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Alkaloid and Non Alkaloid Extracts of *Solanum melongena* Leaves as Green Corrosion Inhibitors on Carbon Steel in Alkaline Medium

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Abstract

The corrosion and inhibition behavior of Carbon steel (CS) in high alkaline solution [Sodium trioxocarbonate (IV)] in the presence of alkaloid and non alkaloid extracts of *Solanum melongena* leaves have been studied using conventional methods - mass loss and gasometric techniques. The results indicate that the extracts inhibit the corrosion of Carbon steel. However, the Alkaloid extract of Solanum melongena leaves (AESML) exhibits higher maximum inhibition efficiency of 81.1% than Non alkaloid extract of Solanum melongena leaves [NAESML] (65.1%) at 3.0 g/L concentration. Inhibition efficiency increase with increasing concentration of extracts but decreased with rise in temperature. Inhibition mechanism was deduced from the activation and thermodynamic parameters that govern the process. Adsorption of extract on the CS was found to obey the Langmuir adsorption isotherm. The phenomenon of physical adsorption is proposed from the obtained thermodynamic parameters.

Key words: Mass loss, thermodynamics, inhibition efficiency, half life, gasometric analysis, adsorption.

Introduction

Most of the industrial cooling water system in refineries, chemical processing plants, petrochemical and fertilizer industries use ground water for coling purposes. In this kind of situation, organic and inorganic inhibitors are used to reduce the corrosive action of acids. Some of the organic inhibitors available are considered to be very toxic and expensive because of its carcinogenic properties. Hence, a need exists for finding the environmentally and eco-friendly formulations for the control of corrosion (Ananda *et al.*, 2005). These have attracted many researchers. The plant extracts are considered as an incredibly rich source of environmentally acceptable corrosion inhibitors. This area of research is of much importance because in addition to being environmentally friendly and ecologically acceptable, that can be extracted by simple procedures with low cost (Pradeep and Mohana, 2013) Corrosion damage can be prevented by using various methods such as upgrading materials, blending of production fluids, process control and chemical inhibition (Ananda *et al.*, 2005).The known effects of most synthetic corrosion inhibitors are

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the motivation for the use of some natural products. Natural products are nontoxic, biodegradable and readily available. So many natural products have been used widely as inhibitors in the corrosion of metals especially mild steel, Aluminum, carbon steel, Uwah *et al.*, 2013 etc. Corrosion inhibition investigation of natural inhibitors is particularly interesting because they are inexpensive, ecologically friendly, and possess no threat to the environment (Okafor *et al.*, 2008 and Uwah *et al.*, 2013).

Experimental

Preparation of Solanum melongena leaves

The required leaves of *Solanum melongena* were dried in a laboratory Oven at a minimal temperature to avoid loss of major organic components of the plant and ground into powder form. The powdered sample was extracted continually with absolute ethanol in a Soxhlet Extractor for over 24 hours. The extract obtained was later heated on a water bath at a temperature of 60°C until most of the ethanol evaporated. 2g of the ethanol extract of the plant was diluted with appropriate volume of the alkaline solution then kept for approximately 24 hours and stored. From the stock solution (2 g/L), inhibition test solutions were prepared to obtain 1.0 g/L, 1.5 g/L, 2.0 g/L, 2.5 g/L and 3.0 g/L for mass loss and gasometric measurements respectively.

Preparation of alkaloid and non-alkaloid plant extracts

Dilute hydrochloric acid (35.5% w/w) and Ammonia solution was used. HCl and NH_3, were preferred because the product formed will be NH_3Cl, which is of no consequence if it contaminates anything since HCl is not as oxidizing as H_2SO_4. However the HCl employed during the experiment was less than 1M, but not weaker than 0.1M (pH 0-1). 20g of the ethanol extract was partitioned between 100ml of chloroform and 100ml of 0.1M HCl solution using a separating funnel. The second part of the separation (fraction at the bottom of the funnel) was used as the non-alkaloid extract. The HCl solution in the float fraction (the fraction at the top of the funnel) from the separating funnel was carefully basify with Ammonia solution and this was taken well above pH 7. A white cloud formed in the solution was noticed indicative of alkaloids presence. Chloroform was immediately added into the basic solution in the separating funnel and 2 nice layers were formed with the lower one (organic) containing the alkaloids. The chloroform layer was eventually separated from mixture and put aside, the chloroform distilled off, and a small quantity of moderately pure alkaloids was obtained. 2g of the alkaloid and non-alkaloid extract were soaked in 0.5litre of 1M HCl solution and kept for 24 hours. The solutions obtained were filtered and stored. From the stock solution, inhibitor test solution of concentrations 1.0 g/L, 1.5 g/L, 2.0 g/L, 2.5 g/L and 3.0 g/L of 5.0 M Na_2CO_3 was prepared. The prepared solutions were then used to study the corrosion inhibition abilities of the extract.

Weight loss measurements

Weighed test specimens were fully immersed separately for 6 days in each of the beakers containing 1.0 g/L, 1.5 g/L, 2.0 g/L, 2.5 g/L and 3.0 g/L extract concentrations, and also alkaline medium (blank). Each of the test specimens were removed every 1day (24 hours) fron the test solution, washed with distilled water, rinsed with ethanol, dried with acetone and re-weighed. Plots of weight loss against exposure time and Concentration were made where corrosion rates were obtained. Surface coverage and inhibition efficiency was calculated from equation (1) and (2) respectively:

$$\Theta = 1 - \frac{W1}{W2} \quad (1)$$

$$IE\% = \theta \, x \, 100 \quad (2)$$

where Θ is the surface coverage, W_1 is the corrosion rate of the blank, W_2 is the corrosion rate of the inhibitor, IE% is the inhibition efficiency.

Hydrogen evolution measurements

In monitoring corrosion studies using this technique, 100 mL of the corrodent (5.0 M Na_2O_3) was introduced into the volumetric flask and the initial volume of the air in the burette was noted. Thereafter, mild steel coupon of dimension 1.20 cm x 0.08 cm x 4.00 cm already weighed was dropped into the pure acid solution and the flask was quickly closed. The volume of the hydrogen gas evolved from the corrosion reaction was monitored by volume changes in the level of paraffin oil in the graduated burette every minute for 30 minutes. In another experiment, a set of fresh specimens were immersed in the flask containing the corrodent at different concentrations each of alkaloid, and non alkalois extracts of *Solanum melongena leaves* (1.0 g/L, 1.5 g/L, 2.0 g/L, 2.5 g/L and 3.0 g/L). The study was conducted at 303K, 313 and 333 K using a thermostat water bath. Each experiment was repeated twice to ensure reproducibility, and the average values were recorded.

Results and Discussion

Mass loss experiments

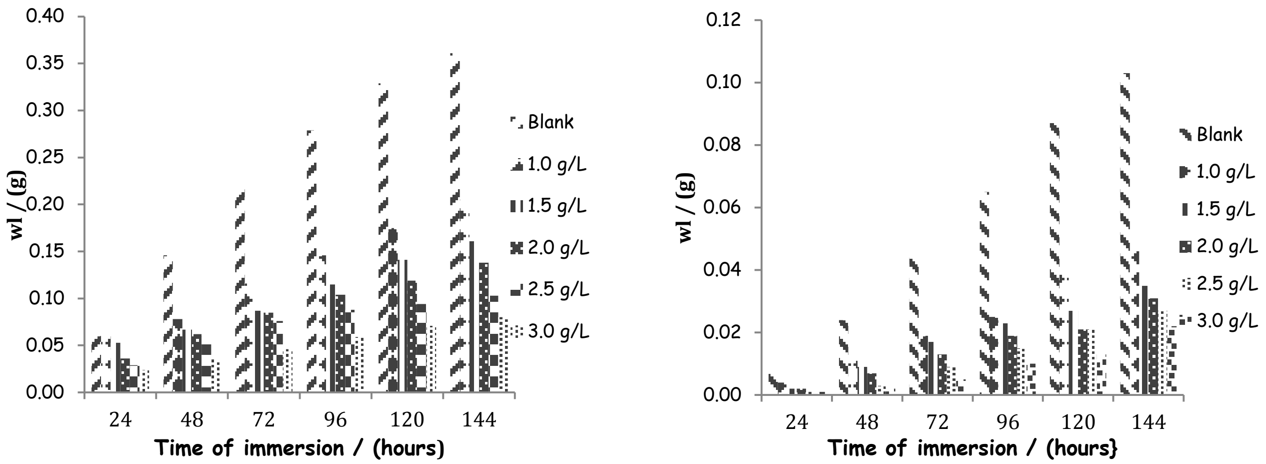
The inhibitor was tested for five different concentrations (1.0 g/L, 1.5 g/L, 2.0 g/L, 2.5 g/L and 3.0 g/L) and the result is presented in Table 1. The addition of inhibitors increased the IE following the time of immersion (Singh *et al.*, 2012). It is observed that the corrosion rates decreased, surface coverage and inhibition efficiency increased with increase in extract concentrations (Fig. 3) according to Ananda *et al*, (2005), Jorge and Singh (2003) and Saratha and Meenaushi (2010). The extracts showed maximum inhibition efficiency of 81.1% for AESML and 65.1% for NAESML, both at an optimum concentration of 3.0 g/L. This may be due to the adsorption of phytochemical constituents of the extracts on the metal surface (Saratha *et al*, 2009; Singh *et al*, 2012; Fatemeh *et al*, 2012).

Weight loss of mild steel was found to decrease with increase in the concentration of *Solanum melongena* extracts indicative that the extract retarded the rate of corrosion in Na_2CO_3 solution (El-Etre *et al.*, 2005; Okafor *et al.,* 2007 and Uwah *et al.*, 2013) as indicated in Table 1 and Figures 2 and 3. Surface coverage (θ) and inhibition efficiency (IE%) increased with increase in AESML and NAESML concentrations, this proved that the corrosion of the metal has been inhibited and a larger fraction of the surface is protected against alkaline attack (El-Etre *et al.*, 2005; Okafor *et al.*, 2007; Uwah *et al.*, 2013 and Ebenso *et al.*, 2008).

Table 1: corrosion rates, surface coverage and inhibition efficiency for CS in the presence and absence of (a) alkaloid and (b) Non alkaloid extracts of *Solanum melongena leaves*.

	*AESML in 5 M Na_2CO_3 solution			**NAESML in 5 M Na_2CO_3 solution		
System	CR ($mg/cm^2/hr$)	θ	IE %	CR ($mg/cm^2/hr$)	θ	IE %
(Blank)	1.460	-	-	1.460	-	-
1.0 g/L	0.721	0.506	50.6	0.983	0.327	32.7
1.5 g/L	0.545	0.627	62.7	0.811	0.445	44.5
2.0 g/L	0.483	0.669	66.9	0.729	0.501	50.1
2.5 g/L	0.336	0.770	77.0	0.555	0.620	62.0
3.0 g/L	0.277	0.811	81.1	0.509	0.651	65.1

* (a), ** (b), CR = Corrosion rate, θ = Surface Coverage, IE% = Inhibition efficiency



(a) (b)

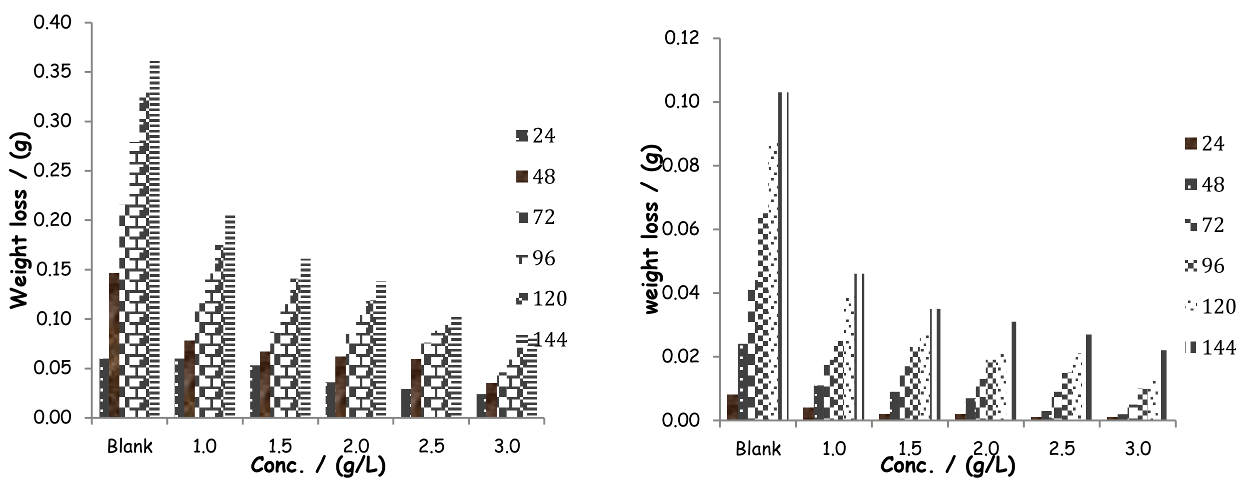
Figure 1: Variation of weight loss with immersion time for CS in the presence and absence of (a) alkaloid and (b) Non alkaloid extracts of *Solanum melongena leaves*.

Effect of temperature

The temperature of the system was varied across the inhibitor concentrations from which the activation energy for the

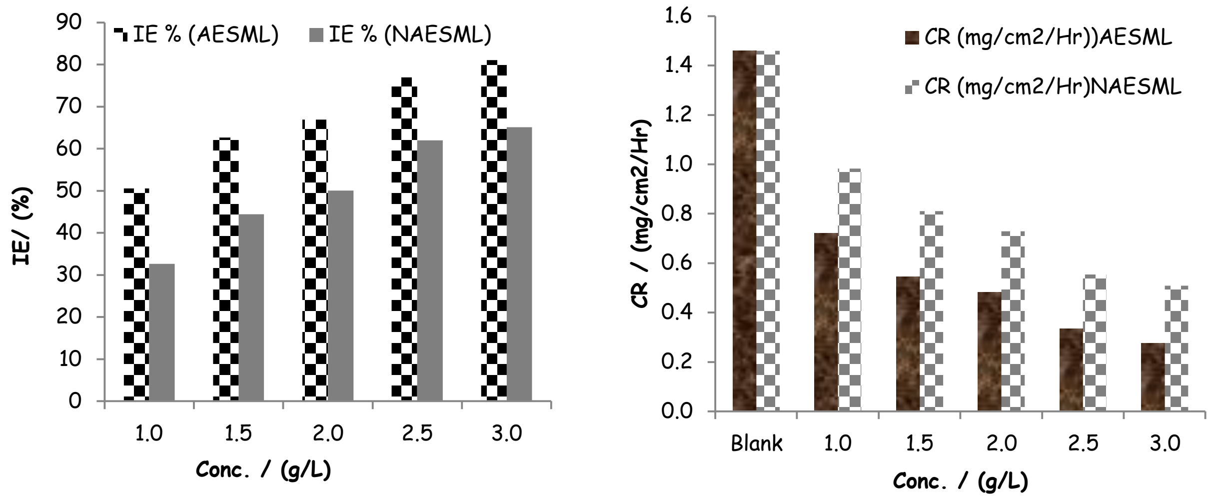
$$\ln R_c = \ln A - \frac{E_o}{RT} \qquad (3)$$

corrosion of mild steel in solutions of Na_2CO_3 was evaluated using the Arrhenius equation given by equation 3. Where Rc is the corrosion rate, Eo is the apparent effective activation energy, R is the general gas constant, and A is the Arrhenius pre-exponential factor (Singh et al., 2010, 2011,2012; Okafor *et al.*, 2008; Ananda *et al.*, 2005). Calculated values of Activation energy between 303 K and 333 K were obtained from the slope of Fig. 4 and presented in Table 2. The values obtained are greater than the value (6.9 $kJmol^{-1}$) obtained for the blank solution indicating that alkaloid and Non alkaloid extracts of *Solanum melongena leaves* retards the corrosion of carbon



(a) (b)

Figure 2: Variation of weight loss with Conc. for CS in the presence and absence of (a) alkaloid and (b) Non alkaloid extracts of *Solanum melongena leaves*.



(a) (b)

Figure 3: Variation of (a) IE (%) and (b) CR with Conc. for CS in in the presence and absence of alkaloid and Non alkaloid extracts of *Solanum melongena leaves*.

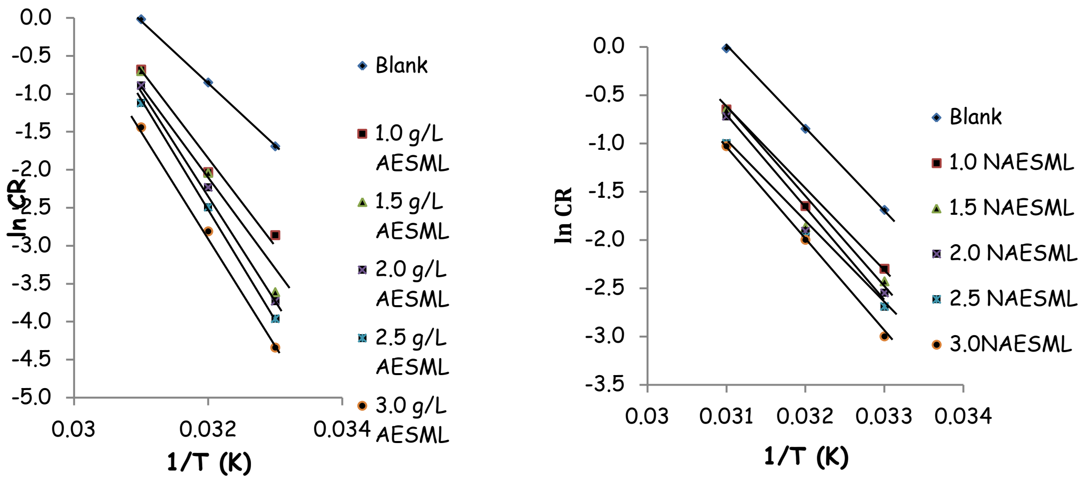
Table 3: Values of activation/thermodynamic parameters for carbon steel in 5 M Na_2CO_3 in the absence and presence of the plant extracts

	AESML				NAESML			
System	Ea (KJ/mol)	ΔH^*_{ads} (KJ/mol)	ΔS^*_{ads} (KJ/mol)	Q_{ads} (KJ/mol)	Ea (KJ/mol)	ΔH^*_{ads} (KJ/mol)	ΔS^*_{ads} (KJ/mol)	Q_{ads} (KJ/mol)
Blank	6.9	66.9	-76.4	-	6.9	66.9	-76.4	-
1.0 g/L	10.0	74.5	-62.0	-36.10	7.0	76.9	-76.4	-3.68
1.5 g/L	11.8	104.7	-35.9	-43.21	7.9	67.8	-76.8	-4.93
2.0 g/L	11.8	104.7	-27.9	-44.14	9.9	78.6	-87.0	-11.24
2.5 g/L	12.1	123.8	-24.1	-55.80	10.5	78.6	-91.4	-12.71
3.0 g/L	14.1	131.3	-21.4	-72.65	15.7	78.6	-99.3	-19.46

Ea= Activation energy ΔH_{ads}=Enthalpy of adsorption ΔS_{ads}=Entropyof adsorption Q_{ads} = Heat of adsorption

steel in Na_2CO_3 solution (El – Etre *et al.*, 2006), (Uwah *et al.*, 2012; Ananda and Singh, 2007). Since the Activation energy which is the energy required to oxidize metal is increased with inhibitor concentration, it implies that more energy has to be supplied to the system for the corrosion to take thus the observed decrease in corrosion rate. The values are also consistent with the data expected for the mechanism of physical adsorption (<80KJmol^{-1}) according to Oguzie *et al.* (2007), Patrick *et al.* (2006) and Okafor *et al.* (2008). Thermodynamic parameters; Enthalpy, ΔH_{ads} , Entropy ΔS_{ads} and Heat of adsorption Q_{ads} of alkaloid and Non alkaloid extracts of *Solanum melongena leaves* on carbon steel was calculated using equations 4 and 5 (transition state equation), which can be written as follows (Parameswari et al., 2012; Uwah *et al.*, 2012; Singh et al., 2010)

$$\frac{CR}{T} = log\ \frac{R}{Nh} + \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT}\log \qquad (4)$$

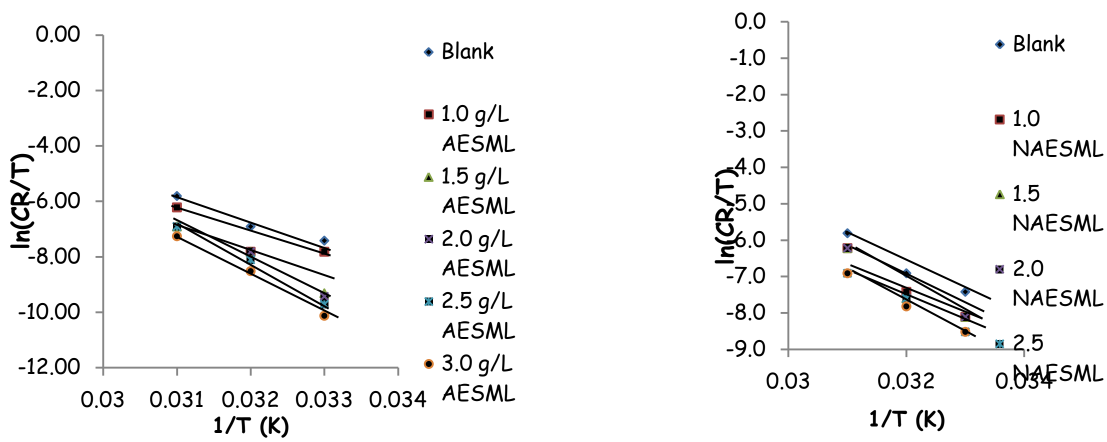


(a) (b)

Figure 4: Arrhenius plots for carbon steel in 5 M Na_2CO_3 solution in the absence and presence of AESML and NAESML extracts of *Solanum melongena leaves* at various temperatures

$$Q_{ads} = 2.303R \log \frac{\theta 2}{1-\theta 2} - \log \frac{\theta 1}{1-\theta 1} \times \frac{T1 \, x \, T2}{T2-T1} KJmol^{-1} \quad (5)$$

where Q^{ads} is the heat of adsorption, R is the universal gas constant, Θ_1 and Θ_2 are the degrees of surface coverage of the inhibitors at temperatures T_1 and T_2 respectively (Oguzie *et al.*, 2007). From equation 4 and 5 values of log (C_R/T) were plotted against $^1/_T$ as shown in Fig. 5 and from the slop and intercept of the plot, values of enthalpy and entropy of adsorption were calculated as shown in Table 2 (Okafor *et al.*, 2008). From the calculated values of ΔH * (Table 2), it can be deduced that the adsorption of the inhibitor on carbon steel surface is exothermic and the reaction becomes less exothermic with increase in inhibitor concentration. The negative values of Q_{ads} indicates that the degree of surface coverage decrease with rise in temperature, supporting the earlier proposed physisorption mechanism for alkaloid and Non alkaloid extracts of *Solanum melongena leaves*. The negative values for ΔS* shows the nonspontanous dissolution of the mild steel and and the increase in its value suggests decrease in disordering in the rate determining step (El-Etre and El-Tantawy, 2006).



(a) (b)

Figure 5: Transition state plots for carbon steel in 5 M Na_2CO_3 solution in the absence and presence of AESML and NAESML extracts of *Solanum melongena leaves* at various temperatures

Table 4: Adsorption parameters for carbon steel in 5 M Na_2CO_3 solutions containing AESML and NAESML extracts of *Solanum melongena* leaves at various temperatures

	AESML				NAESML			
Temp (K)	Equil. Const. k (g/L)	Corr. Coeff. (R^2)	Slope	ΔG^*_{ads} (KJ/mol)	Equil. Const. k (g/L)	Corr. Coef. (R^2)	Slope	ΔG^*_{ads} (KJ/mol)
303	23.981	0.9993	1.061	-444.22	9.569	0.9976	1.336	-315.78
313	9.066	0.9959	1.123	-318.40	5.711	0.9956	1.401	-251.65
333	3.050	0.9514	1.184	-171.33	4.953	0.9867	1.477	-245.85

ΔG^*_{ads} = Standard free energy of adsorption AESML= Alkaloid extract of *Solanum melongena* leaves NAESML= Non alkaloid extract of *Solanum melongena* leaves

Adsorption Isotherm consideration

The surface coverage (θ) values for different concentrations of the inhibitors in Na_2CO_3 medium was evaluated from the weight loss data. The data were tested graphically to find a suitable adsorption isotherm to describe the adsorption characteristics of the extracts (Saratha *et al.*, 2009; Singh *et al.*, 2011; Zuo *et al.*, 2004; Benali *et al.*, 2013. A plot of Log (Θ/C) against Log C (Fig. 6) shows a straight line (R>= 0.9) indicating that adsorption follows the Langmuir adsorption isotherm according to Uwah *et al.*, (2012; Saratha *et al.*, 2009; Oguzie *et al.*, 2007; Okafor *et al.*, 2008; Chaieb *et a*l., 2005). It is also observed that although these plots are linear, the gradients are never unity, contrary to what is expected for ideal Langmuir adsorption isotherm equation. Organic molecules having polar atoms or groups which are adsorbed on the metal surface may interact by mutual repulsion or attraction and this may be advocated as the reason for the departure of the slope values from unity (Ananda and Singh, 2007; Saratha *et al.*, 2009).

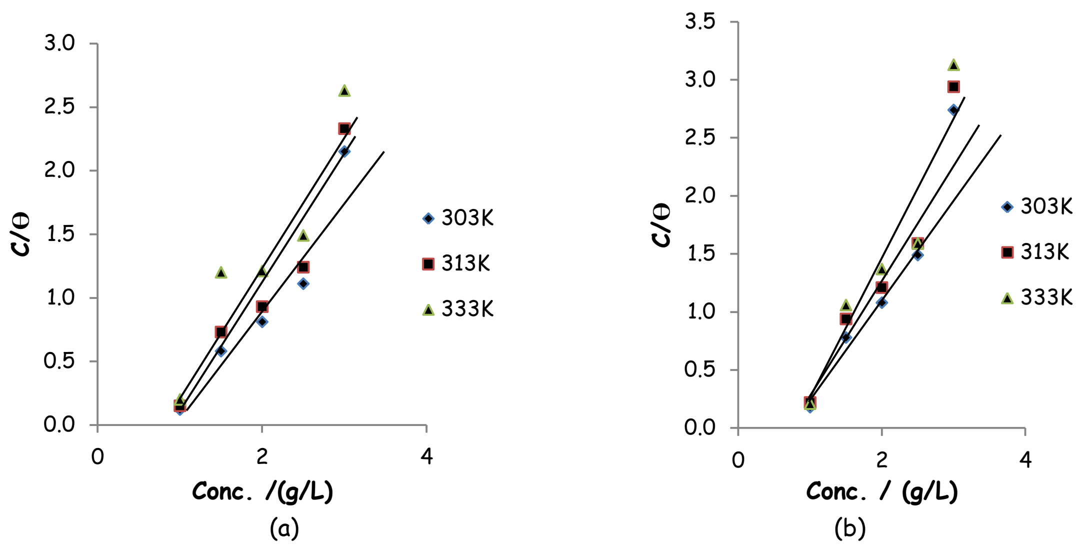


Figure 6: Langmuir adsorption isotherm for AESML and NAESML extracts of *Solanum melongena leaves* at various temperatures

Conclusion

The present study leads to the following conclusions:

The formulation consisting of 2g stock solution of alkaloid and non-alkaloids extracts of *Solanum melongena leaves* offers 81.1 % and 65.1 % inhibition efficiency to carbon steel immersed in 5 M Na2CO3 solution.

Adsorption study reveals that the mechanism of adsorption follows Langmuir

Isotherm which implies a monolayer adsorption calculated from the correlation coefficient of 0.999 approximate.

Thermodynamic study reveals that the inhibition process is a physical adsorption mechanism and not a chemisorption judging from the threshold values of the different thermodynamic parameters.

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