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Corrosion Inhibitive Effects of Withania Somnifera (A medicinal plant) on Aluminium in HCl Solution

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Abstract

Corrosion can be considered either chemical or electrochemical in nature. It decays the metallic properties of metals and lead them unfit for their specific purpose in industry. Corrosion of metals may be prevented by either barrier protection or sacrificial protection or by alloying or by anti rust solution of ligands containing N, S, O, Se and P as hetero atoms. The naturally occurring plant products are eco-friendly, compatible, nonpolluting, less toxic, easily available, biodegradable and economic to be used as corrosion inhibitors. Extract of different parts of plant like seeds, leaves, stem can be used as inhibitor to reduce the corrosion rate of metal like aluminium in acidic media.Corrosion inhibitive effects of naturally occurring Withania Somnifera (Ashwagandha) have been studied in different concentrations of HCl for aluminium. Studies were carried out at two different temperatures of extract of leaves and root of the said plant. Leaves extract has been found more effective corrosion inhibitor at lower temperature. The maximum corrosion inhibition efficiency was found 99.28% for leaves extract at 303K.

Keywords: Corrosion inhibition efficiency, corrosion rate, reaction number, *Withania Somnifera*, alkaloid, surface coverage.

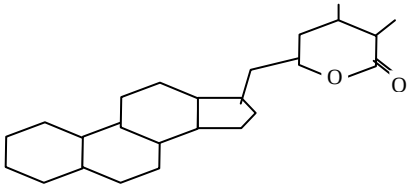
Introduction

Aluminium and its alloys are very important in many industrial as well as household applications due to their corrosion passivity in neutral media and atmospheric conditions due to formation of passive oxide layer on them. Although it is very reactive in emf series but becomes passive on exposure to water and atmosphere but it dissolves in hydrochloric acid liberating H_2 gas.

$$2Al + 6\,HCl + 12\,H_2O \longrightarrow 2\,[Al\,(H_2O)_6\,]Cl_3 + 3H_2$$

Compounds containing N, S and O have been found as good inhibitors due to high basicity and electron density and thus assist corrosion inhibition[1]. O, N and S are the active center for the process of adsorption on the metal surface. The size, orientation, shape and electric charges of the molecule also play a part in the effectiveness of inhibition. Corrosion not only causes enormous loss to the economy of country but also is a major threat to human safety. The government committee on corrosion in U.K. estimated that the total loss to the national economy due to corrosion was 3.5% of GNP. Developed countries dump their scrap due to corroded alloys into sea and oceans and this material produces environmentally adverse effect on flora and fauna of oceans. Gases evolved during corrosion like SO_2, NO_2 causes acid rain which is very harmful for buildings, plants and animals.

In addition to the heterogeneous organic compounds synthesized in laboratory some naturally occurring substances like Ficus virens[2], Delonix regia[3], Ocimum basilicum[4], Caparis deciduas[5], Sansevieria trifascinata[6], Phylanthus amarus[7], Prosopis julifforar[8], Argemone maxicana[9] have been evaluated as effective corrosion inhibitors. The naturally occurring plant products are eco-friendly, compatible, nonpolluting, less toxic, easily available, biodegradable and economic to be used as corrosion inhibitors. These inhibitors have many N, O and S containing alkaloids which are get adsorbed on metal surface which essentially block the discharge of H^+ and dissolution of metal ions. Extract of different parts of plant like seeds, leaves, stem and bark can be used as inhibitor to reduce the corrosion rate of metal like aluminium in acidic media. In the present investigation the inhibition efficiencies of Withania Somnifera have been studied in different concentrations of HCl solution at two temperature i.e. 303 K (30^0 C) and 318K (45^0 C). Withania Somnifera is a very common plant in India and other regions having almost same climatic conditions. Alkaloids and steroidal lactones are the main constituents of Ashwagandha. Plant contains many alkaloids like anaferin, anahygrine, betasisterol, chlorogenic acid, cystein, cuscohygrine, pesudotropine, scopoletin, somniferiene tropanol, withanine, withananine etc. Withaferin A and withanolides A-Y are the main steroidal lactones. The withanolides are a group of naturally occurring C-28 steroidal lactones built on an intact or rearranged ergostane framework in which C-22 and C-26 are appropriately oxidized to form a six membered lactone ring.



Material and Methods

Commercially available aluminium was used for specimen preparation. The specimens were prepared by cutting the aluminium sheet into square shaped pieces having dimension 2.0 × 2.0 × 0.03cm containing a small hole of about 2mm diameter near the upper edge. Specimens were polished to mirror finish by using emery paper. Solutions of HCl were prepared by using double distilled water. All chemicals used were of AR grade. Extract of leaves and root of *Withania Somnifera* was obtained by refluxing the dried leaves and root in soxhlet in ethanol. Solutions of different concentrations of extract were prepared in ethanol.

Each specimen was suspended by a V-shaped glass hook made of capillary and plunge into a beaker containing 50mL of the test solution (HCl) at 303K and at 318K. After the sufficient exposure, test specimens were washed with running water and dried by hot air dryer. Duplicate experiments were performed in each case and mean value of weight loss was determined. The percentage inhibition efficiency was calculated as[10].

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

Where ΔW_u and ΔW_i are the weight loss of the specimen in uninhibited and in inhibited solution respectively. Degree of surface coverage (θ) was calculated as[11].

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

The corrosion rate in mm/yr can be obtained by the following equation[12].

$$\text{Corrosion Rate (mm/yr)} = \frac{\Delta W \times 87.6}{A \times T \times D}$$

Where, ΔW is weight loss in mg, A is area of specimen in cm^2, T is time of exposure in hours, D is density of metal in gm/cm^3.

Results and Discussion

Weight loss data and corresponding values of inhibition efficiency and corrosion rate for leaves and root extract as an inhibitor are given in table-1 and table-2. It is obvious from the table-1 that inhibition efficiency increases with increasing acid strength and it also increases with increasing concentration of leaves extract. The maximum efficiency (i.e.99.28%) has been observed in 2N HCl at highest concentration of inhibitor (i.e.0.8%) for leaves extract at 303K. Observations of inhibition efficiency corresponding to same concentrations of acid and inhibitor at 318K show that efficiency of the inhibitor is less at 318K than that at 303K although the trends are same at 318K. Maximum efficiency at 318K is 98.53% for the same concentration of leaves extract (i.e. 0.8%) for 2N HCl. Variation of inhibition efficiency with concentration of leaves extract for 2N HCl at two different temperatures is shown in figure 1.

Table- 1
Inhibition efficiency (η%) for aluminium in HCl with leave extract of Withania Somnifera at 303K and 318K
Area of specimen: 8.0cm^2

Conc. of inhibitor	0.5N HCl (173 hrs.)			1N HCl (2.25 hrs.)			2N HCl (25 min)		
-	ΔW	η%	C.R.	ΔW	η%	C.R.	ΔW	η%	C.R.
At 303K									
uninhibited	0.207	-	0.7148	0.117	-	31.06	0.279	-	400.680
0.1	0.163	21.27	0.5629	0.043	63.24	11.41	0.007	97.49	10.053
0.2	0.157	24.15	0.5421	0.015	87.17	3.98	0.005	98.2	7.185
0.4	0.154	25.6	0.5321	0.003	97.43	0.796	0.004	98.56	5.744
0.8	0.152	26.57	0.5249	0.002	98.29	0.531	0.002	99.28	2.872
At 318K									
uninhibited	0.324	-	1.118	0.364	-	96.65	0.273	-	652.51
0.1	0.271	16.35	0.9358	0.136	62.63	17.525	0.008	97.06	19.121
0.2	0.257	20.67	0.8875	0.085	76.64	11.68	0.006	97.8	14.341
0.4	0.254	21.6	0.8771	0.039	89.28	0.355	0.005	98.16	11.95
0.8	0.251	22.53	0.8668	0.037	89.83	9.824	0.004	98.53	9.56

Table-2
Inhibition efficiency (η%) for aluminium in HCl with root extract of Withania Somnifera at 303K and 318K
Area of specimen: 8.0cm^2

Conc. of inhibitor	0.5N HCl (173 hrs.)			1N HCl (2.25 hrs.)			2N HCl (25 min)		
	ΔW	η%	C.R.	ΔW	η%	C.R.	ΔW	η%	C.R.
At 303K									
uninhibited	0.207		0.7184	0.117		31.06	0.279		400.680
0.1	0.180	13.04	0.6216	0.062	47.00	16.46	0.009	96.77	12.925
0.2	0.170	17.87	0.5870	0.017	85.47	4.51	0.007	97.49	10.053
0.4	0.155	25.12	0.5350	0.006	94.87	1.59	0.005	98.20	7.180
0.8	0.154	25.60	0.5318	0.004	96.58	1.06	0.004	98.56	5.744
At 318K									
uninhibited	0.324		1.118	0.364		96.65	0.273		652.51
0.1	0.273	15.74	0.9427	0.112	69.23	29.73	0.012	95.60	28.68
0.2	0.262	19.31	0.9047	0.108	70.32	28.67	0.009	96.70	21.51
0.4	0.261	19.44	0.9013	0.098	73.07	26.02	0.007	97.43	16.73
0.8	0.254	20.06	0.8944	0.057	84.34	15.13	0.006	97.80	14.34

Table-3
Surface coverage and log (θ/ 1-θ) for aluminium in HCl with leave extract of Withania Somnifera at 303K and 313K

Conc. Of inhibitor	0.5N HCl(173 hrs.)			1N HCl(2.25 hrs.)			2N HCl(25min..)		
	η%	θ	log (θ/ 1-θ)	η%	θ	log (θ/ 1-θ)	η%	θ	log (θ/ 1-θ)
At 303K									
uninhibited									
0.1	21.27	0.2127	-0.5684	63.24	0.6324	0.2356	97.49	0.9749	1.5893
0.2	24.15	0.2415	-0.4970	87.17	0.8717	0.8321	98.20	0.9820	1.7368
0.4	25.60	0.2560	-0.4633	97.43	0.9743	1.5788	98.56	0.9856	1.8353
0.8	26.57	0.2657	-0.4415	98.29	0.9829	1.7595	99.28	0.9928	2.1395
At 318K									
uninhibited									
0.1	16.35	0.1635	-0.7089	62.63	0.6263	0.6544	97.06	0.9706	1.5187
0.2	20.67	0.2067	-0.5841	76.64	0.7664	0.8567	97.80	0.9780	1.6479
0.4	21.60	0.2160	-0.5599	89.28	0.8928	0.9206	98.16	0.9816	1.7271
0.8	22.53	0.2253	-0.5364	89.83	0.8983	0.9461	98.53	0.9853	1.8263

Table-4
Surface coverage and log (θ/ 1-θ) for aluminium in HCl with root extract of Withania Somnifera at 303K and 313K

Conc. Of inhibitor	0.5N HCl(173 hrs.)			1N HCl(2.25 hrs.)			2N HCl(25min..)		
	η%	θ	log (θ/ 1-θ)	η%	θ	log (θ/ 1-θ)	η%	θ	log (θ/ 1-θ)
At 303K									
uninhibited									
0.1	13.04	0.1304	-0.8240	47.00	0.4700	-0.0522	96.77	0.9677	1.4765
0.2	17.87	0.1787	-0.6624	85.47	0.8547	0.7695	97.49	0.9749	1.5893
0.4	25.12	0.2512	-0.4743	94.87	0.9487	1.2670	98.20	0.9820	1.7368
0.8	25.60	0.2560	-0.4633	96.58	0.9658	1.4509	98.56	0.9856	1.8353
At 318K									
uninhibited									
0.1	15.74	0.1547	-0.7286	69.23	0.6923	0.3522	95.60	0.9560	1.3370
0.2	19.31	0.1931	-0.6210	70.32	0.7032	0.3746	96.70	0.9670	1.4669
0.4	19.44	0.1944	-0.6174	73.07	0.7303	0.4335	97.43	0.9743	1.5788
0.8	20.06	0.2006	-0.6004	84.34	0.8434	0.7312	97.80	0.9780	1.6479

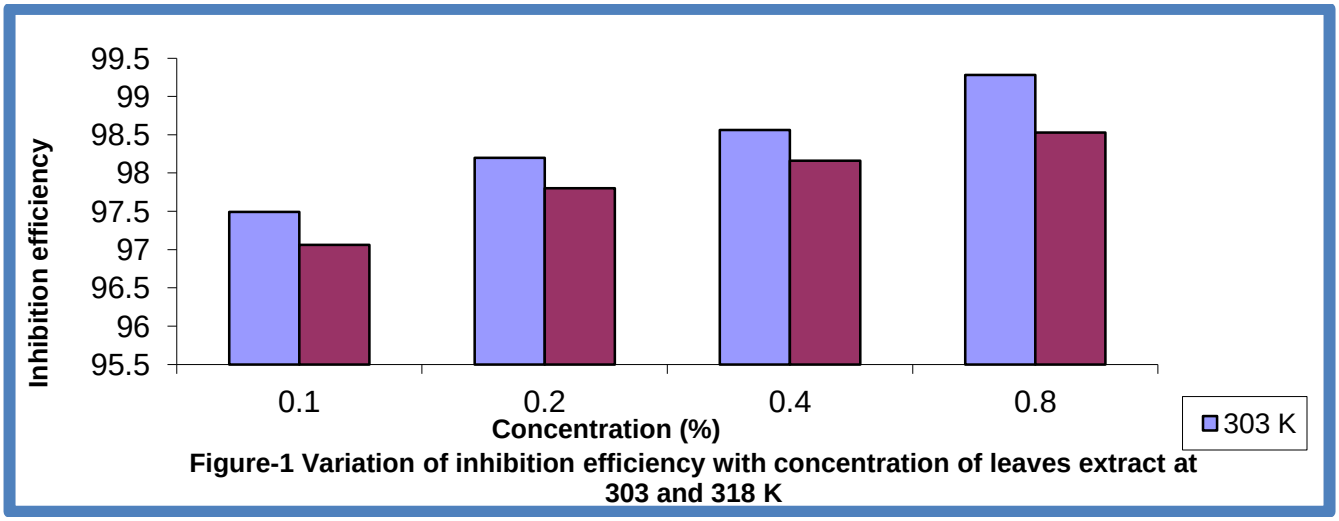


Figure-1 Variation of inhibition efficiency with concentration of leaves extract at 303 and 318 K

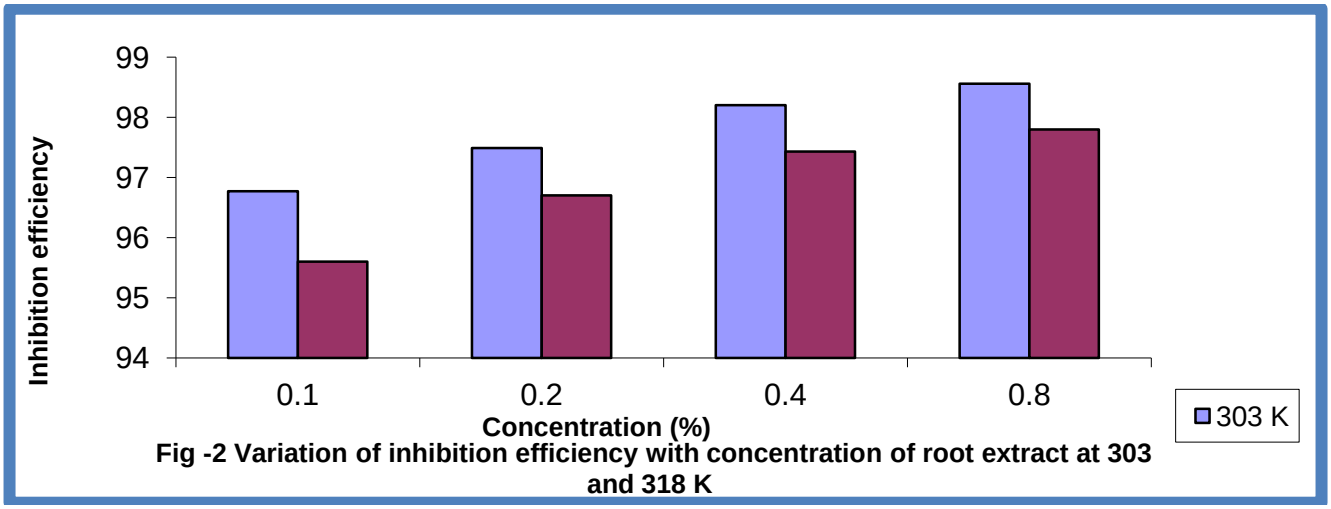


Fig -2 Variation of inhibition efficiency with concentration of root extract at 303 and 318 K

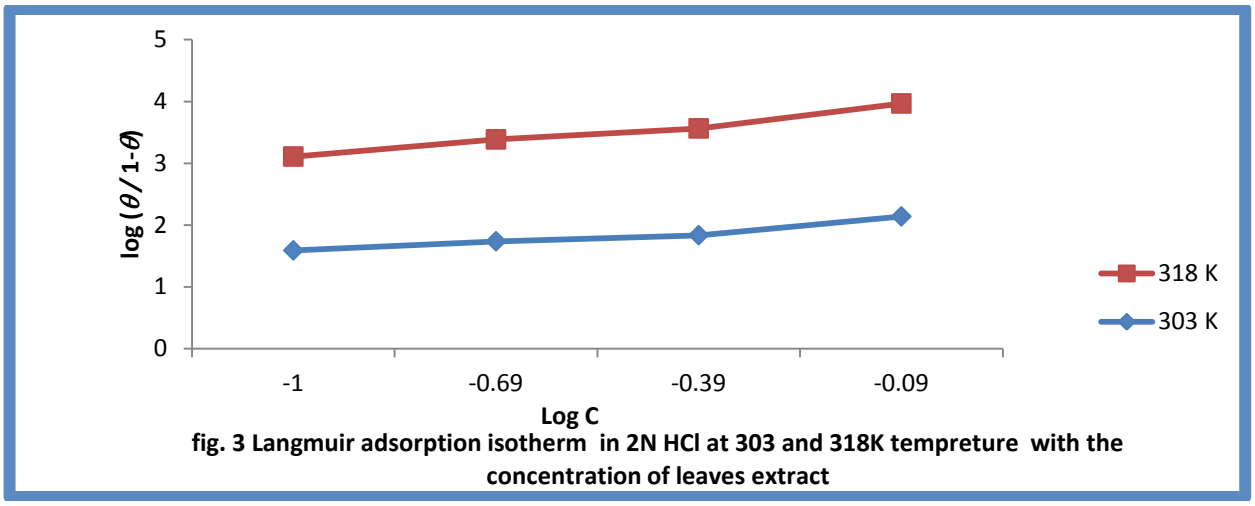


fig. 3 Langmuir adsorption isotherm in 2N HCl at 303 and 318K tempreture with the concentration of leaves extract

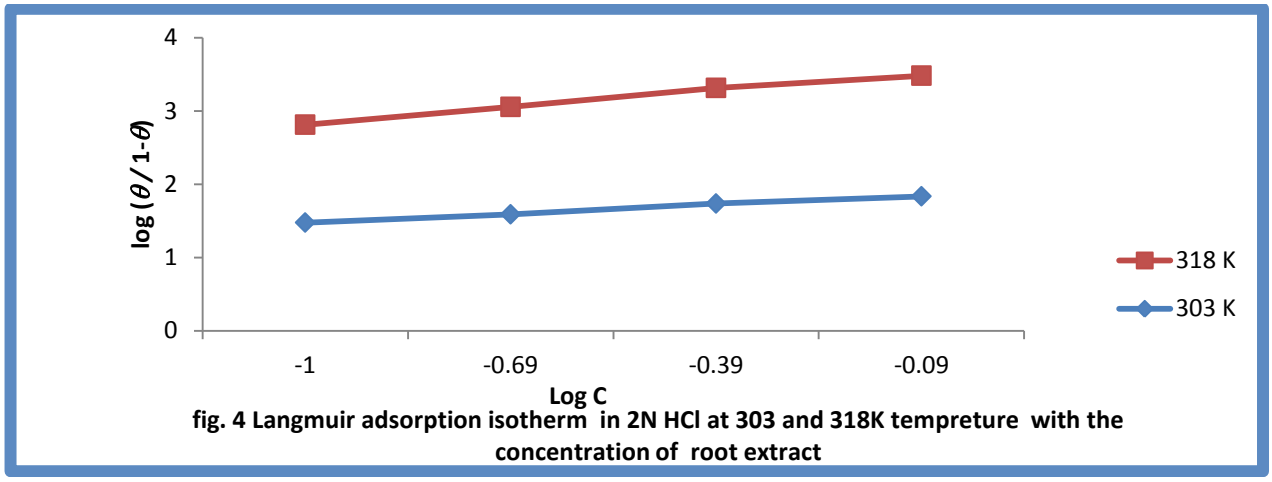


fig. 4 Langmuir adsorption isotherm in 2N HCl at 303 and 318K tempreture with the concentration of root extract

It is clear from the table-2 that root extract also shows excellent inhibition efficiency for aluminium metal in HCl solution .it is obvious from the table that root extract shows same trends as leaves extract with increasing concentration of acid as well as with increasing concentration of inhibitor. Root extract is also more efficient at 303K than 318K as an inhibitor. The maximum efficiency (i.e.98.56%) has been observed in 2N HCl at highest concentration of inhibitor (i.e.0.8%) for root extract at 303K. Variation of inhibition efficiency with concentration of root extract for 2N HCl at two different temperatures is shown in figure 2.

The degree of surface coverage of metal (θ) covered by the adsorption of inhibitor to block the active sites on the surface at various concentrations of inhibitor for different HCl concentrations are shown in table-3 and table -4 for leaves and root extract. It is clear from the tables that degree of surface coverage increases with increasing concentration of inhibitor at both temperatures i.e.303K and 318K, however at 318K the coverage is less than that at 303K. Hoar and Holiday gave the Langmuir adsorption isotherm[13]

$$\log \theta/(1-\theta) = \log A + \log C - Q/2.3\,RT$$

Where:

θ = Surface coverage, A = Temperature dependent constant, C = Bulk concentration of inhibitor (mol /L), Q = Heat liberated in reaction.

According to which a straight line should be obtained if a graph is plotted between log $\theta/(1-\theta)$ versus logC with gradient equal to one. In our investigation the graph is linear but gradient is not equal to unity. This deviation from unit behaviour can be explained on the basis of interaction of the adsorbed molecules on the metal surface. According to Langmuir the adsorbed layer is unimolecular i.e. there is no interaction between adsorbed molecules themselves and between adsorbate and adsorbent molecules. Only then the gradient is unity but in actual practice there is an interaction between adsorbed molecules themselves and between adsorbate and adsorbent molecules that is why the gradient is not unity. Variation of log $\theta/(1-\theta)$ with concentration of leaves and root extract for 2N HCl are shown in figure 3 and figure 4.

Conclusion

The studies on Withania Somnifera as corrosion inhibitor for aluminium in HCl have shown that this widely available plant is a very good corrosion inhibitor for aluminium. Studies have shown that both leaves and root extract show similar trends for different concentrations of acid as well as those of inhibitor. Further it can be concluded from the studies that Withania Somnifera is a better corrosion inhibitor at 303K than at 318K and leaves extract is more efficient than root extract.

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