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Journal of Chemical and Pharmaceutical Research, 2014, 6(1):580-588

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Vitex negundo leaves extract as green inhibitor for the corrosion of aluminium 1N NaOH solution

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ABSTRACT

The present work investigates corrosion inhibition of aluminium in 1N NaOH solution in presence of Vitex negundo (VNL) leaves extract as green corrosion inhibitor by using chemical and electrochemical techniques. It was found that the inhibition efficiency increased with increase of VNL extract and reached the maximum of 72.6% at 900 ppm of VNL extract. The results obtained from chemical and electrochemical measurements were in good agreement. The potentiodynamic polarization studies reveal that the VNL extract act as mixed type inhibitor. Adsorption of VNL extract on the surface of aluminium follows Langmuir adsorption isotherm. The surface characteristics of inhibited and uninhibited aluminium were investigated by scanning electron microscope studies. These results were supported by kinetic and thermodynamic parameters obtained from weight loss data at different temperatures studied.

Keywords: Corrosion inhibitors, *Vitex negundo* leaves extract, Aluminium corrosion, Langmuir adsorption isotherm, Mixed type inhibitor.

INTRODUCTION

Aluminium is one of the world's most abundant metal and is the second to iron in terms of production and consumption. It is one of the most important metals which find extensive domestic as well as industrial applications light weight, strength, recyclability, corrosion resistance, durability, conductivity etc. The corrosion behavior of pure aluminium and its alloys in alkaline solution have been extensively studied in the development of aluminium anodes for aluminium/air batteries [1]. Aluminium corrosion within the battery cause many problem because in most aqueous solutions, the anodic overvoltage for the dissolution of aluminium is very high[2]. In solution containing aggressive anions or in highly alkaline solutions, the dissolution procedure occurs in a much easier way. Although, there is a high amount of dissolution, which is favorable, there arises a problem of high hydrogen evolution which in turn commercial application of the situation. Thus, commercial application of aluminium and its alloys requires minimizing the over voltage for the anodic process, while increasing it for the cathodic process. The use of chemical inhibitors has been limited because of the environmental regulations, and hence plant extracts have become important because they are environmentally acceptable, readily available and renewable source for a wide range of needed inhibitors [3]. For instance, henna leaves [4] gossipium higgutum [5], gum arabic [6] phyllanthusamarus [7], ipomoea involucrate [8], hibiscus sabdoriffa [9] adathoda vasica [10] damisissa [11], brahmi [12], pipali leaves [13] etc., have been studied as effective corrosion inhibitors for aluminium in alkaline medium.

This paper reports the influence of VNL extract on the corrosion of aluminium in 1N alkaline solution by weight loss, gasometric, potentiodynamic polarization and AC-impedance studies to find out the inhibition efficiency of the inhibitors and a suitable mechanism regarding the mode of inhibition was also proposed. Surface examination on the aluminium in the absence and presence of inhibitor was made to confirm the formation film on the surface of aluminium.

EXPERIMENTAL SECTION

Material preparation

Aluminium strips of 4.5cm × 2cm × 0.2cm containing > 99.9 % purity was used for weight loss and gasometric studies. The strips were mechanically polished and degreased with acetone before use. A cyclindrical aluminium rod of the same composition embedded in a Teflon rod with an exposed area of 0.5cm^2 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 *Vitex negundo* leaves (*VNL*) extract

The *Vitex negundo* leaves (Nochi) were collected and cut into small pieces. They were dried in an air oven at 80°C for 2 hrs. The dried leaves were ground well into powder. From this, 10g of the sample was refluxed in 100mL of 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 [14]. The *VNL* extract concentrations of 300 to 900 ppm were prepared using 1N NaOH solution.

Weight loss studies

Weight loss measurements were carried out as described elsewhere [15]. 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 described elsewhere. Weight loss measurements were also performed at various immersion time from 2 hours to 10 hours for the best concentration of the *VNL* 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 (θ) was calculated from the weight loss measurement results using the formula [15];

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

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

Gasometric method

This technique gives accurate results compared to that of conventional weight loss method provided, the inhibitor does not react with hydrogen and the hydrogen penetration into the metal is small compared to the total volume of hydrogen gas. An improved design of the gasometric method as described elsewhere [16]. The specimen was suspended from the hook of the glass stopper and was introduced into the cell containing 100 mL of the experimental solution. The temperature was maintained constant throughout these experiments at 30°C and at constant atmospheric pressure. Volume measurements were made for a period of two hours in all the cases. From the volume of hydrogen gas liberated, the inhibition efficiency was calculated using the formula;

$$\text{Inhibition efficiency (\%)} = \frac{V_0 - V_1}{V_0} \times 100$$

Where, V_0 is the volume of hydrogen evolved in the absence of *VNL* extract and V_I is the volume of hydrogen evolved in the presence of *VNL* extract.

Electrochemical polarization studies
Electrochemical polarization measurements were carried out using Electrochemical analyzer (BioLogic, VSP, France) 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 various concentrations of the *VNL* 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 [17];

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

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

Electrochemical impedance studies
The electrochemical AC-impedance measurements were performed using Electro-chemical analyzer (BioLogic, VSP, France) as described earlier. Experiments were carried out at the open circuit potential for the frequency range of 100kHz to 1mHz.A plot of Z' vs Z" were made. From the plots, the charge transfer resistance (R_t) were calculated and the double layer capacitance (C_{dl}) were then calculated using the following equation [18].

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

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 various concentrations of *VNL* inhibitor. The percentage of inhibition efficiency was calculated using the equation [18];

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

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

Surface examination studies
The aluminium specimens were immersed in 1N NaOH in the absence and presence of the best concentration of *VNL* extract for 2 hours at 30°C. After 2 hours, the specimens were taken out, dried and kept in desiccators. The protective film formed on the surface of aluminium was confirmed by SEM studies with the magnification of 1000x.

RESULTS AND DISCUSSION

Weight loss method
The weight loss method was done with concentrations of *VNL* extract ranging from 300 to 900ppm (Table 1). Rise in concentration of *VNL* extract decreased the corrosion rate of aluminium in 1N NaOH solution and increased the inhibition efficiency, increased from 51.0 % to 72.6 % upto 900ppm.It indicates that 900ppm is the best concentration to get maximum corrosion protection for aluminium in 1N NaOH using *VNL* extract. The effect of inhibition efficiency with various concentrations of VNL extract on aluminium in 1N NaOH is shown in Fig.1.

The effect of immersion time from 2 hours to 10 hours was also studied. The effect of immersion time on percentage inhibition efficiency of aluminium in 1N NaOH at 30°C in presence of an optimum concentration (900ppm) of *VNL* extract is shown in Fig.2 (Table 2). It can be seen that the inhibition efficiency was found to increase from 51.0 % to 72.6 %. Though 65.6 % inhibition efficiency was obtained even at 10 hours of immersion time, the maximum inhibition efficiency was found at 2 hours. Hence, using weight loss method, it was found that *VNL* extract acted as corrosion inhibitor at the best concentration of 900ppm for a period of 2 hours at 30°C.

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

Conc. of VNL Extract (ppm)	Weigh Loss (gm)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)	Surface Coverage (θ)
Blank	0.2424	436.92	-	-
300	0.1187	213.95	51.0	0.510
500	0.0926	166.91	61.8	0.618
700	0.0744	134.10	69.3	0.693
900	0.0664	119.68	72.6	0.726

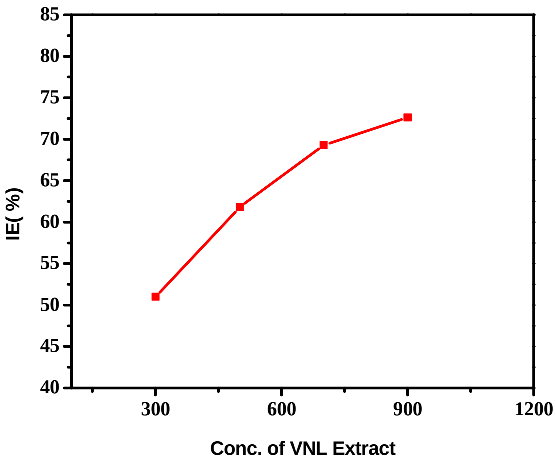

Fig.1 Inhibition efficiency with various concentrations of VNL extract on aluminium in 1N NaOH at 30°C

Table 2 Effect of immersion time on percentage inhibition efficiency of aluminiumin 1N NaOH at 30°C in presence of the best concentration (900ppm) of VNL extract

System	Weight Loss (gm)					IE (%)				
	Time (hrs)					Time (hrs)				
	2	4	6	8	10	2	4	6	8	10
Blank	**0.2424**	**0.3482**	**0.5482**	**0.7262**	**0.8560**	-	-	-	-	-
900 ppm of VNL extract	**0.0664**	**0.1001**	**0.1721**	**0.2382**	**0.2945**	**72.6**	**71.26**	**68.6**	**67.2**	**65.6**

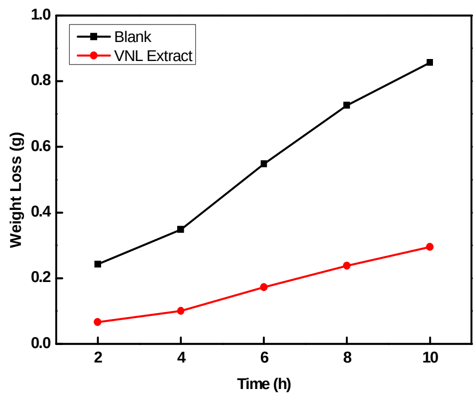

Fig.2 Effect of immersion time on percentage inhibition efficiency of aluminium in 1N NaOH at 30°C in presence of the best concentration (900ppm) of VNL extract

Gasometric method

In the gasometric method, the increase in concentrations of *VNL* extract from 300 to 900ppm decreased the volume of hydrogen gas evolved from 26.4 to 7.3 mL and hence the inhibition efficiency increased from 50.6 to 72.2 % is shown in Table 3. Hence the best concentration of the *VNL* extract was found to be 900ppm. It could be observed that *VNL* extract has better ability to inhibit the corrosion of aluminium in alkaline solution.

Table 3 Inhibition efficiency obtained from gasometric measurements for aluminium in 1N NaOH containing various concentrations of *VNL* extract at 30˚C

Conc. of VNL Extract (% in v/v)	Volume of Hydrogen Gas evolved (mL)	Inhibition Efficiency (%)
Blank	26.4	-
300	13.4	50.6
500	10.4	60.6
700	8.3	68.4
900	7.3	72.2

Electrochemical polarization method

The electrochemical polarization parameters for aluminium in the absence and presence of various concentrations *VNL* extract in 1N NaOH is given in Table 4 and their polarization curves are shown in Fig.3. It can be seen from the table that the corrosion potential was not shifted significantly in presence of the extract suggesting that *VNL* extract control both anodic and cathodic reactions to inhibit the corrosion of aluminium by blocking active sites on the aluminium surface [19]. On the other hand, the corrosion current markedly decreased upon addition of the *VNL* extract. With the addition of the best concentration of *VNL* extract (900ppm), the maximum inhibition efficiency of 71.2 % was observed as in weight loss method. Hence, it is inferred that the inhibition action is of mixed type.

Table 4 Electrochemical polarization parameters for aluminium in 1N NaOH solution in the absence and presence of various concentrations of VNL extract

Conc. of VNL extract (ppm)	E_{corr} (V vs SCE)	I_{corr} (mA/cm^2)	Tafel Slope (mV/decade)		Inhibition Efficiency (%)
			b_a	b_c	
Blank	-1.584	4.46	182	318	---
300	- 1.580	2.221	172	294	50.2
500	-1.570	1.779	170	292	60.1
700	-1.560	1.436	168	288	67.8
900	-1.555	1.284	176	290	71.2

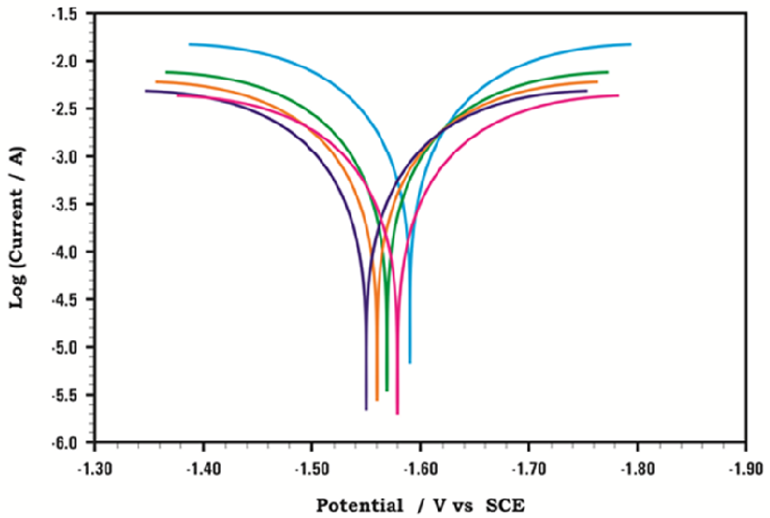

Fig. 3 Electrochemical polarization curves for aluminium in 1N NaOH solution in the absence and presence of various concentrations of VNL extract

AC- impedance measurements

Fig.4 shows the impedance diagrams for aluminium in 1N NaOH in the absence and presence of various concentrations of *VNL* extract and their corresponding impedance parameters are given in Table 5. It can be seen from the Nyquist plots that the curves are almost semicircular appearance followed by an inductive loop at the low frequency region. The semi circular nature of the Nyquist plot is due to the charger – transfer process, mainly control the corrosion of aluminium in 1N NaOH solution. The low frequency inductive loop is due to the growth and dissolution of the surface film [10,20]. In presence of *VNL* extract, the value of R_t increased and the value of C_{dl} decreased. 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 led to increase in the inhibition efficiency. This is due to increase in surface coverage by the adsorbed organic molecules present in the *VNL* extract. The maximum R_t value of 15.84 Ω cm^2 and the minimum C_{dl} value of 7.84µF/cm^2 was obtained at an optimum concentration of 900ppm of the VNL extract, which gave the maximum inhibition efficiency of 71.5 %. This result has good agreement with the results obtained from non-electrochemical methods.

Table 5 Impedance parameters for the corrosion of aluminium in 1N NaOH in the absence and presence of various concentrations of *VNL* extract at 30^{0}C

Conc. Of VNL Extract (ppm)	R_t (Ω cm^2)	C_{dl} (µF/cm^2)	Inhibition Efficiency (%)
Blank	4.52	108.36	---
300	9.12	20.26	50.4
500	11.44	15.20	60.5
700	14.22	12.22	68.2
900	15.84	7.84	71.5

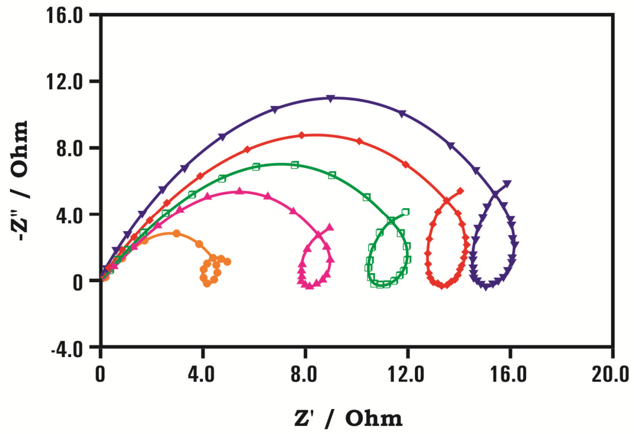

Fig. 4 Impedance diagrams for aluminium in 1N NaOH solution in the absence and presence of various concentrations of *VNL* extract

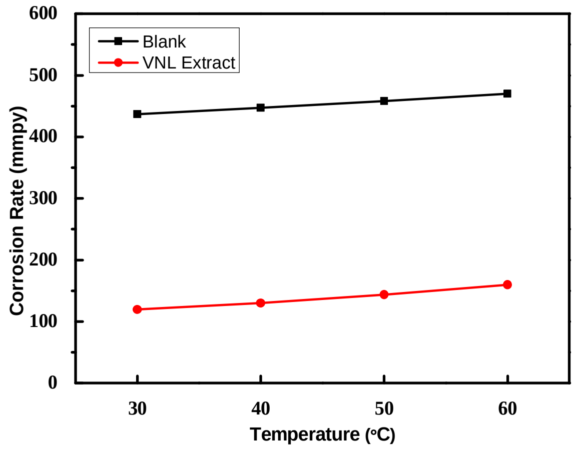

Fig.5 Effect of temperature on the corrosion inhibition efficiency of aluminium in 1N NaOH in presence of the best concentration (900ppm) of *VNL* extract

Effect of Temperatures

The effect of temperature in the range of 30°C to 60°C on the corrosion behaviour of aluminium in 1N NaOH solution in the absence and presence of the best concentration of *VNL* extract was studied using weight loss method as shown in Fig.5 and its results are summarized in Table 6. It can be seen from the table that the increase in corrosion rate was more pronounced with the rise in temperature for the uninhibited alkaline solution than the inhibited solution suggesting that the extract adsorbed on the aluminium surface at all temperatures studied. As the temperature increased from 30°C to 70°C, the inhibition efficiency was found to slightly decrease from 72.6 % to 64.6 %. This shows that the adsorption of the extract on the aluminium may be due to physical adsorption.

Table 6 Corrosion of aluminium in the absence and presence of the best concentration of VNL extract (900 ppm) in 1N NaOH at different temperatures obtained by weight loss method

System	Temperature (°C)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)
Blank	30	436.92	---
	40	447.46	---
	50	458.51	---
	60	470.14	---
900 ppm of VNL extract	30	119.68	72.6
	40	130.28	70.5
	50	144.08	67.8
	60	159.75	64.6

Mechanism of corrosion inhibition

The Arrhenius plot for aluminium immersed in 1N NaOH solution in the absence and presence of the best concentration (900 ppm) of *VNL* extract as shown in Fig. 6. It showing a straight line according to the Arrehenius equation and revealing the effect of temperature. The calculated values of activation energy (E_a) and free energy of adsorption (ΔG°) are shown in Table 6. The activation energy E_a was found to be 1.87 KJ mol^{-1} for blank and increased to 6.73 KJ mol^{-1} in presence of *VNL* extract in 1N NaOH suggesting that the adsorbed organic matter creates a physical barrier to charge and mass transfers, leading to reduction in corrosion rate. The higher value of E_a in presence of the *VNL* extract compared to that in the absence of the extract is due to physical adsorption [10, 20].

Table 7 Calculated values of activation energy (E_a) and free energy of adsorption (ΔG°) in the absence and presence of the best concentration (900 ppm) of *VNL* extract

System	E_a (KJ/mol)			ΔG° (KJ/mol)			
	Temperature (°C)			Temperature (°C)			
	30-40	40-50	50-60	30	40	50	60
Blank	1.87	2.05	2.23	-	-	-	-
900 ppm of VNL extract	6.73	8.52	9.21	-12.85	-12.99	-13.07	-13.08

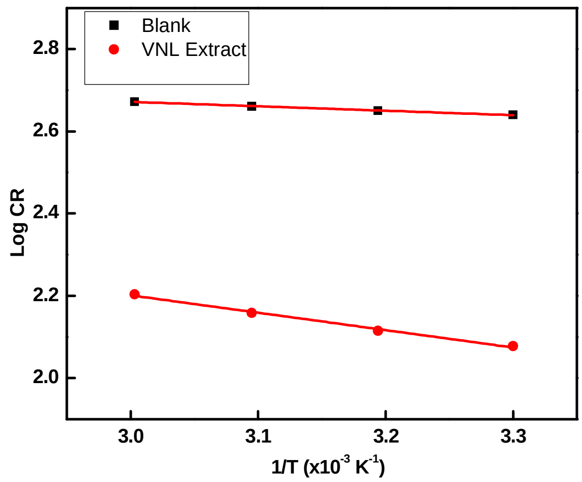

Fig. 6 Arrhenius plots for aluminium immersed in 1N NaOH solution in the absence and presence of the best concentration (900ppm) of *VNL* extract

The negative sign of free energy of adsorption indicates that the adsorption of *VNL* extract on aluminium surface is a spontaneous process. In this study, the $\Delta G°$ values are in the range of -12.85 KJ mol^{-1} to -13.08 KJ mol^{-1}. As the values of free energy of adsorption are less than -20 KJ mol^{-1}, where the mode of inhibition is due to physisorption [21]. The corrosion of aluminium in NaOH solution is a heterogonous one, composed of anodic and cathodic reactions. Based on this, the kinetic analyses of the data studied for a period of 2 hours immersion time were considered. The major constituent present in the VNL extract is the flavonoides [22]. These compounds adsorbed on the aluminium surface made a barrier for charge and mass transfers leading to a decrease in the interaction of aluminium with the corrosive environment. As a result, the corrosion rate of aluminium decreased. The formation of film layer prevented the corrosion of aluminium. The use of adsorption isotherm provides useful insight onto the corrosion inhibition mechanism. The adsorption of various concentrations of VNL extract on the surface of aluminium in 1N NaOH solution followed Langmuir adsorption isotherm (Fig. 7).

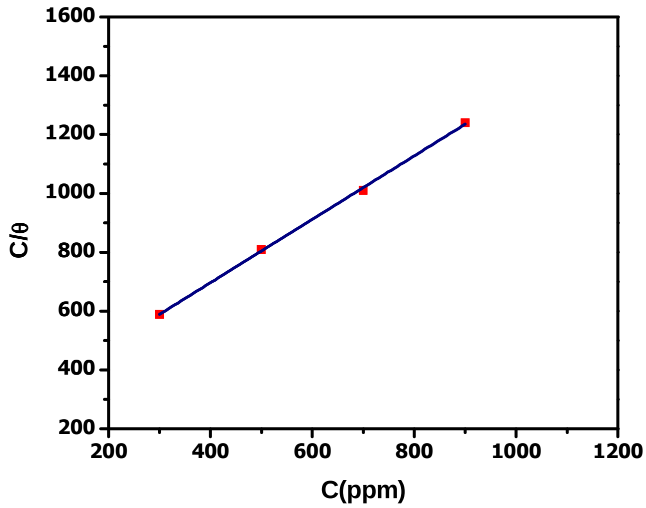

Fig.7 Langmuir adsorption isotherm plot for the adsorption of various concentrations of VNL extract on the surface of aluminium in 1N NaOH solution

Surface Analysis

Surface examination of the aluminium specimens was made using scanning electron microscope (SEM) with the magnification of 1000x is shown in Fig.8 (a & b). The SEM studies showed that the inhibited aluminium surface was found smother than the uninhibited surface due to the formation of protective film on the inhibited aluminium surface.

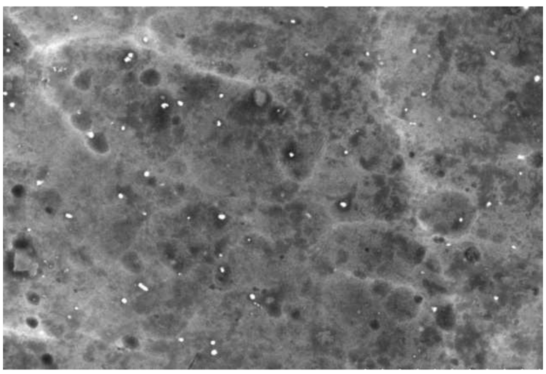

Fig.8 (a) SEM Photograph of aluminium immersed in 1N NaOH solution (blank)

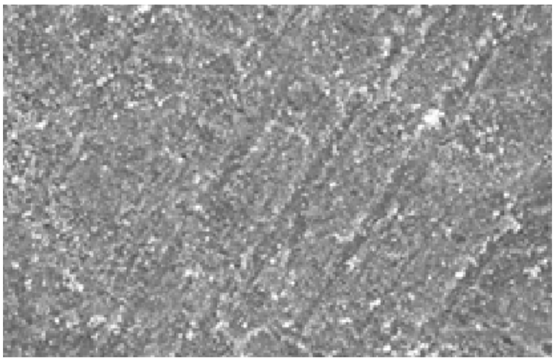

Fig. 8(b) SEM Photograph of aluminium immersed in 1N NaOH solution containing the best concentration (900ppm) of VNL extract

CONCLUSION

The following conclusions are drawn from the above studies;
The *Vitex negundo* leaves (*VNL*) extract perform well in 1N NaOH solution and inhibit the corrosion of aluminium at the best concentration of 900ppm. The *VNL* extract control both anodic and cathodic reactions by blocking the active sites of aluminium surface and thus the inhibitor of mixed type. The *VNL* 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. The scanning electron microscope studies showed that the inhibited aluminium surface was found smother than the inhibited surface due to the formation of protective film on the inhibited aluminium surface.

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