Use of *Azadirachta indica* (AZI) as green corrosion inhibitor against mild steel in acidic medium: anti-corrosive efficacy and adsorptive behaviour

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Abstract

The corrosion inhibition of mild steel in 1 N HCl, H₂SO₄ and HNO₃ solution in the presence of AZI at a temperature of 304 & 313 K was studied using weight loss techniques. The Neem (AZI) works as an inhibitor in the acid surroundings. The results showed that the inhibition efficiency was increased by increasing the inhibitor concentration and reached the maximum at 1000 ppm (72 hr) in 1 N HCl and H₂SO₄ and in HNO₃ solution. The AZI was found to follow Langmuir adsorption isotherm at all the concentrations in different acidic mediums studied. The phenomenon of physical adsorption obtained and the process is spontaneous.

Keywords: mild steel, adsorption, corrosion, inhibitor, green chemistry. Received: January 18, 2017. Published: March 21, 2017. doi: 10.17675/2305-6894-2017-6-2-2

1. Introduction

Mild steel is applicable in industrial and structural applications on a large level. Acid solutions are consistently used in a number of operations in for scrubbing, scraping and storing of steel structure; developments which are calculated as the extensive termination of the metal and it is mandatory to add corrosion inhibitors to govern the corrosion rate for the advancement of surroundings. Most of the Organic heterogeneous compounds holding these elements have been reported to be proficient corrosion inhibitors [1-8]. The corrodent attack can be controlled by an adsorption mechanism with the presence of heteroatom and aromatic rings. A number of authors have been inventing the use of plant parts or extracts as corrosion inhibitor [9-19]. They are readily available, cost effective, non-toxic, biodegradable in nature which drives the attention to work on them as a corrosion inhibitor. Wide list of literature we have found the nurturing use of natural plant origin to inhibit the corrosion of different metals in different mediums (Acid & alkaline) [20-25]. Authors of this paper have published a comprehensive review [26] focusing the potential of *Azadirachta indica* as a green corrosion inhibitor against mild steel, aluminum, and tin, which inspired the authors to carry out the present study. The present study is

designed to investigate the adsorption and inhibiting properties of water extract of leaves of *Azadirachta indica* for the corrosion of mild steel in 1 N HCl, H₂SO₄ and HNO₃ solutions.

Azadirachta indica consists its place in the mahogany family of Meliaceae. Neem rich countries are India, Bangladesh, Thailand, Nepal, and Pakistan. "Tree of the 21st century (Neem)" is well known for its medicinal uses in human day to day life. In India, there are many names for this tree like "Heavenly Tree", "Lifetime enhancing tree", "Environment's Dispensary", "Community Apothecary" [27–30]. The chemical constituents found in the leaves of neem as Nimbin, nimbanene, 6-desacetylnimbinene, nimban-diol, nimbolide, ascorbic acid, n-hexacosanol and aminoacid, 7-desacetyl-7-benzoylazadiradione, 7-desacetyl-7-benzoylgedbenzoylgedunin, 17-hydroxyazadiradione and nimbiol [31–33].

2. Materials and methods

2.1 Materials

The mild steel sheets (98.9%) were cut into $3 \times 2 \times 0.2$ cm dimension to form specific metal coupons. Each coupon was scratched by emery paper in order to obtain a smooth surface, washed with water to make it free from dust and rinsed with acetone to make it dry, for the preservation of treated coupons we transferred them into the desiccator. All components and chemicals used for the experimental work were anlar grade and distilled water was used for their preparation.

2.2 Solutions

Leaves of *Azadirachta indica* were collected from the Sanganer region in Jaipur (Rajasthan). The Leaves were washed and dried, crushed and held in reserve in glass jars till use. Standard solutions of the leaves were equipped by soaking 50 g of the dehydrated and crushed leaves in 1000 ml of, particularly distilled water. The resulted solution was maintained for 24 hours, filtered and stored. From the stock solution (0.05 g/l), we equipped different concentrations [250, 500, 750, 1000 ppm (mg/ml)] solutions [34]. The 1 N HCl solution was equipped by dilution of analytical grade HCl, H_2SO_4 and HNO₃ solutions with distilled water and all trials were passed out in unstirred solutions.

2.3 Weight Loss Method

Weight loss parameters were functioning on the mild steel samples with a four-sided form of size $3 \times 2 \times 0.2$ cm in one normal HCl, H₂SO₄ and HNO₃ solution with and without the addition of different concentrations (250, 500, 750, 1000 ppm) of neem leaves extract. Each sample was evaluated in SHIMADZU (ATX224) electronic balance and then sited in the acid solution (100 ml). The period of the involvement was 6, 24, 48, 72 h at the temperature range 304 & 313 K. Afterward, involvement, the surface of the MS metal coupon was washed with double distilled water and carry on the drying with acetone and the sample was considered one more time weighed in order to calculate inhibition efficiency (*E*%) and the corrosion rate (*CR*). Every testing followed by freshly equipped solution and the solution temperature was thermostatically prescribed at a preferred assessment.

The surface coverage (θ) and inhibition efficiency (*E*%) was determined by using the following equation

$$\theta = w_0 - w_i / w_0 \tag{1}$$

$$E\% = (w_0 - w_i / w_0) \times 100 \tag{2}$$

Where w_i and w_0 are the weight loss values in the presence and absence of inhibitor, respectively. The corrosion rate (*CR*) of mild steel was calculated using the following relation:

$$CR = \frac{\text{weight loss}}{\text{area} \times \text{time} \times \text{density}} \times 8.76 \times 10^4$$
(3)

Where w is corrosion weight loss of mild steel (g), area of the coupon (cm²), t (h), and density of mild steel in (g cm⁻³).

2.4 GC-MS Study

GC-MS investigation was run away with a GC Clarus 500 Perkin Elmer system embracing an AOC-20i auto sampler and gas chromatograph interfaced to a mass spectrometer (GC-MS) apparatus.

2.5 Surface Analysis

External appearance studies of the mild steel surface were commenced by SEM inspection using Nova Nano SEM 450 BRUKER Scanning electron microscope from Malaviya National institute of technology, (MNIT) Jaipur.

3. Results and discussion

Figures 1, 2, 3 indicate the variety of weight loss, IE% and corrosion proportion with the time for the corrosion of mild steel in a solution of [A] 1 N HCl, [B] H_2SO_4 , [C] HNO₃ holding prescribed concentrations of AZI (Neem) at 304 and 313 K. We resolved from the figures that the weight loss of mild steel surges with the increasing duration of contact, but it's caught control with a surge in the concentration of *Azardirachta indica*. Corrosion rates upsurge with an upsurge in temperature. Resulted observations pointed that AZI effective to condense the mild steel corrosion in all three acidic media (1 N HCl H_2SO_4 & HNO₃), but the highest weight loss stated in HNO₃ medium due to HNO₃ acids hyper oxidative behave [35], however, we have seen the inhibition in HNO₃ medium very low, so we can say that inhibitor is more effective in the other acid medium as compare to HNO₃ solution. Consequently, the Tables 1 and 2 show the relative data of standard metal loss, corrosion rate and inhibition efficiency of the corroded samples of mild steel at 304 and 313 K. The maximum efficiency of mild steel (70.2%) has been observed in the highest inhibitor

concentration 1000 ppm at 72 hr at a temperature of 304 K in 1 N HCL, 65.6 % for 72 hr on 1000 ppm in 1 N H₂SO₄ and 52.6% for 72 hr on 1000 ppm in 1 N HNO₃ medium.



Figure 1. Weight loss graphs of mild steel with different concentration of AZI in [A] 1 N HCl, [B] 1 N H₂SO₄ and [C] 1 N HNO₃.



Figure 2. Corrosion rate graphs of MS with different concentration of AZI in [A] 1 N HCl, [B] 1 N H₂SO₄ and [C] 1 N HNO₃.



Figure 3. Inhibition efficiency graphs of MS with different concentration of AZI in [A] 1 N HCl, [B] 1 N H_2SO_4 and [C] 1 N HNO_3 .

Medium	Inhibitor conc.		6 hr	6 hr			24 hr				72 hr		
		Wt. loss (gm)	<i>CR</i> , mm/yr	IE%	Wt. loss (gm)	<i>CR</i> , mm/yr	IE%	Wt. loss (gm)	<i>CR</i> , mm/yr	IE%	Wt. loss (gm)	<i>CR</i> , mm/yr	IE%
	0	0.308	4.0977		0.512	6.806		0.726	9.6403		0.879	11.68	
1 N	250	0.159	2.1156	48.37	0.257	3.420	49.74	0.361	4.8009	50.19	0.433	5.747	50.8
HCl	500	0.142	1.8902	53.87	0.213	2.823	58.52	0.266	3.5392	63.28	0.305	4.052	65.3
	750	0.139	1.8453	54.97	0.208	2.768	59.33	0.242	3.2186	66.61	0.289	3.834	67.1
	1000	0.133	1.7696	56.81	0.178	2.365	65.25	0.234	3.1056	67.78	0.262	3.478	70.2
	0	0.496	65.949		0.625	83.005		0.875	116.29		0.951	126.32	
	250	0.309	41.006	37.82	0.373	49.57	40.27	0.410	54.433	53.19	0.441	58.57	53.6
1 N H₂SO₄	500	0.299	39.733	39.75	0.338	44.864	45.95	0.350	46.487	60.02	0.353	46.95	62.8
24	750	0.264	35.065	46.83	0.263	34.926	57.92	0.340	45.197	61.13	0.340	45.106	64.3
	1000	0.252	33.455	49.27	0.253	33.562	59.56	0.336	44.692	61.56	0.327	43.50	65.6
	0	1.084	144.01		1.210	160.68		1.380	183.38		1.400	185.9	
	250	0.902	119.88	16.75	0.986	131.01	18.46	0.938	124.62	32.23	0.797	105.95	43
1 N HNO₁	500	0.874	116.14	19.35	0.934	124.10	22.76	0.899	119.49	34.84	0.743	98.76	46.9
mog	750	0.856	113.66	21.07	0.896	119.02	25.92	0.817	108.5	40.83	0.715	94.97	48.9
	1000	0.834	110.85	23.02	0.819	108.84	32.25	0.797	105.89	42.25	0.664	88.21	52.6

Table 1. Corrosion parameters of AZI at 304 K in different acidic medium with mild steel at different immersion time periods.

Table 2. Corrosion parameters of AZI at 313 K temperature in different acidic medium with mild steel at different immersion time periods.

Medium	Inhibitor conc.		6 hr			24 hr			48 hr			72 hr	
		Wt. loss (gm)	<i>CR</i> mm/yr	IE%									
1 N HCl	0	0.400	5.314		0.596	7.917		0.726	9.644		0.880	11.688	
	250	0.228	3.023	43.10	0.318	4.230	46.56	0.365	4.847	49.73	0.433	5.749	50.808
	500	0.218	2.900	45.41	0.281	3.728	52.90	0.299	3.965	58.88	0.338	4.484	61.631
	750	0.199	2.642	50.27	0.261	3.460	56.28	0.287	3.818	60.40	0.318	4.229	63.815
	1000	0.165	2.1964	58.67	0.243	3.221	59.30	0.270	3.589	62.78	0.297	3.950	66.21
	0	0.571	75.803		0.722	95.94		0.970	128.88		1.066	141.60	
	250	0.387	51.390	32.20	0.462	61.40	35.99	0.517	68.72	46.68	0.540	71.68	49.374
1 N H₂SO₄	500	0.375	49.836	34.25	0.440	58.43	39.09	0.504	66.97	48.03	0.504	66.99	52.691
2 1	750	0.365	48.438	36.09	0.356	47.24	50.75	0.437	58.058	54.95	0.411	54.54	61.482
	1000	0.339	45.093	40.51	0.317	42.17	56.04	0.418	55.58	56.87	0.395	52.52	62.91
	0	1.140	151.47		1.242	164.96		1.448	192.35		1.522	202.25	
	250	0.969	128.76	14.99	1.044	138.68	15.93	1.029	136.75	28.90	0.903	119.95	40.693
1 N HNO3	500	0.947	125.82	16.93	1.030	136.78	17.08	0.996	132.35	31.19	0.874	116.11	42.59
	750	0.933	123.96	18.16	0.962	127.77	22.54	0.888	117.98	38.66	0.851	113.04	44.111
	1000	0.900	119.61	21.03	0.917	121.79	26.17	0.859	114.17	40.64	0.786	104.44	48.36

3.2 Kinetic studies

Mainly corrosion reactions are first order signifying that it follows a mode [35]

$$-log (weight loss) = k_1 t / 2.303$$
(4)

Where *t* is the period of contact and k_1 is the first order rate constant. Figures 4, 5 and Table 3 shows values and plots for the variation of -log (weight loss) with time for the corrosion of MS in the deficiency and the existence of AZI different concentrations at 304 and 313 K on different intervals (6, 24, 48 and 72 hrs). Received the straight line plots with good R^2 values confirm that *Azardirachta indica* as a good inhibitor for mild steel in different acidic mediums.

Table 3. Kinetic parameters for the corrosion of mild steel in 1 N HCl, H₂SO₄ & HNO₃ containing various concentrations of AZI.

	304 K													
	Conc. (ppm)	В	K	R^2		В	K	R^2		В	K	R^2		
1 N HCl	0	-0.151	0.62	0.96		-0.099	0.395	0.96		-0.039	0.003	0.7		
	250	-0.144	0.91	0.96	1 N H2SO4	-0.05	0.546	0.95		-0.018	0.001	0.9		
	500	-0.109	0.92	0.95		-0.023	0.534	0.832	1 N HNO ₃	0.022	0.008	0.89		
	750	-0.102	0.92	0.94	112004	-0.044	0.634	0.79		0.027	0.018	0.76		
	1000	-0.099	0.95	0.97		-0.046	0.655	0.76		0.031	0.033	0.74		
						313 K								
	Conc. (ppm)	В	K	R^2		В	K	R^2		В	K	R^2		
	0	-0.111	0.482	0.96		-0.094	0.328	0.96		-0.044	0.012	0.97		
	250	-0.089	0.709	0.99		-0.048	0.0446	0.947		0.009	0.018	0.19		
1 N HCl	500	-0.059	0.7	0.98	1 N H₂SO₄	-0.044	0.455	0.88	1 N HNO ₂	0.011	0.012	0.25		
ner	750	-0.065	0.744	0.98	112~04	-0.024	0.469	0.55		0.015	0.03	0.73		
	1000	-0.081	0.826	0.99		-0.031	0.516	0.54		0.02	0.012	0.78		



Figure 4. Variation of -log (weight loss) versus time for the corrosion of mild steel in solutions of 1 N HCl, H₂SO₄ & HNO₃ containing various concentrations of AZI at 304 K temperature.

Effect of temperature

Activation energies help us to know that surface interaction energy E_a for the corrosion of mild steel in the non-existent and in the existences of AZI have estimated using the logarithmic form of the Arrhenius equation, which can be articulated as follows [36].

$$E_{\rm a} = 2.303R \cdot \log\left(\frac{CR_1}{CR_2}\right) / \left(T_1 - \frac{T_2}{T_1 \cdot T_2}\right) \tag{5}$$

Where CR_1 and CR_2 are the corrosion rates of mild steel at the temperatures T_1 (304 K) and T_2 (313 K), respectively, E_a is the triggering/activation energy, and R is the gas constant. Activation energy values (E_a) ranged from 0.04 to 37.66 kJ/mol for mild steel in 1 N HCl medium, 9.04 to 32.1 kJ/mol for MS in H₂SO₄, 2.3 to 15.3 kJ/mol in HNO₃ medium with different concentrations of inhibitor the E_a values are comparably less than 40 kJ/mol. On the whole, minor values of E_a point to an affinity towards physisorption phenomena. Obtained result in Table 4 authorizes that the adsorption of AZI on the surface of MS in 1 N HCl, H₂SO₄ & HNO₃ medium monitors the physisorption.



Figure 5. Variation of -log (weight loss) versus time for the corrosion of MS in solutions of 1 N HCl, H₂SO₄ & HNO₃ containing various concentrations of AZI at 313 K temperature.

Table 4. Calculated values of apparent activation energy (Ea) and Heat of adsorption (Q) of AZI on mild steel in 1 N HCl, H₂SO₄ and HNO₃ medium.

AZI Concentration	Medium		$E_{ m a}$ (kJ	mol ⁻¹)	$Q_{ m ads}~(m kJ~mol^{-1})$					
(ppm)		6 hr	24hr	48 hr	72 hr	6 hr	24hr	48 hr	72 hr	
0		22.86	13.28	0.04	0.04					
250		31.4	18.67	0.857	0.04	-2.14	-2.12	-2.05	-2.06	
500	1 N HCl	37.66	24.44	10	8.909	-2.53	-2.75	-3.17	-3.39	
750		31.58	19.63	15.03	8.496	-2.46	-2.73	-3.67	-3.64	
1000		18.98	27.17	12.72	11.19	-2.35	-3.47	-3.8	-4.18	
0		12.24	12.74	9.04	10.03					
250	$1 \text{ N H}_2 \text{SO}_4$	19.85	18.81	20.49	17.76	-1.89	-1.87	-2.42	-2.36	
500		19.92	23.24	32.1	31.23	-1.91	-2.11	-3.11	-3.33	

750		28.41	26.57	22.01	16.7	-2.29	-2.76	-3.01	-3.23
1000	$1 \text{ N } \text{H}_2\text{SO}_4$	26.25	20.07	19.17	16.57	-2.3	-2.77	-3	-3.39
0		4.447	2.313	4.201	7.396				
250		6.287	4.999	8.165	10.93	-1.93	-1.92	-1.75	-1.86
500	1 N HNO ₃	7.036	8.549	8.987	14.23	-1.88	-1.99	-1.78	-2.05
750		7.631	6.231	7.366	15.3	-1.86	-1.79	-1.8	-2.15
1000		6.687	9.876	6.624	14.84	-1.77	-1.88	-1.81	-2.3

4. Thermodynamics and adsorption study

The heat of adsorption of *Azardirachta indica* on mild steel surface was calculated using the following equation [37]

$$Q_{ads} = 2.303R \left(\log \frac{\theta_2}{1 - \theta_2} - \log \frac{\theta_1}{1 - \theta_1} \right) \times \frac{T_1 T_2}{T_2 - T_1}$$
(6)

Where *R* is the universal gas constant, θ_2 and θ_1 are the degree of surface coverage at the temperatures T_1 (304 K) and T_2 (313 K). In Table 4 we can see the values of Q_{ads} for prescribed concentrations of AZI. We have found negative values of heat adsorption for all concentrations of AZI inhibitor presenting that the adsorption of Neem on the surface of the mild steel is exothermic. We calculate the surface coverage (θ) values by using formula number (1).

If the adsorbent (water & acid) and adsorbate (AZI) are in touch long enough then an equilibrium will be built between the amount of adsorbate in solution and the amount of adsorbate adsorbed. Isotherms made to determine the equilibrium. Communication between the metal surface and inhibitor can be defined by adsorption mechanism. The degree of surface exposure, for the 1 N HCl, H_2SO_4 and HNO_3 mediums with different concentration (250, 500, 750 & 1000 ppm) of AZI inhibitor studied was calculated from the weight loss measurements. The surface coverage values for the inhibitor were fitted into the Langmuir adsorption isotherm model.

$$\frac{C}{\theta} = C + \frac{1}{K_{\text{ads}}} \tag{7}$$

In the formula, *C* stands for the concentration of the inhibitor (AZI), θ is the substantial surface coverage, and K_{ads} denotes the adsorption equilibrium constant. From the intercepts of the straight line C_{inh}/θ – axis, *K* value was considered and from the graph, the value originated can be rationalized by theoretical value. As we knew that the adsorbed molecule decreases the surface area which was accessible for the corrosion reactions to occur.

Figure 6 shows the plot of C/θ against C for [A] 1 N HCl, [B] 1 N H₂SO₄, [C] 1 N HNO₃ at 304 K temperature. Linear plots were obtained indicating that the experimental results fit into Langmuir isotherm. K is the equilibrium constant of adsorption process and C is the concentration of AZI. K is related to the free energy of adsorption by the equation:

$$\Delta G_{\rm ads} = -RT \ln \left(K_{\rm ad} \times 55.5 \right) \tag{8}$$

The plots between C/θ and concentration of inhibitor at 304 K & 313 K is shown in Figures 6 & 7. From the plot, straight lines obtained for AZI show that its adsorption on the mild steel surface follows Langmuir isotherm. The free energy of adsorption values, ΔG_{ads} , were obtained from Eqn. (8). The values obtained are presented in Table 5. Results presented in the table indicate that the values of ΔG_{ads} are negative in all cases. The negative values also point towards an instantaneous adsorption of the inhibitor molecules which are signs of physical adsorption on the surface of the metal [38].



Figure 6. Adsorption isotherms for the AZI on mild steel in different acid medium at 304 K temperature. [A] Langmuir isotherm in 1 N HCl, [B] 1 N H₂SO₄ and [C] 1 N HNO₃.



Figure 7. Adsorption isotherms for the AZI on mild steel in different acid medium at 313 K temperature. [A] Langmuir isotherm in 1 N HCl, [B] 1 N H₂SO₄ and [C] 1 N HNO₃.

Amultad	Medium	Como	T:		30)4K		313K			
isotherm		ppm	(hr)	В	K _{ads} ppm ⁻¹	R^2	ΔG _{ads} kJ mol ⁻¹	В	K _{ads} ppm ⁻¹	R^2	$\Delta G_{ m ads}$ kJ mol $^{-1}$
		250	6	-23.96	528.84	0.97	-26.00011	-51.5	642.22	0.82	-26.49106
Langmuir adsorption isotherm	1 N HCl	500	24	-36.4	524.58	0.98	-25.97967	-37.42	562.32	0.94	-26.15526
		750	48	-40.73	511.12	0.95	-25.91397	-32.41	515.87	0.95	-25.93735
		1000	72	-41.86	505.45	0.98	-25.88578	-35.72	506.06	0.96	-25.88883
	1 N	250	6	-55.59	721.76	0.94	-26.78617	-51.49	832.68	0.97	-27.14749
Langmuir		500	24	-71.55	682.93	0.93	-26.6464	-89.22	791.2	0.96	-27.01834
isotherm	H_2SO_4	750	48	-19.93	475.2	0.74	-25.7298	-35.343	575.96	0.93	-26.21584
isotiterin		1000	72	-26.35	474.43	0.76	-25.7257	-39.46	544.87	0.94	-26.07559
		250	6	-132.4	1595.2	0.97	-28.7906	-153.65	1811.1	0.99	-29.11142
Langmuir	1 N	500	24	-187.1	1515.9	0.98	-28.66172	-219.67	1823.4	0.96	-29.12853
isotherm	HNO ₃	750	48	-67.1	843.18	0.95	-27.17916	-90.387	957.94	0.95	-27.50167
		1000	72	-33.8	609.75	0.98	-26.35993	-31.251	649.38	0.96	-26.51908

Table 5. Parameters for the adsorption of AZI on mild steel surface at 304 K & 313 K temperature.

GCMS analysis

The chromatogram of compounds which were reported in GCMS of Azardiracta indica are following: Phenol, 2-methoxy-4-propyl-; Digitoxin; Cyclohexanol, 4-[(trimethylsilyl)oxy]-, cis-; Hexadecanoic acid, 1,1-dimethylethyl ester; Cyclononasiloxane, octadecamethyl-; Cyclopentanol, 2-cyclopentylidene-; Octadecanoic acid, butyl ester; Cyclononasiloxane, octadecamethyl-; 2,6-Dimethyl-4-nitro-3-phenyl-cyclohexanone; 1,2-Propanediol, 3benzyloxy-1,2-diacetyl-; Heptasiloxane, hexadecamethyl-; 2-(3-Hydroxy-2-nitro-1phenylbutyl)cyclohexane, Succinic acid, 3,7-dimethyloct-6-en-1-yl isobutyl; Butyl myristate; Stearic acid, 3-(octadecyloxy)propyl esters; 1-Penten-3-one, 4,4-dimethyl-1phenyl-: beta-Tocopherol; Retinol, acetate; Andrographolide; trans-Dehydroandrosterone, methyl ether. Clarification on mass spectrum GC-MS was accompanied using the databank of National Institute Standard and Technology (NIST) having more than 62,000 designs. The spectrum of the unfamiliar constituent was paralleled with the spectrum of the known constituent compounds deposited in the NIST library.

From the GC-MS spectrum Of AZI, it is evident that the spectrum of AZI consisted of 33 peaks with various values of retention time (RT) and fragmentation peaks. Because the area below a chromatogram is proportional to the concentration of the analyte, area normalization was carried out in categorize to calculate the percentage constituent of molecules identified in each peak. Long carbon chain or aromatic compounds have reported in GCMS analysis.



Figure 8. GCMS spectrum of Azardirachta indica.

In Figure 8 we can understand the relative inhibitory capacity of Neem (AZI) inhibitor for mild steel corrosion in all acidic mediums, we have found that in all three acidic mediums (1 N HCl, H_2SO_4 and HNO_3) medium inhibitor effectiveness upsurge with increasing concentration but in 1 N HNO₃ we have observed very low inhibition capacity due to hyper oxidative nature. AZI has been initiated to be an active mild steel corrosion inhibitor in 1 N HCl, H_2SO_4 and HNO_3 medium.

Mechanism

The course of mild steel termination in acidic medium, *i.e.* (1 N HCl, 1 N H_2SO_4 and 1 N HNO_3) relies on concentrations of anions in the solution as observed

$$Fe+Cl^{-} \iff (FeCl^{-})_{ads}$$

$$(FeCl^{-})_{ads} \iff (FeCl)_{ads} + e^{-}$$

$$(FeCl)_{ads} \iff FeCl^{+} + e^{-}$$

$$FeCl^{+} \iff Fe^{2+} + Cl^{-}$$

When we add *Azardirachta indica* (AZI) as an inhibitor to acid solution different additional phases are involved depending on the nature of the electrolyte in the mechanism of anodic dissolution:

$$(FeCl^{-})_{ads} + H^{+}AZI \iff (FeCl^{-}H^{+}AZI)_{ads}$$
$$(FeCl^{-}H^{+}AZI)_{ads} \iff (FeH^{+}AZI)_{ads} + Cl^{-}$$

In acidic medium reduction mechanism is not affected by the presence of the inhibitor because hydrogen evolution is activated controlled step. Due to this there is retardation in the rate of the cathodic reaction by the inhibitor and the possible pathways of the cathodic reaction are following

$$Fe + H^{+} + e^{-} \iff (FeH)_{ads}$$

$$Fe + (H^{+}AZI) + e^{-} \iff (FeH AZI)_{ads}$$

$$(FeH)_{ads} + (FeH)_{ads} \iff 2Fe + H_{2}$$

As a conclusion, we can say that there is competition between H^+ and H^+AZI (protonated inhibitor) for the similar active site to get adsorbed on the surface. The corrosion rate is greater in the nitric acid medium, followed by sulfuric acid, and last of all hydrochloric acid. The breakdown visibility in nitric acid is very significant because nitric acid is identified to be a strong oxidizing agent [39].

The primary dislocation of H $^+$ ions from the solutions is followed by HNO₃ reduction relative to the hydrogen evolution since the acid reduction clues to a noticeable drop in free energy.

$$Fe + 4HNO_3 \longrightarrow Fe(NO_3)_2 + 2H_2O + 2NO_2$$

This response clues to the evolution of nitrogen(II) oxide and production of Fe $(NO_3)_2$ which directed to the furtherance coloration of the medium [40, 41]. We consider the same mechanism of inhibition, which has been presented in our recently published research paper on gums [42].

SEM analysis

The surface morphology of treated mild steel examined by electron microscope is shown in Figure 9 for samples (MS) treated with 1 N hydrochloric acid and Figures 10 & 11 for samples (MS) treated with 1 N sulfuric acid and HNO₃ solution. Each figure shows scanning electron micrographs of the tested surfaces with and without inhibitor. All figures show the surface morphology of mild steel. Scanning electron micrograph of plain mild steel shows analogous grooves with moderately light areas, which were identified as a clean surface. Figure 9 shows the surface morphology of plain mild steel and exposed MS to 1 N hydrochloric acid without inhibitor or with inhibitor on best potent efficiency (1000 ppm, 72 hr). Figure 10 shows the surface morphology of plain MS and MS exposed to 1 N H₂SO₄ in the without inhibitor or with inhibitor on best potent efficiency (1000 ppm, 72 hr) and in Figure 11 we obtained the surface morphology of plain MS and MS exposed to 1 N HNO₃ without inhibitor or with inhibitor on best potent efficiency (1000 ppm, 72 hr). In every figure, we can clearly found the more fine surface images which were treated with an inhibitor (AZI) as compared to without inhibitor. In Figure 12 we have plotted the comparative graph analysis of MS corrosion in all three acidic medium hours wisely.



Figure 9. SEM images of mild steel with HCl on 40 µm: [A] Polished MS; [B] MS without inhibitor; [C] MS with inhibitor (1000 ppm, 72 hr).



Figure 10. SEM images of mild steel with H_2SO_4 on $40\mu m$: [A] Polished MS; [B] MS without inhibitor; [C] MS with inhibitor (1000 ppm, 72 hr).



Figure 11. SEM images of mild steel with HNO₃ on 40µm: [A] Polished MS; [B] MS without inhibitor; [C] MS with inhibitor (1000 ppm, 72 hr).



Figure 12. Comparative analysis graphs of AZI inhibitor on mild steel corrosion in 1 N HCl, H₂SO₄ & HNO₃ at [A] 6 hr; [B] 24 hr; [C] 48 hr; [D] 72 hr.

Conclusion

- AZI testified as active and decent corrosion inhibitor for mild steel in prescribed acidic medium.
- We have found that inhibition productivity upsurge with increasing AZI inhibitor concentration in all (1 N HCl, H₂SO₄ & HNO₃) acidic mediums, but the uppermost IE% obtained in HCl medium at 1000 ppm (72 hr) on 304 K temperature. We stated reduction in inhibition on the rise in temperature 313 K.
- We have stated weight loss high and IE% low results in the HNO₃ medium as associated with H₂SO₄ and HCl medium due to HNO₃ hyper oxidizing behave.
- Calculated activation energies and heat of adsorption supports the instances, physical adsorption which followed the Langmuir isotherm.
- According to obtained result, *Azardirachta indica* adsorption on metal surface was spontaneous, exothermic and supported the mechanism of physical adsorption. AZI inhibitor adsorption follows the Langmuir adsorption isotherm for MS with all three acids at 304K & 313 K temperature.

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