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ORIGINAL RESEARCH ARTICLE

CORROSION INHIBITION OF *POLYALTHIA LONGIFOLIA* LEAVES EXTRACT IN 1M HCL SOLUTION ON MILD STEEL

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ABSTRACT

Corrosion is a very common phenomena in the manufacturing as well as chemical process industries. Corrosion has generated wide amount of interest worldwide because of its potential hazards to process equipment and machineries; which often leads to associated downtimes as well as adverse economic and safety consequences. The use of inhibitors is one of the most practical and efficient technique of protection against corrosion. In this work, the corrosion inhibition efficiency of polyalthia longifolia leaves extract in 1M HCl solution on mild steel surface was investigated using the standard gravimetric (weight loss) method. The results indicate that the extract could serve as a good green inhibitor. The inhibition efficiency increases with increase in the inhibitor concentrations. For the mild steel samples investigated in this work, about 70% inhibition efficiency was achieved with only 1.0 ml extract solution per 40 ml of 1.0 M HCl solution after five (5) days; and under same conditions, increasing the amount of extract by fivefold yielded only 10% increase in the inhibition efficiency for the same test period. The inhibition efficiency was also found to significantly increase with time of exposure for the first 48 hours of the experiment, but the increase was rather gradual at later times for all levels of extract concentrations

1.0 Introduction

Corrosion is an increasingly serious and costly problem that can lead to plant and equipment failures, leakages in oil and gas pipelines as well as failure of steel bridges, ships, and buildings. These failures range from being an annoyance to being catastrophic. Failures caused by corrosion could lead to a direct failure of a component which could then affect the entire system; and can not only be very expensive in terms of down-time to repair, or replace plant and equipment, but can also be costly in terms of productivity, health or even loss of human life, as well as damage to the environment (Lekan et al., 2013).

Corrosion phenomena, control and prevention are unavoidable major scientific issues that must be addressed daily as long as there is increasing needs of metallic materials in all facets of technological development (Loto et al., 2012). The consequences of corrosion are many and varied, and the effects of corrosion on the safe, reliable and efficient operation of equipment or structures are often more serious than simple loss of a mass of a metal. Equipment failure of various kinds leading to the necessary expensive replacements may occur even though the amount of metal destroyed is quite small (Umoren, 2009). It is an ever present and unceasing problem, often hard to eradicate totally. Metallic deterioration progresses rather fast after the destruction or penetration of the passive barrier, which is followed by a number of reactions that alter the constituents and behaviour of both the superficial metal surface and the immediate environment (Adegoke, 2015). This is observed in, for example, oxides formation, gradual metal cation diffusion into the coating matrix, local pH changes and electrochemical potential.

The costs attributed to corrosion damage of all kinds have been estimated to be of the order of 3 to 5% of the industrialized countries' gross national product (GNP). The total annual cost of corrosion in the oil and gas production industry is estimated to be 1.375 billion dollars, broken down into 589 million dollars in surface pipeline and facility costs, 463 million dollars annually in downhole tubing expenses, and another 320 million dollars in capital expenditure related to corrosion (Lekan et al., 2013).

Nigeria, a major user of ferrous and non-ferrous metal is also experiencing its own fair share of corrosion problems. One of the major industrial sectors in Nigeria experiencing this problem is the oil and gas industry. Research work on the analysis of oil pipeline failures in oil and gas industries in the Niger delta area of Nigeria was carried out to ascertain the causes of these failures. Information on pipeline conditions was gathered for the period between 1999 and 2010. Observations showed that the major causes of failure include: ageing, corrosion, mechanical failures – welding defects, pressure surge problems, stress, wall thickness, etc. The report's recommendations emphasized measures to minimize these failures (Achebe, 2012).

In practice corrosion can never be eliminated, but can be hindered to a reasonable level. Due to problems from corrosion that are confronting industries; several methods of corrosion control and prevention have been investigated and tested. For example, cathodic protection, lubrication, anodic protection, alloying, coating and corrosion inhibition among others. The choice and application of any method is based on its efficiency, economic factors and the nature of the corrosive environment (Njoku, 1998).

2.0 Corrosion Inhibitors

The use of inhibitors is one of the most practical methods for protection against corrosion in corrosive environments. Inhibitors are substances that directly or indirectly coat a film on a metal surface to protect it from its environment. Most inhibitors are adsorbed by the metal surface from a solution or dispersed, but some are applied directly as coatings. Generally, the dissolution of metal can be suppressed by the action of adsorptive inhibitors which may prevent the adsorption of the aggressive ions, by the formation of a more resistant film on the metallic surface (El-Maghraby, 2009).

Recently, there have been growing interest on some environmentally friendly substances; especially from natural resources that could be used to control/prevent incessant corrosion problems, aside the conventional synthesized inorganic and organic chemicals; which often have adverse impacts on the environment (Adegoke, 2015). Many researches have been conducted on some green inhibitors with promising outcomes (Rani and Basu, 2012; Loto et al., 2012).

The use of natural corrosion inhibitors has been advocated because of the prohibitive cost, toxic nature and environmental unfriendliness of some of the chemical-based corrosion inhibitors. More so, the green inhibitors are readily available, cheap and renewable source of materials. Several researchers have investigated and elucidated the application of various plants extract for corrosion inhibition (Patni et al., 2013; Onen et al., 2013; Angel et al., 2014). Plant parts that have been used include leaves, bark, fruit and roots. In many cases, the corrosion inhibition effects of some of the plants 'extracts have been attributed to the presence of tannin in their bioactive constituents. Also associated with the presence of tannin in the extracts is the bitter taste in the bark and/ or leaves of these plants (Loto et al., 2012).

In this study, corrosion inhibition efficacy of *polyalthia longifolia* leaves extract in hydrochloric acid solution on mild steel was investigated. The choice of mild steel as the test specimen was because of its wide usage and good mechanical properties.

3.0 Materials and Methods

3.1 Materials and Equipment

Fresh leaves of *polyalthia longifolia* plant were collected from around University of Maiduguri campus. Commercial grade concentrated hydrochloric acid, ethanol and acetone were purchased from a local store in Maiduguri metropolis. Mild steel coupon specimens were prepared in Mechanical Engineering workshop, University of Maiduguri. Strings and distilled water were obtained from the Chemical Engineering Departmental laboratory.

The equipment used include digital balance (EK5055 Camry Industries Ltd, Zhongshan), mini digital scale (S-EDS-0146), electric grinder (Sonik, Japan), soxhlet extractor (EX5/83-Quickfit, Avantor VWR, Singapore), Water bath (Gallenkamp, UK), silicon carbide paper (P60D, P220D, G60D) and glass wares (Pyrex) were obtained from the Chemical Engineering Departmental laboratory.

3.2 Methods

3.2.1 Preparation of the leaves sample

The fresh leaves of *Polyalthia longifolia* collected, were washed with water to clean them from dusts and other deposits. The leaves were then chopped into smaller pieces and allowed to dry for four days to achieve 91% moisture content reduction. The dried leaves were then grounded to powder for easy extraction.

3.2.2 Extraction

The ground leaves of *Polyalthia longifolia* was extracted with the use of a small scale soxhlet extractor with methanol as solvent. The soxhlet extractor consists of a main extractor, thimble (round bottom flask), a reflux condenser and an electric heater (Vasudha and Shanmuga, 2013).

3.2.3 Preparation of mild steel specimen

The mild steel sheet used was prepared in the Mechanical Engineering workshop, University of Maiduguri. The steel sheet was cut into several small pieces of uniform dimension of 20mm x 40mm and the coupon specimens were descaled by wire brushing. The specimens were mechanically polished with emery paper abrasive for a smoother surface, washed with acetone, air dried and kept in a desiccator to avoid contact with impurities for subsequent analyses.

3.2.4 Experimental Procedure

The simple standard weight loss method as described in (Ayssar, et al., 2012) was adopted. Six (6) 250ml glass beakers were cleaned thoroughly, dried and labelled A-F respectively. Forty milliliters (40ml) of diluted HCl were measured and poured into each beaker. Similarly, 1ml, 2ml, 3ml, 4ml, and 5ml of the *Polyalthia longifolia* extract solution was pipetted and added into the five beakers labelled A-E respectively. No extract solution was added to the sixth beaker labelled F, and therefore left as control. Thirty (30) mild steel coupons (with dimension specified earlier) were individually cleaned with distilled water, and then washed with acetone, dried and weighed. The coupons were each tied with a string to a small stick that will enable them to suspend when placed across the mouth of the beaker. The weighed coupons were then lowered into the beakers, five (5) coupons per beaker, at room temperature. The first set of the coupons (one coupon from each beaker) were retrieved from the acid corrodent after 24 hours. Similarly, the second set retrieved after 48 hours, the third set after 72 hours and the fourth set after 96 hours and finally the last set after 120 hours. Each coupon was individually cleaned with distilled water, and then with acetone. dried and weighed. The weight loss, Δm (g) was calculated (Aminu et. al., 2015) using equation (1).

$$\Delta m = m_b - m_a \tag{1}$$

Where m_b (g) and m_a (g) are the weights before and after immersion in the test solutions respectively.

3.2.5 Corrosion Rate

The corrosion rate was calculated from weight loss of the coupons (Sheeba, et. al, 2014) at room temperature for various concentrations and immersion times using equation (2).

$$CR = \frac{\Delta m}{St} \tag{2}$$

Where S = surface area of the coupon (cm^2), t = immersion time (h), CR = corrosion rate ($mg/cm^2.h$)

3.2.6 Inhibition Efficiency

The inhibition efficiency of the green inhibitor was calculated from weight loss measured for different inhibitor concentrations using Equation (3) modified from (Vasudha and Shanmuga, 2013).

$$\mathrm{IE} = [1 - (\frac{CR_{inh}}{CR_{corr}})] \times 100 \tag{3}$$

where: IE = Inhibition Efficiency (%)

CR_{inh} = Corrosion Rate in the presence of extract ($mg/cm^2.h$)

CR_{corr} = Corrosion Rate without extract ($mg/cm^2.h$)

4.0 Results and Discussion

4.1 Weight Loss and Corrosion Rate

Figure 1 illustrates the weight loss of the mild steel samples immersed in 1M HCl solution with various amounts of the extract solution, compared to the weight loss of the steel sample when immersed in the control (1M HCl solution without extract). The results indicate gradual weight loss of steel sample at the onset of the experiment up to 24 hours of exposure to the corrodent. It could be seen however, that the weight loss of the sample was more than halved by the addition of only 1ml of the extract solution after 24 hours. The weight lost generally increases with time of exposure as the steel gets corroded over time, but the increase remains gradual for all levels of extract solution compared to loss in mass of the steel when there was no extract in which the weight loss significantly increases with time. For instance, it could be seen from Figure 1 that with no extract solution added, the mild steel samples weight loss was about 7.4% after 24 hours and 88.6% after 120 hours. Whereas the observed weight loss with addition of 1ml and 5ml extract solution were 4.5% and 2.0% after 24 hours respectively; and the reduction in mass of the steel samples were 36.5% and 18.7% after 120 hours respectively. This is indicative of the effect of the addition of the extract solution in inhibiting the ability of the corrodent to impair the surface of the mild steel that ultimately led to the weight loss. Similar observations were reported on the effect of weight loss of mild steel by aqueous extract of *Polyalthia longifolia* leaves in various concentration of H_2SO_4 solution (Vasudha and Shanmuga, 2014).

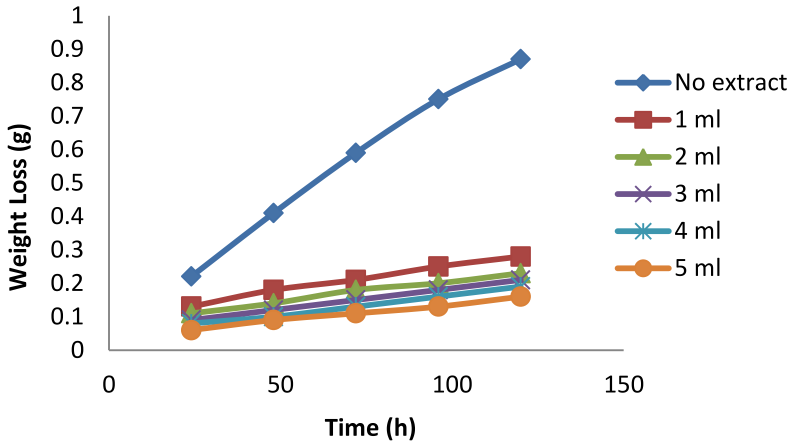

Fig. 1. Reduction in the mass of mild steel in 1M HCl solution with and without addition of *Polyalthia longifolia* leaves extract.

On the other hand, it could be observed from Figure 2 that the corrosion rates increase with reduction in the amount of extract solution. For no extract solution the corrosion rate ranges from 1.2 - 0.8 mg/cm^2/h over the period of the experiment. But the corrosion rate is approximately halved by the addition of just 1.0 ml extract solution, falling to the range of 0.7 - 0.3 mg/cm^2/h. With the addition of 5ml extract solution the corrosion rate significantly reduces to the range of 0.3 - 0.2 mg/cm^2/h. This reduction in the corrosion rates could be attributed to possibility of adsorption of bioactive inhibitor molecules on the metal surface forming a thin coating film that grows with time on the metal surface which hinders corrosive attack on the metal thereby reducing weight loss of the specimen. Similar trends were observed in previous findings (Yawas, 2005) and (Nwabanne and Okafor, 2011).

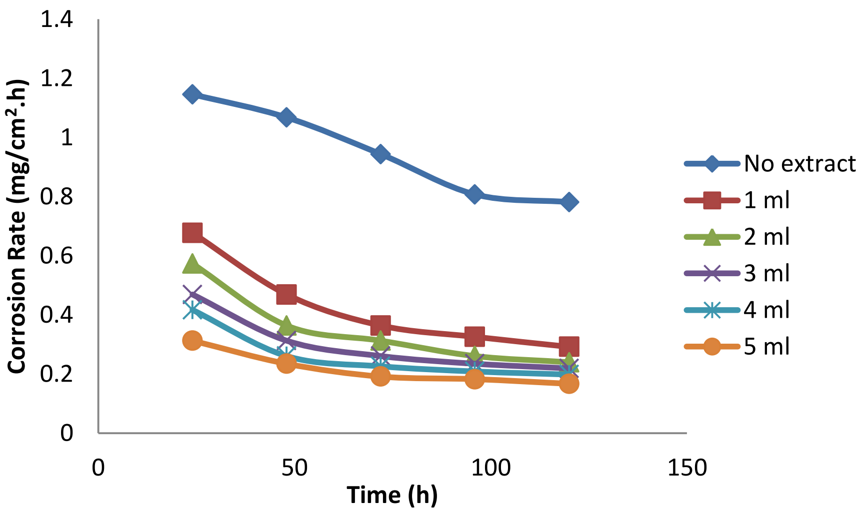

Fig. 2. Effect of amount of *Polyalthia longifolia* leaves extract on the corrosion rate of mild steel in 1M HCl solution.

The effect of concentration of *Polyalthia longifolia* leaves extract on the corrosion rates could further be amplified as illustrated in Figure 3. The figure presents the influence of the concentration of the extract on the corrosion rate at periodic intervals for the various extract levels investigated. The results confirm that the corrosion rate strongly decreases with increase in the amount of inhibitor extract in mild HCl solution, indicative of the significant dependence of the extent of the corrosion on the amount of the inhibitor extract in the system. Similar behaviour of aqueous extract of *Polyalthia longifolia* leaves on the corrosion rate of mild steel in dilute H_2SO_4 solution was observed in previous works (Vasudha and Shanmuga, 2014). Generally, it could be observed that the corrosion rate is significantly decreased by approximately 50% after 24 hours of the experiment for all level of the extract solution, after which the decrease in the corrosion rate was rather gradual with time for all level of the extract concentration used.

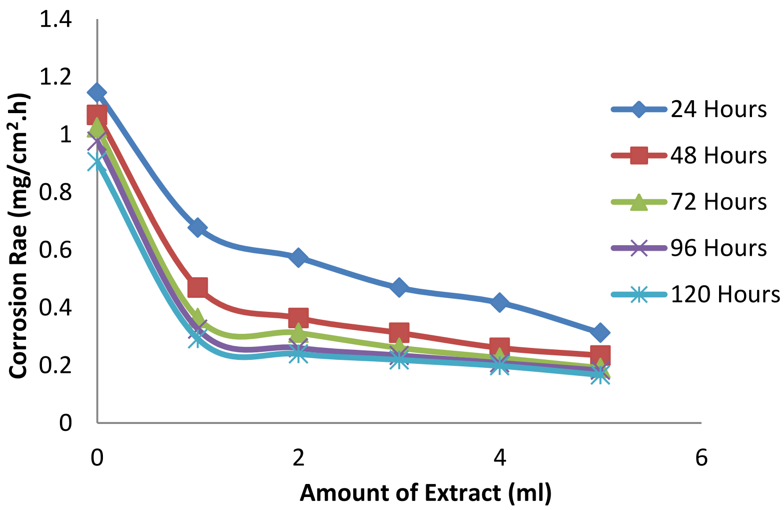

Fig. 3. Effect of amount of *Polyalthia longifolia* leaves extract on the corrosion rate of mild steel in 1M HCl solution for different immersion times.

4.2 Inhibition Efficiency

Figure 4 illustrates the variation of the inhibition efficiency of the *Polyalthia longifolia* leaves extract solution with time for various level of the extract solution. It could be noted that the inhibition efficiency generally increases with increase in the amount of the extract solution. It is noteworthy that the inhibition efficiency did not increase appreciably with increase in the amount of extract solution at the late stage of the experiment. This is likely because at the beginning of the experiment, the mild steel surface was mainly exposed to the acid corrodent, and increasing the amount of the extract has significant effect in preventing attack on the surface thereby increasing the inhibition efficiency. For instance, using 1.0 ml extract solution achieved inhibition efficiency of about 41% after 24 hours and 70% after 5 days respectively. Whereas, the corresponding inhibition efficiency using 5.0 ml extract solution was approximately 70% after 24 hours and 80% after 5 days respectively. Overall, the inhibition efficiency increases gradually over time for all extract levels, and almost plateaued leading to no appreciable increase in inhibition efficiency with time after about 3 days of the experiment. As asserted earlier, this could be attributed to the fact that initially the metal surface was largely exposed to the corroding medium, and there is rapid loss in mass of the sample, and at the same time there is rapid adsorption of the extract molecules on the surface, thus increasing the inhibition efficiency. However, as the metal surface gets coated with the adsorbed molecules of the extract, only little surface of the metals gets attacked for corrosion, and correspondingly small amount of the extract solution further gets adsorbed for corrosion inhibition, and consequently increase in the inhibition efficiency stagnated.

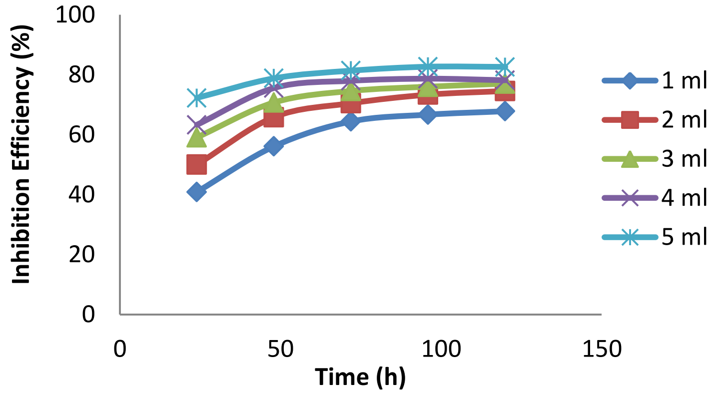

Fig. 4. Effect of amount of *Polyalthia longifolia* leaves extract on the corrosion inhibition efficiency in 1M HCl solution on mild steel.

Figure 5 illustrates the influence of *Polyalthia longifolia* extract concentration on the inhibition efficiency for various immersion times. It could be seen that the inhibition efficiency monotonically increases with increase in the extract concentration for various immersion times. For instance, using only 1ml of extract solution the inhibition efficiency of about 40% was achieved after 24 hours, which then increased to more than 70% after 5 days.

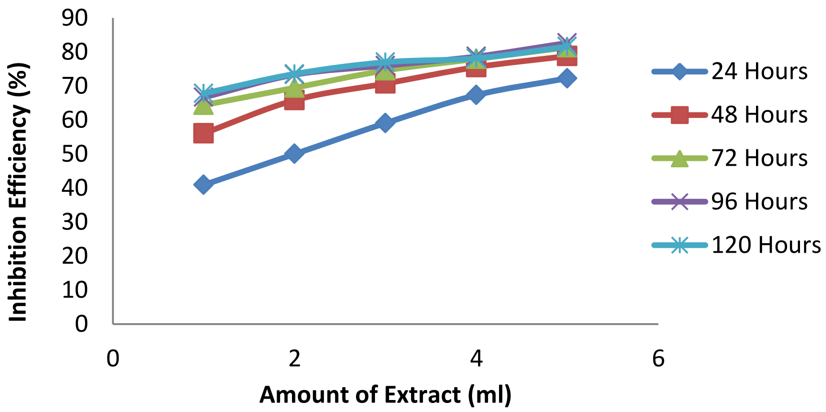

Fig. 5. Effect of amount of *Polyalthia longifolia* leaves extract on the corrosion inhibition efficiency in 1M HCl solution on mild steel for different immersion times.

5.0 Conclusion

The solvent extract from *Polyalthia longifolia* leaves was found to be effective green corrosion inhibitor that inhibits the corrosion of mild steel in 1M HCl solution under room conditions. The *Polyalthia longifolia* extract significantly influence the corrosion of mild steel due to the adsorption of the plant extract on the steel surface; which creates a thin film coating that effectively blankets the surface of the steel from the corrodent attack, thereby inhibiting the corrosion. The corrosion inhibition efficiency of the plant extract was found to moderately increase with increase in amount of extract. It was found that with 1ml of the extract solution, the inhibition efficiency of nearly 70% was achieved after five (5) days. Furthermore, the inhibition efficiency significantly increases with time of exposure at initial times. However, the increase becomes gradual and nearly plateaued over time as the steel surface gets coated with the adsorbed plant extract for all levels of extract solution investigated.

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