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Corrosion Inhibition of Aluminium by *Capparis decidua* in Acidic Media

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Abstract: The inhibition efficiency of ethanolic extract of different parts of *Capparis decidua* (Ker) in acidic medium has been evaluated by mass loss and thermometric methods. Values of inhibition efficiency obtained from the two methods are in good agreement and are dependent upon the concentration of inhibitor and acid.

Keywords: Corrosion, Inhibition, Aluminium, *Capparis decidua*.

Introduction

Aluminium being various corrosive agents subject an industrially important metal to corrosion in service, of which aqueous acids are most harmful. The corrosion of aluminium and its alloys in acidic solution has been studied. The effect of nitrogen containing heterocyclic compounds on the dissolution of aluminium has also been evaluated. Organic compounds containing nitrogen have been found to function as very effective corrosion inhibitors. The efficiency of these compounds as corrosion inhibitors can be attributed to the number of mobile electron pair present, the orbital character of free electrons and electron density around the nitrogen atoms. In the present investigation the inhibitive effect have been evaluated of ethanolic extract of fruit, stem bark and root bark of *Capparis decidua*. The extracts of *Capparis decidua* work as green inhibitor, which are nontoxic and biodegradable. Ker is commonly used in the Indian system of medicine. Its stem bark, root bark, fruit, seeds, young shoots and even buds are endowed with medicinal properties. The seeds are cooling, laxative, refrigerant, leaves and young shoots are purgative, stem bark is cooling astringent and fruit is laxative and digestive. Because of the toxic nature and high cost of some chemicals currently in use it is necessary to develop environmentally

acceptable and less expensive inhibitors. Natural product can be considered as a good source for this purpose. To reduce the corrosion problem in environment inhibitive effects of various naturally occurring substances like *Datura stramonium*[2], *Calotropis gigantea, Capparis decidua*[3], *Prosopis juliflora*[4] have been evaluated as effective corrosion inhibitors. The average composition of ripe fruit is as following

Moisture	65%
Protein	17%
Fat	05%
Carbohydrate	71%
Fiber	01%
Ca	210 mg/100 g
P	360 mg
Fe	06 mg
Vitamin C	100 mg/100 g

Experimental

2 Kg of plant material in natural condition was air dried for 8 to 10 days in shade. Then grained and powdered. 300g of finely powdered dried material was taken in a 1000mL round bottom flask and sufficient quantity of ethyl alcohol was added to cover the powder completely. The RBF was covered with stopper and left for 48h. Then the resulting paste was refluxed for 48h. Then it was filtered. The reaction procedure for extraction was repeated for maximum extraction. The filtrate was collected and then separated ethyl alcohol with the help of distillation unit. To clean the stuff obtained it was boiled with activated charcoal (2g) to remove gung and pure plant extract is obtained. 2kg of plant material in natural condition was air dried for 8 to 10 days in shade. Then grained and powdered. 300g of finely powdered dried material was taken in a 1000ml round bottom flask and sufficient quantity of ethyl alcohol was added to cover the powder completely. The RBF was covered with stopper and left for 48h. Then the resulting paste was refluxed for 48hours. Then it was filtered. The reaction procedure for extraction was repeated for maximum extraction. The filtrate was collected and then separated ethyl alcohol with the help of distillation unit. To clean the stuff obtained it was boiled with activated charcoal (2g) to remove gung and pure plant extract is obtained.

Specimen preparation

Rectangular specimens of aluminium of dimension 2.5X1.5X0.02 cm containing a small hole of 2mm diameter near the upper edge were employed for the determination of corrosion rate. Specimens were cleaned by buffing to produce a mirror finish with the help of emery paper and were then degreased. Each specimen was suspended by a glass hook and immersed in a beaker containing 50mL of test solution at 23 ^{0}C and left exposed to air. Evaporational losses were made up with doubly distilled water. After the test specimens were cleaned with benzene. Duplicate experiments were performed in each case and mean values of the Weight loss were calculated.

Test solution preparation

The acidic solution was prepared by using doubly distilled water. All chemicals were used of analytical reagent quality.

The percentage inhibition efficiency was calculated[5] as

$I=100(\Delta Mu-\Delta Mi/\Delta Mu)$

Where ΔMu and ΔMi are the mass loss of the metal is uninhibited and inhibited solution respectively.

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

$\theta = \Delta Mu-\Delta Mi/\Delta Mu$

Where θ surface coverage and ΔMu and ΔMi are the mass loss of the metal in uninhibited and inhibited acid.

The **corrosion rate** is mmpy (mili miles per year) can be obtained by the following equation

Corrosion rate (mmpy) = (Mass loss*87.6) / (Area*Time*Metal density)

Where mass loss is expressed in mg, area is expressed in cm^2 of metal surface exposed, time is expressed in hours of exposure, metal density is expressed in $g/cm^3$and 87.6 is conversion factor.

Inhibition efficiency was also determined using a thermometric technique. This involved the immersion of single specimens measuring 2.5X1.5X0.02 cm in a reaction chamber containing 50 mL of test solution. Temperature changes were measured at interval of one minute using a thermometer with a precision of 0.5ºC.The temperatures increased slowly at first then rapidly and attained a maximum temperature was recorded percentage inhibition efficiencies were calculated[6] as

$\eta=100(RNfree-RNi)/RNfree$

Where RNi and RNfree are the reaction number in the presence and absence of inhibitors respectively and RN ($^{\circ}C$/min) is defined as

$RN=(Tm-To)/t$

Where Tm and To are the maximum and initial temperature respectively and '*t*' is the time required to reach the maximum temperature.

Results and Discussion

The inhibition efficiency (%) calculated from the mass loss measurement for hydrochloric acid and sulphuric acid and inhibitor are given in tables. It is observed that the inhibition efficiency increases with increase in the concentration of inhibitor and decreases with increases in acid strength. The corrosion rate decreases with increases in concentration of inhibitor. The maximum effeciency was obtained in low acid concentration. The inhibitors have shown the efficiency in the range. Capparis *decidua* fruit extract shows minimum 51.99% inhibition efficiency and maximum 98.49% for 0.5N hydrochloric acid but 1N hydrochloric acid solution show minimum efficiency 32.27% and maximum 65.17% and 2N hydrochloric acid solution show minimum efficiency 33.95% and maximum 55.56%. *Capparis decidua* stem bark extract shows minimum 38.92% inhibition efficiency and maximum 93.52% for 0.5N for hydrochloric acid but 1N hydrochloric acid solution show minimum efficiency 27.07% and maximum 64.09% and 2N hydrochloric acid solution show minimum efficiency 25.42% and maximum 53.22%. *Capparis decidua* root bark extract shows minimum 31.05% inhibition efficiency and maximum 94.44% for 0.5N for hydrochloric acid but 1N hydrochloric acid solution show minimum efficiency 27.74% and maximum 63.10 % and 2N hydrochloric acid solution show minimum 36.38 % and

maximum 57.68% (Table 3). *Capparis decidua* fruit extract shows inhibition effeciency minimum 23.10% and maximum 77.84% for 0.5N for sulphuric acid but 1N sulphuric acid solution show minimum 24.08% and maximum 62.20% and 2N sulphuric acid solution show minimum 46.07% and maximum 55.62%. *Capparis decidua* stem bark extract shows inhibition effeciency minimum 24.52% and maximum 76.23% for 0.5N for sulphuric acid but 1N sulphuric acid solution show minimum 15.86% and maximum 56.62% and 2N sulphuric acid solution show minimum 48.19% and maximum 56.12%.

Table 1. Mass loss and corrosion rate (mmpy) for aluminium in hydrochloric acid solution with given inhibitor addition at room temperature for *Capparis decidua*.

	0.5N HCl		1N HCl		2N HCl	
	Mass loss	Mmpy	Mass loss	Mmpy	Mass loss	Mmpy
Uninhibited	0.1729		0.3136		0.4812	
Fruit extract						
0.08	0.0830	0.0149	0.2124	0.0383	0.3178	0.0572
0.16	0.0410	0.0073	0.1906	0.0343	0.2843	0.0512
0.24	0.0270	0.0020	0.1764	0.0317	0.2662	0.0479
0.36	0.0138	0.0024	0.1444	0.0260	0.2378	0.0428
0.40	0.0026	0.0004	0.1092	0.0019	0.2138	0.0385
Stem bark extract						
0.08	0.1056	0.0146	0.2287	0.0407	0.2987	0.0538
0.16	0.0852	0.0153	0.2017	0.0363	0.2765	0.0498
0.24	0.0552	0.0099	0.1794	0.0323	0.2568	0.0462
0.36	0.0306	0.0055	0.1492	0.0268	0.2442	0.0440
0.40	0.0112	0.0020	0.1126	0.0202	0.2079	0.0374
Root bark extract						
0.08	0.1192	0.0214	0.2265	0.0408	0.3061	0.0551
0.16	0.0872	0.0157	0.2057	0.0370	0.2958	0.0537
0.24	0.0535	0.0096	0.1809	0.0326	0.2573	0.0463
0.36	0.0292	0.0052	0.1357	0.0244	0.2289	0.0412
0.40	0.0096	0.0017	0.1157	0.0208	0.2036	0.0366

Capparis decidua root bark extract shows inhibition effeciency minimum 24.24% and maximum 76.79% for 0.5N for hydrochloric acid but 1N sulphuric acid solution show minimum 18.91% and maximum 59.60% and 2N sulphuric acid solution show minimum 45.63% and maximum 56.53%. (Table 4). *Capparis decidua* fruit extract shows inhibition efficiency minimum 82.58% for 5N hydrochloric acid and maximum 94.98% for 3N acid solution. Capparis *decidua* stem bark extract shows inhibition efficiency minimum 83.88% for 5N hydrochloric acid and maximum 94.61 % for 3N for hydrochloric acid. *Capparis decidua* root bark extract shows inhibition efficiency minimum 84.31% for 5N hydrochloric acid and maximum 94.79% for 3N acid(Table 5). *Capparis decidua* fruit extract shows inhibition efficiency minimum 73.57% for 5N sulphuric acid and maximum 81.76% for 3N sulphuric acid solution. Capparis *decidua* stem bark extract shows inhibition efficiency minimum 71.91% for 5N sulphuric acid and maximum 83.37 % for 3N for sulphuric hydrochloric acid. *Capparis decidua* root bark extract shows inhibition efficiency minimum 75.39% for 5N sulphuric hydrochloric acid and maximum 83.50% for 3N sulphuric acid (Table 6).

Table 2. Mass loss and corrosion rate (Mmpy) for aluminium in sulphuric acid solution with given inhibitor addition at room temperature for *Capparis decidua.*

	0.5N H_2SO_4		1N H_2SO_4		2N H_2SO_4	
	Mass loss	Mmpy	Mass loss	Mmpy	Mass loss	Mmpy
Uninhibited	0.1056		0.2421		0.4137	
Fruit extract						
0.08	0.0812	0.0146	0.1838	0.0331	0.2231	0.0402
0.16	0.0704	0.0126	0.1548	0.0279	0.2149	0.0387
0.24	0.0631	0.0113	0.1369	0.0246	0.2001	0.0360
0.36	0.0397	0.0071	0.1263	0.0227	0.1993	0.0359
0.40	0.0234	0.0042	0.0915	0.0164	0.1836	0.0330
Stem bark extract						
0.08	0.0797	0.0143	0.2037	0.0367	0.2212	0.0398
0.16	0.0682	0.0122	0.1916	0.0345	0.2143	0.0386
0.24	0.0601	0.0108	0.1601	0.0288	0.2011	0.0362
0.36	0.0353	0.0063	0.1348	0.0242	0.1963	0.0353
0.40	0.0251	0.0045	0.1050	0.0189	0.1815	0.0327
Root bark extract						
0.08	0.0800	0.0144	0.1963	0.0353	0.2249	0.0405
0.16	0.0712	0.0128	0.1859	0.0335	0.2107	0.0379
0.24	0.0611	0.0110	0.1513	0.0272	0.2077	0.0374
0.36	0.0373	0.0067	0.1378	0.0248	0.1947	0.0350
0.40	0.0245	0.0017	0.0978.	0.0176	0.1798	0.0324

Table 3. Surface coverage and inhibition efficiency for aluminium in hydrochloric acid solution with given inhibitor addition at room temperature for *Capparis decidua*.

	0.5N HCl		1N HCl		2N HCl	
	Surface coverage	η,%	Surface coverage	η,%	Surface coverage	η,%
Uninhibited	0.1729		0.3136		0.4812	
Fruit extract						
0.08	0.5199	51.99	0.3227	32.27	0.3395	33.95
0.16	0.7678	76.78	0.3922	39.22	0.4019	40.19
0.24	0.8438	84.38	0.4375	43.75	0.4467	44.67
0.36	0.9201	92.01	0.5395	53.95	0.5058	50.58
0.40	0.9849	98.49	0.6517	65.17	0.5556	55.56
Stem bark extract						
0.08	0.3892	38.92	0.2707	27.07	0.2542	25.42
0.16	0.5072	50.72	0.3568	35.68	0.3983	39.83
0.24	0.6807	68.07	0.4279	42.79	0.4345	43.45
0.36	0.8230	82.30	0.5240	52.40	0.4462	44.62
0.40	0.9352	93.52	0.6409	64.09	0.5322	53.22
Root bark extract						
0.08	0.3105	31.05	0.2774	27.74	0.3638	36.38
0.16	0.4906	49.06	0.3440	34.40	0.3859	38.59
0.24	0.6905	69.05	0.4213	42.13	0.4652	46.52
0.36	0.8311	83.11	0.5672	56.72	0.5243	52.43
0.40	0.9444	94.44	0.6310	63.10	0.5768	57.68

Table 4. Surface coverage and inhibition efficiency for aluminium in sulphuric acid solution with given inhibitor addition at room temperature for *Capparis decidua*.

	0.5N H_2SO_4		1N H_2SO_4		2N H_2SO_4	
	Surface coverage	η,%	Surface coverage	η, %	Surface coverage	η, %
Uninhibited	0.1056		0.2421		0.4137	
Fruit extract						
0.08	0.2310	23.10	0.2408	24.08	0.4607	46.07
0.16	0.3333	33.33	0.3605	36.05	0.4805	48.05
0.24	0.4024	40.24	0.4345	43.45	0.5182	51.38
0.36	0.6240	62.40	0.4783	47.83	0.5255	52.55
0.40	0.7784	77.84	0.6220	62.20	0.5562	55.62
Stem bark extract						
0.08	0.2452	24.52	0.1586	15.86	0.4653	46.53
0.16	0.3541	35.41	0.2085	20.85	0.4819	48.19
0.24	0.4308	43.08	0.3387	33.87	0.5138	51.38
0.36	0.6657	66.57	0.4432	44.32	0.5255	52.55
0.40	0.7623	76.23	0.5662	56.62	0.5612	56.12
Root bark extract						
0.08	0.2424	24.24	0.1891	18.91	0.4563	45.63
0.16	0.3257	32.57	0.2321	23.21	0.4906	49.06
0.24	0.4214	42.14	0.3750	37.50	0.4979	49.79
0.36	0.6467	64.67	0.4308	43.08	0.5293	52.93
0.40	0.7679	76.79	0.5960	59.60	0.5653	56.53

Table 5. Reaction number and inhibition efficiency for aluminium in hydrochloric acid solution with given inhibitor addition at room temperature for Capparis decidua

	3N HCl		4N HCl		5N HCl	
	RN	η, %	RN	η, %	RN	η, %
Uninhibited	2.528		4.528		6.815	
Fruit extract						
0.08	1.615	33.70	1.898	58.57	3.721	45.39
0.16	1.138	53.28	1.793	60.86	2.264	66.77
0.24	0.897	63.17	1.413	69.16	2.016	70.41
0.36	0.538	77.91	0.725	84.11	1.863	72.66
0.40	0.122	94.98	0.232	94.92	1.187	82.58
Stem bark extract						
0.08	1.583	35.01	1.901	58.50	4.010	41.15
0.16	1.102	54.76	1.688	63.16	2.139	68.61
0.24	0.883	63.73	1.255	72.60	1.889	72.28
0.36	0.520	78.64	0.782	82.19	1.742	74.43
0.40	0.131	94.61	0.356	92.22	1.098	83.88
Root bark extract						
0.08	1.601	34.27	1.941	57.62	3.971	41.73
0.16	1.018	58.21	1.782	61.10	2.298	66.28
0.24	0.790	67.56	1.364	70.22	1.764	74.11
0.36	0.493	79.75	0.699	84.74	1.569	76.97
0.40	0.126	94.79	0.364	92.05	1.069	84.31

Table 6. Reaction number and inhibition efficiency for aluminium in sulphuric acid solution with given inhibitor addition at room temperature for Capparis decidua

	3N HCl		4N HCl		5N HCl	
	RN	η,%	RN	η,%	RN	η,%
Uninhibited	0.0976		0.1683		0.3251	
Fruit extract						
0.08	0.0488	50.00	0.1015	39.69	0.1752	46.10
0.16	0.0361	63.01	0.0821	51.21	0.1531	52.90
0.24	0.0292	70.08	0.0678	59.71	0.1342	58.72
0.36	0.0194	80.12	0.0539	67.97	0.1052	67.64
0.40	0.0178	81.76	0.0345	79.50	0.0859	73.57
Stem bark extract						
0.08	0.0421	56.85	0.0910	45.92	0.1763	45.77
0.16	0.0346	64.54	0.0877	47.89	0.1541	52.59
0.24	0.0287	70.59	0.0667	60.36	0.1352	58.41
0.36	0.0187	80.84	0.0542	67.79	0.1113	65.76
0.40	0.0172	82.37	0.0329	80.45	0.0913	71.91
Root bark extract						
0.08	0.0463	52.56	0.0977	41.94	0.1757	45.95
0.16	0.0357	63.42	0.0863	48.72	0.1539	52.66
0.24	0.0269	72.43	0.0644	61.73	0.1356	58.28
0.36	0.0192	80.32	0.0540	67.91	0.1037	68.10
0.40	0.0161	83.50	0.0315	81.40	0.0800	75.39

Generally the adsorption of organic molecules involves O, N and S atoms. This process may block active sites hence, decrease the corrosion rate. In the present study it is assuming that the plant extract are adsorbed on the metal surface and decreases the surface area available for cathodic and anodic reaction to take place.

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Conclusions

From the present investigation, the following conclusion can be drawn

- The rate of corrosion of mild steel and aluminium in hydrochloric acid and sulphuric acid is a function of the concentration of *Capparis decidua*.
- The inhibition increases with increased additive concentration.
- *Capparis decidua* ethanolic extract is a corrosion inhibitor and can be replace toxic chemicals.

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