Journal of Materials and Environmental Science
ISSN : 2028-2508
e-ISSN : 2737-890X
CODEN : JMESCN

J. Mater. Environ. Sci., 2023, Volume 14, Issue 12, Page 1504-1516

http://www.jmaterenvironsci.com

The Corrosion Behavior of Extracts of *Cymbopogon Citratus* (*Lemon Grass*) on Mild Steel in Oil of Vitriol and Caustic Soda Environments

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Received *07 Nov 2023,*
Revised *03 Dec 2023,*
Accepted *06 Dec 2023*

Keywords:
- ✓ *Corrosion;*
- ✓ *Engineering mild steel, ;*
- ✓ *Tetraoxosulphate (VI) Acid;*
- ✓ *Sodium Hydroxide;*
- ✓ *Cymbopogon citratus (Lemon grass)*

Citation*: Nwangbo T. N., Idenyi, N. E., Idu H. K., Aburu, C.M., Imoh, U.R., Dania, D., Nwachukwu, U. (2023) The Corrosion Behaviour of Extracts of Cymbopogon Citratus (Lemon Grass) on Mild Steel in Oil of Vitriol and Caustic Soda Environments, J. Mater. Environ. Sci., 14(12), 1504-1516*

Abstract: The Weight Loss Technique of corrosion analysis was adopted in the study of the corrosion behaviour of engineering mild steel in acidified and hydrolyzed media using Cymbopogon citratus (Lemongrass) extracts. The engineering mild steel rods were cut into Sixty-four (64) test coupons, each measuring 15 mm in length x 10 mm in diameter and their initial weights noted. Lemongrass extract was obtained using Reflux method and then added in volumes of 10 mL, 15 mL and 20 mL respectively into Sixteen (16) beakers containing each of 0.5 M H_2SO_4, 1.0 M H_2SO_4, 0.5 M NaOH and 1.0 M NaOH with 4 of the beakers containing plain H_2SO_4 and NaOH as controls. Four (4) coupons suspended with nylon strings were fully immersed in each of the beakers. The setup was allowed to remain for a period of 28 days (672 hours) with a coupon withdrawn from each beaker every 7 days (168-hourly) and subsequently processed for corrosion rate characterization using standard laboratory procedures and the final weight noted. The data of the weight loss values were recorded and computations made the corrosion penetration rate using the formula $Cpr = \frac{K\Delta W}{\rho At}$; for inhibition efficiency, IE % using $IE\% = \left[\frac{CR_a - CR_p}{CR_a}\right] \times 100$; and Langmuir adsorption isotherm using $\theta = \left[\frac{CR_a - CR_p}{CR_a}\right]$. Plots of Corrosion Penetration Rate (CPR) against Extract Concentration (mL); and Langmuir adsorption isotherms (using Surface Coverage Area, Θ against Extract Concentration) were constructed using ORIGIN and then critically analysed. The results obtained showed that the corrosion rate profile obeyed the trends that are associated with passivating metals beginning with an initial steep rise in corrosion rate which progressively declines with increasing exposure time. The inhibition efficiency also suggests that lemon grass has good inhibition potentials while the Langmuir adsorption isotherms confirm that the inhibitor species in Lemon grass adsorbed strongly and was evenly spread over the entire metal surface. In comparative terms, the inhibitive potency of Cymbopogon flexuosus (lemon grass) in NaOH surpasses that in the H_2SO_4 at different volumes of the extract. We therefore conclude from the foregoing that Lemon grass can be exploited as a veritable green inhibitor for use in the oil and gas industry and such other chemicals handling plants where corrosion is of great concern.

1. Introduction

Fontana (1987) defined corrosion as the deterioration and the loss of materials due to chemical or electrochemical process. Among the various forms of corrosion it is the presence of water contact that causes the corrosion of such material. Although mild steel is greatly used in many engineering construction, it has been on record that mild steel can corrode in both acidic media (Bouklah *et al.*, 2006; Singh and Murkherjee, 2010; Prabakaran *et al.*, 2016), and non-acidic media (Ibrahim *et al.*, 2017; Miron *et al.*, 2014). This corrosive effect on different engineering mild steel materials in various aspects of engineering construction is quite worrisome (Elmsellem *et al.*, 2014a; Dafali *et al.*, 2002). In addition, it imposes economic consequences of repair, damages, collapse, reconstruction and treats to life. Scientist and material engineers cannot seat arms locked to watch these important materials corrode forever. The first evidence of natural product used as corrosion inhibitors in 1930's, was when extracts of *Chelidonium majus* (Celadine) and other plants were used in H_2SO_4 pickling baths. Successful developments of researches to obtain natural corrosion inhibitors are growing as quickly as the environmental consciousness is gaining ground (Pandian *et al.*, 2008; Shammanol *et al.*, 2022; Es'haghi *et al.*, 2018). The best way to make safe a metallic material in acidic medium is to use an inhibitor (organic or mineral) to reduce and/or stop the corrosion process (Zarrok *et al.*, 2012; Hmamou *et al.*, 2012). Researchers are reoriented to natural compounds called friendship of environment (Abboud *et al.*, 2009; Dandia *et al.*, 2013; Elmsellem *et al.*, 2014b).

There are several extraction methods for green inhibitors that have been employed over time by researchers. For instance, decoction and infusion methods have been used in the study of the effects of aqueous extracts of spent coffee grounds on the corrosion of carbon steel in a 1 M HCl (Torres *et al.*, 2011). Zhou *et al.* (2023) used soxhlet extraction at 95°C for the study of green corrosion inhibitor extracted from waste feverfew root for carbon steel in H_2SO_4 solution, while soaking, heating, reflux, enzymatic hydrolysis, soxhlet and ultrasonic methods were cited as having been used in the extraction of organic inhibitors (Shang and Zhu, 2021). Furthermore maceration, infusion, decoction, digestion and percolation were reported as traditional extraction methods by Mirairio and Vazquez (2020).

The Lemongrass (*Cymbopogon citratus*) is a tropical plant native to South and Southeast Asia, valued for its culinary, medicinal, and aromatic properties. It has found wide applications for culinary, medicinal and aromatic uses (Shah *et al.*, 2011; Santin *et al.*, 2009). Lemongrass contains various phytochemical constituents that contribute to its aroma, flavor, and potential medicinal properties. Some of the key phytochemicals found in lemongrass include citral, geraniol, limonene, flavonoids, tannins and phenolic compounds. These phytochemical constituents make lemongrass not only a popular culinary herb but also a plant with potential health benefits due to its antioxidant, anti-inflammatory, and antimicrobial properties (Oladeji *et al.*, 2019; Shaikh *et al.*, 2019; Skaria *et al.*, 2007).

Extracts from lemongrass have also shown promise as effective corrosion inhibitors. The citral and geraniol possess inhibitive properties against metal corrosion. These compounds have been studied for their ability to form a protective layer on metal surfaces, reducing the rate of corrosion (El-Katori and Hashem, 2022). Lemongrass extracts have been explored in research as a potential eco-friendly and cost-effective alternative to synthetic corrosion inhibitors for various industries, including the automotive and oil sectors. However, while it shows promise, further research and testing are ongoing to determine its effectiveness under different conditions and on various metal types (Nwigwe and Nwoye, 2023; Abdel-Gaber *et al.*, 2014). This work therefore seeks to extend the research frontiers on green corrosion inhibition generally and in specifics, the effect of lemongrass in tetra-oxo-sulphate (VI) acid and caustic soda.

2. Methodology

2.1 Materials

The materials used for the study were: mild steel rod, sieve, plastic containers, bowls, dry leaves of Cymbopogon citratus, emery paper, distilled water, filter papers, tetraoxosulphate (VI) acid (H_2SO_4)

and sodium hydroxide base (NaOH) solution, cello tape, nylon thread, electronic weighing balance (Tapson's Scientific Instruments Co. Model=TAPT 3000 G), hack saw and hand file beakers, measuring cylinder, hacksaw and blades, vernier caliper and measuring tape.

2.2 Material preparation of mild steel and leaf extracts

The leaves of *Cymbopogon citratus* were obtained from the neighbourhood vicinity in Abakaliki, Ebonyi State, Nigeria. They were thoroughly washed in water to remove dust and sand particles. The leaves and seeds were shade dried separately for 96 hours, so as to enrich the active principles in them by reducing their moisture content (Saratha *et al*., 2009). The dried leaves were converted to powder by pounding using a mortar and pestle (Plates 1-3). The powdered samples were sieved with a sieve (150 µm mesh size). The sieved samples of leaves of *Cymbopogon citratus* were stored in polythene bags until needed for corrosion studies. Extraction of active ingredients in the leaves of *Cymbopogon citratus* plant were done using the Reflux method (Nwigbo *et al*., 2012, Finšgar *et al*., 2017).

Plate 1: Fresh leaf of Lemon grass

Plate 2: dried leaf of Lemon grass

Plate 3: Powder of lemon grass

30 grams of the powdered leaves were measured using an electronic balance into four round bottom flasks. 1.0M H_2SO_4, 0.5M H_2SO_4, 1.0M NaOH and 0.5M NaOH solution were respectively added to each of the measured samples in the four flasks. The resulting mixtures were boiled for 90 minutes, on a gas burner. The content of each flask was filtered using a filter paper. The filtrates were taken as the stock solution. Mild steel coupons were produced from mild steel rod. The mild steel rod was cut into one hundred and forty-four test specimens, each of dimensions (10mm x 5mm x 5mm). The surfaces of the test specimens were polished with abrasive paper to produce smooth surface and to remove any trace of contaminants. The test specimens were degreased in ethanol, washed thoroughly in deionized water and rinsed with acetone. The washed specimen was air dried (Eddy *et al*., 2011, Ehujiro *et al*., 2014) to remove any moisture that might be present on the test specimens.

The required concentration of the extract (10 ml, 15 ml and 20ml) were respectively measured from the stock solution of leaves of *Cymbopogon citratus* and added to each of the beakers containing the corrodent in each set. No inhibitor was added to the first beaker in each set. Four pre-weighed specimens were tied with nylon string, coded and totally immersed in each of the beakers. The setup was allowed to stand for 672 hours. Periodically, after every 168 hours, one sample was withdrawn from the corrodent; washed with distilled water; rinsed in ethanol to remove corrosion products; air dried; and re-weighed. The difference in weight of the coupon was taken as the weight loss. The Subsequently, the corrosion rates in mm/yr. were computed using Eqn.1:

$$CR = \frac{87.6W}{\rho At} \qquad \text{Eqn.1}$$

Where W = weight loss (mg); ρ = density of specimen (g/cm^3), A = area of specimen (cm^2) and t = period of immersion (hours).

The inhibition efficiencies (IE %) of the inhibitors were computed using Eqn.2.

$$IE\% = \left(\frac{CR_a - CR_p}{CR_a}\right) \times 100 \qquad \text{Eqn.2}$$

CR_p = Corrosion rate in the presence of inhibitor and CR_a = Corrosion rate in its absence.

Closely associated with inhibition efficiency is the Langmuir isotherm adapted for this study. Simplistic assumption was made to the effect that the surface coverage of the adsorbed layer (θ) is related to inhibition efficiency as shown in Eqn.3:

$$\theta = \left[\frac{CR_a - CR_p}{CR_a}\right] \qquad \text{Eqn.3.}$$

3. Results and Discussion

The results of the experimentation are shown in Figures 1 – 12.

Corrosion Penetration Rate (mmpy)

Figures 1, 4, 7 and 10 represent the corrosion penetration rate profiles for varying concentrations of *Cymbopogon citratus* in the two-corrosion media at the various molarities studied. The general observation inferred here is that the normal trend of corrosion behavior of passivating metals is obtained. Passivation entails the complete shielding of the metal surface by a layer of corrosion film which drastically reduces the influence of the corrosion media from direct contact with the metal surface. At the onset of corrosion, the attack occurs so rapidly that the corrosion rate rises significantly, peaks at some point when the corrosion product begins to adhere on the metal surface, and subsequently begins to decline as the exposure time increases, by which time a total encasement of the metal surface by the oxide film results.

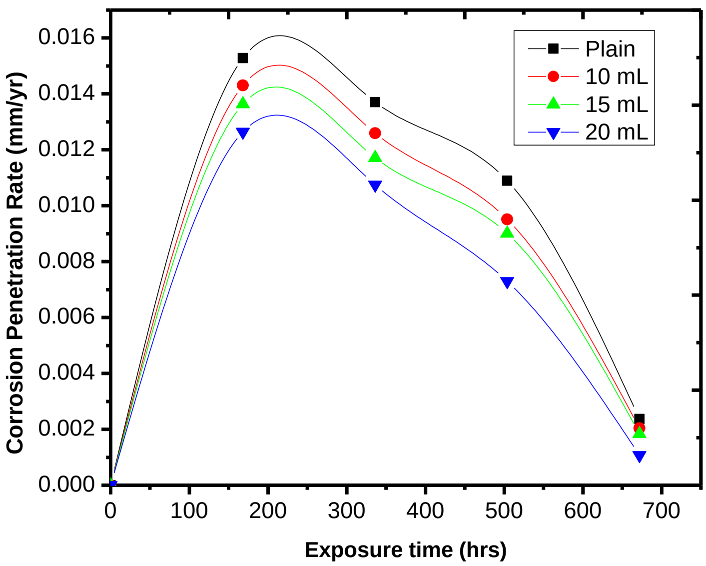

Figure 1. Corrosion penetration rates against exposure time for *Cymbopogon citratus* in 0.5 M H_2SO_4

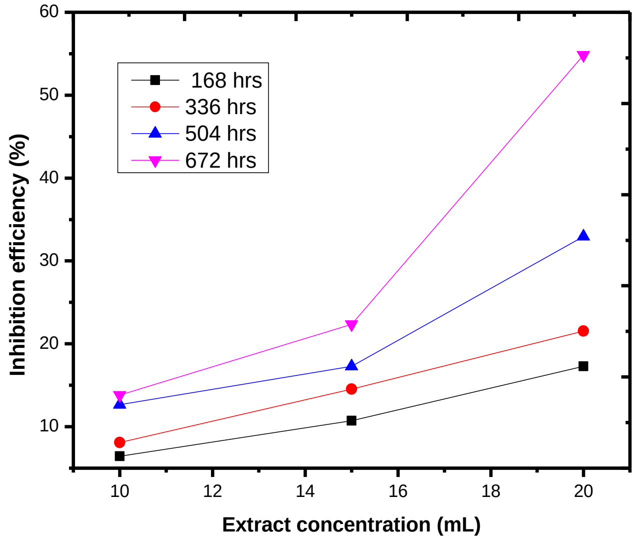

Figure 2. Inhibition Efficiencies of varying concentrations of *Cymbopogon citratus* on mild steel in 0.5 M H_2SO_4

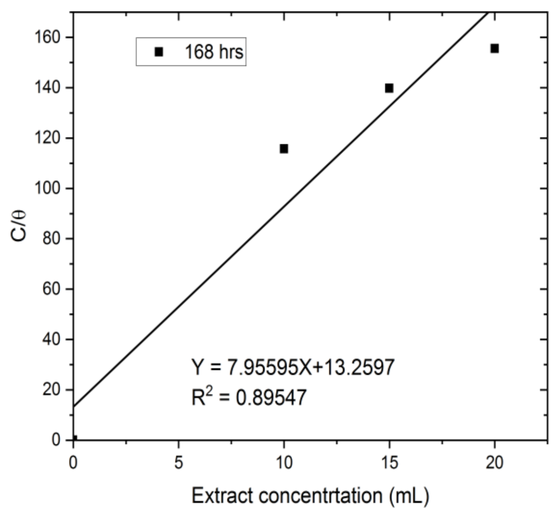

Figure 3. Langmuir adsorption isotherms of varying concentrations of *Cymbopogon citratus* on mild steel in 0.5M H_2SO_4

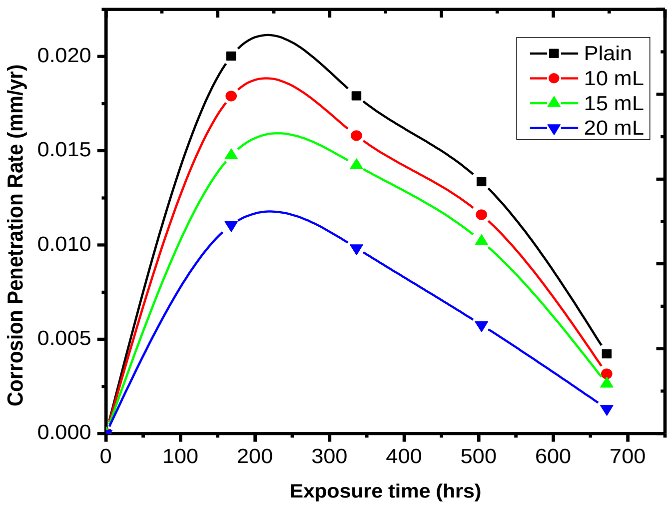

Figure 4. Corrosion penetration rates against exposure time for *Cymbopogon citratus* in 1.0 M H_2SO_4

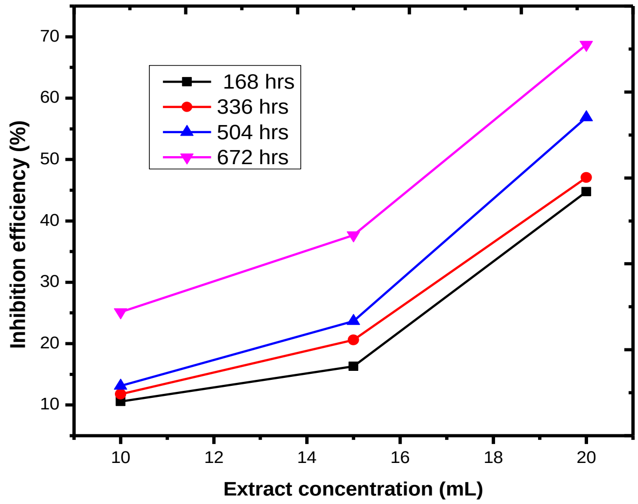

Figure 5. Inhibition Efficiencies of varying concentrations of *Cymbopogon citratus* on mild steel in 1.0 M H_2SO_4

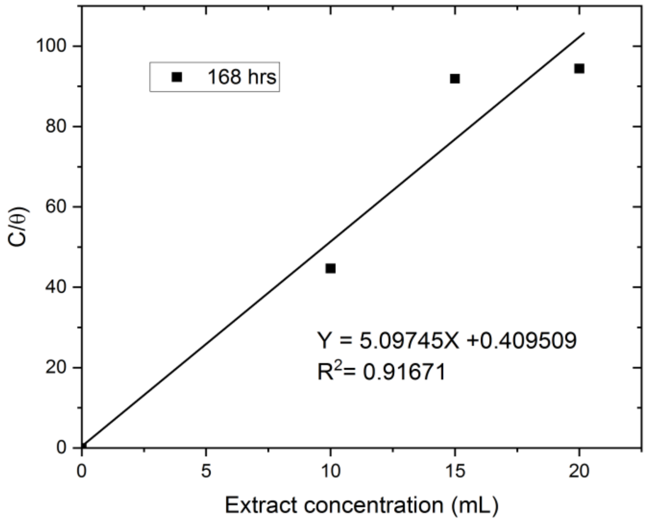

Figure 6. Langmuir adsorption isotherms of varying concentrations of *Cymbopogon citratus* on mild steel in 1.0M H_2SO_4

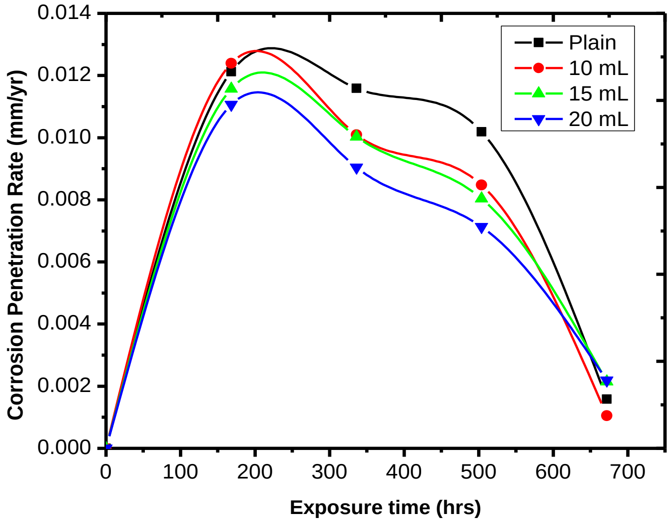

Figure 7. Corrosion penetration rates against exposure time for *Cymbopogon citratus* in 0.5 M NaOH.

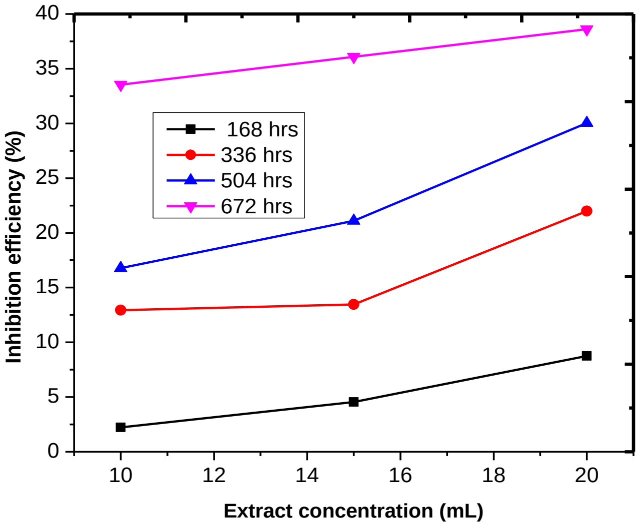

Figure 8. Inhibition Efficiencies of varying concentrations of *Cymbopogon citratus* on mild steel in 0.5 M NaOH.

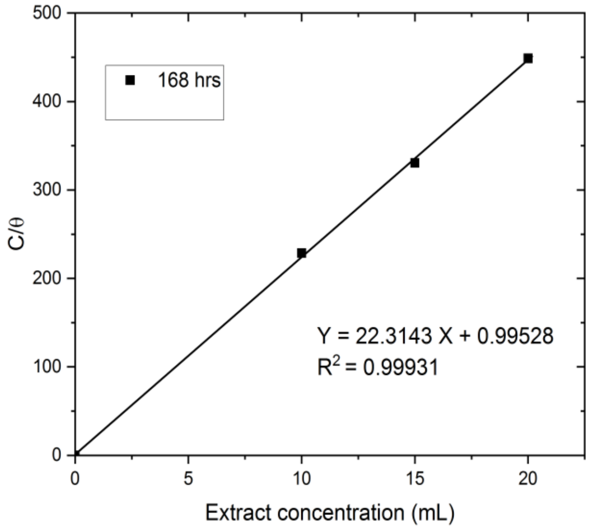

Figure 9. Langmuir adsorption isotherms of varying concentrations of *Cymbopogon citratus* on mild steel in 0.5M NaOH

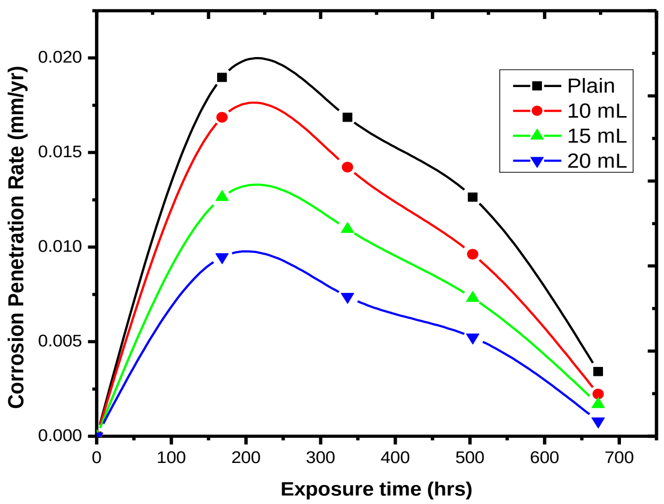

Figure 10. Corrosion penetration rates against exposure time for *Cymbopogon citratus* in 1.0 M NaOH.

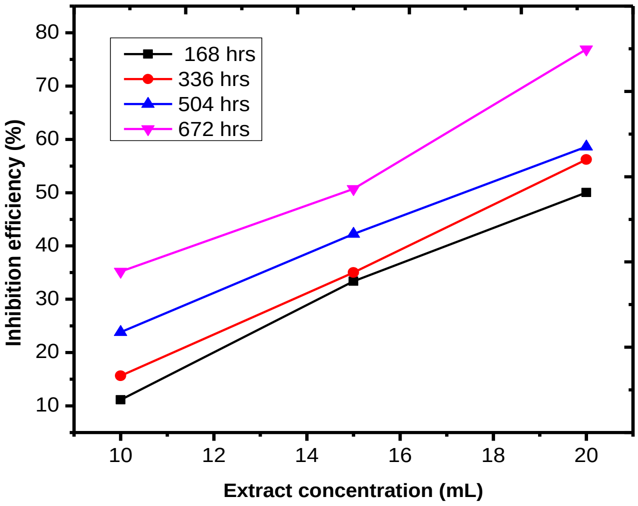

Figure 11. Inhibition Efficiencies of varying concentrations of *Cymbopogon citratus* on mild steel in 1.0 M NaOH.

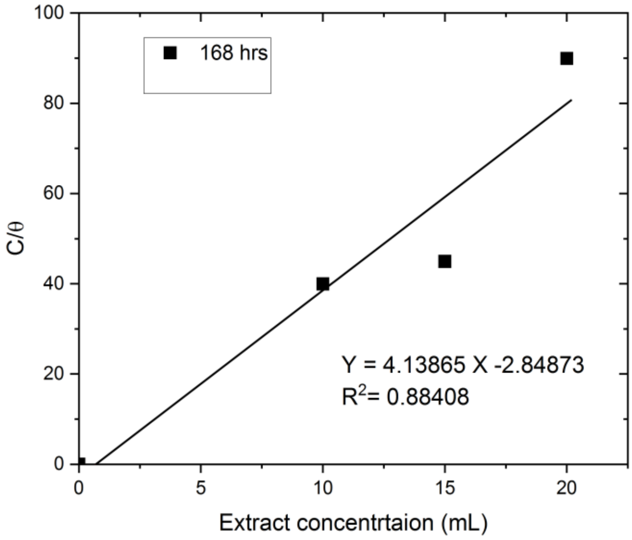

Figure 12. Langmuir adsorption isotherms of varying concentrations of *Cymbopogon citratus* on mild steel in 1.0M NaOH

As a time dependent phenomenon, for a constant inhibitor concentration, the behavior is somewhat parabolic (Idenyi *et al.*, 2009; Ekuma *et al.*, 2010; Nwankwo *et al.*, 2013; Nwankwo *et al.*, 2014; Idu *et al.*, 2015; Ifeanyichukwu *et al.*, 2023; Adagashi *et al*., 2023). It is apparent from the figures that the corrosion penetration rate (CPR) is directly proportional to the concentration of the extract, leading to the fact that the 20mL extract volume showed the least values of the CPR in all the media. The most plausible interpretation of this behavior is that lemongrass is an effective green corrosion inhibitor. Comparatively however, the passivation phenomenon is more pronounced in the caustic soda media (NaOH) than in oil of vitriol (H_2SO_4). This is expectedly so because acids in general contain more corrosion activating radicals than bases.

Inhibition Efficiency (IE %)

The inhibition efficiencies (expressed in percentages) of the extracts in each of the media are represented in Figures 2, 5, 8 and 11. A critical analysis of the plots reveals the direct linear proportionality between inhibition efficiency and extract concentration (if lines of best fit were taken).

The change in slopes at observed points along the lines of plots is attributable to several factors, including but not limited to the surface morphology of the corrosion coupons. Changes in surface morphology (roughness, texture and composition) can influence the adsorption process in several ways: surface area, adsorption sites, transport and diffusion, corrosion rate and protection. It is important to establish the fact that all the coupons used for this work were ribbed mild steel rods as such, it is expectedly going to lead to ineffective overall adsorption. Specific surface morphologies may provide protective barriers or hinder access of corrosive species to the metal surface, thereby affecting the kinetics of adsorption and desorption of the corrosion species on the surface (Toloei *et al.*, 2013; Saleikahrizsangi *et al.*, 2021; Li and Li, 2006; Alam *et al.*, 2023; Gajdacsi and Cegla, 2016; Alshamsi and AlBlooshi, 2019; Chen *et al.*, 2022). Analytically, it can be seen that the exposure time frame of 672 hours presented the best efficiencies in all the media. This is understandably true because adsorption and adhesion being time-dependent variables seem to be more efficient and effective (if the kinetics parametrics are uniform over the duration of the experiment

Langmuir Adsorption Isotherm (Surface Area Coverage)

In Figures 3, 6, 9 and 12 we have the Langmuir adsorption isotherms showing the surface area coverage (ϴ) against the extract concentration in mL. Equation 3 of this work establishes a mathematical relationship between surface area coverage and inhibition efficiency, which is simplistically $E = 100.\theta$. That being the case, it can easily be inferred that inhibition efficiency is a hundredfold of surface area coverage. Therefore, it is easily explainable to say that the plot of the Langmuir adsorption isotherm should linearly increase with increase in media concentration (Salasi *et al.*, 2007; Yetri *et al.*, 2015). In the figures shown above, the surface coverage area is highest at the 672 hour-period in all the media, with caustic soda showing better coverage than oil of vitriol. If the line of best fits are plotted, the graphs should be straight lines, but the associated problems of surface morphologies and corrosion kinetics make the observed changes in slopes inevitable. This phenomenon has earlier been exhaustively discussed under inhibition efficiency above. Further works that address this understanding exist (Liu, 2006; Doğan *et al.*, 2006). As mentioned above that natural extract contains numerous components at different contents as citral, geraniol, limonene, flavonoids, tannins and phenolic compounds. These molecules are rich in heteroatoms as O, N, S… as well as aromatic rings which facilitate the adsorption process at the metal surface to create a barrier against the arrival of aggressive ions (H^+) and dissolved oxygen (O_2). The multiadsorption is widely called synergistic intermolecular adsorption effect (Khadom *et al.*, 2022; Lrhoul *et al.*, 2023)

Conclusion

This work has reasserted the fact that acids and bases are high corrosive mediums. However their corrosive potency is a function of their concentrations with acids having more corrosion radicals. Also established is the fact that *Cymbopogon citratus* (Lemongrass) is a veritable green corrosion inhibitor with inhibition potency increasing as its concentration in the media increases. These findings therefore conclusively suggests that *Cymbopogon citratus* can serve as a cost-effective and eco-friendly alternative to the hazardous and oftentimes expensive synthetic inhibitors widely used in our oil and gas industries to ameliorate the devastating impacts of corrosion.

Acknowledgement: The authors acknowledge the invaluable supports from Ebonyi State University, Abakaliki (EBSU), the Scientific Equipment Development Institute, Enugu (SEDI-E), the National Agency for Science and Engineering Infrastructure, Abuja (NASENI) and the Taraba State University, Jalingo (TSU).

Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest.
Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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