



Corrosion Inhibitive Dynamics of *Pennisetum Purpureum* (Elephant Grass) on Aluminum Metal in Acidic Media

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ABSTRACT

This work describes the inhibiting dynamics of elephant grass (*Pennisetum purpureum*) leaves extract on the corrosion of aluminum metal in 0.5 M HCl and 2 M HNO₃ media. The corrosion effect was studied using different concentrations of 0 - 60% v/v for both 0.5 M HCl and 2 M HNO₃ by adopting weight loss technique at varying temperature of 40⁰C and 60⁰C. Phytochemical screening was used to evaluate the anti – nutrients present in the inhibitor extract. Phytochemical analysis of the leaves detected the presence of tannins (++) , saponins (+) , steroids (+) and glycosides (+). Inhibition efficiency was found to increase with increasing inhibition concentration and decreasing temperature. The addition of halides to the extract enhanced the inhibition efficiency due to synergistic effect which improved adsorption of cationic species present in the extract and was in the order KCl < KBr < KI suggesting possible role of radii of the halide ions. Thermodynamic parameters determined showed that adsorption of *P. purpureum* on the metal surface is an endothermic and non – spontaneous process and that the adsorption was via a physisorption mechanism as a result of the existence of van der Waal's force (weak force) between the adsorbate and the adsorbent. The results showed that the leaves extract is a good inhibitor for aluminum metal in both acid media and better performance was obtained in medium.

Keywords: corrosion, inhibition, synergism, aluminum, physisorption, thermodynamics

INTRODUCTION

Corrosion is a major destructive process affecting the performance of metallic materials in applications in many construction sectors. Corrosion is a naturally occurring phenomenon commonly defined as deterioration of metal surfaces caused by the electrochemical reaction with the surrounding environmental conditions (Ating *et al.*, 2010).

Corrosion inhibitors are either organic or inorganic compounds, or more commonly formulations thereof that are added in small amounts to a corrosive environment in order to delay or decrease the corrosion process at the surface (Palou *et al.*, 2014). Organic compounds containing nitrogen atoms are commonly used to reduce the corrosion attack on aluminum in acidic media. These compounds can adsorb on the metal surface, block the active sites on the surface and thereby reduce the corrosion attack. The efficiency of these compounds as corrosion inhibitors can be attributed to the number of mobile electron pair present, the pi orbital character of free electrons and the electron density around the heteroatom like O, N or S (Abdallah *et al.*, 2005; Popova *et al.*, 2003).

Due to the fact that equipment constructed with materials resistant to corrosion are very expensive, it is common to use corrosion inhibitors as a practical, economical and simple alternative. The corrosion inhibitors formulations generally are made up of one or more active ingredients and suitable vehicles

(other additives and solvents) that encourage compatibility with the environment and make viable the active transport to the area to be protected (metal surface).

It is an established fact in surface chemistry that surface reactions are strongly affected by the presence of foreign molecules. Corrosion processes, being surface reactions, can be controlled by compounds known as inhibitors which adsorb on the reacting metal surface. Generally corrosion inhibitors may be divided into three broad classes namely, oxidizing, precipitating and adsorption inhibitors (Lebe *et al.*, 2014). The term adsorption refers to molecules attached directly to the surface, normally only one molecular layer thick, and not penetrating into the bulk of the metal itself. Adsorption inhibitors are usually organic substances containing heteroatoms with high electron density such as nitrogen, sulfur and oxygen and the presence of unsaturated bonds or aromatic rings in the molecular surface of the inhibitors favors adsorption on corroding metal surface. The adsorption is influenced by the nature and the surface charge of the metal, the type of corrosion media and the molecular structure of the inhibitor (Oguzie, 2006).

A corrosion inhibitor, when added in minute quantity slows down the rate of corrosion of a metal or a metal alloy. Corrosion inhibitors may act in a number of ways; it may restrict the rate of anodic process or the cathodic process or both by simply blocking active sites on the metal surface. Alternatively it may act by increasing the potential of the metal surface so that the metal enters the passivation region where a natural oxide film forms. A further mode of action of some inhibitors is that the inhibiting compounds contribute to the formation of a thin layer on the surface which stifles the corrosion process.

It is known that some corrosion inhibitors and their derivatives are toxic and pollute the environment (Manahan, 1999). There is therefore the need to explore new non – toxic, environmental friendly, ecologically acceptable and inexpensive corrosion inhibitor substitutes. Among the alternative of corrosion inhibitors, natural products of plant origin have been shown to be quite efficient as corrosion inhibitors (Lebe *et al.*, 2014; Oguzie, 2006; Abiola *et al.*, 2009).

Elephant grass is a tall grass that originally came from Africa (Uganda) in 1913. It is commonly called Napier grass, Uganda grass and belongs to genus of pennistum and species *purpureum*. It grows in dense clumps of up to 10 feet tall. It does reproduce sexually but the seeds are very small and do not germinate well. The grass mainly reproduces mainly through its rhizomes (root – like underground stem that produce roots below and sends up shoots to the surface) (Butterworth, 1965).

Aluminum is an element with the symbol Al, a group 13 element in period 3 with atomic number 13; it is a silvery white, soft, ductile metal. It resists corrosion when pure in spite of its chemical activity because of a thin surface layer of oxide.

Nowadays aluminum metal has become an important part of our life due to its extensive use for applications in household as well as its use as building materials and various industrial operations. There is need to stop and reduce the rate at which this metal corrode, this can be achieved through the use of inhibitors.

The study of corrosion rate of aluminum using plant extract has been done by several scientists. There is therefore the need to explore new non – toxic, environmental benign, ecologically acceptable and inexpensive corrosion inhibitors.

The aim of this work is to replace toxic corrosion inhibitors with pennistum *purpureum* extract which are of plant origin and are usually non – toxic, readily available, inexpensive and environmentally friendly. The actions of the leaf extract as inhibitor in both 1 M HCl and 2 M HNO₃ over a range of inhibitor concentration and solution temperature, as well as synergistic effects of halides have been studied. The phytochemical screening of the plant extract has also been evaluated.

MATERIALS AND METHODS

Sample Collection and Preparation

The metal coupons in this study used was pure Aluminum metal, which was obtained from First Aluminum Company, Trans-Amadi, Port – Harcourt, Rivers State, Nigeria. The metal sheet was cut into a specific dimension of 2 cm x 4 cm x 0.1 cm. Each coupon was perforated to give a hole of same diameter, at about 0.5 cm from the length of the coupon, to allow the passage of the thread.

The metal coupons were brushed and washed with distilled water and were afterwards degreased in acetone to remove impurities before taken the initial weight and was identified using alphabetical letters.

Preparation and Characterization of Elephant grass (P. Purpureum)

The elephant grass leaves used for this study were obtained from around the Faculty of Social Sciences, University of Port – Harcourt, Rivers State. It was identified by the department of Plant Science and Biotechnology of the University of Port – Harcourt as *P. purpureum*. The flesh matured leaves were washed using tap water, and then rinsed with distilled water. The leaves were then cut into smaller parts of about 6 cm length and oven dried at a temperature of 100⁰C for 105 minutes (1 hour 45 minutes). Then after was ground into fine powder for better surface area and stored in a desiccator awaiting analysis. Phytochemical screening for tannins was carried out using the method described by Evans and Trease, (2009) while glycosides, alkaloids by Sofowora, (1993) and saponins by Harborne, (1973).

Preparations of Stock Solution of Elephant Grass Extract using 0.5 M HCl and 2 M HNO₃ and Procedure

Chemicals used for this study are of Analytical grade. Ground elephant grass (10 g) weighed and poured into 500 mL flat bottom flask and 400 mL of 0.5 M HCl standard solution was added into it and was heated under reflux with a condenser (quick fit) using a hot plate regulated at 50⁰C for three (3) hours. This was repeated for 3 times to get a volume of 1,200 mL (1.2 liters) volume of stock solution of plant extract.

After 3 hours the elephant grass solution was allowed to cool overnight and filtered using a filter paper to get a clear solution. It was then pour into a 1000 mL volumetric flask. Similarly, 2 M HNO₃ was equally used to prepare the stock solution repeating the procedures above. The test inhibitor, *P. purpureum* was used in the concentration range 10 – 60 % v/v, while 0.05 M of the halide ions was used. Gravimetric experiments were conducted on test coupons of dimension 2 x 4 x 0.1 cm. Tests were conducted under total immersion conditions in 400 ml of test solutions at 40⁰C and 60⁰C. The pre – cleaned and weighed coupons were suspended in beakers containing the test solutions using glass hooks and rods. All tests were made in aerated solutions and were run in triplicate. To determine weight loss with respect to time, the coupons were retrieved from test solutions at 1 – 5 hrs intervals appropriately cleaned, dried and re – weighed. The weight loss was taken to be the difference between the weight of the coupons at a given time and its initial weight.

RESULTS AND DISCUSSION

Phytochemical Screening of the Extract

Phytochemical analysis of the leaves detected tannins (++) , saponins (+), steroids (+) and glycosides (+).

Effect of Immersion Time on Corrosion Rate

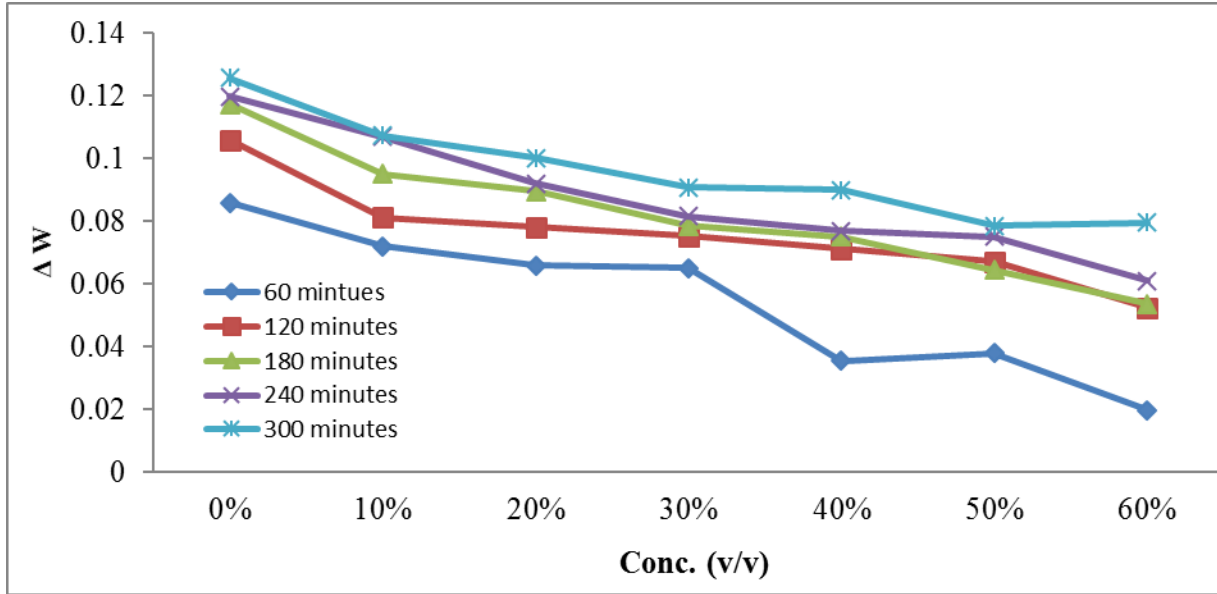


Figure 1: ΔW with concentration in 0.5 M HCl at 40°C

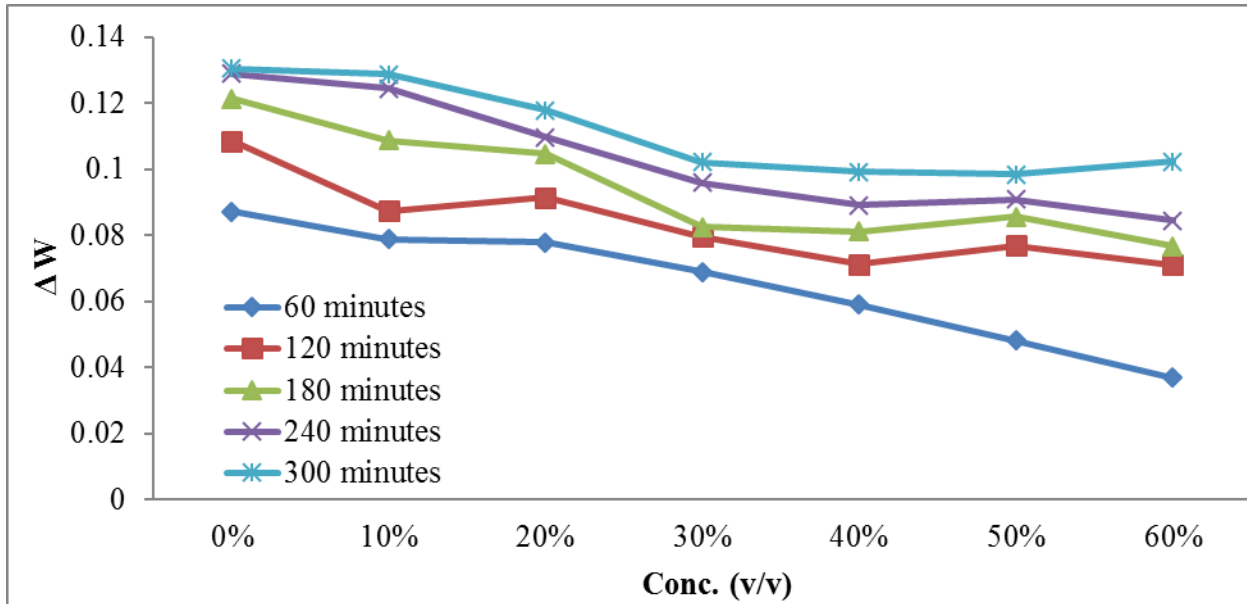


Figure 2: ΔW with concentration in 0.5 M HCl at 60°C

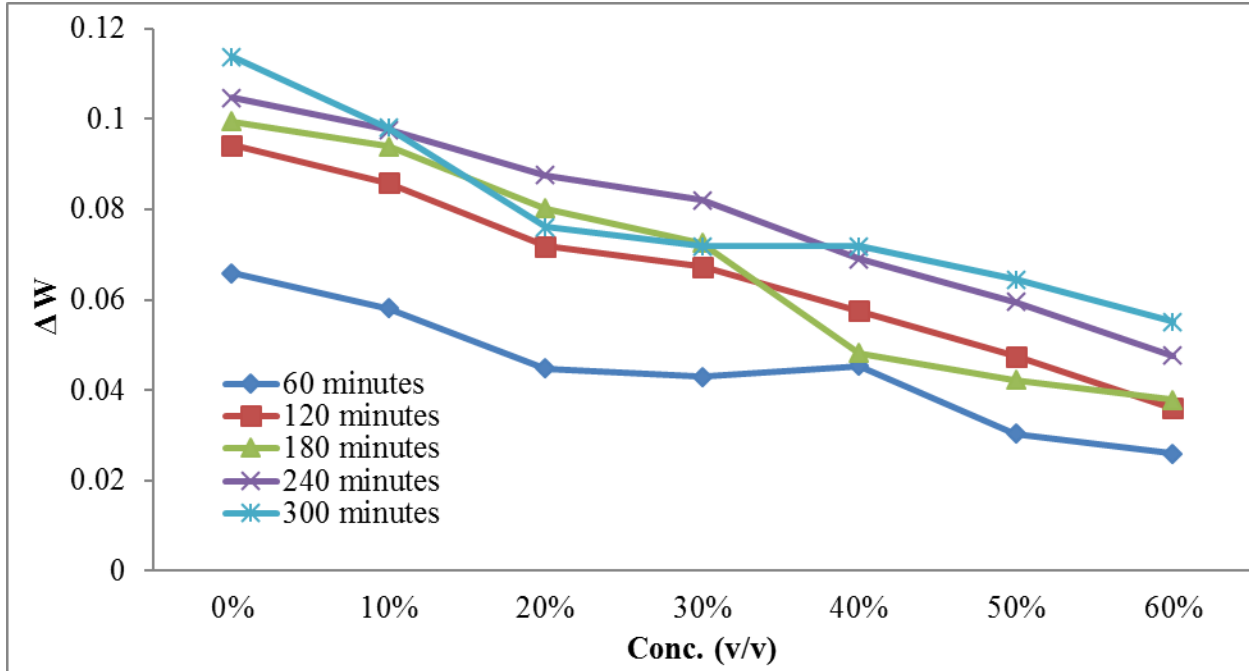


Figure 3: ΔW with concentration in 2 M HNO_3 at $40^\circ C$

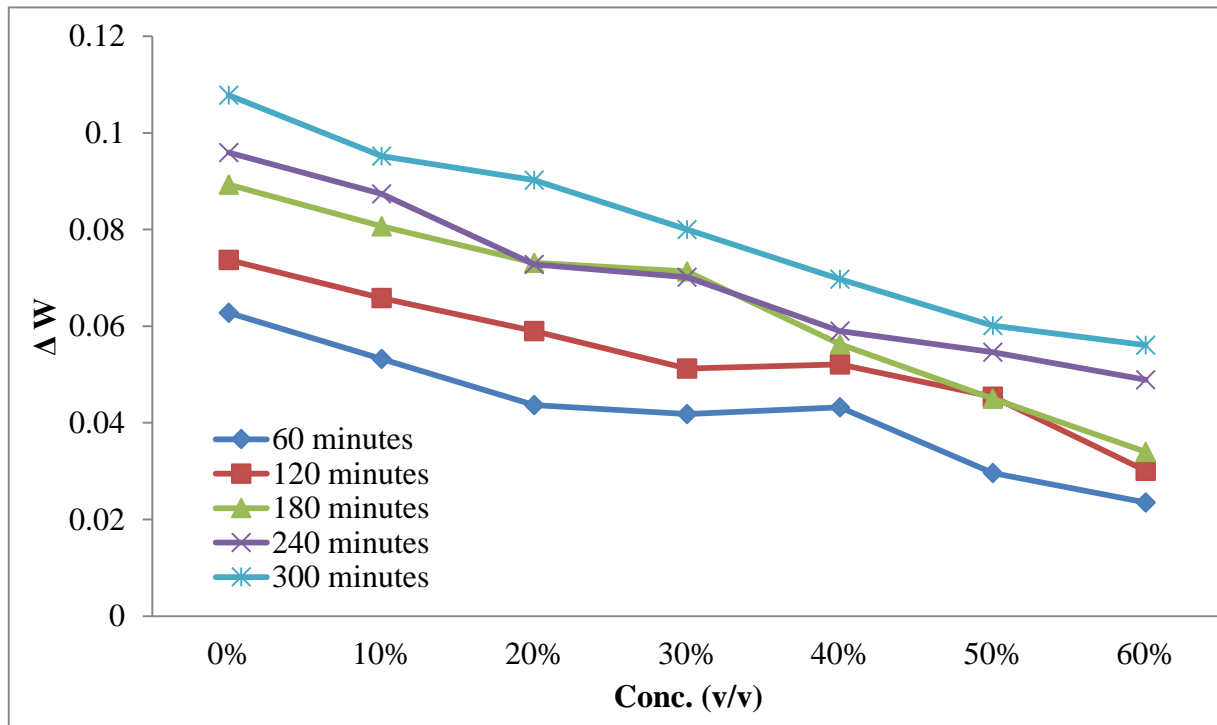


Figure 4: ΔW with concentration in 2 M HNO_3 at $60^\circ C$

Weight loss measurement of aluminum metal subjected to acidic media in the absence and presence of *P. purpureum* extract were made at various time intervals. The effect of change in weight loss as a function of the concentration is presented in Figures 1 – 4.

The results obtained showed that increasing concentration decrease weight loss with respect to time. The implication is that the *P. purpureum* worked effectively as a corrosion inhibitor.

Inhibition Efficiency

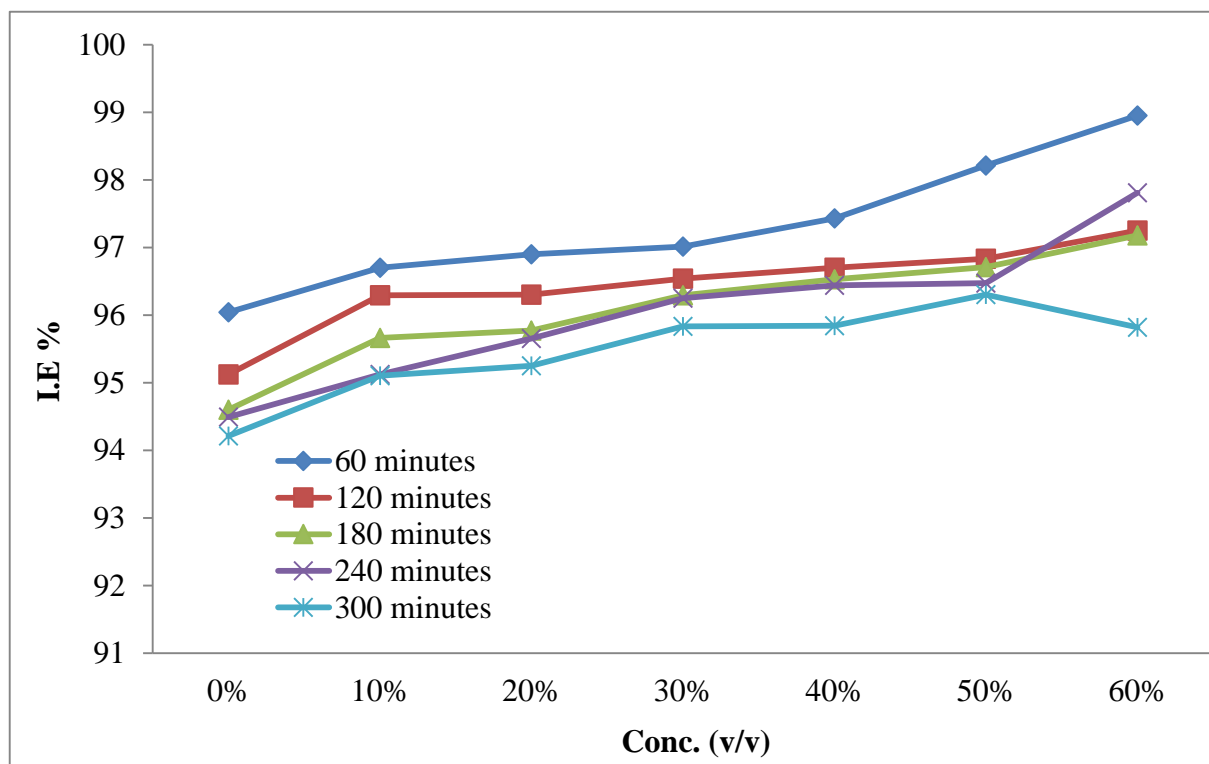


Figure 5: Inhibition efficiency of *P. purpureum* at 40°C in 0.5 M HCl extract solution with respect to varying time interval.

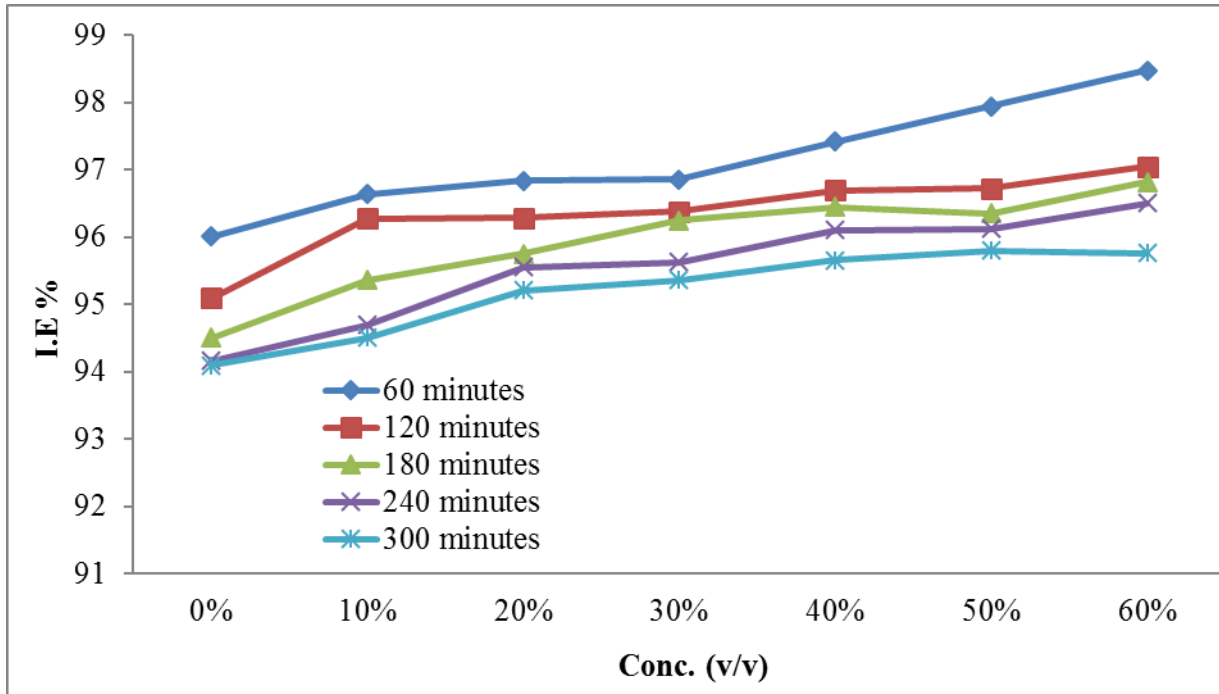


Figure 6: Inhibition efficiency of *P. purpureum* at 60°C with 0.5 M HCl solution with respect to varying time interval

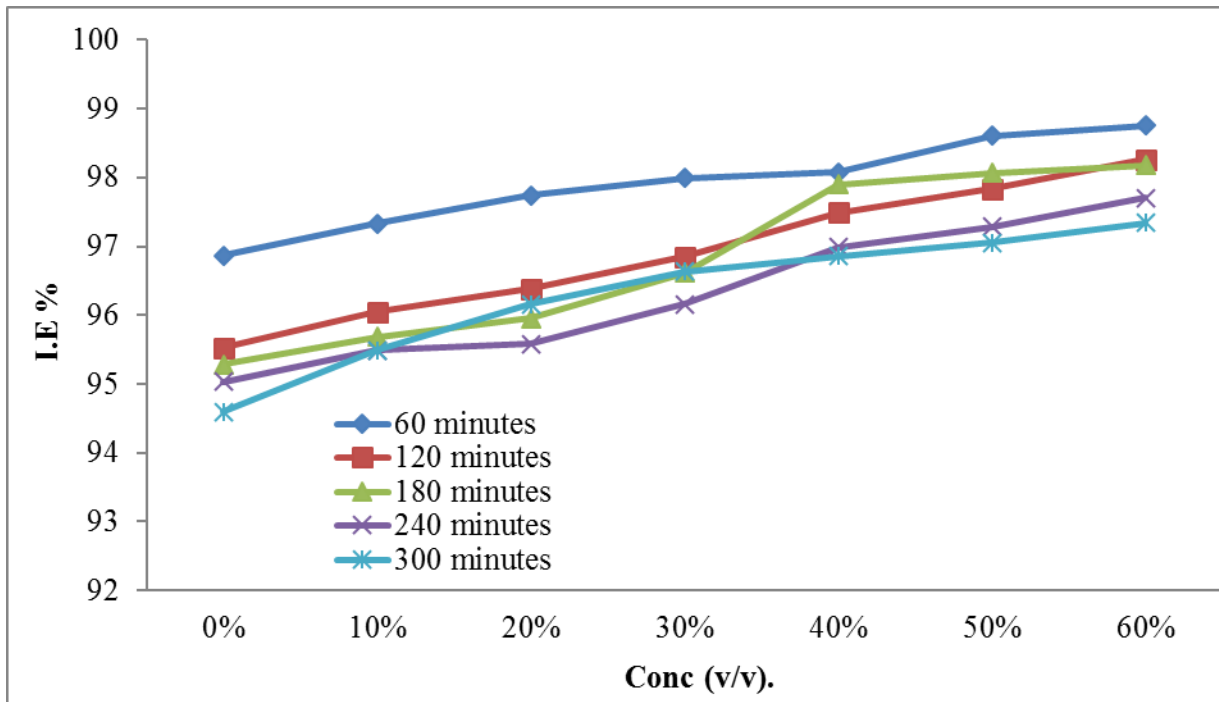


Figure 7: Inhibition efficiency of *P. purpureum* at 40°C with 2 M HNO₃ solution with respect to varying time interval

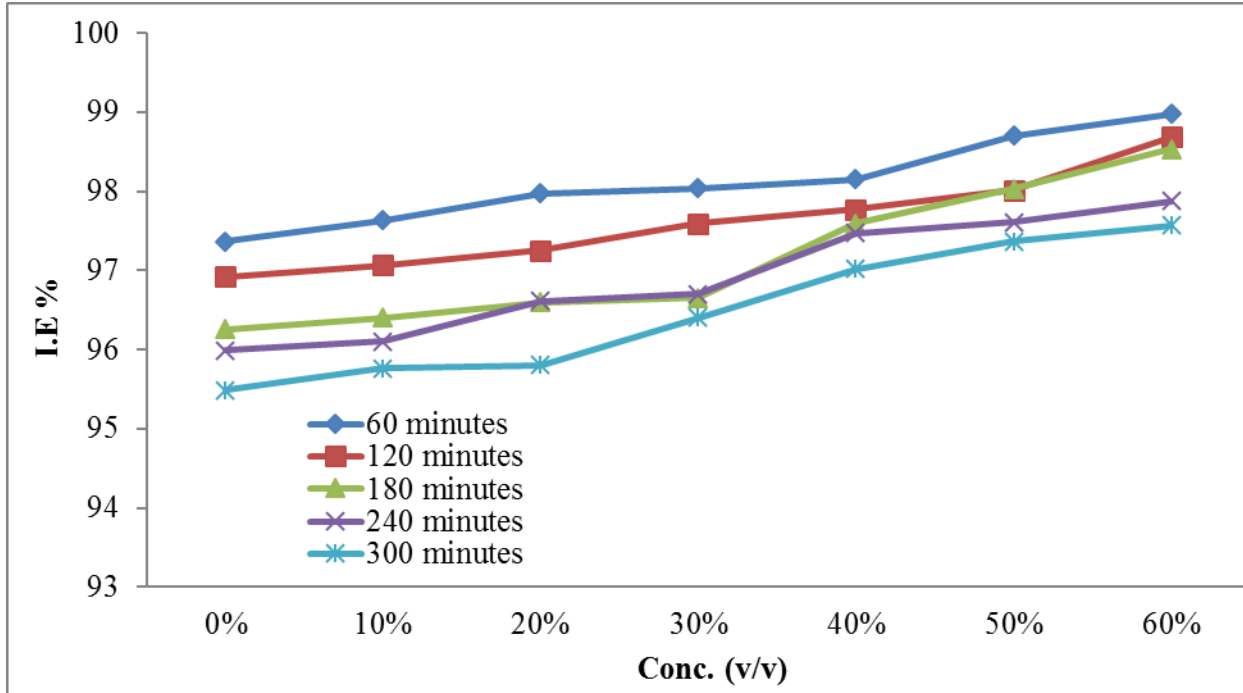


Figure 8: Inhibition efficiency of *P. purpureum* at 60°C with 2 M HNO₃ solution with respect to varying time interval

The percentage inhibition efficiency (IE, %) for the weight loss measurement was calculated using the inhibition efficiency formula shown in equation 1 and 2. The degree of surface coverage (Θ) of *P. purpureum* extract on aluminum metal in acidic media was evaluated from:

$$IE = 100 \times 1 - \left(\frac{W_F - W_I}{W_I} \right) \dots\dots\dots 1$$

$$\Theta = 1 - \left(\frac{W_F - W_I}{W_I} \right) \dots\dots\dots 2$$

Where W_F and W_I are the final and initial weight loss of aluminum metal.

The result showed that the extract retarded acidic corrosion of the aluminum metal. The results further revealed that the surface coverage and inhibition efficiencies increased with increasing inhibition concentration at both temperatures.

The effect of temperature on the corrosion behavior of aluminum metal in the absence and presence of *P. purpureum* extract was investigated and are presented in Figures 5 – 8. It can be clearly noticed that the inhibition efficiency of *P. purpureum* extract was higher in 0.5 M HCl than in 2 M HNO₃ over the concentration range studied, suggesting that the nature of the acidic anion influences metal – inhibitors interaction. In the presence of strong acids, some inhibitor species become protonated. The surface charge on aluminum in acidic solution is positive at the corrosion potential and specific adsorption of chloride ions of HCl renders the metal surface more negative and susceptible to adsorption of protonated inhibitor species compared to HNO₃. Thus the adsorption of the protonated species on the metal surface will be enhanced in HCl, leading to higher inhibition efficiencies.

Adsorption Isotherm Behavior

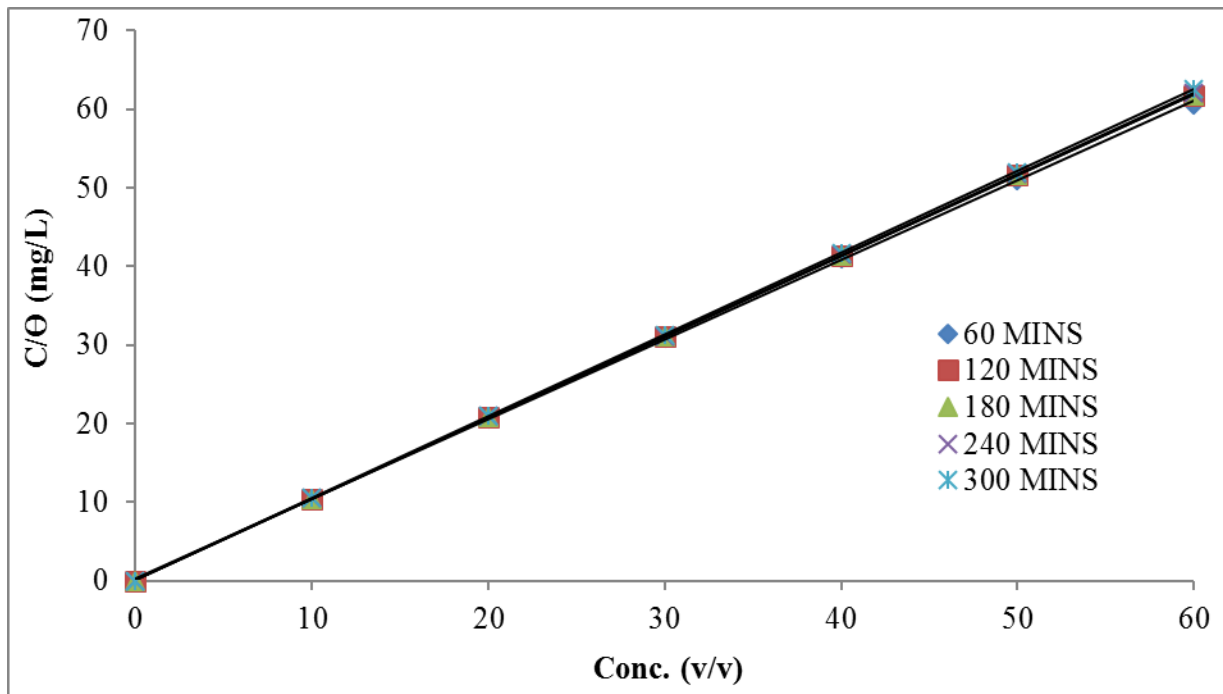


Figure 9: Plot of C/Θ against different concentration of 0.5 M HCl extract solution at 40°C

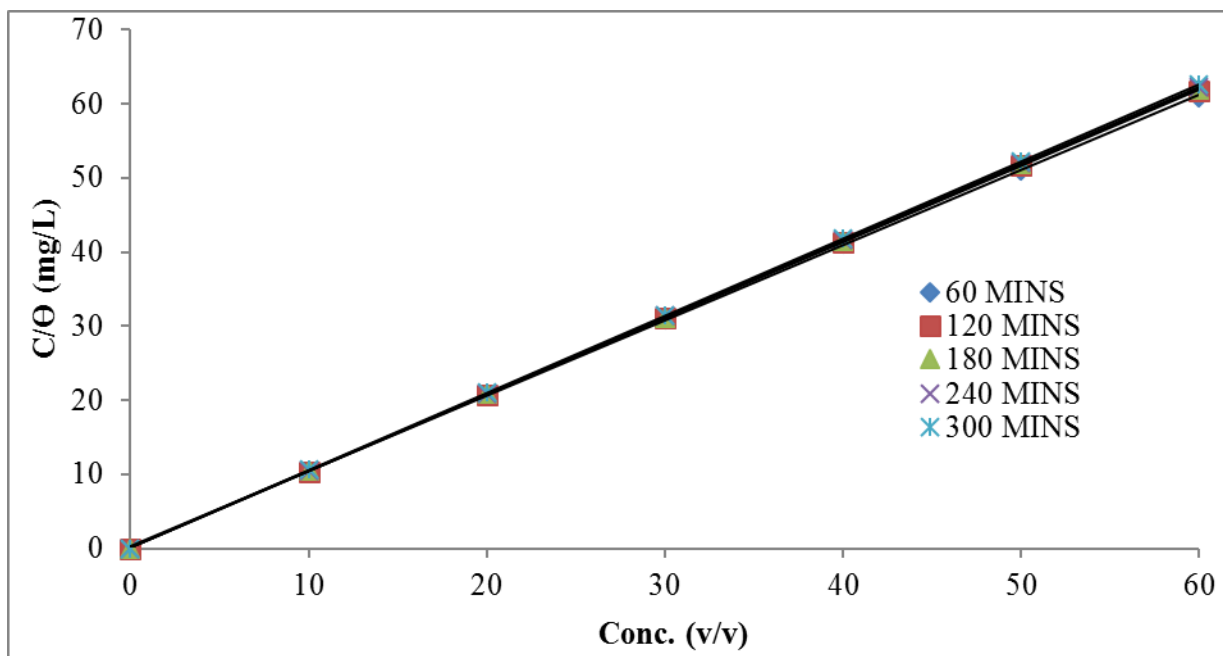


Figure 10: Plot of C/Θ against different concentration of 0.5 M HCl extract solution at 60°C

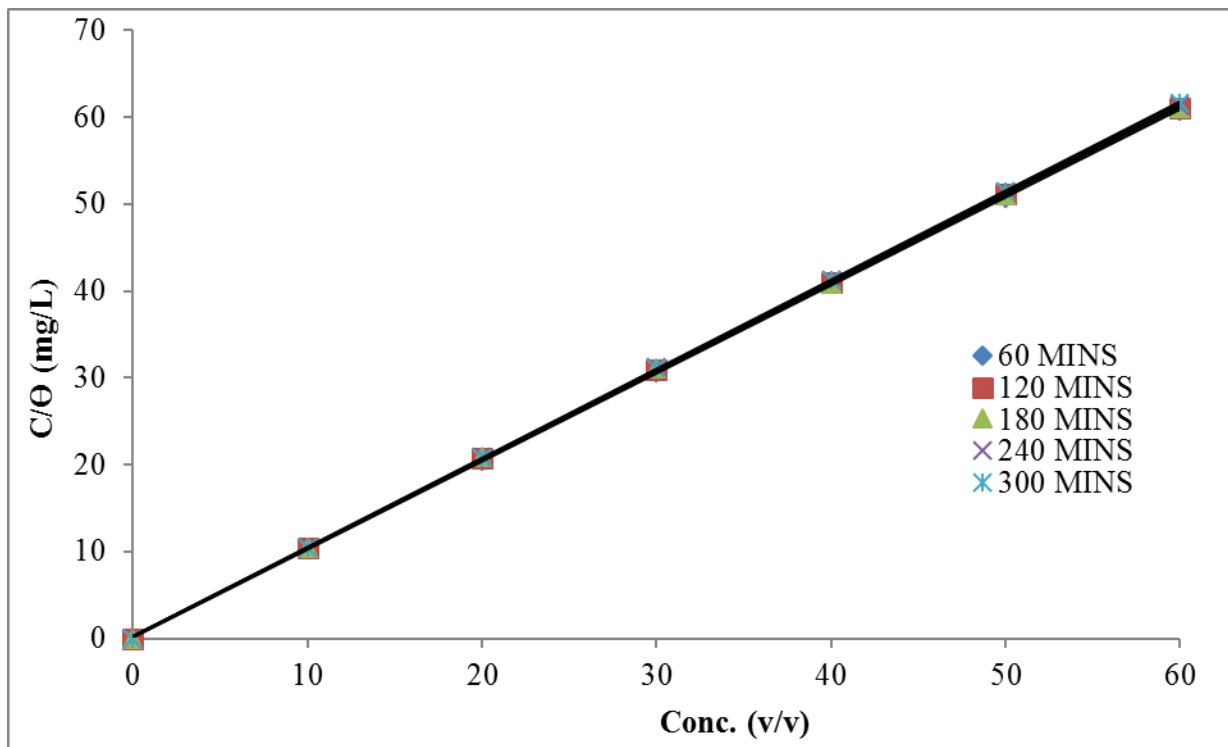


Figure 11: Plot of C/Θ against different concentration of 2 M HNO₃ extract solution at 40°C

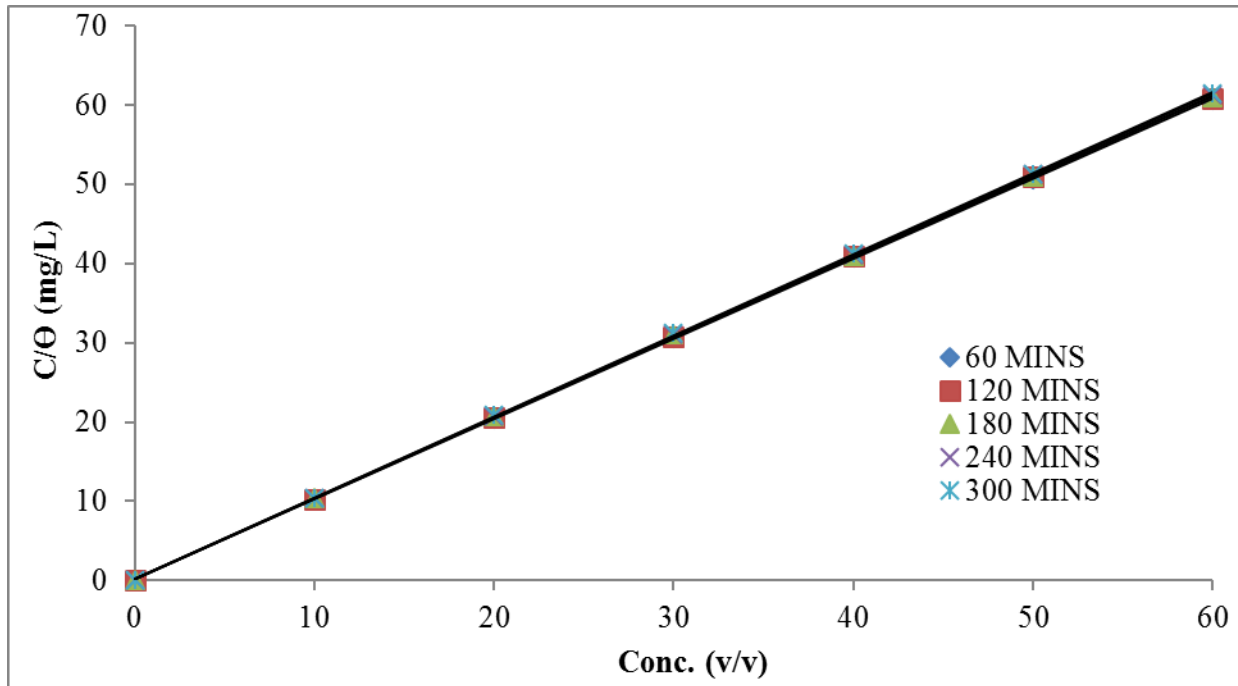


Figure 12: Plot of C/Θ against different concentration of 2 M HNO₃ extract solution at 60°C

Experimental and theoretical studies have shown that the protective action of organic substances during metal corrosion is based on the adsorption ability of their molecules, where the resulting adsorption film prevents the metal surface from corroding (Bouklah *et al.*, 2006). Therefore, Langmuir adsorption isotherm expression was employed in this study and it is given as:

$$\frac{C}{\theta} = \frac{1}{K} + C \dots\dots\dots 3$$

The above equation relates the surface coverage (θ) and inhibitor concentration (C) with adsorption equilibrium constant, K , at the different temperatures. The plots of $\frac{C}{\theta}$ versus C for 0.5 M HCl and 2 M HNO₃ are represented in Figures 9 - 12 and the values of K are calculated from the intercept of the plot. The correlation coefficient (R^2) values which were all above 0.9999 showed a good fit of the experimental data and suggests that the adsorption of *P. purpureum* extract on aluminum metal surface followed the Langmuir adsorption isotherm equation (Orubite – Okorosaye and Oforika, 2004).

Negative activation energy values obtained, which showed that increase in temperature, decreased the rate of corrosion. It implies that the reaction is reversible. More so, the increase in time variation decreased the activation energy.

In addition standard Gibbs free energy was calculated from the expression below:

$$\Delta G^\circ = -RT \ln K \dots\dots\dots 4$$

Where ΔG° is the standard Gibbs free energy change, R is gas constant, T is temperature, K is adsorption equilibrium constant.

The standard Gibbs free energy obtained gave positive values which showed that adsorption of *P. purpureum* on the metal surface is an endothermic and non – spontaneous process.

Table 1: Calculated values of K, correlation coefficient (R²), and activation energy (E_a) in 0.5 M HCl extract solution at 40⁰C and 60⁰C

Time (minutes)	40 ⁰ C			60 ⁰ C		
	K	R ²	E _a	K	R ²	E _a
60	0.2729	0.9999	-19.3846	0.2229	0.9999	-19.4612
120	0.1143	1	-19.7082	0.0957	1	-19.7407
180	0.1657	1	-19.7139	0.1304	1	-19.7828
240	0.1454	1	-19.7733	0.1525	1	-19.8422
300	0.0764	1	-19.9284	0.1018	1	-19.9686

Table 2: Calculated values of K, correlation coefficient (R²), and activation energy (E_a) in 2 M HNO₃ extract solution at 40⁰C and 60⁰C

TIME (minutes)	40 ⁰ C			60 ⁰ C		
	K	R ²	E _a	K	R ²	E _a
60	0.1414	1	-19.3846	0.1429	1	-19.3559
120	0.2421	0.9999	-19.4803	0.1721	0.9999	-19.4324
180	0.2857	0.9999	-19.4478	0.2582	0.9999	-19.4401
240	0.2643	0.9999	-19.5856	0.1850	1	-19.5473
300	0.1629	1	-19.6622	0.2257	0.9999	-19.6009

Table 3: Calculated standard Gibbs free energy values at 40°C and 60°C in 0.5 M HCl and 2 M HNO₃ extract solution on aluminum metal.

TIME (MINUTES)	ΔG^0 (KJ/mol)			
	0.5 M HCl		2 M HNO ₃	
	40°C	60°C	40°C	60°C
60	3379.4531	4155.7003	5090.4865	5386.5425
120	5644.1641	6496.5331	3691.0883	4871.7820
180	4677.8006	5639.9723	3260.1726	3748.6905
240	5017.8938	5206.5319	3462.7798	4671.6700
300	6692.4775	6325.4587	4722.1498	4121.1391

Effect on Halides

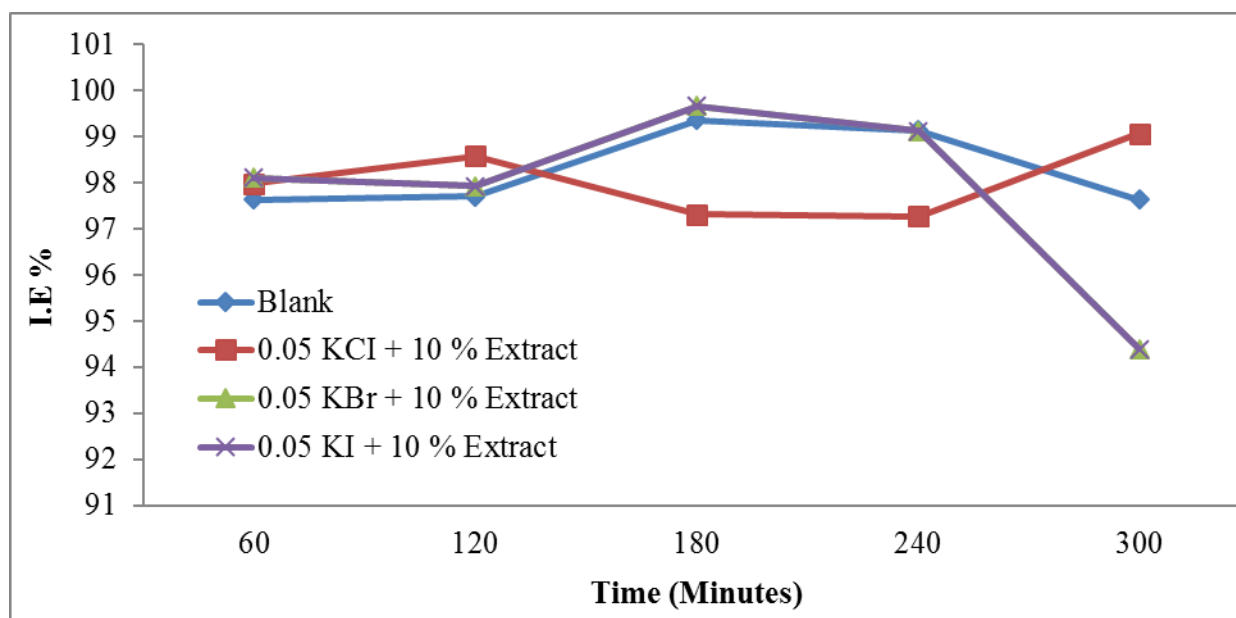


Figure 13: A plot of percentage inhibition efficiency with time showing the effect of halides in 0.5 M HCl at 40°C

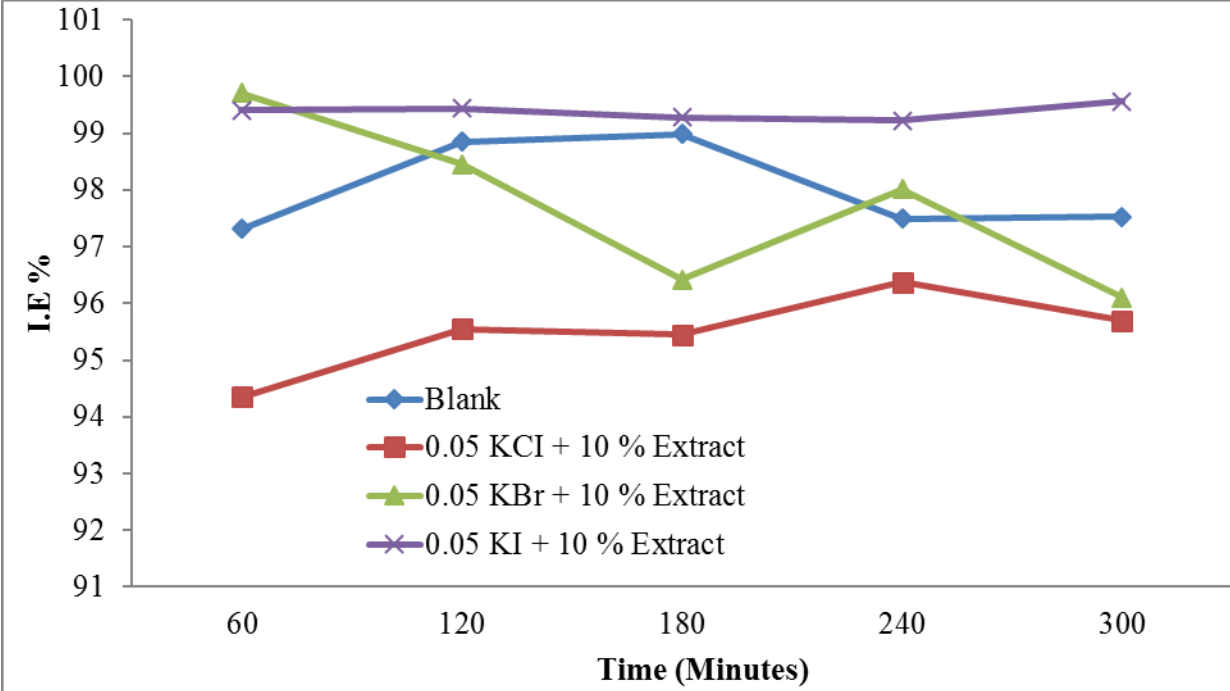


Figure 14: A plot of percentage inhibition efficiency with time showing the effect of halides in 0.5 M HCl at 60°C.

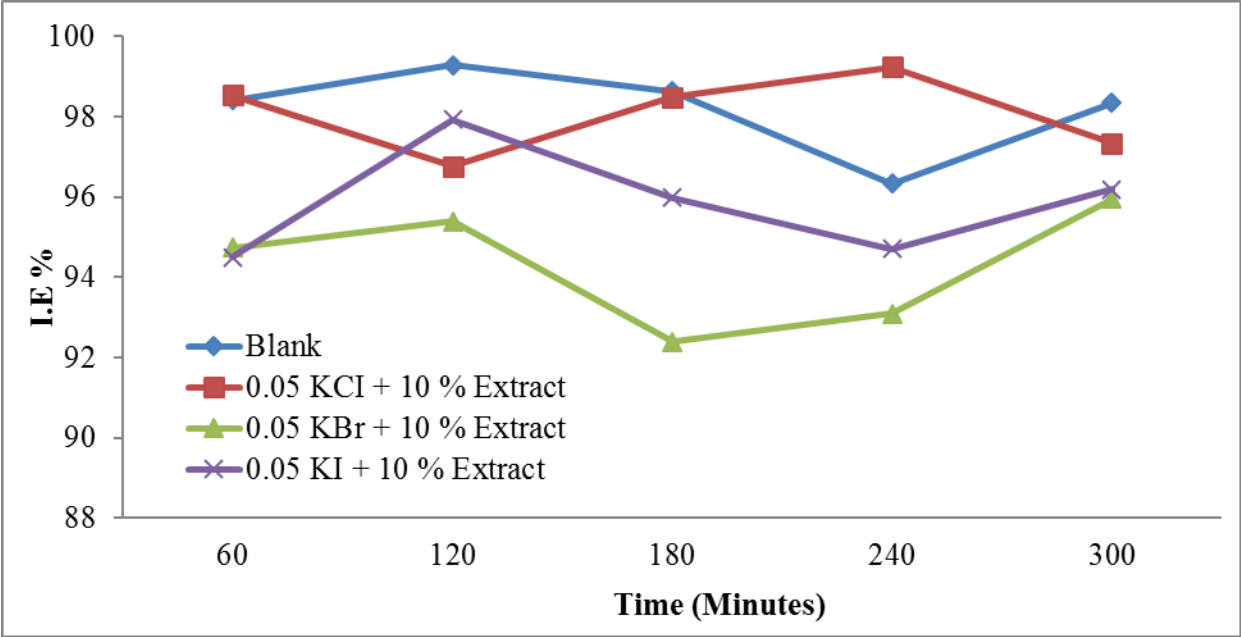


Figure 15: A plot of percentage inhibition efficiency with time showing the effect of halides in 2 M HNO₃ at 40°C.

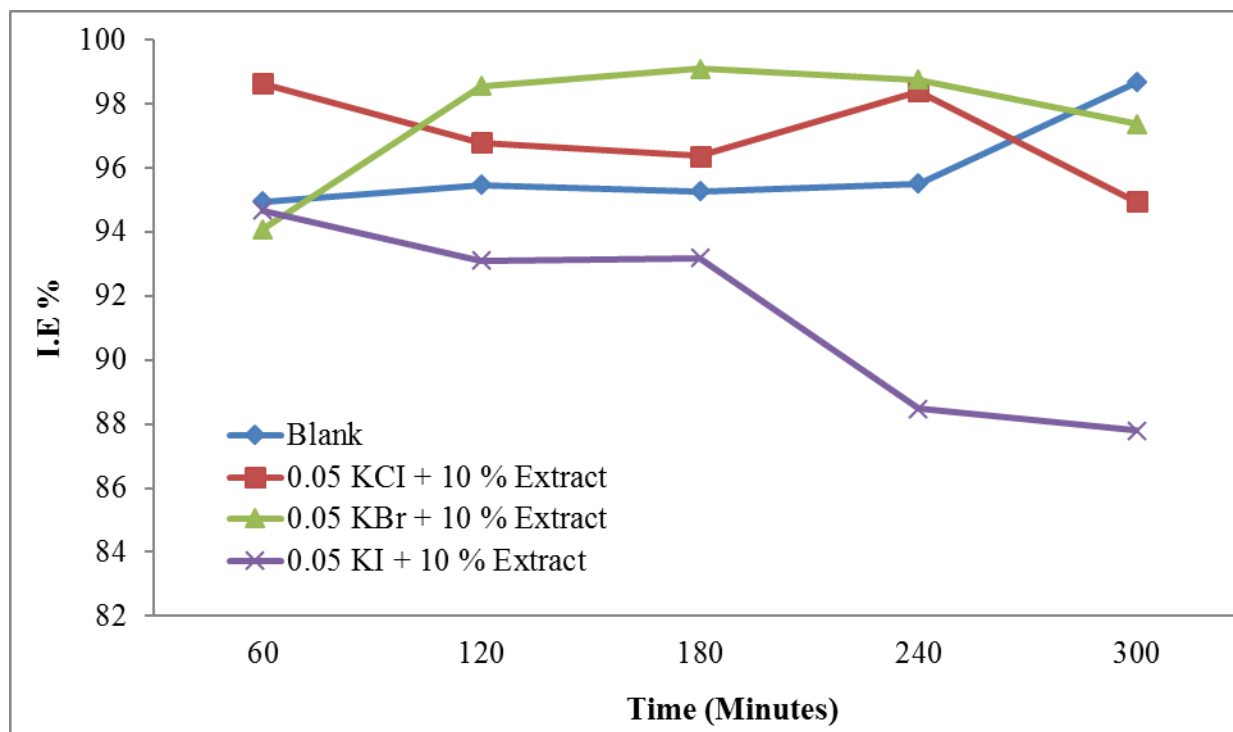


Figure 16: A plot of percentage inhibition efficiency with time showing the effect of halides in 2 M HNO₃ at 60°C.

The values of the percentage inhibition efficiency for 5×10^{-2} M of KCl, KBr and KI in the presence of various concentrations of inhibitors are presented in Figures 13 – 16.

The inhibition efficiency of *P. purpureum* extract was significantly improved in the presence of halide ion in both acid media and at both temperatures studied (Oguzie, 2006; Oguzie *et al.*, 2005; Ebenso, 2003). The results obtained illustrated that the adsorption of protonated species in *P. purpureum* extract was enhanced through ion pair interactions with the halide ions forming an intermediate bridge between the metal surface and the inhibitor. This observation is in line with the work done by Lebe *et al.*, (2014) and Popova *et al.*, (2003).

CONCLUSION

The inhibition of aluminum metal by *P. purpureum* leaf extract in 0.5 M HCl and 2 M HNO₃ at varying temperature of 40°C and 60°C showed that inhibitor efficiency increased with increase in *P. purpureum* extract concentrations and synergistically increased in the presence of KCl. Temperature studies revealed a decrease in inhibition efficiency with rise in temperature. Time variation studies also revealed a decrease in inhibition efficiency with increase in time.

Comparative analyses of the results from both acid solutions suggest that protonated species in the extract play a predominate role in the inhibitive behavior observed, with the predominant effect being the physical adsorption of protonated species. Physical adsorptions (physiosorption) occurs when the force of attraction existing between the adsorbate and adsorbent are vander Waals forces (weak forces) therefore this type of adsorption can easily reverse by heating or decreasing the pressure.

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