Inhibition of the Corrosion of Mild Steel in Acid Media by Naturally Occurring *Acacia Senegal*

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Abstract: The inhibition of corrosion of mild steel in HCl solution by naturally occurring *Acacia senegal* has been studied in relation to the concentration of inhibitor and concentration of corrosive medium. It has been observed that the *Acacia senegal* alcoholic extract acts as a good corrosion inhibitor in hydrochloric acid solution and the adsorption of the extract provides a good protection against mild steel corrosion.

Keywords: Corrosion, Inhibitors, *Acacia Senegal*, HCl, Langmuir adsorption isotherm.

Introduction

Corrosion is the destructive attack on a metal or metal alloy by chemical or electrochemical reaction with its environment¹. Corrosion of metal is a major industrial problem that has attracted a lot of investigators in recent years²⁻⁴. Corrosion inhibitors are of great practical importance, being extensively employed in minimizing metallic waste in engineering materials³. Many current corrosion control methods use coating and conversion layers which contain toxic and environmentally hazardous material. There is a great need to find a non toxic replacement that is compatible with current industrial technologies. Well known as non toxic compound and due to their availability and relatively low cost, naturally substances find various applications in many fields. Like tannin, beet root^{5,6}, saponin⁷, tamarind, tea-leaves, pomegranate juice peels^{8,9} and the mixture of the later three sapindus, trifolianus and acacia concianna¹⁰, swertiw aangustefolia¹¹ and prosopis juliflora¹² which have been evaluated as effective corrosion inhibitor.

Mild steel find a variety of application owing to its excellent strength and workability. The corrosion of steel has long been an important problem causing losses in excess of US\$ 100 billion annually worldwide. The corrosion inhibitor of mild steel in different acid media has been studies by various authors¹³⁻¹⁶. In the present work, an attempt has been made to study the influence of varying concentration of constitues and substitute extracts of

Acacia senegal the corrosion rate of mild steel in 0.1 N hydrochloric acid to 5 N hydrochloric acid. *Acacia senegal* belongs to the fabaceae family. Its seed are dried and preserved for human consumption¹⁷. Causing partial destruction of many alkaloids including atropine, hyoscyamine, scopolamine, homatropine, morphine, apomorphine, cocaine and physostigmine, gum acacia might be viewed as a possible antidote. It is pharmaceutically used mainly in the manufacture of emulsions and in making pills and troches, as demulcent for inflammation of the throat or stomach and as masking agent for acrid tasting substance such as capsicum, also as a film forming agent in peel off masks. The alkaloids found in *Acacia senegal* include less than .1% DMT and NMT in leaf¹⁸⁻¹⁹.

Figure 1. Atropine

Figure 2. Esarine (Physostigmine) An
acetylcholinesterase inhibitor (alkaloid) 2003
A.M. Helmenstine

Figure 3. Hyoscyamine

Figure 4. Homatropine

Experimental

For the mass loss determination, rectangular specimen of mild steel of size 1.5x2.5x.025 cm were so cut from a sheet having chemical composition as carbon (0.14%), manganese (0.32%), sulphur (0.05%), tungsten (0.02%) and rest mild steel. 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 than suspended with the help of glass hooks in borosil beakers containing 50 mL of corrosive electrolyte for complete immersion test. The solution of 0.1 N to 5 N HCl 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. The solvent is distilled off and residue treated with inorganic acid. Where, the base is extracted as their soluble salt. The free bases are liberated by the addition of any base and extracted with various solvent *eg.* ether, chloroform, *etc.* The mixture of base thus obtained is separated by various methods into the individual compound²⁰.

The test specimens were studied for complete immersion test in different acid solution at 298 ± 1 K temperatures with and without inhibitor, after removal of the corrosion product. The duration of immersion time is 24 h and is indicated in respective Tables. After the immersion period the specimen was cleaned carefully as per champion. Corrosion rate (mmpy), inhibition efficiency ($\eta\%$), rate constant and half life were calculated from this mass loss data. The results are depicted in respective Table. The inhibitor efficiency ($\eta\%$) is calculated as²¹.

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

Where the Mu is the mass loss of metal in uninhibited acid and Mi ; mass loss of metal in inhibited solution. The degree of surface coverage (θ) can be calculated as

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

Where θ is surface coverage and ΔMu and ΔMi are the mass loss of the metal in uninhibited and inhibited acid. The corrosion rate in miles per year can be obtained by the following equation²².

$$\text{Corrosion rate} = \frac{\text{mass loss} \times 87600}{\text{Area} \times \text{time} \times \text{density}} \quad (3)$$

Where mass loss in gram, Area is in of metal surface exposed time is expressed in hours of exposure and metal density is expressed in gram/cm^3 .

The corrosion current (i) can be calculated as²³ –

Corrosion current (i) = Corrosion rate $\times F / n$

Where F is faraday (96500) and n is number of electron. The inhibitive action and the compound will also be investigated by using mylius thermometric method. This involved the immersion of single specimens ($2.5 \times 1.5 \times 0.025$ cm) in a reaction chamber containing 50 mL. of solution at initial temperature 298 ± 0.1 K. Temperature changes were measured at intervals of 5 min using thermometer with a precision of 0.01 K. The temperature increased slowly at first then rapidly and attained a maximum value before falling. The minimum temperature was recorded the percentage inhibition efficiencies in this case were calculated²⁴.

$$\eta = 100 (RN_{\text{free}} - RN_i) / RN_{\text{free}} \quad (4)$$

Where RN_i and RN_{free} are the reaction number in the presence and absence of inhibitor respectively and RN (K Min^{-1}) is defined as

$$RN = (T_m - T_o) / t \quad (5)$$

Where T_m and t_o is the maximum and initial temperature respectively and t is the time required to reach the maximum temperature in minutes.

Results and Discussion

All the inhibitors have reduced the corrosion rate to a significant extent. Corrosion rate, inhibition efficiency, surface coverage, corrosion current, rate constant, half life with or without inhibitor are show in Tables 1-4.

Effect of concentration- The $\eta\%$ calculated from the mass loss measurement for. 1 N to 1 N HCl solution. It is found that the inhibition efficiency increases with increases of inhibitor concentration for different plant extracts from 0.12% to 0.6% from the mass loss data. It was concluded that the plant extracts act as a good inhibitor for mild steel in HCl solution. Table show that the leaf extract of *Acacia senegal* has maximum inhibition efficiency.

Kinetic parameter- From Tables 1-4, the rate constant at 298K show a general decrease with increases inhibitor concentration, inhibitor efficiency, half life of the metal -corrodent-inhibitor system. Similar trend in kinetic data has been reported by several investigators and indicate that a good inhibitor is one that is able to increase the time of conversion of metals to corrosion products. Table show increases in half life when inhibitors are present, which further support the assertion that the natural product are corrosion inhibitors for mild steel in HCl solution.

Table 1. Effect of extract of different parts of plants *Acacia Senegal* on mass loss data for corrosion of mild steel in 0.1 N HCl at 298±1K Effective area of specimen: 7.50 cm² Immersion time 24 h

Inhibitor concentration	Mass loss, mg	Inhibition efficiency, $\eta\%$	Surface coverage θ	Corrosion rate	Corrosion current	Rate constant	Half life
Uninhibited	40.3	0.00	0.0000	2.50	80263.88	0.0022	315.94
Leaf extract							
0.12	16.2	59.80	0.5980	1.00	32264.89	0.0009	798.47
0.24	13.5	66.50	0.6650	0.84	26887.40	0.0007	959.84
0.36	10.1	74.94	0.7494	0.63	20115.76	0.0005	1285.77
0.48	6.7	83.37	0.8337	0.41	13344.12	0.0004	1942.48
0.60	3.9	90.32	0.9032	0.24	7767.47	0.0002	3343.06
Seed extract							
0.12	18.1	55.09	0.5509	1.12	36049.04	0.0010	713.77
0.24	15.3	62.03	0.6203	0.95	30472.39	0.0008	845.93
0.36	12.4	69.23	0.6923	0.77	24696.58	0.0007	1045.73
0.48	10	75.19	0.7519	0.62	19916.60	0.0005	1298.71
0.60	6.8	83.13	0.8313	0.42	13543.29	0.0004	1913.79
Bark extract							
0.12	17.3	57.07	0.5707	1.07	34455.71	0.0009	747.17
0.24	13.7	66.00	0.6600	0.85	27285.74	0.0007	945.70
0.36	11.6	71.22	0.7122	0.72	23103.25	0.0006	1118.42
0.48	8.4	79.16	0.7916	0.52	16729.94	0.0004	1547.67
0.60	6	85.11	0.8511	0.37	11949.96	0.0003	2170.07
Root extract							
0.12	16.5	59.06	0.5906	1.02	32862.38	0.0009	783.80
0.24	13.2	67.25	0.6725	0.82	26289.91	0.0007	981.84
0.36	10.8	73.20	0.7320	0.67	21509.92	0.0006	1201.89
0.48	8	80.15	0.8015	0.50	15933.28	0.0004	1625.47
0.60	4.8	88.09	0.8809	0.30	9559.97	0.0003	2714.68
Gum extract							
0.12	15.3	62.03	0.6203	0.95	30472.39	0.0008	845.93
0.24	11.6	71.22	0.7122	0.72	23103.25	0.0006	1118.42
0.36	9.2	77.17	0.7717	0.57	18323.27	0.0005	1412.36
0.48	6.4	84.12	0.8412	0.40	12746.62	0.0003	2033.92
0.60	3.6	91.07	0.9107	0.22	7169.97	0.0002	3622.34

Table 2. Effect of extract of different parts of plants *acacia Senegal* on mass loss data for corrosion of mild steel in 0.2 N HCl at 298±1K, Effective area of specimen: 7.50 cm² Immersion time 24 h

Inhibitor concentration	Mass loss mg	Inhibition efficiency, $\eta\%$	Surface coverage, θ	Corrosion rate	Corrosion current	Rate constant	Half life
Uninhibited	75.3	0.00	0.0000	4.66	149971.97	0.0042	165.12
Leaf extract							
0.12	35.7	52.59	0.5259	2.21	71102.25	0.0019	357.74
0.24	27.3	63.75	0.6375	1.69	54372.31	0.0015	470.41
0.36	22.8	69.72	0.6972	1.41	45409.84	0.0012	564.91
0.48	16	78.75	0.7875	0.99	31866.55	0.0009	808.56
0.60	10.1	86.59	0.8659	0.63	20115.76	0.0005	1285.77
Seed extract							
0.12	34.6	54.05	0.5405	2.14	68911.42	0.0019	369.38
0.24	29.4	60.96	0.6096	1.82	58554.79	0.0016	436.20
0.36	25.6	66.00	0.6600	1.59	50986.49	0.0014	502.20
0.48	21	72.11	0.7211	1.30	41824.85	0.0011	614.05
0.60	15.8	79.02	0.7902	0.98	31468.22	0.0008	818.90
Bark extract							
0.12	33.1	56.04	0.5604	2.05	65923.93	0.0018	386.50
0.24	27.1	64.01	0.6401	1.68	53973.98	0.0015	473.94
0.36	23.3	69.06	0.6906	1.44	46405.67	0.0013	552.61
0.48	17.3	77.03	0.7703	1.07	34455.71	0.0009	747.17
0.60	12	84.06	0.8406	0.74	23899.92	0.0006	1080.86
Root extract							
0.12	33.8	55.11	0.5511	2.09	67318.09	0.0018	378.32
0.24	25.6	66.00	0.6600	1.59	50986.49	0.0014	502.20
0.36	21.8	71.05	0.7105	1.35	43418.18	0.0012	591.21
0.48	16.5	78.09	0.7809	1.02	32862.38	0.0009	783.80
0.60	11.2	85.13	0.8513	0.69	22306.59	0.0006	1158.67
Gum extract							
0.12	31.6	58.03	0.5803	1.96	62936.44	0.0017	405.25
0.24	24.8	67.07	0.6707	1.54	49393.16	0.0013	518.67
0.36	20.3	73.04	0.7304	1.26	40430.69	0.0011	635.51
0.48	15.8	79.02	0.7902	0.98	31468.22	0.0008	818.90
0.60	9.7	87.12	0.8712	0.60	19319.10	0.0005	1339.13

Table 3. Effect of extract of different parts of plants *acacia Senegal* on mass loss data for corrosion of mild steel in 0.5 N HCl at 298±1K, Effective area of specimen: 7.50 cm² Immersion time 24 h

Inhibitor concentration	Mass loss mg	Inhibition efficiency, $\eta\%$	Surface coverage θ	Corrosion rate	Corrosion current	Rate constant	Half life
Uninhibited	98.5	0.00	0.0000	6.10	196178.47	0.0056	124.19
Leaf extract							
0.12	49.7	49.54	0.4954	3.08	98985.48	0.0027	254.58
0.24	39.5	59.90	0.5990	2.45	78670.55	0.0021	322.51
0.36	32.7	66.80	0.6680	2.02	65127.27	0.0018	391.33

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0.48	22.7	76.95	0.7695	1.41	45210.67	0.0012	567.43
0.60	15.5	84.26	0.8426	0.96	30870.72	0.0008	834.91
Seed extract							
0.12	45.6	53.71	0.5371	2.82	90819.68	0.0025	278.23
0.24	39	60.41	0.6041	2.41	77674.72	0.0021	326.75
0.36	33.4	66.09	0.6609	2.07	66521.43	0.0018	382.95
0.48	29.5	70.05	0.7005	1.83	58753.96	0.0016	434.70
0.60	20.6	79.09	0.7909	1.28	41028.19	0.0011	626.13
Bark extract							
0.12	45.6	53.71	0.5371	2.82	90819.68	0.0025	278.23
0.24	39	60.41	0.6041	2.41	77674.72	0.0021	326.75
0.36	33.4	66.09	0.6609	2.07	66521.43	0.0018	382.95
0.48	29.5	70.05	0.7005	1.83	58753.96	0.0016	434.70
0.60	20.6	79.09	0.7909	1.28	41028.19	0.0011	626.13
Root extract							
0.12	45.3	54.01	0.5401	2.80	90222.18	0.0025	280.13
0.24	38.4	61.02	0.6102	2.38	76479.73	0.0021	331.99
0.36	32.5	67.01	0.6701	2.01	64728.94	0.0018	393.79
0.48	24.6	75.03	0.7503	1.52	48994.83	0.0013	522.96
0.60	18.7	81.02	0.8102	1.16	37244.03	0.0010	690.60
Gum extract							
0.12	44.3	55.03	0.5503	2.74	88230.52	0.0024	286.65
0.24	35.4	64.06	0.6406	2.19	70504.75	0.0019	360.84
0.36	30.5	69.04	0.6904	1.89	60745.62	0.0016	420.17
0.48	24.6	75.03	0.7503	1.52	48994.83	0.0013	522.96
0.60	16.7	83.05	0.8305	1.03	33260.72	0.0009	774.31

Table 4. Effect of extract of different parts of plants *acacia Senegal* on mass loss data for corrosion of mild steel in 1 N HCl at 298±1K, Effective area of specimen: 7.50 cm² Immersion time 24 h

Inhibitor concentration	Mass loss, mg	Inhibition efficiency $\eta\%$	Surface coverage, θ	Corrosion rate	Corrosion current	Rate constant	Half life
Uninhibited	129.2	0.00	0.0000	8.00	257322.42	0.0075	92.60
Leaf extract							
0.12	72.1	44.20	0.4420	4.46	143598.66	0.0040	172.83
0.24	56.9	55.96	0.5596	3.52	113325.43	0.0031	221.29
0.36	49.7	61.53	0.6153	3.08	98985.48	0.0027	254.58
0.48	35.2	72.76	0.7276	2.18	70106.42	0.0019	362.94
0.60	25.3	80.42	0.8042	1.57	50388.99	0.0014	508.26
Seed extract							
0.12	60.1	53.48	0.5348	3.72	119698.74	0.0033	209.05
0.24	51.6	60.06	0.6006	3.19	102769.64	0.0028	244.89
0.36	45.2	65.02	0.6502	2.80	90023.01	0.0025	280.77
0.48	40	69.04	0.6904	2.48	79666.38	0.0022	318.37
0.60	29.7	77.01	0.7701	1.84	59152.29	0.0016	431.71

Contd...

Bark extract							
0.12	60.7	53.02	0.5302	3.76	120893.74	0.0033	206.90
0.24	50.3	61.07	0.6107	3.11	100180.48	0.0028	251.44
0.36	43.9	66.02	0.6602	2.72	87433.86	0.0024	289.34
0.48	33.5	74.07	0.7407	2.07	66720.60	0.0018	381.79
0.60	25.8	80.03	0.8003	1.60	51384.82	0.0014	498.24
Root extract							
0.12	59.4	54.02	0.5402	3.68	118304.58	0.0033	211.62
0.24	50.3	61.07	0.6107	3.11	100180.48	0.0028	251.44
0.36	42.6	67.03	0.6703	2.64	84844.70	0.0023	298.43
0.48	33.5	74.07	0.7407	2.07	66720.60	0.0018	381.79
0.60	23.2	82.04	0.8204	1.44	46206.50	0.0012	555.02
Gum extract							
0.12	60.7	53.02	0.5302	3.76	120893.74	0.0033	206.90
0.24	47.8	63.00	0.6300	2.96	95201.33	0.0026	265.04
0.36	41.3	68.03	0.6803	2.56	82255.54	0.0022	308.09
0.48	36.1	72.06	0.7206	2.24	71898.91	0.0020	353.68
0.60	27.1	79.02	0.7902	1.68	53973.98	0.0015	473.94

The variation of reaction number with inhibitor concentration, presented graphically in (Figure 6-9), show reaction number decreases with increasing inhibitors concentration. Adsorption isotherm - Adsorption plays an important role in the inhibition of metallic corrosion by inhibitors. Many investigators have used the Langmuir adsorption isotherm to study inhibitors characteristics²⁵.

Figure 5. Langmuir adsorption isotherm of leaves extract for mild steel in hydrochloric acid with inhibitor concentration

Figure 6. Variation of reaction number vs. Concentration with all five inhibitors in 2 N hydrochloric acid solution in mild steel

Figure 7. Variation of reaction number vs. Concentration with all five inhibitors in 3 N hydrochloric acid solution in mild steel

Figure 8. Variation of reaction number vs. Concentration with all five inhibitors in 4 N hydrochloric acid solution in mild steel

Figure 9. Variation of reaction number vs. Concentration with all five inhibitors in 5 N hydrochloric acid solution in mild steel

Langmuir adsorption isotherm-

$$\log [\theta / 1 - \theta] = \log A + \log C - (\theta / 2.3RT) \quad (6)$$

Should give a straight line of unit gradient for the plot of $(\theta/1-\theta)$ versus $\log C$ where θ is surface coverage, A is a temperature independent constant and C is concentration of the inhibitor. The corresponding plot Figure 5 is linear but the gradients are not equal to unity as would be expected for the Langmuir adsorption isotherm equation.

A wide range of substance can inhibit the corrosion of metal in aqueous acid solution. These include relative simple substance such as C, P, Br and I ions and many organic compounds, particularly those containing element such as N, O, S, P, As and Se. The primary step in the action of inhibition in acid solution is generally agreed to be adsorbed on the metal surface. Beside electrostatic interaction, inhibitor can bond to metal surface by electron transfer to the metal to form a co-ordinate type of link. This process is favored by the presence in the metal surface of vacant electron orbital of low energy, such as may be found in transition metal. Electron transfer from the adsorbed species is favored by the presence of loosely bound electrons, such as may be found in anions and neutral organic molecules containing lone pair of electron or π electron system associated with multiple bonds or aromatic rings. In organic compound suitable lone pair of electrons for co-ordinate bonding occur in functional groups containing elements C, N, S. the tendency to stronger co-ordinate bond formation by these elements with decreasing electro negativity in the order $O < N < S < Se$ ²⁶⁻²⁷ and depends also on the nature of the functional groups containing these elements. The structure of the rest of the molecule can affect co-ordinate bond formation by its influence on the electron density at the functional group²⁸⁻³⁰.

In the present study it is assuming that total alkaloids of the natural products are adsorbed on the metal surface and decrease the surface area available for cathodic and anodic reactions to take place.

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Conclusion

The study of plant extract has shown them to be effective inhibitors of the corrosion of iron in acid solution. Both mass loss and thermometric determinations have shown that the inhibition efficiency increases with increasing inhibitor concentration over the range 0.12%-0.60% and with increasing acid concentration within the range 0.1 N to 5 N hydrochloric acid solution. Adsorption of these compounds on iron obeyed Langmuir adsorption isotherm. It is concluded that the plant extract of *Acacia senegal* is a good corrosion inhibitor for iron in acidic solution. 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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