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Corrosion Inhibition Effect of Arial Parts of Euphorbia Caducifolia for Aluminium in HNO_3

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ABSTRACT

Corrosion is a natural process, which converts a refined metal to a more chemically-stable form, such as its oxide, hydroxide, or sulfide. The most common kinds of corrosion result from electrochemical reactions. It can be prevented if the metal is coated with something which does not allow moisture and oxygen to react with it. It can be controlled by either alloying or by anti rust solutions. The naturally occurring plant products are eco-friendly, compatible, nonpolluting, less toxic, easily available, biodegradable and economic to be used as corrosion inhibitor. *Euphorbia caducifolia* has been selected to study its corrosion inhibition efficiency. It is easily available in any season. It is native to Thar Desert of India and located on rocky terrain, hills. It is used for treatment of bleeding wound, cutaneous eruption, urinary problems, kidney stones, rheumatic pain, bronchitis, jaundice, diabities, stomach pain, hernia etc. It is also called "Thor" and "Danda-thor". It contains caudicifolin) norcycloartane type triterpene, cyclocaducinol, triterpenes euphol, tirucallol and cycloartenol. Corrosion inhibition efficiency of arial parts of *Euphorbia caducifolia* was studied for aluminium in HNO_3. Maximum inhibition efficiency was found 92.17% in 1N HNO_3acid with 0.8% leaf corrosion inhibitor whereas it was 90.53% for stem and 89.94% for flower with same concentration of inhibitor i.e. 0.8%. Inhibition efficiency was studied in different concentration of acid (1N, 1.5N, 2N and 2.5N) with different concentration of inhibitor (0.2%, 0.4%, 0.6% and 0.8%). Weight loss and thermometric methods were used. Inhibition efficiency was found to be increase with increase in concentration of inhibitor and decrease with increase in acid strength.

Introduction

Corrosion is a natural process, which converts a refined metal to a more chemically-stable form, such as its oxide, hydroxide, or sulfide. The most common kinds of corrosion result from electrochemical reactions. It affects almost all the metals and decays the metallic properties of metals. It is unavoidable process but It can be prevented if the metal is coated with something which does not allow moisture and oxygen to react with it. it can be controlled by either alloying or by using corrosion inhibitors (anti rust solution)[1].

Aluminium alloys with a wide range of properties are used in engineering structures. The strength and durability of aluminium alloys vary widely, not only as a result of the components of the specific alloy, but also as a result of heat treatments and manufacturing processes. A lack of knowledge of these aspects has from time to time led to improperly designed structures and gained aluminium a bad reputation.

In the acid, oxidation of metal occurs and hydrogen gas evolved. In the environment so many harmful gases and acids are present in the air which disintegrate and degrade the metal and alloy by corrosion. In industries acids are widely used in many processes so we need to use corrosion inhibitors which prevent or decrease the loss of metal.

A number of N and S containing ligands have been synthesized [2-5] which are found as effective corrosion inhibitors. Some heterocyclic compounds and their derivatives have been also used for metals as corrosion inhibitors in acidic media[6-9]. Epoxy esters inhibit the corrosion of aluminium and reduce evolution of hydrogen gas in aqueous solution of alkaline media[10.] Schiff bases are good corrosion inhibitors[11-12]. Mannich bases are also investigated as good corrosion inhibitor[13-15]. All the above components are good corrosion inhibitors but these are costly, toxic, pollutant and harmful so we need eco-friendly inhibitors.

The naturally occurring plant products are eco-friendly, compatible, nonpolluting, less toxic, easily available, biodegradable and economic to be used as corrosion inhibitor. A number of natural products extracted from plants are also found effective corrosion inhibitor like: *Argemone mexicana*[16], *Withania somnifera*[17], *Holly Basil*[18-19], *ocimum sanctum*[20] etc.

Euphorbia caducifolia is a Euphorbiaceae species native to Thar Desert of India, where latex of *E. caducifolia* (ECL) is used by the local inhabitants for treatment of bleeding wound, cutaneous eruption and other skin diseases[21]. Isolated fraction of E. caducifolia (IFEC) and latex of E. caducifolia (ECL) were tested against S. aureus, M. luteus, B. subtilis, E. coli, S. typhi, A. niger and C. albicans[22]. Flower extract of *Euphorbia caducifolia*[23]is found effective corrosion inhibitor for iron in different acidic media like sulphuric acid, nitric acid and hydrochloric acid. Leaf, stem and flower extract of *Euphorbia caducifolia*[24] are also effective corrosion inhibitor for aluminium in HCL. In the proposed investigation

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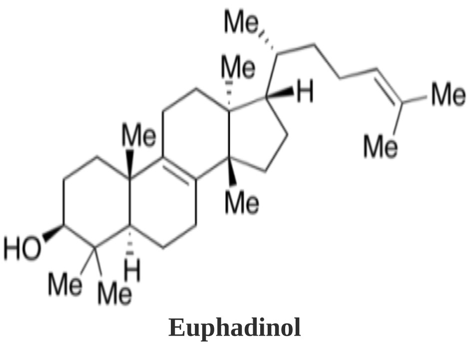
Euphorbia caducifolia extract will be used as corrosion inhibitor in nitric acid on aluminium.

Plant Description

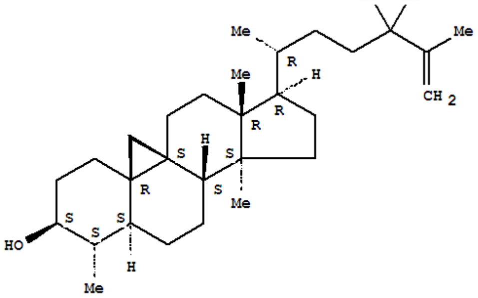
Euphorbia caducifolia is native to Thar desert of India and located on rocky terrain, hills. It is also called "Thor" and "Danda-thor".

Extract of *euphorbia caducifolia* is widely used in medicines. It is used for treatment of bleeding wound, cutaneous eruption, urinary problems, kidney stones, rheumatic pain, bronchitis, jaundice, diabetes, stomach pain, hernia etc.

It contains caudicifolin[25] (8,14-epoxy-17-hydroxy-11,13(15)-abietadien-15,12-olide) norcycloartane type triterpene, cyclocaducinol, triterpenes euphol, tirucallol and cycloartenol[26].



Euphadinol



Cyclocaducinol

Experimental

Square specimen of aluminium of dimension 2.5x2.5 cm^2 containing a small hole of about 2mm diameter near the upper edge were used for studying of corrosion. Different solutions of HNO_3 were prepared using double distilled water.

Each specimen was suspended by a V shaped glass hook made of fine capillary tube and immersed in the beaker containing 100 ml of uninhibited and different concentration of inhibited test solutions. After the sufficient exposure, the specimen were taken out, washed thoroughly with running water and then dried with hot air dryer and then the final weight of each specimen was taken.

The percentage inhibition efficiency was calculated[27] as

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

and surface coverage (θ) was calculated as

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

Where ΔW_u is weight loss of metal in acid solution in the absence of inhibitor and ΔW_i is weight loss of metal in acid solution in the presence of known amount of inhibition.

The Corrosion rate (CR) in mm/yr can be obtained by following equation

$$R_{corr.} = \frac{\Delta W \times 87.6}{D \times A \times T}$$

Where Δ W = weight loss in milligrams, D = metal density in g $/cm^3$, A = area of sample in cm^2, T= time of exposure of the metal sample in hours.

Inhibition efficiency was also determined by thermometric method. In this method a specimen was immersed in a reaction chamber containing 100ml of solution at an initial temperature of 25°C. Temperature change were measured using a thermometer. Initially temperature increased slowly, then rapidly and attain a maximum value before falling. The maximum temperature was recorded. Percentage inhibition efficiency were calculated as

$$\eta\% = \frac{RN_f - RN_i}{RN_f} \times 100$$

Where RN_f and RN_i are the reaction number in the absence and presence of inhibitor respectively and reaction number is defined as

$$RN = \frac{T_m - T_i}{t}$$

Where T_m and T_i are maximum and initial temperature and t is the time (in minutes) required to reach the maximum temperature.

Result and Discussion

Weight loss, percentage inhibition efficiency, surface coverage and corrosion rate in 1N, 1.5N, 2N and 2.5N HNO_3 solution with different concentration of leaf, stem and flower extract inhibitor are given in table1 and table 2.

Table 1. Weight loss data (△W) and percentage inhibition efficiency (%) for aluminium in1N and 1.5N $HNO_3$with inhibitor of leaf, stem and flower extract.

Temperature : 25 ± 0.1^{0}C   Area of Specimen : 13 cm^2

1N HNO_3 (360 hours)						1.5N HNO_3 (312 hours)					
Conc. Of inhibitor (%)	**ΔW (g)**	**I.E. (η%)**	**Surface Coverage (θ)**	**Corrosion Rate**	**Log (θ/1-θ)**	**Conc. Of inhibitor (%)**	**ΔW(g)**	**I.E. (η%)**	**Surface Coverage (θ)**	**Corrosion Rate**	**Log (θ/1-θ)**
Leaf						**Leaf**					
Uninhibited	0.5216			0.00361		Uninhibited	0.5132			0.00410	
0.2	0.0771	85.21	0.8521	0.00053	0.76052	0.2	0.0959	81.31	0.8131	0.00076	0.63853
0.4	0.0696	86.64	0.8664	0.00048	0.81191	0.4	0.0825	83.92	0.8392	0.00066	0.71758
0.6	0.0526	89.91	0.8991	0.00036	0.94991	0.6	0.0701	86.34	0.8634	0.00056	0.80076
0.8	0.0408	92.17	0.9217	0.00028	1.07082	0.8	0.0526	89.75	0.8975	0.00042	0.94231
Stem						**Stem**					
0.2	0.0855	83.61	0.8361	0.00059	0.70768	0.2	0.1017	80.17	0.8017	0.00081	0.60669
0.4	0.0784	84.96	0.8496	0.00054	0.75196	0.4	0.0925	81.97	0.8197	0.00074	0.65766
0.6	0.0659	87.35	0.8735	0.00045	0.83917	0.6	0.0801	84.38	0.8438	0.00064	0.73255
0.8	0.0494	90.53	0.9053	0.00034	0.98044	0.8	0.0632	87.68	0.8768	0.00050	0.85229
Flower						**Flower**					
0.2	0.1026	80.32	0.8032	0.00071	0.61080	0.2	0.1149	77.61	0.7761	0.00092	0.53986
0.4	0.0930	82.16	0.8216	0.00064	0.66326	0.4	0.1064	79.26	0.7926	0.00085	0.58224
0.6	0.0722	86.15	0.8615	0.00050	0.79380	0.6	0.0955	81.39	0.8139	0.00076	0.64082
0.8	0.0524	89.94	0.8994	0.00033	0.95135	0.8	0.0748	85.42	0.8542	0.00059	0.76780

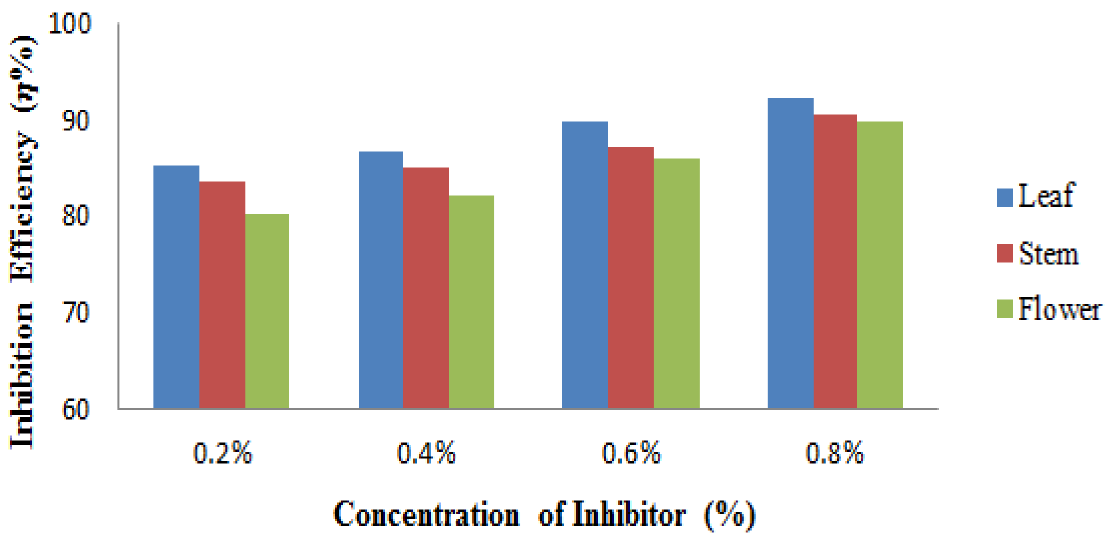


Fig.1 Variation of inhibition efficiency with concentration of leaf, stem and flower extract for aluminium in 1N HNO_3.

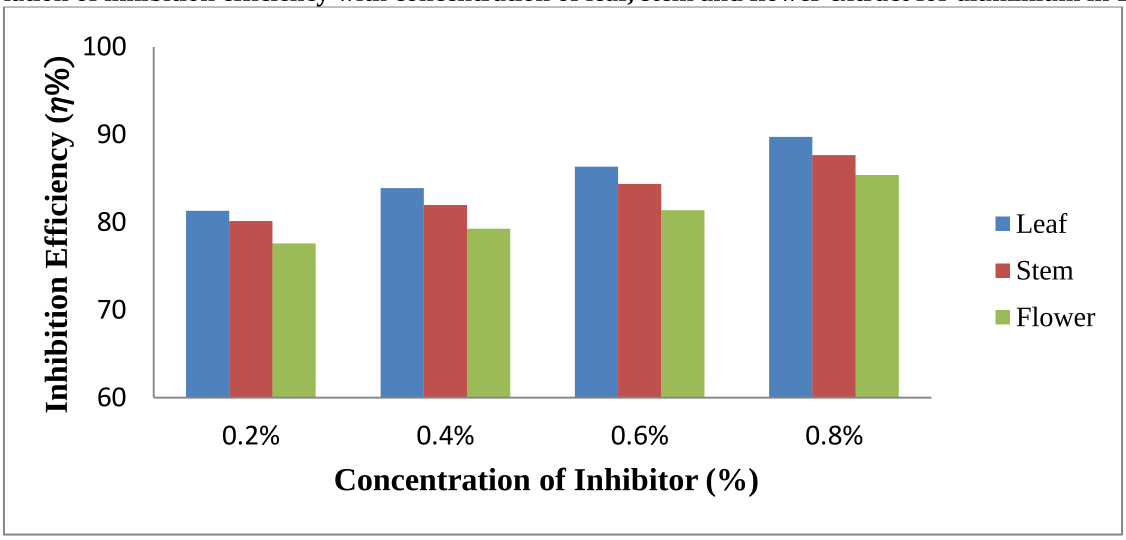


Fig 2. Variation of inhibition efficiency with concentration of leaf, stem and flower extract for aluminium in 1.5N HNO_3.

Table 2. Weight loss data (△W) and percentage inhibition efficiency (%) for aluminium in 2N and 2.5N HNO_3 with inhibitor of leaf, stem and flower extract

Temperature : 25±0.1^{0}C — Area of Specimen : 13 cm^2

2N HNO_3 (264 hours)						2.5N HNO_3 (216 hours)					
Conc. of inhibitor (%)	**ΔW (g)**	**I.E. (η%)**	**Surface Coverage (θ)**	**Corrosion Rate**	**Log (θ/1-θ)**	**Conc. of inhibitor (%)**	**ΔW (g)**	**I.E (η%)**	**Surface Coverage (θ)**	**Corrosion Rate**	**Log (θ/1-θ)**
Leaf						**Leaf**					
Uninhibited	0.5236			0.00494		Uninhibited	0.5187			0.00599	
0.2	0.1277	75.61	0.7561	0.00120	0.49136	0.2	0.1418	72.66	0.7266	0.00163	0.42449
0.4	0.1154	77.96	0.7796	0.00109	0.54866	0.4	0.1333	74.29	0.7429	0.00154	0.46082
0.6	0.1026	80.39	0.8039	0.00097	0.61272	0.6	0.1186	77.13	0.7713	0.00137	0.52795
0.8	0.0891	82.97	0.8297	0.00084	0.68770	0.8	0.1092	78.93	0.7893	0.00126	0.57357
Stem						**Stem**					
0.2	0.1500	71.34	0.7134	0.00141	0.39605	0.2	0.1538	70.35	0.7035	0.00177	0.37523
0.4	0.1328	74.62	0.7462	0.00125	0.46836	0.4	0.1424	72.54	0.7254	0.00164	0.42187
0.6	0.1191	77.24	0.7724	0.00112	0.53067	0.6	0.1340	74.16	0.7416	0.00154	0.45787
0.8	0.1050	79.93	0.7993	0.00099	0.60016	0.8	0.1201	76.84	0.7684	0.00138	0.52084
Flower						**Flower**					
0.2	0.1538	70.61	0.7061	0.00145	0.38066	0.2	0.1638	68.42	0.6842	0.00189	0.33577
0.4	0.1430	72.68	0.7268	0.00135	0.42493	0.4	0.1508	70.91	0.7091	0.00174	0.38696
0.6	0.1290	75.36	0.7536	0.00122	0.48550	0.6	0.1392	73.16	0.7316	0.00160	0.43549
0.8	0.1177	77.51	0.7751	0.00111	0.53736	0.8	0.1300	74.93	0.7493	0.00150	0.47550

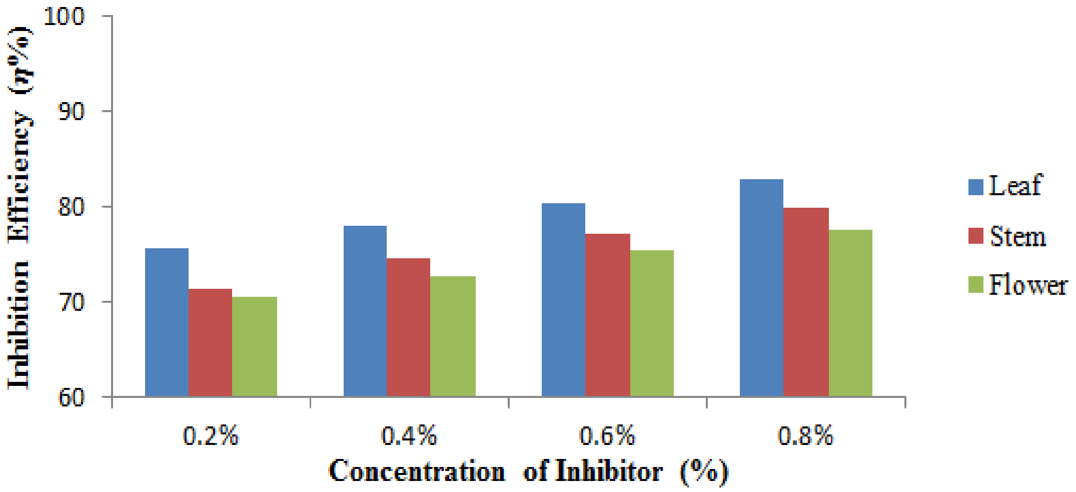


Fig 3. Variation of inhibition efficiency with concentration of leaf, stem and flower extract for aluminium in 2N HNO_3.

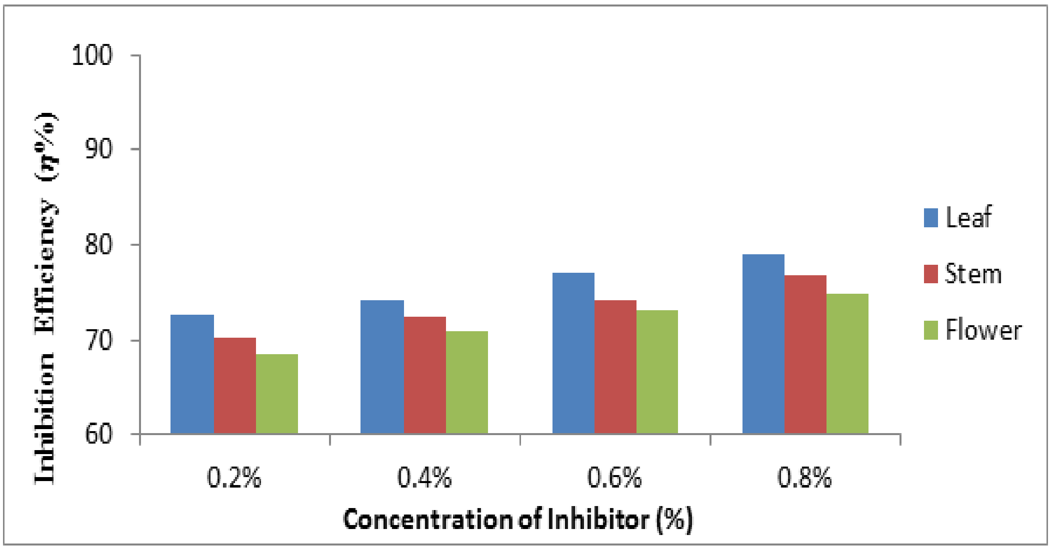


Fig 4. Variation of inhibition efficiency with concentration of leaf, stem and flower extract for aluminium in 2.5N HNO_3.

Table 3. Reaction number (RN) and inhibition efficiency (%) for aluminium in 2N, 3N and 4N HNO_3 with inhibitor of leaf, stem and flower extract.

Conc.	2N HNO_3		3N HNO_3		4N HNO_3	
	RN	I.E. (%)	RN	I.E. (%)	RN	I.E. (%)
Leaf						
Uninhibited	0.3654		0.6456		0.9412	
0.2	0.1702	53.42	0.3297	48.92	0.5159	45.18
0.4	0.1638	55.16	0.3128	51.54	0.4994	46.94
0.6	0.1485	59.34	0.2959	54.17	0.4870	48.25
0.8	0.1370	62.51	0.2663	58.74	0.4472	52.48
Stem						
0.2	0.1820	50.18	0.3555	44.93	0.5517	41.38
0.4	0.1731	52.63	0.3432	46.83	0.5370	42.94
0.6	0.1597	56.29	0.3252	49.62	0.5152	45.26
0.8	0.1481	59.46	0.2976	53.89	0.4877	48.18
Flower						
0.2	0.1965	46.21	0.3733	42.17	0.6005	36.19
0.4	0.1803	50.64	0.3532	45.29	0.5796	38.42
0.6	0.1720	52.92	0.3380	47.64	0.5445	42.14
0.8	0.1617	55.75	0.3147	51.25	0.5150	45.28

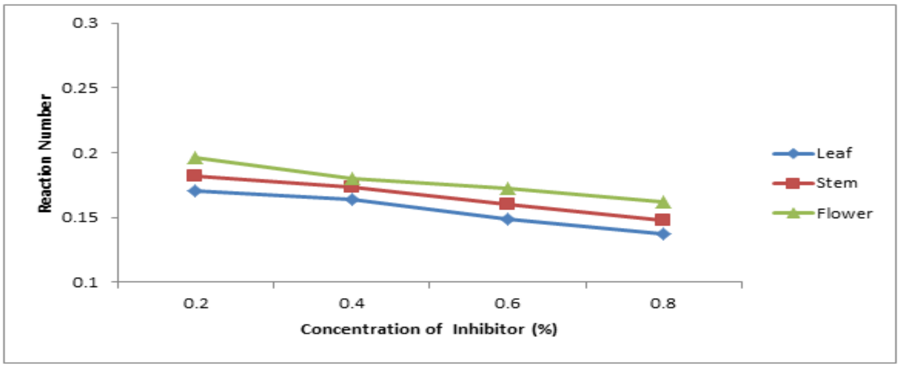


Fig 5. Variation of reaction number with concentration of leaf, stem and flower extract for aluminium in 2N HNO_3.

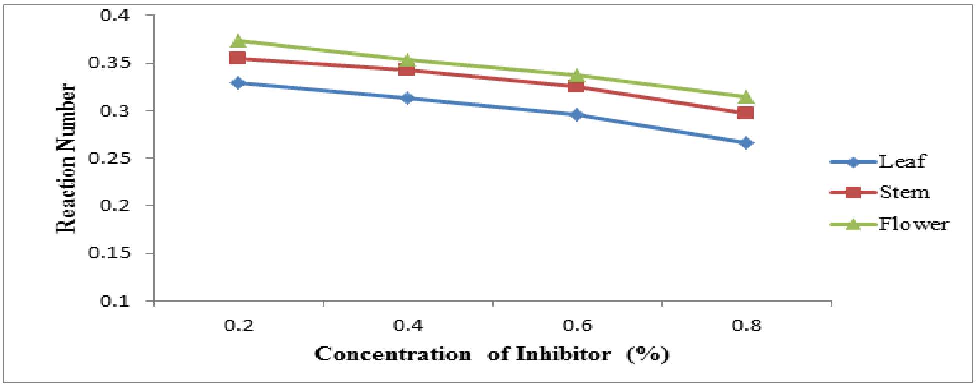


Fig 6. Variation of reaction number with concentration of leaf, stem and flower extract for aluminium in 3N HNO_3.

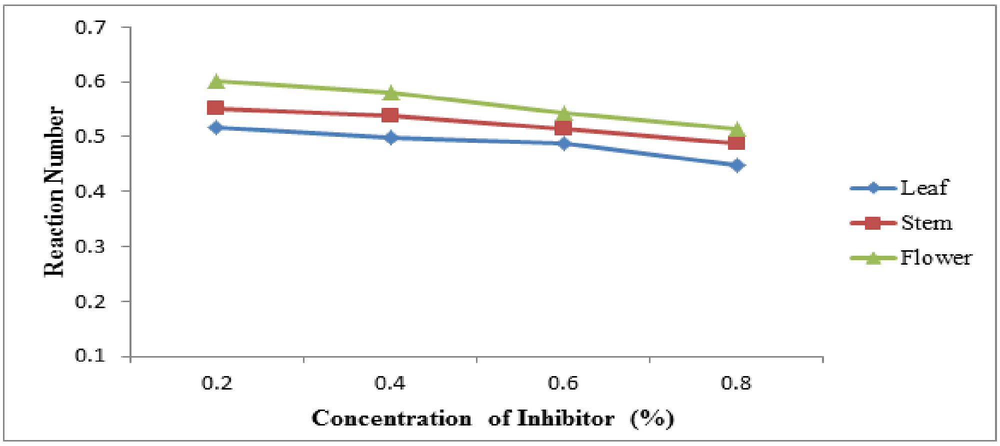


Fig 7. Variation of reaction number with concentration of leaf, stem and flower extract for aluminium in 4N HNO_3.

It can be seen from tables that inhibition efficiency of inhibitor increases with increasing concentration of inhibitor. The Maximum inhibition efficiency 92.17% was obtained in 1N HNO_3 at an inhibitor concentration of 0.8% for flower extract. Maximum inhibition efficiency for stem extract was found 90.53% 1N HNO_3 with 0.8% corrosion inhibitor whereas maximum Inhibition efficiency for flower extract in 1N HNO_3 was obtained 89.94% with 0.8% corrosion inhibitor. The result shows that leaf extract have higher inhibition efficiency in HNO_3 than stem and flower.

The variation of percentage inhibition efficiency with inhibitor concentration is depicted graphically in fig-1, 2, 3 and 4 in 1N, 1.5N, 2N and 2.5N acid strength respectively for leaf, stem and flower extract. It indicates that the inhibition efficiency increases with increasing inhibitor concentration.

From table 1 and table 2 it is clear that the surface coverage increase with increasing concentration of inhibitor and corrosion rate decrease with increasing concentration of inhibitor.

Inhibition efficiencies were also determined by using thermometric method.Thermometric experiments were carried out at higher concentrations of acid i.e. 2N, 3N and 4N because no appreciable changes of temperature were observed at lower concentrations of acid. Results summarized in table 3 show a good agreement with the results obtained by weight loss method.The variation of reaction number (RN) with inhibitor concentration is depicted graphically in fig. 5,6 and 7 for HNO_3. The maximum inhibition efficiency was obtained with the highest concentration of leaf extract inhibitor at lowest concentration of acid. Inhibition efficiency increases with increasing concentration of inhibitor and decreases with increasing concentration of acid. Both methods (weight loss as well as thermometric) show same trends in corrosion efficiency and results are in good agreement with each others.

Conclusion

A study of extract of euphorbia caducifolia has shown that to be better corrosion inhibitor for aluminium in HNO_3.

Weight loss and thermometric methods were shown that inhibition efficiency of plant extract increases with increasing inhibitor concentration over the range 0.2% to 0.8% and and decreases with decreasing concentration of acid. The maximum inhibition efficiency was found up to 92.17% for aluminium in 1N HNO_3 at a concentration of 0.8% for leaf extract whereas it was 90.53% for stem extract and 89.94% for flower extract with same concentration i.e. 0.8%. Thus, it was concluded that leaf extract is a better corrosion inhibitor in HNO_3 than stem and flower extract.

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