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# Investigation of Corrosion Inhibition Potential of Selected Biological Inhibitors

T. H. Udoh[1, *], M.U. Sunday

[1,2]*Chemical/Petrochemical Engineering Department, Akwa Ibom State University, Uyo, Akwa Ibom, NIGERIA*

**Abstract**
*In this paper, corrosion inhibition potential of two biological compounds namely azadirachta indica and enzyme on corrosion of mild steel was investigated. The weight loss analysis method was used to assess the corrosion losses in mild steel exposed to saline solutions with or without inhibitors over a period of 576 days and the corrosion rates, inhibitors' efficiencies and surface coverage were determined. The results showed that the rate of corrosion of mild steel generally does not change significantly after 400 days of continuous exposure to the same solution. Addition of enzyme to low and high saline solutions significantly reduced the corrosion rate of mild steel relative to the use of saline solutions alone. High corrosion inhibition efficiency was observed with the application of enzyme and its efficient concentration was found to be 2 wt.% in both low and high saline solutions. The corrosion inhibition of azadirachta indica was however found to be more efficient in low saline solution and an optimum concentration of 2 wt.% was efficient in this environment but in high saline solution, higher concentration of 10 wt.% is required for efficient corrosion inhibition.*

**Keywords:** Corrosion inhibitor, azadirachta indica, enzyme, mild steel and saline solutions.

## 1.0 INTRODUCTION

Corrosion process involves degradation of metallic materials through chemical or electrochemical reaction with their environment [1]. Metallic products such as pipes and flowlines are refined products of natural metals that had existed as stable ores of oxides, and corrosion is basically a natural way of reversing the unnatural process to its original form. Since corrosion is a natural phenomenon, it is almost impossible to prevent its occurrence hence, corrosion control is an apparent economical solution [2]. Oil production systems are complex systems with different component parts and failure in any of these components can result in life and environmental threats. Also, every component in oil and gas field is susceptible to corrosion attacks right from the casing string to the production platform. Different factors contribute to corrosion process in oil production systems such as oxygen that is present everywhere; water and carbon-dioxide that are produced or injected during recovery process; acid used around the wellbore to reduce formation damage or scale etc. All these can initiate or expedite corrosion process in oil production systems [2]. Furthermore, corrosion is of great interest in oil and gas industries because their products are transported from the reservoir to the storage through different metallic pipes and flowlines. Corrosion of these components can result in leakage of flammable and toxic products to the immediate environment. This is a potential danger to lives as well as great economical loss for the affected company. The produced oil from the reservoir is emulsion in nature because of the presence of dispersed aqueous solution in the continuous oil phase. This aqueous solution usually contains salts of different concentrations and compositions. Also, crude oil contains other non-hydrocarbon compounds such as oxygen, sulfur, nitrogen, and metals. Hence, it is difficult to predict the corrosiveness of crude oil based on its physicochemical composition due to the complexity of its chemistry [3].

Over the years, different measures have been used to control corrosion such as surface coatings and painting, use of cathodic protection as well as the use of corrosion inhibitors. Some of these measures for example, painting and coating are not feasible in some cases due to their intricate shapes or due to the possibility of chemical reactions. The use of corrosion inhibitors has been identified as one of the most practical ways of controlling corrosion [4]. Addition of small concentration of corrosion inhibitors to a corrosive medium is said to reduce corrosion through the formation of monomolecular layer between the metallic surface and corrosive agent. Corrosion inhibitors are usually classified based on their sources (as organic or

***Corresponding author **(Tel:** +234 (0) 8066519248**)**

**Email addresses:** *tinuolaudoh@aksu.edu.ng* (T. H. Udoh), and michaelsunday@aksu.edu.ng (M.U. Sunday)

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inorganic) and methods of production (as synthesized or extracted). The use of some conventional corrosion inhibitors such as chromates and lead are now being restricted due to their hazardous and non-degradable nature that constitutes environmental threat [5]. Hence, more studies are researching on green organic corrosion inhibitors as substitute for synthesized inorganic inhibitors. The use of different plant extracts such as Justicia gendarussa [6], khillar [7], olive leaves [8], Phyllanthus amaratus [9], Musa paradisica peel [10] and Murraya koenigii leaves [11] have been explored. The efficiency of green organic corrosion inhibitors has been associated with the presence of organic compounds with some atoms such as nitrogen (N), oxygen (O), phosphorus (P) and sulfur (S). The stated order of increase in their corrosion inhibition efficiency is P>S>N>O [5].

The green organic inhibitors modify corrosion process through their interfacial adsorption at the metal-solution interface [12]. This adsorption process can be physisorption that involves electrostatic ionic bonding or chemisorption that involves strong chemical bonds between non-ionic inhibitor molecules and the metal. The efficiency of these organic inhibitors is said to be enhanced with the displacement of one of the hydrogen atoms attached to carbon in the heterocyclic ring by either of -CHO, -NO, -COOH or $-NH_2$. Previous studies have shown that the efficiency of green organic inhibitors is strongly influenced by their structure, concentration, system temperature and exposure duration [5, 13]. Although these studies are advocating the use of green inhibitors, but their efficiencies must be ascertained in the laboratory and field trials to know the suitability of an inhibitor to a given system. Most of the previous studies on green inhibitors were carried out in hydrochloride acid (HCl) aqueous environment. For example, Garcia et al. [4] investigated the use of ethanolic extract of the Pachycormus discolor leaves to control corrosion of carbon steel and their results showed that ethanolic exhibited a good performance as corrosion inhibitor for carbon steel exposed to HCl aqueous solutions when 2% (v/v) concentration was used. The recent study by Agu [1] also demonstrated the efficiency of extract of azadirachta indica to reduce corrosion of mild steel in acidic environment. Taj et al. [14] however investigated the potential of green inhibitors extracted from leaves and root of medicinal plants on mild steel corrosion control in synthetic ocean water and their results show good corrosion protection. This corrosion control phenomenon has not been fully understood and hence, prompts further research. The aim of this paper is to investigate the potentials of azadirachta indica and enzyme as inhibitors of corrosion of mild steel in saline environments that are relevant to hydrocarbon reservoirs. Azadirachta indica has been identified as a good acid corrosion inhibitor based on its high content of tannin and series of complex triterpene glycosides but it has not investigated in saline solutions [1]. The enzyme corrosion inhibition especially in saline environment has not been investigated to the best of our knowledge but it has the properties associated with corrosion inhibitors presented by Popoola [5] and it has been used for enhanced oil recovery and well stimulation processes [14, 15].

## 2.0 MATERIAL AND METHOD

### *2.1 Materials and sample preparation*

The compositional breakdown of the saline solutions used for the mild steel corrosion investigations in this study is presented in Table 1. The brine solutions were prepared with reagent grade NaCl, $CaCl_2$, $MgCl_2.6H_2O$ and $Na_2SO_4$ salts in distilled water. Two saline solutions of 0.5 and 1 molarity (M) were used as representative of injection and formation brines, respectively that are commonly used in hydrocarbon production system. These brines normally have direct contact with the flowlines during hydrocarbon production and water injection processes.

**Table 1:** Compositional breakdown of saline solutions.

| Components | 0.5 M Brine | 1.0 M Brine |
|---|---|---|
| NaCl | 28.08 | 56.16 |
| $CaCl_2$ | 2.10 | 4.20 |
| $MgCl_2$ | 0.10 | 0.05 |
| $Na_2SO_4$ | 0.01 | 0.02 |

The material used as a representative of a flowline in this study is mild steel coupons with compositional breakdown presented in Table 2. The coupons used had the same dimensions of 5 cm by 4 cm and thickness of 0.80 mm. The coupons surfaces were first smoothened with emery paper having a grit size 220. They were then neatly wiped with cotton wool repeatedly, weighed immediately and thereafter immersed in the experimental vessels containing relevant saline solutions with and without inhibitors.

The two green corrosion inhibitors used in this study are azadirachta indica extract and enzyme. The extract of the azadirachta indica was produced following the procedures detailed in [1] with 800 g of fleshly grounded azadirachta indica leaves that was dissolved in 1000 mL of distilled water. The comprehensive chemical composition of azadirachta indica leaf extract is presented in [16]. The enzyme used in this study is a 100% concentrate of greenzyme solution prepared from DNA of oil eating microbes, it was supplied by Biotech Processing supply

Dallas, Texas. The compositional analysis of this enzyme is presented in the previous study by Udoh [17].

**Table 2:** Percentage composition of mild steel [1]

| Component | % |
|---|---|
| C | 0.150 – 0.190 |
| Mn | 0.60 – 0.9 |
| P | ≤0.025 |
| S | ≤0.02 |
| Si | ≤0.03 |
| Cr | ≤0.15% |

### *2.2 Experimental method*

The weight loss analysis method was used to assess the corrosion losses in the mild steel exposed to saline environments in the absence and presence of corrosion inhibitors in this study. Eighteen coupons of the same size, two corrosion inhibitors (azadirachta indica and enzyme) and two saline solutions (0.5 M and 1.0 M) were used. Each of the coupon was initially weighed and then immersed in 50 mL of relevant saline solution to which different concentrations (0, 1 wt.%, 2 wt.%, 5 wt.% and 10 wt.%) of the inhibitors were added. Each of the coupons were weighed again after cleaning the corrosion deposit on them every 72 hours of continuous immersion in solutions. The differences in the weights of the coupons were used to calculate the corrosion rates (CR), efficiencies of corrosion inhibitors (E) and surface coverage of the inhibitors (θ) using Equations 1-3 [1, 15]:

$$CR\ (mgcm^{-2}h^{-1}) = \frac{W}{At}, \quad (1)$$

$$E\ (\%) = \frac{CR_0 - CR}{CR_0} x\ 100, \quad (2)$$

$$\theta = \frac{CR_0 - CR}{CR_0}, \quad (3)$$

Where $W$ is difference in initial and final weights of coupons (mg), $A$ is area of the coupons ($cm^2$) and $t$ is the time during which the coupons were immersed in the solutions (h), $CR_0$ and $CR$ represent the corrosion rates ($mgcm^{-2}h^{-1}$) without and with inhibitors, respectively.

## 3.0 RESULTS AND DISCUSSION

The results of the corrosion rates of the coupons immersed in 0.5 M saline solutions with and without inhibitors of different concentrations over a period of 576 h and the efficiencies of these inhibitors are presented in Figure 1. A progressive increase in corrosion rate (0.01-0.057 $mgcm^{-2}h^{-1}$) of mild steel was observed when it was in saline environment without corrosion inhibitors over the period investigated. The addition of different concentrations of enzyme to this saline solution however reduced the corrosion rate of mild steel drastically to below 0.01 $mgcm^{-2}h^{-1}$ irrespective of the concentration used. The efficiency of enzyme as an inhibitor of corrosion of mild steel increases with its contact time with mild steel. High inhibition efficiencies (>80%) were observed with all the enzyme concentrations investigated in the saline solution thereby signifying the concentration independence of the enzyme's corrosion inhibition process. Hence, the use of high concentration of enzyme may not be needful in this saline solution since good corrosion inhibition can be achieved with the application of low concentration.

On the contrary, the use of azadirachta indica as corrosion inhibitor of mild steel tends to be concentration dependent. The addition of 1 wt.% azadirachta indica to the 0.5 m saline solution resulted in an initial increase in corrosion of mild steel from 0.01 $mgcm^{-2}h^{-1}$ to 0.18 $mgcm^{-2}h^{-1}$ relative to the use of saline solution alone (Figure 1a). The continuous exposure of the mild steel to azadirachta indica in saline solution however reduced its corrosion rate to that of the saline solution alone after more than 500 h of exposure. This signifies the inefficiency of 1 wt.% azadirachta indica to inhibits corrosion of mild steel in this saline solution hence, the efficiency plot could not be presented due to very high negative values. The use of higher concentration of azadirachta indica however significantly reduced the corrosion rate of mild steel to below 0.01 $mgcm^{-2}h^{-1}$ expect at very high concentration of 10 wt.% when 0.016 $mgcm^{-2}h^{-1}$ was attained. In the same vein, high inhibition efficiency of azadirachta indica was observed with increase in contact time with mild steel.

The results of the corrosion rates of the mild steel immersed in 1.0 M saline solutions with and without the inhibitors are presented in Figure 2. In this saline environment, lower corrosion rate (0.01-0.175 $mgcm^{-2}h^{-1}$) was observed relative to the 0.5 M saline solution in the absence of inhibitors. The addition of different concentrations of enzyme to the saline solution also reduced the corrosion rate of mild steel to below 0.01 $mgcm^{-2}h^{-1}$. Signifying the potential of enzyme to inhibit the corrosion of mild steel in high saline solution although its efficiencies at different concentrations were below 60% and the least efficiency was observed with the highest concentration (10 wt.%). The application of different concentrations of azadirachta indica as corrosion inhibitor in this saline solution however seems to be inefficient expect at very high concentration of 10 wt.% when lower corrosion rate was attained with low efficiency.

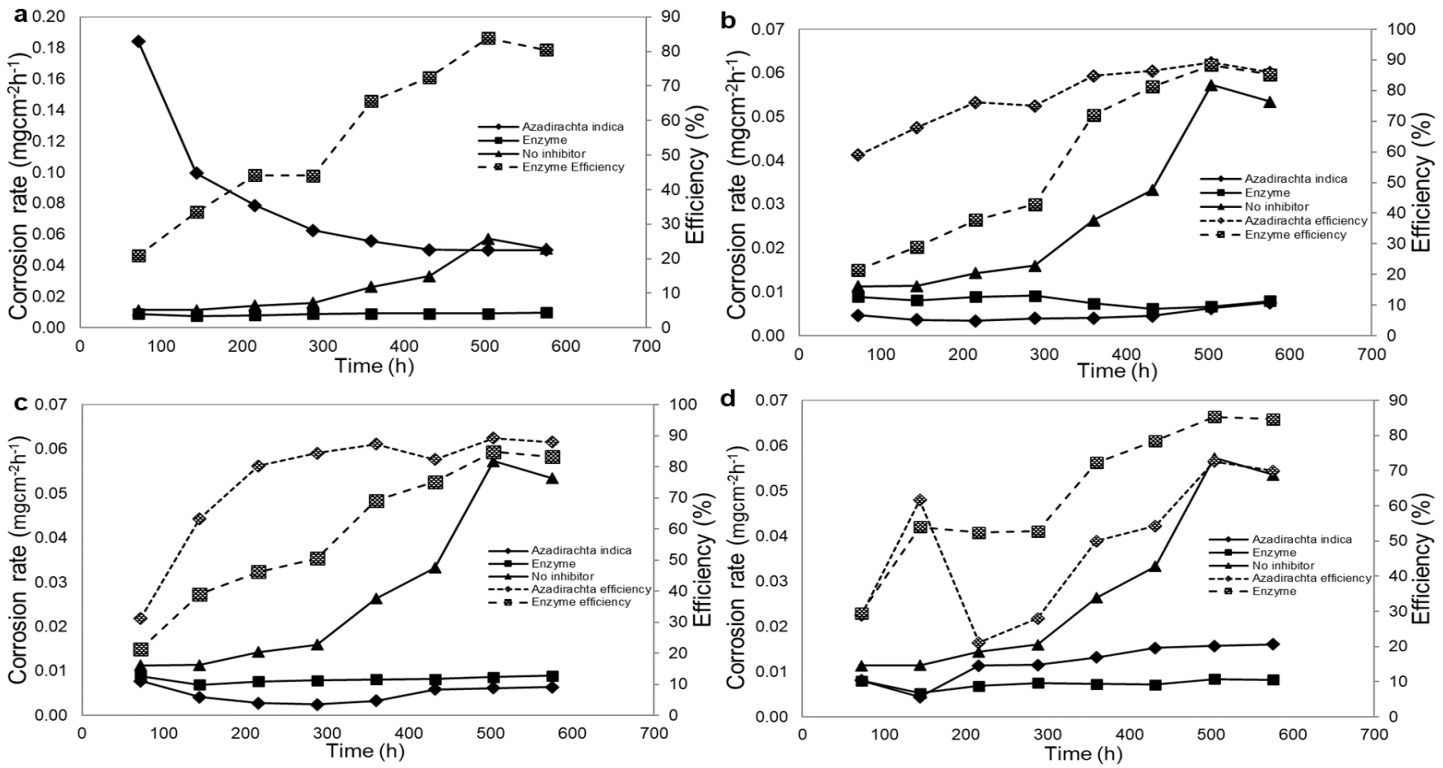


**Figure 1:** The corrosion rate of mild steel immersed in 0.5 M saline environment with and without corrosion inhibitors and the efficiencies of the inhibitors for (a) 1% concentration, (b) 2% concentration, (c) 5% concentration and (d) 10% concentration.

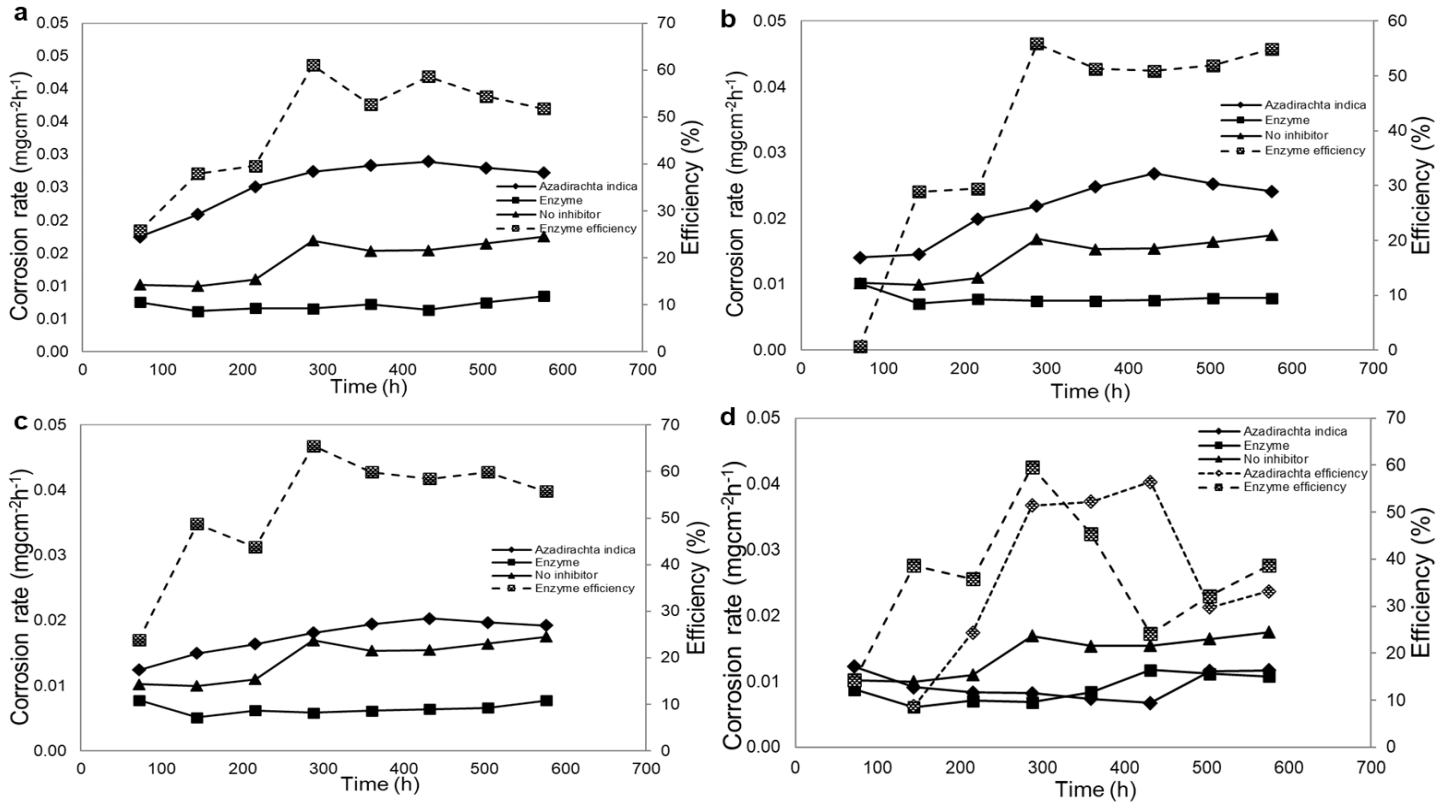


**Figure 2:** The corrosion rate of mild steel immersed in 1 M saline environment with and without corrosion inhibitors and the efficiencies of the inhibitors for (a) 1% concentration, (b) 2% concentration, (c) 5% concentration and (d) 10% concentration.

This shows the sensitivity of azadirachta indica to high salt concentration present in this saline environment. Relating the results of the corrosion rates of mild steel in this saline solution to that of 0.5 M saline solution, the corrosion inhibition efficiencies of both enzyme and azadirachta indica were lower in high saline solution, suggesting the possibility of salts molecules effect or interference in inhibitors-mild steel surface interactions.

To better understand the mild steel corrosion inhibition process of enzyme and azadirachta indica, their respective surface coverage in the two saline environments were calculated and presented in Figure 3. The result of the application of 1 wt.% of azadirachta indica in 0.5 M saline solution was not included in Figure 3a due to its very high negative values (up to -15.27) that makes the readability of the plots difficult. It is evident from the results that azadirachta indica was more efficiency in low saline solution than high saline solution. This suggest that it has more surface coverage on the mild steel thereby limiting its interaction with the active salt molecules in the saline solution and hence, reduces its corrosion rate. Its surface coverage was however limited in high saline solution with high molecular salt concentration but the used of very high concentration of 10 wt.%, azadirachta indica was able to penetrate and cover the mild steel surface.

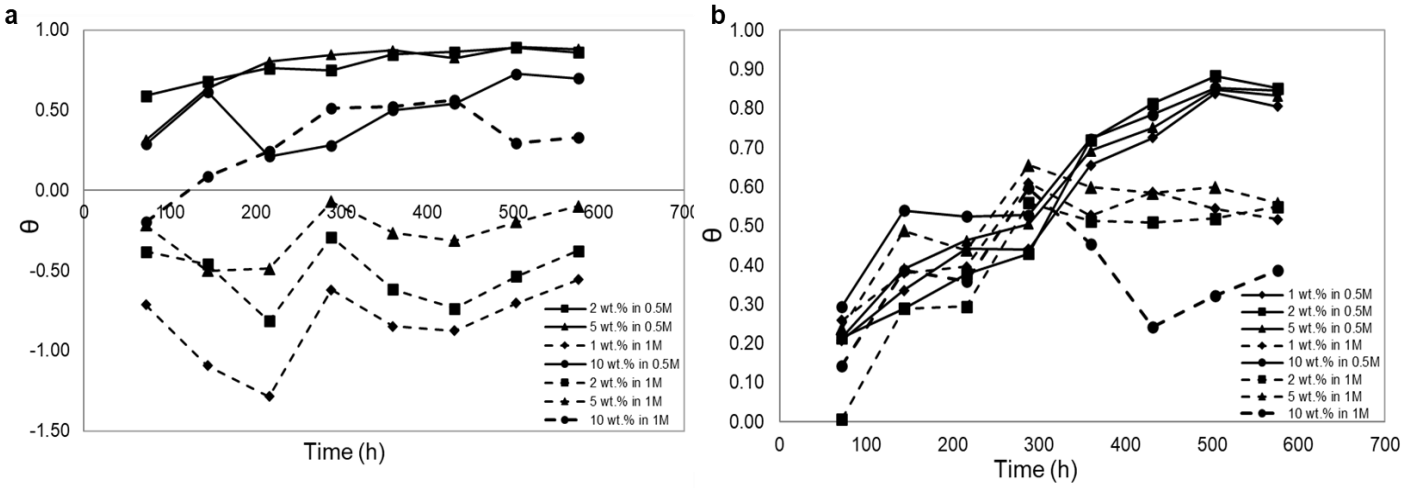


**Figure 3:** Effect of varied concentrations of corrosion inhibitors on their surface coverage of mild steel immersed in (a) 0.5 M brine and (b) 1 M brine with enzyme and azadirachta extract inhibitors.

The observed occurrence of limited surface coverage of azadirachta indica in the high saline solution can be attributed to excess surface coating of mild steel by salt molecules that prevents direct contact of azadirachta indica with its surface. The use of enzyme as inhibitor in both low and high saline solutions was characterised by progressive increase in surface coverage that seems to stabilize after prolonged contact with the mild steel surface. Higher surface coverage was observed in 0.5 M saline solution relative to the 1 M saline solution. This further shows the possibility of interference of the salt molecules in interactions of these corrosion inhibitors and mild steel surface. The enzyme however showed high tolerance for the saline environment than azadirachta indica. This is consistent with previous study by Udoh and Vinogradov [18] that showed that enzyme has high activity in high salinity brines. Also, from all tests carried out, it was obvious that corrosion rate of mild steel does not change significantly after 400 days of continuous exposure to solutions.

Furthermore, the high efficiency of enzyme to inhibit mild steel corrosion observed in this study may be associated with its molecular composition. According Popoola [5], the presence of organic compounds with some atoms such as nitrogen, oxygen, phosphorus, and sulfur in corrosion inhibitor enhance its inhibition efficiency. The compositional analysis of the enzyme used in this study that was presented in the previous study by Udoh [17] showed that nitrogen and oxygen atoms are present in the enzyme. However, from the compositional analysis of azadirachta indica presented by Garba and Mungadi [16], only phosphorus is present. This probably explains the reduced performance observed with the application of azadirachta indica in high saline solution relative enzyme. Relating the efficiencies of enzyme and azadirachta indica inhibitors to their respective concentrations as demonstrated in Figure 4 shows that 2 wt.% concentration of enzyme is efficient for inhibiting the corrosion of mild steel in 0.5 M and 1 M saline environments while for azadirachta indica, 2 wt.% concentration is efficient for inhibiting corrosion of mild

steel in 0.5 M saline environment but higher concentration of about 10 wt.% will be required for its corrosion inhibition in 1 M saline environment.

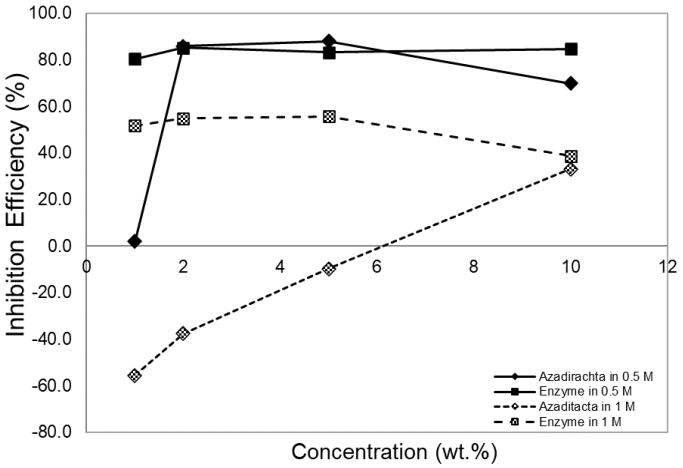


**Figure 4:** The effect of concentration of corrosion inhibitors on their efficiencies in 0.5 M and 1 M saline solutions environment.

## 4.0 CONCLUSION

This study presents a novel potential of the application of biological based corrosion inhibitors (enzyme and azadirachta indica) to flowline exposed to high saline environment that is relevant to hydrocarbon reservoirs. The results of this study show that:

- When corrosion inhibitors are not added to saline solutions that mild steel is exposed to, its corrosion rate increases with increase in contact time but reduces with increase in the salinity of the solution.
- Addition of enzyme inhibitor to low and high saline solutions to which mild steel is exposed to reduces its corrosion rate and enzyme corrosion inhibition efficiency increases with increase in contact time.
- Addition of azadirachta indica inhibitor to low saline solution is also efficient in reducing the corrosion rate of mild steel, but its efficiency reduces in high saline solution expect at very high concentration.
- The low concentration of 2 wt.% is enough for enzyme to efficiently reduce mild steel corrosion in low and high saline solutions while 2 wt.% concentration of azadirachta indica can efficiently reduce it corrosion rate in low saline solution but high concentration of 10 wt.% is required for its efficient corrosion inhibition in high saline environment.

## ACKNOWLEDGMENTS

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## REFERENCES

[1] Agu, P. C. "Inhibition of the corrosion of mild steel in acidic environment using azadirachta indica leaf extracts as inhibitor.," Federal University of Technology, Owerri, 2010.

[2] Brondel, D., Edwards, R., Hayman, A., Hill, D., Mehta, S. and Semerad, T. "Corrosion in the oil industry," *Oilfield review*, 6(2), 1994, pp. 4-18.

[3] Groysman, A. "Corrosion problems and solutions in oil, gas, refining and petrochemical industry," *Koroze a ochrana materialu*, 61(3), 2017, pp. 100-117.

[4] García, R., Valdez, B., Schorr, M., Carrillo, M., Carrillo, I., Gutiérrez, G. and Márquez, E. "Green Corrosion Inhibitor," in *XI* National Association of Corrosion Engineers *International, Central Mexico Section International Congress*, Mexico, 2012.

[5] Popoola, L. T. "Organic green corrosion inhibitors (OGCIs): a critical review," *Corrosion Reviews*, 37(2), 2019, pp. 71-102.

[6] El-Etre, A. Y. "Khillar extract as inhibitor for acid corrosion of SX 316 steel.," *Applied Surface Science*, 252(24), 2006, pp. 8521–8525.

[7] El-Etre, A. Y. "Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves.," *Journal of Colloid Interface Science*, 314(2), 2007, pp. 578–583.

[8] Ji, G., Anjum, S., Sundaram, S. and Prakash, R. "Musa paradisica peel extract as green corrosion inhibitor for mild steel in HCl solution.," *Corrosion Science*, 90, 2015, pp. 107–117.

[9] Okafor, P. C., Ikpi, M. E., Uwaha, I. E., Ebenso, E. E., Ekpe, U. J. and Umoren, S. A. "Inhibitory action of Phyllanthus amaratus extracts on the corrosion of mild steel in acidic media.," *Corrosion Science*, 50(8), 2008, pp. 2310–2317.

[10] Quraishi, M. A., Singh, A., Singh, V. K., Yadav, D. K. and Singh, A. K. "Green approach to corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by the extract of Murraya koenigii leaves". *Materials chemistry and Physics*, 122(1), 2010, pp. 114-122.

[11] Satapathy, A. K., Gunasekaran, G., Sahoo, S. C., Amit, K. and Rodrigues, P. V. "Corrosion inhibition by Justicia gendarussa plant extract in hydrochloric acid solution.," *Corrosion Science*, 51(12), 2009, pp. 2848–2856

[12] Marzorati, S., Verotta, L. and Trasatti, S. P. "Green corrosion inhibitors from natural sources and biomass wastes," *Molecules*, 24(1), 2019, pp. 48.

[13] Taj, S., Siddekha, A., Papavinasam, S. and Revie, R. W. Some natural products as green corrosion inhibitors, presented in *National Association of*

*Corrosion Engineers, International Corrosion Conference Series*, 076301- 0763013, 2007.

[14] Udoh, T. and Vinogradov, J. "A Synergy between Controlled Salinity Brine and Biosurfactant Flooding for Improved Oil Recovery: An Experimental Investigation Based on Zeta Potential and Interfacial Tension Measurements," *International Journal of Geophysics*, 2019, pp. 1-15.

[15] Wang, W. "Experimental Study of Oil Displacement by the Bio-enzyme at the Third Type Reservoirs of Sabei Blocks," presented in *Power and Energy Engineering Conference (APPEEC)*, Asia-Pacific, 2010.

[16] Garba, S. and Mungadi, H. U. "Quantitative chemical compositions of neem (Azadirachta indica) leaf aqueous," *International Journal of Research and Scientific Innovation*, 6(7), 2019, pp. 114-119.

[17] Udoh, T. H. "Comparative Study on Adsorption of Biologically Generated Surface Active Agents on Carbonate and Sandstone Rock Surfaces," *International Journal of Current Research and Academic Review*, Vol. 7, Number 2, 2019, pp. 23-36.

[18] Udoh, T. and Vinogradov, J. "Experimental Investigations of Behaviour of Biosurfactants in Brine Solutions Relevant to Hydrocarbon Reservoirs," *Colloids and Interfaces*, 3(1), 2019, pp. 1-24