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Assessment of Internal Pipeline Corrosion Using Vernonia Amygdalina

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Abstract
Previous research efforts usually consider external corrosion of the pipes in the presence of seawater, which is typical of offshore operations. In this study, the corrosion inhibition potentials of Vernonia amygdalina leaf extract was investigated to understand its efficacy in tackling internal corrosion in pipelines. Fresh leaves of bitter leaf plant were collected from a nearby farm, from which the extracts were produced using ethanol solvent. The gravimetric method was carried out at various concentrations of the plant extracts using mild steel, aluminum and galvanized steel samples cut into rectangular coupons (30cm x 20cm). The various concentrations consisting of 4ml, 6ml and 8ml of inhibitors were used to testaluminum, mild steel and galvanized steel samples in 100ml crude oil with 1.0 M of H_2SO_4. From the obtained results, there was a direct relationship between internal corrosion rate of the metals studied and their exposure time in the corrosive medium. For all the metals studied, there was an inverse relationship between the internal corrosion rate and the concentration of Vernonia amygdalina leaf extract in the corrosive medium. In addition, the observed inhibition efficiencies for aluminum were 31.11%, 46.67% and 57.78% at 4ml, 6ml and 8ml inhibitor concentrations respectively. Inhibition efficiencies for mild steel were 31.43%, 45.71% and 62.86%, while galvanized steel had the highest inhibition efficiencies of 44%, 64% and 72% at 4ml, 6ml and 8ml inhibitor concentrations respectively.
Keywords: *Vernonia amygdalina, Corrosion inhibition, Green inhibitors, Internal corrosion, Mild steel, Galvanized steel, Aluminum*

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1. Introduction

Pipelines are system of interconnected pipes designed to transport liquids, gases or solid/liquid mixtures over long distances. Corrosion causes huge safety concerns and economic damage. It is of vital importance that these pipelines do not corrode since accompanied with pipeline failure are potential explosions, human and economic risk and environmental disaster. Corrosion reduces the structural integrity of pipelines, makes it deteriorate and overtime spill its content into the environment, thereby rendering it an unsafe channel for transporting toxic and hazardous fluids (Achebe *et al.*, 2015).

Corrosion is the deterioration and gradual destruction of the component of a material as a result of the chemical or electrochemical reactions of the material and its environment. A general definition of corrosion is the degradation of material through environmental interactions; this includes manmade and naturally occurring structures. Metallic materials tend to corrode when exposed in aqueous environments which are either water or moist soil as the case may be. This environment acts as the electrolyte and corrosion occur as an electrochemical process (Umarani and Ngobiri, 2021). Corrosion can be classified as dry and wet corrosion, chemical and electrochemical corrosion. Most corrosion problems encountered fall into five basic categories: uniform or general corrosion, localized corrosion, metallurgical induced corrosion, mechanically assisted corrosion and stress corrosion cracking. These five basic types of corrosion can be broken down into eight visually identifiable forms. They include the general or uniform corrosion, galvanic corrosion, crevice corrosion and pitting corrosion. Others are inter-granular corrosion, microbiologically influenced corrosion, erosion corrosion and stress cracking corrosion (Nitonye *et al.*, 2020).

Corrosion inhibitors are additive/chemicals that can reduce the rate of corrosion. Inhibitors act to slow down the anodic or cathodic reaction by the formation of a protective film on the system confined in a corrosive environment.

Corrosion inhibitors are generally classified into three, including anodic, cathodic and organic inhibitors. Anodic inhibitors (also called passivation inhibitors) act by a reducing anodic reaction, that is, blocks the anode reaction and supports the natural reaction of passivation of the metal surface, which is due to the formation of a film adsorbed on the metal. In general, the inhibitors react with the corrosion product initially formed, resulting in a cohesive and insoluble film on the metal surface. Cathodic corrosion inhibitors prevent the occurrence of the cathodic reaction of the metal. The cathodic inhibitors form a barrier of insoluble precipitate over the cathode. This restricts the metal's contact with the environment even if it is completely immersed, thereby preventing the occurrence of corrosive reactions. Due to this, the cathodic inhibitor is independent of concentration and is considerably more secure than the anodic inhibitor. Organic corrosion inhibitors are naturally-occurring molecules exhibiting a strong affinity for metal surfaces with good inhibition efficiency and low environmental risk. These inhibitors build up a protective hydrophobic film of adsorbed molecules on the metal surface, which provides a barrier to the dissolution of the metal in the electrolyte. They are usually meant to be soluble or dispersible in the medium surrounding the metal.

Environment-friendly corrosion inhibitors include biopolymers, plant extracts, chemical medicines, ionic liquids, polyethelyne glycols, multicomponent reaction inhibitors, ultrasound, microwave inhibitors, and green solvent inhibitors. These inhibitors were introduced to replace the environmentally hazardous chromates. Extracts of plant materials top the list. The plant extracts are environmentally friendly, non-toxic and readily available. These extracts contain many ingredients and several organic compounds which have polar atoms such as O, N, P and S. They are adsorbed onto the metal surface through these polar atoms, thereby forming protective films. Among the different parts of plants, the extracts of leaves are most commonly tested as they have showed the highest protection efficiency. In most of the plants, the synthesis of phytochemicals mostly takes place in leaves and therefore leaves are the part of plants that are richest in phytochemicals. Similar to organic corrosion inhibitors, phytochemicals are generally rich in electron donor sites called active or adsorption sites. These electron rich sites of phytochemicals include polar functional groups and multiple bonds. Using these electron rich sites, phytochemicals form strong bonding with the metallic surface, especially through coordination bonding, and behave as strong ligands.

Currently, organic compounds are established as one of the most effective and profitable methods of corrosion inhibition because of their associated efficiency, economy, ecology and environmental friendliness. Organic corrosion inhibitors are also used for different industrial applications (Verma *et al.*, 2021). However, there are numerous challenges of using these organic inhibitors. One of the biggest challenges of using organic corrosion inhibitors is their limited solubility, especially in polar electrolytes. Because of their hydrophobic nature, organic corrosion inhibitors, especially compounds containing aromatic rings and non-polar hydrocarbon chains, show limited solubility which adversely affects their protection efficiency.

Recent research outputs have equally considered the use of green corrosion inhibitors capable of delaying corrosion reactions in metals. Particularly, there has been increasing research in the use of natural products, such as plant extracts, to obtain eco-friendly corrosion inhibitors. Chitosan, a biopolymer with exceptional environmentally friendly properties, gained significant attention as a sustainable corrosion inhibitor (CI) for metallic surfaces. Despite its inherent advantages, its limited solubility has posed challenges to its widespread application. To address this limitation, a water-soluble chitosan salt (CS) was developed and demonstrated as an effective green CI for N80 pipeline steel in artificial seawater (Kumar et al., 2024). However, its temperature-dependent behaviour and involving multiple chemical processes to develop suggests a need for further optimization. The rationale behind the use of various plant extracts is due to the presence of various phytochemicals in plants that are equally hydrophilic in nature. This scenario informed the choice of investigating the corrosion inhibition properties of the leaf extracts of a widely grown plant like *Vernonia amygdalina.* The inhibition potential was tested on metal samples representative of pipeline construction materials. Various researchers have considered using bitter leaf extracts as corrosion inhibitors (Avwiri and Igho, 2003; Nitonye *et al.*, 2018; Umarani and Ngobiri, 2021). An experimental result on the Vernonia amydalina extract demonstrated an optimal inhibition efficiency of 83.9% at a temperature of 47.3°C, an inhibitor concentration of 12.10 mg/mol, and a duration of 7.5 seconds. This result suggests that Vernonia amydalina is an effective inhibitor, Díaz-Jiménez (2024). Pipes made of aluminium and galvanized steel were not considered in the experiment. Limited literature exists on the performance of Vernonia amydalina on the internal corrosion of pipes made of aluminium and galvanized steel in the presence of seawater and in acidic solutions. This study investigates the efficacy of bitter leaf (*Vernonia amygdalina*) extracts as internal corrosion inhibitor in pipelines.

2. Materials and methods

Gravimetric analysis was used in testing the efficacy of Vernonia Amygdalina as a corrosion inhibitor. Gravimetric analysis in corrosion involves measuring the mass change of a material due to corrosion processes. This technique typically includes exposing a metal sample to a corrosive environment, and then weighing it before and after exposure to quantify the amount of material lost. The data helps assess corrosion rates and determine the effectiveness of protective coatings or inhibitors. The materials and equipment used are: sand paper, distilled water, acetone, thread, sieve, filter paper, tissue paper, soft brush, beakers, ethanol, sulphuric acid, measuring cylinder, broomsticks, crude oil, electronic weighing balance, vernonia amygdalina leaves, aluminium, mild and galvanized steel coupons, electronic grinding machine, and laboratory oven.

2.1 Extraction of the plant extracts (Vernonia amygdalina)

100g of fresh leaves of bitter leaf plant were oven-dried before grinding to increase the surface area and stored in a closed container. The ground plant leaves were measured and soaked in 400ml of ethanol. At the end of the 48 hours the plant mixture was filtered. The filtrate obtained is a mixture of the plant extract and the ethanol. The ethanol solvent was distilled off. The concentrated plant extract was weighed and stored for the corrosion inhibition study.

2.2 Metal coupon preparation

The mild steel, aluminium and galvanized steel samples were cut into rectangular coupons (30cm x 20cm). The coupons were cleaned followed by polishing with emery paper to expose shining polished surface. To remove any oil and organic impurities, the coupons were degreased with acetone and washed with distilled water, dried in air and then stored in desiccators. Accurate weight of each coupon was taken using electronic weighing balance and the initial weight was recorded. The above procedure was carried out on a total of 12 coupons including 4 coupons of aluminium, 4 coupons of mild steel and 4 coupons of galvanized steel. Holes were made at the top of each coupon to allow a thread passed through. The thread was tied to a broom stick marked with corresponding label. The stick acts as a handle for controlling the coupon (taking it in and out of crude).

2.3 Gravimetric (weight loss) method

The weight loss method was carried out at various concentrations of the plant extracts. According to this method, weighed mild steel, aluminium and galvanized steel coupons were separately immersed in open beakers containing 100 ml of crude oil with a constant concentration of 1.0 M H_2SO_4 and 0 ml inhibitor. Nine other beakers were equally prepared comprising of 3 beakers each of 4 ml, 6 ml and 8 ml of inhibitors and containing 100 ml crude oil with 1.0 M of H_2SO_4.

The coupons were inserted into the beakers having 0 ml, 4 ml, 6 ml and 8 ml inhibitor for each metal type. After 24 hrs, the metals were then removed from the crude, rinsed in ethanol, degreased in acetone, and later measured to obtain the current weight. Afterward, the measured coupons were reintroduced into the corrosive crude environment and the corrosion rate was calculated. The above steps were repeated for 5 days and results were recorded daily. The experiments were carried out at room temperature. Weight loss was calculated after every 24 hours using the formula:

$$\Delta W = W_o - W_i \quad (1)$$

where W_o is the initial coupon weight, W_i coupon weight at time I and i = 1-5 days.

2.4 Calculation of corrosion rate and inhibition efficiency

The corrosion rate is a function of weight loss (Δw), area of coupon, density of material, and exposure time (Samson et al., 2018). Here, it is assumed that the weight loss is singularly due to the corrosive environment the coupons were introduced. In addition, any resulting internal corrosion of the coupon is highly negligible. According to According to Ocheri et al. (2020), the corrosion rate is:

$$C_r = \frac{KW}{ATD} \quad (2)$$

where, W = mass loss (g), K = corrosion constant = 8.76×10^4 (mm/yr), A = area of specimen (cm^2), D_1 = density of steel (g/cm^2) = 7.86 g/cm^3, T = time of exposure in hours and D_2 = density of Al (g/cm^2) = 2.7 g/cm^3. Another variable used for evaluating the efficacy of corrosion inhibitors is the inhibition efficiency. It measures the ability of the inhibitor to stop corrosion from taking place. This variable is usually expressed in percentage for easy comprehension. The percentage inhibition efficiency was calculated using the relationship:

$$p = \left(1 - \frac{\Delta W_2}{\Delta W_1}\right) X\ 100 \quad (3)$$

The degree of surface coverage was obtained using:

$$\Theta = \frac{\Delta W_1 - \Delta W_2}{\Delta W_1} \quad (4)$$

where ΔW_1 and ΔW_2 are weight loss in the absence and presence of extract, respectively.

3. Results and discussion

From Fig. 1, a clear trend can be observed between corrosion rate and exposure time. The graph actually depicts a direct relationship between corrosion rate and the amount of time the aluminum coupons were exposed to the corrosive medium. This relationship is expectedly so since corrosion in general has been described as a spontaneous chemical reaction, of which its reaction rate would normally increase as reaction time increases given sufficient reactant (metal coupon). This explains why the corrosion rates generally increased with increase in exposure time both in the absence or presence of *Vernonia amygdalina* leaf extract.

Another striking observation from Fig. 1 is the influence of *Vernonia amygdalina* leaf extract concentration on the corrosion rates of aluminum coupons. From the graph, it can be noticed that there was a significant reduction in the corrosion rate in the presence of *Vernonia amygdalina* leaf extract, as depicted by the lower corrosion curves compared to the case of 0 ml extract. In fact, addition of the extract succeeded in stagnating the corrosion rate for the first 48 hrs of exposure before the corrosion rate started increasing. The corrosion rate also decreased further with increasing inhibitor concentration, thereby signifying an inverse relationship between extract concentration and corrosion rate. This behaviour is suggestive of the internal corrosion inhibition ability of *Vernonia amygdalina* leaf extract in aluminum crude oil pipelines.

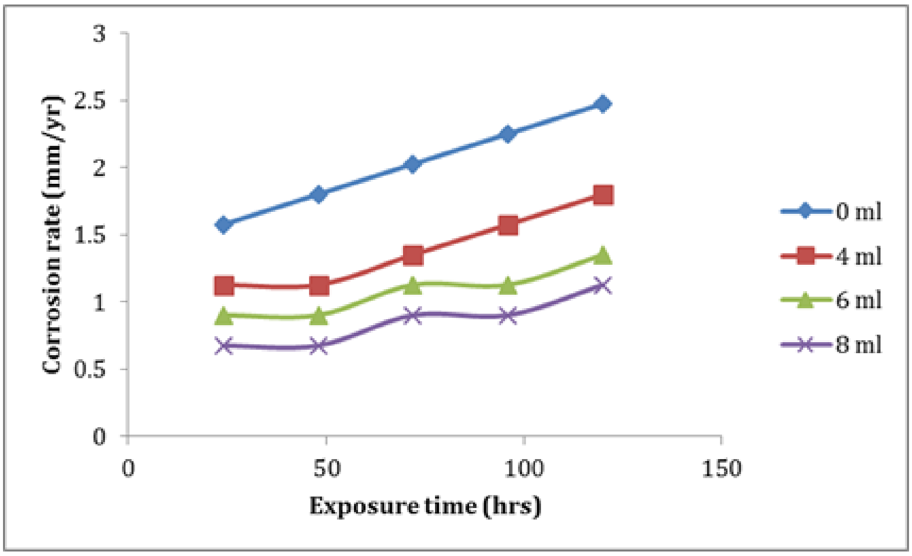

Fig. 1: Plot of Aluminum corrosion rate against time at various concentrations of *Vernonia amygdalina* leaf extract

From Fig. 2 it was observed that there was a significant reduction in mild steel corrosion rate as *Vernonia amygdalina* leaf extract was added to the crude oil, which is depicted by the increasingly lower corrosion curves compared to the absence of extract. This further validates the internal corrosion inhibition ability of *Vernonia amygdalina* leaf extracts in mild steel crude oil pipelines. In addition, the presence of *Vernonia amygdalina* leaf extracts also helped in stagnating the corrosion rate for the first 48 hrs of exposure at all concentrations of the extract. However, the corrosion rate equally remained constant between 72 and 96 hrs of exposure for both 4 and 6 ml *Vernonia amygdalina* leaf extract concentrations. But for 8 ml *Vernonia amygdalina* leaf extracts concentration, the corrosion rate remained constant for the first 72 hrs. The above inhibitive observations can obviously be attributed to the presence of *Vernonia amygdalina* leaf extracts in the corrosive medium, which is indicative of its corrosion inhibition ability on mild steel. Since the crude oil corrosive medium utilized in this study is synonymous (in terms of exposure) with internal environment of crude oil pipelines, *Vernonia amygdalina* leaf extracts can therefore be applied as internal corrosion inhibitors in mild steel pipelines. Hence, validates a similar research which shows Vernonia amydalina extract demonstrated an optimal inhibition efficiency of 83.9% at a temperature of 47.3°C, an inhibitor concentration of 12.10 mg/mol, and a duration of 7.5 seconds, Díaz-Jiménez (2024).

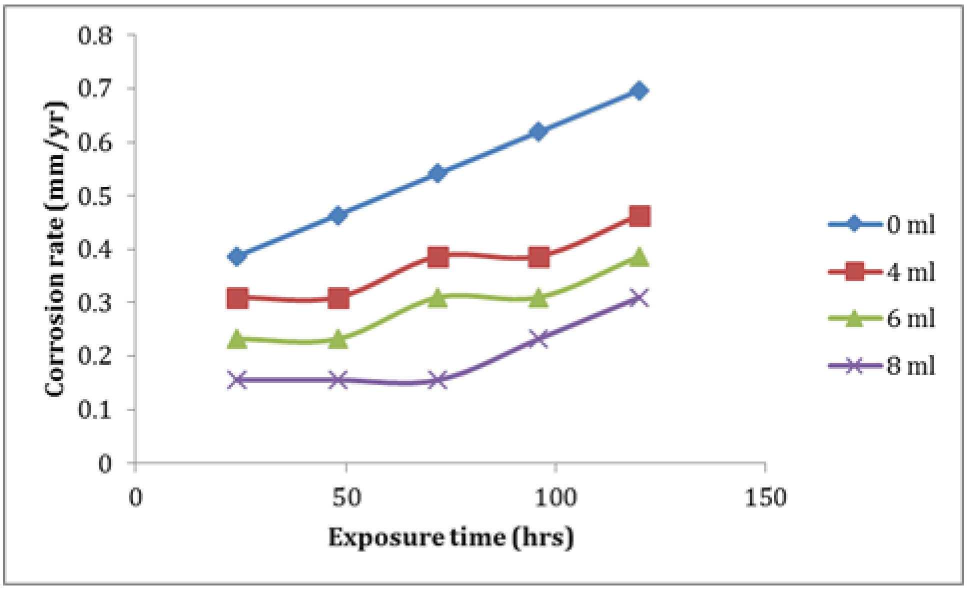

Fig. 2: Plot of Mild Steel Corrosion rates against time at various concentrations of *Vernonia amygdalina* leaf extract

From the Fig. 3, it can equally be noticed that there was a significant reduction in the corrosion rate as the galvanized steel was immersed in the crude oil containing *Vernonia amygdalina* leaf extract. This was observed from the generally lower corrosion curves compared to the absence of extract. In addition, the presence of *Vernonia amygdalina* leaf extracts equally helped in stagnating the corrosion rate for the first 48 hrs of exposure at all concentrations of the extract. Similar to mild steel, the corrosion rate also remained momentarily constant after 72 hrs of exposure for both 4 and 6 ml *Vernonia amygdalina* leaf extracts concentrations. The corrosion rates remained constant until after 96 hrs of exposure before increasing again. But for 8 ml *Vernonia amygdalina* leaf extracts concentration, the corrosion rate remained constant for the first 72 hrs similar to mild steel, before increasing after 72 hrs. However, unlike mild steel, the corrosion rate later became constant again after 96 hrs. The above inhibitive observations are obviously attributed to the presence of *Vernonia amygdalina* leaf extracts in the corrosive medium, which is equally indicative of its corrosion inhibition ability on galvanized steel. Since a crude oil corrosive medium is synonymous with internal parts of flowing crude oil pipelines, *Vernonia amygdalina* leaf extracts can therefore be applied as internal corrosion inhibitors in galvanized steel pipelines.

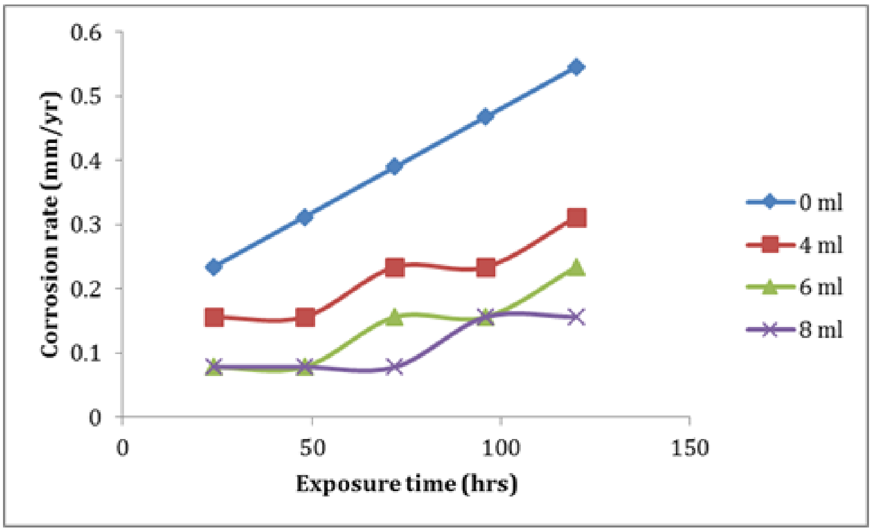

Fig. 3: Plot of galvanised steel corrosion rate against time at various concentrations of *Vernonia amygdalina* leaf extract

Fig. 4 shows the total weight loss recorded at different *Vernonia amygdalina* leaf extract concentrations throughout the experiments for the various metal types studied. From the bar chart, it can be deduced that as the inhibitor concentration increased, there was a simultaneous reduction in the total weight loss recorded, which characterizes corrosion. This suggests an inverse relationship between total weight loss and *Vernonia amygdalina* leaf extract concentration, and of course, the corrosion inhibitive property of *Vernonia amygdalina* leaf extract. This observation was possible because higher inhibitor concentration means more inhibitive capacity, which in effect slows down the rate of the corrosive chemical reaction taking place. When the corrosive reaction that causes weight loss is retarded, less metal material will eventually be lost to corrosion.

Also, the relative susceptibility of the various metal samples to corrosion can equally be gauged from the bar chart depicted in Fig. 4. For each *Vernonia amygdalina* leaf extract concentration, aluminum coupons had the highest recorded total weight loss, followed by mild steel. The high susceptibility of aluminum can be attributed to its unalloyed nature, unlike steel (an alloy of iron and carbon), which has a lower likelihood of corrosion compared to unalloyed iron. But galvanized steel consistently posted the least total weight loss among the metals. The low susceptibility of galvanized steel can be traced to the efficacy of the galvanization treatment it previously received, which is a process whereby a coating of zinc is electrochemically applied to steel for protection against corrosion. This explains why galvanized steel suffered the least corrosion among the studied metal types.

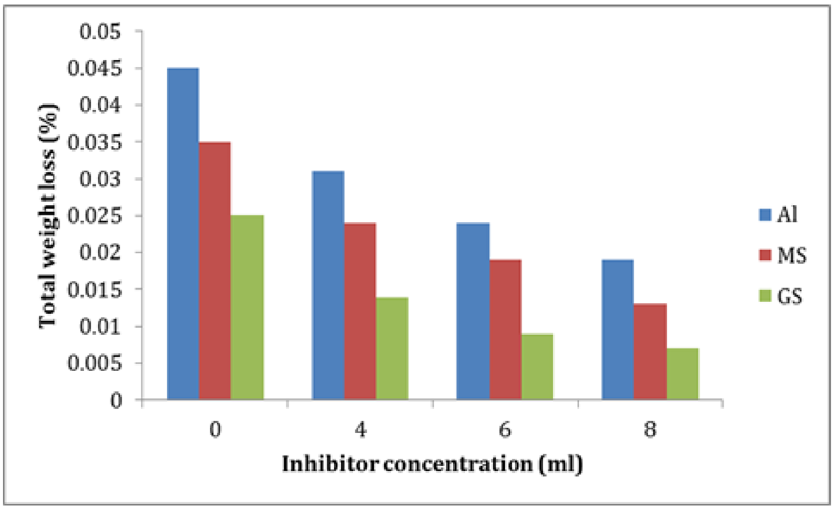

Fig. 4: Total weight loss of various metals at different *Vernonia amygdalina* leaf extract concentrations

Fig. 5 shows the inhibition efficiency of *Vernonia amygdalina* leaf extract at different concentrations on various metals. From the bar chart, it can be observed that inhibition efficiency varied among the metals, but the highest inhibition efficiency was recorded in galvanized steel. This results basically corroborates the earlier result reported in Figure 4 about the comparatively low susceptibility of galvanized steel coupons. The connection between the two results can be explained by the inverse relationship between weight loss (which characterizes corrosive reactions) and inhibitive performance or efficiency. The inverse relationship signifies that less material loss will likely be recorded in the presence of a corrosion inhibitor of high inhibitive efficiency and vice versa. In addition, a definitive direct proportionality can equally be deduced between inhibition efficiency and *Vernonia amygdalina* leaf extract concentration for each metal. Such that for each metal, inhibitive efficiency increased as concentration increased. This observation only shows that higher *Vernonia amygdalina* leaf extract concentration would directly lead to better internal corrosion inhibitive performance among the metals.

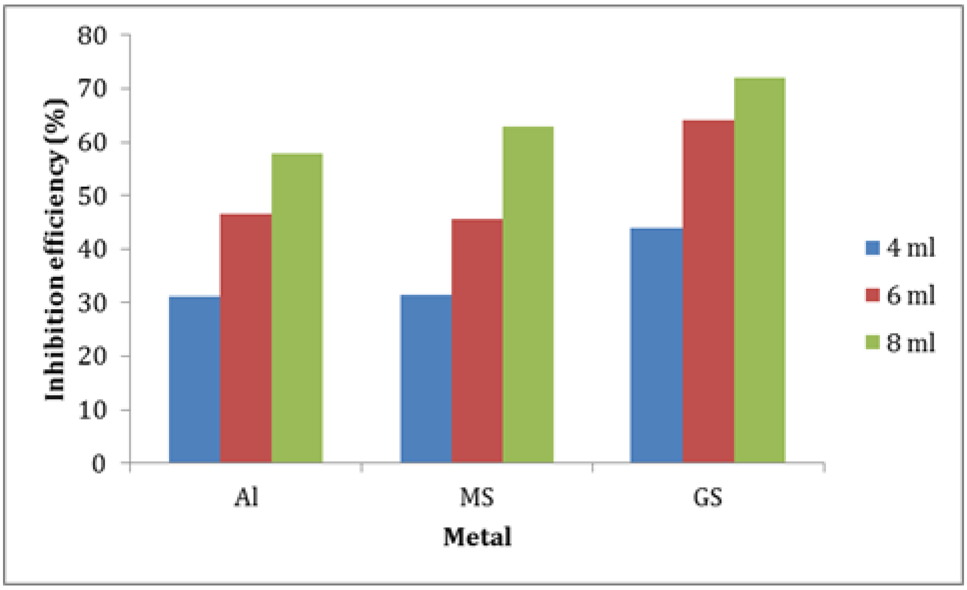

Fig. 5: Inhibition efficiency *Vernonia amygdalina* leaf extract at different concentrations on various metals

4. Conclusion

From the study, the following conclusion can be reached.

(a) There exists a direct relationship between internal corrosion rate of the metals studied and their exposure time in the corrosive medium.

(b) For all the metals studied, there was equally an inverse relationship between internal corrosion rate and *Vernonia amygdalina* leaf extract concentration in the corrosive medium.

(c) From the obtained results, there was also direct a direct relationship between inhibitive performance of *Vernonia amygdalina* leaf extract and its concentration in the corrosive medium.

(d) Among the metals studied, galvanized steel showed the least susceptibility to internal corrosion in the presence of *Vernonia amygdalina* leaf extract, followed by mild steel. While aluminum showed the highest susceptibility to internal corrosion in the presence of *Vernonia amygdalina* leaf extract.

(e) The similarity in inhibitive performance of *Vernonia amygdalina* leaf extract recorded for both mild and galvanized steel confirms their similar chemical composition, which indicates that they are actually different physical forms of the same substance (steel).

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