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Investigation of *Vangueria agrestis* Leaf Extract as a Corrosion Inhibitor for Aluminium and Mild Steel in Acidic and Basic Media

Femi Emmanuel Awe[1], Kabiru Ado[1], Umar Alhaji Adamu[1*]

Department of Chemistry, Nigerian Defence Academy Kaduna.

***Corresponding author:** Email: adamukrg@gmail.com, +2348032574713

Abstract

The inhibition efficiency of *Vangueria agrestis* leaf extract was evaluated by weight loss measurements across a concentration range of 0.1 g/L to 0.7 g/L. The effect of temperature and thermodynamic parameters on the inhibition mechanism was determined experimentally at 303 K, 313 K, 323 K and 333 K with a constant immersion period of 3 hours. Potentiodynamic polarization method was used; the corrosion potentials (E_{corr}) and corrosion current densities (I_{corr}) were studied. The result revealed that % inhibition efficiency increased with increase in concentration of the extract in both medium, this indicates the inhibitive effect of the extract. On the other hand % inhibition efficiency decreased with increase in temperature. The highest % inhibition efficiencies of the leaves extract were found to be 93.63 % for mild steel in acidic and 95.43 % for aluminium in basic medium both at 303 K and 0.7 g/L. The lowest % inhibition efficiencies were 36.29 % and 33.39 % for mild steel in 0.5 M HCl and aluminium in 0.5 M NaOH both at 333 K and concentration of 0.7 g/L of the extract. The ΔG_{ads} values obtained were between (-11.02 kJ/mol and -20.03 kJ/mol), below -40 kJ/mol indicating physical adsorptions. Langmuir adsorption isotherm fitted this research. The FTIR result indicated the presence of C-H and O-H stretching which attributed to the inhibition of the extract on the coupons. The surface morphology study of the coupons in the presence and absence of the inhibitor has proved the inhibition effect of the extract on the coupons, this has to do with the adsorption of the inhibitor molecules on the surface of the coupons resulting in the formation of protective layers preventing the attack of corrosive substances. Therefore, *Vangueria agrestis* leaves extract is effective green corrosion inhibitor for mild steel and aluminium in aggressive media.

Key Words: Adsorption, Corrosion inhibition, Extract, Mild Steel, Weight loss.

1.0 Introduction

Mild steel and aluminium are extensively used across industries such as chemical processing, automotive, machinery, petroleum and construction because of their desirable properties (malleability, hardness, ductility, luster, and high melting and boiling points). However, mild steel exhibits poor resistance to corrosion in aggressive environments, which raises significant concerns [1]. Preserving the useful properties of these metals therefore requires attention [1,2,3]. Common, effective approaches to corrosion

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protection include applying protective coatings and using corrosion inhibitors [4,5]. Corrosion, known as the gradual degradation of a metal due to reaction with its environment is widely recognized as a major cause of loss of metallic performance [6]. Cost-effective mitigation depends on a clear understanding of corrosion causes; a range of factors have been identified as contributing to corrosion [7].Corrosion originates from electrochemical interactions between a metal and its environment, producing reaction products on the metal surface. No single method has been established that completely halts corrosion of metals and alloys [8]. Consequently, addressing metal deterioration caused by corrosion is an important area of study. The use of corrosion inhibitors can substantially reduce costs associated with replacing corroded components [9]. Because corrosion proceeds via electrochemical mechanisms, understanding electrochemistry and physical metallurgy is essential: the structure and composition of metallic materials strongly influence their corrosion behavior [10]. A corrosion inhibitor is a substance that slows corrosion by adsorbing onto a metal surface, either through physical adsorption (charge transfer between a charged inhibitor and the charged metal surface) or by electron donation from inhibitor molecules into vacant metal d-orbitals [5,9]. Recent research has focused on plant extracts as corrosion inhibitors because they contain numerous organic compounds (e.g., alkaloids and heterocyclic compounds such as flavonoids) with oxygen, sulfur and nitrogen functional groups that enhance inhibitory potential [11,12,13,14]. Plant extracts also include tannins, cellulose and polycyclic phytochemicals that can form protective films on metal surfaces [10,15]. This study investigates the potential of *Vangueria agrestis* leaves extract as a corrosion inhibitor for mild steel in 0.5 M HCl and for aluminium in 0.5 M NaOH using weight-loss and potentiodynamic techniques. To our knowledge, *Vangueria agrestis* leaves extract has not previously been studied as a corrosion inhibitor.

The use of aqueous extract of *Acanthopanax senticosus* leaves as a corrosion inhibitor for carbon steel in acidic media was conducted [16]. The study reported that the maximum protection of 98.79 % was achieved at an extract concentration of 150 mg/L. The impact of rosemary extract on the corrosion behavior of mild steel in an acidic (HCl) medium was investigated [17]. The electrochemical results suggest that rosemary extract acts as a mixed inhibitor, providing 92 % corrosion prevention. The presence of the inhibitor provided 87 % protection when the mild steel was immersed in the acidic environment after 6 hours. In another study [18] using extract from *Fatsia japonica* leaves as inhibitor to prevent the corrosion of carbon steel in concrete, the inhibition activity determined by electrochemical method was 89.6 % at 1000 mg/L and it was observed to increase with increase in immersion time [18].

2.0 Materials and Methods

Mild steel and aluminium sheets were purchased from Panteka market located at Tudun Wada, Kaduna, Kaduna State Nigeria. Analar grade of sodium hydroxidepelletes (NaOH of 98 % purity), HCl (with purity of 35 % of the stock solution) and ethanol 99.5 % were purchased from Johnext chemical store and medical equipment, Kano road, Kaduna while double distilled water were gotten from Chemistry Department of Kaduna Polytechnic Tudun Wada, Kaduna.

Samples of *Vangueria agrestis* leaves were obtained from Kuriga area of Chikun local government, Kaduna, Kaduna State, Nigeria. Other materials used in carrying out this research includes; 250 cm^3 beakers, 1000 cm^3 volumetric flask, stirrer, 1000 cm^3 measuring cylinder, petri dish with lid, desiccator, thermostat, water bath, soxhlet extractor, weighing balance machine and bristle brush which were gotten from the Department of Chemistry, Nigerian Defence Academy, Kaduna were also used.

2.1 Experimental procedure

In this research, mild steel consisting of Fe 97.99 %, Mn 0.8 %, S 0.04 %, P 0.03 % and C 0.24 % and aluminium sheet 99.9 % pure as test metals were obtained from Panteka market of Kaduna metropolis, Kaduna, Nigeria. The metals were mechanically pressed cut and formed different coupons with the dimension 3 cm × 3 cm each for gravimetric and electrochemical studies. The coupons were polished with # 400 to # 1200 grade of emery abrasive paper, washed with ethanol, cleaned in acetone, air dried and preserved in desiccators [19].

All reagents used in the course of this research work were of analytical grade, distilled water was employed in the preparation of 0.5 M HCl and 0.5 M NaOH solutions for the weight loss measurements and the potentiodynamic polarization studies using concentration of the extract from 0.1 g/L to 0.7 g/L [8,20].

2.2 Extraction of the plant

Fresh *Vangueria agrestis leaves* were collected, identified and issued voucher number (NDA/BIOH/2024/24) by herbarian in the Department of Biological sciences, Nigerian Defence Academy, Kaduna. The sample was washed thoroughly and all the undesired (dirt) materials were removed, the washed *Vangueria agrestis* leaves were air-dried at room temperature for 7 days. The dried leaves were then pulverized using mortar and pestle. The powdered *Vangueria agrestis* leaves was subsequently sieved to obtain uniform particle size and extracted using 99.5 % pure, Analytical-grade ethanol (Sigma-Andrich) in a Soxlet apparatus at 65^0C for 21 hours, the resulting solution was concentrated using rotary evaporator. The extract yield (%) was calculated to be 20 %. The concentrated solution formed was stored at 4^0C in an air tied sterile container and used as the stock inhibitor solution [21]. The concentrations of the stock inhibitor solution prepared were 0.1, 0.3, 0.5, and 0.7 gdm^{-3} to

assess the effective performance of the inhibitor on corrosion protection [4].

2.3 Gravimetric (weight loss) measurements

The weight loss measurements were conducted in conical flasks containing 100 mL of 0.5 M HCl and 0.5 M NaOH separately. Coupons of measured weight were inserted in the flasks and covered with aluminium foil paper both in the presence and absence of the extract. The flasks were then placed into a water bath at temperature of 303 K. The corrosion product were removed from test samples by washing it with distilled water and rinsed in ethanol. The specimens were then washed further with acetone. The experiments were repeated at 313 K, 323 K and 333 K for 3 hours each. The new weight of the coupons were recorded using electronic balance (Sensitivity = ± 0.1 mg). Corrosion rate, surface coverage and percentage inhibition efficiencies (%IE) using the concentration of the extracts at 0.1, 0.3, 0.5 and 0.7 g/L were calculated using the following equations alongside with those without inhibitors [19,22].

$$CR = \frac{Kw}{DAt} \qquad 1$$

Where, CR is the corrosion rate and is calculated in mils per year (mm/y), w is the weight loss (mg), K is constant, D is the density of the coupons (7.85 g/cm^3 for mild steel and 2.7 g/cm^3 for aluminium), A is the surface area of the metals used (9 cm^2), and t is the immersion time (3 hours).

$$\text{Surface Coverage } (\theta) = \frac{CR_o - CR_i}{CR_o} \qquad 2$$

Where, CR_i = Corrosion rate in the presence of inhibitor and CR_o = Corrosion rate in the absence of inhibitor.

$$CIE = \frac{CR_o - CR_i}{CR_o} * 100\% \qquad 3$$

Where, CIE is corrosion inhibition efficiency (%), CR_o is the corrosion rate without inhibitor (mm/y) and CR_i is the corrosion rate with inhibitor (mm/y) respectively.

The weight loss measurements were obtained according to ASTM G31-72, which is the standard methodology for this technique in the laboratory [23].

2.4 Fourier Transform Infra Red Analysis (FTIR)

FTIR analysis was performed by using a Shimadzu spectrophotometer in the spectral region between 4000 and 500 cm^{-1}, the functional groups present in *Vangueria agretis* leaves extract and that of the film formed on the metals surfaces after corrosion were recorded. Changes such as peak shifts, disappearance of new peaks were examined and assessed the phytochemicals in the extract interaction [24].

2.5 Scanning Electron Microscopy Analysis (SEM)

Scanning electron microscopy analysis was carried out to examine the surface morphology of the metals specimens after electrochemical measurements in the corrosive media in the absence and presence of the inhibitor. The potentiodynamic polarization experiment was performed using a conventional three-electrode

electrochemical cell consisting of the metal specimen as the working electrode, a platinum counter electrode, and a Saturated Calomel Electrode as the reference electrode. Prior to polarization measurements, the system was allowed to stabilize at the open circuit potential for about 30 minutes to ensure a steady electrochemical state and to allow adequate adsorption of the inhibitor molecules on the metal surface. The polarization scan was then conducted within a potential window of −250 mV to +250 mV relative to the open circuit potential at a scan rate of 1 mV s^{-1}. The SEM micrograph of the metal surface exposed to the corrosive solution without inhibitor revealed severe surface damage characterized by rough morphology, corrosion pits, and cracks, indicating intense corrosion attack under the applied electrochemical conditions. In contrast, the SEM image of the metal surface in the presence of *Vangueria agrestis* leaves extract displayed a relatively smoother and more uniform surface with significantly reduced pits and defects. This improved morphology suggests that the inhibitor molecules adsorbed onto the metals surfaces during the stabilization period, forming a protective film that suppressed both anodic metal dissolution and cathodic reactions within the applied potential range. The SEM observations therefore corroborate the electrochemical results, confirming the effectiveness of the plant extract as a corrosion inhibitor. The surface morphologies of the coupons were observed using SEM (JEOL, JSM-6400) [25,26].

2.6 Significance of the Study

This research identifies *Vangueria agretis* leaves extract as a novel, eco-friendly corrosion inhibitor. The finding expands the pool of natural inhibitors available for corrosion control and offer new possibilities for green chemistry applications.

3.0 Results and Discussion

3.1 Weight Loss Measurements

The data obtained from the weight loss measurements are given in Table 1 and 2 respectively. The results indicate that inhibition efficiency increases with concentration up to 0.7 g/L; this suggests the attainment of adsorption saturation where the metals surfaces reached maximum occupancy of inhibitor molecules, forming stable monolayer films that isolate the metals from the corrosive media. The surface coverage values (θ) were calculated from the inhibition efficiency obtained at different concentrations of the inhibitor. The results show that surface coverage increases with increasing inhibitor concentration, indicating enhanced adsorption of inhibitor molecules on the metals surfaces. This increased adsorption leads to the formation of a protective film that reduces direct contact between the metals and the corrosive media, thereby decreasing the corrosion rates.

Table 1: Corrosion rate, Surface coverage and Inhibition efficiency of *Vangueria agrestis* leaves extract on mild steel in 0.5 M HCl

Temperature (K)	***Concentration (g/L)***	***ΔW (mg)***	***Corrosion rate (mm/y)***	***Inhibition efficiency (%IE)***	***Surface Coverage (θ)***
303K	Blank	123	51.78	-	-
	0.1	21	8.67	82.35	0.8235
	0.3	17	7.01	86.27	0.8627
	0.5	14	5.78	90.19	0.9019
	0.7	8	3.30	94.41	0.9441
313K	Blank	169	68.70	-	-
	0.1	66	27.30	61.43	0.6143
	0.3	61	25.20	64.29	0.6429
	0.5	52	21.50	70.00	0.7000
	0.7	40	16.50	75.71	0.7571
323K	Blank	228	94..20	-	-
	0.1	126	52.00	44.68	0.4468
	0.3	122	50.40	46.81	0.4681
	0.5	117	48.30	48.94	0.4894
	0.7	109	45.00	52.13	0.5213
333K	Blank	289	119.30	-	-
	0.1	184	76.00	36.67	0.3667
	0.3	179	73.90	38.33	0.3833
	0.5	172	71.00	40.83	0.4083
	0.7	162	66.9	44.17	0.4417

The results for the gravimetric measurements obtained, generally revealed that the inhibition efficiency increases with increase in concentration of the extract, confirming that *Vangueria agrestis* leaves extract is an adsorption inhibitor on mild steel in 0.5 M HCl. The inhibition efficiencies were also found to reduce as the temperature increased; the observed decrease with increasing temperature suggests that the extent of adsorption of the inhibitor on the mild steel surface is predominantly physisorption. In comparison with the results obtained from previous researchers indicates that, the results are in agreement with the findings reported by [27].

Table 2: Corrosion rate, Surface coverage and Inhibition efficiency for *Vangueria agrestis* leaves extract on aluminium in 0.5 M NaOH

Temperature (K)	Concentration (g/L)	ΔW (mg)	Corrosion *rate* (mm/y)	Inhibition efficiency (%IE)	Surface Coverage (θ)
303K	Blank	175	210.32	-	-
	0.1	26	31.25	85.14	0.8514
	0.3	19	22.83	89.15	0.8915
	0.5	14	16.83	91.99	0.9199
	0.7	8	9.61	95.43	0.9543
313K	Blank	225	270.39	-	-
	0.1	86	103.32	61.83	0.6183
	0.3	81	97.32	64.01	0.6401
	0.5	74	88.96	67.09	0.6709
	0.7	62	74.5	72.45	0.7245
323K	Blank	293	352.10	-	-
	0.1	167	200.70	42.99	0.4299
	0.3	162	194.60	44.73	0.4473
	0.5	158	189.90	46.07	0.4607
	0.7	146	175.40	50.18	0.5018
333K	Blank	364	437.30	-	-
	0.1	243	291.30	33.39	0.3339
	0.3	238	286.00	34.59	0.3459
	0.5	231	277.60	36.52	0.3652
	0.7	222	266.80	38.99	0.3899

The highest % inhibition efficiency of the leaves extract was found to be 95.43 % at 303 K and 0.7 g/L concentration for aluminium in basic medium while the lowest % inhibition efficiency was recorded as 33.39 % for the *Vangueria agrestis* leaves extract on aluminium in 0.5 M NaOH at 333 K and concentration of 0.1 g/L of the leaves extract. The result shows dependency of corrosion rate with temperature and concentration. The rate increases with temperature but decreases as the concentration of the inhibitor increases. At lower temperature (303 K), the inhibitor molecules strongly adsorbed on to the aluminium surface, this leads to the formation of a protective layer that hinders the diffusion of corrosion species (Na^+ and OH^-). This results in high inhibition efficiency (95.43 %) and reduced the corrosion rate. At higher temperature (333 K), the protective layer weakens due to partial desorption of inhibitor molecules from the metal surface. The metal-inhibitor interaction becomes less stable, allowing more aggressive ions to penetrate the surface, leading to high corrosion rate and lower inhibition efficiency, the result obtained is in good agreement with that reported by [28].

3.2 Effect of concentration

The various concentrations of *Vangueria agrestis* leaves extract used in this research are presented in Table 1 and 2, that is 0.1 g/L, 0.3 g/L, 0.5 g/L

and 0.7 g/L. Corrosion rate decreases with an increase in concentration of the extract. Moreover, looking at the table clearly, it can be seen that inhibition efficiency increases with an increase in concentration of the extract. This shows that more inhibitor molecules are adsorbed on the surfaces of the studied metals at high concentration leading to the formation highly protective film on surfaces of the studied metals [8,24,28].

3.3 Effect of temperature

It is observed that at lower temperature the inhibitor molecules strongly adsorbed onto the surfaces of the metals, forming a compact protective layer that hinders the diffusion of corrosive species, this resulted to have maximum inhibition. At higher temperatures, the protective layers weaken due partial desorption of inhibitor molecules from the metals surfaces. The metals-inhibitor interaction become less stable, allowing more aggressive ions to penetrate the surface, leading to a maximum corrosion rate and lower inhibition efficiency [24,29].

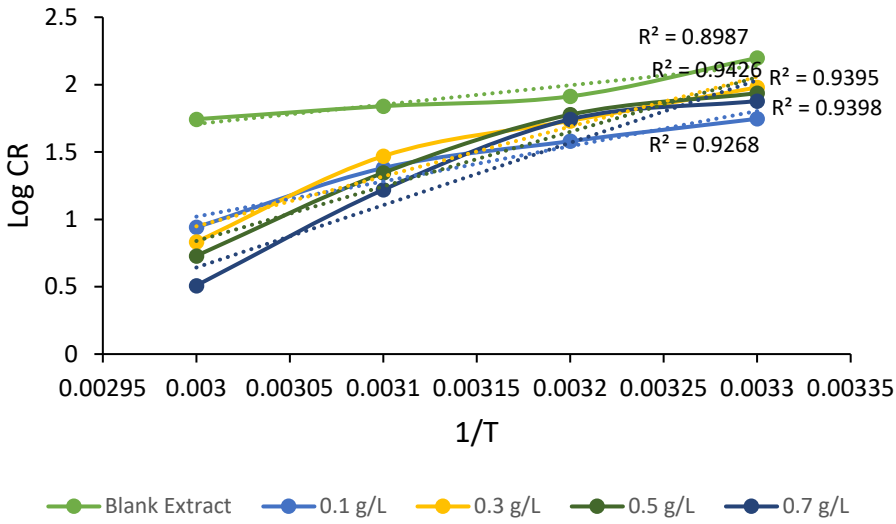


Figure 1: Isotherm for *Vangueria agrestis* leaf extract on mild steel in 0.5 M HCl

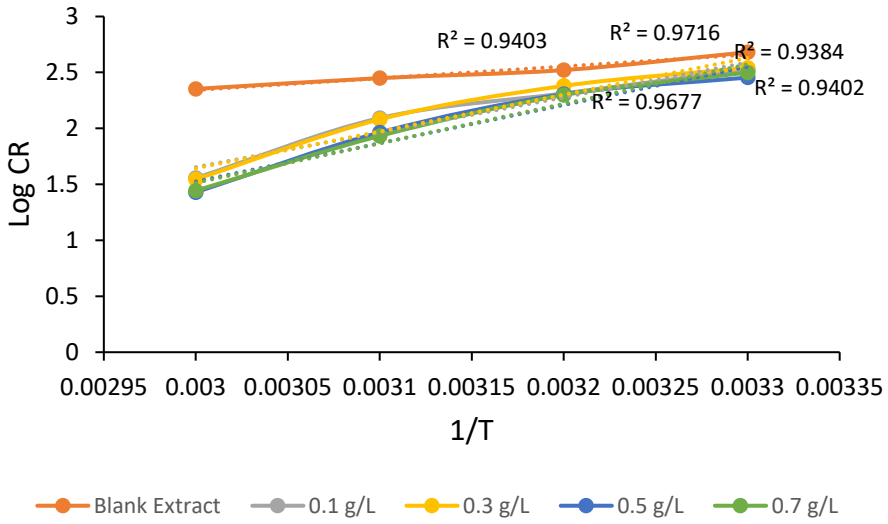


Figure 2: Isotherm for *Vangueria agrestis* leaves extract on aluminium in 0.5 M NaOH

3.5 Thermodynamic study

The thermodynamic parameters obtained from the adsorption studies provide important information about the mechanism of interaction between the inhibitor molecules and the metals surfaces. The negative values of the Gibbs free energy of adsorption (ΔG_{ads}) indicate that the adsorption process of the inhibitor molecules on the metals surfaces is spontaneous. The magnitude of ΔG_{ads} also provides insight into the nature and strength of interaction between the inhibitor molecules and the metals surfaces. Generally, values around −20 kJ/mol or less negative suggest electrostatic interaction between charged inhibitor molecules and the charged metal surface (physisorption), whereas values around −40 kJ/mol or more negative indicate chemical interaction through charge sharing or transfer between the inhibitor molecules and the metal surface (chemisorption). The adsorption process involves the displacement of water molecules previously adsorbed on the metal surface by the inhibitor molecules present in the solution. This solvent displacement leads to the formation of an adsorbed protective layer that isolates the metal surface from the corrosive environment. The interaction between the inhibitor molecules and the metals surfaces result in the formation of a compact adsorption films, which reduce the accessibility of aggressive ions to the metal surface. For the adsorption of ethanolic extract of *Vangueria agrestis* on the mild steel and aluminium surfaces; thermodynamic of interest were enthalpy of adsorption (ΔH_{ads}), entropy of adsorption (ΔS_{ads}) and the standard Gibb's free energy of adsorption (ΔG_{ads}). The transition state equation was used and determined two of the thermodynamic parameters (enthalpy of adsorption and entropy of adsorption).

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right) \quad 4$$

Where, CR is the corrosion rate for mild steel in 0.5 M HCl and aluminium in 0.5 M NaOH solutions, R is gas constant, T is the temperature, N is the Avogadro's number, and h is the Planck constant. ΔS_{ads} is the entropy of the adsorption and ΔH_{ads} is the enthalpy of adsorption of the inhibitor on mild steel and aluminium surfaces. Taking the natural logarithm (ln) of both sides of eqn. 4, eqn. 5 was obtained;

$$\ln(CR/T) = \ln(R/Nh) + \Delta S_{ads}/R - \Delta H_{ads}/RT \quad 5$$

The slopes and intercept of the transition state plot in Figure 1 and 2 is equal to $-\Delta H_{ads}/R$ and $\log(R/Nh) + \Delta S_{ads}/R$, respectively. Values of the standard changes in entropy and enthalpy calculated from the intercepts and slopes of the plots are recorded in Table 3 and 4 respectively [28].

Table 3: Calculated activation energy and thermodynamic parameters for the corrosion process of mild steel in the presence and absence of *Vangueria agrestis* leaves extract in 0.5 M HCl .

Concentration (g/L)	***Ea (kJmol^{-1})***	***ΔH^{o} (kJmol^{-1})***	***ΔS^{o} (Jmol^{-1}K^{-1})***
Blank	23.82	10.35	49.85
0.1	59.52	25.84	95.28
0.3	63.43	27.54	100.37
0.5	68.62	29.79	107.08
0.7	73.09	36.07	125.96

Table 4: Calculated activation energy and thermodynamic parameters for the corrosion process of aluminium in the presence and absence of *Vangueria agrestis* leaves extract in 0.5 M NaOH

Concentration (g/L)	***Ea (kJmol^{-1})***	***ΔH^{o} (kJmol^{-1})***	***ΔS^{o} (Jmol^{-1}K^{-1})***
Blank	20.49	08.89	50.15
0.1	61.20	26.58	102.39
0.3	63.43	27.54	112.66
0.5	76.48	33.21	122.48
0.7	79.73	39.39	141.18

As shown in Table 3 and 4, the activation energy (*Ea)* is higher for the inhibited process than for an uninhibited process; that is the activation energy (*Ea)* increases as the concentration of the inhibitor extract increases. The observation could be due to formation of adsorptive films as earlier reported by [8]. This result suggests that the corrosion inhibition by *Vangueria agrestis* leaves extract is feasible because of the increase in energy barrier for the metals dissolutions. The formation of a thin film on the metals surfaces serve as a barrier to both energy and mass transfer, which increases the activation energy (*Ea)*. Therefore, the results show that the adsorption of *Vangueria agrestis* for the metals both in acidic and basic media is by physical

adsorption. Previous studies have shown that, an increase in activation energy (*Ea)* with increasing inhibitor concentration or an activation energy (*Ea)* value lower than 80 kJ/mol, typically indicates physical adsorption. In contrast, activation energy values greater than 80 kJ/mol are generally associated with chemical adsorption. The higher activation energy values observed in the presence of the inhibitor in both media are attributed to the increased energy barrier for the corrosion process. This observation also suggests the possible formation of a complex compound between the inhibitor molecules and the metal surface, which is consistent with earlier reports [20]. Furthermore, the present results agree with findings that support a previous physical adsorption mechanism [20,24,30].

The enthalpy and entropy change of activation (ΔH^o_{ads} and ΔS^o_{ads}) values obtained in the absence and presence of inhibitor were all seen positive in both media and the values also increases with the addition of the extract. The positive values of the entropies change suggest disorderliness of the processes [31].

A spontaneous adsorption process is defined when ΔH^o is negative and ΔS^o_{ads} is positive or when, ΔH^o_{ads} is less than $T\Delta S^o_{ads}$. Therefore, spontaneous adsorption of *Vangueria agrestis* leaves extract onto mild steel and aluminium surfaces is favored [31]. This result suggests that the corrosion inhibition by *Vangueria agrestis* leaves extract is feasible because of the increase in energy barrier for the metals dissolutions [20].

Table 5: Calculated thermodynamic parameters ΔG_{ads} for the corrosion process of mild steel in the presence of *Vangueria agrestis* leaves extract in 0.5 M HCl

Concentration (g/L)	***ΔG$_{ads}$ (kJ/mol)***			
	303K	**313K**	**323K**	**333K**
0.1	-19.88	-17.59	-16.38	-15.95
0.3	-17.61	-15.07	-13.59	-13.09
0.5	-16.73	-14.42	-12.46	-11.93
0.7	-17.71	-14.42	-11.92	-11.46

Table 6: Calculated thermodynamic parameters ΔG_{ads} on the corrosion process of aluminium in the presence of *Vangueria agrestis* leaves extract in 0.5 M NaOH at different temperatures

Concentration (g/L)	***ΔG$_{ads}$ (kJ/mol)***			
	303K	**313K**	**323K**	**333K**
0.1	-19.72	-15.25	-16.43	-16.03
0.3	-17.03	-15.43	-13.62	-13.12
0.5	-16.73	-14.55	-12.54	-11.85
0.7	-17.71	-14.78	-11.92	-11.18

The calculated Gibbs free energy of adsorption (ΔG_{ads}) values range from -11.18 to -19.88 kJ/mol. The negative magnitudes confirm that the adsorption of *Vangueria agrestis* leaves extract onto the aluminium and mild steel surfaces is a spontaneous process. These results are consistent with a physical adsorption mechanism; established literature suggests that ΔG_{ads} values more positive than -20 kJ/mol are indicative of physisorption, whereas values more negative than -40 kJ/mol signify chemisorption [22,27].

3.6 Adsorption isotherm

The experimental inhibition for the corrosion of mild steel in 0.5 M HCl and aluminium in 0.5 M NaOH solutions increases with increase in the concentration of the *Vangueria agrestis* leaves extract; this can be explained by the adsorption of the constituents of the extract on the metals surfaces. Different adsorption isotherm models (Langmuir, Freundlich and Temkin) were applied using the experimental data obtained from the weight loss measurements. Of all the adsorption isotherm models, Langmuir adsorption isotherm was the one found best fitted for the extract on the metals in the entire medium.

$$\text{Freundlich: } \text{Log } \theta = \text{Log } K + n\text{Log } C \quad (6)$$

$$\text{El-Awady: } \text{Log } (\theta/1-\theta) = y\text{Log } C + \text{Log } K \quad (7)$$

$$\text{Langmuir: } C/\theta = 1/K + C \quad (8)$$

$$\text{Temkin: } \theta = \text{In } C + \text{In } K \quad (9)$$

Where, K is the equilibrium constant for adsorption process which reflects the extent of interaction between the inhibitor and the metals surfaces and C is the concentration of the inhibitor. $\Delta G_{ads}$was calculated using the following equation

$$\Delta Gads = -RT \ln(55.5\ K_{ads}) \quad (10)$$

Where, R is molar gas constant (8.314 J/K), T is temperature in Kelvin and value 55.5 is the molar concentration of water in solution [32].

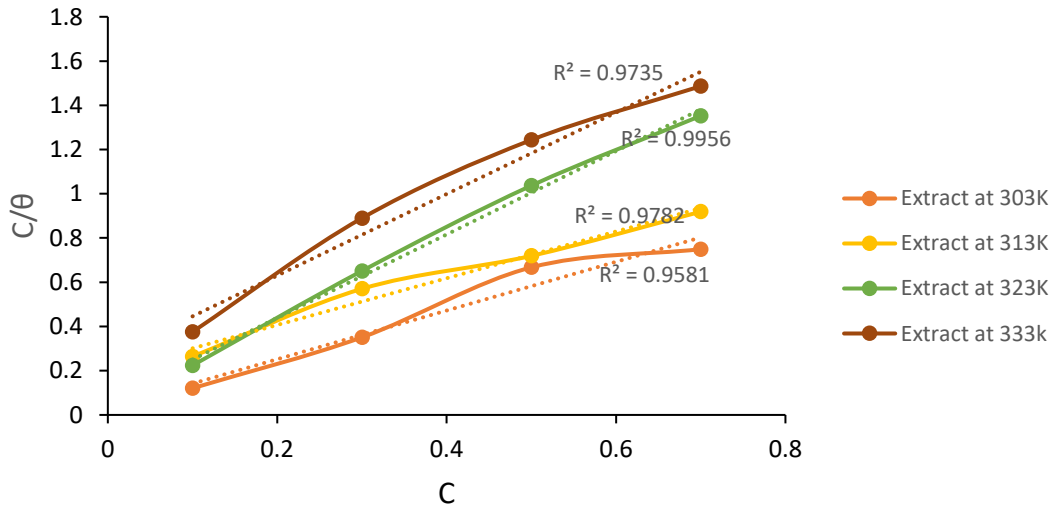


Figure 3: Langmuir Isotherm for *Vangueria agrestis* leaves extract on mild steel in 0.5M HCl

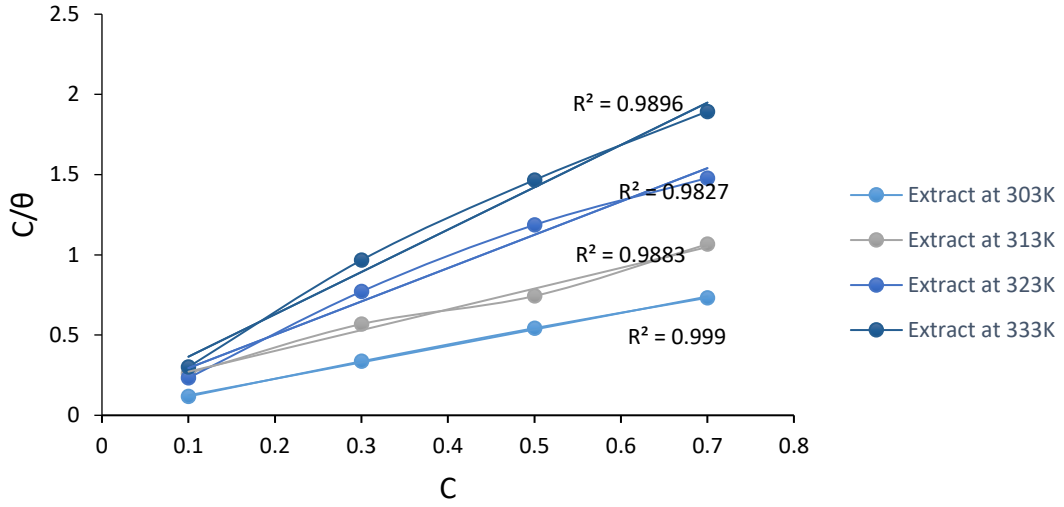


Figure 4: Langmuir Isotherm for *Vangueria agrestis* leaves extract on aluminium in 0.5 M NaOH

The plots of surface coverage (C/θ) against concentration (C) yield straight lines as shown in Figure 3 and 4 yields straight lines with linear regression (R^2) values close to unity, these support the assumption that the adsorption of the extract on mild steel in 0.5 M HCl and aluminium surfaces in 0.5 M NaOH solution follows the Langmuir adsorption isotherm [28].

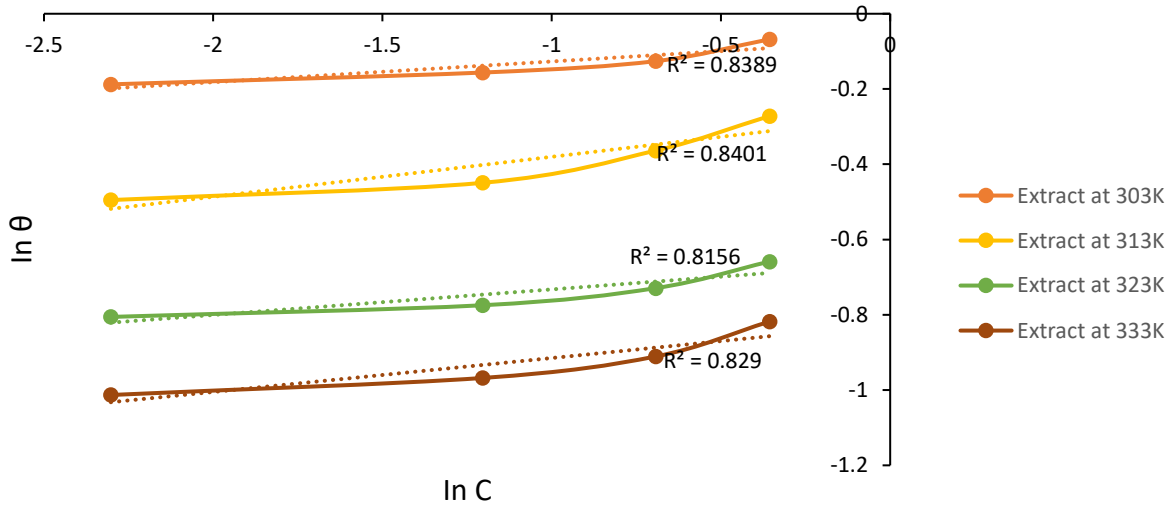


Figure 5; Freundlich Isotherm for *Vangueria agrestis* leaves extract on mild steel in 0.5M HCl

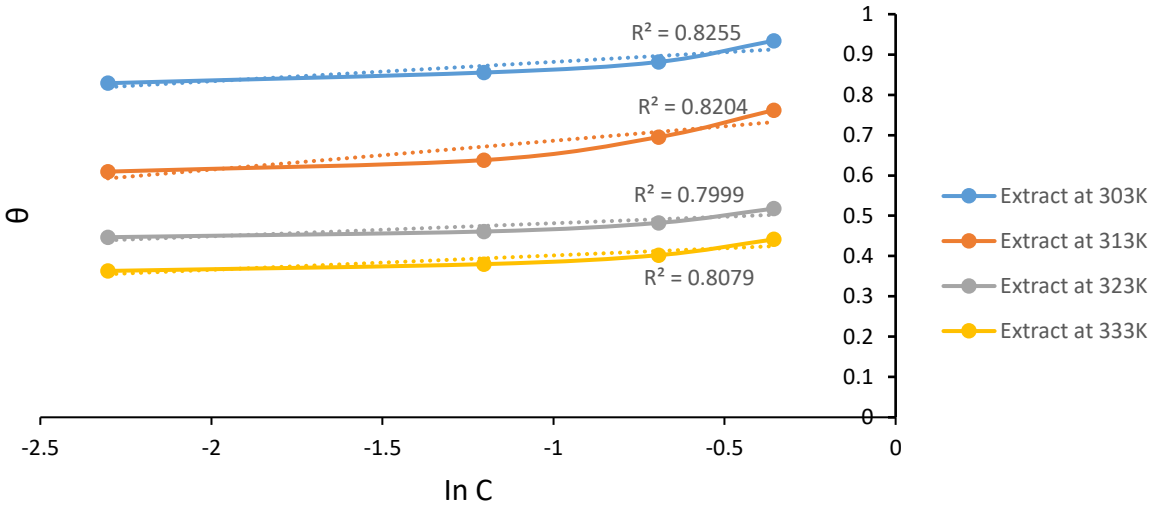


Figure 6: Temkin Isotherm for *Vangueria agrestis* leaves extract on mild steel in 0.5M HCl

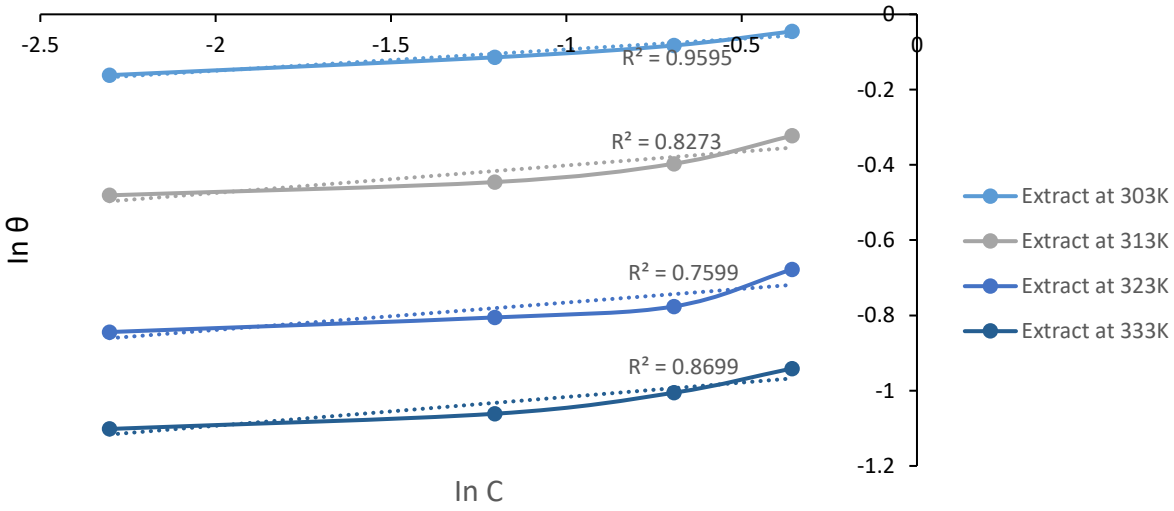


Figure 7: Freundlich Isotherm for *Vangueria agrestis* leaves extract on aluminium in 0.5M NaOH

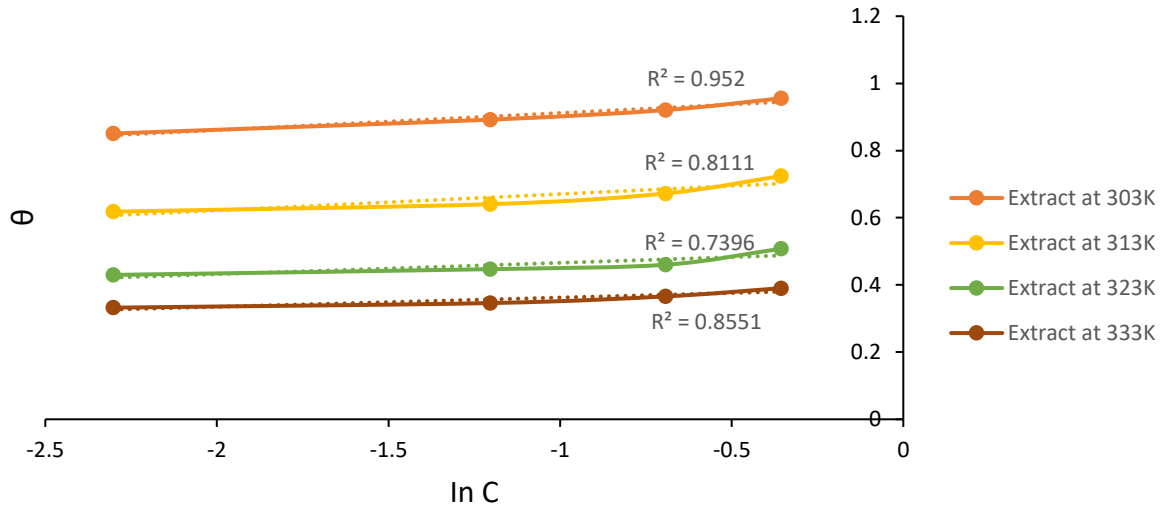


Figure 8: Temkin Isotherm for *Vangueria agrestis* leaves extract on aluminium in 0.5M NaOH

3.7 Potentiodynamic Polarization Results

The potentiodynamic polarization curves show that the addition of the inhibitor significantly reduces the corrosion current density (I_{corr}) compared with the blank solution, indicating effective inhibition of the corrosion process. The shift in corrosion potential (E_{corr}) in the presence of the inhibitor is relatively small (less than ±85 mV), suggesting that the inhibitor acts as a mixed-type inhibitor affecting both anodic metal dissolution and cathodic hydrogen evolution reactions. However, the observed shift of E_{corr} towards more negative potentials indicates that the inhibitor exhibits a stronger influence on the cathodic reaction, implying that the cathodic process is predominantly suppressed. Furthermore, the variation in both anodic and cathodic Tafel slopes confirms that the inhibitor reduces the overall corrosion rate through adsorption on the metals surfaces and formation of a protective film [33].

Table 7: Potentiodynamic polarization parameters for mild steel in 0.5 M HCl solution in the absence and presence of *Vangueria agrestis* leaves extract.

Concentration (g/L)	***-E_{corr} (mV)***	***I_{corr}(mAcm^{-2})***	***Bc(mV/dec)***	***βa(mV/dec)***	***IE(%)***
Blank	177.4	92.33	968.3	3171.7	-
0.1	139.5	47.34	216.1	333.5	48.73
0.3	144.7	12.41	239.7	890.2	86.56
0.5	105.6	6.38	436.5	287.2	93.09
0.7	95.3	2.81	589.4	208.9	96.96

Table 8: Potentiodynamic polarization parameters for aluminium in 0.5 M NaOH solution in the absence and presence of *Vangueria agrestis* leaves extract.

Concentration (g/L)	-E_{corr} (mV)	I_{cor}(mAcm^{-2})	Bc(mV/dec)	Ba(mV/dec)	IE(%)
Blank	369	8105	95	166	-
0.1	388	1342	84	182	83
0.3	346	884	94	175	83
0.5	319	503	96	147	89
0.7	295	307	104	115	96

From Table 7 and 8, E_{corr} is the corrosion potential, I_{corr} is the corrosion current density, *IE(%)* is the corrosion inhibition efficiency, ***βc*** represent the cathodic Tafel slope and *βa* represent the anodic Tafel slope. It can be seen that, the corrosion current density (I_{corr}) reduces with the addition of the extract concentration in both medium, this suggests that *Vangueria agrestis* leaves extract act as effective corrosion inhibitor for mild steel in 0.5 M HCl and aluminium in NaOH solutions. Generally, an inhibitor can be tagged as either anodic or cathodic, but when a shift in corrosion potential (E_{corr}) due to inhibitor is more than 85 mV, the inhibitor used is said to be a mixed type inhibitor [34]. In this research, the corrosion potential (E_{corr}) recorded is greater than 85 mV. Therefore, the inhibitor used act as mixed type inhibitor [2,5,34].

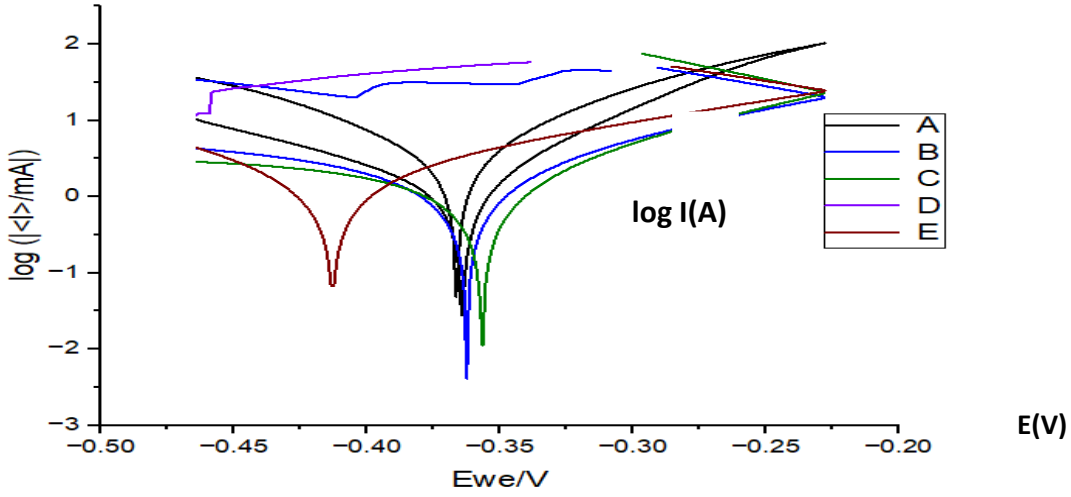


Figure 9: Potentiodynamic polarization curves of mild steel in 0.5 M HCl in the presence of different concentrations of *Vangueria agrestis* leaves extract.

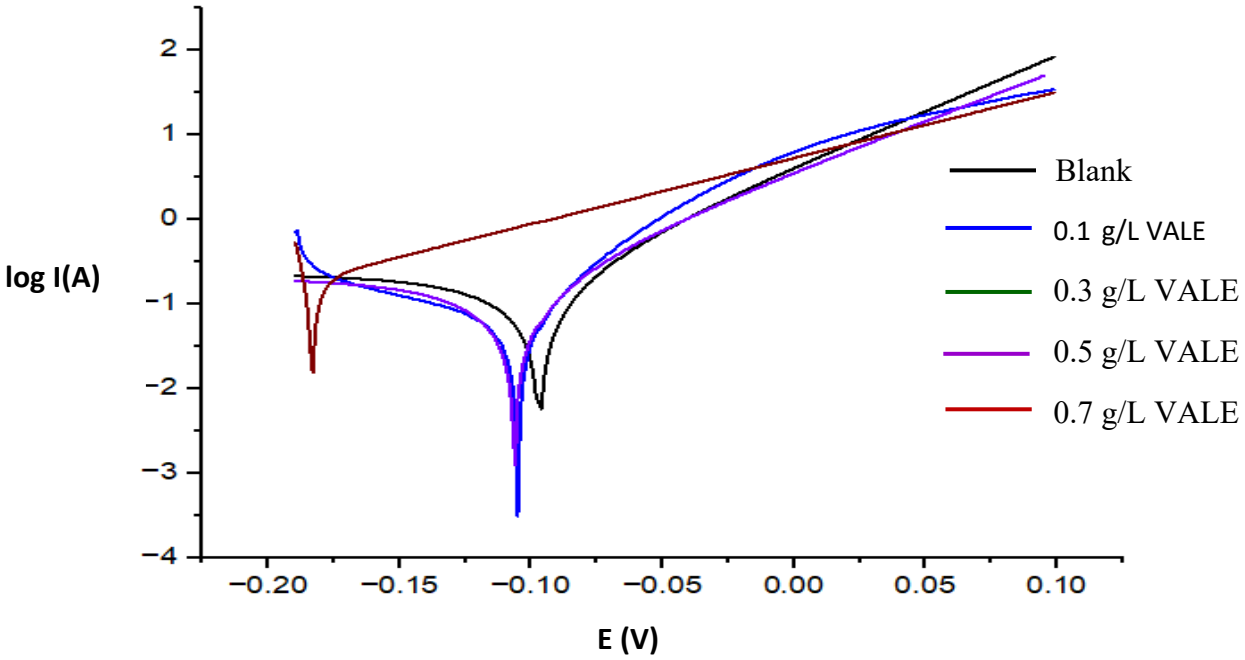


Figure 10: Polarization curves for the corrosion of aluminium in 0.5 M NaOH in the presence of different concentration of *Vangueria agrestis* leaves extract.

The Potentiodynamic polarization plots for various concentrations of *Vangueria agrestis* leaves extract are presented in table 9 and 10. From the Tables, VALE means *Vangueria agrestis* leaves extract. In the presence of inhibitor, the cathodic and anodic Tafel slopes are more or less equal, suggesting that *Vangueria agrestis* leaves extract acts as a mixedtype inhibitor. From the plots, the transition from the active zone to the passivating zone, as the corrosion potential increases to the passivation potential proves the formation of a passivating film [9,35,36].

3.8 FTIR of *Vangueria agrestis* leaves extract

The Fourier Transform Infrared Spectroscopy (FTIR) technique is widely employed to identify the functional groups and types of bonding present in organic corrosion inhibitors adsorbed on metal surfaces [37]. The FTIR spectrum of *Vangueria agrestis* leaves extract revealed several characteristic absorption bands corresponding to different functional groups. A broad absorption band observed around 3902.5 cm^{-1} was attributed to O–H or N–H stretching vibrations, while the band around 1919.6 cm^{-1} corresponded to C–H stretching vibrations. The –C=C– stretching vibration exhibited a strong absorption peak at 1774.2 cm^{-1}, and S=O bending

vibration was recorded at 1408.9 cm^{-1}. In addition, the structural vibrations of aromatic rings were assigned to absorption bands at 1667 cm^{-1} and 1449 cm^{-1}.

These results indicate the presence of oxygen and nitrogen atoms in functional groups such as O–H, N–H, C=C, and aromatic rings in the *Vangueria agrestis* leaves extract. These functional groups were absent in the corrosion products formed on the mild steel surface, suggesting that the extract satisfies the general structural requirements of an effective corrosion inhibitor as reported in previous studies.

Furthermore, the C=N stretching and S=O bending vibrations, which appeared in the FTIR spectrum of the *Vangueria agrestis* leaves extract at 1688.5 cm^{-1} and 1408.9 cm^{-1}, respectively, were also absent in the spectrum of the surface product of aluminium immersed in 0.5 M NaOH and mild steel in 0.5 M HCl solutions in the presence of the inhibitor. This observation indicates that the *Vangueria agrestis* leaves extract molecules were adsorbed onto the surfaces of both aluminium and mild steel through these functional groups, leading to the formation of a protective layer that inhibits corrosion [6,8,24].

3.9 Result of SEM Analysis

The scanning electron microscopy micrograph of the mild steel coupons immersed in 0.5 M HCl and 0.5 M NaOH at 303 K for an immersion period of 3 hours in the absence and presence of 0.7 g/L *Vangueria agrestis* leaves extract are shown in Plates 1 - 4. It can be seen that the mild steel and aluminium surfaces were extremely damaged as a result of the attack of the corrosive media in the absence of the inhibitor visible in Plate 1 and 3. Carefully looking at the Plates, it can be also observed that the metal coupon surface immersed in the presence of inhibitor is in better condition resulting in smooth surface when compared with the surfaces of the coupons immersed in the corrosive media alone that is without the use of inhibitor. These developments have to do with the formation of good protective films by the inhibitor on the mild steel and aluminium surfaces which in turn were responsible for the inhibition of corrosion [9,38].

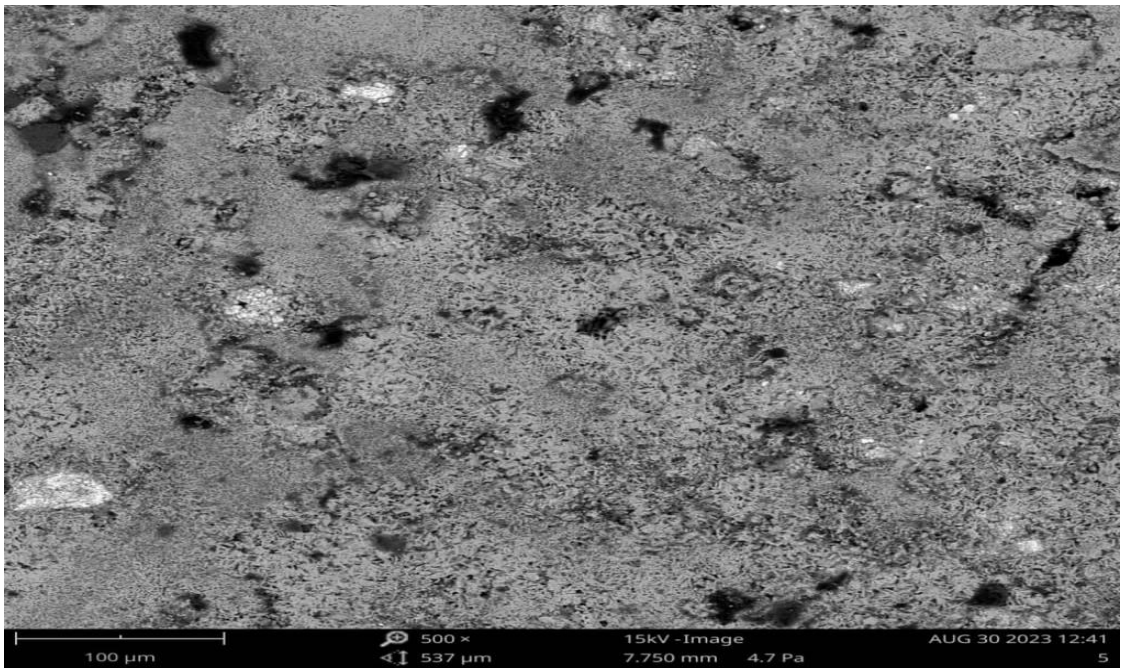


Plate 1: SEM image of mild steel after 3 hours immersion in 0.5M HCl at 303 K without inhibitor (Blank) at 500 × magnification.

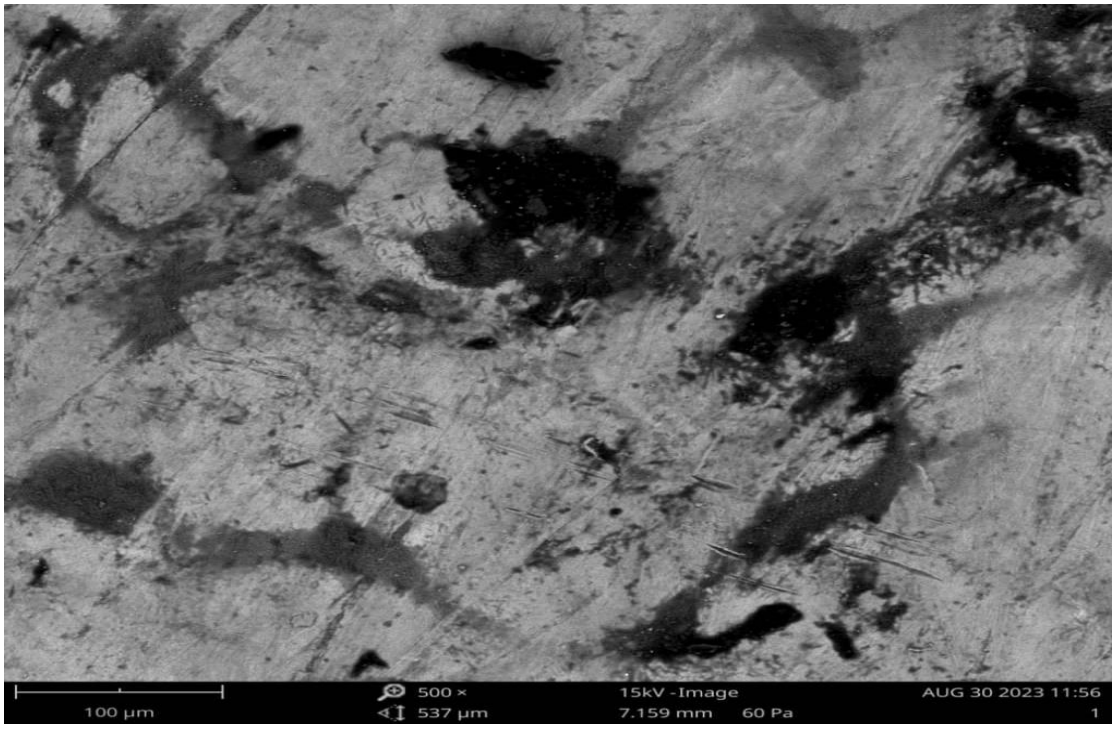


Plate 2: SEM image of mild steel surface after 3 hours immersion at 303 K in 0.5M NaOH in the presence of 0.7 g/L *Vangueria agrestis* leaves extract at 500 × magnifications.

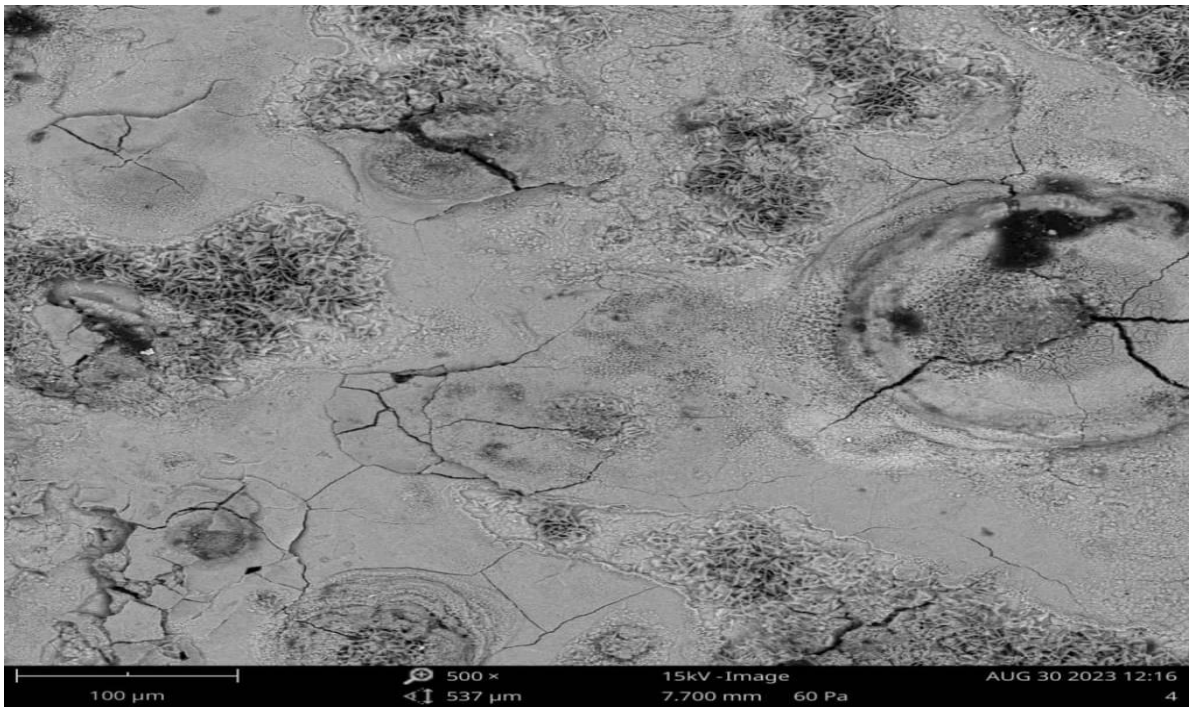


Plate 3: SEM image for aluminium in 0.5M NaOH without inhibitor **(**Blank**)** at 500 × magnifications.

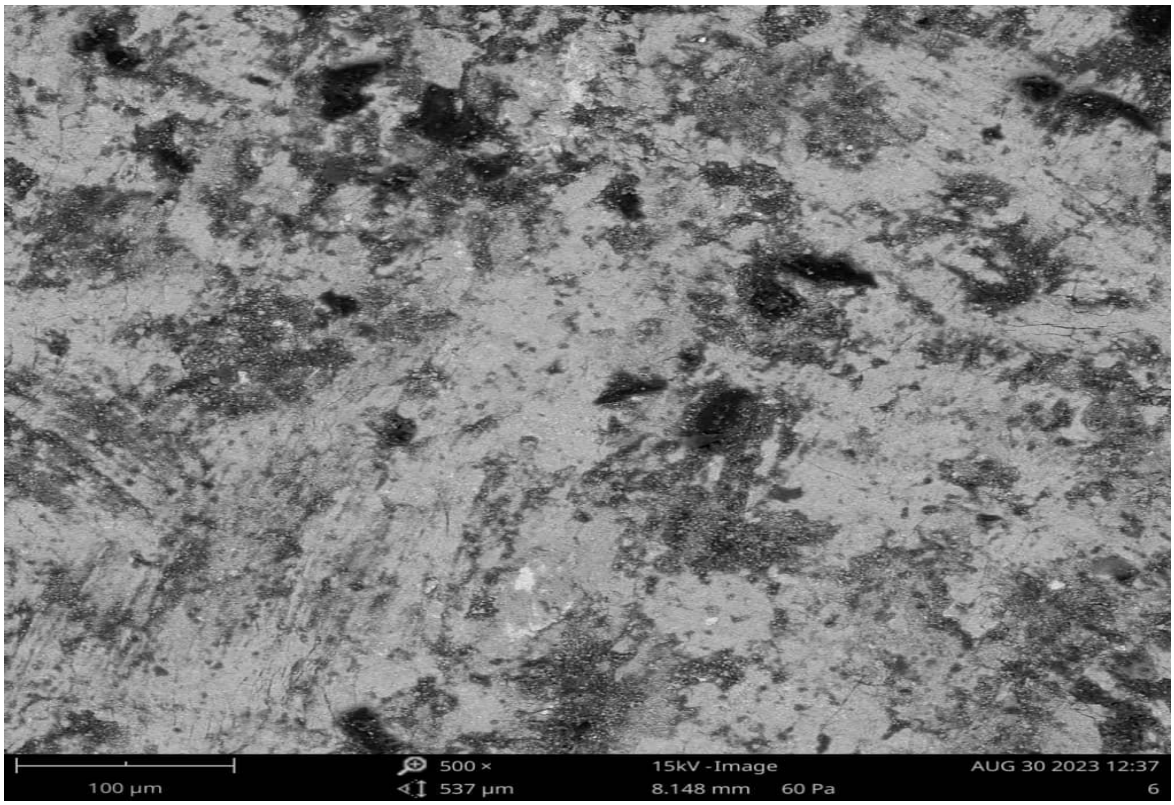


Plate 4: SEM micrographfor aluminium in 0.5M NaOH in the presence of 0.7 g/L *Vangueria agrestis* leaves extract at 500 × magnifications.

4.0 Conclusion

The potential of *Vangueria agrestis* leaves extract as corrosion inhibitor in 0.5 M HCl for mild steel and 0.5 M NaOH for aluminium were investigated. The results obtained show a general trend of decreasing in corrosion rate as the inhibitor extract concentration increases while the corrosion rate decreased with increase in temperature. The inhibition effect of the studied plant extract on the metals coupons could be attributed to the presence of C-H and O-H groups due to stretching found from FTIR analysis which are responsible for the adsorption on the surfaces of the coupons. The adsorptive nature of the research were all suggested to be physisorption (physical adsorption) and spontaneous. The Tafel polarization measurements conducted suggest that the inhibitor behave as mix type. SEM examination shows that the surfaces of the metals coupons immersed in 0.5 M HCl and 0.5 M NaOH in the presence of the plant extract gave smooth surfaces unlike the coupons immersed in the corrosive media in the absence of the plant extract resulted in having rough surfaces. Therefore, this research contributed that, *Vangueria agrestis* leaves extract can now be considered as eco-friendly and effective green corrosion inhibitor for mild steel and aluminium.

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