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Mangifera indica Leave Extracts as Organic Inhibitors on the Corrosion of Zinc Sheet in 5 M H_2SO_4 Solution

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KEYWORDS: Langmuir adsorption, *Mangifera indica*, Zinc sheet, Alkaloids, Inhibition efficiency, Tannins, H_2SO_4

ABSTRACT: The inhibition efficiency and adsorption characteristics of alkaloids, flavonoids and tannins extracts of *Mangifera indica* leaves in controlling corrosion of Zinc sheet in 5 M hydrogentetraoxosulphate (VI) acid solution has been evaluated by gasometric method. The formulation consisting of 2 g/L of extract offers 96.2%, 85.3% and 70.6% inhibition efficiencies (alkaloids, flavonoids and tannins respectively) at 30^0C to Zinc metal immersed in 5 M hydrogentetraoxosulphate (VI) acid solution. Judging from the trend in inhibition efficiency against temperature, it can be deduced that the adsorption process was physisoption being that corrosion rate increased while inhibition efficiency decreased with temperature. Adsorption mechanism followed the Langmuir adsorption isotherm being that the correlation coefficient was found to be approximately unity i.e. 0.9237. © JASEM

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Introduction

To be realistic, corrosion can only be reduced significantly or delayed to a reasonable extent. Controlling of the pH or ion concentration of the solution or controlling the metal solution interface had a number of ways to achieve the reduction in the rate of corrosion over the years. This is achieved through the addition of small quantity of chemicals called inhibitors, that either encourage film formation or form a barrier like layer on the metal surface and by so doing stop or slow down the rate of metal decomposition (Obot et al., 2011).

Throughout the ages, plants have been used by human beings for their basic needs such as shelters, production of food stuffs, fertilizers, flavors and fragrance, clothing, medicines and last but not the least, as corrosion inhibitors as noted by Benali et al., (2013). The use of corrosion inhibitors is the most economical and practical method in reducing corrosive attack on metals. Corrosion inhibitors are chemicals either synthetic or natural which when added in small quantity to an environment, decrease the rate of attack by the environment on metals (Lebrini et al., 2011).

In order to find out non-toxic, cheap and effective green corrosion inhibitors from renewable sources, in the present study, I report the Inhibition Properties and Adsorption Characteristics of Three Leave Extracts viz: Alkaloids, Flavonoids and Tannins of *Mangifera indica L*. on the Corrosion of Zinc in 5 M H_2SO_4 Solution. Literatures showed that these extracts of *Mangifera indica L* had never been studied for their corrosion inhibition properties and adsorption characteristics which triggered me in conducting this research on mild steel in 5 M H_2SO_4 using weight loss deduced from gasometric analysis.

MATERIAL AND METHODS

Preparation of Specimens: The Zinc sheet for the experiment was obtained from System Metals Inc., Calabar – Nigeria. The metal was press cut into sheets of dimension 2.0 cm x 0.08cm x 4 cm, then polished to a mirror finish with emery paper of grade #600 and #1200 and then degreased with acetone and stored in a desiccator.

Preparation of Crude Leaf Extract: The leaves of *Mangifera indica L* obtained from a plot in Murray, Calabar South – Nigeria were washed and dried in an Oven at 50^0C. The dried leaves were later grind into power with a very fine particle size. The powered leaves were extracted with a Soxhlet extractor using methanol for over days and the product obtained was evaporated using a water bath at 60^0C. The crude

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extract obtained was used to prepare alkaloids, flavonoids and tannins.

Preparation of Alkaloid, Flavonoids and Tannin extracts: Hydrochloric acid used during the experiment was less than 1 M, but not weaker than 0.1 M. 15g of the methanol extract was partitioned between 100 ml of chloroform and 0.1 M HCl solution in a separating funnel. Two non-homogeneous layers were obtained and the top fraction was basified with ammonia solution and a white precipitate formed in the solution was indicative of the presence of alkaloids. Addition of chloroform to the basic solution produced two nice layers of which the lower one is the organic component (alkaloids).The chloroform layer was separated from the mixture and distilled off while 2g of the alkaloid was weighed out for the experiment.

Flavonoids were determined by weighing 2g of the crude extract into a beaker and extracted with 50 cm^3 of 100% methanol at room temperature for about 2 hours. The solution was filtered using a filter paper while the filtrate was evaporated to dryness over a water bath.

Tannins were obtained by extracting the powdered leaves with acetone and left for 24 hours after which the mixture was filtered with filter paper. The product obtained was condensed with a rotary evaporator and subsequently dried with freeze drier to obtain Tannin fraction.

Gasometric Method and Procedure: Polished Zinc specimens in triplicate were immersed in 100 ml of the solutions containing various concentrations (0.5 g/L, 1.0 g/L, 2.5 g/L, 4.0 g/L and 7.5 g/L) of the inhibitor for 1 hour each using a gasometric assembly at temperatures of 303, 313 and 323K. The weight of the specimens before and after immersion was determined using weighing balance, after being washed with double distilled water, rinsed with ethanol and dried with acetone. The inhibition efficiency was calculated from equation 1:

$$IE\ (\%) = 100\ [1 - (\frac{W2}{W1})]\ \% \qquad 1$$

where W_1 is the corrosion rate in the absence of the inhibitor, and W_2 is the corrosion rate in the presence of the inhibitor.

RESULTS AND DISCUSSION

Effect of inhibitor concentration: From Table 1a - c, it is noticed that corrosion rate decreases as inhibitor concentration increases (Figs. 1a – c) and inhibition efficiency increases with increase in extract concentration as well as decrease in temperature. This suggests that the methanolic extract of *Mangifera indica L* significantly reduce the corrosion of Zinc (Obot et al., 2011). FIG.2a - c shows the variation of inhibition efficiency with extract concentration for Zinc in 5 M H_2SO_4 solutions containing AEMIL (Alkaloid extract of *Mangifera indica L)*, FEMIL (Flavonoid extract of *Mangifera indica L)* and TEMIL (Tannin extracts of *Mangifera indica L*). This indicates that the plant extracts mitigate the corrosion of Zinc in 5 M H_2SO_4 solutions and that the extent of corrosion inhibition depends on the amount of the extract present (Xiaoyuan and Singh, 2010). It is also observed that inhibition efficiency increases in the order AEMIL > FEMIL > TEMIL .This suggests that alkaloid extract of *Mangifera indica L* are adsorbed more on the metal surface thereby protecting metal from the action of corrodent. This is in line with the previous report by Singh and Anaya (2007). This phyto-chemical is believed to be adsorbed on to the metal surface through its basic oxygen present in the heterocyclic ring of the compounds

Table. 1: Calculated values of Corrosion rate, Surface coverage and Inhibition efficiency from weight loss hydrogen evolution of (a) Alkaloids (b) Flavonoids and (c) Tannins on Zinc metal in 5M H_2SO_4 solution.

	Corrosion Rate (cm/min)			Surface Coverage (θ)			Inhibition Efficiency (%)		
Extract Conc	303K	313K	**323K**	303K	313K	**323K**	303K	313K	**323K**
Blank	0.135	0.260	**0.347**	-	-	-	-	-	-
0.5 g/L	0.065	0.140	**0.202**	0.52	0.46	**0.42**	51.9	46.2	**41.9**
1.0 g/L	0.063	0.126	**0.192**	0.53	0.52	**0.45**	53.1	51.7	**44.5**
2.5 g/L	0.031	0.070	**0.115**	0.77	0.73	**0.67**	77.0	73.1	**66.8**
4.0 g/L	0.019	0.056	**0.101**	0.86	0.79	**0.71**	85.9	78.6	**70.9**
7.5 g/L	0.005	0.040	**0.094**	0.96	0.85	**0.73**	96.2	84.7	**72.9**

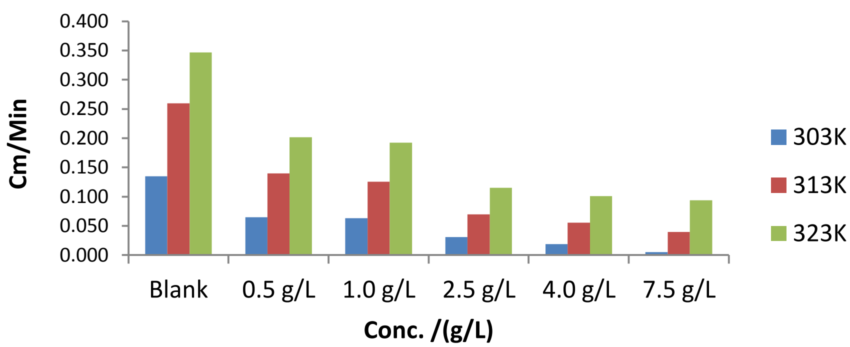
(a)

	Corrosion Rate (cm/min)			Surface Coverage (θ)			Inhibition Efficiency (%)		
Extract Conc	303K	313K	**323K**	303K	313K	**323K**	303K	313K	**323K**
Blank	0.135	0.260	**0.347**	-	-	-	-	-	-
0.5 g/L	0.071	0.152	**0.215**	0.47	0.41	**0.38**	47.3	41.4	**37.9**
1.0 g/L	0.061	0.123	**0.175**	0.55	0.53	**0.49**	54.7	52.8	**49.5**
2.5 g/L	0.050	0.095	**0.153**	0.63	0.63	**0.56**	63.0	63.4	**55.8**
4.0 g/L	0.032	0.074	**0.133**	0.76	0.71	**0.62**	76.4	71.4	**61.6**
7.5 g/L	0.020	0.059	**0.123**	0.85	0.77	**0.64**	85.3	77.2	**64.4**

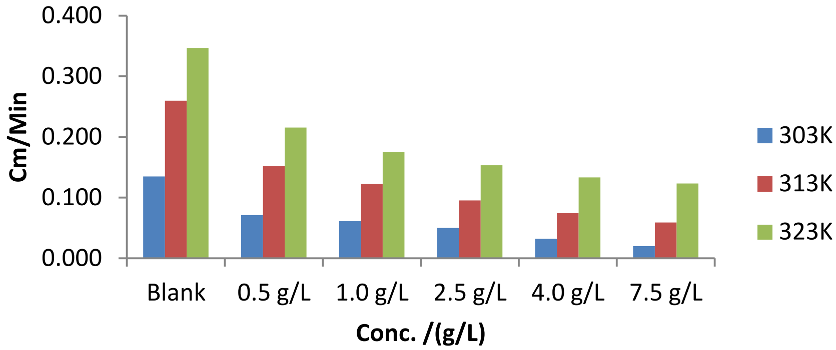
(b)

	Corrosion Rate (cm/min)			Surface Coverage (θ)			Inhibition Efficiency (%)		
Extract Conc	303K	313K	**323K**	303K	313K	**323K**	303K	313K	**323K**
Blank	0.135	0.260	**0.347**	-	-	-	-	-	-
0.5 g/L	0.092	0.179	**0.254**	0.32	0.31	**0.27**	31.6	31.3	**26.7**
1.0 g/L	0.074	0.154	**0.231**	0.45	0.41	**0.33**	44.9	40.9	**33.3**
2.5 g/L	0.052	0.132	**0.211**	0.61	0.49	**0.39**	61.3	49.0	**39.0**
4.0 g/L	0.047	0.100	**0.197**	0.65	0.61	**0.43**	65.0	61.5	**43.3**
7.5 g/L	0.040	0.085	**0.148**	0.71	0.67	**0.57**	70.6	67.4	**57.3**

(c)



(a)



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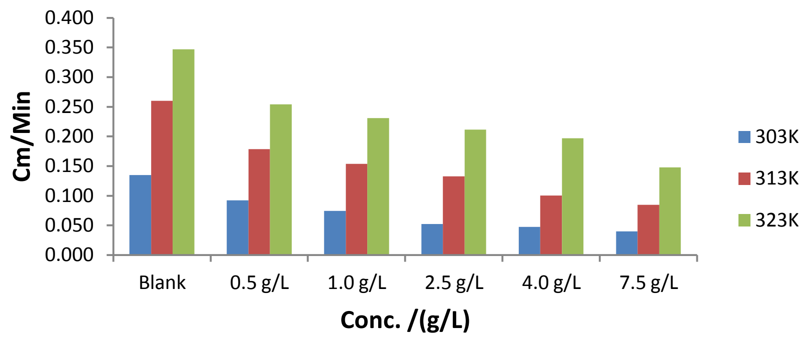

(b)

Fig. 1: Variation of corrosion rate with extract concentration for (a) alkaloids (b) flavonoids and (c) tannins on Zinc sheet in 5 M H_2SO_4 solutions.

Effect of Temperature on inhibitor concentration: In Table 1 the inhibition efficiency was found to decrease with rise in temperature. The temperature of the system was varied across the AEMIL, FEMIL and TEMIL concentrations studied. It was observed that the inhibition efficiency is temperature dependent; this is evident in the general decrease in efficiency with temperature. This also suggests that the adsorption phenomenon is a physical adsorption. The above observation agrees with that of Lebrini et al., (2011) which indicates that the mechanism is a physical adsorption mechanism

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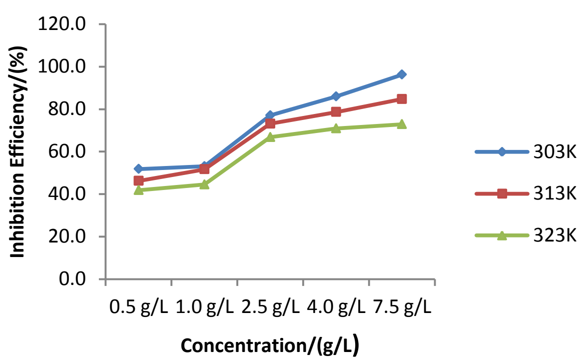

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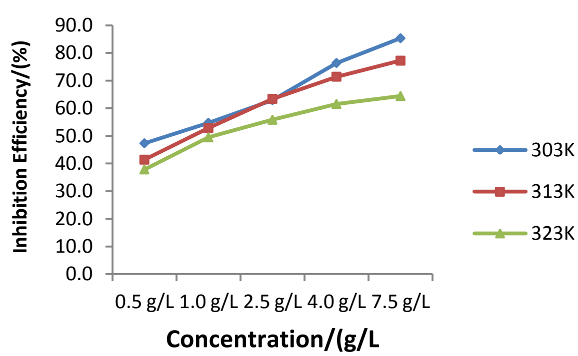

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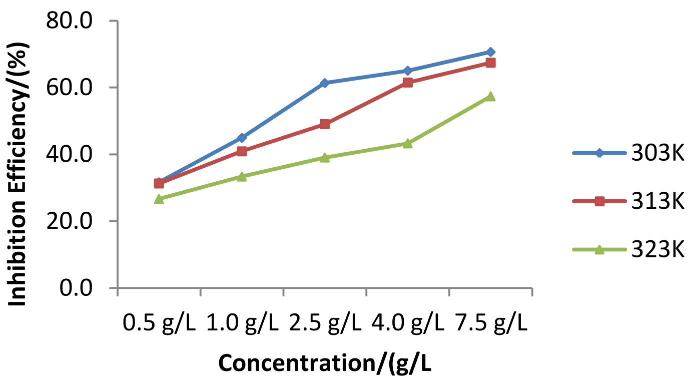
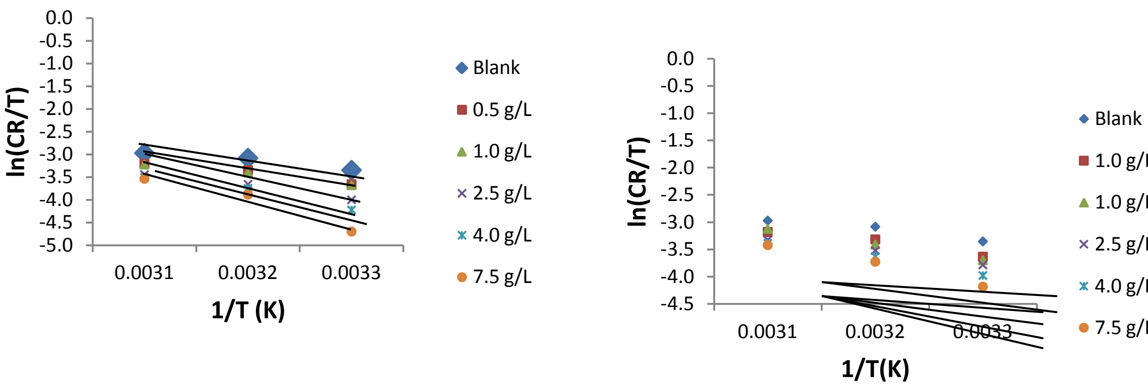


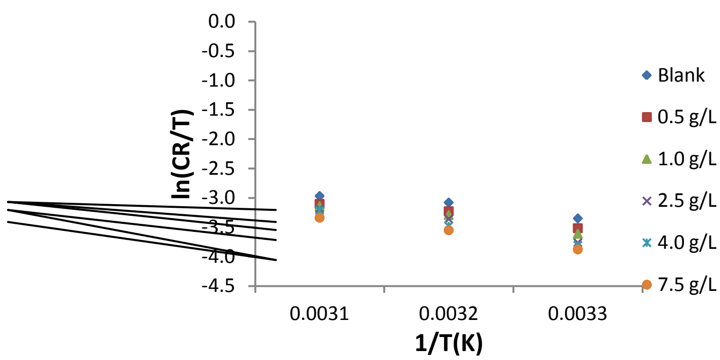
(c)

Fig. 2: Variation of inhibition efficiency with extract concentration for (a) alkaloids (b) flavonoids and (c) tannins on Zinc coupons in 5 M H_2SO_4 solutions.

3Thermodynamic consideration



(a)



(b)

Fig. 2: Eyring transition state plots for Zinc in 5 M H_2SO_4 solutions in the absence and presence of (a) AEMIL, (b) FEMIL and (c) TEMIL

The activation energy for the data obtained in Table 2 was calculated out of the equation 2:

$$Ea = 2.303R \left[\frac{T1T2}{T2-T1} \ x \ log\frac{K2}{K1}\right] \quad (2)$$

Where Ea is the activation energy, R is the gas constant, T is the standard temperature and K represent the corrosion rates.

Increased activation energy (Ea) in inhibited solutions compared to the control experiment implies that the inhibitor is physically adsorbed on the metal surface (Bendahou et al., 2006). It is observed from Table 2 that Ea values were higher in the presence of leaf extracts compared to the control solution leading to an increase in their corrosion rates.. The Ea values support the earlier proposed physisorption mechanism. The values for the enthalpy and entropy of adsorption were obtained from the plot of log(CR/T) against 1/T derived from the transition state equation 3:

$$\log\frac{CR}{T} = log\ \frac{K}{Nh} + \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \qquad 3$$

where CR is the corrosion rate, R is the gas constant, N is the Avogadros constant, h is the plank constant, K the Bolzman constant, T is the absolute temperature, ΔS is the change in entropy and ΔH is the change in enthalpy (Singh et al., 2012).

The positive values of ΔH reveals that the dissolution of the metal is endothermic (Ugi et al., 2014).This also suggests that mild steel dissolution requires less energy in 5 M H_2SO_4 in the presence of all the extracts. The change in entropy ΔS, was found to be greater than zero. This implies that the reaction is irreversible. It is obvious that, the complete desorption of the inhibitor is difficult. The shift towards negative values of entropy implies that disordering decreases on going from reactants to the activated complex according to Singh *et al.,* (2012).

Table 2: Thermodynamic data for Zinc in 5 M H_2SO_4 in the blank and presence of the leave extracts of *Mangifera indica L*

AEMIL			FEMIL			TEMIL		
ΔH^*_{ads} (kJ/mol)	ΔS^*_{ads} (kJ/mol)	Ea (kJ/mol)	ΔH^*_{ads} (kJ/mol)	ΔS^*_{ads} (kJ/mol)	Ea (kJ/mol)	ΔH^*_{ads} (kJ/mol)	ΔS^*_{ads} (kJ/mol)	Ea (kJ/mol)
15.65	-26.63	56.85	15.88	-26.86	56.85	17.21	-28.19	56.85
18.96	-29.94	81.28	18.87	-29.85	78.30	19.38	-30.36	70.92
18.96	-29.96	83.97	65.56	-76.54	86.39	19.38	-30.36	76.39
23.11	-34.09	107.06	69.56	80.54	93.97	24.11	-35.09	82.5
29.64	-40.62	115.40	81.36	-92.34	102.95	24.69	-35.67	88.13
48.26	-59.24	125.00	96.75	-107.73	109.79	22.46	33.44	97.53

Adsorption characteristics: The possible adsorption mode was investigated by testing the experimental data obtained with several adsorption isotherms (Saratha and Menakshi, 2010). Such investigations will greatly throw more light to understanding of the corrosion inhibition mechanism. It is suspected that the inhibition of metal corrosion occurred as a result of the adsorption of the active principles of the extracts onto the metal surface. The experimental data for AEMIL, FEMIL and TEMIL fitted the Langmuir adsorption isotherm model. The Langmuir adsorption isotherm is given by the equation 4:

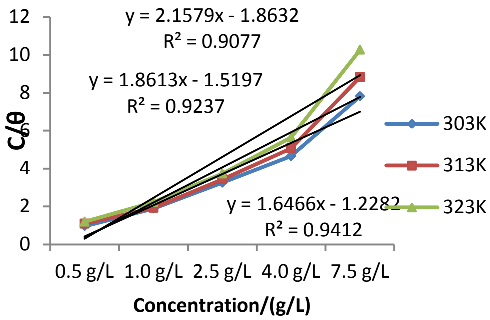
$$\frac{C}{\theta} = \frac{1}{K} + C \qquad 4$$

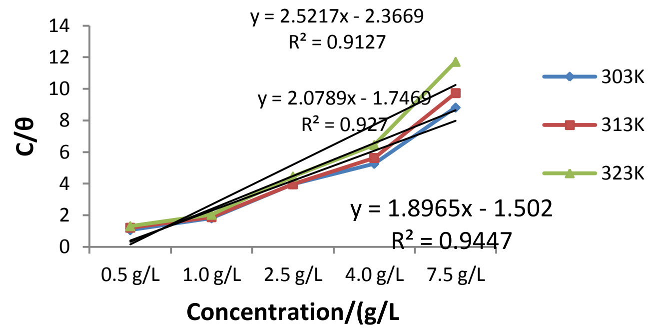
where, θ is the surface coverage, C is the concentration, K is the equilibrium constant of adsorption process (Ugi, 2014; Singh et al., 2010). The plot of C/θ against C is shown in FIG 1a - c. Linear plot were obtained across the temperatures studied. The values of the adsorption rate constant (K_{ads}) from the isotherm and the correlation factors (R) were estimated from Fig 1. The correlation factors obtained from the plots were close to unity (0.9077 to 0.9412) for AEMIL, (0.9127 to 0.9447) for FEMIL and (0.9147 to 0.9746). This indicates strict adherence to the principles underlying the derivation of Langmuir isotherm (Ugi, 2014).

The inhibition process is generally attributed to adsorption of inhibitor species unto the metallic surface. The linear plots have the value of slops ranging between 1.64 – 2.88 for the experimental temperatures of 303, 313 and 323 K. This results could also indicate that some constituents of *Mangifera indica* leaves extracts units occupied more than one adsorption site on the zinc sheet surface. Adherence to Langmuir suggests formation of monolayer of adsorption and no interaction between the adsorbed species (Benali et al., 2013; Singh et al., 2012; Fatemeh et al., 2012).

The highest inhibition efficiencies for AEMIL, FEMIL and TEMIL obtained at 7.5 g/L are 96.2%, 85.3% and 70.6% respectively. The order for the corrosion rate in the presence of the inhibitor for the extracts is Tannins > Flavonoids > Alkaloids.

(a)





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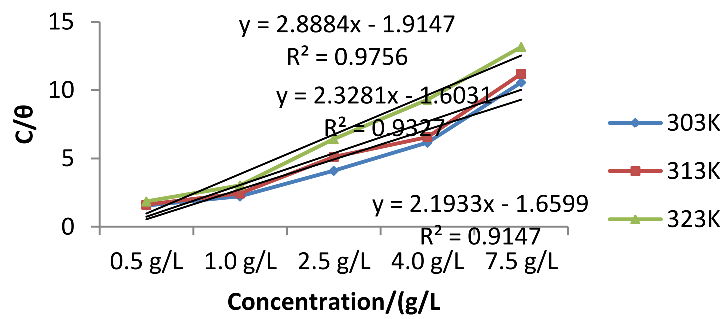

(c)

Fig.3: Langmuir adsorption isotherm for (a) Alkaloids (b) Flavonoids and (c) Tanning on Zinc coupons in 5 M H_2SO_4

Conclusion:Alkaloids, Flavonoids and Tannin extracts of *Mangifera indica* leaves has been confirmed as reliable corrosion inhibitors for Zinc sheets in 5.0 M H_2SO_4(96.2%, 85.3% and 70.6%) respectively, over a wide range of concentrations (0.5g/L – 7.5g/L). Inhibition efficiency increases for longer immersion periods at an increasing concentration. The adsorption of active components of inhibitor obeys Langmuir adsorption isotherm confirming that the inhibitor acts through a simple physical adsorption mechanism.

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