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Influence of aqueous extract of *Sida acuta* leaves on corrosion inhibition of aluminium in alkaline solution

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ABSTRACT

An aqueous extract of Sida acuta leaves (SAL) was prepared and its influence on corrosion inhibition of aluminium in 1N NaOH solution was studied using chemical and electrochemical methods. It was found that the inhibition efficiency increases with the increasing the concentration of Sida acuta extract upto 900ppm. Electrochemical measurements revealed that SAL extract acts as a mixed type inhibitor. Adsorption of SAL extract was found to follow Langmuir adsorption isotherm. The results obtained from chemical and electrochemical measurements were in good agreement. The protective film formed on the surface of aluminium by the adsorption of water-soluble chemical constituents of SAL extract was confirmed by using scanning electron microscopy studies. These results were supported by kinetic and thermodynamic parameters obtained from weight loss data at various temperatures studied.

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

INTRODUCTION

Aluminium is one of the most abundant metals after iron. It is used in a large number of applications by itself and in a wide range of alloys. It can be used as an anode material for power sources with high energy densities. The corrosion behavior of pure aluminium and its alloys in alkaline solution has been extensively studied for the development of aluminium anode for Al/Air battery [1]. It has been reported that the damage of aluminium by self corrosion in alkaline solution. This can be substantially reduced by employing corrosion inhibitors. Nowadays, the use of chemical inhibitors has been limited due to environmental regulations, and hence, plant extracts have again become important because they are environmentally acceptable, readily available, eco-friendly and renewable materials. Natural products such as henna leaves [2], gossipium higgutum [3], gum arabic [4] phyllanthus amarus [5], ipomoea involucrate [6], hibiscus sabdoriffa [7], adathoda vasica [8] damisissa [9], brahmi [10], pipali leaves [11] etc., have been studied as effective corrosion inhibitors for aluminium in alkaline environment.

This paper reports the influence of aqueous extract of *Sida acuta* leaves for the corrosion inhibition of aluminium in 1N sodium hydroxide solution by chemical and electrochemical techniques. The effect of temperature on the corrosion rate of aluminium in presence of an optimum concentration of SAL extract was investigated and some thermodynamic parameters for activation process were also computed and discussed.

MATERIALS AND METHODS

Material preparation
Aluminium strips of 4.5×2cm ×0.2cm containing > 99.9 % purity were used for weight loss and gasometric 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 $0.5cm^2$ was used for electrochemical studies. Analar grade NaOH and double distilled water were used to prepare the solutions.

Preparation of sidaacuta leaves extract
The *Sida acuta* leaves (Aruvamanai poondu) were taken and cut into small pieces and 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 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 [8]. The inhibitor concentrations of 300 to 900ppm were prepared using 1N NaOH solution.

Weight loss studies
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 inhibition efficiency were calculated using the following equations;

Corrosion rate (mmpy) = kW/ATD

Where, $k = 8.76\times10^4$ (constant), W = weight loss in g, A= area in square cm, T= time in hours and D= density in gm / cu.cm (2.70)

Inhibition Efficiency (%) = $W_B - W_I / W_B$ X100

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 different immersion time from 2 hours to 10 hours for the best concentration of SAL extract at 30°C. From the initial and final weight of the specimen, the weight loss of the specimen was calculated and the inhibitor efficiency at different immersion times was calculated.

Determination of surface coverage
The degree of surface coverage (θ) was calculated from the weight loss measurement results using the following 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 SAL extract, W_I is the weight loss in the presence of the SAL extract. The data were tested graphically for fitting a suitable isotherm.

Electrochemical polarization studies
Tafel 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 SAL extract from a cathodic potential of – 1800 mV to an anodic potential of – 1300 mV (vs SCE) at a sweep rate of 1mV/sec. From the polarization curves, Tafel slopes, corrosion potential and corrosion current were calculated. The inhibitor efficiency was calculated using the formula [8];

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

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

AC-Impedance studies

The electrochemical AC-impedance measurements were performed using Electrochemical analyzer (BioLogic, VSP, France) as described earlier. Experiments were carried out at the open circuit potential in the frequency range of 100kHz to 1 mHz. A plot of Z' vs Z" were made. From the plots, the charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were 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 various concentrations of SAL extract. The percentage of inhibition efficiency was calculated using the equation;

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

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

Surface examination studies

The aluminium specimens were immersed in 1N NaOH in the absence and presence of the best concentration of SAL extract for 2 hour at 30°C. After 2 hour, 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 corrosion parameters obtained from weight loss measurements for aluminium in 1N NaOH solution containing various concentrations of *Sida acuta* leaves extract are given in Table-1. It was found that with the rise in concentration of *Sida acuta* leaves extract from 300 to 900 ppm, the weight loss of aluminium decreased, and the inhibition efficiency increased from 47.9 % to 67.1 %. This result indicated that 900 ppm is the best concentration to get corrosion protection for aluminium in 1N NaOH using *Sida acuta* leaves extract. This trend may result from the fact that adsorption is enhanced with increase in concentration of *Sida acuta* leaves extract. As a result, more inhibitor molecules are adsorbed on the metal surface reduces the surface area available for the attack of the aggressive OH^- ions from the alkaline solution for corrosion. The variation of inhibition efficiency with various concentrations of *Sida acuta* 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 SAL extract

Conc. of SAL Extract (ppm)	Weigh Loss (gm)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)	Surface Coverage (θ)
Blank	0.2424	436.92	-	-
300	0.1262	227.47	47.9	0.479
500	0.1086	195.75	55.2	0.552
700	0.0942	169.79	61.1	0.611
900	0.0798	143.83	67.1	0.671

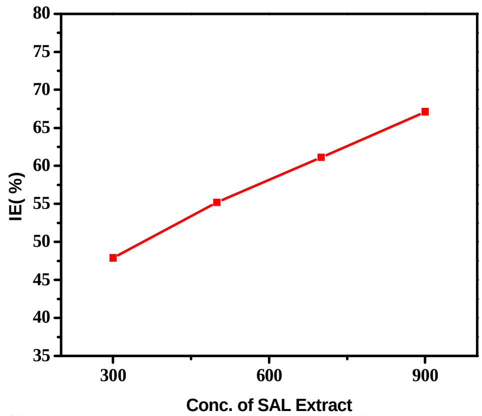

Fig.1 Variation of inhibition efficiency with various concentrations of SAL extract on aluminium in 1N NaOH solution

The effect of immersion time from 2 to 10 hours was also studied. The inhibition efficiency was found to decrease from 67.1 % to 61.2 %.The slight decrease in inhibition efficiency at longer immersion time is due to an increase in cathodic or hydrogen evolution kinetics or an increase in concentration of Al^{3+}ions. The effect of immersion time on percentage inhibition efficiency of aluminium in 1N NaOH at 30^0C in presence of an optimum concentration (900 ppm) of *Sida acuta* leaves extract is given in Table-2 (Fig.2). Though 61.2 % 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 *Sida acuta* leaves extract acted as corrosion inhibitor for aluminium in 1N NaOH medium at the best concentration of 900 ppm for a period of 2 hours at 30^0C.

Table 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 SAL 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 SAL extract	0.0797	0.1191	0.1995	0.2745	0.3321	67.1	65.8	63.6	62.2	61.2

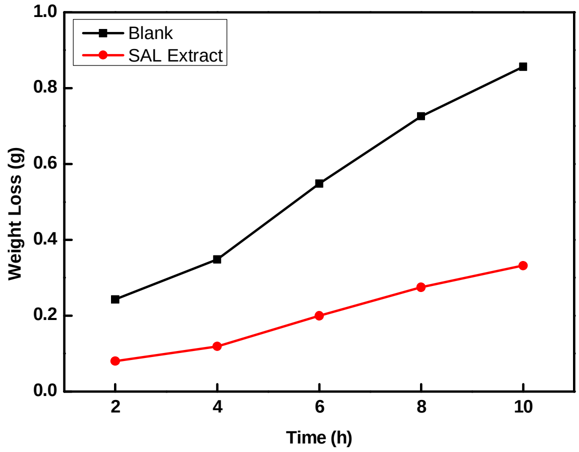

Fig.2 Effect of immersion time on percentage inhibition efficiency of aluminium in 1N NaOH at 30°C in presence the best concentration (900ppm) of SAL extract

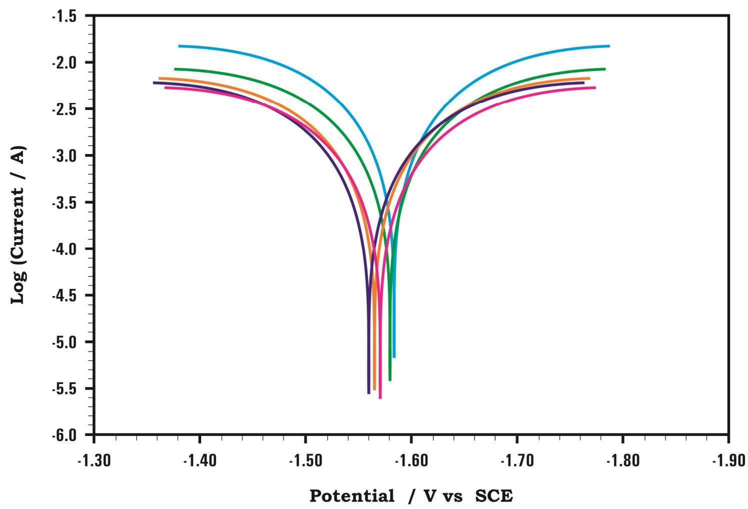

Fig.3 Electrochemical polarization curves for aluminium in 1N NaOH solution in the absence and presence of various concentrations of SAL extract

Electrochemical polarization method

Fig.3 shows the polarization curves for aluminium in 1N NaOH solution in the absence and presence of various concentrations of *Sida acuta* leaves extract and their corresponding electrochemical 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 *Sida acuta* leaves extract control both anodic and cathodic reactions to inhibit the corrosion of aluminium by blocking active sites on the surface of aluminium . This showed that the inhibition action is of mixed type [15]. 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 the SAL extract (900 ppm) and the maximum inhibition efficiency of 66.0 % was observed as in weight loss method.

Table 3 Electrochemical polarization parameters for aluminium in 1N NaOH solution in the absence and presence of various concentrations of SAL extract

Conc. of SAL Extract (ppm)	E_{corr} (V vs SCE)	I_{corr} (mA/cm^2)	Tafel Slope (mV/decade) b_a	b_c	Inhibition Efficiency (%)
Blank	-1.584	4.46	182	318	---
300	-1.582	2.417	174	294	45.8
500	-1.570	2.243	170	290	49.7
700	-1.565	1.819	168	282	59.2
900	-1.560	1.516	170	286	66.0

AC-Impedance measurements

Fig.4 shows the nyquist plots for aluminium in 1N NaOH in the absence and presence of various concentrations of *Sida acuta* 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. The low frequency inductive loop is due to the growth and dissolution of the surface film [16]. In fact, the presence of *Sida acuta* 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 values of R_t and the decrease in the values of C_{dl} with an increase in concentration of inhibitor led to increase in the inhibition efficiency. This is due to increase in surface coverage by the inhibitor. The maximum R_t value of 13.36 Ωcm^2 and the minimum C_{dl} value of 12.32$\mu F/cm^2$ was obtained at the optimum concentration 900ppm of the extract gave a maximum inhibition efficiency of 66.2 %. This result has good agreement with the results obtained from non-electrochemical weight loss and electrochemical Tafel polarization methods.

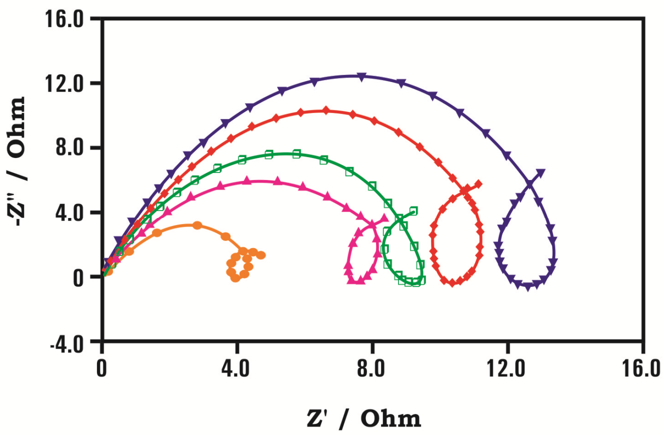

Fig. 4 Impedance diagrams for aluminium in 1N NaOH solution in the absence and presence of various concentrations of SAL extract

Table 4 Impedance parameters for the corrosion of aluminium in 1N NaOH in the absence and presence of various concentrations of SAL extract at 30^{0}C

Conc. of SAL Extract (ppm)	R_t (Ω cm^2)	C_{dl} (μF/cm^2)	Inhibition Efficiency (%)
Blank	4.52	108.36	---
300	8.46	25.82	46.6
500	9.10	20.20	50.3
700	11.22	16.44	59.7
900	13.36	12.32	66.2

Effect of Temperature

Table 5 shows the corrosion rate and inhibition efficiency of aluminium in 1N NaOH solution in the absence and presence of the SAL extract at different temperatures ranging from 30^{o}C to 60^{o}C. 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 [17]. The effect of temperature on the corrosion inhibition of aluminium in 1N NaOH in presence of an optimum concentration of *Sida acuta* leaves extract as shown in Fig.5.

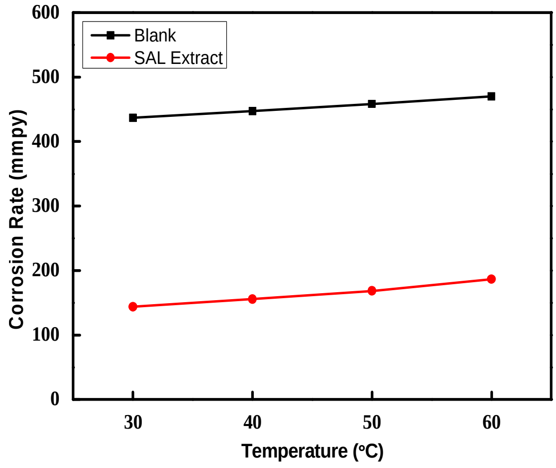

Fig.5 Effect of temperatures on the corrosion inhibition efficiency of aluminium in 1N NaOH in presence of the best concentration (900ppm) of SAL extract

Table 5 Corrosion of aluminium in the absence and presence of the best concentration of SAL 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 SAL extract	30	143.83	67.1
	40	155.89	64.7
	50	168.68	62.3
	60	186.82	58.6

Mechanism of corrosion inhibition

The Arrhenius plot for aluminium immersed in 1N NaOH solution in the absence and presence of an optimum concentration (900ppm) of *Sida acuta* 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 [17];

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

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 the best concentration of SAL extract were calculated from the following Arrhenius equation [18];

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\,[1/T_1 - 1/T_2]$$

Where, k_1 and k_2 are the corrosion rates at temperatures T_1 and T_2, respectively.

The inhibition of *Sida acuta* leaves extract may be due to the presence of the major alkaloid, quindoline and cryptolepine which containing nitrogenous compounds and methyl groups [19]. The structures of quindoline and cryptolepine are shown in Fig.7(a & b). The inhibition mechanism involved in this is due to the adsorption of inhibitor on the surface of aluminium and forming a compact protective thin layer on the aluminium surface. It provokes the corrosion of aluminium in 1N NaOH solution.

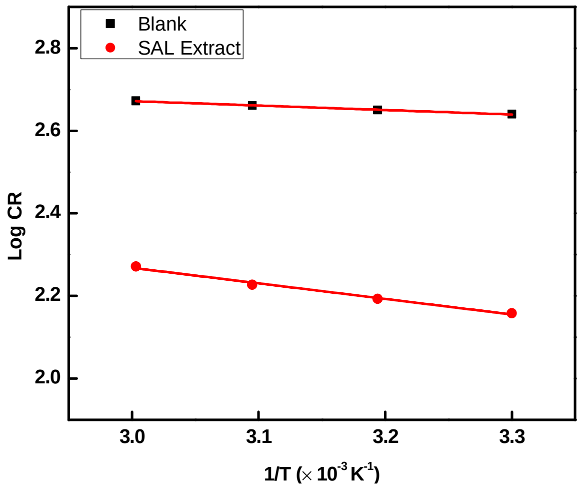

Fig. 6 Arrehenius plots for aluminium immersed in 1N NaOH solution in the absence and presence of the best concentration (900ppm) of SAL extract

(a)

(b)

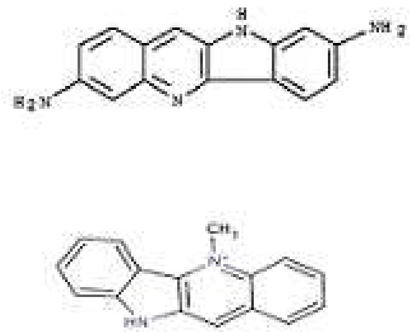

Fig. 7 Structure of (a) Quindoline and (b) Cryptolepine

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 these 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 *Sida acuta* leaves extract are shown 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 *Sida acuta leaves* extract on the surface of aluminium in 1N NaOH solution follows Langmuir adsorption isotherm (Fig.8).

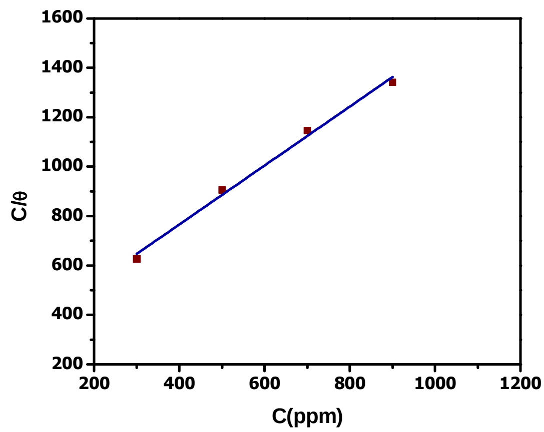

Fig.8 Langmuir adsorption isotherm plot for the adsorption of various concentrations of SAL extract on the surface of aluminium in 1N NaOH solution

Surface Analysis

Surface examination of the aluminium specimens were made using 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 an optimum concentration of the *Sida acuta 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). In the absence of SAL extract, the corroded aluminium surface with etched grain boundaries is clearly seen. In the presence of SAL extract, almost 66 % of protected aluminium surface are seen.

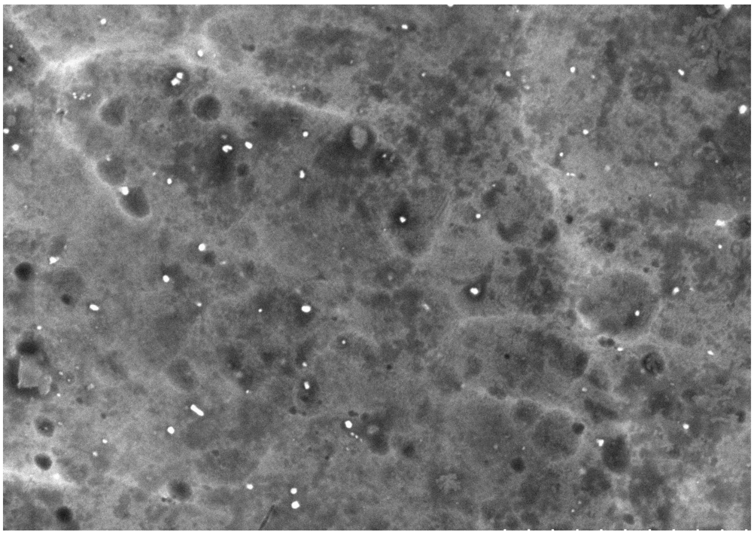

Fig. 9(a) SEM Photograph of aluminium immersed in 1N NaOH solution (Blank)

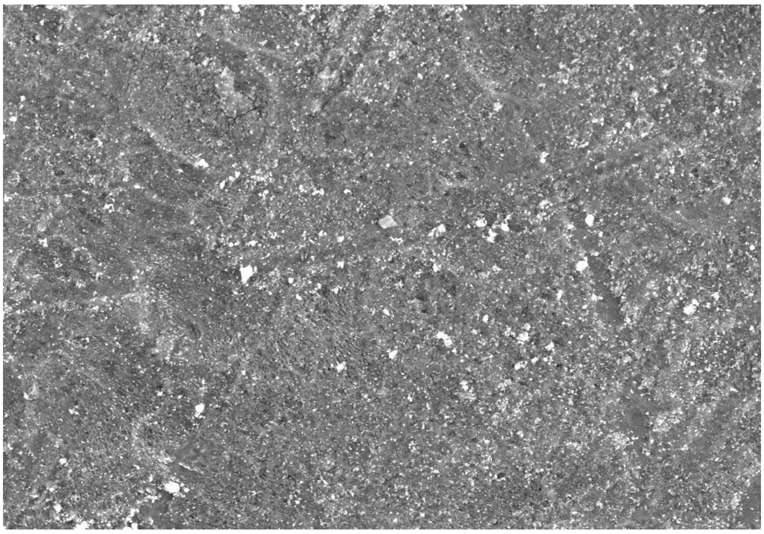

Fig.9(b) SEM Photograph of aluminium immersed in 1N NaOH solution containing the best concentration (900) of SAL *extract*

CONCLUSION

The following conclusions are drawn from the above studies;

The aqueous extract of *Sida acuta* leaves perform well in 1N NaOH solution and inhibit the corrosion of aluminium and the inhibition efficiency increases with increasing concentration of SAL extract. The SAL extract control both anodic and cathodic reactions by blocking the active sites of aluminium surface and thus the inhibitor of mixed type. Electrochemical impedance plots indicated that the charge transfer resistance increased in concentration of SAL extract. The SAL 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.

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