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# Effect of Temperature on Inhibitory Efficacy of *Azadirachta indica* Fruit on Acid Corrosion of Aluminium

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**Abstract**: *Azadirachta indica* (Neem) is one of the most versatile medicinal plants having wide spectrum of biological activity. The *Azadirachta indica* fruit is rich nimbin, nimbinin, nimbidin, metiantriol (triterpenoid), azadirone, epoxyazadiradione etc. The inhibitory efficacy of ethanolic extract of *Azadirachta indica* fruit (EE*Ai*F) has been investigated at room as well as elevated temperatures and the IE % has been observed significantly high (92.37 %) at room temperature at concentration 1.052g/L. The experimentations has been carried out on acid corrosion of Aluminium using weight loss measurement. The high inhibitive effect is attributed due to these photochemical present in the extract. Efficiency of the inhibitor increases with the increasing concentration of inhibitor. The thermodynamic parameters for *Azadirachta indica* fruit extract indicate that the process was spontaneous and the active constituents have been physically adsorbed onto the metal surface. The adsorptive behavior of the inhibitor at room and higher temperatures has been further endorsed by carrying out FT-IR spectroscopy.

Keywords: Aluminium, Azadirachta indica, Acid corrosion, FT-IR Spectroscopy, Kinetic and Thermodynamic Parameters

#### I. INTRODUCTION

Aluminium is an active metal i.e. its nature is to oxidize very quickly. This particular quality is actually the key to its ability to resist corrosion. Aluminium's oxide film is tenacious, hard, and instantly self-renewing, but it is not always completely impervious to corrosion. This layer can become unstable when exposed to extreme pH levels. When the environment is highly acidic or basic, breakdown of the protective layer can occur, and its automatic renewal may not be fast enough to prevent corrosion [1-2].

Corrosion inhibitors are the substances added to the corrosive medium to reduce the rate of its attack on the metal or alloy [3] and these may be inorganic or organic compounds [4-9]. The inorganic compounds such as chromates inhibit the corrosion process via formation of passive oxide film on the metal surface and thus prevent the corrosive medium to attack the bar metal. On the other hand, the organic compounds adsorb on the metal surface forming a barrier between the metal and the corrosive environment. Inhibition of metallic corrosion, now-a-days is mainly focused to cater the environmental regulations as well as economic. Unfortunately, most of the effective corrosion inhibit the corrosion process. Most of the naturally occurrence substances are safe and can be extracted by simple and cheap procedures. Many of the natural resources, such as, henna, natural honey, *Trigonella foenum graceums*, tulsi, opuntia, oils extracted from different parts of different plants have proved their inhibitive ability towards metal corrosion in different aggressive media [10-20].

The *Azadirachta indica* fruits extract is non-toxic and biodegradable, hence, its usages would help to reduce the economic cost of corrosion control as well as decrease the subsequent environmental threats. The chemical constituents of *Azadirachta indica* fruit mainly are nimbin, nimbinin, nimbidin, metiantriol (triterpenoid), azadirone, azadiradionolide, meliacinin, limocin, epoxyazadiradione and the inhibitive effect is attributed due to these photochemical present in the extract [21-25].



### Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

#### Vol. 2, Issue 12, December 2013

In the present work, the effect of elevation in temperature on inhibitory efficacy of *Azadirachta indica* fruit for acid corrosion of aluminium has been investigated at different immersion periods i.e. 6 and 72 h.

Structures of the active constituents of Azadirachta indica fruit



#### Preparation of Test Coupons:

Commercially available aluminium was used for specimen preparation with 98 % purity. The specimens were prepared by cutting the aluminium sheet into rectangular shaped pieces having dimension 3.0 x 2.0 x 0.16cm containing a small hole of about 0.12mm diameter near the upper edge. Specimens were polished to mirror finish by using emery paper. *Test Solutions & Experimentation:* 

Solutions of HCl were prepared by using bi-distilled water. All chemicals used were of AnalR grade. Ethanolic extraction of *Azadirachta indica* fruits (EEA*i*F) was obtained by refluxing the dried fruits in soxhlet extractor (as procedure adopted earlier [14-20]. Each specimen was suspended by the glass hook and plunge into a beaker containing 50 mL of the test solution and different concentrations of the inhibitor (EEA*i*F). The investigation has been carried out at different elevated temperatures (303K to 353K). After fixed intervals of exposure time period, test specimens were washed with running water and dried by hanging the washed specimens in desiccators for sufficient time period. *Surface morphological analysis:* 

Fourier- Transform infrared (FTIR) spectroscopy: The spectra were recorded with the 8400s Shimadzu, Japan spectrometer. The samples were prepared using KBr and the analysis was done by scanning the samples through a wave number range of 400 to  $4000 \text{ cm}^{-1}$ .

#### Chemical (Weight Loss) Measurement:

To get more information about the performance of the inhibitor and the nature of adsorption isotherm which can be used to explain the adsorption and activation processes, the experimentations have been carried at various elevated temperatures, in the range 303-353K, in absence and presence of inhibitor at various concentrations at 6 and 72 h immersion periods. Various corrosion and adsorptive parameters, viz., corrosion rate ( $\rho_{corr}$ ) (mmy<sup>-1</sup>), percentage inhibition efficiency (IE %), fractional surface coverage ( $\Theta$ ), adsorption equilibrium constant ( $K_{ad}$ ) etc. have been evaluated using following equations and the results have been tabulated in table 1.

$$\& IE = \left[ \left( \Delta W_u - \Delta W_i \right) / \Delta W_u \right] \ge 100$$
<sup>(1)</sup>

7983





### Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

#### Vol. 2, Issue 12, December 2013

where  $\Delta W_u$  is weight loss without inhibitor and  $\Delta W_i$  is weight loss with inhibitor. The degree of surface coverage ( $\theta$ ) has been calculated as:

$$(\theta) = \left( \left( \Delta W_{u} - \Delta W_{i} \right) / \Delta W_{u} \right)$$

(2)

The corrosion rate ( $\rho_{corr}$ ) (mmy<sup>-1</sup>) has been obtained by following equation

 $Corrosion rate (mmy<sup>-1</sup>) = (\Delta W \times 87.6) / area x time x metal density$ (3) where  $\Delta W$  weight loss expressed in mg, area expressed in cm<sup>2</sup> of metal surface exposed, time expressed in hours of exposure and metal density expressed in g/cm<sup>3</sup>

exposure and metal density expressed in g/cm.	
TABLE- I	
Corrosion Parameters of EEAiF for Acid Corrosion of Aluminium at 6 and 72h Immersions at Elevated Temperatures	

	Temp.	EEA <i>i</i> F		6	h			72h		
(g/L)         Weigh loss (mg)         Corroston (mg)         Inibition (mg)         Adsorption (mg)         Weigh (mg)         Corroston (mg)         Inibition (mg)         Adsorption (mg)         Efficiency (mg)         Equilibrium (mg)         Efficiency (mg)         Eduilibrium (mg)           303         A0         15         5.03         -         131         3.66         -           A1         0.052         12         4.02         20.00         2.38         68         1.90         48.09         8.81           A3         0.2630         10         3.35         33.33         1.90         42         1.17         67.94         8.06           A4         0.520         9         3.02         40.00         1.43         10         0.28         92.37         11.50           A0         20         6.71         -         160         4.47         -         -           A1         0.0526         17         5.70         15.00         3.35         130         3.63         18.75         4.39           313         A2         0.052         15         5.03         2.500         1.77         31         0.87         80.62         3.96           A0         0.50	(±1K)	Concentration	W/ 1 /	G .	T 1 '1 '.'	A 1	W. 1 /	a ·	T 1 1 1 1	A 1
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		(g/L)	Weight	Corrosion	Inhibition	Adsorption	Weight	Corrosion	Inhibition	Adsorption
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			loss	rate ( $\rho_{corr}$ )	Efficiency	Equilibrium	loss	rate ( $\rho_{corr}$ )	Efficiency	Equilibrium $C_{\text{equilibrium}}$
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		4.0	(IIIg) 15	(IIIIIy)	(% IE)	Constant $(\mathbf{K}_{ad})$	(IIIg) 121	(IIIIIY)	(% IE)	Constant $(\mathbf{K}_{ad})$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		A0	13	3.03	12.22	2.02	151	3.00	20.52	0.26
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		A1 0.0320	15	4.30	15.55	2.92	91	2.34	30.33	0.30
A3         0.2050         10         3.33         1.50         42         1.17         07.94         8.00           A4         0.2500         9         3.02         40.00         1.27         28         0.78         78.63         6.99           A5         0.7890         7         2.35         53.33         1.45         16         0.45         87.79         9.11           A6         1.0520         6         2.01         60.00         1.43         10         0.28         92.37         11.50           A0         20         6.71         -         -         160         4.47         -         -           A1         0.0526         17         5.70         15.00         3.35         130         3.63         18.75         4.39           A2         0.1052         15         5.03         25.00         3.17         100         2.79         37.50         5.70           A3         0.2630         13         4.36         35.00         1.55         43         1.20         73.12         3.45           A6         1.0520         7         2.35         65.00         1.77         31         0.87         80.62	303	A2 0.1032	12	4.02	20.00	2.38	42	1.90	48.09	8.06
A4         0.320         9         3.02         44.000         1.27         28         0.78         78.03         0.599           A5         0.780         7         2.35         53.33         1.145         16         0.46         87.79         9.11           A6         1.0520         6         2.01         60.00         1.43         10         0.28         92.37         11.50           A1         0.0526         17         5.70         15.00         3.35         130         3.63         18.75         4.39           A2         0.1052         15         5.03         25.00         3.17         100         2.79         37.50         5.70           A3         0.2630         13         4.36         35.00         2.05         75         2.10         53.12         4.31           A4         0.5200         1         3.69         45.00         1.55         43         1.20         73.12         3.45           A6         1.0520         7         2.35         65.00         1.77         31         0.87         80.62         3.96           A2         0.1052         22         7.38         18.52         2.16	505	A5 0.2050	10	3.33	33.33	1.90	42	1.17	79.62	8.00 6.00
A3         0.7850         7         2.53         33.33         143         16         0.43         87.79         9.17           A6         10520         6         201         60.00         1.43         110         0.28         92.37         11.50           313         A0         20         6.71         -         -         160         4.47         -         -           313         A2         0.052         15         5.03         25.00         3.35         130         3.63         18.75         4.39           A1         0.0526         17         5.03         25.00         3.17         100         2.79         37.50         5.70           A3         0.630         13         4.36         35.00         2.05         75         2.10         53.12         4.31           A4         0.5260         11         3.69         45.00         1.55         43         1.20         73.12         3.45           A6         10520         7         2.35         65.00         1.77         31         0.87         80.62         3.96           A1         0.0526         24         8.05         11.11         2.38		A4 0.3200	9	3.02	40.00 52.22	1.27	20	0.78	/ 8.03	0.99
A0 $10^{\circ}$ $11^{\circ}$ $10^{\circ}$ $11^{\circ}$ $10^{\circ}$ $11^{\circ}$ $10^{\circ}$ $2.79^{\circ}$ $37.50^{\circ}$ $5.70^{\circ}$ A3 $0.260^{\circ}$ $11^{\circ}$ $3.60^{\circ}$ $2.05^{\circ}$ $5^{\circ}$ $2.10^{\circ}$ $5^{\circ}$ $3.12^{\circ}$ $43.11^{\circ}$ A4^{\circ} $0.27^{\circ}$ $9^{\circ}$ $2.35^{\circ}$ $65.00^{\circ}$ $1.77^{\circ}$ $31^{\circ}$ $0.80^{\circ}$ $3.12^{\circ}$ $3.12^{\circ}$ $3.12^{\circ}$ $3.12^{\circ}$ $40^{\circ}$ $0.526^{\circ}$ $24^{\circ}$ $80.62^{\circ}$ $3.6^{\circ}$ $61.0^{\circ}$ $11.11^{\circ}$ $2.38^{$		AS 0.7890	1	2.55	<u> </u>	1.43	10	0.43	07.79	9.11
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		A0 1.0520	20	<b>2.01</b>	00.00	1.43	10	0.28	92.37	11.50
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		AU	20	0./1 5.70	-	- 2.25	100	4.47	-	-
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	313	A1 0.0320	1/	5.70	15.00	2.55	100	2.03	10.73	4.39
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	515	A2 0.1032	13	3.03	25.00	2.05	75	2.79	57.30	3.70
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		A5 0.2050	15	4.50	35.00	2.03	73	2.10	62.50	4.51
A6 $1.35$ $4.3$ $1.20$ $73.12$ $3.43$ A6 $1.0520$ 7 $2.35$ $65.00$ $1.77$ $31$ $0.87$ $80.62$ $3.96$ $A0$ $27$ $9.05$ -         - $27$ $6.99$ -         - $A1$ $0.0526$ $24$ $8.05$ $11.11$ $2.38$ $24$ $5.84$ $16.40$ $3.73$ $A2$ $0.1052$ $22$ $7.38$ $18.52$ $2.16$ $22$ $5.11$ $26.80$ $3.48$ $A3$ $0.2630$ $19$ $6.37$ $29.63$ $1.60$ $19$ $3.91$ $44.00$ $2.99$ $A4$ $0.5260$ $16$ $5.36$ $40.74$ $1.31$ $16$ $2.93$ $58.00$ $2.63$ $A6$ $0.520$ $10$ $3.36$ $62.96$ $1.62$ $10$ $1.68$ $76.00$ $3.01$ $A0$ $35$ $11.73$ $ 405$ $11.5$		A4 0.3200	11	3.09	43.00	1.50	42	1.08	72.12	2.15
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		AS 0.7890	9	3.02	55.00	1.55	45	1.20	75.12	3.43
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		A0 1.0520	27	2.35	05.00	1.//	27	6.00	80.02	3.90
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		A0	27	9.03	-	-	27	5.99	-	-
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	373	A1 0.0520	24	7 29	11.11	2.36	24	5.04	26.80	3.73
AS         0.2830         19         0.37         29.03         1.60         19         5.91         440.0         2.99           A4         0.5260         16         5.36         40.74         1.31         16         2.93         58.00         2.63           A5         0.7890         13         4.36         51.85         1.37         13         2.29         67.20         2.60           A6         1.0520         10         3.36         62.96         1.62         10         1.68         76.00         3.01           333         A0         35         11.73         -         -         405         11.32         -         -           A1         0.0526         32         10.73         08.57         1.78         358         10.00         11.60         2.50           A2         0.1052         29         9.72         17.14         1.97         310         8.66         23.45         2.91           A3         0.2630         25         8.38         28.57         1.52         250         6.99         38.27         2.36           A4         0.5260         22         7.38         37.14         1.12         190 </td <td>525</td> <td>A2 0.1032</td> <td>10</td> <td>7.38</td> <td>18.32</td> <td>2.10</td> <td>10</td> <td>2.01</td> <td>20.80</td> <td>3.48</td>	525	A2 0.1032	10	7.38	18.32	2.10	10	2.01	20.80	3.48
A4         0.5200         16         3.56         40.74         1.51         16         2.95         38.00         2.65           A5         0.7890         13         4.36         51.85         1.37         13         2.29         67.20         2.60           A6         1.0520         10         3.36         62.96         1.62         10         1.68         76.00         3.01           A0         35         11.73         -         -         405         11.32         -         -           A1         0.0526         32         10.73         08.57         1.78         358         10.00         11.60         2.50           A2         0.1052         29         9.72         17.14         1.97         310         8.66         23.45         2.91           A3         0.2630         25         8.38         28.57         1.52         250         6.99         38.27         2.36           A4         0.5260         22         7.38         37.14         1.12         190         5.31         53.09         2.15           A5         0.7890         18         6.04         48.57         1.20         150         4.19		A3 0.2030	19	5.26	29.03	1.00	19	2.02	44.00 58.00	2.99
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		A4 0.3200	10	J.30	40.74 51.95	1.31	10	2.93	58.00	2.03
A6 $1.0520$ $10$ $3.36$ $62.96$ $1.62$ $10$ $1.68$ $70.00$ $3.01$ 333A0 $35$ $11.73$ $405$ $11.32$ A1 $0.0526$ $32$ $10.73$ $08.57$ $1.78$ $358$ $10.00$ $11.60$ $2.50$ A2 $0.1052$ $29$ $9.72$ $17.14$ $1.97$ $310$ $8.66$ $23.45$ $2.91$ A3 $0.2630$ $25$ $8.38$ $28.57$ $1.52$ $250$ $6.99$ $38.27$ $2.36$ A4 $0.5260$ $22$ $7.38$ $37.14$ $1.12$ $190$ $5.31$ $53.09$ $2.15$ A5 $0.7890$ $18$ $6.04$ $48.57$ $1.20$ $150$ $4.19$ $62.96$ $2.15$ A6 $1.0520$ $14$ $4.69$ $60.00$ $1.43$ $108$ $3.02$ $73.33$ $2.61$ A0 $50$ $16.76$ $600$ $16.76$ A1 $0.0526$ $47$ $15.76$ $6.00$ $1.21$ $544$ $15.20$ $9.33$ $1.96$ A2 $0.1052$ $42$ $14.08$ $16.00$ $1.81$ $490$ $13.69$ $18.33$ $2.13$ $343$ $A3$ $0.2630$ $38$ $12.74$ $24.00$ $1.20$ $430$ $12.01$ $28.33$ $1.50$ $A4$ $0.5260$ $32$ $10.73$ $36.00$ $1.07$ $320$ $8.94$ $46.67$ $1.66$		AS 0.7890	15	4.30	51.85	1.37	15	2.29	76.00	2.00
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		A0 1.0520	25	<b>3.30</b>	02.90	1.02	405	11.00	/0.00	3.01
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		A0	33	10.72	- 08 57	- 1.79	259	11.32	- 11.60	- 2.50
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	333	A1 0.0520	32	0.73	17.14	1.70	210	8 66	22.45	2.30
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	555	A2 0.1032	29	9.72	17.14	1.97	250	6.00	23.43	2.91
A4         0.3200         22         7.38         37.14         1.12         190         5.31         53.09         2.15           A5         0.7890         18         6.04         48.57         1.20         150         4.19         62.96         2.15           A6         1.0520         14         4.69         60.00         1.43         108         3.02         73.33         2.61           A0         50         16.76         -         -         600         16.76         -         -           A1         0.0526         47         15.76         6.00         1.21         544         15.20         9.33         1.96           A2         0.1052         42         14.08         16.00         1.81         490         13.69         18.33         2.13           343         A3         0.2630         38         12.74         24.00         1.20         430         12.01         28.33         1.50           A4         0.5260         32         10.73         36.00         1.07         320         8.94         46.67         1.66		A3 0.2030	23	7 38	20.37	1.52	100	5.31	53.00	2.30
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		A4 0.3200	18	6.04	48 57	1.12	150	J.J1 / 10	62.06	2.15
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		A6 1 0520	10	4 69	60.00	1.20	108	3.02	73 33	2.13
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		Δ0	50	16.76	-	-	600	16.76	-	- 2.01
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		A1 0.0526	47	15.76	6.00	1.21	544	15.70	9 33	1.96
343         A3         0.2630         38         12.74         24.00         1.07         430         12.01         28.33         1.50           A4         0.5260         32         10.73         36.00         1.07         320         8.94         46.67         1.66		A2 0 1052	42	14.08	16.00	1.21	490	13.20	18 33	2.13
A4         0.5260         32         10.73         36.00         1.07         320         8.94         46.67         1.66	343	A3 0 2630	38	12.74	24.00	1.01	430	12.01	28.33	1.50
		A4 0 5260	32	10.73	36.00	1.23	320	8.94	46.67	1.50
		A5 0 7890	28	9 39	44 00	1.07	240	6.71	60.00	1.00
A6         1050         20         7.38         56.00         1.21         190         5.31         68.33         2.05		A6 1 0520	20	7 38	56.00	1.00	190	5 31	68 33	2.05
A0 60 20.12 940 26.26		A0	60	20.12	-	-	940	26.26	-	-
A1 0.0526 57 19.11 5.00 1.00 870 24.31 7.45 1.53		A1 0.0526	57	19.11	5.00	1.00	870	24.31	7.45	1.53
A2 0.1052 53 17.77 11.67 1.26 830 23.19 11.70 1.26		A2 0.1052	53	17.77	11.67	1.36	830	23.19	11.70	1.26
353 A3 0.2630 48 16.09 20.00 0.95 760 21.23 19.15 0.90	353	A3 0.2630	48	16.09	20.00	0.95	760	21.23	19.15	0.90
A4 0.5260 45 15.09 25.00 0.63 700 19.56 25.53 0.65		A4 0.5260	45	15.09	25.00	0.63	700	19.56	25.53	0.65
A5         0.7890         41         13.75         31.67         0.59         600         16.76         36.17         0.72		A5 0.7890	41	13.75	31.67	0.59	600	16.76	36.17	0.72



### Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

#### Vol. 2, Issue 12, December 2013



Fig: 1(a). IE (%) vs concentration of EEA*i*F (g/L) at different temperatures (303-353K) at 6h immersion period.

Figures 1(a) and (b) clearly indicate an increase in inhibition efficiency with increasing concentration of the inhibitor. The maximum efficiency (92.37%) has been observed at highest inhibitor concentration (1.052g/L) at 72 h at room temperature (303 K). At elevated temperature (353 K), IE % reduces to 41.67%. With an elevation in temperature, due to the thermal aggitation, the desorption process of the adsorbed constituents of the inhibitor increases, leading to a decrease in the inhibition efficacy of EEAiF (table I).



Fig: 1(b). IE (%) vs concentrations of EEAiF (g/L) at different temperatures (303-353K) at 72h immersion period.



Fig:2(a). Corrosion rate vs concentrations of EEA*i*F (g/L) at different temperature (303-353K) at 6h immersion period.



### Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization) Vol. 2, Issue 12, December 2013



Fig:2 (b). Corrosion rate vs concentrations of EEA*i*F at different temperature (303-353K) at 72h immersion period.

Figures 2(a) and (b) indicate an increase in the corrosion rate with an increase in temperature. A decrease in the degree of surface coverage has been observed with increasing temperature owing to the desorption of the inhibitor molecules onto the aluminium surface.

#### Kinetic /thermodynamic Treatment of Weight Loss Results:

Assuming that the corrosion rate of aluminium and the concentration of the EEA*i*F obey the kinetic relationship, expressed by the equation:

#### $\log \rho_{corr} = \log k + B \log C$

(4)

where k is the rate constant and equals to  $\rho_{corr}$  at inhibitor concentration of unity; B is the reaction constant which, in the present case, is a measure for the inhibition effectives and C is the concentration of EEA*i*F in g/L.



Fig. 3 (a). log  $\rho_{\text{corr}}$  vs log C at 6h immersion periods.

Fig. 3 (b). log  $\rho_{corr}$  vs log C at 72h immersion periods.

The plot of log  $\rho_{corr}$  vs. log C at various temperature for 6 and 72 h immersions resulted in straight lines (Figs-3 a & b). The kinetic parameters (k and B) have been calculated using equation 4 and the results have been tabulated in table-II. The straight lines with negative slopes were obtained, indicative that the rate of corrosion process is inversely proportional to EEA*i*F concentration, i.e. EEA*i*F becomes more effective as its concentration is increased. At each temperature a linear variation was observed, confirming the first order kinetics. At elevated temperature, with an



(5)



### International Journal of Innovative Research in

### Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

#### Vol. 2, Issue 12, December 2013

increase in the concentration of the inhibitor, the decrease in corrosion rate is very low (also low values of B), indicating that the desorption process is swift.

TABLE – II

The kinetic parameters (k and B) for EEAiE at 6 and 72 h immersions at different temperatures							
Temperature		6h			72h		
(K)	В	K	$\mathbb{R}^2$	В	k	$\mathbb{R}^2$	
303	-0.244	2.269	0.917	-0.695	0.386	0.941	
313	-0.266	2.773	0.907	-0.437	1.066	0.945	
323	-0.265	4.018	0.888	-0.393	2.042	0.937	
333	-0.246	5.559	0.89	-0.369	3.724	0.922	
343	-0.225	9.840	0.9	-0.334	6.383	0.894	
353	-0.142	12.912	0.907	-0.193	14.962	0.743	

#### Energy of Activation:

The weight loss measurements were conducted in the temperature range of 303-353K in the absence and presence of different concentrations of EE*Ai*F in 0.5N HCl for aluminium. The dependence of corrosion rate on temperature can be expressed by Arrhenius equation [14-20]:

#### $\log CR = \log A - E_a/2.303RT$

where CR is the corrosion rate, A is Arrhenius constant, R is a molar gas constant and T is temperature(K). A plot of log CR ( $\rho_{corr}$ ) against 1/T resulted straight lines (figs. 4 a & b) in 0.5N HCl in absence and presence of different concentrations of EE*Ai*F. Activation energy values, Ea were calculated from the slope of the plots of figure 4 and are summarized in table III.



Fig: 4(a). log  $\rho_{corr}$  vs 1/T (K) at 6h immersion period.

Fig: 4(b). log  $\rho_{corr}$  vs 1/T (K) at 72h immersion period.

TABLE – III	
Thermodynamic Parameters at 6 and 72 h immersion period	ods

	Thermodynamic r araneters at 0 and 72 if initiersion periods								
Concentration (g	;/L)		6h 72h						
		(Ea)	$\Delta H$	$\Delta S$	(Ea)	$\Delta H$	$\Delta S$		
		$(kJ mol^{-1})$	$(kJ mol^{-1})$	(J/mol k)	$(kJ mol^{-1})$	$(kJ mol^{-1})$	(J/mol k)		
	A0	23.61	-21.06	-162.08	33.92	-31.42	-131.52		
A1 0.05	526	25.49	-22.94	-157.22	38.30	-35.75	-119.79		
A2 0.10	052	25.64	-23.09	-157.56	42.30	-39.75	-108.95		
A3 0.26	530	26.92	-24.37	-154.77	48.22	-45.67	-92.92		
A4 0.52	260	27.48	-24.93	-154.19	51.57	-49.04	-84.86		
A5 0.78	890	29.85	-27.32	-148.45	56.74	-54.21	-71.63		
A6 1.05	520	29.91	-27.36	-150.13	58.57	-56.31	-67.97		

The enthalpy,  $\Delta H$  and entropy of adsorption,  $\Delta S$  were obtained from the Transition state equation:  $\log \rho_{corr} / T = [\log (R/Nh) + (\Delta S/ 2.303R)] - \Delta H / 2.303 RT$  (6) where h is Planck's constant, N is the Avogadro's number.



### Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

#### Vol. 2, Issue 12, December 2013

Figure 5 illustrates the plot of log (CR/T) as a function of 1/T for aluminium (a) at 6 h and (b) 72 h immersion periods. Straight lines were obtained with a slope of  $(-\Delta H/R)$  and an intercept of log  $(R/Nh) + (\Delta S/2.303R)$  from which the values of  $\Delta H$  and  $\Delta S$  were calculated.

The calculated values have been presented in Table III for aluminium in 0.5N HCl without and with varying concentration of EEAiF. The value of  $E_a$  increases in the presence of the inhibitor as compared to the free acid solution for aluminium corrosion. The increase in  $E_a$  in the presence of inhibitor has been associated with physisorption of the adsorptive film onto the metal surface.



Fig: 5 (b)  $\log(\rho_{corr}/T)$  vs 1/T at 72 h immersion period.

#### Thermodynamic Parameters:

#### With the expression: $\mathbf{K} = 1/55.5 \exp \left[-\Delta G^{o}_{ads}/\mathbf{RT}\right]$

(7)

the free energy of adsorption values,  $\Delta G^{o}_{ads}$  were obtained and the results have been tabulated in Table- IV (a & b). Results presented in the Tables indicate that the values of  $\Delta G^{o}_{ads}$  are negative in all cases. The negative values indicate a spontaneous adsorption of the inhibitor molecules. Generally, values of  $\Delta G^{o}_{ads}$  up to -20 kJ mol<sup>-1</sup> are consistent with electrostatic interaction between charged molecules and a charged metal (which indicates physical adsorption) while those more negative than  $-40 \text{ kJ mol}^{-1}$  involves charge sharing or transfer from the inhibitor components to the metal surface to form a coordinate type of bond (which indicate chemisorption).

The thermodynamic parameters  $\Delta H$  and  $\Delta S$  for adsorption of EEAiF on aluminium can be calculated from the following equation:  $\Delta \mathbf{G}^{\circ} = \Delta \mathbf{H}^{\circ} - \mathbf{T} \Delta \mathbf{S}^{\circ}$ (8)

where  $\Delta H$  and  $\Delta S$  are the enthalpy and entropy of adsorption process. The calculated values are given in Table IV (a & b).

TABLE – IV (a)

Thermodynamic Parameters ( $\Delta H^{o}_{ads}, \Delta G^{o}_{ads}, \Delta S^{o}_{ads}$ ) for 6 h immersion at different temperature									
Concen.(g/L)		$\Delta G^{o}_{ads} kJ mol^{-1}$							
	303K	313K	323K	333K	343K	353K	kJmol <sup>-1</sup>	Jmol <sup>-1</sup> K <sup>-1</sup>	
A0	-	-	-	-	-	-			
A1 0.0526	-12.82	-13.60	-13.11	-12.72	-12.01	-11.79	-22.36	0.029	
A2 0.1052	-12.30	-13.45	-12.85	-12.99	-13.15	-12.46	-12.86	0.060	
A3 0.2630	-11.74	-12.32	-12.05	-12.28	-11.98	-11.64	-13.20	0.003	
A4 0.5260	-10.72	-11.60	-11.51	-11.44	-11.64	-10.45	-12.41	0.003	
A5 0.7890	-11.05	-11.59	-11.62	-11.62	-11.44	-10.23	-15.55	0.013	
A6 1.0520	-11.01	-11.93	-12.07	-12.10	-12.00	-10.65	-27.36	0.004	

TABLE - IV (b)

Thermod	ynamic	Parameters	$(\Delta H^{o}_{ads},$	$\Delta G^{o}_{ads}$	$\Delta S^{o}_{ads}$	) for	72 h	immersic	on at	different	tempe	erature	
													1

Concn. (g/L)		$\Delta H^{o}_{ads} kJ$	$\Delta S^{o}_{ads}$					
	303K	313K	323K	333K	343K	353K	mol <sup>-1</sup>	Jmol <sup>-1</sup> K <sup>-1</sup>
A0	-	-	-	-	-	-		
A1 0.0526	-15.47	-14.30	-14.32	-13.65	-13.37	-13.04	-28.66	0.044
A2 0.1052	-15.60	-14.98	-14.14	-14.08	-13.62	-12.47	-32.72	0.056





### Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 2, Issue 12, December 2013

A3 0.2630	-15.38	-14.25	-13.73	-13.49	-12.62	-11.48	-36.56	0.070
A4 0.5260	-15.02	-13.45	-13.38	-13.24	-12.91	-10.53	-35.78	0.069
A5 0.7890	-15.69	-13.67	-13.35	-13.25	-13.29	-10.82	-37.34	0.073
A6 1.0520	-16.27	-14.03	-13.75	-13.78	-13.50	-12.20	-34.44	0.062

#### Adsorption Isotherm

Adsorption isotherm provides useful insights into the mechanism of corrosion inhibition. The adsorption equilibrium constant, K<sub>ad</sub>, is expressed as:

#### $\mathbf{K}_{ad} \mathbf{C} = \boldsymbol{\theta} / (\mathbf{1} - \boldsymbol{\theta})$

(9)

where C is the concentration of EEAiF in g/L;  $\theta$  the fractional surface coverage and K<sub>ad</sub> is the adsorption equilibrium constant. The fractional surface coverage,  $\theta$ , was evaluated. The fractional surface coverage  $\theta$ , and the adsorption equilibrium constant K<sub>ad</sub>, was found large at higher concentration of EEAiF, hence it is concluded that higher concentration of EEAiF is essential for maximum adsorption over aluminium metal surface. It is essential to determine empirically which adsorption isotherm fits best to the surface coverage data in order to use the corrosion rate measurements to calculate the thermodynamic parameters pertaining to inhibitor adsorption. Different adsorption models were considered for the best fit of experimental data. The best fitted straight line was obtained for the plot of  $C_{inh}/\theta$  versus  $C_{inh}$  with slopes around unity. This suggests that the adsorption of EEAiF on the metal surface obeyed Langmuir adsorption isotherm, mathematically expressed as: (10)

 $(C / \theta) = C + 1 / K_{ad}$ 

where, C is the concentration of the inhibitor (EEA*i*F),  $\theta$  is the fractional surface coverage, and K<sub>ad</sub> is the adsorption equilibrium constant. From the intercepts of the straight line Cinh/O-axis, K value was calculated and from graph the value came can be justify by theoretical value. It is based on the assumption that the adsorbed molecule decreases the surface area available for the corrosion reactions to occur.



Fig: 6(a). Plot of C/ $\Theta$  vs C at different temperature at 6h immersion period. Fig: 6(b)Plot of C/ $\Theta$  vs C at different temperature at 72 h immersions.

		TABLE- V								
The correlation coefficient and slopes from Langmuir adsorption isotherm at different temperature										
Temperature	6h		72h							
(K)	Correlation	K (adsorption	Correlation	K (adsorption						
	coefficient (R <sup>2</sup> )	coefficient)	coefficient (R <sup>2</sup> )	coefficient)						
303	0.965	2.439	0.998	7.874						
313	0.968	2.873	0.991	4.673						
323	0.956	2.012	0.993	3.389						
333	0.948	1.724	0.988	2.532						
343	0.931	1.362	0.964	1.805						
353	0.922	1.095	0.737	1.116						



# International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization) Vol. 2, Issue 12, December 2013

The degree of linearity of Langmuir adsorption isotherm as measured by value of  $R^2$  in the range (0.999  $\ge r^2 \ge 0.737$ ) is nearly equal to one and slope is almost unity, monolayer of the inhibitor species must have been attached to aluminium surface without lateral interaction between the adsorbed species.

#### Surface Morphological Analysis:

*FT-IR Spectroscopy:* The formation of the adsorbed protective film over the surface of copper coupon was further established by carrying out FT-IR spectroscopic investigations. FT-IR was conducted on 8400 Shimadzu, Japan FT-IR spectrometer in the IR range from 4000 to 400 cm<sup>-1</sup>. The FT-IR spectrum of the protective film was recorded by carefully removing the film, mixing it with KBr & making the pellet.



Fig: 7 (b). FTIR spectra of adsorbed film of EEAiF onto Aluminium surface in 0.5 N HCl containing 1.052g/L EEAiF

Fig. 7 (b) shows the changes in the spectrum of EEFgF after its adsorption onto the metal surface and undoubtedly illustrates that some of the peaks have disappeared completely while some have shifted to higher frequencies region, justifying the adsorption phenomenon taking place over the solid metal surface.

#### Proposed Mechanism for Inhibition by EEAiF

Corrosion of aluminium in 0.5N HCl is retarded in presence of different concentrations of the *Azadirachta indica* extract. The results clearly showed that the inhibition mechanism involves blocking of aluminium surface by inhibitor molecules via adsorption. In general, the phenomenon of adsorption is influenced by the nature of metal and chemical structure of inhibitor. The values of thermodynamic parameters for the adsorption of inhibitors provide valuable information about the mechanism of corrosion inhibition. The adsorption mechanism of extract on aluminium surface involves a physisorption. It means that the extract is able to electrostatically adsorb on the metal surface. The temperature study (303-353K) shows that at higher temperature desorption of the inhibitor from the metal surface occur. The Kinetic and thermodynamic parameters also confirm that there is electrostatic kind of interaction between the extract and metal surface. *Azadirachta indica* fruit extracts contain significant high concentrations of alkaloids, fatty acids, and nitrogen and oxygen-containing compounds. Chemical constituents of *Azadirachta indica* fruit mainly are



### Science, Engineering and Technology

#### (An ISO 3297: 2007 Certified Organization)

#### Vol. 2, Issue 12, December 2013

nimbin, nimbinin, nimbidin, metiantriol (triterpenoid), azadirone, epoxyazadiradione and the inhibitive effect is attributed due to these photochemical present in the extract. The adsorption of these organic molecules occurred due to the formation of a links between aluminium atoms, involving the displacement of water molecules from metal surface, and the lone pairs present on N- and O- atoms of the heterocyclic rings. It can be concluded that, due to the suitable inhibitive characteristics of compounds present in Azadirachta indica extract it is effective inhibitor for aluminium corrosion.

#### **III. CONCLUSION**

From the study, it was concluded that ethanol extract of Azadirachta indica fruit has good adsorptive propensity for the metal (aluminium) surface. The inhibition of the corrosion of aluminium by ethanol extract of the fruits of Azadirachta indica is due to the phytochemical constituents of the extract. Analyses of the temperature effect on inhibition efficiency as well as comparison of corrosion activation energies in absence and presence of inhibitor give some insight into the possible mechanism of inhibitor adsorption. Decrease in inhibition efficiency with rise in temperature, with correspondingly increase in corrosion activation energy in the presence of inhibitor compared to its absence, is ascribed to physical adsorption mechanism. The adsorption of ethanol extract of the fruits of Azadirachta indica is spontaneous and occurred according to the mechanism of physical adsorption. The experimental data fit into the Langmuir adsorption isotherm. The formation of monolayer of adsorption as described by Langmuir adsorption isotherm also supported this assertion. The FT-IR spectra confirm that the extract inhibit the corrosion of aluminium by being adsorbed on the surface of aluminium and that there is interaction between the inhibitor and the surface. In view of the findings, it may be concluded that the ethanolic extract of Azadirachta indica fruit can be considered as a source of relatively cheap, eco-friendly and effective acid corrosion inhibitor to a certain elevation in temperature.

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#### REFERENCES

- J. Dubey, P. Sharma, A. Chaturvedi, R. K. Upadhyay, "Effect of Temperature on Corrosion Inhibition Efficiency of Withania Somnifera [1] (Ashwagandha) on Aluminium in HCl Solution", J. Corros. Sci. Engg., vol. 13 (1) pp. 1466, 2010.
- Christian Vargel, Corrosion of Aluminium, Oxford, Elsevier: UK, 2004. [2]
- Vedula S. Sastri, Corrosion Inhibitors: Principles and Applications, John Wiley & Sons: England, 1998. [3]
- [4] Shankar Lal Meena, Mohit Sharma, Alka Sharma, I. K. Sharma, and P. S. Verma, "Effect of Some Surface-Active Agents on Corrosion of Aluminium in acidic medium", Bull. Electrochem ., vol. 20 (4) pp. 183-185, 2004.
- M. Iannuzzi, G.S. Frankel, "Mechanisms of Corrosion Inhibition of AA2024-T3 by Vanadates", Corros. Sci. Vol. 49, pp. 2371–2391, 2007. [5]
- K. A. Yasakau, M. L. Zheludkevich, M. G. S. Ferreira, "Lanthanide Salts as Corrosion Inhibitors for AA5083. Mechanism and Efficiency of [6] Corrosion Inhibition", J. Electrochem. Soc., vol. 155 (5) pp. C169-C177, 2008. A. Yurt, S. Ulutas, H. Dal, "Electrochemical and Theoretical Investigation on the Corrosion of Aluminium in Acidic Solution Containing
- [7] Some Schiff Bases", Appl. Surf. Sci., vol. 253 (2) pp. 919-925, 2006.
- Da-Quan Zhang, Qi-Rui Cai, Li-Xin Gao, Kang Yong Lee, "Effect of Serine, Threonine and Glutamic Acid on the Corrosion of Copper in [8] Aerated Hydrochloric Acid Solution", Corros. Sci., vol. 50 (12) pp.3615-3621, 2008.
- A. R. Yazdzad, T. Shahrabi, M. G. Hosseini, "Inhibition of 3003 Al Alloy Corrosion by Propargyl Alcohol and Tartrate Ion and their [9] Synergistic Effects in 0.5% NaCl Solution", Mater. Chem. Phys., vol.109 (2-3) pp. 199-205, 2008.
- S. A. Umoren, "Inhibition of aluminium and mild steel corrosion in acidic medium using *Gum Arabic*", Cellulose, vol. 15, pp. 751-761, 2008. 1101
- A. Ostovari, S. M. Hoseinieh, M. Peikari, S. R. Shadizadeh, S. J. Hashemi, "Corrosion inhibition of mild steel in 1M HCI solution by henna [11] extract : A comparative study of the inhibition by henna and its constituents (Lawsone, gallic acid,  $\alpha$ -D- Glucose and Tannic acid)", Corros. Sci., vol. 51, pp. 1935-1949, 2009.
- R. Khandelwal, S. Sahu, S. K. Arora, S. P. Mathur; Study of corrosion inhibition efficiency of naturally occurring plant Cordia Dicotoma on [12] aluminium in acidic media; J. Corros. Sci. Engg, vol. 13 (12), pp. 1466, 2010.
- M.Hazwan hussin, M. Jain Kassim, "Thermodynamic characterisation of mild steel corrosion and inhibition adsorption of Uncaria gambir and [13] catechin in 1M HCl", J. Corrs. Sci. Engg., vol. 13(18) 2010.
- Alka Sharma, P.S. Verma, I.K.Sharma, Rekha N Nair, Proc. World Acad. Sci. Eng. Technol. (PWASET) vol. 39, pp. 745, 2009. [14]
- [15] Rekha N. Nair, Shashi Sharma, I.K. Sharma, P.S. Verma, Alka Sharma, "Inhibitory efficacy of Piper Nigrum Linn. Extract on corrosion of AA1100 in HCl", RASAYAN J. Chem., vol. 3 (4) pp. 783-795, 2010.
- Swati Yadav, Guddi Choudhary, Alka Sharma, "Green Approach to Corrosion Inhibition of aluminium and copper by Ziziphus mauritiana [16] Fruit Extract in Hydrochloric Acid Solution", Int. J. ChemTech Res., vol. 5 (4) pp. 1815-1823, April-June 2013.
- [17] Alka Sharma, Rekha N. Nair, Prassan Singh Pratihar, Swati Yadav and P S Verma, "Investigation of anti-corrosive propensity of Mangifera indica Linn. On AA1100 employing chemical and electrochemical methods", Chem News Letter, vol. 2 (2) pp. 105-115, July-December 2012.



### Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

#### Vol. 2, Issue 12, December 2013

- [18] Alka Sharma, Rekha N Nair, Arpita Sharma, Guddi Choudhury, "Combating Aluminium Alloy Dissolution by employing Ocimum tenuiflorum leaves extract", Int J Adv Sci Tech Res, vol. 6 (2) pp.713-729, 2012.
- [19] Alka Sharma and P S Verma, "Corrosion An inevitable but controllable process", Chem News Letter, vol. 1 (1) pp. 14-15, January-June 2012.
- [20] Shashi Sharma, Prassan S Pratihar, Rekha N Nair, P S Verma, Alka Sharma, "Influence of ion-additives on inhibitory action of extract of *Trigonella foenum graceums* seeds for AA6063 in acid medium", RASAYAN J. Chem., vol. 5 (1) pp. 16-23, 2012.
- [21] Peter C. Okafor, Eno E. Ebenso, Udofot J.Ekpe, "Azadirachta Indica Extracts as Corrosion Inhibitor for Mild Steel in Acid Medium", Int. J. Electrochem. Sci., vol. 5, pp. 978 993, 2010.
- [22] Sanjay K. Sharma, Ackmez Mudhoo, Gargi Jain, Jyoti Sharma, "Corrosion inhibition and adsorption properties of *Azadirachta indica* mature leaves extract as green inhibitor for mild steel in HNO<sub>3</sub>", Green Chemistry Letters and Reviews, vol. 3(1), pp.7-15, 2010.
- [23] C. A. Loto, R. T. Loto, A. P. I. Popoola, "Effect of neem leaf (*Azadirachita indica*) extract on the corrosion inhibition of mild steel in dilute acids", Int. J. Phy. Sci., vol. 6 (9), pp. 2249-2257, 2011.
   [24] T. V. Sangeetha, M. Fredimoses, "Inhibition of Mild Copper Metal Corrosion in HNO<sub>3</sub> Medium by Acid Extract of *Azadirachta Indica* Seed",
- [24] T. V. Sangeetha, M. Fredimoses, "Inhibition of Mild Copper Metal Corrosion in HNO<sub>3</sub> Medium by Acid Extract of Azadirachta Indica Seed", E-J. Chem., vol. 8 (S1) pp. S1-S6, 2011.
- [25] N. O. Eddy, P. A. P. Mamza, "Inhibitive and Adsorption Properties of Ethanol Extract of Seeds and Leaves of Azadirachta Indica on the Corrosion of Mild Steel in H<sub>2</sub>SO<sub>4</sub>", Portug. Electrochimica. Acta, vol. 27(4) pp. 443-456, 2009.