



## The effect of aqueous extract of *Adathoda vasica* leaves on corrosion inhibition of aluminium in alkaline solution

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### ABSTRACT

The effect of aqueous extract of *adathoda vasica* leaves (AVL) on corrosion inhibition of aluminium in 1N NaOH solution was studied using chemical and electrochemical techniques. It was found that the inhibition efficiency increased with the increase of *adathoda vasica* extract upto 800 ppm. Beyond this concentration there is no improvement in the inhibition efficiency. Electrochemical measurements revealed that AVL extract acts as a mixed type inhibitor. Adsorption of AVL extract was found to follow Langmuir adsorption isotherm. The results obtained from chemical and electrochemical measurements are in reasonably good agreement. The protective film formed on the surface of aluminium by the adsorption of water-soluble chemical constituents of AVL extract was confirmed using scanning electron microscopy studies.

**Keywords:** Corrosion inhibitors, *Adathoda vasica* leaves extract, Aluminium corrosion, Langmuir adsorption isotherm, Mixed type inhibitors.

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### INTRODUCTION

Aluminium presently finds extensive use in industrial as well as domestic applications due to its lightweight, strength, recyclability, corrosion resistance, durability, formability and conductivity. The pickling of aluminium in caustic alkali solution before anodizing or to give an attractive matt finish is common practice [1]. Alkali destroys the protective aluminium film very quickly because OH<sup>-</sup> ions are positively adsorbed [2] and hence the dissolution rate of aluminium is very high. To inhibit the dissolution of aluminium in such aggressive solutions, small quantity of corrosion inhibitors can be added to reduce the corrosion. Many research works have also been done using chemical compounds as inhibitors to reduce corrosion [3].

Nowadays, the use of chemical inhibitors has been limited because due to environmental regulations, plant extracts have again become important because they are environmentally acceptable, readily available and renewable source for a wide range of needed inhibitors plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. By using leaves extracts, inhibitive properties of mild steel in acid medium was studied [4,5]. For instance henna leaves [6] *gossypium higgutum* [7], gum arabic [8] *phyllanthus amarus* [9], *ipomoea involucre* [10], *hibiscus sabdoriffa* leaves [11] have been studied as effective corrosion inhibitors for aluminium in alkaline medium. This paper reports the influence of aqueous extract of *adathoda vasica* leaves for the corrosion of aluminium in 1N alkaline solution by chemical and electrochemical techniques. The effect of temperature on the corrosion rate of aluminium in presence of an optimum concentration of the extract was also investigated and some thermodynamic parameters for activation process were computed and discussed.

## EXPERIMENTAL SECTION

### Material preparation

Aluminium strips of 4.5% and 2cm × 0.2cm containing 1.5% Pb, 0.1% Ga, 1% In and the remainder Al were used for weight loss, gasometric and hydrogen permeation studies. The strips were mechanically polished and degreased with acetone before use. A cylindrical aluminium rod of the same composition embedded in a Teflon rod with an exposed area of 0.5cm<sup>2</sup> was used for potentiodynamic polarization studies and AC impedance measurements. Analar grade NaOH and double distilled water were used to prepare the solutions.

### Preparation of leaves of *adathoda vasica* extract

The leaves of *adathoda vasica* were taken and cut into small pieces and they were dried in an air oven at 80°C for 2 hrs. They were ground well into powder. From this 10g of the sample was refluxed in 100mL distilled water for 1 hour. The refluxed solution was filtered carefully and the filtrates were heated on water bath to evaporate fully the moisture content to get the dried compound [12]. The inhibitor concentrations of 200, 400, 600, 800 and 1000ppm were prepared using 1N NaOH solution.

### Techniques used for the study

#### Weight loss measurements

Weight loss measurements were carried out as described elsewhere [12]. Aluminium specimens were immersed in 100ml of inhibited and uninhibited solutions for 2 hours at 30°C. The corrosion rate (mmpy) and the inhibition efficiency were calculated using the following equations;

$$\text{Corrosion rate (mmpy)} = KW/ATD$$

Where,  $K = 8.76 \times 10^4$  (constant),  $W$  = weight loss in g,  $A$  = area in square cm,  $T$  = time in seconds and  $D$  = density in gm / cu.cm (2.70)

$$\text{Inhibition Efficiency (\%)} = W_B - W_I / W_B \times 100$$

Where,  $W_B$  and  $W_I$  are weight loss per unit time in the absence and presence of inhibitors.

Weight loss measurements were also performed at various immersion time from 2 hours to 24 hours in an optimum concentration of AVL extract at 30°C. From the initial and final weight of the specimen, the loss in weight was calculated and the efficiency of inhibitor at various immersion time was calculated.

#### Determination of surface coverage

The degree of surface coverage ( $\theta$ ) was calculated from the weight loss measurement results using the formula [13];

$$\text{Surface coverage } (\theta) = \frac{W_B - W_I}{W_B}$$

Where,  $W_B$  is the weight loss in the absence of the extract,  $W_I$  is the weight loss in the presence of the extract. The data were tested graphically for fitting a suitable isotherm.

#### Potentiodynamic polarization studies

Potentiodynamic polarization measurements were carried out using EG &G PAR potentiostat / galvanostat (Model - 173) analyzer a universal programmer in a conventional three – electrode glass cell. A platinum foil of surface area 2cm<sup>2</sup> was used as the auxiliary electrode and a saturated calomel electrode as the reference electrode. Both anodic and cathodic polarization curves were recorded in the absence and presence of an optimum concentration of the extract from a cathodic potential of –1900 mV to an anodic potential of – 1300 mV (vs SCE) at a sweep rate of 1mV per second. From the polarization curves, Tafel slopes, corrosion potential and corrosion current were calculated. The inhibitor efficiency was calculated using the formula;

$$\text{IE (\%)} = \frac{I_{\text{Corr}} - I_{\text{Corr}}^*}{I_{\text{Corr}}} \times 100$$

Where,  $I_{\text{corr}}$  and  $I_{\text{corr}}^*$  are corrosion current in the absence and presence of AVL extract.

**Electrochemical Impedance studies**

The electrochemical AC-impedance measurements were performed using EG & G Electrochemical impedance analyzer (model – 6310) with M38 software as described earlier. Experiments were carried out at the open circuit potential for the frequency range of 100kHz to 10mHz. A plot of  $Z'$  vs  $Z''$  were made. From the plots, the charge transfer resistance ( $R_t$ ) were calculated and the double layer capacitance were then calculated using the equation [14].

$$C_{dl} = 1 / 2\pi f_{max} R_t$$

Where  $R_t$  is charge transfer resistance and  $C_{dl}$  is double layer capacitance. The experiments were carried out in the absence and presence of an optimum concentration of inhibitor. The percentage of inhibition efficiency was calculated using the equation [15].

$$IE (\%) = \frac{R_t^* - R_t}{R_t^*} \times 100$$

Where  $R_t^*$  and  $R_t$  are the charge transfer resistance in the presence and absence of AVL extract.

**RESULTS AND DISCUSSION****Weight loss method**

The weight loss studies was performed with various concentrations of *adathoda vasica* leaves extract ranging from 200-1000 ppm to study the influence of various concentrations of *adathoda vasica* leaves extract and immersion time on the corrosion inhibition of aluminium in 1N NaOH solution at 30°C for a period of 2 hours. The corrosion parameters obtained from weight loss measurements for aluminium in 1N NaOH solution containing various concentrations of *adathoda vasica* leaves extract are given in Table -1. It was found that with the rise in concentration of *adathoda vasica* leaves extract from 200 to 800 ppm, the weight loss of aluminium decreased, and the inhibition efficiency increased from 65.8 % to 81.5 %. Beyond this concentration (800 ppm), there is no improvement in the inhibition efficiency. This result indicated that 800 ppm is the optimum concentration to get maximum corrosion protection for aluminium in 1N NaOH using *adathoda vasica* leaves extract. The variation of inhibition efficiency with various concentrations of *adathoda vasica* leaves extract on aluminium in 1N NaOH as shown in Fig.1.

**Table -1 Corrosion parameters obtained from weight loss measurements for aluminium in 1N NaOH solution containing various concentrations of AVL extract**

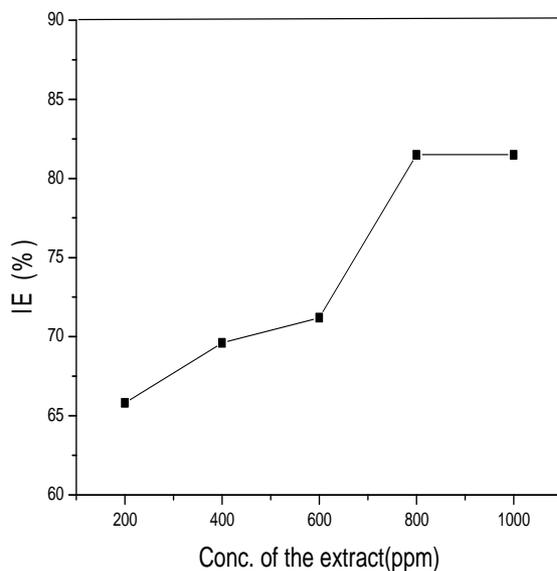
Conc. of AVL Extract (ppm)	Weigh Loss (gm)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)	Surface Coverage ( $\theta$ )
Blank	0.3734	757.17	---	---
200	0.1456	295.24	65.8	0.61
400	0.1135	230.15	69.6	0.69
600	0.1077	218.39	71.2	0.71
800	0.0690	139.92	81.5	0.85
1000	0.0690	139.92	81.5	0.85

The effect of immersion time from 2 hours to 24 hours was also studied. The inhibition efficiency was found to decrease from 81.5 % to 66.2 %. The effect of immersion time on percentage inhibition efficiency of aluminium in 1N NaOH at 30°C in presence of an optimum concentration (800 ppm) of *adathoda vasica* leaves extract is given in Table-2 (Fig.2). Though 66.2% inhibition efficiency was obtained even at 24 hours of immersion time, the maximum inhibition efficiency was found at 2 hours. Hence, using weight loss method, it was found that *adathoda vasica* leaves extract acted as corrosion inhibitor for aluminium in 1N NaOH medium at an optimum concentration of 800 ppm for a period of 2 hours at 30°C.

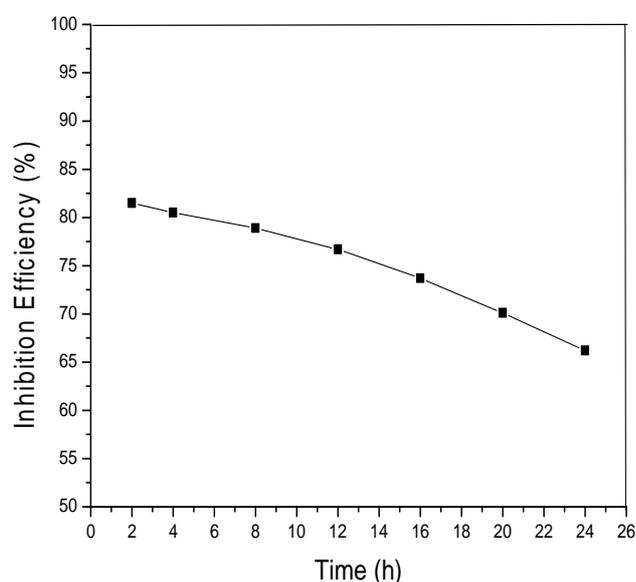
**Potentiodynamic polarization method**

Fig.3 shows the polarization curves for aluminium in 1N NaOH solution in the absence and presence of an optimum concentration of *adathoda vasica* leaves extract and their corresponding potentiodynamic polarization parameters are given in Table 3. It can be seen from the table that the corrosion potential was not shifted significantly in presence of the extract suggesting that the *adathoda vasica* leaves extract control both anodic and cathodic reactions to inhibit the corrosion of aluminium by blocking active sites on the aluminium surface. Hence, it is inferred that

the inhibition action is of mixed type [16]. On the other hand, the corrosion current density was markedly decreased upon the addition of the extract in 1N NaOH solution. The extent of its decrease increased with the addition of 800 ppm of the extract and the maximum inhibition efficiency of 81.5% was observed as in weight loss method.



**Fig.1** Variation of inhibition efficiency with various concentrations of AVL extract on aluminium in 1N NaOH solution



**Fig.2** Effect of immersion time on percentage inhibition efficiency of aluminium in 1N NaOH at 30°C in presence of an optimum concentration (800ppm) of AVL extract

**Table – 2** Effect of immersion time on percentage inhibition efficiency of aluminium in 1N NaOH at 30°C in the presence of an optimum concentration (800ppm) of AVL extract

System	Inhibition Efficiency (%)						
	Time (h)						
	2	4	8	12	16	20	24
800 ppm of AVL Extract	81.5	80.5	78.6	76.7	73.7	70.1	66.2

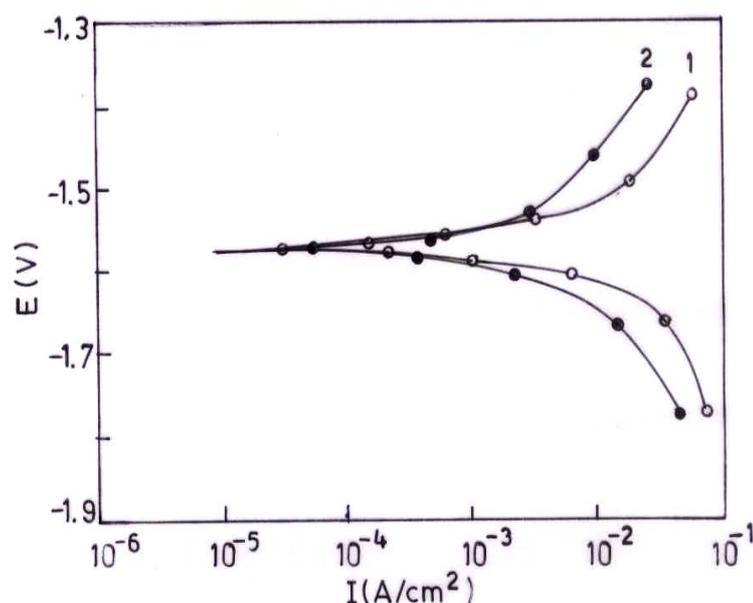


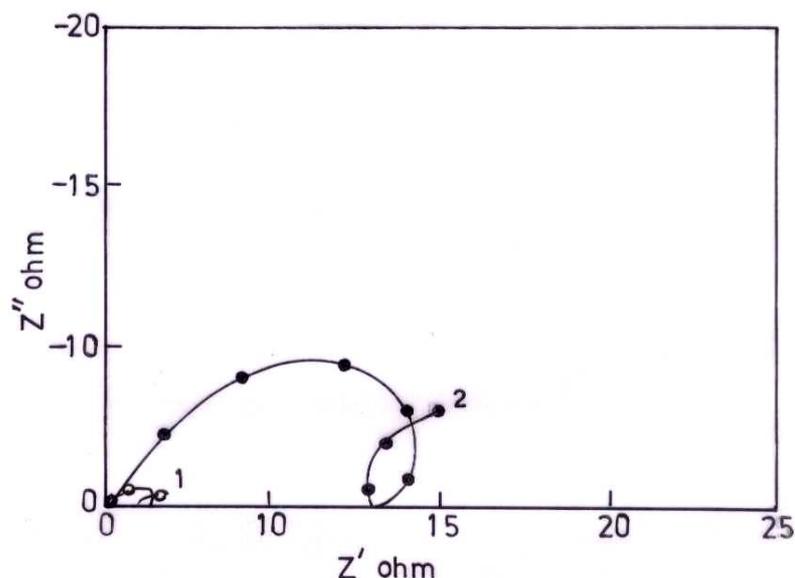
Fig. 3 Potentiodynamic polarization curves for aluminium in 1N NaOH solution in the absence and presence of an optimum concentration of AVL extract (1)Blank (2) 800 ppm of AVL extract

Table -3 Potentiodynamic polarization parameters for aluminium in 1N NaOH solution in the absence and presence of an optimum concentration of AVL extract

Conc. of AVL Extract (ppm)	$E_{corr}$ (V vs SCE)	$I_{corr}$ (mA/cm <sup>2</sup> )	Tafel Slope (mV/decade)		Inhibition Efficiency (%)
			$b_a$	$b_c$	
Blank	-1.572	8.21	318	207	---
800	-1.572	1.52	312	204	81.5

#### AC-impedance measurements

The corrosion behaviour of aluminium in 1N NaOH in the absence and presence of *adathoda vasica* leaves extract was investigated by AC-impedance method to find out the charge transfer resistance ( $R_t$ ) and double layer capacitance ( $C_{dl}$ ). From these parameters, the inhibition efficiency was calculated. Fig.4 shows the Nyquist plots for aluminium in 1N NaOH in the absence and presence of an optimum concentration of *adathoda vasica* leaves extract and their corresponding impedance parameters are given in Table 4. It can be seen from the figure that the obtained Nyquist plots are almost semicircular in nature followed by an inductive loop at the low frequency region. The semicircular nature of the Nyquist plot is due to the charge-transfer process, mainly controls the corrosion of aluminium. Deviations of perfect circular shape are often referred to the frequency dispersion of interfacial impedance. This anomalous phenomenon may be attributed to the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena. The low frequency inductive loop is due to the growth and dissolution of the surface film [17]. In fact, the presence of *adathoda vasica* leaves extract enhanced the value of  $R_t$  in alkaline solution and the values of double layer capacitance are brought down to the maximum extent in the presence of inhibitor. The decrease in  $C_{dl}$  showed that the adsorption of the inhibitor took place on the aluminium surface in alkaline solution. The increase in the value of  $R_t$  with the inhibitor led to increase in the inhibition efficiency. The maximum  $R_t$  value of 14.20  $\Omega$  cm<sup>2</sup> and minimum  $C_{dl}$  value of 24.62  $\mu$ F/cm<sup>2</sup> was obtained at the optimum concentration 800 ppm of the extract gave a maximum inhibition efficiency of 81.7%. This result has good agreement with the results obtained from non-electrochemical weight loss method and electrochemical potentiodynamic polarization and AC-impedance methods.



**Fig. 4** Impedance diagrams for aluminium in 1N NaOH solution in the absence and presence of an optimum concentration of AVL extract (1) Blank (2) 800ppm of AVL extract

**Table – 4** Impedance parameters for the corrosion of aluminium in 1N NaOH in the absence and presence of an optimum concentration of AVL extract at 30°C

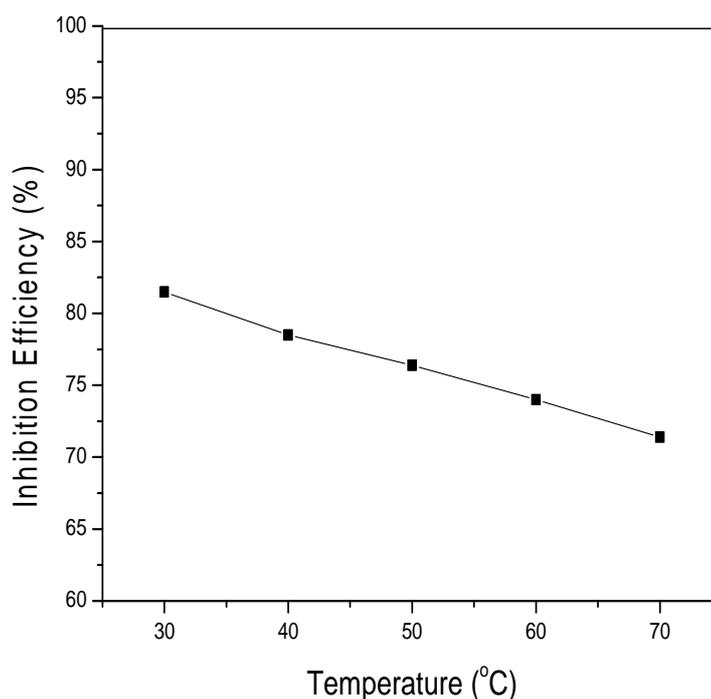
Conc. of AVL Extract (ppm)	$R_t$ ( $\Omega \text{ cm}^2$ )	$C_{dl}$ ( $\mu\text{F}/\text{cm}^2$ )	Inhibition Efficiency (%)
Blank	2.56	82.12	---
800	14.20	24.62	81.7

#### Effect of Temperature

The effect of temperature in the range of 30°C to 70°C on the corrosion behaviour of aluminium in 1N NaOH solution in the absence and presence of an optimum concentration of the extract was studied using weight loss method. Table-5 shows the corrosion rate and inhibition efficiency of aluminium in 1N NaOH solution in the absence and presence of the AVL extract at different temperatures. It can be seen from the table that the increase in corrosion rate is more pronounced with the rise in temperature for the uninhibited alkaline solution than the inhibited solution suggesting that the extract was adsorbed on the aluminium surface at all temperatures studied [6]. The effect of temperature on the corrosion inhibition of aluminium in 1N NaOH in presence of an optimum concentration of *adathoda vasica leaves extract* as shown in Fig.5.

**Table -5** Corrosion of aluminium in the absence and presence of an optimum concentration of AVL extract (800 ppm) in 1N NaOH at various temperatures obtained by weight loss method

System	Temperature (°C)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)
Blank	30	757.17	---
	40	964.02	---
	50	1172.42	---
	60	1404.66	---
	70	1697.76	---
800 ppm of AVL extract	30	139.92	81.5
	40	207.26	78.5
	50	276.70	76.4
	60	365.20	74.0
	70	485.60	71.4



**Fig.5 Effect of temperature on the corrosion inhibition efficiency of aluminium in 1N NaOH in presence of an optimum concentration (800ppm) of AVL extract**

#### Mechanism of corrosion inhibition

The Arrhenius plot for aluminium immersed in 1N NaOH solution in the absence and presence of an optimum concentration (800ppm) of *adathoda vasica leaves* extract as shown in Fig.6. The plot of logarithm of the corrosion rate versus the reciprocal of absolute temperature gave a straight line. According to the Arrhenius equation [18-20];

$$\ln r = A - E_a / RT$$

Where  $r$  is the corrosion rate,  $A$  is the constant frequency factor and  $E_a$  is the apparent activation energy. The values of activation energy ( $E_a$ ) for the corrosion process in the absence and presence of an optimum concentration of the extract were calculated from the Arrhenius equation;

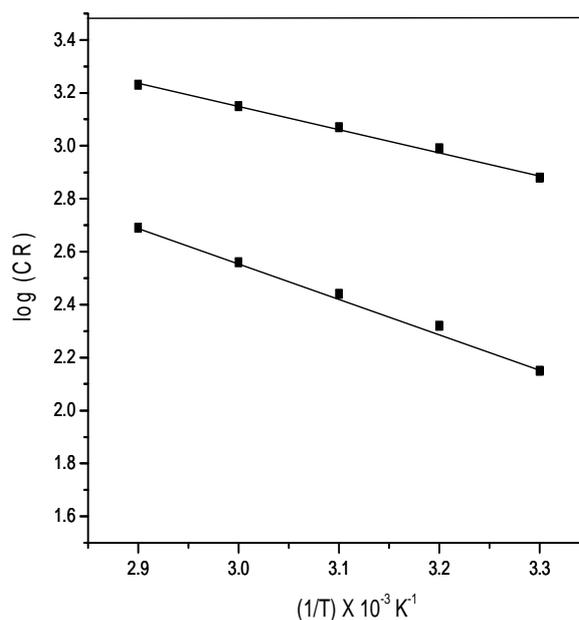
$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303 R} [1/T_1 - 1/T_2]$$

Where,  $K_1$  and  $K_2$  are the corrosion rates at temperatures  $T_1$  and  $T_2$  respectively.

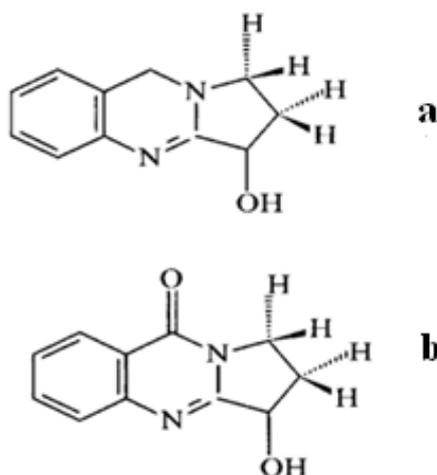
The free energy of adsorption ( $\Delta G^\circ$ ) used to find out the interaction of adsorption molecules and metal surface, was calculated using the equation;  $\Delta G^\circ = -RT \ln (K/55.5)$ . The value of 55.5 is the concentration of water in solution expressed in molar. The value of  $K$  can be calculated using the equation;  $K = \theta / (1-\theta) C$ . The enthalpy of adsorption ( $\Delta H$ ) was calculated using the equation;  $\Delta H = E_a - RT$  and the entropy of adsorption ( $\Delta S$ ) was calculated using the equation;  $\Delta G^\circ = \Delta H - T\Delta S$ .

The calculated values of activation energy ( $E_a$ ), enthalpy of adsorption ( $\Delta H$ ), free energy of adsorption ( $\Delta G^\circ$ ) and entropy of adsorption ( $\Delta S$ ) are shown in Table-6. The activation energy  $E_a$  was found to be  $17.42 \text{ KJ mol}^{-1}$  for 1N NaOH solution and increased to  $27.54 \text{ KJ mol}^{-1}$  in the presence of *adathoda vasica leaves* extract. The adsorbed organic matter provided a physical barrier to charge and mass transfer, leading to reduction in corrosion rate. The higher value of  $E_a$  in presence of the extract compared to that in the absence of the extract was attributed to physical adsorption [21]. The negative sign of free energy of adsorption indicates that the adsorption of *adathoda vasica leaves* extract on aluminium surface is a spontaneous process [22]. It is well known that the value of  $\Delta G^\circ$  around  $-20 \text{ KJ mol}^{-1}$  or lower are consistent with the electrostatic interaction between organic charged molecules and the

charged metal (physisorption) and those around  $-40 \text{ KJ mol}^{-1}$  or higher involved charge sharing or transfer from the organic molecules to the metal surface to form a co-ordinate type of bond (chemisorption) [23]. In this case, the  $\Delta G^\circ$  values were in the range  $-14.40$  to  $-14.70 \text{ KJ mol}^{-1}$  and hence the adsorption could be physisorption. The positive values of enthalpy of adsorption ( $\Delta H$ ) suggests that the reaction is endothermic and the adsorption of the extract on the metal surface takes place. Entropy of adsorption ( $\Delta S$ ) remained a positive and this is due to the formation of an ordered stable layer of the inhibitor molecule on the aluminium. Positive values of entropy indicates that the reaction was spontaneous and feasible [24]. From the literature survey, it was found that vasicine and vasicinone are the principal alkaloids present in the leaves extract of *adathoda vasica* [25]. The inhibition of *adathoda vasica leaves extract* may be due to the presence of the major alkaloid, vasicine and vasicinone which containing nitrogenous compounds and hydroxyl groups. The structures of vasicine and vasicinone are shown in Fig.7(a & b). The inhibition mechanism involved in this is due to the adsorption of inhibitor on the surface of the metal and forming a compact protective thin layer on the aluminium surface. It provokes the corrosion of aluminium in 1N NaOH solution.



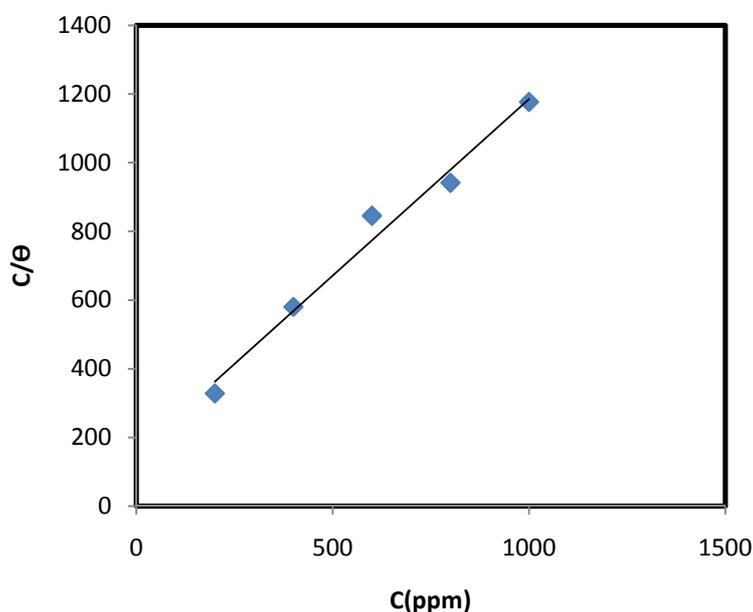
**Fig. 6** Arrhenius plots for aluminium immersed in 1N NaOH solution in the absence and presence of an optimum concentration (800ppm) of AVL extract (1) Blank (b) 800ppm of AVL extract



**Fig. 7** Structure of (a) Vasicine and (b) Vasicinone

**Table – 6** Calculated values of activation energy ( $E_a$ ), enthalpy of adsorption ( $\Delta H$ ), free energy of adsorption ( $\Delta G^\circ$ ) and entropy of adsorption ( $\Delta S$ ) in the absence and presence of an optimum concentration of AVL extract

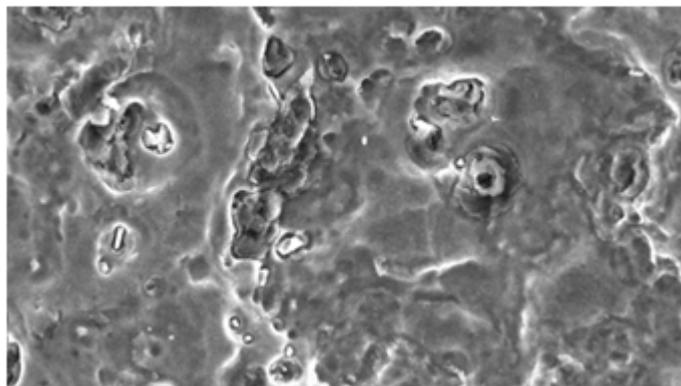
System	Temp. (K)	$E_a$ ( $\text{KJ mol}^{-1}$ )	$\Delta G^\circ$ ( $\text{KJmol}^{-1}$ )	$\Delta H$ ( $\text{KJmol}^{-1}$ )	$\Delta S$ ( $\text{KJmol}^{-1}$ )
Blank	303	17.42	---	14.90	---
	313		---	14.81	---
	323		---	14.73	---
	333		---	14.65	---
	343		---	14.56	---
800 ppm of AVL Extract	303	27.54	-14.42	25.02	0.130
	313		-14.40	24.93	0.126
	323		-14.54	24.86	0.122
	333		-14.63	24.77	0.118
	343		-14.70	24.69	0.115

**Fig.8** Langmuir adsorption isotherm plot for the adsorption of various concentrations of AVL extract on the surface of aluminium in 1N NaOH solution

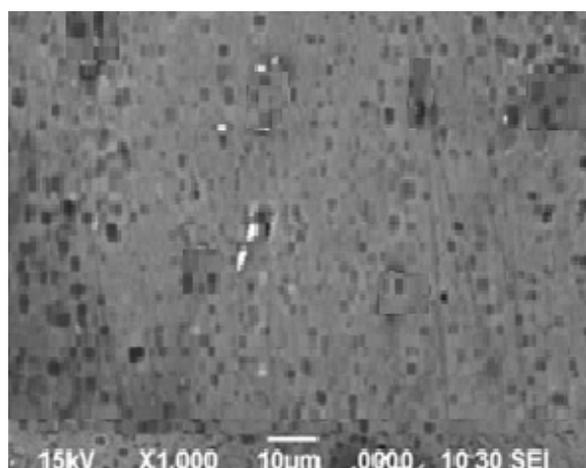
The adsorption of these compounds on the aluminium surface made a barrier for mass and charge transfers. This situation led to the protection of aluminium surface from the action of aggressive ions of the alkaline solution. The degree of protection increased with surface coverage by the adsorbed molecules. As the extract concentration increased, the number of adsorbed molecules on the surface increased. Surface coverage ( $\theta$ ) which was estimated from the inhibition efficiency values using weight loss method, could be used to represent the fraction of the surface occupied by the adsorbed molecules. The values of surface coverage ( $\theta$ ) for various concentrations of *adathoda vasica leaves* extract are given in Table-1. The use of adsorption isotherm provides useful insight into the corrosion inhibition mechanism. A plot of  $C/\theta$  versus  $C$  gave a straight line with unit slope suggests that the adsorption of various concentrations of *adathoda vasica leaves* extract on the surface of aluminium in 1N NaOH solution follows Langmuir adsorption isotherm (Fig.8).

#### Surface Analysis

Surface examination of the aluminium specimens were made using JEOL –Scanning electron microscope (SEM) with the magnification of 1000X. The aluminium specimens after immersion in 1N NaOH solution for 2 hours at 30°C in the absence and presence of optimum concentration of the *adathoda vasica leaves* extract were taken out, dried and kept in a desiccator. Their surface was examined by SEM studies are shown in Fig.9 (a & b).



**Fig. 9(a)** SEM Photograph of aluminium immersed in 1N NaOH solution (blank)



**Fig.9(b)** SEM Photograph of aluminium immersed in 1N NaOH solution containing an optimum concentration (800) of AVL extract

### CONCLUSION

The following conclusions are drawn from the above studies;

- The aqueous extract of adathode vasica leaves perform well in 1N NaOH solution and inhibit the corrosion of aluminium at an optimum concentration of 800ppm.
- The AVL extract control both anodic and cathodic reactions by blocking the active sites of aluminium surface and thus the inhibitor of mixed type.
- The AVL extract inhibit the corrosion of aluminium in 1N NaOH solution by strong adsorption of its chemical constituents on the aluminium surface obeys Langmuir adsorption isotherm.

### REFERENCES

- [1] Ehteram A Noor. *J. Appl. Electrochem.*, **2009**, 39, 1465
- [2] UR Evans; Edward Arnold. *An Introduction to Metallic Corrosion*, London, **1983**, 69
- [3] Arvnabh Mishra; D R Godhani; Anil Sanghani. *J.Chemical & Pharmaceuticals Research.*, **2011**, 2, 388-396
- [4] Tedjani Yahia Namoussa; Segni Ladjel; Nouredine Gherraf; Mohamed Ridha Ouahrani. *J.Chemical & Pharmaceuticals Research.*, **2010**, 4, 808-811
- [5] Samir Hameurlaine; Nouredine Gherraf; Abdelkader Benmnine; Amar Zellagui. *J.Chemical & Pharmaceuticals Research.*, **2010**, 4, 819-825
- [6] HAl Sehaibani. *Mat.-Wiss.U, Werkstoff Tech.*, **2000**, 31,1060
- [7] Olugegun K Abiola; JOE Otaigbe; OJ Kio, *Corros. Sci.*, **2009**, 51, 1899.
- [8] SA Umoren;IB Obot. *Anti-Corrosion Methods and Materials*, **2006**, 53, 277.
- [9] Olesegun K Abiola; JOE Otaigbe; OJ.Kio. *Corros. Science*, **2009**, 51, 2790.
- [10] IB Obot; NO Obi. Egbedi, *Portugaliae Electrochemica Acta*, **2009**, 27, 517.
- [11] Enteram A Noor. *J.Appl.Electrochem.*, **2009**, 39, 1465.

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- [12] Olesegun K Abiola; JOE Otaigbe; OJ Kio. *Corros. Sci.*, **2009**, 51, 1879.
- [13] R Hariharaputhran; A Subramania; AA Antony; T Vasudevan; SVK Iyer; *British Corrosion J.*, **1998**, 33, 214.
- [14] AR Saithya Priya; VS Muralidharan ; A Subramania. *Corrosion*, **2008**, 64, 541
- [15] T Gowrani; K Parameswari; A Selvaraj; A Subramania. *Anti-Corrosion Methods and Materials*, **2004**, 51, 414.
- [16] A Subramania; R Sathiya priya; K Saminathan; VS Muralidharan. *J.Applied Electrochem.*, **2004**, 34, 693.
- [17] Ehteram A Noor. *J. Appl. Electrochem.*, **2009**, 39, 1465.
- [18] CB Breslin; WM Carnol. *Corros. Sci.*, **1993**, 33, 327.
- [19] MG A Khedr; MS Lashien. *Corros. Sci.*, **1992**, 33, 137.
- [20] T Szauer; A Brandt. *Electrochim. Acta*, **1981**, 26, 1209.
- [21] T Gowrani; J Yamuna; K Parameswari; S Chitra; A Subramania. *Anti- Corrosion Methods and Materials*, **2004**, 51, 414.
- [22] KO. Orubit; NC Oforka. *J.Appl. Sc. Environ.Mgt.*, **2004**, 8, 57.
- [23] Yan Li *Applied Surface Sc.*, **2005**, 252, 1245.
- [24] G Morotti; F Guid; G Grion. *Corros. Sci.*, **2004**, 46, 387.