COMPARATIVE STUDY OF CORROSION INHIBITION EFFICIENCY OF NATURALLY OCCURRING ECOFRIENDLY VARIETIES OF HOLY BASIL (TULSI) FOR TIN IN HNO_3 SOLUTION

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Abstract: *Weight loss technique has been used to study the corrosion inhibition efficiency of tin in HNO_3 solution by using the leaves and stem extract of different varieties of Holy Basil viz. ocimum basilicum (E_B), ocimum cannum (E_C) and ocimum sanctum (E_S). The results show that all the varieties under study are good corrosion inhibitors, among which leaves extract of E_B is the most effective. Corrosion inhibition efficiency increases with increasing concentration of inhibitor and it also increases with increasing concentration of HNO_3 solution. Inhibition efficiency was found maximum up to 95.83% for tin in 3.0 M HNO_3 solution, with 0.6% leaves extract whereas it was 81.25% in same concentration of HNO_3 solution for stem extract.*

Keywords: *Inhibitors, inhibition efficiency, weight loss, surface coverage.*

1. INTRODUCTION

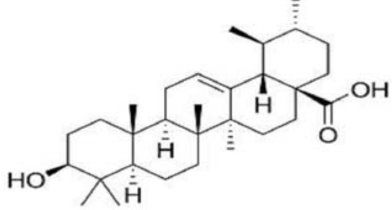
Tin and its alloys are found useful for many engineering applications because of their lightness and strength, thermal and electrical conductivity, heat and light reflectivity and hygienic and non-toxic qualities. Tin is a reactive metal according to the electrochemical series (Eo= -0.14V), but it is non reactive in moisture due to the formation of a stable oxide film on its surface. Tin is not attacked by pure water but dissolves in aqueous acids with the liberation of hydrogen gas. Acids like hydrochloric acid, sulphuric acid etc. are used for drilling operation, pickling and descaling. Many workers have studied corrosion of tin in HNO_3 solution.

Holy basil is a very common plant in India. It is antibacterial, anti-fungal and is used as an air purifier and anti-malarial from ancient times in Indian homes. Powder of its stem and leaves is used as medicine in balancing blood glucose management, to maintain a healthy digestive system, to encourage the efficient use of oxygen, to enhance the efficacy of many therapeutic treatments etc.

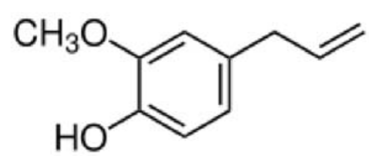
The importance of the study lies in the fact that natural plant products are non-polluting, ecofriendly, economic, less toxic and easily available than synthetic organic compounds. They are biodegradable and so can be used without any side adverse effects.

The chemical composition of ocimum sanctum is highly complex, containing many vitamins like A and C, calcium, zinc, iron, chlorophyll along with many other phytonutrients which are present in the extract of ocimum sanctum.

The major chemical constituents responsible for physico-chemical action of ocimum sanctum are volatile oil (0.1 to 0.9%), eugenol (60-70%), cavacrol (about 3.0%), eugenol methyl ether (20%) and other minor chemical constituents of ocimum sanctum are like alkaloids, glycoside, saponin, tannin, maleic acid, ursolic acid, citric acid and tartaric acid.



Ursolic acid



Eugenol

β-bisabolene (13-20%), methyl chavicol (3-19%), 1-8 cineole (9-33%), α- bisabolene (4-7%), α- terpineol (1.7-7%), campestrol, cholesterol, stigma sterol, β- sisterol and methyl ester of common fatty acid were the main constituents of the oil which are found in there species.

Generally, the organic compounds containing hetero atoms like nitrogen, oxygen and sulphur etc. have been found to be very effective corrosion inhibitors [5-7]. The efficiency of these compounds depends upon the electron density of hetero atoms. The inhibition efficiency also depends upon the number of adsorption active centers in the molecule, their charge density, molecular size and mode of adsorption and formation of metallic complexes. Atoms such as nitrogen, oxygen and sulfur are capable of forming coordinate covalent bond with metal owing to their free electron pairs. Compounds with π bonds like aldehydes, ketones, imines also generally exhibit good inhibitive properties due to interaction of π orbital with metal surface.

In addition to the heterogeneous organic compounds[1-5] like Schiff's bases, Mannic bases etc. which are synthesized in laboratory assist in inhibition, there are also some naturally occurring substances like Tarmerind tea leaves, Beet root[6, 7], Saponin [8], Terminalia bellerica[9], Oxandra asbeckii[10], Argemone Mexicana[11], Betanin[12], Henna [13], Wheat[14], Ginger [15], Marraya koeningii[16], Garlic extract [17], Ananas sativum[18], etc. have also been evaluated as effective corrosion inhibitors. The present study deals with the study of three varieties of Holy basil i.e. ocimum basilicum, ocimum sanctum and ocimum canum which are most common as corrosion inhibitors of Al in the most corrosive medium of HCl solution.

Several surface modification techniques such as ion implantation, surface laser melting, have been employed to improve pitting corrosion resistance of stainless steel by Momeni et. al.[19]. EXD analysis of the surface area of as received and electropolished specimens showed modification in surface roughness during electropolishing was the main reason of pitting corrosion improvement. Scanning micropy investigation of polarized specimens beyond the pitting potential revealed that in as-receives specimen pits were nucleated in at and in the vicinity of surface scratches that was created during surface abrading. Scanning electron microscopy examination of anodically polarized of sensitized specimen at 700 mV prior and after oxalic acid etching revealed large stable pits with lacy cover and also open pits with deep crevice for etched specimens studied by Moayed et. al.[20]. An investigation of the electrochemical noise generation during Stress Corrosion Cracking (SCC) of 70-30 Brass in Matton's was conducted by Sermi et. al.[21]. It is shown that 70-30 Brass has characteristic noise behavior during SCC that is step-by step change in current and potential up to the final stage of fracture and this may be used for SCC monitoring.

2. EXPERIMENTAL

The rectangular specimens of tin of dimensions 2.0cm × 2.0cm × 0.014 cm containing a small hole of about 2 mm diameter near the upper edge were cut from a large sheet of pure tin. The solutions of HNO_3 acid were prepared using double distilled water. All chemical used were of analytical reagent grade. Different inhibitor solutions were prepared in absolute ethanol. The extracts of leaves and stem of three varieties were obtained by refluxing the dried leaves and stem in a soxhlet using ethanol as solvent for sufficient time.

Each specimen was suspended with a V-shaped glass hook made of fine capillary and plunged into a beaker containing 50 mL of the test solution (HNO_3 acid) at room temperature. After sufficient exposure, the test specimens were taken out, washed with running water and dried with hot air dryer. Experiments were repeated in each case and the mean value of the weight loss was calculated. The percentage inhibition efficiency was calculated using the following formula [22].

$$\eta\% = \frac{\Delta Wu - \Delta W_i}{\Delta Wu} \times 100$$

Where ΔW_u and ΔW_i are the weight loss of the metal in uninhibited acid and in inhibited solution respectively. The corrosion rate (CR) in mm/y can be calculated by the following equation [23].

$$\text{Corrosion rate (mm/y)} = \frac{\Delta W \times 87.6}{A \times T \times d}$$

Where, ΔW is weight loss in mg, A is area of specimen in cm², T is time of exposure in hours and d is density of metal in g/cm³

The degree of surface coverage π by inhibitor can be calculated as

$$\theta = \frac{\Delta Wu - \Delta W_i}{\Delta Wu}$$

Where ΔW_u and ΔW_i are the weight loss of the metal in uninhibited acid and in inhibited solution, respectively.

3. RESULTS AND DISCUSSION

Weight loss, percentage inhibition efficiency, corrosion rate and surface coverage in 3M HNO_3 solution with different inhibitors of leaves extract are given in table 1. It can be seen from the table that the inhibition efficiency of the inhibitor increases with increasing concentration of inhibitor. The maximum inhibition efficiency (95.33%) was obtained for ocimum basilicum (EB) at an inhibitor concentration of 0.6% in 3.0M HNO_3 solution for leaves extract whereas it was 81.25% in 3M HNO_3 solution with same

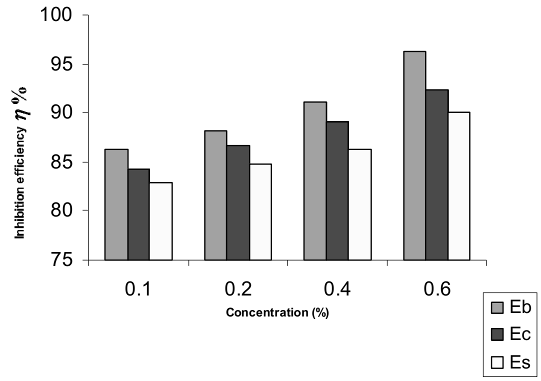


Fig. 1. Variation of inhibition efficiency with concentration of leaves extract for Tin in 3.0M HNO_3

Table 1. Weight loss data (ΔW) and percentage inhibition efficiency (η%) for Tin in 3.0 M HNO_3 solution with given inhibitor additions of leaves extract.

Temperature: $25 \pm 0.1^{o}C$ **Exposore time: 7 min.**

Inhibition conc.(%)	ΔW (mg)	I.E. (η %)	Surface coverage (θ)	Corrosion rate (mm/yr)	log [θ/ 1-θ]
Uninhibited	210			3153.60	
Ocimum basilicum (E_B)					
0.1	29	86.19	0.8619	435.50	0.7952
0.2	25	88.09	0.8809	375.43	0.8690
0.4	17	91.09	0.9109	255.29	1.0095
0.6	8	96.19	0.9619	120.14	1.4022
Ocimum canum (E_C)					
0.1	33	84.28	0.8428	495.57	0.7292
0.2	28	86.66	0.8666	420.48	0.8126
0.4	23	89.04	0.8904	345.39	0.9097
0.6	16	92.38	0.9238	240.27	1.0836
Ocimum sanctum (E_S)					
0.1	36	82.85	0.8285	540.62	0.6840
0.2	32	84.76	0.8476	480.55	0.7452
0.4	29	86.19	0.8619	435.50	0.7952
0.6	21	90.00	0.9000	315.36	0.9542

Table 2. Weight loss data (ΔW) and percentage inhibition efficiency (η%) for Tin in 3.0N HNO_3 solution with given inhibitor additions of stem extract.

Temperature: 273 ± 0.1 K **Exposure time: 7 min.**

Inhibitor conc.(%)	ΔW (mg)	I.E. (η %)	Surface coverage (θ)	Corrosion rate (mm/yr)	log [θ / 1-θ]
Uninhibited	285			4279.88	
Ocimum basilicum (E_B)					
0.1	114	60.00	0.6000	1711.95	0.1760
0.2	99	65.26	0.6526	1486.69	0.2738
0.4	86	69.82	0.6982	1291.47	0.3642
0.6	77	72.98	0.7298	1156.32	0.4315
Ocimum canum (E_C)					
0.1	120	57.89	0.5789	1802.05	0.1382
0.2	108	62.10	0.6210	1621.85	0.2144
0.4	98	65.16	0.6516	1471.68	0.2719
0.6	85	70.17	0.7017	1276.45	0.3714
Ocimum sanctum (E_S)					
0.1	125	56.14	0.5614	1877.14	0.1072
0.2	112	60.70	0.6070	1681.92	0.1887
0.4	106	62.10	0.6210	1591.81	0.2144
0.6	92	67.71	0.6771	1381.57	0.3215

concentration i.e. 0.6% for stem extract as shown in table 2. The results show that there is more inhibition efficiency of ocimum basilicum than ocimum canum and ocimum sanctum in HNO_3 solution. The variation of percentage inhibition

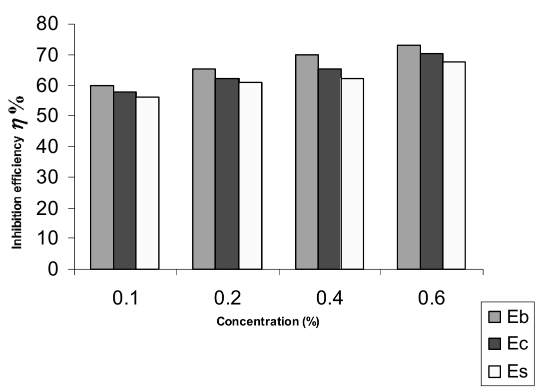


Fig. 2. Variation of inhibition efficiency with concentration of stem extract for Tin in 3.0 M HNO_3

efficiency (η%) with inhibitor concentration is depicted graphically in fig. 1 for leaves extract and in fig. 2 for stem extract in 3.0 M HNO_3 solution. Variation of percentage inhibition efficiency (η%) with the concentration of inhibitor indicate that the inhibition efficiency increases with increasing inhibitor concentration. From table 1 it is clear that the surface coverage (θ) increases with increasing concentration of inhibitor.

Adsorption plays an important role in the inhibition of metallic corrosion by organic inhibitors. Many investigators have used the Langmuir adsorption isotherm to study inhibitor characteristics [24, 25]. Assuming that the inhibitors adsorbed on the metal surface decrease the surface area available for cathodic and anodic reaction to take place. Hoar and Holliday[24] have shown that the Langmuir isotherm,

$$\text{Log}\,[\theta / 1\text{-}\theta] = \log A + \log C - [Q/2.303\,RT]$$

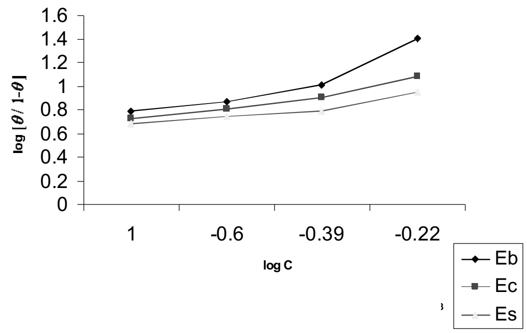


Fig. 3. Langmuir adsorption isotherm for Tin in $3.0MHNO_3$ with inhibitor concentraction for leaves extract

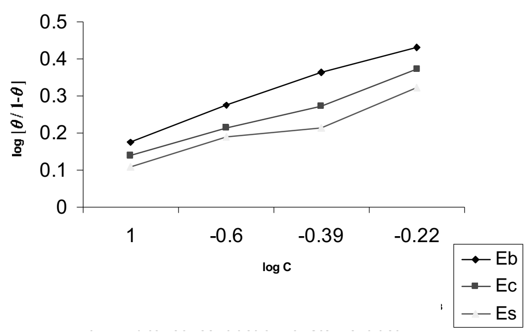


Fig. 4. Langmuir adsorption isotherm for Tin in $3.0MHNO_3$ with inhibitor concentraction for stem extract

should give a straight line of unit gradient for the plot of log [θ/1-θ] versus log C, where A is a temperature independent constant, C is the bulk concentration of the inhibitor (percentage) and Q is the heat evolved during adsorption.

The corresponding plots, shown in fig. 3 and fig. 4 for 3.0M HNO_3 for leaves and stem extract are linear but the gradients are not equal to unity as would be expected for the ideal Langmuir adsorption isotherm equation. This deviation from unity may be explained on the basis of the interaction among the adsorbed species on the metal surface. It has been postulated in the derivation of the Langmuir isotherm equation that the adsorbed molecules do not interact with one another but this is not true in the case of organic molecule having polar atoms or groups which are adsorbed on the anodic and cathodic sites of the metal surface. Such adsorbed species may interact by mutual repulsion or attraction. Thus, it is also possible for inhibitor molecule those are adsorbed on anodic and cathodic sites to interact with metallic surface as well as with each other.

4. CONCULSION

A study of three varieties of holy basil viz. ocimum basilicum(E_B), ocimum cannum (E_C) and ocimum sanctum(E_S)has shown them to be better corrosion inhibitor for Tin metal in H_2SO_4 solution. E_B has proved to be an excellent inhibitor for Tin in HNO_3 acid due to the presence of methyl eugenol terpenoid (75.69%).

Weight loss method has shown that inhibition efficiency of holy basil increases with increasing inhibitor concentration over the range 0.1% to 0.6% the maximum inhibition efficiency was found up to 95.83% for tin in 3.0M HNO_3 acid at a concentration of 0.6% for leaves extract whereas it was 81.25% for stem extract with same concentration of acid strength. Thus, it was concluded that leaves extract is a better corrosion inhibitor than stem extract.

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