrial technologies with their availability and relatively low cost, naturally substances. A lot of investigations have been done to work out on the use of natural plant extracts as corrosion inhibitors for Aluminium [2-5]. In the present work, an attempt has been made to study the influence of varying concentration of alcoholic extracts of fruits, leaves and stem constituents of plant *Tribulus Terrestris* on the corrosion rate of aluminium in sulphuric acid. The *Tribulus Terrestris plant* belongs to the zygophyllaceae family. *Tribulus terrestris* is an annual creeping herb widespread in large area of India, China, eastern Asia, and extends into western Asia and southern Europe. In Ayurvedic medicine, *Tribulus terrestris* is referred to as *Gokshura* or *Chhota Gokshura* for the treatment of lower back pain, sciatica, inflammation of the pelvic and sacral region, dry cough and respiratory disorders [6,7].

2. EXPERIMENTAL

For the study of corrosion inhibition efficiency of *Tribulus terrestris*, mass loss method has been employed.

Specimen preparation – The aluminium sheets of Gauge 25 (0.045cm) were purchased from local market. For the mass loss determination, rectangular specimen of aluminium of size 3.0 x 2.5 cm, were cut from a sheet containing a small hole of about 3mm diameter near upper edge were used for experiment. To clean the specimens were abraded with various grades of wax coated emery paper (1/0,2/0,3/0,4/0) and successively washed with benzene and soap and distilled water and finally with acetone then dried and weight. The metal coupons were then suspended with the help of glass hooks in borosil beakers containing 50 ml of corrosive electrolyte for complete immersion test.

Test solution preparation - The solution of 1.0 N H_2SO_4 were prepared using doubly distilled water. The Senegal extract was obtained by dried the parts of plants, then finely powdered and extracted with boiling methanol in a Soxhlet appratus.

To observe the influence of various parameters, Inhibition efficiency (IE%), degree of surface coverage (θ) and corrosion rate (mmpy) were calculated by mass loss method.

The inhibitor efficiency (IE%) can be calculated as [8]

$$IE\% = 100(\Delta Mu - \Delta Mi / \Delta Mu) \quad (1)$$

The degree of surface coverage (θ) can be calculated as

$$\theta = \Delta Mu - \Delta Mi / \Delta Mu \quad (2)$$

Where, ΔMu = mass loss of metal in uninhibited acid and ΔMi = mass loss of metal in inhibited solution

The corrosion rate(CR) in milli meter per year can be obtained by the following equation [9].

$$CR = \frac{8.76x10^4 x\Delta M}{A\,x\,T\,x\,D} \quad (3)$$

Where, mass loss in gram, Area is in cm^2 of metal surface, exposed time is expressed in hours and metal density is expressed in $gram/cm^3$. The density of aluminium sheets is 2.7 gm/ cm^3.

Adsorption Isotherm

Langmuir Adsorption Isotherm equation shown as

$$\log(\theta/1-\theta) = \log C + \log K_{ads} \quad (4)$$

Where, C is concentration of inhibitor, θ is surface coverage and K_{ads} is adsorption equilibrium constant.
According to Langmuir Adsorption Isotherm straight line should be obtained when a graph is plotted between log(θ/1-θ) versus log C with gradient equal to one with the intercept equal to –log K_{ads} for the extract.

3. RESULTS AND DISCUSSION

Corrosion behavior of aluminium in 1.0 N concentration of sulphuric acid with and without inhibitor has been studied and the results are depicted in the Table -1. It is found that the inhibition efficiency increases with increases of inhibitor concentration for different plant extracts from 0.12%to 0.60% from the mass loss data as shown in Figure 1. The increase in inhibition efficiency may be due to the fact that the inhibition action takes place via adsorption of inhibitor molecule on metal surface [10]. So the IE of any substance is mostly expressed as relative reduction in corrosion rate and that depends on the amount of adsorbed inhibitor on metal surface. It is presumed that the corrosion reactions are nullified from the active sites of metal surface by covering it adsorbed inhibitor species, whereas the corrosion reactions take place usually on the inhibitor free area. Therefore, the inhibition efficiency is directly proportional to the fraction of surface covered with adsorbed substances [11]. In other words, we can say as concentration increases more number of inhibitor molecule are adsorbed on metal surface which results in larger surface coverage and the inhibitor molecule screen the coated part of metal surface from surrounding corrodent.

Inhibition efficiency α Inhibitor concentration

Table 1. Gravimetric parameters of aluminium in 1.0N H_2SO_4 with various concentrations of the inhibitor at 303±1 K.

Effective area of specimen – 15.0 cm^2 Immersion Time – 24 hrs.

Concentration of inhibitor w/v (%)	Mass loss, ΔM (mg)	Corrosion Rate, CR (mmpy)	Surface coverage, θ	Inhibition Efficiency, IE (%)
Blank	32.01	2.885	-	-
Fruit extract				
0.12	16.8	1.515	0.4749	47.49
0.24	14.7	1.321	0.5421	54.21
0.36	12.8	1.154	0.6000	60.00
0.48	11.3	1.017	0.6475	64.75
0.60	10.4	0.941	0.6738	67.38
Leaf extract				
0.12	17.5	1.579	0.4527	45.27
0.24	14.8	1.336	0.5369	53.69
0.36	13.6	1.230	0.5737	57.37
0.48	12.0	1.078	0.6263	62.63
0.60	11.0	0.987	0.6579	65.79
Stem extract				
0.12	19.0	1.711	0.4069	40.69
0.24	16.3	1.469	0.4908	49.08
0.36	14.8	1.330	0.5390	53.90
0.48	13.1	1.183	0.5899	58.99
0.60	12.7	1.142	0.6042	60.42

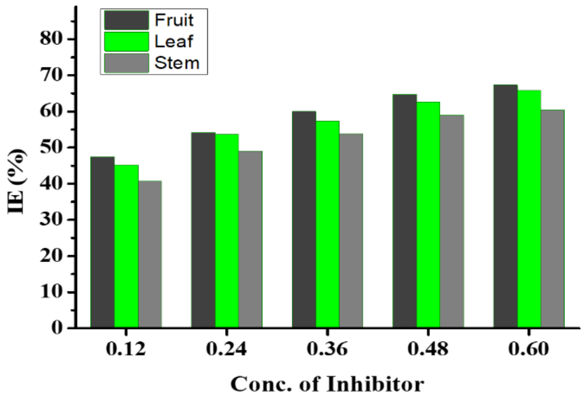

Figure 1: Variation of Inhibitor efficiency with extracts concentration for aluminium in 1N H_2SO_4 solution containing different parts of plant.

It was concluded that the plant extracts act as a good inhibitor for aluminium in acid solutions. Table-1 show that the inhibition efficiency is highest for fruit extract for followed by leaf and stem extract.

Fruit > Leaf > Stem

Langmuir Adsorption Isotherm

The Langmuir Adsorption Isotherm are plotted between log(θ/1-θ) versus log C shown in Figure 2. In present investigation, the plots are linear but gradient is not equal to unity. The deviation from unity behaviour can be explained on the basis of interaction of the adsorbed molecule on the metal surface. According to Langmuir, the adsorbed layer is unimolecular i.e. there is no interaction between adsorbed molecules themselves and between adsorbate and adsorbent molecules. There may be an interaction between adsorbed molecules themselves and between adsorbate and adsorbent molecules, that's why the gradient is not unity [12].

The estimated values of adsorption equilibrium constant (K_{ads}) and Gibbs free energy (ΔG^0_{ads}) are given in Table 3. K_{ads} is calculated from intercept of Langmuir Adsorption Isotherm and ΔG^0_{ads} is calculated by following equation.

$$\Delta G^0_{ads=} - RT ln(55.5\, K_{ads}) \quad (5)$$

Where, $\Delta G^0_{ads=}$ change in Gibbs free energy, Kads = adsorption equilibrium constant, T = absolute temperature, R = universal gas constant (8.314 J K^{-1} mol^{-1}), 55.5 =concentration of water (mol/litre)

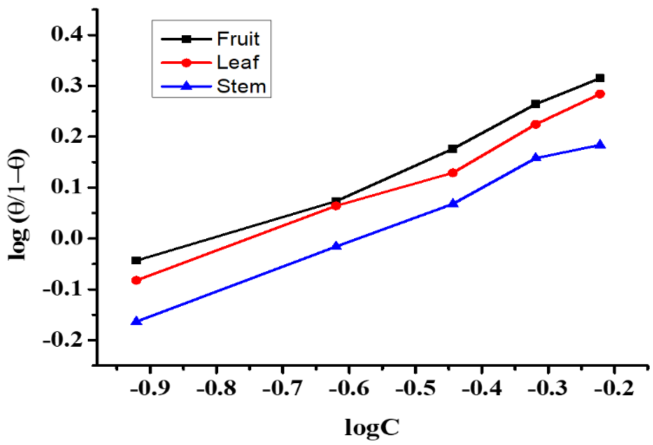

Figure 2: Langmuir adsorption isotherm curve for aluminium in 1.0N H_2SO_4 with *Tribulus terrestris* extract.

The negative values of $\Delta G°_{ads}$ ensure the spontaneity of adsorption process and stability of the adsorbed layer on the aluminium surface [13]. Generally, the values of $\Delta G°_{ads}$ around -20 kJ/mol or lower are consistent with physiosorption [14], while those around -40kJ/mol or higher involve chemisorptions. As shown in the Table, results obtained indicate that the values of $\Delta G°_{ads}$ are negative in all cases and are less than 20 kJ/mol. This is consistent with literature survey and therefore authenticates physical adsorption. This implies that the plant extracts adhere on the surface of the corroding system and so gives a very strong inhibitor.

Table – 2 Change in K_{ads} and $\Delta G°_{ads}$ for aluminium in 1.0 N H_2SO_4 with given inhibitor

Inhibitor	**K_{ads}**	**(ΔG^0_{ads}) ($KJmol^{-1}$)**
Fruit	1.0115	-10.15
Leaf	1.0241	-10.18
Stem	1.0322	-10.20

Conclusion

- It is concluded that the plant extract of *Tribulus Terrestris* is a good corrosion inhibitor for aluminium in sulphuric acid solutions.
- Inhibition Efficiency (IE%) increases with inhibitor concentration and maximum inhibition efficiency was observed for the fruit extract at the concentration of 0.60% w/v at 303K.
- The adsorption of different concentrations of the plant extract on the surface of the aluminium in 1N H_2SO_4 acid follows Langmuir adsorption isotherm.
- The negative sign of the free energy of adsorption indicates that the adsorption of the inhibitors on the aluminium surface was a spontaneous process and was found to be physisorption.
- This type of inhibitor are eco-friendly, biodegradable and less toxic therefore these type of inhibitors can be used to replace toxic chemicals.

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