

# Sulphuric Acid Corrosion of Mild Steel in Leave Extracts of *Cnidoscolus aconitifolius* Plant

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## Abstract

Alkaloid and nonalkaloids extracts of *Cnidoscolus aconitifolius* leaves is reported as corrosion inhibitor of mild steel in HCl. Conventional weight loss measurements and Tafel polarization techniques are employed to study the effect on mild steel corrosion in H<sub>2</sub>SO<sub>4</sub> solutions. The weight loss result revealed that both plant extracts are excellent corrosion inhibitors. Electrochemical polarization data revealed that mixed mode of inhibition. The increase in %IE with change in concentration of the extracts suggests the strong adsorption of active molecules leading to the formation of a protective layer on the mild steel surface. It was found that adsorption of both leaf extracts followed Langmuir adsorption isotherm model.

**Keywords:** Weight loss, Langmuir isotherm, activation energy, corrosion current density, inhibition efficiency, *Cnidoscolus aconitifolius*.

## 1. Introduction

So many industrial processes for example acid descaling, acid washing, acid pickling as well as oil well acidification employ extensively industrial acids of various concentration which lead to corrosion damage in a long run. This corrosion damage is an electrochemical corrosion process on the metallic material and often time's organic inhibitors containing hetero – atoms like nitrogen, oxygen, sulphur are used in mitigating the corrosion attack as a result of the aggressiveness of these acids. The known hazardous effect of most synthetic corrosion inhibitors is the motivation for the use of some natural products. The use of chemical inhibitors has been limited because of the environmental threat, recently, due to environmental regulations. Plant extracts have become important because they are environmentally acceptable, inexpensive, readily available and renewable sources of materials, and ecologically acceptable (Singh et al., 2010).

The effectiveness and flexibility of these organic inhibitors on corrosion attack of metals have been reported by Okafor and Zheng (2009), Liu et al., (2009), Singh et al., (2012), Ugi (2014).

Notable heterocyclic organic inhibitors are extracts of medicinal (herbal) plants which are known to contain heterocyclic compounds like alkaloids, tannins, flavonoids, saponins, phenols, etc. and are used as corrosion inhibitors of steel (especially mild steel) in acidic solutions, especially for corrosion protection of oil and gas pipelines (Eddy et al., 2015; Obi-Egbedia, 2011).

The inhibiting action of these plant extracts is attributed to their to the mild steel/solution interface. However, it has been reported that the extent of adsorption of these organic inhibitors is greatly influenced by the nature and surface charge of the metal, the adsorption mode, chemical structure of the inhibitor, reaction temperature and pressure as well as composition of the aggressive solution (Okafor and Zheng, 2009; Okafor et al., 2008; Shalabil et al., 2014; Uwah et al., 2013).

In this paper, two organic inhibitors extracted from the leaves of *Cnidoscolus aconitifolius* were chosen to investigate their inhibition performances in fighting the corrosion of mild steel in 2 M H<sub>2</sub>SO<sub>4</sub> solutions. Furthermore, the inhibition action of the inhibitors were correlated with potentiodynamic polarization analysis in anticipation that the information will be helpful in the design of new inhibitors with higher inhibition efficiency in acidic solutions.

## 2. Experimental

### 2.1 Preparation of metal

Corrosion tests were performed on a mild steel of the following percentage composition: Fe 99.30%, C 0.076%, Si 0.026%, Mn 0.192%, P 0.012%, Cr 0.050%, Ni 0.050%, Al 0.023%, and Cu 0.135%. Prior to all measurements, the mild steel specimens were abraded successively with silicon carbide paper from 600 to 1200 grades. The specimens were washed with double distilled water, rinsed in ethanol, degreased with acetone and finally air dried. The aggressive solution of 2.0 M H<sub>2</sub>SO<sub>4</sub> was prepared by dilution of analytical grade with double distilled water and all experiments were carried out in unstirred solutions. The rectangular specimens with dimension 5.0 x 4.0 x 0.08 cm<sup>2</sup> were used in weight loss experiments and of size 1.0 x 1.0 cm<sup>2</sup> (exposed) were used for electrochemical measurements.

### 2.2 Preparation of inhibitors

The leaves of *Cnidoscolus aconitifolius* used was obtained in Calabar, Nigeria. These were dried in an oven at

50° C. The dried leaves were ground into powder. 200 g of the powder was extracted with 250 cm<sup>3</sup> of absolute ethanol in a soxhlet extactor until almost all the extract was removed, and the ethanol evaporated using a water bath. 20 g of the ethanol extract was partitioned between 200 ml of chloroform and 200 ml of 2.0 M HCl solution using a separating funnel. The filtrate fraction was used as the non-alkaloid extract. The float fraction from the separating funnel was further basified using 200 ml of ammonia and partitioned using 150 ml of chloroform the float was taken as the alkaloid extract. 5 g of the alkaloid and non-alkaloid extracts were soaked in 0.5 Litre of 0.5 M H<sub>2</sub>SO<sub>4</sub> solution and kept for over a day. The solutions thus obtained were filtered and stored. From the stock solutions of 5 g/L concentration, inhibitor test solutions of concentration: 0.5, 1.0, 1.5, 2.5 and 4.0 g/L were prepared. The prepared solutions were then used to study the corrosion inhibition abilities of the extracts.

### 2.3 Weight loss method

Weight loss measurements were performed on the Mild Steel coupons of dimension 5cm x 0.08cm x 4cm in 5.0 M H<sub>2</sub>SO<sub>4</sub> solutions with and without different concentrations (0.5, 1.0, 1.5, 2.5 and 4.0 g/L) of alkaloid and nonalkaloid extracts. Each mild steel coupon was weighed with a digital analytical balance and then suspended with the aid of glass rods in the acid solution contained in a 100mL beaker. The duration of immersion was 6 hours. After immersion the surface of the metal was washed with distilled water using a bristled brush to scrub the surface followed by rinsing with absolute ethanol followed by acetone and air dried. The sample was then weighed again to calculate the weight loss. This process was repeated progressively for 6 hours. The Corrosion rate (CR) of the mild steel was obtained from the slope of the graph of weight loss per surface area against time of exposure (Fig 2). Surface coverage ( $\theta$ ) and Inhibition efficiency (IE%) were calculated using the following equations 1 and 2.

$$\theta = \frac{CR_o - CR_i}{CR_o} \quad 1$$

$$IE\% = \frac{CR_o - CR_i}{CR_o} \times 100 \quad 2$$

where CR<sub>o</sub> and CR<sub>i</sub> are the corrosion rate values in presence and absence of the inhibitor, respectively.

### 2.4 Potentiodynamic polarization

Measurements were carried out in the 1 M H<sub>2</sub>SO<sub>4</sub> solution with different concentrations of the tested inhibitor (Blank, 0.5 and 4.0 g/L) by varying the electrode potential from -250 to + 250 mV against corrosion potential at a scan rate of 1 mV s<sup>-1</sup>. Corrosion current densities were obtained from the linear Tafel plots and the inhibition efficiency evaluated from the measured I<sub>corr</sub> values obtained using:

$$IE\% = \frac{I_{corr}^o - I_{corr}^i}{I_{corr}^o} \times 100 \quad 3$$

where I<sub>corr</sub><sup>o</sup> and I<sub>corr</sub><sup>i</sup> represent the corrosion current density in control and in presence of corrodent respectively.

## 3. Result and discussion

### 3.1 Weight loss result

Different concentrations of AECAL and NAECAL were used to study the weight loss of mild steel in 2.0 M solution of H<sub>2</sub>SO<sub>4</sub>. After 6 hours of immersion at room temperature, the weight loss was found to be decreasing with concentration (Fig. 1) and increasing with time of immersion (Fig. 2). Inhibition efficiency of the mild steel was determined in the presence and absence of the plant extracts and the results are shown in Table 1. It was observed that the corrosion rate of the mild steel decreases on increasing the concentration of the extracts up to 4.0 g/L. This result is in accordance with those of Raja *et al.*, (2013); Soltain *et al.*, (2012); Singh *et al.*, (2010). The increase in adsorption of the inhibitor on the mild steel surface is attributed to the behavior just identified above, and this reduces the surface area that is available for direct attack on the metal surface according to Ugi, (2014); Obi-Egbedia (2011). The % IE at different concentrations of the plant extracts increases with increase in inhibitor concentration (Table 1). This is due to decrease in the dissolution process of the MS in 2.0 M H<sub>2</sub>SO<sub>4</sub> solution. The presence of diverse phytochemical constituents in the extracts is also responsible for the inhibitive effects of the extracts. The better % IE of the AECAL over the NAECAL is attributed to the presence of organic compounds of high molecular weight with heteroatoms and pie centres.

Table 1 Corrosion rates, surface coverage and inhibition efficiency for MS in the presence and absence of (a) alkaloid and (b) Non alkaloid extracts of *Cninidoscolus aconitifolius* leaves.

Systems	AECAL			NAECAL		
	CR (mg/cm <sup>2</sup> /min)	Surface Coverage (Θ)	IE (%)	CR (mg/cm <sup>2</sup> /min)	Surface Coverage (Θ)	IE (%)
Blank (2M H <sub>2</sub> SO <sub>4</sub> )	0.163	-	-	0.163	-	-
0.5 g/L	0.087	0.464	46.4	0.100	0.387	38.7
1.0 g/L	0.036	0.779	77.9	0.093	0.429	42.9
1.5 g/L	0.019	0.883	88.3	0.039	0.761	76.1
2.5 g/L	0.012	0.926	92.6	0.019	0.883	88.3
4.0 g/L	0.005	0.969	96.9	0.017	0.896	89.6

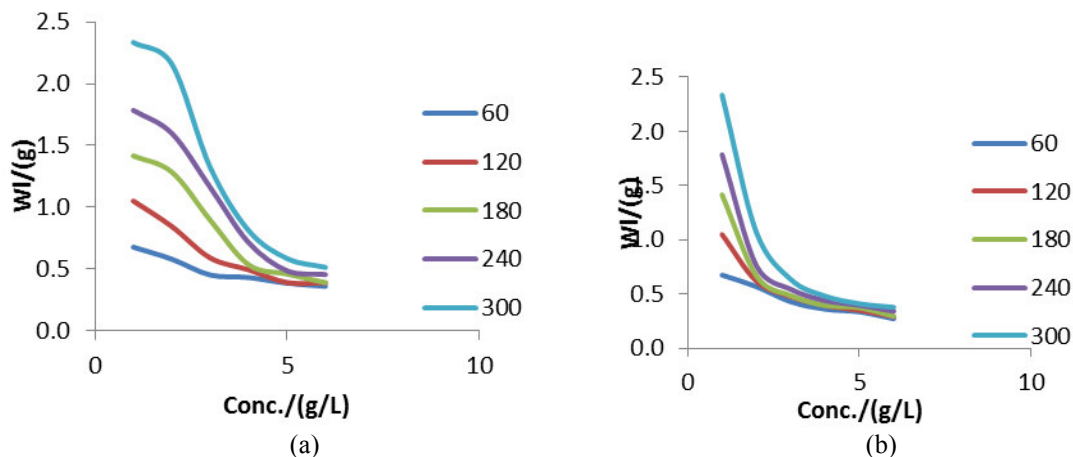


Fig. 1. Variation of weight loss with Conc. for MS in the presence and absence of (a) NAECAL and (b) AECAL

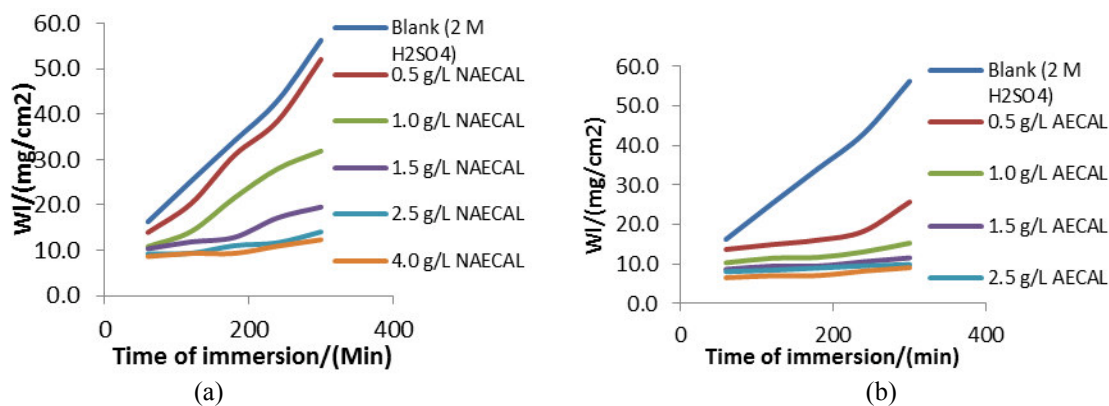


Fig. 2. Variation of weight loss with immersion time for MS in the presence and absence of (a) NAECAL and (b) AECAL

### 3.2 Temperature effects

In the present study, the values for  $\Delta G_{ads}$  for both AECAL and NAECAL on the mild steel surface are in the

ranges of -53 and -58 kJmol<sup>-1</sup> (Table 2), suggesting the combination of both physical and chemical adsorption (Pradeep and Mohana, 2013). However, the negative values of  $\Delta G_{ads}$  suggest spontaneous adsorption and stability of the inhibitors on the metal surface. The  $\Delta G_{ads}$  was deduced from equation 4.

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \quad 4$$

where 55.5 is the concentration of water in solution (molL<sup>-1</sup>), R is the universal gas constant and T is the absolute temperature.

The values of  $\Delta H_{ads}$  and  $\Delta S_{ads}$  were obtained from the plot of  $\Delta G_{ads}$  versus T which gave a straight line (Fig. 3a and b) with a slope of  $-\Delta S_{ads}$  and intercept of  $\Delta H_{ads}$ . The values of  $\Delta H_{ads}$  obtained for both AECAL and NAECAL were negative (Table 2), indicating that adsorption of the inhibitor is an exothermic process. The values of  $\Delta S_{ads}$  obtained are also negative in the adsorption process (Table 2) suggesting that the solvent entropy is reduced by the presence of the inhibitors according to Deng and Li, (2012); Pradeep and Mohana, (2013).

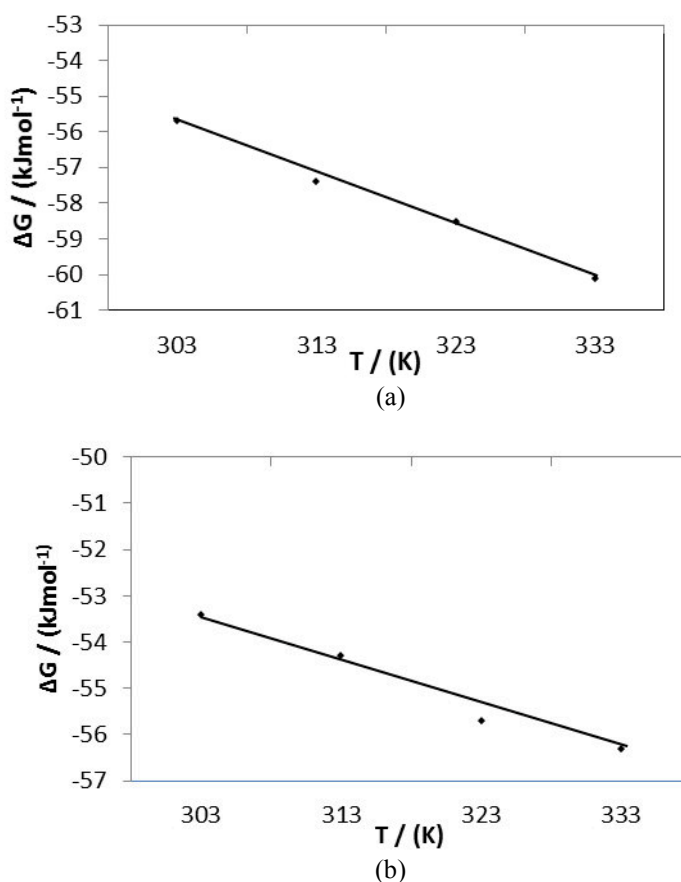


Fig. 3. Plots of Gibbs free energy versus absolute temperature for mild steel in 2.0 M H<sub>2</sub>SO<sub>4</sub> solutions in the absence and presence of (a) AECAL and (b) NAECAL.

Table 2. Thermodynamic parameters for adsorption of AECAL and NAECAL extracts on MS in 2.0 M H<sub>2</sub>SO<sub>4</sub> solutions at different temperatures from Langmuir adsorption isotherm obtained from gasometric analysis result.

Temp.(K)	AECAL				NAECAL			
	K <sub>ads</sub> (gmol <sup>-1</sup> )	ΔG <sub>ads</sub> (kJmol <sup>-1</sup> )	ΔH <sub>ads</sub> (kJmol <sup>-1</sup> )	ΔS <sub>ads</sub> (kJmol <sup>-1</sup> )	K <sub>ads</sub> (gmol <sup>-1</sup> )	ΔG <sub>ads</sub> (kJmol <sup>-1</sup> )	ΔH <sub>ads</sub> (kJmol <sup>-1</sup> )	ΔS <sub>ads</sub> (kJmol <sup>-1</sup> )
303	179.1	-53.4			264.7	-55.7		
313	155.3	-54.3	<b>-52.4</b>	<b>-101.8</b>	259.2	-57.4	<b>-54.3</b>	<b>-143.1</b>
323	147.4	-55.7			231.9	-58.5		
333	122.9	-56.3			225.0	-60.1		

### 3.3 Potentiodynamic polarization result

The anodic and cathodic polarization curves of mild steel electrode in H<sub>2</sub>SO<sub>4</sub> medium with and without the various concentrations of alkaloids and non alkaloid extracts are presented in Fig. 4a and b. This type of plots have been produced earlier by Khaledl and El-Sherik (2013); Taylor (2012). The electrochemical parameters such as corrosion potential ( $E_{corr}$ ) and corrosion current density ( $I_{corr}$ ) were obtained from the intercession of anodic and cathodic Tafel slopes of the polarization curves and this values are shown in Table 3. It is obvious from Fig. 4 that both the cathodic and anodic curves showed lower current densities in the presence of the extract than those recorded in the free solution (2 M H<sub>2</sub>SO<sub>4</sub>). This is a confirmed indication that both extracts inhibits the corrosion reaction of the mild steel according to Eddy et al., (2015); Liu et al., (2009). From the results obtained, the changes of  $E_{corr}$  are less than 85mV for the studied plant extracts, this suggest that both AECAL and NAECAL act as a mixed type inhibitor for the corrosion of mild steel in H<sub>2</sub>SO<sub>4</sub> medium (Shalabil et al., 2014; Singh et al., 2012; Okafor et al., 2011).

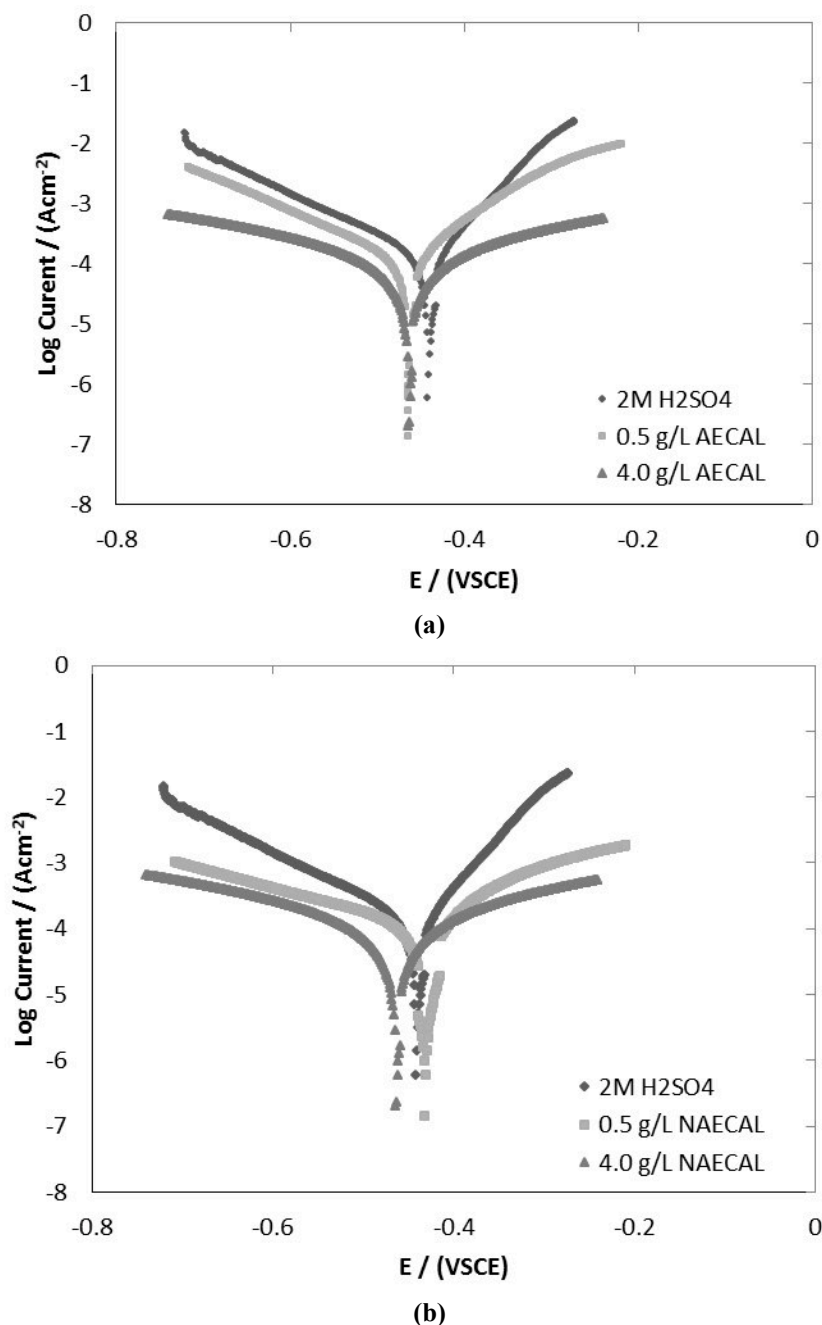


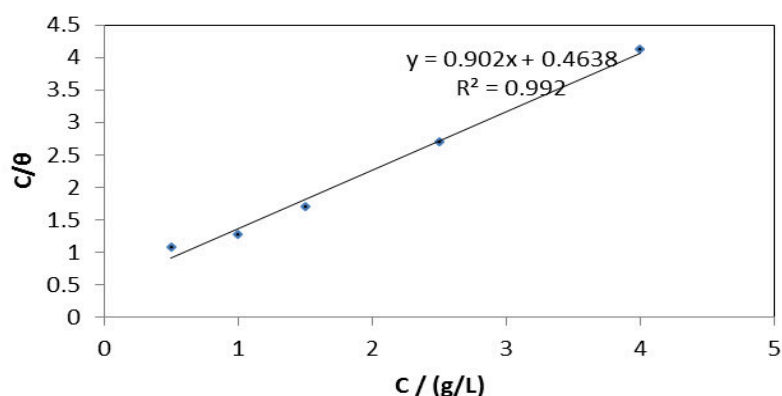
Fig. 4. Polarization curves for mild steel in 2.0 M H<sub>2</sub>SO<sub>4</sub> solutions in the absence and presence of (a) AECAL and (b) NAECAL at 303 K.

Table 3 Potentiodynamic polarization parameters for mild steel in 2.0 M H<sub>2</sub>SO<sub>4</sub> solutions containing AECAL and NAECAL at 303 K

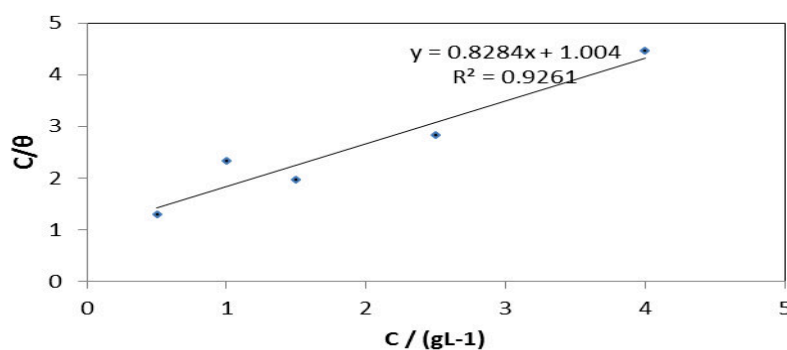
Systems	AECAL			NAECAL		
	$-E_{corr}$ (mV)	$I_{corr}$ ( $\mu\text{Acm}^{-2}$ )	% IE <sub>i</sub>	$-E_{corr}$ (mV)	$I_{corr}$ ( $\mu\text{Acm}^{-2}$ )	% IE <sub>i</sub>
Blank (2M H <sub>2</sub> SO <sub>4</sub> )	569.72	2571.1	-	569.72	2571.1	-
0.5 g/L	594.98	1488.6	42.1	576.17	1574.8	38.8
4.0 g/L	611.43	219.9	91.4	589.65	376.3	85.3

### 3.4. Adsorption consideration

To be aware of the mechanism of corrosion inhibition, it is necessary to investigate the adsorption behaviour of the inhibitor on the metal surface (Ebenso et al., 2008; Patel et al., 2013). To this end, the data were tested graphically by fitting to various isotherms including Langmuir adsorption isotherm. From the results, the best fit was obtained from Langmuir adsorption isotherm (Figs. 5a and b) for both AECAL and NAECAL. To judge the best fitted isotherm, the correlation coefficient values were used. This procedure was applied in the corrosion inhibition of metals by (References). In the current study, the strong correlation ( $R^2 > 0.99$ ) indicates that the adsorption of both AECAL and NAECAL on mild steel surface was in good agreement with the Langmuir isotherm (Raja et al., 2013; Uwah et al., 2013).



(a)



(b)

Fig. 5 Langmuir adsorption isotherm for mild steel in 2.0 M H<sub>2</sub>SO<sub>4</sub> solutions in the absence and presence of (a) AECAL and (b) NAECAL at 303 K derived from weight loss result

## 4. CONCLUSION

1. Both extracts are good inhibitors of mild steel in H<sub>2</sub>SO<sub>4</sub> solutions. However, the AECAL inhibited more than the NAECAL owing to its good adsorption on the metal surface compared to NAECAL.

2. The results obtained by weight loss and polarization measurements are in good agreement with each other.
3. The adsorption of the AECAL and NAECAL on mild steel was identified to have obeyed the Langmuir adsorption isotherm.
4. The values of  $\Delta G_{ads}$  calculated suggests the adsorption of both extracts on the mild steel is the combination of both physisorption and chemisorption.

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