# Corrosion Inhibitive Characteristics of *Vernonia amygdalina* (Bitter Leaf) on Mild Steel in Seawater

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**Abstract** The corrosion inhibitive characteristics of *Vernonia amygdalina* (Bitter leaf) extract on mild steel in seawater were investigated using gravimetric method. The parameters studied were effects of inhibitor concentration and time on weight loss and corrosion rates (CR) of the coupons. Different inhibitor concentrations ranging from 0-25% were added to the corrosive medium and allowed for specific durations. Investigations carried out revealed that at higher concentrations, CR did not reduce correspondingly. Furthermore, results show that weight loss values for samples tested in solutions without inhibitor were much higher than those in solutions with inhibitor. Furthermore, plots of weight loss and corrosion rate against time of immersion revealed that generally, weight loss was inversely proportional to CR. Although, the CR generally decreased with time for almost all the concentrations investigated, weight loss values consistently increased with time. An indication that the inhibitor was gradually losing its effectiveness with time and requires more inhibitor being added to the corrosive medium at regular intervals if the effectiveness of the inhibitor must be sustained.

**Keywords** Corrosion inhibitor, *Vernonia Amygdalina*, mild steel, seawater

## 1. Introduction

A combination of the unique mechanical properties and economic viability of Mild Steel (MS) has made it one of the most versatile construction materials used in various industrial applications viz; petroleum production and refining, marine applications, chemical processing, construction, metal processing and other industries [1-2]. However, it is highly prone to corrosion [1] when exposed to chloride media and seawater is one of such. Although, the major chemical constituents of seawater are relatively consistent worldwide, it is a complex chemical system affected by many factors such as concentration and access of dissolved oxygen, salinity, biological activity and several pollutants [2] all of which could influence, in isolation or combined, the behavior of MS in seawater. It is crucial that the risk of failure of materials made of MS is subdued since they are often disastrous, life threatening and of high economic loss [3]. Corrosion, in its various forms is often a major contributing factor to such catastrophic failures. The nature and veracity of MS corrosion is often dependent amongst others, on the pH of the corrosive medium and the corrosion process. In seawater, the predominate presence of Cl⁻ ions is a major driving force behind its corrosive behavior. The use of pipelines as a means of transporting fluids over long distances is an age long practice [4]. This is because they are considered relatively safer routes compared to other modes of conveying natural gas needed for our daily energy requirements. Pipelines are made of several materials *e.g*., steel, aluminum, copper, etc. The choice of material depends on a number of factors, and these include: cost, durability, strength, resistance to corrosion, accessibility etc. Although, MS is versatile and possesses most of the aforementioned properties, it often suffers devastating

corrosion when exposed to most aggressive media. Corrosion is the deterioration and gradual destruction of a material as a result of the chemical or electrochemical reactions of this material and its environment. The consequences of corrosion are often numerous, and the effects on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass of the metal [5]. Consequently, the need to control corrosion of MS continues to be a major concern to the engineer [3,6] as failure of various kinds may occur and expensive replacements required even though the amount of metal destroyed may be small [5]. Besides, it is pertinent to obtain real time environment performance data of MS in order to aid effective design of mitigation programme and prediction of its service life [2]

An attractive way of combating corrosion is the use of corrosion inhibitors [7-12]. Most of the efficient inhibitors are organic compounds that contain in their structures mostly nitrogen, sulphur or oxygen atoms and function via adsorption of the molecules on the metal surface creating a barrier to corrosive attacks [13]. It has been reported [7,8] that *V. Amygdalina* possesses such characteristics. *V. Amygdalina* is a plant commonly available in most African and Asian countries. The leaves, roots and stems are edible. The leaves are often used to prepare vegetable soup and the roots as chewing stick in some parts of Nigeria [7]. Although, the use of *V. Amygdalina* as corrosion inhibitor has been reported [7-9] elsewhere, there is paucity in this regard in natural environments such as seawater. Hence, this work seeks to study the effect of using *V. Amygdalina* extract on MS coupons submerged in seawater**.** The choice of bitter leaf was driven by the fact that it is a major nutritional vegetable used in most African households. Its processing generates a lot of waste water (the plant extract) that could be recycled as a useful and ready green inhibitor for industrial applications.

## 2. Materials and Methods
The investigations were carried out based on ASTM G13: A recommended standard practice for laboratory immersion corrosion testing of materials.

### 2.1. Test Apparatus
MS specimens; corrosive medium-seawater, 2M concentration of *Vernonia Amygdalina* (bitter leaf) extract solution, distilled water, plastic bowl, top-loading electronic chemical weighing balance, measuring cylinder, beakers, rubber threads, acetone, wooden sticks.

### 2.2. Sample Preparation
MS samples were cut to size with dimensions of 35 x 30 x 1mm. All cut and sheared edges were ground to prevent them from becoming sites for preferential attack. This was followed by finishing of the sample surface with grit abrasive paper (sand paper). Samples were then rinsed in distilled water, degreased in acetone and air dried. Degreasing was done to remove any dirt, oil or grease that might interfere with the investigations. After drying, specimens were weighed simultaneously to obtain their initial weights. The volume of test solution was relatively large (a solution volume-to-specimen area of 30 ml/cm$^2$) enough to avoid any appreciable changes in corrosivity during the test, either through exhaustion of corrosive constituents or accumulation of corrosion products. The method of supporting the specimens ensured the insulation of the specimen from each other physically and electrically, and also from the plastic container used.

### 2.3. Preparation of Inhibitor
1200g of *V. Amygdalina* leaves were plucked, weighed and crushed. 600cl of water was added to the crushed leaves. The mixture was put in a filter cloth and squeezed with hand to filter out the active ingredients responsible for corrosion inhibition. With this, 2M concentration of *V. Amygdalina* extract was prepared.

### 2.4. Experimental procedure
MS coupons were immersed in different plastic containers containing 400ml of seawater with pH value of 7.25 without inhibitor as the control solution. Each set of the specimen were looped about a wooden stick with the aid of rubber strings. The specimens were suspended by the strings and completely immersed in the test medium with different percentage concentrations of inhibitor ranging from 5%, 10%, 15%, 20%, and 25% respectively. For purposes of minimal error, air tight electronic balance was used to weigh the coupons before and after each experiment.

**2.5. Determination of Corrosion Rate**

The corrosion rate (CR) in mm/yr is given by

$$CR = \frac{K \times W}{A \times T \times D}$$

Where,

*W = mass loss (g)*

*K = corrosion rate constant = 8. 76 x 10$^4$*

*A = area of specimen (cm$^2$)*

*D = density of MS (g/cm$^2$) = 7.86g/cm$^3$*

*T = time of exposure in hours.*

**3. Results and Discussion.**

**3.1. Effect of inhibitor concentration on weight loss**

Fig 1 shows the relationship between weight loss, inhibitor concentration and time of immersion. The results show that there is a gradual increase in weight loss with increase in immersion time although with a small gradient. Furthermore, it is evident that weight loss values for experiments carried out without inhibitor in the bath were much higher than those with inhibitor. With respect to inhibitor concentration, although 20% exhibited the lowest weight loss values, there appear not to be any distinct trend between those of 5% and 10% inhibitor concentrations.
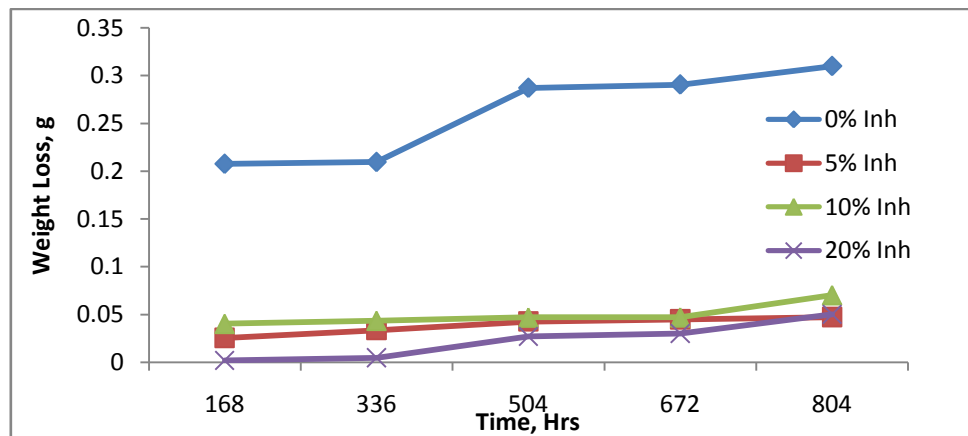


*Figure 1: Weight loss against time for mild steel in salt water with 0%, 5%, 10%, 20% inhibitor concentrations*

**3.2. Effect of inhibitor concentration on CR**

Fig 2 shows the relationship between the rate of mild steel corrosion and inhibitor concentration in the corrosive medium for various durations.The results indicate a consistent decrease in CR with increase in inhibitor concentration. The mode of inhibition is probably via adsorption of the inhibitor molecules onto the MS surface. Inhibitors generally proffer protection to surfaces by the formation of thin layers. Decrease in the CR with increase in inhibitor concentration may not be unconnected to a possible increase in thickness of the adsorbed inhibitor layer.

Mass transfer of the corrosive Cl$^-$ species to the MS surface in an unagitated medium is likely via diffusion. Since diffusion is a function of thickness, the thicker the inhibitor layer, fewer the chances of the corrosive species reaching the surface of the metal to cause any further damage. Plants of natural origin have organic compounds such as amino acids, tannins, and alkaloid which have inhibitive effect. The principle of inhibition is the adsorption of the phytochemical molecules in the plant on the surface of the metal resulting in the displacement of water molecules at the corroding surface [9]. However, with no inhibitor in the corrosive medium, the CR decreased linearly with increase in time. Although, there was a sharp decrease from 0 - 5% inhibitor, the decrease tends to equilibrate between 5% and 15% while there was no marked decrease from 15% - 25% inhibitor with time. This is an indication that at inhibitor concentrations of 15%, the inhibitor concentration for maximum protection had not been attained. The reason for this behaviour may be that after a

particular concentration the inhibitor may have reached its maximum performance [9] ; often referred to as the critical concentration. The inhibitive action of some plant extracts on the corrosion of metal in acid medium increased with increasing concentration of the plant extract up to a critical concentration and decreased afterwards with time [14]. It is generally assumed that adsorption of the inhibitor at the metal/aggressive solution interface is the first step in the inhibition mechanism [15]. It is possible that the inhibitor acts by adsorbing and blocking the available active centres for steel dissolution [9].
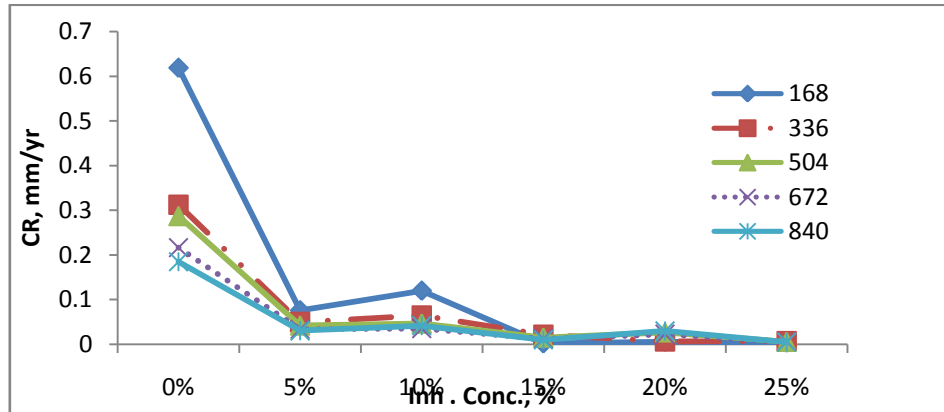


*Figure 2. Effect of inhibitor concentration on the corrosion rate of MS in seawater for different durations ranging from 168 -840 hours.*

### 3.3. Effect of inhibitor concentration on weight loss and corrosion rate

Weight loss and CRs were compared for each concentration of *V. Amygdalina* for all the durations investigated. Figs 3-7 show weight loss and CRs as a function of time with weight loss on the primary axis and CRs on the secondary axis for inhibitor concentrations of 0%, 5%, 10%, 15%, and 25% respectively. The general trend in each of these figures indicates that weight loss is inversely proportional to corrosion rates for the ranges of inhibitor concentrations investigated. The consistent increase in weight loss with time in all cases is an indication that $Cl^-$ ions in sea water aggressively attacked the mild steel surface causing it to corrode with time. However, reverse is the case in corrosion rates, where CRs are consistently on the decrease. This is probably due to the formation of corrosion products on the surface of the mild steel thereby providing an oxide film of initial corrosion products. These corrosion products may have formed an impermeable barrier for further attacks hence reducing the rate of corrosion. Also, for longer durations, there is the general tendency for an increase in corrosion products in the corrosive medium some which could act as limitations on the pathways of the corrosive $Cl^-$ ions thereby reducing their corrosive impact with time.
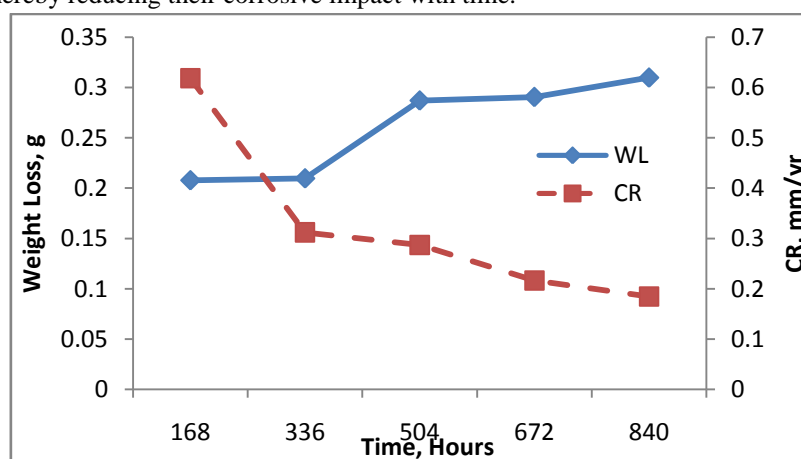


*Figure 3: Effect of time on weight loss and corrosion rate of mild steel in seawater without inhibitor*
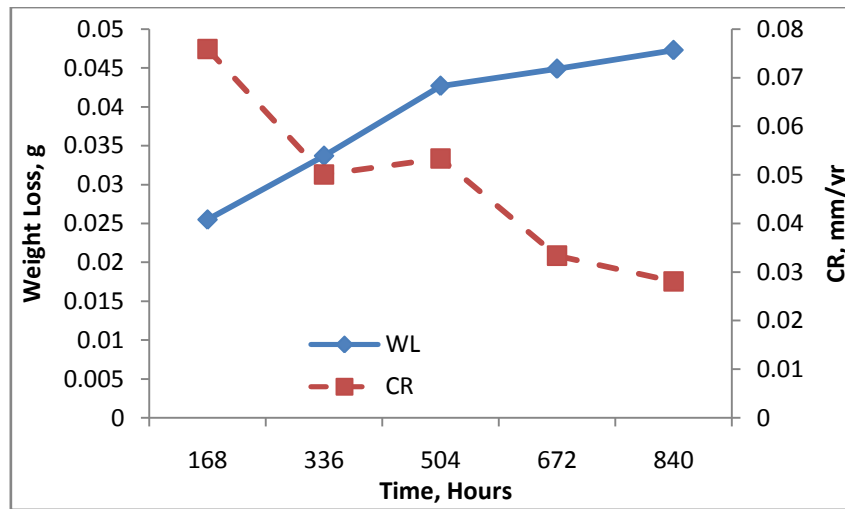
*Figure 4: Effect of time on weight loss and corrosion rate of mild steel in seawater with 5% inhibitor.*
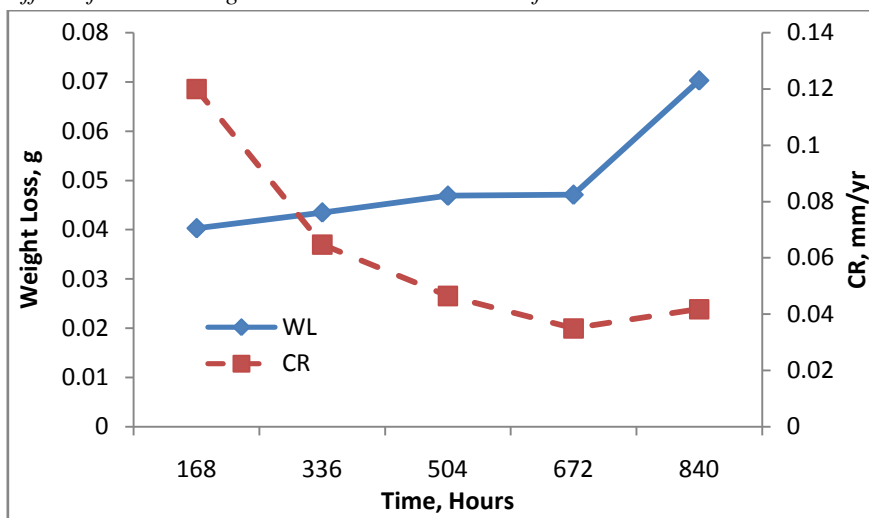


*Figure 5: Effect of time on weight loss and corrosion rate of mild steel in seawater with 10% inhibitor*
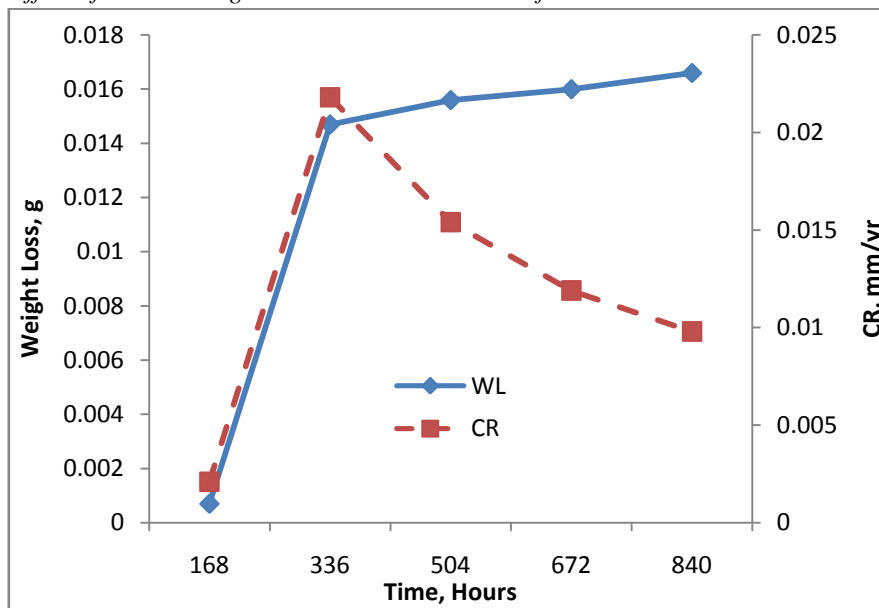


*Figure 6: Effect of time on weight loss and corrosion rate of mild steel in seawater with 15% inhibitor*

Furthermore, apart from Fig 7 with 25% inhibitor concentration, Figs 3,4,5,6 all shows relatively consistent trends where weight loss and CRs intercept at approximately 336 hours. While those of Fig 7 with 25% inhibitor intercepts at approximately 650 hours. This is an indication that at 25% inhibitor concentration, *V. Amygdalina* may no longer be effective as a corrosion inhibitor. Instead, it may have become detrimental as weight loss values continuous to increase. Furthermore, Fig 7 shows a different trend in corrosion rate when compared to those of Figs 3,4,5 and 6. It shows a sharp increase in corrosion rate to a maximum and then a decrease. At inappropriate and excessively high concentrations, instead of being beneficial, surface active compounds such as surfactants and inhibitors could become detrimental [16].
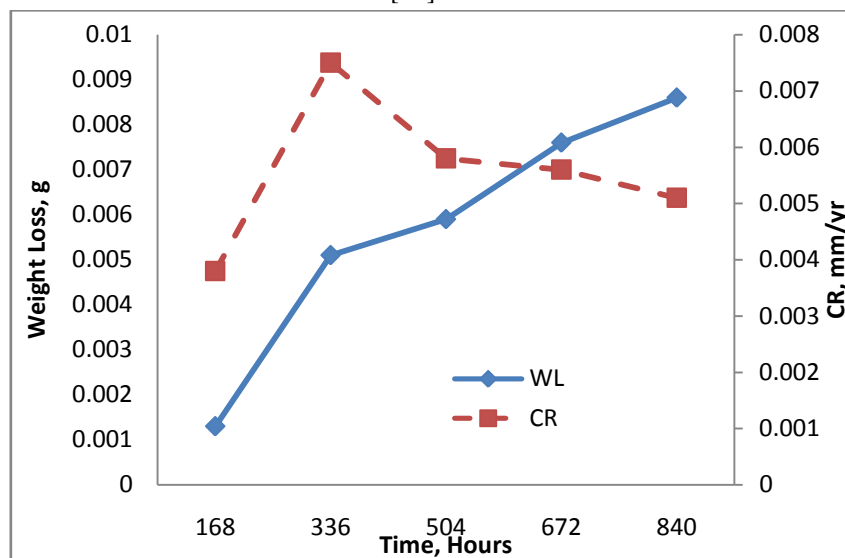


*Figure 7: Effect of time on weight loss and corrosion rate of mild steel in seawater with 25% inhibitor*

### 3.3. Effect of immersion time on the CR

Figs 3-7 show the effect of immersion time on the CR of mild steel. The overall trend indicates that bath concentrations ranging from 0-10% inhibitor exhibited a continuous decrease in corrosion rate with increasing time of immersion. However, for higher inhibitor concentrations of 15% and 25% there is the tendency for an initial increase to a maximum, then a decrease with time. This behavior appears to be in agreement with literature [16] that at excessively high concentrations, inhibitors become detrimental. Generally, inhibitors have been reported [16] to work more effectively at lower concentrations and detrimental when excessively high. Also, as can be seen from Figs 3-7, corrosion rates were consistently higher in all cases at a relatively shorter duration from 168-336 hrs than for longer durations. Indicating the aggressiveness of the corrosive species at shorter durations but as corrosion products begins to form with time they become less aggressive possibly due to build up of corrosion products in the corrosive medium and/or formation of surface oxides as impermeable thin films on the surface of MS.

### 4. Conclusion

The study reveals that *Vernonia Amygdalina* is an effective corrosion inhibitor of MS in seawater. The mode of inhibition may have, amongst others, been through the reaction of the corrosive medium and the inhibitor by neutralizing the chloride radicals present in seawater to form sparingly soluble salts. This action could retard the corrosion process of the coupons and be useful in combating corrosion of steel pipes. Also, displacement of water molecules by the inhibitor and adsorption onto the MS may have played a major role in the inhibition process.

Furthermore, optimum inhibition of coupons was observed between 15-25% of the inhibitor. Although, the CR generally decreased with time in almost all the concentrations investigated, weight loss values consistently increased with time. This is an indication that the inhibitor was gradually losing its effectiveness; meaning more inhibitors should be added into the corrosive medium at regular intervals if the effectiveness of the inhibitor

must be sustained. It is also crucial to apply the right concentration of inhibitor since it appears to be detrimental at excessively high inhibitor concentrations.

### 4.1. Recommendations

From the results of this research, it is recommended that; to sustain the effectiveness of the inhibitor, more should be added to the corrosion medium at regular intervals. Also, the right concentration of inhibitor should always be applied as the need arises.

### Acknowledgement

### References

[1]. Mobin, M., Aslam, R., Zehra, S., Ahmad, M., Bio-/Environment-Friendly Cationic Gemini Surfactant as Novel Corrosion Inhibitor for Mild Steel in 1 M HCl Solution, https://www.researchgate.net/publication/310836648_Bio-Environment-Friendly_Cationic_Gemini_Surfactant_as_Novel_Corrosion_Inhibitor_for_Mild_Steel_in_1_M_HCl_Solution.

[2]. Sekunowo, O.I, Durowaye, S.I., Lawal, G.I. (2017), Potentiodynamic Corrosion Study of Mild Steel in Seawater and 1M HCl, NSE Technical Transaction 51(1), 85-91.

[3]. Alawode, A.J., and Ogunleye I.O. (2011), Maintenance, Security and Environmental Implications of Pipeline Damage and Ruptures in the Niger Delta Region. Pacific Journal of Science and Technology. 12(1):565-573

[4]. Okiongbo, K. S and Ogobiri, G. (2013), Predicting Soil Corrosivity along a Pipeline Route in the Niger Delta Basin Using Geoelectrical Method: Implication for Corrosion Control, Engineering 5,237-244.

[5]. Omotiama, M. and Onukwuli, O. D. (2015), Inhibitive and adsorption properties of leaves extract of bitter leaf (Vernonia Amygdalina) as corrosion inhibitor of Aluminium in 1.0M NaOH. Der Pharma Chemica, 7(11), 373-383

[6]. Okoroafor, C. (2004), Cathodic Protection as a Means of Saving National Asset. Journal of Corrosion Science and Technology. 1 (1): 1-6

[7]. Awe, I. C., Abdulrahaman A.S., Ibrahim H. K., Kareem A. G., Adams S. M (2015), Inhibitive Performance of Bitter Leaf Root Extract on Mild Steel Corrosion in Sulphuric Acid Solution, American Journal of Materials Engineering and Technology, 3(2), 35-45

[8]. Obiukwu, O. O., Opara I. O., Oyinna B. C. (2013), Corrosion Inhibition of Stainless Steel Using Plant Extract Vernonia Amygdalina and Azadirachta Indica, The Pacific Journal of Science and Technology, 4(2), 31-35

[9]. Oluseyi A. K., Oluwatoyin A. C., Abimbola A. A., Ayorinde F., Abiola E. O., Moriamo J. O. (2012), Eco-Friendly Impact of Vernonia Amygdalina as Corrosion Inhibitor on Aluminium in Acid Media. Chemistry Journal, 02(04), 153-157

[10]. Al-Mhyawi, S. R. (2014), Inhibition of mild steel corrosion using Juniperus plant as green inhibitor. African Journal of Pure and Applied Chemistry, 8(1), 9-22

[11]. Rajeev, P., Surendranathan A. O., Murthy, Ch. S. N. (2012), Corrosion mitigation of oil well steels using organic inhibitors-A review, J. Mater. Environ. Sci. 3(5), 856-869

[12]. Tuaweri, T. J., Ogbonnaya, E. A., Onyemaobi, O.O. (2015), Corrosion Inhibition of Heat Treated Mild Steel with Neem Leave Extract in a Chloride Medium, International Journal of Research in Engineering and Technology, 4(6), 404-409

[13]. Umoren, S.A., Eduok, U.M, Solomon, M.M., Udoh, A.P. (2016), Corrosion inhibition by leaves and stem extracts of Sida Acuta for mild steel in 1M $H_2SO_4$ solution investigated by chemical and spectroscopic techniques. Arabian Journal of Chemistry, Vol.9, S209-S224

[14]. Abdel-Gaber, A.M., Abd-El-Nabey, B.A., Sidahmed, I.M., El-Zayady, A.M., and Saadawy, M. (2006), Kinetics and thermodynamics of aluminium dissolution in 1.0M sulphuric acid containing chloride ions. Corr. Sci. 48(9), 2765-2779

[15]. Niu, L., Hu Z., Fenghua W., Suxiang W., Xiaoli C., Pengpeng L. (2005), Corrosion inhibition of iron in acid solutions by quarternary ammonium halides: correlation between inhibition efficiency and molecular structure. Appl. Surf. Sci. 252(5), 1634-1642

[16]. Tuaweri, T.J and Wilcox G.D (2006), Behaviour of Zn-SiO$_2$ electrode position in the presence of N,N-dimethyldodecylamine, Surf. & Coat. Technol. 2000, 5921-5930