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Sulphuric Acid Catalysed Corrosion Inhibitory Activity of Aerial Parts of Euphorbia Neriifolia Linn on Aluminium

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ABSTRACT

Corrosion is a natural destructive process, in which metal loss their properties through unwanted chemical or electrochemical attack by its environment, in this process metals revert back to their natural and lower energy state which is more stable than the pure state of metals, it showed that corrosion is a reverse chemical process of extraction of metals. In the refining process, energy is added to the ore to produce the pure metal. Aluminium is one of the most important metals on the earth which is widely used for different kind of activities. Generally aluminium metal exists in the forms of their oxide and it has high corrosion resistance to atmosphere and pure water but it is corroded adversely in presence of acidic environment. The corrosion inhibition of aluminium by *Euphorbia Neriifolia linn* in different solution of sulphuric acid was investigated by using weight less and thermometer method at 301K temperature. The findings of the study shows that the inhibition inefficiency was maximum (93.11%) for highest concentration (0.7%) of stem extract in lowest strength of sulphuric (1N) and inhibition efficiency was minimum (74.82 %) for lowest concentration of flower extract (0.1%) in 3N sulphuric acid and the study showed that the inhibition efficiency increases with increase in the concentration of extract of plant in H_2SO_4 solution. The study shows that extract of *Euphorbia Neriifolia linn* is an efficient natural corrosion inhibitor in acidic medium and the stem extract is better inhibitor than leaves and flower extract of the plant.

Introduction

Corrosion is a physio-chemical interaction between a metal and its environment which results in changes in the properties of the metal and often leads to impairment of the function of metal, the environment, or the technical system of which there form a part Corrosion degrade the metallic properties of metal and alloys and makes them unfit for specific role[1]. Aluminium is one of the most important metals on the earth which is widely used in different region of the society. The special characteristics of aluminium like low density, good conductor of heat and electricity are made it important metal and it is widely used in aerospace industry, transportation industry and building industry. Generally aluminium metal exists in the forms of their oxides compounds and it has high corrosion resistance to atmosphere and in pure water but it corroded adversely in acidic environment. Corrosion decreases the chemical and physical properties of the metal and hence the metal has loss their usable properties [(2-8)]. Heterocyclic compound containing O,N,S and P atoms have been used as corrosion inhibitors in acidic media because the compound contains aromatic rings with free π-electron pair for sharing with metal and donating their electron to the surface of metal and hence they forms a coordinate bond between metal and inhibitor that reduces the corrosion rate. In this process inhibitor acts as nucleophile while metal acts as electrophile centres. The electron density, orientation, size and shape of molecule play significant role in the effectiveness of inhibition. In this mechanism, the inhibitor got adsorbed on the active centre of the metal surface and blocked the active corrosion site on the metal surface, due to this liberation of H^+ ions and dissociation of metal is stopped in the acidic media, consequently the corrosion of metal stops.Schiff bases and mannish bases are also investigated as good corrosion inhibitor [(9-10)]. The above organic compounds are good corrosion inhibitors but these are very costly, pollutant, toxic and harmful that's why we need eco-friendly inhibitors. Natural occurring plant products are easily available, less toxic, economic, eco-friendly and biodegradable so they are widely used as corrosion inhibitors without any harmful effects [(11-13)], some examples of natural corrosion inhibitor like: *Argemone Mexicana*, *Olea europaea* [(14)], *Withania somnifera*, *Holly basil* [(15)] etc.

Plant Description

Euphorbia neriifolia linn plant was selected for this study. The plant is a xerophyte shrub which is commonly available in desert climatic condition of India. The plant belongs to euphorbiaceae species. Geographical condition of Rajasthan is very favourable for growing this plant and it is known as thoar or sehund in locally and milk hedge in English.

The plant extract is bitter in taste, pungent laxative and carminative and improves appetite. It is useful in abdominal trouble, bronchitis, tumor, delirium, lucoderma, piles, inflammation, enlargement of spleen, enema, ulcer and it is also use for ear disorder. The plant extract contains, sugar,

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flavonoids, tannins, triterpesnoids, alkaloids and saponins etc. [16-21].

Materials and Methods

Experimental

Commercially available aluminium sheet was used for this study. Square shaped specimen of aluminium sheet having dimension 2.5 × 2.5 cm^2 containing small hole of about 2mm diameter near the upper edge were used for experiments.

Plant Extract

Euphorbia neriifolia linn was identifying with help of subject expert and its aerial part was collected from theme park Botanical garden, Regional Institute of Education, Ajmer. The whole plant including stem, leaves and flower were air dried at room temperature, and then grinned to make powder. The extract of stem, leaves, and flower were obtained by refluxing the dried powder of the aerial parts of plant in soxhlet unit in ethanol with refluxing for sufficient time (15-25) hrs.

Fig 1. *Euphorbia Neriifolia linn*

Chemical Used

1N, 2N, 3N solutions of H_2SO_4 were prepared using for experimental study and there acid solutions were used for corrosion analysis, in this study we have used 0.1, 0.3, 0.5 and 0.7 percentage composition solutions of stem, leaves and flower extract as inhibitors.

Method

Weight loss method: Each specimen was suspended by a V-shaped glass hook made of fine capillary and plunged into a beaker containing 100 mL of the test solution at room temperature. After the sufficient exposure, test specimens were washed with running tap water and dried with hot air dryer. Duplicate experiments were performed in each case and mean value of weight loss was calculated. The percentage inhibition efficiency (η%) was calculated [22-24] by using following equation:

$$\eta\% = 100\left[\frac{(\Delta W_u - \Delta W_i)}{\Delta W_u}\right]$$

Where ΔW_u and ΔW_i are the weight loss of the metals in absence and presence of inhibitor solution, respectively. The degree of surface coverage (θ) was calculated by using following equation:

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

Langmuir adsorption isotherm equation should give a straight line of unit gradient for the plot [θ / 1- θ] versus log C, where θ is surface coverage; A is a temperature independent constant and C is concentration of inhibitor. The corresponding plot Figure (for aluminium Fig, no 3, 5, 7) is linear but the gradients are not equal to unity as would be expected for the Langmuir adsorption isotherm equation. As Langmuir adsorption isotherm is related with formation of the monolayer on metal surface and it also characteristic of physical adsorption or electrostatic adsorption and the slope of graph indicates the adsorption phenomenon of inhibitors according to kinetic thermodynamic.

Thermometric method

Inhibition efficiencies were determined by using thermometric method technique. This involved the immersion of single specimen of area 13cm^2(both sides) in reaction chamber containing 100 mL solution of acid at an initial temperature of 301K. Experiments were carried out in 1N, 2N, 3N, H_2SO_4 acid solutions in absence and presence of different concentration of inhibitor viz. 0.1%, 0.3%, and 0.5% and 0.7%. Thermometer bulb and specimen were completely immersed in test solution in a beaker; the beaker was kept in a thermally insulated chamber. Temperature changes were measured at definite intervals using thermometer with a precision of 0.1^0C, the temperature increased slowly at first, then rapidly and attained a maximum value before failing the maximum temperature was recorded.

The reaction number(R N) is calculated [25-27] by using following equation:

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

Where T_m and T_i are maximum and initial temperatures, respectively and t is the time in minutes required to attain maximum temperature. The percentage inhibition efficiencies (η%) were obtained by using following equation:

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

Where $RN_{f,}$ and RNi are reaction numbers in the absence and in the presence of inhibitor respectively. The corrosion rate (CR) in mm/year can be calculated [28-30] by using the following equation:

$$R\ corr. = \frac{(\Delta W \times 87.6)}{(A \times T \times d)}$$

Where ΔW is weight loss in mg, A is surface area of specimen in cm^2; t is time of exposure in hrs. and d is density of metal in g /cm^3.

Result and Discussion

The corrosion rate of aluminium in sulphuric acid (1N, 2N, 3N) solutions were studied by using weight loss method and themo- metric method in absence and presence of, stem, leaves and flower extract of *Euphorbia neriifolia linn* plant at 301K temperature and percentage inhibition efficiency were calculated in both the conditions. We can see and observed from the Table-1, 2, and 3 that inhibition efficiency decreases with increasing strength of sulphuric acid and inhibition efficiency increases with increasing concentration of extract in strength of each acid solution and rate of corrosion increases with increasing acid strength.

The maximum efficiency has been observed in lowest strength of H_2SO_4 i.e. 1N H_2SO_4 with highest concentration of inhibitor i.e. of 0.7% (93.11%) for stem extract and it was for leaves (91.46%),whereas it was (89.73%) for flower extract in same H_2SO_4 concentration. The corrosion rate has been observed maximum in blank solution i.e. 0.9120 for 3N

H_2SO_4 and it decreased with the increasing concentration of inhibitor in H_2SO_4 solution of different strength. Corresponding variation of inhibition efficiencies with concentration of inhibitor are shown in Fig.1a-b, 2a-b, and 3a-b for 1N, 2N, and 3N H_2SO_4 solution respectively. In this phenomenon the adsorption reaction is depends on chemical composition of inhibitors that contains various heterocyclic compounds like alkaloids, flavonoids, steroids and tannins etc. which has higher electronegative atoms like O, N and S having with lone pair electrons, these atoms forms co-ordinate bond with metal and stopped the discharge of H^+ ions and dissolution of metal ion in acidic media and hence the corrosion reaction of metal reduces in the presence of inhibitors.

In the Fig.1b, 2b and 3b, study by using Langmuir isotherm which shows graphic slope (y) between log (ɵ /1- ɵ) and logarithm of corrosion inhibitor concentration, in the value 1/y represents the number of actives site on metal surface covered by corrosion inhibitors and it is higher for stem extract and lower for flower extract of plant.

Conclusion

The study of aerial part of *Euphorbia neriifolia linn* showed that its extract would be good corrosion inhibitor for tin in different strength of sulphuric acid solution, the findings of the study shows that the inhibition inefficiency was maximum (93.11%) for highest concentration (0.7%) of stem extract in lowest strength of sulphuric (1N) and inhibition efficiency was minimum (74.82 %) for lowest concentration of flower extract (0.1%) in 3N sulphuric acid. Results indicate that the inhibition efficiency increases with the increase in the concentration of inhibitor in H_2SO_4 acid solutions and it was concluded that extract of stem is better corrosion inhibitor than the leaves and flower extract of *Euphorbia neriifolia linn*.

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Table 1. Weight loss data (Δw), inhibition efficiency (η%), surface coverage (θ) and corrosion rate for Aluminium in 1N H_2SO_4 acid with various inhibitors extract concentration of aerial parts of *Euphorbia neriifolia linn* plant.

Temperature : 301±0.1^{0}C Time of Exposure: (0.75 hrs) Area of Specimen :13cm^2

Concentration (%)	Weight Loss (Δw) in g	Inhibition Efficiency (I.E.) (η%)	Surface Coverage (θ)	Corrosion Rate in (mm/yr)	$\log\left(\frac{\theta}{1-\theta}\right)$
Stems					
Uninhibited	0.3691			0.0034	
0.1	0.0521	85.88	0.8588	0.0005	0.7840
0.3	0.0441	88.05	0.8805	0.0004	0.8673
0.5	0.0339	90.81	0.9081	0.0003	0.9918
0.7	0.0254	93.11	0.9311	0.0002	1.1307
Leaves					
0.1	0.0579	84.31	0.8431	0.0006	0.7302
0.3	0.0535	85.50	0.8550	0.0005	0.7705
0.5	0.0431	88.32	0.8832	0.0004	0.8786
0.7	0.0315	91.46	0.9146	0.0003	1.0146
Flowers					
0.1	0.0674	81.73	0.8173	0.0006	0.6506
0.3	0.0579	84.31	0.8431	0.0005	0.7302
0.5	0.0485	86.85	0.8685	0.0004	0.8081
0.7	0.0392	89.73	0.8973	0.0003	0.9413

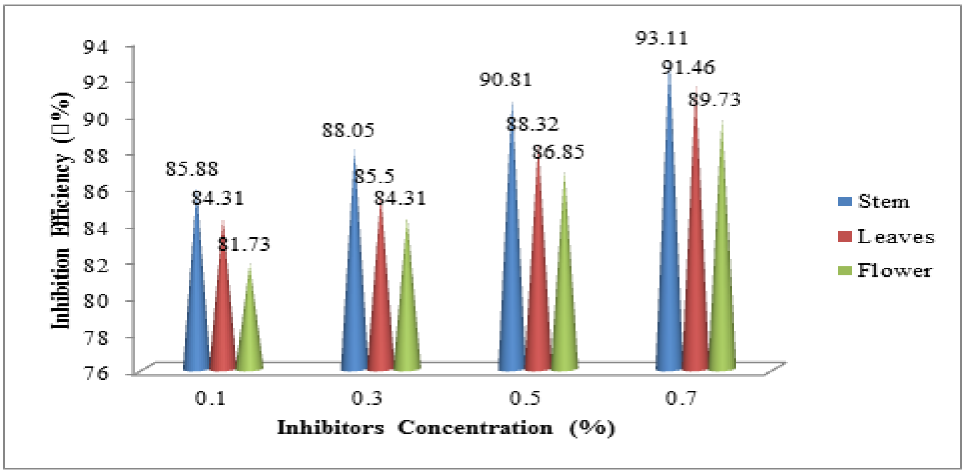

Fig 2 (a). Variation of inhibition efficiency with various concentrations of inhibitors for Aluminium in 1N H_2SO_4 acid solution

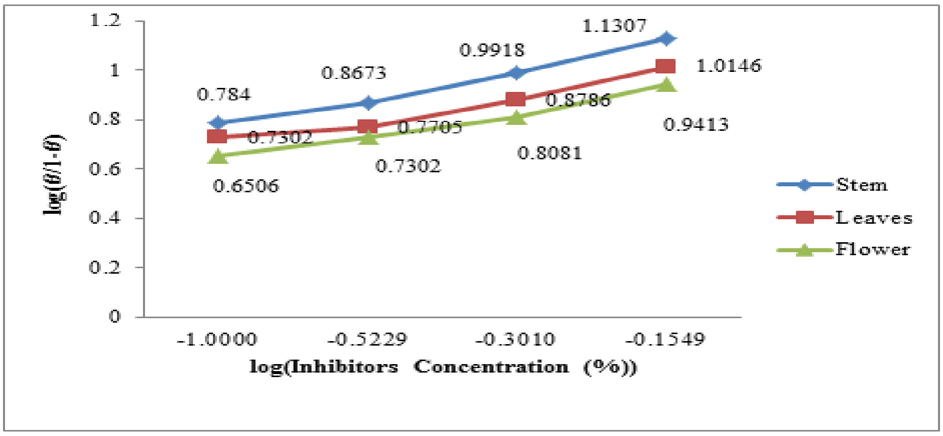

Fig 2 (b). Langmuir adsorption isotherm for Aluminium in 1N H_2SO_4 acid solution

Table 2.Weight loss data (Δw), inhibition efficiency (η%), surface coverage (θ) and corrosion rate for Aluminium in 2N H_2SO_4 acid solution with various inhibitors extract concentration of aerial parts of *Euphorbia neriifolia linn* plant.
Temperature : 301±0.1^{0}C Time of Exposure: (0.25 hrs) Area of Specimen :13cm^2

Concentration (%)	**Weight Loss (Δw) in g**	**Inhibition Efficiency (I.E.) (η%)**	**Surface Coverage (θ)**	**Corrosion Rate in (mm/yr)**	$\log\left(\frac{\theta}{1-\theta}\right)$
Stems					
Uninhibited	0.3846			0.0054	
0.1	0.0696	81.90	0.8190	0.0010	0.6555
0.3	0.0591	84.63	0.8463	0.0008	0.7408
0.5	0.0486	87.36	0.8736	0.0007	0.8395
0.7	0.0381	90.09	0.9009	0.0005	0.9586
Leaves					
0.1	0.0761	80.21	0.8021	0.0010	0.6077
0.3	0.0655	82.96	0.8296	0.0009	0.6873
0.5	0.0549	85.72	0.8572	0.0007	0.7783
0.7	0.0443	88.48	0.8848	0.0006	0.8853
Flowers					
0.1	0.0821	78.65	0.7865	0.0011	0.5662
0.3	0.0715	81.40	0.8140	0.0010	0.6411
0.5	0.0609	84.16	0.8416	0.0008	0.7253
0.7	0.0503	86.92	0.8692	0.0007	0.8225

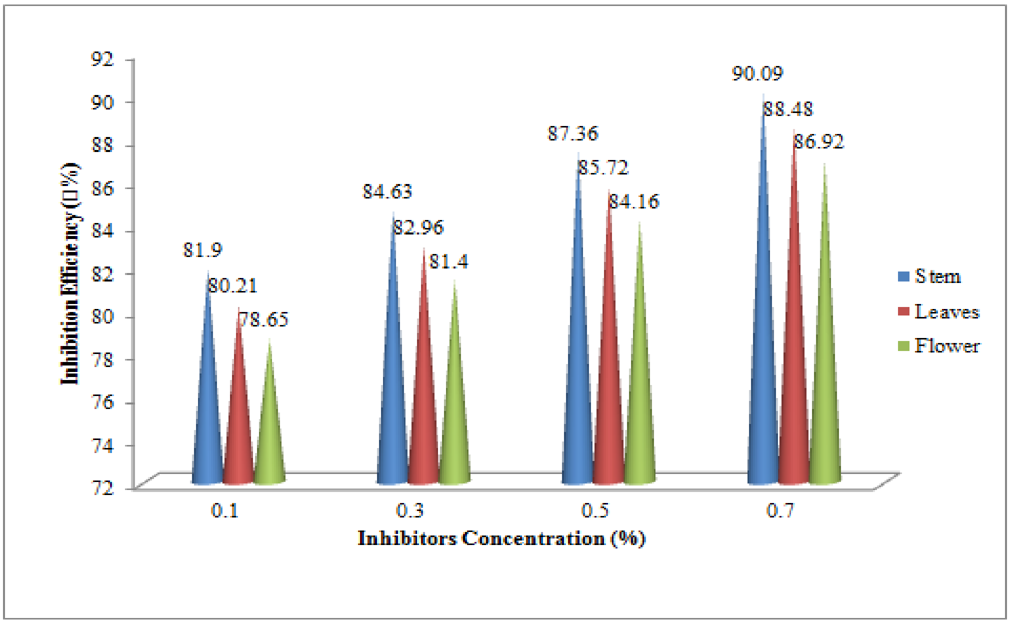

Fig 3 (a). Variation of inhibition efficiency with concentration of inhibitors for Aluminium in 2N H_2SO_4 acid solution

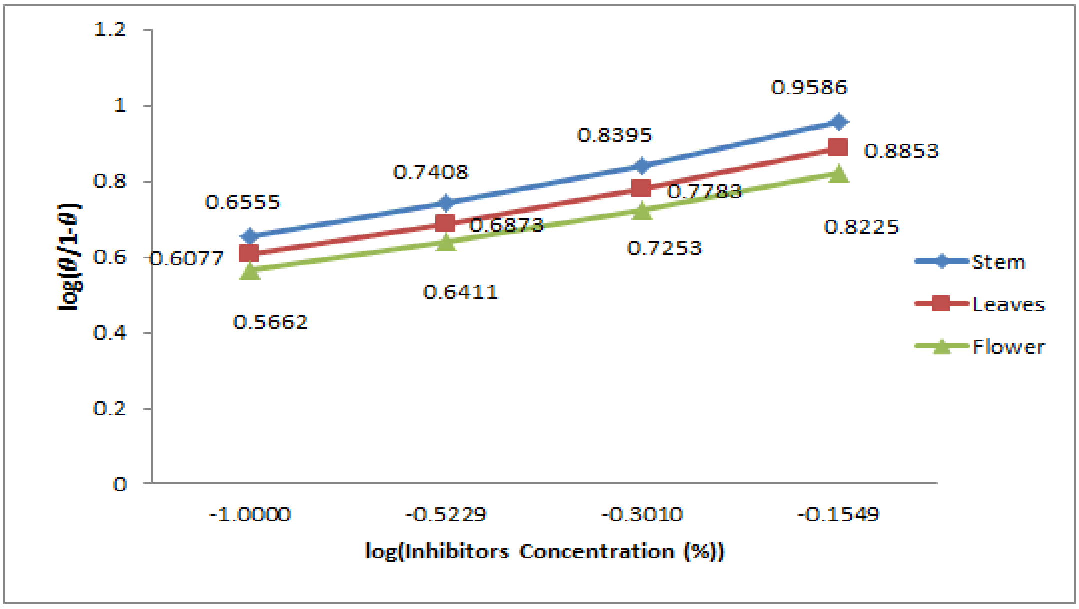

Fig 3 (b). Langmuir adsorption isotherm for Aluminium in 2N H_2SO_4 acid solution

Table 3. Weight loss data (Δw), inhibition efficiency (η%), surface coverage (θ) and corrosion rate for Aluminium in 3N H_2SO_4 acid solution with various inhibitors extract concentration of aerial parts of *Euphorbia neriifolia linn* plant.
Temperature : 300±0.1^{0}C Time of Exposure: (0.133 hrs) Area of Specimen :13cm^2

Concentration (%)	Weight Loss (Δw) in g	Inhibition Efficiency (I.E.) (η%)	Surface Coverage (θ)	Corrosion Rate in (mm/yr)	$\log\left(\frac{\theta}{1-\theta}\right)$
Stems					
Uninhibited	0.4016			0.0074	
0.1	0.0871	78.31	0.7831	0.0016	0.5575
0.3	0.0765	80.95	0.8095	0.0014	0.6283
0.5	0.0658	83.61	0.8361	0.0012	0.7076
0.7	0.0552	86.25	0.8625	0.0010	0.7974
Leaves					
0.1	0.0941	76.56	0.7656	0.0017	0.5140
0.3	0.0834	79.23	0.7923	0.0015	0.5814
0.5	0.0727	81.89	0.8189	0.0013	0.6553
0.7	0.0621	84.53	0.8453	0.0011	0.7375
Flowers					
0.1	0.1011	74.82	0.7482	0.0018	0.4729
0.3	0.0904	77.49	0.7749	0.0016	0.5368
0.5	0.0798	80.12	0.8012	0.0014	0.6053
0.7	0.0691	82.79	0.8279	0.0012	0.6821

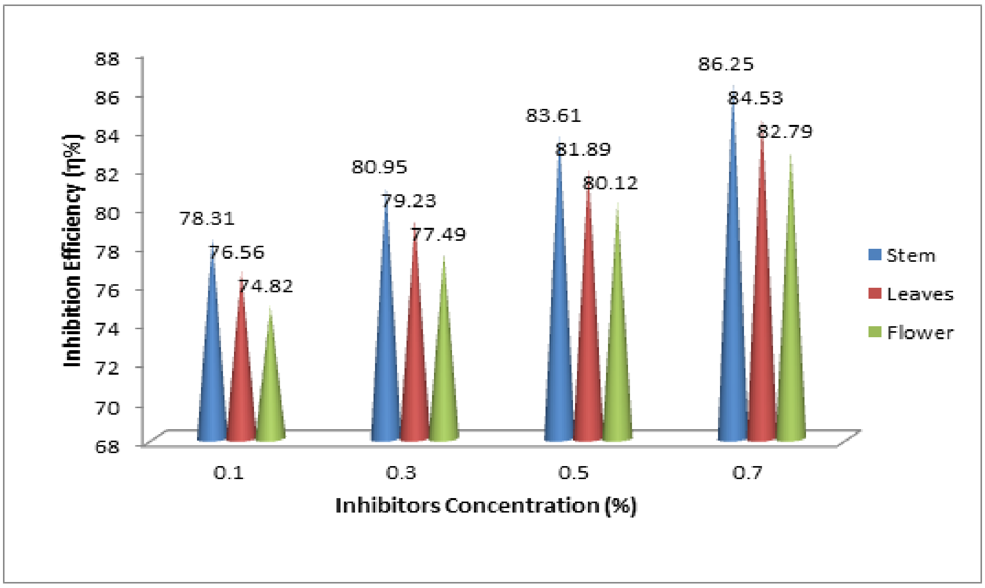

Fig 4 (a). Variation of inhibition efficiency with various concentrations of inhibitors for Aluminium in 3N H_2SO_4 acid solution

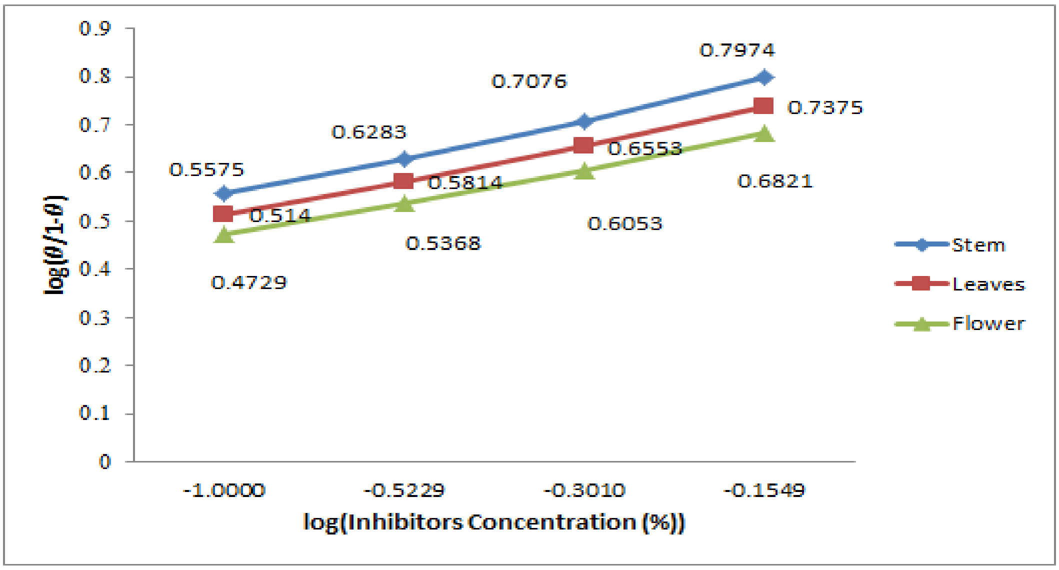

Fig 4 (b). Langmuir adsorption isotherm for Aluminium in 3N H_2SO_4 acid solution

Table 4. Reaction number (RN) and Inhibition efficiency (%) for Aluminium in 1N, 2N and 3N H_2SO_4 acid with various concentration of inhibitors

Temperature: 300±0.1^{0}C Area of Specimen: 13cm^2

Inhibitor Concentration (%)	1N H_2SO_4		2N H_2SO_4		3N H_2SO_4	
	RN Reaction Number	I.E.(%) Inhibition Efficiency	RN Reaction Number	I.E.(%) Inhibition Efficiency	RN Reaction Number	I.E.(%) Inhibition Efficiency
Stems						
Uninhibited	0.3402		0.6205		0.9120	
0.1	0.1507	55.84	0.3102	50.00	0.4962	45.59
0.3	0.1417	58.34	0.2933	52.73	0.4798	47.39
0.5	0.1327	60.99	0.2762	55.48	0.4674	48.75
0.7	0.1232	63.78	0.2465	60.27	0.4276	53.11
Leaves						
0.1	0.1625	52.23	0.3360	45.85	0.5322	41.64
0.3	0.1560	54.14	0.3237	47.83	0.5175	43.25
0.5	0.1495	56.05	0.3152	49.20	0.4957	45.65
0.7	0.1430	57.96	0.2781	55.18	0.4682	48.66
Flowers						
0.1	0.1796	47.20	0.3558	42.98	0.5810	36.29
0.3	0.1726	49.26	0.3337	46.22	0.5601	38.58
0.5	0.1656	51.05	0.3285	47.05	0.5250	42.43
0.7	0.1586	53.38	0.3052	50.81	0.4956	45.65

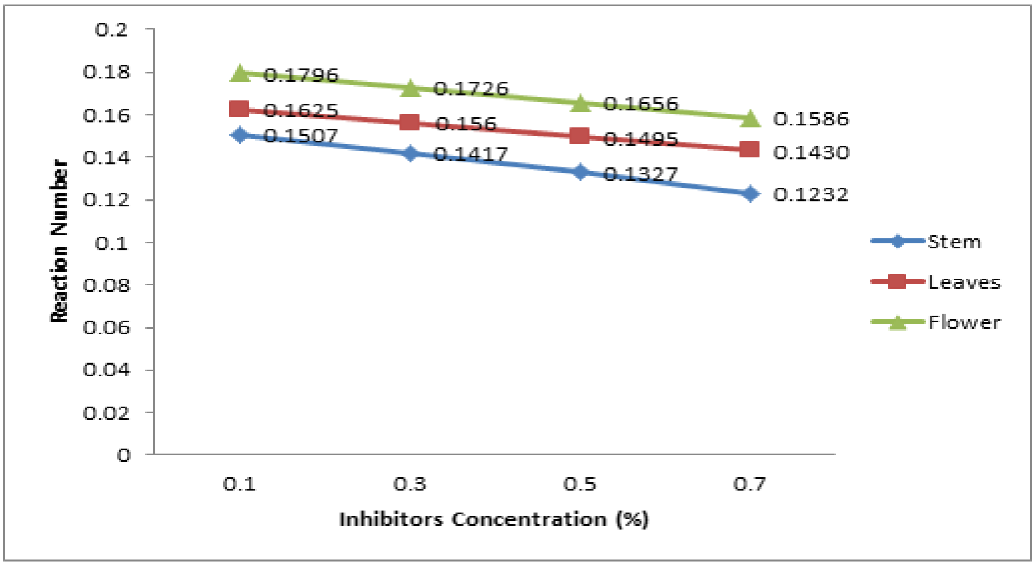

Fig 5 (a). Variation of Reaction Number with various concentrations of inhibitors for Aluminium in 1N H_2SO_4 acid solution

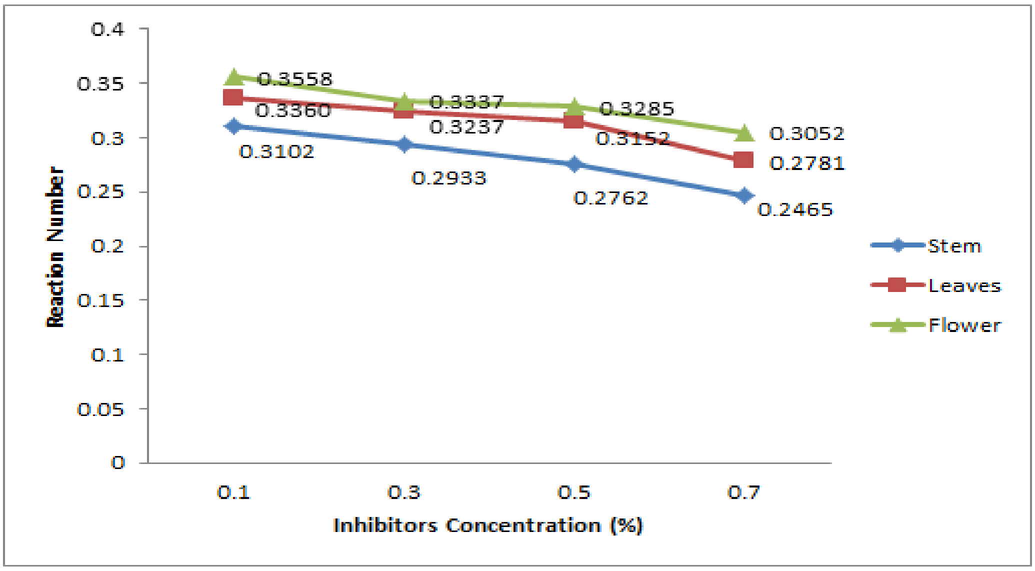

Fig 5 (b). Variation of Reaction Number with various concentrations of inhibitors for Aluminium in 2N H_2SO_4 acid solution

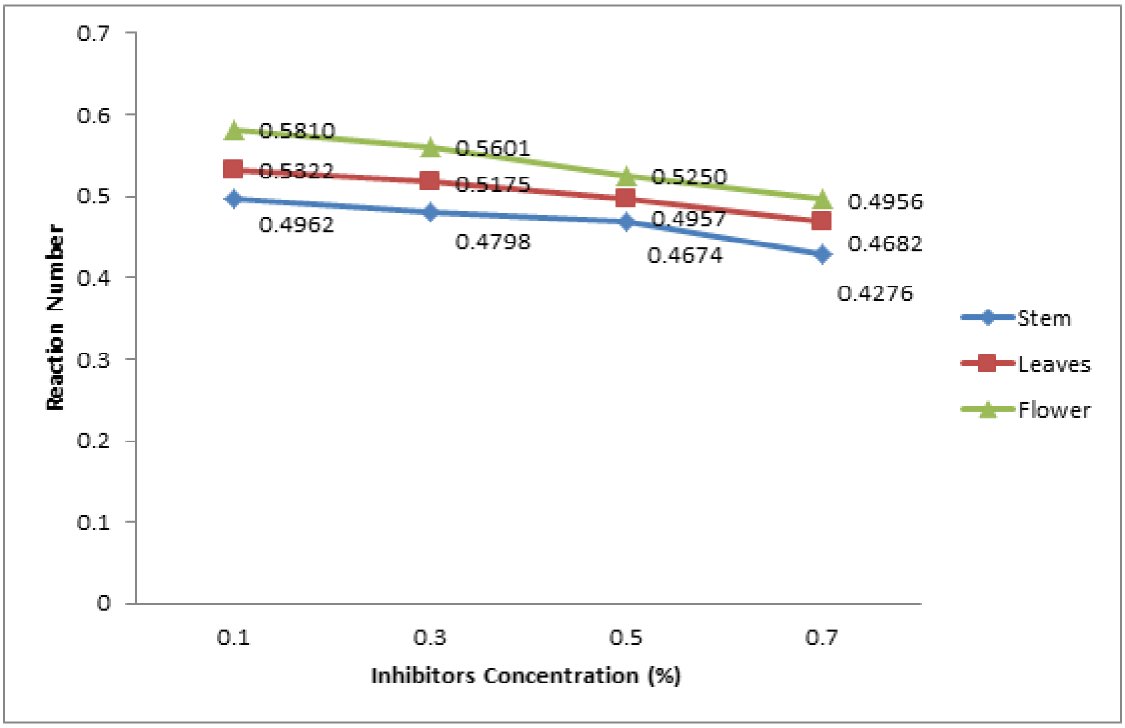

Fig 5 (c). Variation of Reaction Number with various concentrations of inhibitors for Aluminium in 3N H_2SO_4 acid solution

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