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ABSTRACT

The inhibitory efficiencies of methanolic leaf extract of *Irvingia gabonensis* and the role of a halide ion as an enhancement on the inhibition of aluminium corrosion in HCl medium were studied at varying acid concentrations of 0.01M, 0.05M, 0.1M under the influence of 3% NaCl. Result of the studies carried out by weight loss technique showed that *I. gabonensis* is highly an efficient inhibitor for the corrosion of aluminium in HCl acid environment and its inhibitory efficiencies increases with respect to the time of exposure.. It was observed from the study that in the absence of the plant extracts, the weight loss increases rapidly indicating an increase in corrosion rate from 0.003g to 0.026g as acid concentration was increased from 0.01M to 0.1M. Conversely, when the plant extract was introduced, there were remarkable decrease in weight loss from 0.001g at 0.01M of HCl to 0.021g at 0.1M, showing a decrease in corrosion of the metal. Experimental data proved that the highest corrosion rates were observed at the highest acid strength pointing that at a concentration of 0.1M HCl, 19% efficiency was attained and a maximum efficiency of 67% was obtained at 0.01MHCl showing a correlation between concentration and inhibition of metal. It was also revealed that the inhibitory efficiency of *I. gabonensis* in HCl medium was magnificently increased when a salt of halide ion was introduced showing a weight loss of 0.01g through 0.003g as acid strength increased from 0.01M to 0.1M. This could be attributed to that the fact that halide ion facilitates the adsorption of organic cations during metal corrosion by forming intermediate bridges between the metal surface and the positive end of the organic inhibitor and this forms a protective hydrophilic film on the metal surface which provided a barrier to the dissolution of the metal into the acid medium.

KEYWORDS: green inhibitor, corrosion rate, concentration, halide ion, inhibitory efficiency.

INTRODUCTION

Acid solutions are widely used in acid cleaning, stimulation of oil wells, and the elimination of localized deposits (tartar not uniformly spread, rust, bacterial deposits, etc.). The aggressiveness of these acid solutions leads to the use of corrosion inhibitors which are indispensable in order to limit the attack of metallic materials. Of the commercially available acids, hydrochloric acid is the most frequently used and is increasingly replacing sulphuric acid [1]. Corrosion is seen as the interaction (electrochemical reaction) of a metal with the surrounding environment, causing a slow,

steady and irreversible deterioration in the metal, in both physical and chemical properties [2]

Corrosion inhibitors are substances when added in small concentration to corrosive media decrease or prevent the reaction of the metal system. The use of corrosion inhibitors as a means of protection is necessary in many industrial cases: surface preparation, transport and storage of metals, cooling circuits, rehabilitation of reinforced concrete, painting and cathodic protection [3]. The characteristic of corrosion inhibitors depends on the chemical moiety of the molecule, type of functional groups and the electron density at the donor atoms. Organic compounds, containing

heteroatom's (N, O, S, and P), electronegative functional groups, π -electrons and aromatic rings as electron density rich centres which are considered as good adsorptive centres[4]. These heterocyclic organic inhibitors get adsorb on the steel surface or form protective insoluble layer and block corrosion sites, which reduces contact of corroding material with the corrosive medium [5]. The current trend is towards friendly inhibitors of the environment. These inhibitors must be non-toxic and capable of ensuring good protection of metals and alloys. [6]. Factors that cause corrosion include reactivity of metal, pressure of impurities, presence of air, moisture, gases like sulphur dioxide (SO₂) and carbon dioxide (CO₂) and presence of electrolytes. Corrosion prevention and retardation are aimed at addressing these factors [7].

The molecules most often used as corrosion inhibitors are nitrogen, sulphur, oxygen and phosphorous containing compounds. These compounds get adsorbed onto the surface of metal from the bulk of environment forming a film at the metal surface. Organic inhibitors generally have heteroatoms. Oxygen, Nitrogen, Sulphur and Phosphorus are found to have higher basicity and electron density and thus act as corrosion inhibitor. Oxygen, Nitrogen, and Sulphur are the active centres for the process of adsorption on the metal surface. The inhibition efficiency should follow the sequence $O < N < S < P$. The existing data showed that most organic inhibitors are adsorbed on the metal surface by displacing water molecules on the surface and forms a compact barrier. Availability of non-bonded electron (lone pair) and p-electrons in inhibitor molecules facilitate electron transfer from the inhibitor to the metal. A coordinate covalent bond involving transfer of electrons from inhibitor to the metal surface may be formed. The strength of the chemisorptions bond depends upon the electron density on the donor atom of the functional group and also the polarisability of the group. When Hydrogen atom attached to the Carbon in the ring is replaced by a substituent group (-NH₂, -NO₂, -CHO, or -COOH) it improves inhibition. The electron density in the metal at the point of attachment changes resulting in the retardation of the cathodic or anodic reactions. Electrons are consumed at the cathode and are furnished at the anode.

I. gabonensis an African wild/bush mango, is a perennial plant, habitat in the humid forest zone of west/central Africa [8].

I. gabonensis contains several organic compounds of high molecular weight with hetero atoms such as tannins, saponins, alkaloids, anthraquinones and phenols which are capable of physicochemical adsorption on metal surfaces [9].

EXPERIMENTATION:

Irvingia gabonensis leaves were collected and identified at Micheal Okpara University of Agriculture, Umudike. The leaves samples were thoroughly washed using de-ionized water were allowed to dried at room temperature for 4 weeks and were milled using a blender to expose the surface area for extraction. Then, 2.5 litres of methanol were poured into 210g of *Irvingia gabonensis* and was left for 2 days in order to guarantee proper extraction. The mixture was filtered using Whatman No. 1 filter paper for three consecutive times and the solvent was then allowed to evaporate using rotatory evaporator at 25°C so as to obtain the concentrate of *I. gabonensis*. A total mass of 0.5g of *I. gabonensis* extract was weighed using electronic weighing balance. Different concentrations of HCl such as 0.01M, 0.1M and 0.05M were all prepared from stock solution using serial dilution. The Aluminium coupon which was collected from Ariaria market in Aba, Abia state Nigeria, was cut into pieces having a dimension of 2cm x 2cm x 1cm with a total surface area 4cm². A small hole was bored near the upper edge of the coupons using a punch electric drilling machine for suspension of the coupons. The coupons were then sand papered until a mirror polished surfaces were obtained. The coupons were de-greased with ethanol, washed with de-ionized water, dried in acetone and their initial weights recorded in grams. The coupons were finally suspended using the fishing lines for the weight loss study.

Weight Loss Method

This involves the immersion of coupons in the media under investigation and retrieving them at specified durations and checking the weight loss in grams. Each coupons was tied and suspended from horizontally placed fishing lines on top of a designated beaker(s) containing 250ml of different concentrations of HCl with or without plant extracts and / or 3% NaCl. Each weighed coupons was suspended such that it was totally immersed in the solution without touching either the side or bottom of the containers. The immersed weighed coupons were left uncovered to react freely with

the atmosphere and the duration of immersion was noted. After the expiration of time allowed, then the reacted coupons were washed gently and properly in water and methanol, dried with a cotton wool and dipped in acetone to remove every moisture and oxygen. Thereafter, each of the dried coupons was carefully reweighed on the electronic balance to obtain a new weight and the weight loss was carefully deduced.

$$\text{corrosion rate (cm/hr)} = \frac{\text{Weight loss}}{\text{Area} \times \text{time}} \dots\dots\dots(1)$$

$$\text{inhibitor efficiency (IE\%)} = \frac{R_o - R}{R_o} \times 100\% \dots\dots\dots(2)$$

Where; R_o = Corrosion rate uninhibited
 R = Corrosion rate inhibited.

RESULTS AND DISCUSSIONS.

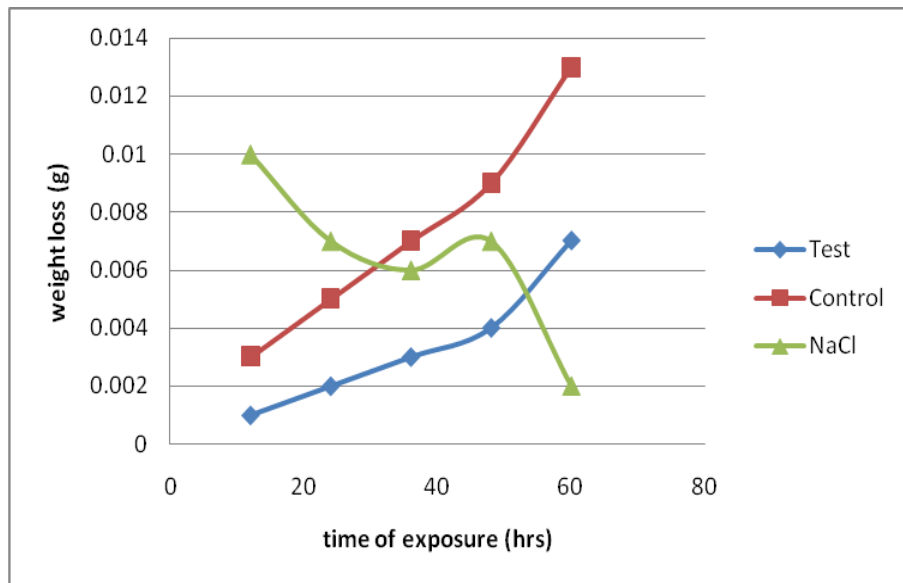


Fig 1: Plot of weight loss against time of exposure for 0.01M HCl for the control, test samples and with NaCl.

Fig 1. shows that in the absence of the plant extract (control), there was a rapid increase in weight loss from 0.003g through 0.013g but when *I. gabonensis* methanolic extract was introduced (test), there was a slow increase in weight loss from 0.001g to 0.007g which leads to a decrease in corrosion rate. Corrosion Inhibition is further enhanced when 3%NaCl solution was introduced, speeding up a decrease in weight loss from 0.01g to 0.002g within the same duration from 12hrs to 60hrs.

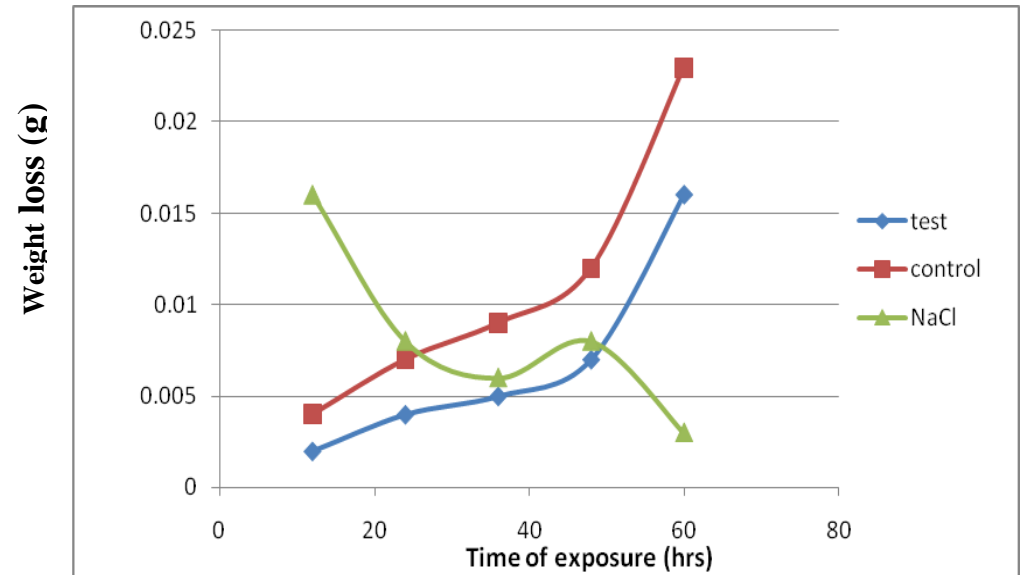


Fig2: Plot of weight loss against time of exposure for 0.05M HCl for the control, test samples and with NaCl

The efficacy of a halide ion enhanced inhibitory action of *I. gabonensis* was further exposed when the strength of the corroding material was increased from 0.01M to 0.05M under the same reaction conditions as illustrated in figure 2 above. Here, the Aluminium metal of the control exhibited a very sharp increase in weight loss from 0.004g to 0.023g. However, the presence of *I. gabonensis* retards this progressive acceleration from 0.002g to 0.016g, showing a reduction in inhibitory

efficiency from 49% to 30% revealing that as time progresses from 12hrs to 60hrs, corrosion also increases. Nevertheless, this trend was terminated with the introduction of a halide ion making the weight loss to decrease appreciably from 0.016g to 0.003g yielding enhanced inhibition efficiency.

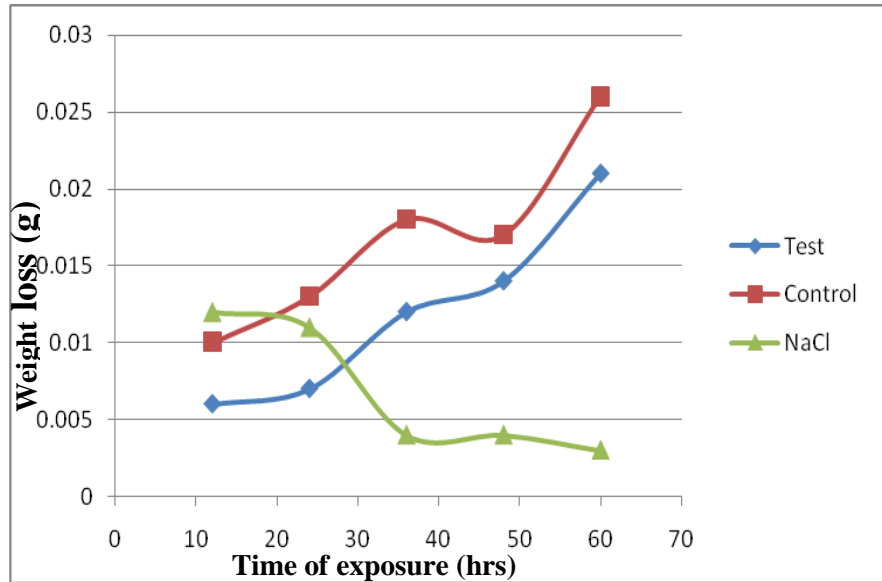


Fig3: Plot of weight loss against time of exposure for 0.1M HCl for the control, test samples and with NaCl

The anti-corrosion activity of *I. gabonensis* further re-awakened in the presence of a halide ion even when the concentration of HCl was further increased from 0.05M to 0.1M in such a manner that the increased acid strength did not prevent this plant extract from forming a protective insoluble layer which blocks the corrosion site in the Aluminium. To that effect, the weight loss recorded with NaCl falls from 0.012g to 0.003g instead of 0.006g to 0.021g as observed with *I. gabonensis* extract.

On a general note, the effect of increase in concentration of HCl acid medium on the inhibition efficiency of *I. gabonensis* over time duration was also analysed. Results shows that as time of exposure increases from 12hrs to 60hrs, the inhibition efficiencies of *I. gabonensis* extract also decreases at all levels of acid concentrations under study.

Similarly, an increase in acid concentration has a corresponding increase in corrosion rate and hence reduces inhibition efficiencies. For instance, from Fig 4; it was observed that the inhibitor efficiency increases for the acid concentration of 0.01M HCl from 46% to 67%, the concentration of 0.05M HCl increases from 30% to 49% and the concentration of 0.1M HCl moves from 19% to 39% as the time of exposure decreases from 60hrs to 12hrs.

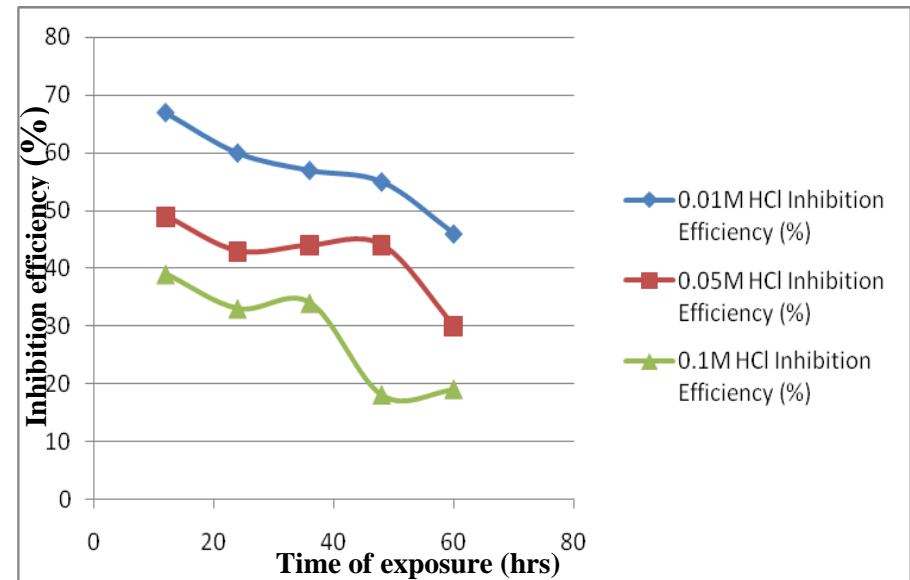


Fig 4: Plot of inhibitor efficiency against time of exposure

CONCLUSION.

Experimental results show that over an acid concentration range of 0.01M to 0.1M, there was a rapid increase in weight loss as time progresses from 12hrs to 60hrs in the corrosion of Aluminium in the blank. However, corrosion rate was reduced upon the introduction of the extract of *I. gabonensis*. Furthermore corrosion inhibition was further achieved and enhanced when 3%NaCl solution was introduced to the reaction mixture.

The *I. gabonensis* extract build up a protective hydrophobic film adsorbed molecules on the Aluminium surface which provides a barrier to the dissolution of the metal in the acid. The halide ion re-activates further the active sites of *I. gabonensis* extract which facilitates the adsorption of organic material unto the metal thereby preventing further reaction of the metal with its acid environment by forming intermediate bridges between the metals surface and the positive end of the organic inhibitor. On the other hand, Increase in acid concentration and time of exposure however decreases the percentage inhibition efficiency of metal under study.

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