Corrosion Inhibition Performance Of Alkaloid Extracts Of Calendula Officinalis (Pot Marigold) Plant On Aluminium, Carbon Steel And Zinc In 5 M Nitric Acid Solution

Ugi, B. U.

Obeten, M. E.

Department of Chemical Sciences,
Cross River University of Technology, Calabar, Nigeria

Magu, T. O.

Uwah, I. E.

Department of Pure and Applied Chemistry,
University of Calabar, Calabar, Nigeria

Abstract: Alkaloid extract of Pot Marigold (Calendula officinalis) leaves was investigated as corrosion inhibitor of carbon steel, aluminium and zinc metals in 5 M HNO₃ acid solutions using conventional weight loss, electrochemical polarization and electrochemical impedance spectroscopy studies. The weight loss results showed that the plant extract is an excellent corrosion inhibitor to all the metals tested, electrochemical polarization data revealed the mixed mode of inhibition and the results of electrochemical impedance spectroscopy have shown that the change in the impedance parameters, charge transfer resistance and double layer capacitance, with the change in concentration of the extract is due to the adsorption of active molecules leading to the formation of a protective layer on the surface of they metals. A physical adsorption mechanism was recorded by the inhibitor /metal interface and the Langmuir adsorption isotherm was well obeyed judging from the good correlation of the data to the isotherm. The inhibitor proved to be a stabled one on both metals and a spontaneous reaction process was recorded from the data of the Gibbs free energy.

Keywords: Weight loss, Langmuir isotherm, Gibbs free energy, anodic slope, inhibition efficiency, Calendula officinalis.

I.   INTRODUCTION

The use of plant extracts as inhibitors for the corrosion of metals/alloys, has gained very wide interest among researchers in recent times (Eddy et al., 2010; Ugi et al., 2016) Acid solutions are often used in industries for cleaning, discaling, and pickling of metallic structures. These are processes which are normally accompanied by considerable dissolution of the metal (Nnanna *et al.* 2010; Brinda et al., 2015). Introduction of inhibitors is one of the methods for protecting corrosion especially in acid solutions to prevent unexpected metal dissolution and acid consumption (Zhanga et al., 2009) The use of chemical as inhibitors has been minimized because of the environmental consequences. Plant extracts have become important because they are environmentally acceptable, inexpensive, readily available and renewable sources of materials. In very many cases the inhibitive effect of some plants extracts has been attributed to the presence of alkaloids

in their chemical constituents (Loto *et al.* 2011; Oguzie et al., 2009; Ochoa et al., 2013). *Calendula officinalis* is a plant in the genus Calendula of the family Asteraceae. It is probably native to southern Europe, though its long history of cultivation makes its precise origin unknown, and it may possibly be of garden origin. *Calendula officinalis* is a short-lived aromatic herbaceousperennial, growing to 80 cm (31 in) tall, with sparsely branched lax or erect stems. The leaves are oblong-lanceolate, 5–17 cm (2–7 in) long, hairy on both sides, and with margins entire or occasionally waved or weakly toothed. The inflorescences are yellow, comprising a thick capitulum or flowerhead 4–7 cm diameter surrounded by two rows of hairy bracts. Pot marigold florets are edible. They are often used to add color to salads or added to dishes as a garnish and in lieu of saffron. The leaves are edible but are often not palatable. They have a history of use as a potherb and in salads. The present study is aimed at investigating the inhibiting effects of alkaloid extract of Pot Marigold

(*Calendula officinalis)* leaves (AECOL) on the corrosion of mild steel in HCl solution at different temperatures using gravimetric and gasometric techniques.

II. EXPERIMENTAL

A. DRESSING OF WORKING ELECTRODES

The electrodes (Carbon steel, aluminium and zinc) were resized to a dimension of 4 cm x 0.08 cm x 2.0cm for weight loss analysis; and 1 cm^2 x 1 cm^2 for the electrochemical measurements (electrochemical impedance spectroscopy and potentiodynamic polarization). The working electrode obtained from System Metal shop in Calabar, Nigeria was carefully polished with different grades of emery paper to obtain a mirror surface, washed with distilled water, rinsed with ethanol, degreased in acetone and air dried then stored in a desiccator.

B. PREPARATION OF INHIBITORS

Fresh samples of Pot Marigold (*Calendula officinalis)* leaves were collected from a bush in Obudu, Cross River State, Nigeria. An MEMMERY UNB – 500 laboratory Oven was used to dry the leaves at a temperature of 50ºC to avoid loss of major organic components of the plant. They were then ground to obtain a fine texture for extraction. 250 g powdered sample was continually extracted using 200 cm3 absolute methanol in an extractor (Soxhlet) for 72 hours. The extract obtained was later heated on a STUART SB – 162 heat stirrer machine at a temperature of 323 K until most of the ethanol evaporated. 35 g crude thanol extract was shared into 200 ml chloroform and 200 ml 0.5 M HCl acids through the aid of a separating funnel and allowed for 90 minutes. The tailing fraction was collected, evaporated of chloroform and used as the non-alkaloid fraction. The HCl solution in the float fraction was diluted with ammonia solution and this was taken well above pH 7. Chloroform was immediately added and the layer with the chloroform eventually taken away for the funnel and distilled off. A small quantity of moderately pure alkaloids was obtained and used as the Alkaloid fraction. The content thus obtained was filtered and preserved. 2.5 g/L was measured out of the stock solution for the preparation of different concentrations of inhibitor (0.5 g/L, 1.5 g/L, 2.0 g/L, 3.0 g/L and 5.0 g/L) which were now used for the corrosion inhibition investigation.

C. WEIGHT LOSS METHOD

Gravimetric analysis were carried out to study the effect of addition of different concentrations of inhibitor on the aluminium, carbon steel and zinc corrosion in 5 M HNO$_3$ at different temperatures (313 - 333K). The test coupons were weighed and immersed in 100 ml electrolytic solution for 1 hour in the absence and presence of various concentration of inhibitor at studied temperatures. After immersion time the coupons of various metals were picked out, cleaned with distilled water, and dried in hot air oven for 5 minutes. The specimens were weighed using electronic balance (sensitivity

up to 0.0001gm). The corrosion rate (R$_i$) in mgcm^{-2} h^{-1} of inhibitor were obtained graphically from a plot of weight loss against time. Inhibition efficiency (%IE) of inhibitors were calculated from the following equation 1:

$$IE\% = \left(\frac{R_o - R_i}{R_o} \right) x100 \qquad \text{........................ 1}$$

where R_o and R_i are the corrosion rates in the absence and presence of the plant extracts.

D. ELECTROCHEMICAL METHODS

Experiments were conducted using a conventional three-electrode cell assembly with the counter electrode made of a platinum foil and the reference electrode being a saturated calomel electrode (SCE) connected to the cell externally through a Luggin capillary tube positioned close to the working electrodes (carbon steel, aluminium and zinc) to minimize the ohmic potential drop. The glass cell was filled with 250 ml of the test solution and the working electrode immersed for 30 minutes prior to each experimental measurement to attain a steady state. EIS measurements were carried out over the frequency range of 100 kHz to 10 mHz with a signal amplitude perturbation of 5 mV at the corrosion potential. The potentiodynamic polarization sweeps were conducted at a sweep rate of 0.5 mV/s. The solution and metal coupon were changed after each sweeps. For each experimental condition, two measurements were performed to estimate the repeatability.

III. RESULTS

A. WEIGHT LOSS RESULT

The material loss expressed as the corrosion rate for the coupons (carbon steel, aluminium and zinc) in 5.0 M HNO$_3$ solutions containing different concentrations of alkaloid extracts of *Calendula officinalis* leaves (AECOL) as a function of inhibitor concentration is presented in Figs. 3.1a - c. This plots are in accordance with the works of Tosun and Ergun (2006), Vijayalakshmi et al., (2011), Lebrini et al., (2011). It is observed that the corrosion rates decreased with the increase in concentration of AECOL, indicating that the extent of inhibition is dependent on the amount of extract present (Loto et al., 2011; Saratha and Vasudha, 2010, Adeyemi and Olubomehin, 2010). The results obtained are shown in Table 3.1 and indicate that the plant extracts show a significant inhibitive effect on both metals in HNO$_3$ solutions. Also from Table 3.1, it is observed that the inhibition efficiencies increase with increase in AECOL concentration. This indicates that the phytochemical components of the extracts are adsorbed onto the metal surface resulting in the blocking of the reaction sites, and protection of the mild steel surface from the attack of the corrosion active ions in the acid medium (James and Akaranta 2010, Adeyemi and Olubomehin, 2010, Nnanna et al., 2010). Comparing the inhibition efficiencies of the extract on the different metals, it is observed that the efficiencies follow the trend: Carbon steel (98.0 %) > Zinc (86.9 %) > Aluminium (76.5 %). This shows that the yield of the phytochemicals in the plant extracts

responsible for the inhibition of the corrosion reactions depend not only on the plant type but also on the type of surface. This finding is in line with previous reports (Chidiebere et al., 2015, Ferreira et al., 2004, Alaneme 2011).
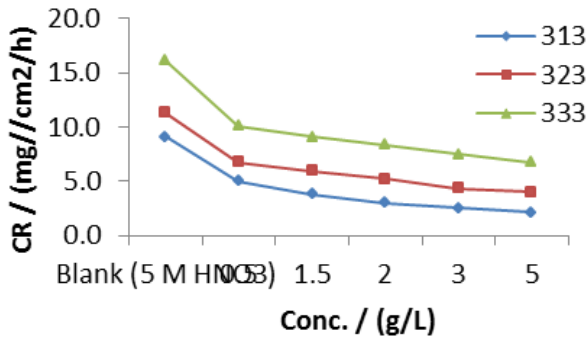

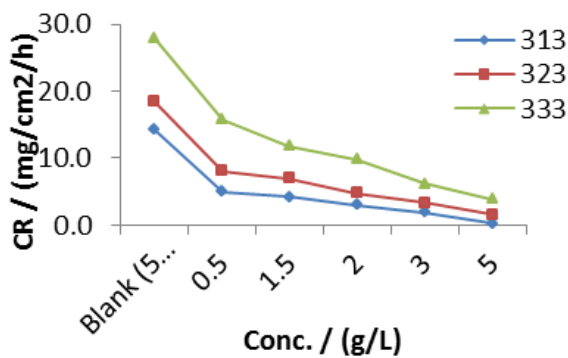*Figure 3.1a: Corrosion rate of Aluminium against inhibitor concentrations*

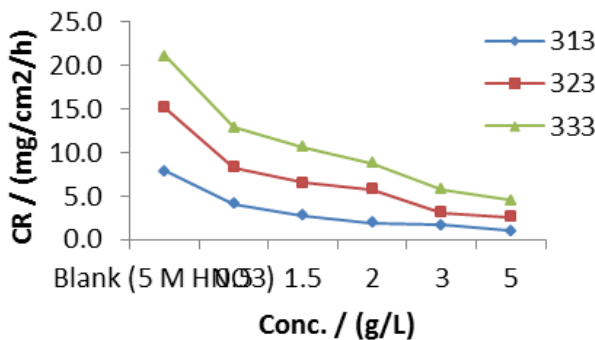*Figure 3.1b: Corrosion rate of carbon steel against inhibitor concentrations*

Figure 3.1c: Corrosion rate of Zinc against inhibitor concentrations

Table 3.1: Corrosion parameters of aluminium, carbon steel and zinc in 5 M HNO₃ solution in the absence and presence of AECOL at different concentration and temperatures, obtained from gravimetric analysis.

	Conc. (g/L)	CR (mg/cm2/h)			θ			% IE		
		313K	323K	333K	313 K	323 K	333 K	313 K	323 K	333 K
ALUMINIUM	Blank (1 M HCl)	9.101	11.320	16.160	-	-	-	-	-	-
	0.5 g/L	5.011	6.771	10.090	0.449	0.402	0.376	44.9	40.2	37.6
	1.5 g/L	3.778	5.980	9.105	0.585	0.472	0.437	58.5	47.2	43.7
	2.0 g/L	2.999	5.219	8.354	0.670	0.539	0.483	67.0	53.9	48.3
	3.0 g/L	2.521	4.333	7.472	0.723	0.617	0.538	72.3	61.7	53.8
	5.0 g/L	2.135	3.999	6.761	0.765	0.647	0.582	76.5	64.7	58.2
CARBON STEEL	Blank (1 M HCl)	14.171	18.376	27.910	-	-	-	-	-	-
	0.5 g/L	5.000	8.090	15.744	0.647	0.560	0.436	64.7	56.0	43.6
	1.5 g/L	4.177	6.997	11.796	0.705	0.619	0.577	70.5	61.9	57.7
	2.0 g/L	3.016	4.713	9.793	0.787	0.744	0.649	78.7	74.4	64.9
	3.0 g/L	1.894	3.278	6.195	0.866	0.822	0.778	86.6	82.2	77.8
	5.0 g/L	0.286	1.542	3.847	0.980	0.916	0.862	98.0	91.6	86.2
ZINC	Blank (1 M HCl)	7.896	15.090	21.100	-	-	-	-	-	-
	0.5 g/L	4.121	8.274	12.840	0.478	0.452	0.391	47.8	45.2	39.1
	1.5 g/L	2.759	6.488	10.576	0.651	0.570	0.499	65.1	57.0	49.9
	2.0 g/L	1.924	5.761	8.758	0.756	0.618	0.585	75.6	61.8	58.5
	3.0 g/L	1.709	3.101	5.727	0.784	0.794	0.729	78.4	79.4	72.9
	5.0 g/L	1.038	2.558	4.517	0.869	0.830	0.786	86.9	83.0	78.6

B. ELECTROCHEMICAL IMPEDANCE RESULTS

The corrosion measures of carbon steel, aluminium and zinc in 5.0 M HNO₃ solutions, in absence and the presence of various concentrations of alkaloid extracts of *Calendula officinalis* leaves were also investigated by EIS technique. The resultant Nyquist plots are shown in Fig 3.2a - c. Again in this case also, there was a gradual increase in the diameter of each semicircle of the Nyquist plot due to the increase in the number of inhibitive molecules present in the extract when the concentration was raised from 0.5 to 5 g/L (Hui et al., 2013; Khaled and Al-Mobarak, 2012). This increase of the diameters has clearly shown that the R_{ct} values were also increased from 110 – 450 Ohms.cm² (aluminium), 379 – 1100 Ohms.cm² (carbon steel) and 290 – 667 Ohms.cm² (zinc) at the highest concentration of 5.0 g/L due to the formation and gradual improvement in compactness of the barrier layer of the inhibitive molecules adsorbed, and as a result the acid corrosion rates of the metals were steadily decreased (Kamal and Gopolakrishma, 2012; Ugi et al., 2016).
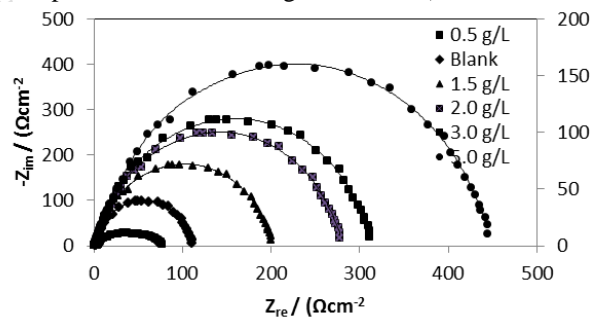

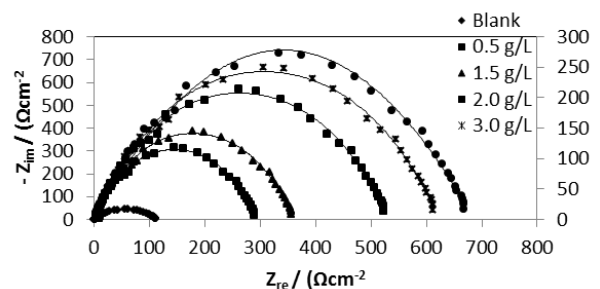*Figure 3.2a: Nyquist plots for the adsorption of AECOL on Aluminium in 5 M HNO₃*

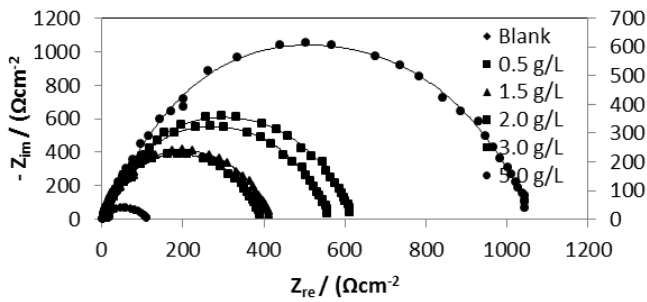*Figure 3.2b: Nyquist plots for the adsorption of AECOL on Zinc in 5 M HNO₃*

Figure 3.2c: Nyquist plots for the adsorption of AECOL on carbon steel in 5 M HNO₃

Table3.2 embodies various parameters such as R_{ct}, double layer capacitance (C_{dl}) and IE (E_R %). It was observed that there was a gradual decrease in values of C_{dl} with increase in the concentration from 0.5 to 5.0 g/L of the extract. This considerable decrease has confirmed that the inhibitive molecules of the extracts were adsorbed on the surface and have decreased the roughness of both metal surfaces created due to corrosion by 5.0 M HNO₃ solution (Jeeval et al., 2014, Gopal et al., 2012,. The values of E_R % were calculated by using the equation 2:

$$IE\% = \frac{Ri_{ct} - Ro_{ct}}{Ri_{ct}} \times 100 \qquad \text{....................... 2}$$

It is obvious that the impedance behaviour profile was unaltered by the change in alkaloid extracts of *Calendula officinalis* leaves concentration, indicating a similar metal disolution mechanism with and without the extracts (Khaled and El-Sharik, 2013) At all concentrations of the inhibitor, the high frequency semicircle represent the parallel combination of the double layer capacitance (C_{dl}) and a charge transfer resistance (R_{ct}) which is associated with some steps in the metal disolution that is inhibited in the presence of the extracts considering the fact that charge transfer resistance exhibited its maximum inhibtion efficiency for the metals (Ugi et al., 2016, Hui et al., 2013, Khaled and El.Sharik, 2013.

	Conc. (g/L)	Rct (Ωcm⁻²)	Cdl (μFcm⁻²)	% IE
	Blank (1 M HCl)	90	0.020	-
ALUMINIUM	0.5 g/L	110	0.016	18.1
	1.5 g/L	200	0.007	55.0
	2.0 g/L	280	0.004	67.9
	3.0 g/L	310	0.003	71.0
	5.0 g/L	450	0.002	80.0
CARBON STEEL	Blank (1 M HCl)	100	0.011	-
	0.5 g/L	397	0.002	73.6
	1.5 g/L	409	0.002	75.6
	2.0 g/L	568	0.001	82.4
	3.0 g/L	610	0.0009	83.6
	5.0 g/L	1100	0.0004	90.9
ZINC	Blank (1 M HCl)	110	0.048	-
	0.5 g/L	290	0.0009	62.1
	1.5 g/L	350	0.0005	68.6
	2.0 g/L	520	0.0002	78.9
	3.0 g/L	605	0.0002	81.8
	5.0 g/L	667	0.0001	83.5

Table 3.2: Results from IES experiment showing charge transfer resistance, double layer capacitance and %IE for the adsorption of AECOL on aluminium, carbon steel and zinc.

C. POTENTIODYNAMIC POLARIZATION RESULTS

The polarization behaviour of carbon steel, zinc and aluminum electrodes in 5.0 M HNO₃ solutions in the absence and presence of different concentrations of alkaloid extracts of *Calendula officinalis* leaves at a scan rate of 1.0 mV s_1 and at 25 ± 1 C is shown in Fig. 3.3a - c. These polarization curves demonstrate, as a first sight, that in presence of alkaloid extracts of *Calendula officinalis* leaves the cathodic and anodic branches of the polarization curves are shifted towards lower currents to similar extent, probably as a consequence of the blocking effect of the adsorbed inhibitor molecules (Khaled and Gopolakrishma, 2012). The observed decrease in cathodic and anodic currents was the greatest for carbon steel electrode followed by zinc and then aluminium. As it can be seen from Table 3.3, the anodic and cathodic reactions are affected by the AECOL. Based on this result, AECOL inhibit corrosion by controlling both anodic and cathodic reactions (mixed-type inhibitors). Meaning that the addition of AECOL reduces the anodic dissolution of all the metals and also retards the cathodic reactions. The curvature of the anodic polarization curves may be attributed to passivation and pitting (Eddy et al., 2010; Hui et al., 2013, Jeeval et al., 2014). It follows from Fig. 3.3a - c. that the shapes of the polarization plots for inhibited electrodes are not substantially different from those of uninhibited electrodes. The presence of each inhibitor decreases the corrosion rate but does not change other aspects of the behaviour. This means that the inhibitor does not alter the electrochemical reactions responsible for corrosion (Khaled and E/ - Sherik, 2013). The inhibitive action of this inhibitor on the three metals therefore may be related to its adsorption and formation of a barrier film on the electrode surface, protecting them from corrosion.
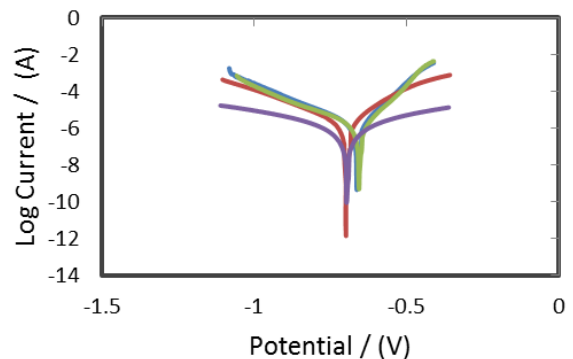

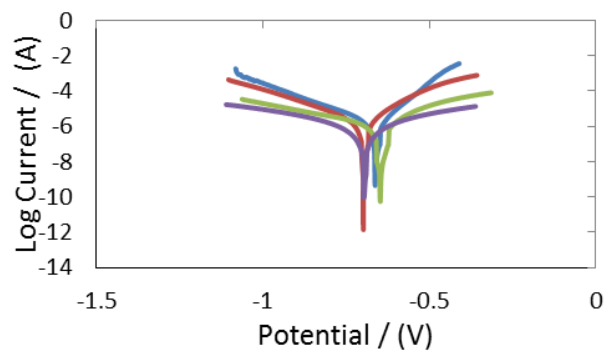*Figure 3.3a: Tafel plots for the adsorption of AECOL on aluminum in 5 M HNO₃*

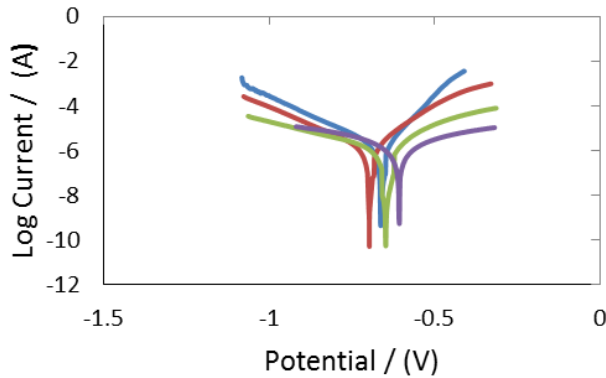*Figure 3.3b: Tafel plots for the adsorption of AECOL on Zinc in 5 M HNO₃*

Figure 3.3c: Tafel plots for the adsorption of AECOL on carbon steel in 5 M HNO₃

	Conc. (g/L)	I_{corr} (mAcm⁻²)	E_{corr} (mV)	βc (mV/dec)	βa (mV/dec)	IE (%)
CARBON STEEL	Blank (5 M HNO₃)	7.811	-917	228	156	-
	0.5 g/L	2.551	-772	217	111	67.3
	2.0 g/L	0.892	-543	165	108	88.6
	5.0 g/L	0.373	-229	128	90	95.2
ZINC	Blank (5 M HNO₃)	6.666	-716	196	112	-
	0.5 g/L	2.091	-553	141	101	68.6
	2.0 g/L	1.824	-397	121	91	72.6
	5.0 g/L	1.172	-211	94	65	82.4
ALUMINIUM	Blank (5 M HNO₃)	4.292	-656	155	107	-
	0.5 g/L	2.101	-444	128	98	51.0
	2.0 g/L	1.622	-319	117	75	62.2
	5.0 g/L	1.211	-219	88	52	71.8

Table 3.3: Results from PDP experiment showing parameters for the adsorption of AECOL on aluminium, carbon steel and zinc.

D. ADSORPTION CONSIDERATION

A direct relationship between inhibition efficiency (%IE) and the degree of surface coverage θ can be assumedfor the different concentrations of the inhibitor. The degree of surface coverage for the different concentrations of alkaloid extracts of *Calendula officinalis* leaves has been evaluated from the weight loss measurements in 5.0 M HNO₃. The data were tested graphically by fitting to various adsorption isotherms including Freundlich, Temkin, Langmuir and Frumkin isotherms. The correlation coefficient (R^2) was used to determine the best fit isotherm which was obtained for Langmuir. According to this isotherm, θ is related to the inhibitor concentration by the following Eq. 3 (Shama et al., 2015; Shalabil et al., 2014; Atta et al., 2014)

$$\frac{c}{\theta} = \frac{1}{K} + C \qquad \text{...................................3}$$

where θ is the surface coverage, C is the concentration, K_{ads} is the equilibrium constant of adsorption process. K_{ads} is related to the standard Gibbs free energy of adsorption ΔG^o_{ads} by the Eq. 4 (Murthy and Vijayaragaden, 2014; Habib et al., 2015) The data was obtained from Fig. 3.4a - c. The intercept of the lines in Fig. 3.4a - c yielded K_{ads} in (dm³ mol⁻¹), and the corresponding standard Gibbs free energy of adsorption in (kJ mol⁻¹) was then calculated from Eq. 5 (Kadhum et al., 2014; Santhini and Jeyaraj, 2012):

$$k = \frac{1}{55.5} \exp \frac{-\Delta G_{ads}}{RT}$$

$$\Delta G^o_{ads} = - RT \ln(55.5K_{ads}) \text{ ....5}$$

where R in (J mol⁻¹ K⁻¹) is the gas constant, T (K) is the temperature, and $C_{solvent}$ is the molar concentration of the solvent, which in this case, is water. Using this equation, the various adsorption parameters are obtained from the studied isotherm including the standard Gibbs free energy of adsorption of alkaloid extracts of *Calendula officinalis* leaves on the metal surfaces were calculated and listed in Table 3.4. Fig. 3.4a - c shows the plot of C/θ versus C and linear plots were obtained for the different concentrations of AECOL indicating that the adsorption of this inhibitor followed Langmuir isotherm. This result is in accordance with those of Saedah and Al-Mhyawi, (2014), Gopal et al., (2012), Eddy et al., (2010). The various adsorption parameters obtained from this isotherm are listed in Table 3.4. It is seen from Table 3.4 that the correlation coefficients are very good and K_{ads} values increases with increasing temperature showing that the molecules of the inhibitors were adsorbed on both metal surfaces. Results presented in the Table 3.4, indicate that the values of ΔG^o_{ads} are negative. The negative values signify adsorption of the inhibitor molecules via mixed adsorption mechanism (Hui et al., 2013). It is also seen that the values of ΔG^o_{ads} increased with an increase in inhibitor concentrations, a phenomenon which indicates that the adsorption of the inhibitor onto the surfaces was favorable with increasing AECOL concentrations (Shama et al., 2015; Shalabil et al., 2014). Literature demonstrates that the values of standard Gibbs free energy of adsorption in aqueous solution around -20 kJ mol⁻¹ or lower (more positive) indicate adsorption with electrostatic interaction between the adsorbent and adsorbate (physisorption), while those around or higher (more negative) than -40 kJ mol⁻¹ involve charge sharing between the molecules and the metal (chemisorption) (Atta et al., 2014; Chidiebere et al., 2015; Eddy et al., 2010)
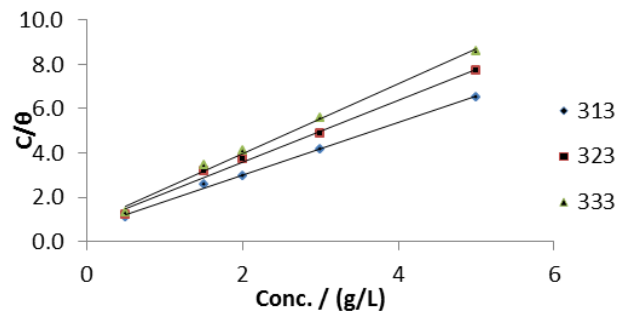

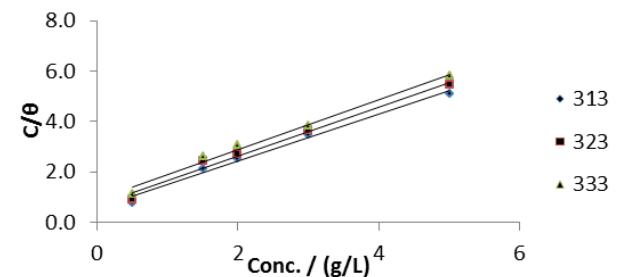*Figure 3.4a: Langmuir isotherm plots for the adsorption of AECOL on aluminium in 5 M HNO₃*

Figure 3.4b: Langmuir isotherm plots for the adsorption of AECOL on carbon steel in 5 M HNO₃
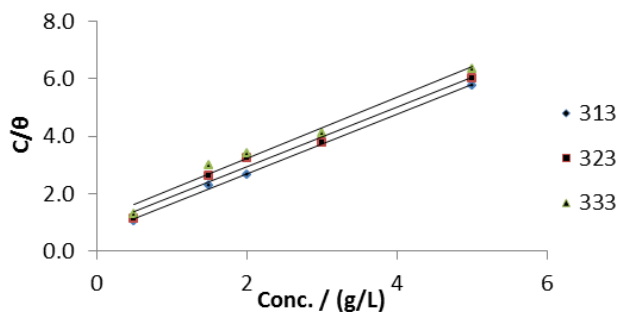
Figure 3.4c: Langmuir isotherm plots for the adsorption of AECOL on zinc in 5 M HNO$_3$

Temp. (K)	ALUMINIUM				CARBON STEEL				ZINC			
	k (g/L)	R^2	Slope	ΔG*$_{ads}$ (kJ/mol)	k (g/L)	R^2	Slope	ΔG*$_{ads}$ (kJ/mol)	k (g/L)	R^2	Slope	ΔG*$_{ads}$ (kJ/mol)
313	0.625	0.997	1.184	-9.029	0.555	0.987	0.935	-8.727	0.625	0.996	1.038	-9.029
323	0.800	0.992	1.393	-9.966	0.678	0.985	0.976	-9.531	0.860	0.980	1.038	-10.156
333	0.839	0.993	1.574	-10.404	0.908	0.987	0.995	-10.617	1.070	0.978	1.069	-11.062

Table 3.4: Results from Langmuir isotherm showing parameters for the adsorption of AECOL on aluminium, carbon steel and zinc.

IV. CONCLUSION

This work reveals that alkaloid extracts of *Calendula officinalis* leaves inhibited the corrosion of both carbon steel, zinc and aluminium in 5 M HNO$_3$ solution. The inhibition efficiency was found to increase with increase in extract concentration and decrease with increase temperature. The %IE followed the order Carbon steel (98.0 %) > Zinc (86.9 %) > Aluminium (76.5 %). The adsorption of AECOL extract onto the metal surfaces best fit the modified Langmuir adsorption isotherm. The negative values of ΔG0ads reflect the spontaneity of the corrosion inhibition process. Based on the decrease in the inhibition efficiency with increase in temperature, physical adsorption mechanism has been proposed for the adsorption of the leaf extract.

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