Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Pelagia Research Library

Der Chemica Sinica, 2015, 6(9):14-24

Pelagia Research Library

ISSN: 0976-8505
CODEN (USA) CSHIA5

Corrosion inhibition of aluminium in alkaline solution using aqueous extract of *Tridax procumbens leaves*

[1]G. Kiruthiga* and [2]Shanmugam Rajendran

[1] Dept. of Chemistry, Imayam Arts and Science College for Women, Kannanur, Thuraiyur
[2]Dept. of Chemistry, Periyar E. V. R. College (Autonomous), Tiruchirappalli

---

ABSTRACT

The influence of aqueous extract of Tridax procumbens leaves (TPL) on corrosion of aluminium in 0.5 NaOH solution was studied using chemical and electrochemical techniques. It was found that the inhibition efficiency increased with the increase of Tridax procumbens extract upto 900 ppm. Beyond this concentration there is no improvement in the inhibition efficiency. Electrochemical measurements revealed that TPL extract acts as a mixed type inhibitor. Adsorption of TPL 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 TPL extract was confirmed using scanning electron microscopy studies.

Keywords: Corrosion inhibitors, *Tridax procumbens* leaves extract, Aluminium corrosion, Langmuir adsorption isotherm, mixed type inhibitor.

INTRODUCTION

Aluminium presently finds extensive use in industrial as well as domestic applications due to it lightweight, strength, durability and formability. By nature, aluminium is a highly reactive material. It has a very high affinity with oxygen [1]. When a new aluminium surface is exposed in the presence of air (or an oxidising agent), it very rapidly acquires a thin, compact, hard, tightly adhering, protective, self healing film of aluminium oxide (about 0,5µ in air). In non-stagnant water, thicker films (of hydrated oxide) are produced. Alkali destroys the protective aluminium film very quickly because OH^- ions are positively adsorbed [2] and hence dissolution rate of aluminium is very high. The presence of the oxide layer makes aluminium very suitable for many applications. This film is relatively inert chemically. It is on the inactivity of the surface film that the good corrosion resistance of aluminium depends [3].

The use of chemical inhibitors has been limited because of the environmental threat. 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. The green inhibitors are the alkaloids and flavonoids and other natural products obtained from natural sources like plant. It can be extracted by simple procedures with low cost and also includes synthetic compounds with negligible toxicity. By using leaves extracts, inhibitive properties of mild steel, carbon steel, aluminium in acid as well as basic medium was studied [4,5]. For instance *bamboo leaf extract* [6], *cocosnucifera* L. [7], *rosemary oil* [8], pine apple leaves *(ananascomosus L.)* [9], *olive leaves* [10], Natural honey [11] have been studied as effective corrosion inhibitors in medium. This is reports the influence of aqueous extract of *Tridax procumbens* leaves extract for the corrosion of aluminium in 0.5N alkaline solution by cnemical and electrochemical techniques. The effect of temperature on the corrosion rate of aluminum in presence of an optimum concentration of the extract was also investigated and some thermodynamic parameters for activation process were computed and discussed.

MATERIALS AND METHODS

Material preparation

Aluminium specimens of 4.1cm× 1.1cm × 0.11cm containing 0.348% Fe, 0.080% Cr, 0.024% Mn, 0.023% Tl, 0.021% Zn, 0.015% Cu and remainder Al were used for the weight loss studies.. The aluminium specimens for the electrochemical measurements were machine cut into test electrodes of dimensions, 4.1cm × 1.1cm × 0.11cm and coated with epoxy resin (araldite) leaving a surface area of 1 cm^2. The corrosive medium, 0.5M NaOH solution was prepared from analytical reagent grade NaOH and distilled water.

Preparation of extract of *Tridax procumbens* leaves

The *Tridax procumbens* leaves extract (TP) were collected and cut into small pieces and they were dried in an air oven at 70^{o}C for 1h. They were ground well into powder. From this, 20g of the sample was refluxed with in 100ml distilled water for 1hour. The refluxed solution was filtered carefully and the filtrates were heated on sand bath to evaporate fully the moisture content to get the dried inhibitor sample [12]**.** The inhibitor concentrations of 100, 200, 300, 400, 500, 600,700, 800 and 900ppm were prepared in double distilled water using 0.5M NaOH solution.

Techniques used for the study

Weight loss measurements

Weight loss measurements were carried out as described elsewhere [13]**.** Aluminium specimens were immersed in 100ml of inhibited and uninhibited solutions for 1 hrs at 30^{o}C. The corrosion rate (mmpy) and the inhibition efficiency were calculated using the following equations:

$$\textbf{Corrosion Rate (mmpy)} = \frac{\mathbf{kW}}{\mathbf{ATD}}$$

where, K = 87.6 (constant), W = weight loss (mg), A = area (cm), T = time (h), D = density in (g/cm^3)

$$\textbf{Inhibition Efficiency (\%)} = (\mathbf{W_B – W_I / W_B}) \times \mathbf{100}$$

where, W_B and W_1 are weight loss per unit time in the absence and presence of TP .

Weight loss measurements were also performed at various immersions from 1h to 24h in an optimum concentration of the TP at 30^{o}C. From the initial and final weight of the specimen, the loss in weight was calculated and the efficiencies of inhibitor at various immersion times were calculated.

Determination of surface coverage

The degree of surface coverage (θ) was calculated from the weight loss measurement results using the formula [14];

$$\textbf{Surface Coverage}(\boldsymbol{\theta}) = \frac{\mathbf{W_B - W_1}}{\mathbf{W_B}}$$

Where, W_B is the weight loss in the absence of the extract, W_1 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 & PAR potentiostat/galvanostat (Model 173) analyzer a universal programmer in a conventional three- electrode glass cell. A platinum foil of surface area 2cm^2 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 TPL

from a cathodic potential of -1700mV to an anodic potential of -500mV (vs. SCE) at a sweep rate of 1mV per second. From the polarization curves, Tafel slopes, corrosion potential and corrosion current were calculated.
The inhibition efficiency was calculated using the formula;

Inhibition Efficiency (%) = (I_{corr} – I^*_{corr} / I_{corr})×100

Where, I_{corr} and I^*_{corr} are corrosion current in the absence and presence of TPL extract

Electrochemical Impendance studies

The cell set up was the same as that used for polarization measurements. A time interval of 10 to 15 minutes was given for the system to attain a steady state open circuit potential. Then over this steady state potential, A.C. potential of 10mV was superimposed. The A.C. frequency was varied from 100MHz to KHz. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms for various frequencies. The R_{ct} and C_{dl} values were calculated.[15]

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

Where $R_{ct}$is charge transfer resistance and Cdl 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 *TPL* extract ranging from 100-900 ppm to study the influence of various concentrations of *TPL* extract and immersion time on the corrosion inhibition of aluminium in 0.5N NaOH solution at 30^0C for a period of 2 hours. The corrosion parameters obtained from weight loss measurements for aluminium in 0.5N NaOH solution containing various concentrations of *TPL* extract are given in Table -1. It was found that with the rise in concentration of *TPL* extract from 100 to 900 ppm, the weight loss of aluminium decreased, and the inhibition efficiency increased 42.38% to 93.35%. Beyond this concentration (900 ppm), there is no improvement in the inhibition efficiency. This result indicated that 900 ppm is the optimum concentration to get maximum corrosion protection for aluminium in 0.5N NaOH using *TPL* extract. The variation of inhibition efficiency with various concentrations of *TPL* extract on aluminium in 0.5N NaOH as shown in Fig.1.

Table -1 Corrosion parameters obtained from weight loss measurements for aluminium in 0.5N NaOH solution containing various concentrations of TPL extract

Concentration of Inhibitor (ppm)	Weight loss(mg)	Corrosion rate, $C_{R\ (mmpy)}$	IE%	Surface coverage area, θ
Blank	0.2515	404.63	-	-
100	0.1449	233.12	42.38	0.42
200	0.1145	184.21	54.47	0.54
300	0.0916	147.37	63.57	0.63
400	0.0663	106.66	73.63	0.73
500	0.049	78.83	80.51	0.8
600	0.0333	53.57	86.75	0.86
700	0.0241	38.77	90.41	0.9
800	0.0205	32.98	91.84	0.91
900	0.0167	26.86	93.35	0.93

The effect of immersion time from 2 hours to 24 hours was also studied. The inhibition efficiency was found to decrease from 93.35 % to 82.52 %. The effect of immersion time on percentage inhibition efficiency of aluminium in 0.5N NaOH at 30^0C in presence of an optimum concentration (900 ppm) of *TPL* extract is given in Table-2 (Fig.2). Though 82.52% 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 *TPL* extract acted as corrosion inhibitor for aluminium in 0.5N NaOH medium at an optimum concentration of 900 ppm for a period of 2 hours at 30^0C.

Potentiodynamic polarization method

Fig.3 shows the polarization curves for aluminium in 0.5N NaOH solution in the absence and presence of an optimum concentration of *TPL* 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 *TPL 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 0.5N NaOH solution. The extent of its decrease, increased with the addition of 800ppm of the extract and the maximum inhibition efficiency of 67.86% was observed as in weight loss method.

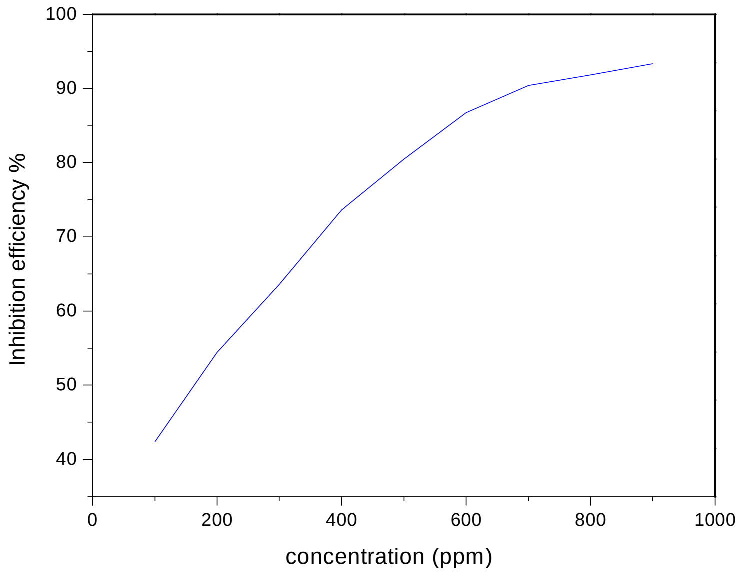

Fig.1 Variation of inhibition efficiency with various concentrations of TPL extract on aluminium in 0.5NNaOH solution

Table – 2 Effect of immersion time on percentage inhibition efficiency of aluminium in 0.5N NaOH at 30°C in the presence of an optimum concentration (900ppm) of TPL extract

System	**Inhibitor Efficiency (%)**							
	Time (h)							
	1	**2**	**3**	**4**	**5**	**6**	**7**	**24**
900ppm of TPL Extract	92.1	93.3	92.2	92.1	92.5	91.4	90.1	82.52

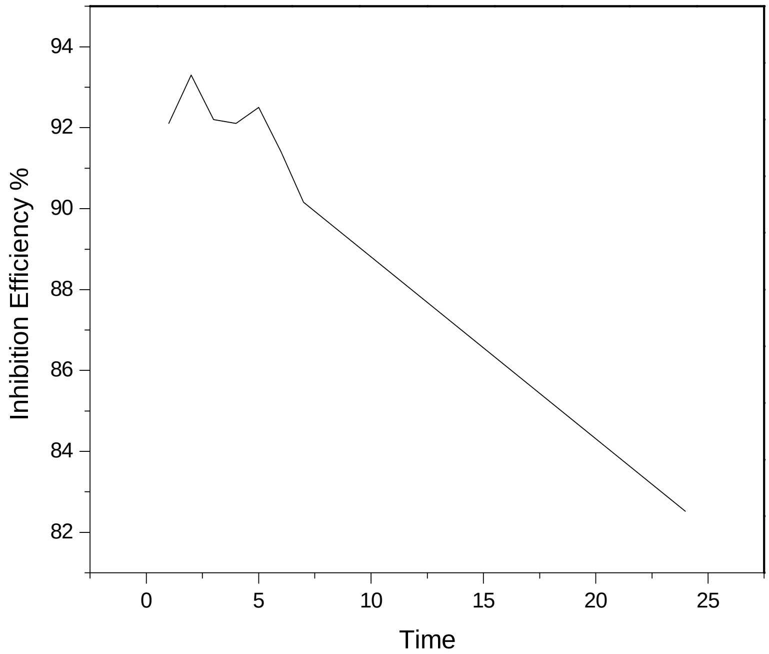

Fig.2 Effect of immersion time on percentage inhibition efficiency of aluminium in 0.5N NaOH at 30°C inpresence of an optimum concentration (900ppm) of TPL extract

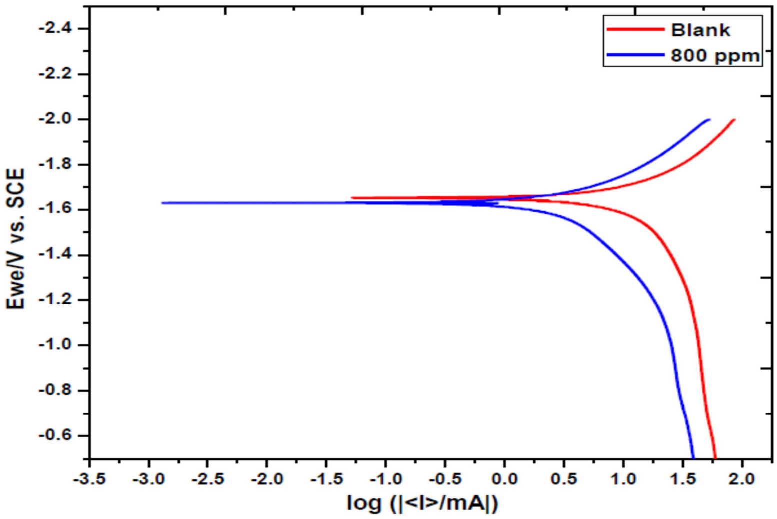

Fig. 3 Potentiodynamic polarization curves for aluminium in 0.5N NaOH solution in the absence and presence of an optimum concentration of TPL extract (1)Blank (2)800ppm of TPL extract

Table -3 Potentiodynamic polarization parameters for aluminium in 0.5N NaOH solution in the absence and presence of an optimum concentration of TPL extract

Inhibitor (ppm)	Tafel				
	E_{corr}(mV)	I_{corr}(mA)	IE%	β_a (mV)/dec	β_c (mV)/dec
Blank	-1647.775	8133.057	-	435.4	269.4
800(TP)	-1616.017	2613.731	67.86	391	239.9

AC-impedance measurements

The corrosion behavior of aluminum in 0.5N NaOH in the absence and presence of *Tridax procumbens* 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. The AC impedance Nyquist graphs (Fig.4) for aluminium in 0.5N NaOH in the absence and presence of an optimum concentration of *Tridax procumbens* 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 semi circular in nature due to charge – transfer process mainly control the corrosion of aluminium. From the Nyquist data it can be seen that there is an increase in the charge transfer resistance or polarization resistance (R_{ct}) values and decrease in double layer capacitance (C_{dl}) values in presence of inhibitors, indicating that there is a stable adsorption layer formed on the aluminium metal surface. The maximum R_{ct} value of 7.834Ω cm^2 and minimum C_{dl} value of 20.33 μF/cm^2 were obtained at the optimum concentration 900ppm of the extract gave a maximum inhibition efficiency of 70.73%. This result has good agreement with the results obtained from non-electrochemical weight loss method and electrochemical potentiodynamic polarization and AC – impedance methods.

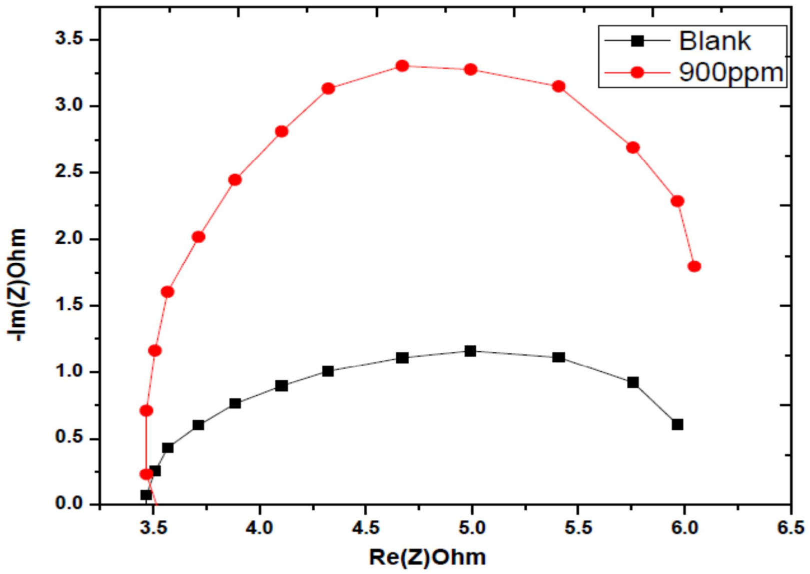

Fig.4 Impedance diagrams for aluminium in 0.5N NaOH solution in the absence and presence of an optimum concentration of TPL extract (1) Blank (2) 900ppm of TPL extract

Table – 4 Impedance parameters for the corrosion of aluminium in 0.5N NaOH in the absence and presence of an optimum concentration of TPL extract at 30^{0}C

Inhibitor (ppm)	Nyquist		
	R_{ct} (ohm cm^2)	IE %	C_{dl} (μF/cm^2)
Blank	2.293	-	0.101
900(TP)	7.834	70.73	20.33

Effect of Temperature

The effect of temperature in the range of 30^{0}C to 70^{0}C on the corrosion behavior of aluminium in 0.5N 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 0.5N NaOH solution in the absence and presence of the TPL 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 0.5N NaOH in presence of an optimum concentration of *Tridax procumbens leaves extract as* shown in Fig.5

Table -5 Corrosion of aluminium in the absence and presence of an optimum concentration of TPL extract (900ppm) in 0.5N NaOH at various temperatures obtained by weight loss method

System	Temperature (^{0}C)	Corrosion Rate (mmpy)	Inhibition Efficiency(%)
Blank	30	385.16	-
	40	681.51	-
	50	1011.65	-
	60	1793.24	-
	70	2116.94	-
900ppm of TPL Extract	30	30.24	92.14
	40	80.76	88.14
	50	174.07	82.79
	60	427.31	76.1
	70	888.63	57.9

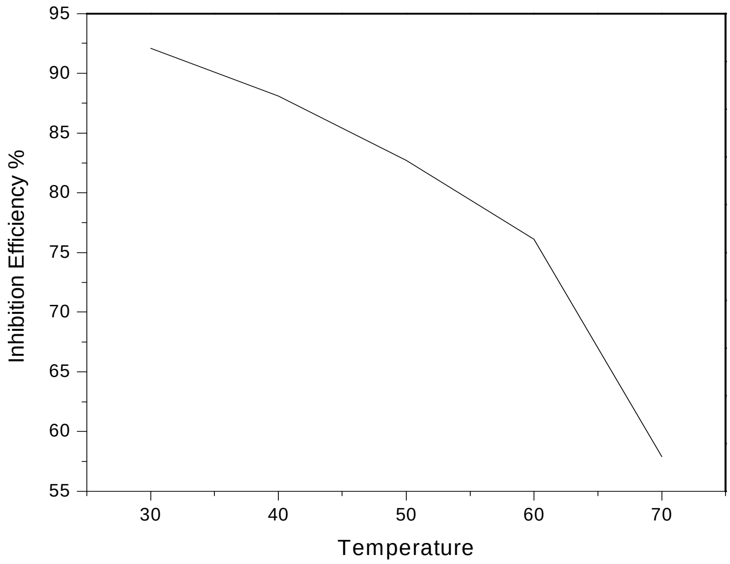

Fig.5 Effect of temperature on the corrosion inhibition efficiency of aluminium in 1N NaOH in presence of an optimum concentration of AVL extract

Mechanism of corrosion inhibition

The energy of activation, E_a and enthalpy, ΔH values calculated for the corrosion processes in the absence and presence of the inhibitors are given in the Tables.6. The E_a and ΔH values for the corrosion processes, in the presence of inhibitors are higher (more positive) than those of the blank. Higher the values of E_a in presence of the extract compared to that in the absence of the extract was attributed to physical adsorption [17]. The negative values of heat of adsorption (Q_{ads}) prove that the adsorption of the inhibitors on the metal surface is a spontaneous process [18]. The positive value of enthalpy of adsorption ΔH suggests that the reaction is endothermic and the adsorption of the extract on the metal surface takes place. From literature survey, it was found that Pyrrolizidine Alkaloids containing nitrogenous compounds present in the leaves extract of *Tridax procumbens* [19] as shown in fig. 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 0.5N NaOH solution.

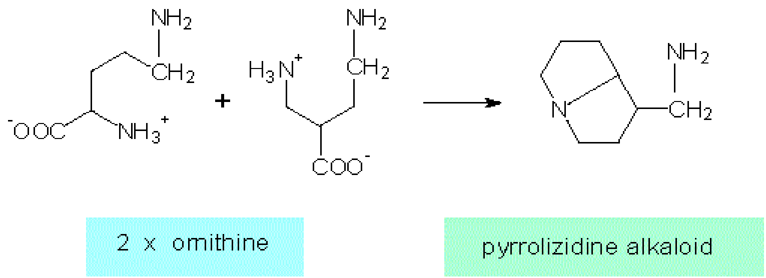

Table.6 Calculated values of activation energy(E_a), enthalphy of adsorption (ΔH), and Q_{ads} in the absence and presence of an optimum concentration of TPL extract

Thermodynamic parameters for the adsorption of TP on aluminium surface [Temperature range 313K -333K]

Conc. Of inhibitor (ppm)	Ea ($kJmol^{-1}$)	ΔH ($kJmol^{-1}$)	Qads ($kJmol^{-1}$)
Blank	39.29	36.77	-
900	71.22	68.7	-37.67

Thermodynamic parameters for the adsorption of TP on aluminium surface [Temperature range 313K -333K]

Conc. Of inhibitor (ppm)	Ea ($kJmol^{-1}$)	ΔH ($kJmol^{-1}$)	Qads ($kJmol^{-1}$)
Blank	41.19	39.32	-
900	72.19	69.59	-36.39

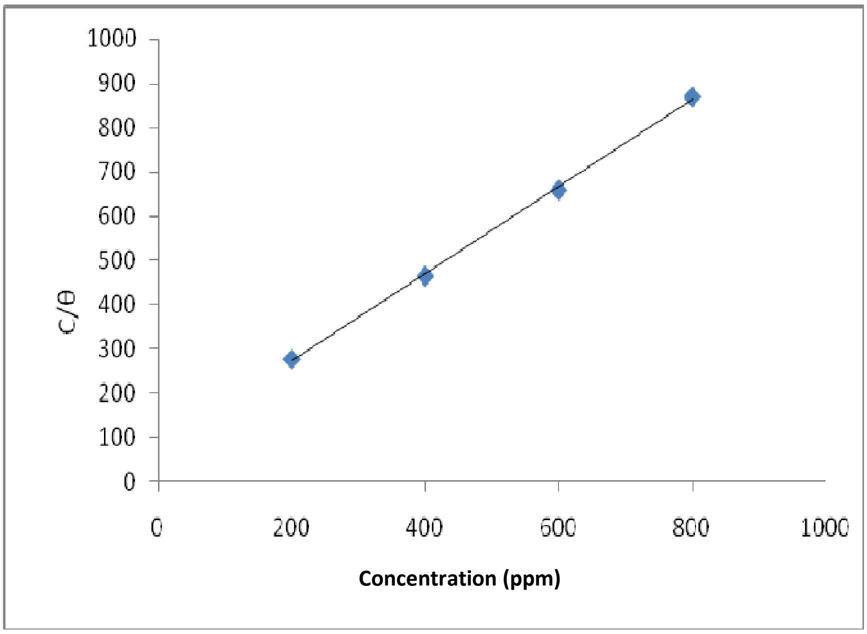

Figure – 6: Langmuir adsorption isotherm of various concentration of TPL

The adsorption of these compounds on the aluminum 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 (θ) 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 (θ) for various concentrations of *Tridax procumbens leaves* extract are given in Table-1. The use of adsorption isotherm provides useful insight into the corrosion inhibition mechanism. A plot of C/θ versus C gave a straight line with unit slope suggests that the adsorption of various concentrations of *Tridax procumbens 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 VAGH3 SBH –Scanning electron microscope (SEM) with the magnification of 1000X. The aluminium specimens after immersion in 1N NaOH solution for 2 hours at30°C in the absence and presence of optimum concentration of the *Tridax procumbens 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).

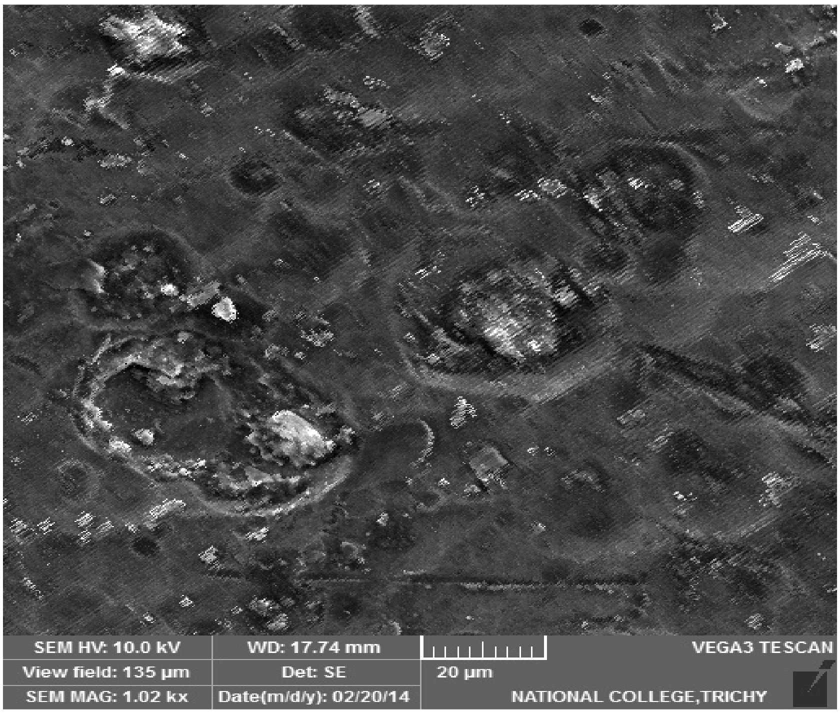

Fig.7: SEM image of aluminium (pure metal)

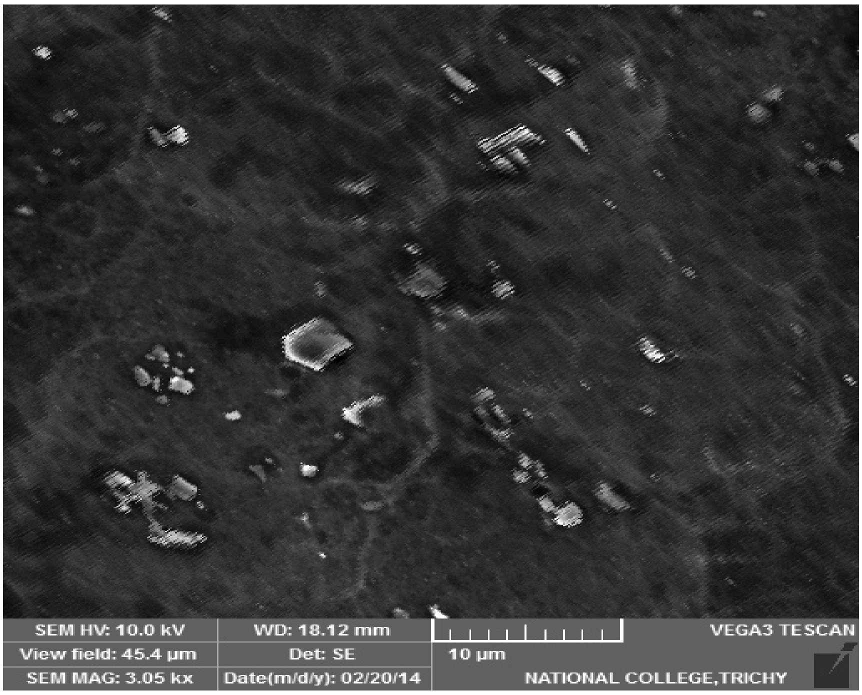

Fig.7a: SEM image of aluminium immersed In 0.5M NaOH solution

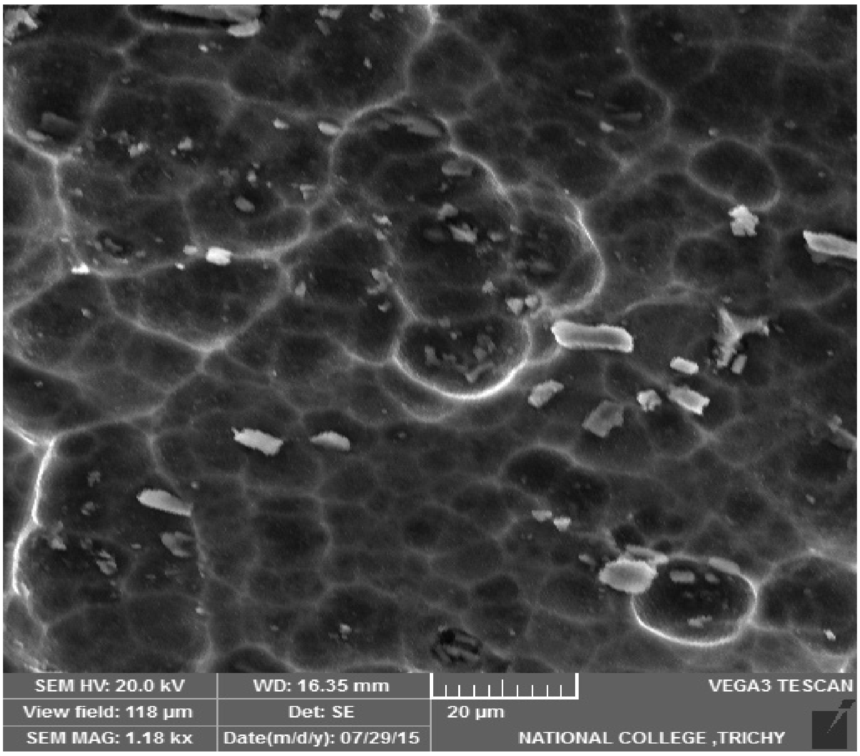

Fig.7b: SEM image of aluminium immersed In 0.5M NaOH solution with TPL extract

CONCLUSION

The results obtained in the present investigation can be summarized as given below:
❖ The present study deals with the corrosion inhibition of aluminium by using green inhibitor, viz., *Tridax procumbens* leaves extract in 0.5M NaOH medium.
❖ When an aqueous solution of TPL is used as inhibitor, it has a maximum of 93.35% IE for 2h duration at 30^0C of 900ppm concentration.
❖ The TPL extract control both anodic and cathodic reactions by blocking the active sites of aluminium surface and thus the inhibition is of mixed type.
❖ The TPL extract inhibit the corrosion of aluminium in 0.5N NaOH solution by strong adsorption of its chemical constituents on the aluminium surfaces obeys Langmuir Adsorption Isotherm.

REFERENCES

[1] Riggs OL, Nathan CC, Corrosion Inhibitors, NACE, Houston, TX, **1973**.
[2] Arvnabh Mishra, Godhani DR, Anil Sanghani *J.Chemical & Pharmaceuticals Research*, **2011**, 2, 388-396.
[3] Evans UR, Edward Amold, *An Introduction to Mettallic Corrosion*, London, **1983**, 69
[4] Othman NK, Mohamad N, *Material Physic.*, 1528, 243-247 (**2012**).
[5] Abiola OK, Otaigbe JOE, Kio OJ, *Corros. Sci.*, 51, 1879, (**2009**).
[6] Xianghong Li, Shuduan Deng, Hui Fu, *Corros. Sci.*, 62, 163-175 (**2012**).
[7] Abiola OK, Tobun Y, *Chinese Chem. Lett*, 21(12), 1149-1452 (**2012**).
[8] Bendahou M, Benabdellah M, Hammouti B, *Pigment & Resin Tech.*, 35(2), 95-100 (**2006**).
[9] Ekanem UF, Umoren SA, Udousoro II, Udoh AP, *J. Mater. Sci.*, 45(20), 5558-5566 (**2010**).
[10] El – Etre, *Corros. Sci.*, 45, 2485 (**2005**).
[11] Rosliza (**2009**), Inhibition on corrosion
[12] Abiola OK, Otaigbe JOE, OJ Kio OJ, *Corros. Sci.*, **2009**, 51, 1879.
[13] Gowrani T, Parameswari K, Selvaraj A, Subramania A, *Anti-Corrosion Methods and Materials*, **2004**, 51, 414.
[14] Hariharaputhran R, Subramania A, Antony AA, Vasudevan T, Iyer SVK, British *Corrosion J.*, **1998**, 33, 214.
[15] SaithyaPriya AR, Muralidharan VS, Subramania A, *Corrosion*, **2008**, 64, 541
[16] Subramania A, Sathiyapriya R, Saminathan K, Muralidharan VS, *J Applied Electrochem.*, **2004**, 34, 693.
[17] Gowrani T, Yamuna J, Parameswari K, Chitra S, Subramania A, *Anti- Corrosion Methods and Materials*, **2004,** 51, 414.
[18] Orubit KO, Oforka NC, *J Appl. Sc. Environ.Mgt*., **2004**, 8, 57.
[19] Prakashsolanki, Manisha Khan, *Golden Research Thoughts*, **2010**, 4(1) 1-5.
[20] Ehteram A Noor, J *Appl. Electrochem.*, **2009,** 39, 1465.