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The Corrosion Behavior of *Cnidoscolus aconitifolius* (Chaya) Leaf Extract on Mild Steel in H_2SO_4 and Brine (NaCl Solution) Environments

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Abstract

The inhibition efficacies of extracts of *Cnidoscolus aconitifolius* (Chaya) leaves in the corrosion of mild steel were investigated in H_2SO_4, and NaCl media. Weight loss method was employed to determine corrosion rate. The ribbed mild steel rod was cut into forty (40) coupons, each measuring 16 mm (diameter) by 8 mm (length) and their initial weights taken and noted. Twenty (20) beakers containing 0.5M and 1.0M each of H_2SO_4 and NaCl solution separately with varying volumes of the extracts ranging from 5ml to 20ml were set up with four (4) coupons in each beaker fully immersed using nylon strings. The set up was allowed to stand for an exposure time of 672hrs with a coupon withdrawn from each beaker every 168 hours and processed using standard procedures before being reweighed using digital weighing balance. The weight difference for each coupon was obtained and used for corrosion rate calculation using the formula, $CPR = \frac{K\Delta W}{\rho At}$. Other corrosion parameters were also obtained using the relevant formulae: inhibition efficiency, $IE\% = \frac{CR_c - CR_i}{CR_c} \times 100$ and surface coverage, $\theta = \frac{CR_c - CR_i}{CR_c}$.The results obtained indicated that the normal corrosion rate profile for passivating metals was followed with the weight loss by the coupons being higher in the control media than those ones in the inhibited media. It was also observed that increase in volumes of these extracts from 5ml to 20ml decreased the corrosion rate of mild steel in the media. We found that in both media *Cnidoscolus aconitifolius* (Chaya) exhibited high inhibition efficiencies of 78.14% in H_2SO_4 and 64.15% in NaCl at extract concentration of 20 ml. Plots of the Langmuir adsorption isotherms suggest uniform surface covering of the adsorbent molecules at equilibrium state of the adsorbate–adsorbent system, with very strong adsorption forces. Based on these findings, the results suggest that *Cnidoscolus aconitifolius* (Chaya) leaves extract is a veritable green inhibitor for both acidic and salt media and can be a suitable alternative to the synthetic inhibitors widely used in the oil and gas industry.

Keywords: Inhibition efficiencies, *Cnidoscolus aconitifolius* (Chaya) leaves, Weight loss, Corrosion, Mild steel, Tetraoxosulphate (VI) acid (H_2SO_4) and Sodium hydroxide (NaCl) solution.

INTRODUCTION

Corrosion has been severally defined in various ways by several authors (Fontana, 1986; Uhlig, 2004; Callister, 1997; Ahmad, 2006; Elmsellem *et al*., 2014; Fernandez *et al*., 2015; Harsimran, 2021). In all the cases, one thing stands out – electrochemical reaction. Naturally, metals exist as oxides, sulphides and carbonates, generally called ores. So when processed into pure metals, they acquire energy and become unstable (Ekuma *et al*., 2010). Thus, throughout their service life, they "struggle" to return to their natural stable states. One process through which this is accomplished is by corrosion (Idenyi *et al*., 2009). Several forms of corrosion exist relative to the environment (Callister, 1997). The cost of corrosion is colossal and more experienced by the industrialized nations expectedly (Kumar *et al*., 2018; Gerhadus *et al*., 2016; Hou *et al.*, 2017; Bhaskaran *et al.*, 2016). Therefore engineers and scientists are constantly engaged in efforts to prevent or at least control corrosion in the industry, especially the oil and gas sector (Singh and Murkherjee, 2010). Part of these prevention and/or control efforts involve the use of corrosion inhibitors (Raja and Sethuraman, 2008). Synthetic inhibitors have been in use for several decades but with its attendance consequences which includes environmental degradation, highly costs and health hazards from their toxicity (Malarvizhi and Selvaraj, 2018; Kadhim *et al*., 2021; Oreko and Batet, 2022). For these reasons, research into the possible use green corrosion inhibitors, mostly of plant origin has been on the front burner in recent times (El-Ibrahim *et al*., 2018). Examples of the use of extracts of plant parts as corrosion inhibitors abound (Miron *et al*., 2014; Shammanol *et al*., 2022; Es'haghi *et al*., 2018). The extraction methods have also expanded to accommodate such processes as decoction, reflux, Soxhlet, etc (Torres *et al*., 2011; Zhou *et al*., 2023; Shang and Zhu, 2021; Miralrio and Vazquez, 2020).

Cnidoscolus aconitifolius, commonly known as chaya or tree spinach, is a leafy green shrub native to Mexico's Yucatan Peninsula and parts of Central America. It belongs to the Euphorbiaceae family, known for its diverse range of species. Chaya typically grows up to 6-8 feet tall, occasionally reaching heights of 12 feet (Grubben and Denton, 2004). Its leaves are the most prominent feature, resembling those of a maple or a split-lobed hand with deep green coloration. Each leaf can measure around 6-8 inches in diameter and has serrated edges. The leaves are rich in nutrients like vitamins A, C, and K, as well as minerals like iron, calcium, and protein, making them a valuable addition to diets, especially in regions with limited food resources (Ross-Ibarra and Molina-Cruz, 2002; Webster and Huft, 1988). Chaya is known for its hardiness, adapting well to various soil types and climates, thriving in tropical and subtropical regions. It's drought-resistant and can withstand periods of dryness, making it a sustainable crop in arid environments.

Chaya, or *Cnidoscolus aconitifolius*, contains various phytochemicals, including:

Flavonoids: These are antioxidants known for their potential health benefits, including anti-inflammatory and antioxidant properties. They contribute to the plant's defense mechanisms against stressors. Alkaloids: Chaya contains alkaloids, including tannins and saponins, which are bioactive compounds that may have medicinal properties. Some alkaloids have been studied for their potential effects on human health. Triterpenes: These compounds are found in the leaves of chaya and are known for their diverse biological activities, including anti-inflammatory and antimicrobial properties. Sterols: Chaya contains sterols, which are plant-based compounds with potential cholesterol-lowering effects and other health benefits. Phenolic compounds: These compounds, such as phenolic acids and lignans, are known for their antioxidant properties and potential health-promoting effects. Many of these phytochemicals contribute to chaya's potential health benefits (Kuti and Konuru, 2004; Kuti and Torres, 1996). However, it's crucial to note that chaya contains toxic compounds, such as hydrocyanic glycosides, in its raw state. Therefore, traditional preparation methods involve cooking or boiling the leaves to remove these toxins before consumption, making it safe and nutritious for eating (Abdala-Roberts and Parra-Tabla, 2005; Villaseňor, 2016; Brako and Zarucchi, 1993; Acevedo-Rodriguez and Strong, 2012; Aguilar and Murillo, 2008; Arango *et al*., 2000).

Several species of Chaya have been investigated for inhibition potentialities (Maragatham and Vizhi, 2015; Maragatham *et al*., 2018; Vizhi *et al*., 2018; Bilgiç, 2022). Ugi *et al*., (2023) worked on the inhibition behavior of isolated alkanoids in *Cnidoscolus aconitifolius* using HCl and H_2SO_4 only. This work therefore is aimed at exploring and exploiting the capabilities of Chaya as a potential alternative green inhibitor to replace the synthetic inhibitors currently in use particularly in the oil and gas industry.

Chaya plant

Dried Chaya leaves

Chaya powder

METHODOLOGY

Materials

The materials used in this investigation were mild steel rod, vernier calliper, meter rule, 40 gram of powdered leaves of *Cnidoscolus aconitifolius*, electronic weighing balance, 20 beakers, filter, funnel, 0.5 M and 1.0 M of tetraoxosulphate (vi) acid and sodium chloride solution. Others are distilled water, measuring cylinder, acetone, syringe, masking tape, beakers, knife, razor blade, thermometer, retort stand and inextensible string.

Preparation of the Mild Steel

The mild steel rod was mechanically cut into cylindrical shapes of dimension; 16 mm (diameter) and 8 mm (length). The specimen (coupons) were cleaned and stored in the desiccators to prevent re-oxidation.

Preparation of the Leave Extracts

The leaves of Chaya were thoroughly washed in distilled water and air dried to let off the moisture. After that, the leaves were ground into powder. A 40 g weight of the Chaya was measured and poured into a 1000 ml capacity beaker and then, 200 ml of distilled water was poured into the beaker and its contents. The beaker with its contents was covered with a lid and placed on the standard thermostatic hot plate at constant temperature of 80^0 C. The system was allowed to boil for 3 hours, after which the hot plate was turned off and the beaker allowed to cool to room temperature. The extracts were filtered with a filter and funnel and then stocked in plastic containers.

Weight Loss Technique:

This method employed is empirical in which the initial weight of each of the coupons was determined using weighing balance and then immersed in the experimental solution (in quadruplet) with the help of the strings. The coupons were allowed to remain in the solution for a period of 672 hours before they were being taken periodically (every 168 hours), one each from the solutions containing no extract and the ones containing various concentrations of the plant extract. Every of the sample withdrawn from the beaker was washed, dried and reweighed to determine the final weight. At the end of the experimental period, the corrosion rate as well as inhibition efficiencies of the extracts were calculated.

Subsequently, the corrosion rates in mm/yr. were computed using Eqn.1.

$$CPR = \frac{k\Delta W}{\rho At} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(Eqn.1)}$$

Where W = weight loss (mg); ρ *= density of specimen (g/cm³), A = area of specimen (cm²), t = period of immersion (hours) and* k *= a proportionality constant with a value of 87.6 for corrosion rate unit in mmpy (millimetres per year) and 534 for corrosion rate unit in mpy (mils per year).*

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

$$IE\% = \frac{CR_c - CR_i}{CR_c} x100 \quad \ldots\ldots\ldots\ldots \text{(Eqn.2)}$$

Where CR_i *= Corrosion rate in the presence of inhibitor and* CR_c *= Corrosion rate in the absence of the inhibitor.*

Closely associated with inhibition efficiency is the Langmuir adsorption isotherm adapted for this study. A 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.

$$\theta = \frac{CR_c - CR_i}{CR_c} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(Eqn. 3)}$$

Where, CR_i = Corrosion rate in the presence of inhibitor, CR_c = Corrosion rate in the absence of the inhibitor and θ = coverage of the adsorbate on the metal surface.

RESULTS AND DISCUSSION

RESULTS

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

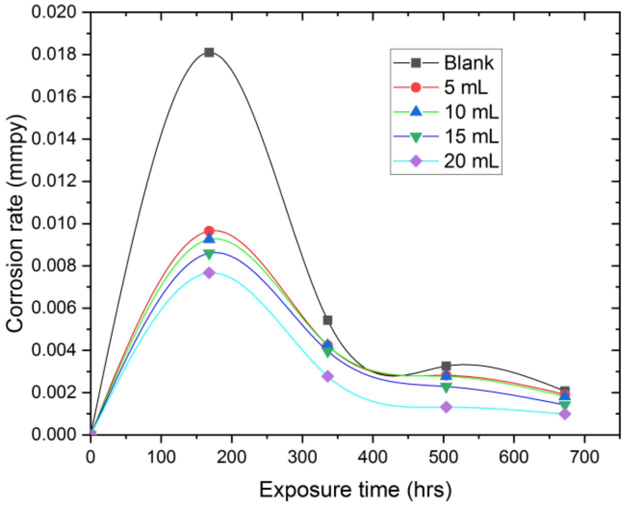

Fig 1: The corrosion penetration rate against exposure time for *Cnidoscolus aconitifolius* in 0.5 M H_2SO_4

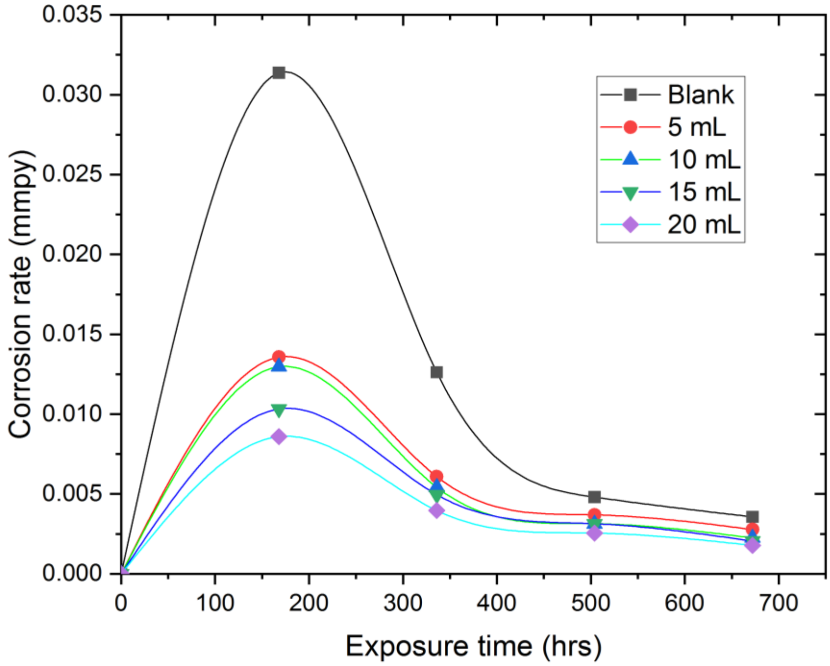

Fig 2: The corrosion penetration rate against exposure time for *Cnidoscolus aconitifolius* in 1.0 M H_2SO_4

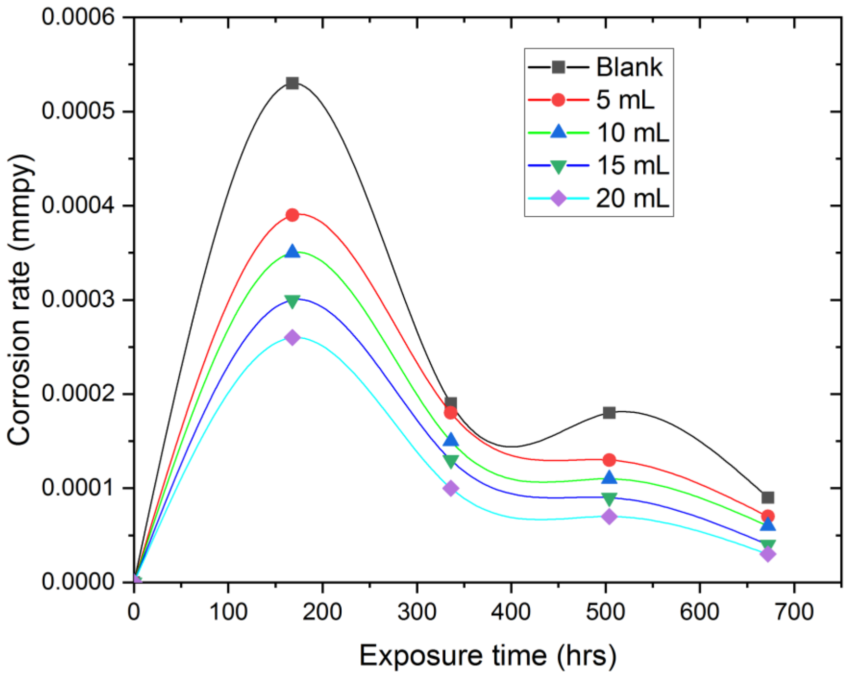

Fig 3: The corrosion penetration rate against exposure time for *Cnidoscolus aconitifolius* in 0.5 M NaCl solution

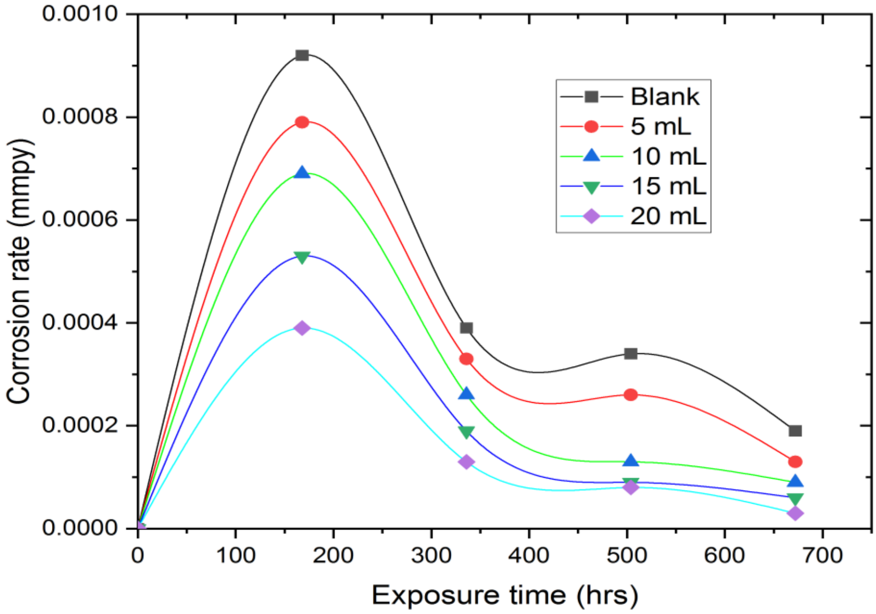

Fig 4: The corrosion penetration rate against exposure time for *Cnidoscolus aconitifolius* in 1.0 M NaCl solution

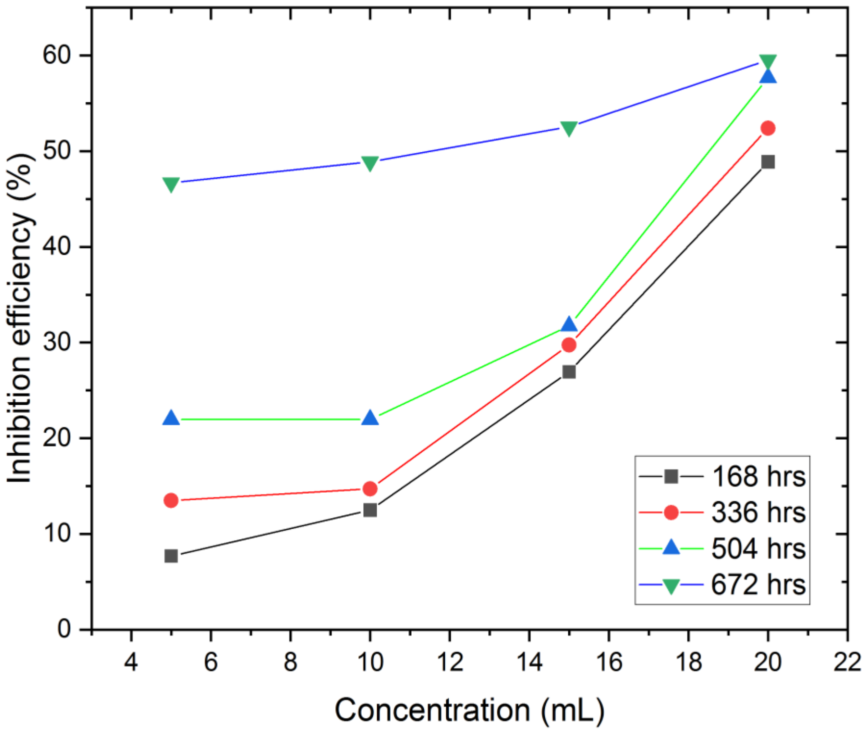

Fig 5: Inhibition efficiency against extract concentration for *Cnidoscolus aconitifolius* in 0.5 M H2SO4

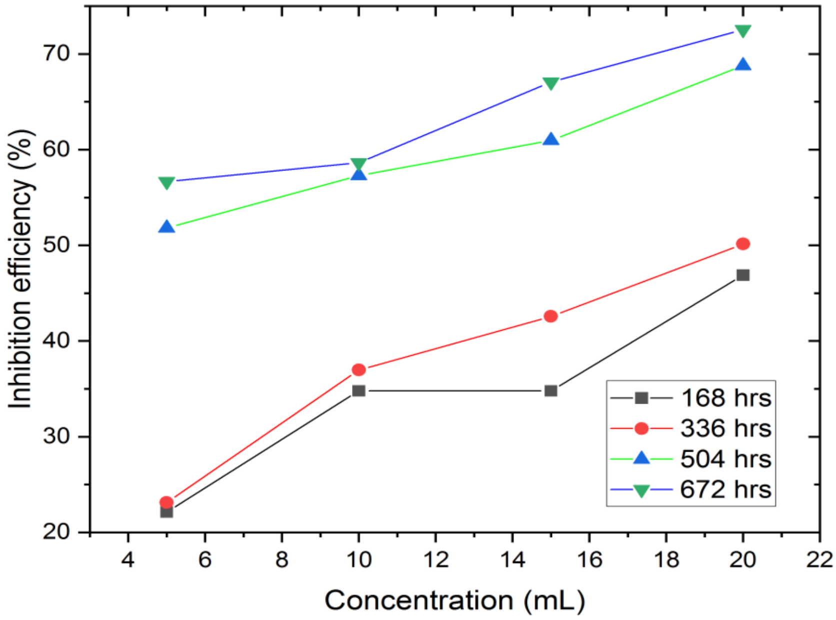

Fig 6: Inhibition efficiency against extract concentration for *Cnidoscolus aconitifolius* in 1.0 M H2SO4

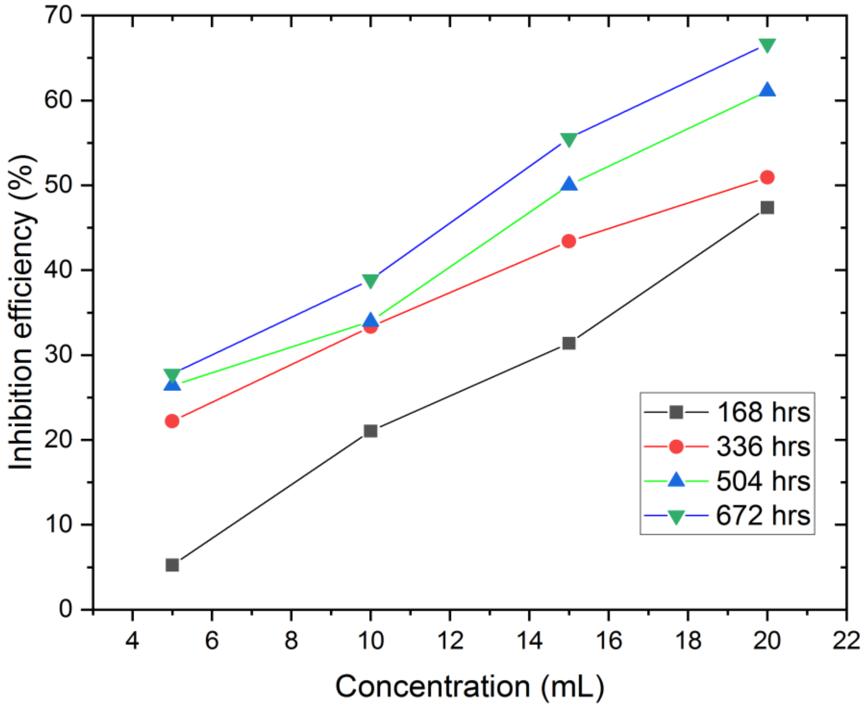

Fig 7: Inhibition efficiency against extract concentration for *Cnidoscolus aconitifolius* in 0.5 M NaCl solution

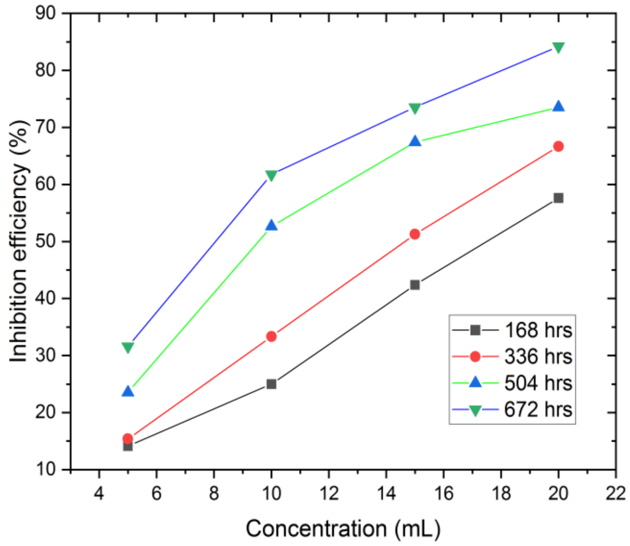

Fig 8: Inhibition efficiency against extract concentration for *Cnidoscolus aconitifolius* in 1.0 M NaCl solution

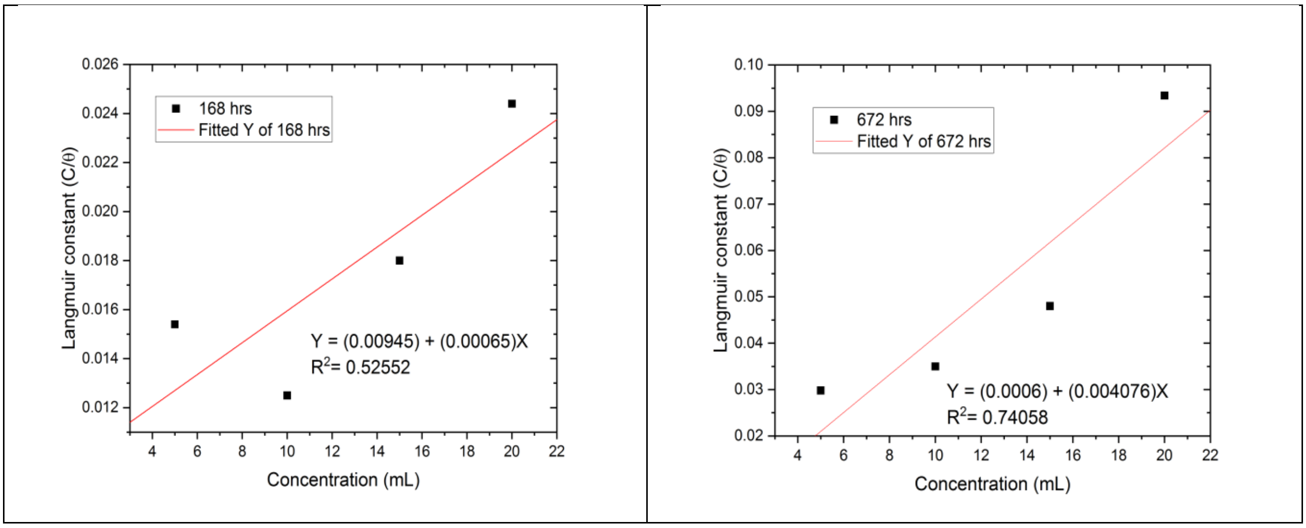

Fig 9: The Langmuir adsorption isotherms for *Cnidoscolus aconitifolius* in 0.5 M H_2SO_4 at 168 and 672 hours exposure times

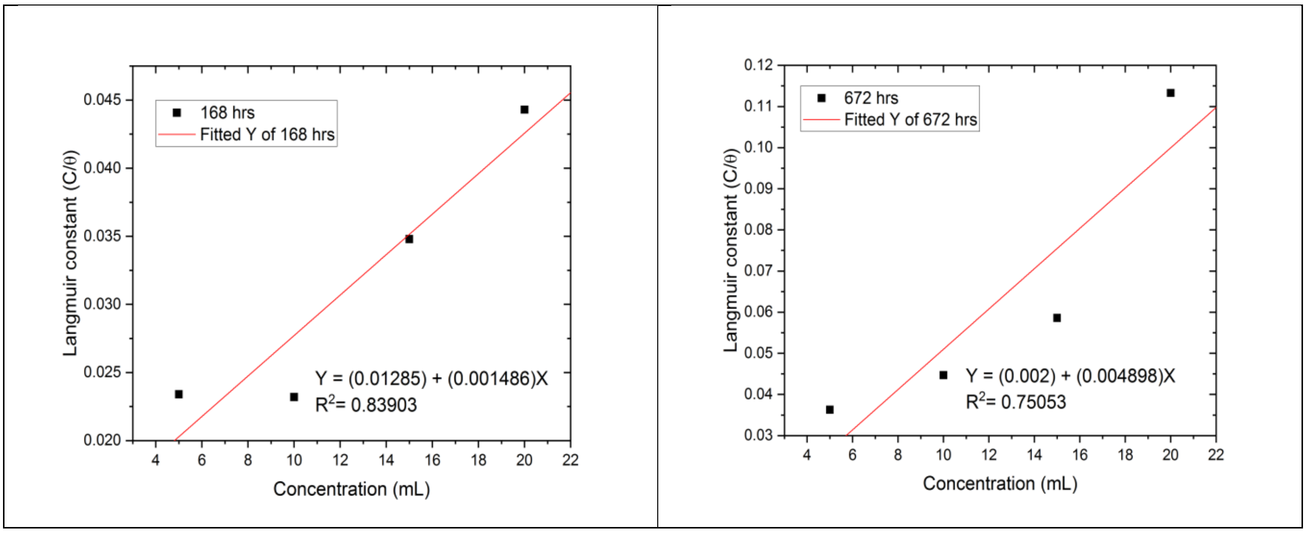

Fig 10: The Langmuir adsorption isotherms for *Cnidoscolus aconitifolius* in 1.0 M H_2SO_4 at 168 and 672 hours exposure times

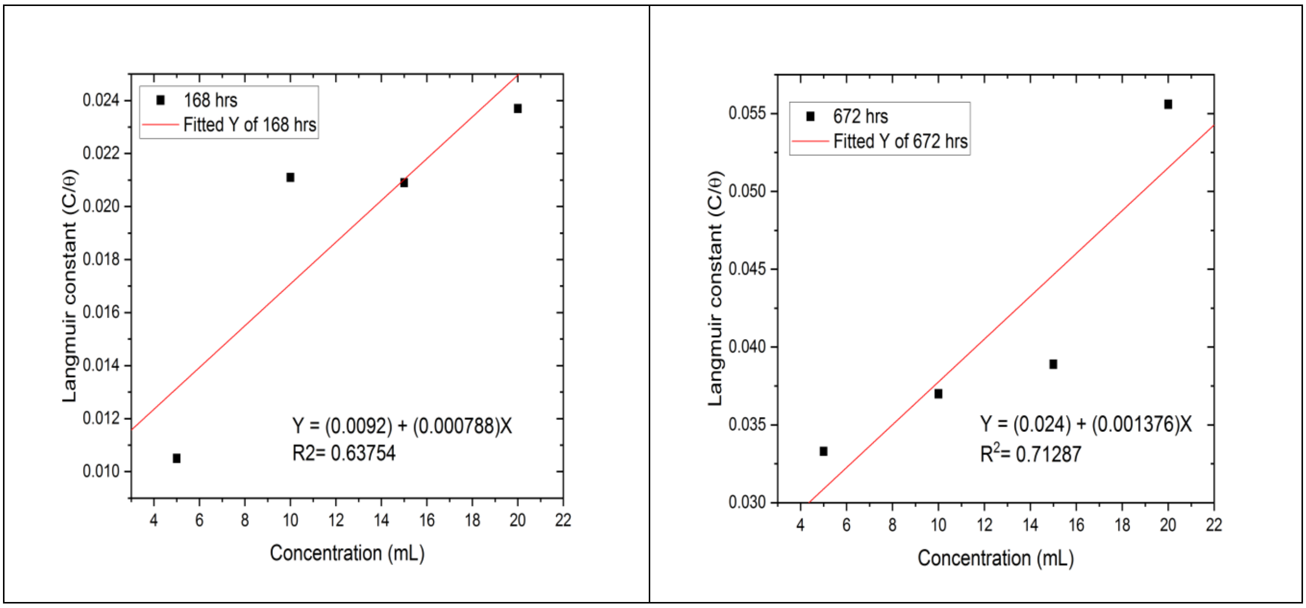

Fig 11: The Langmuir adsorption isotherms for *Cnidoscolus aconitifolius* in 0.5 M NaCl solution at 168 and 672 hours exposure times

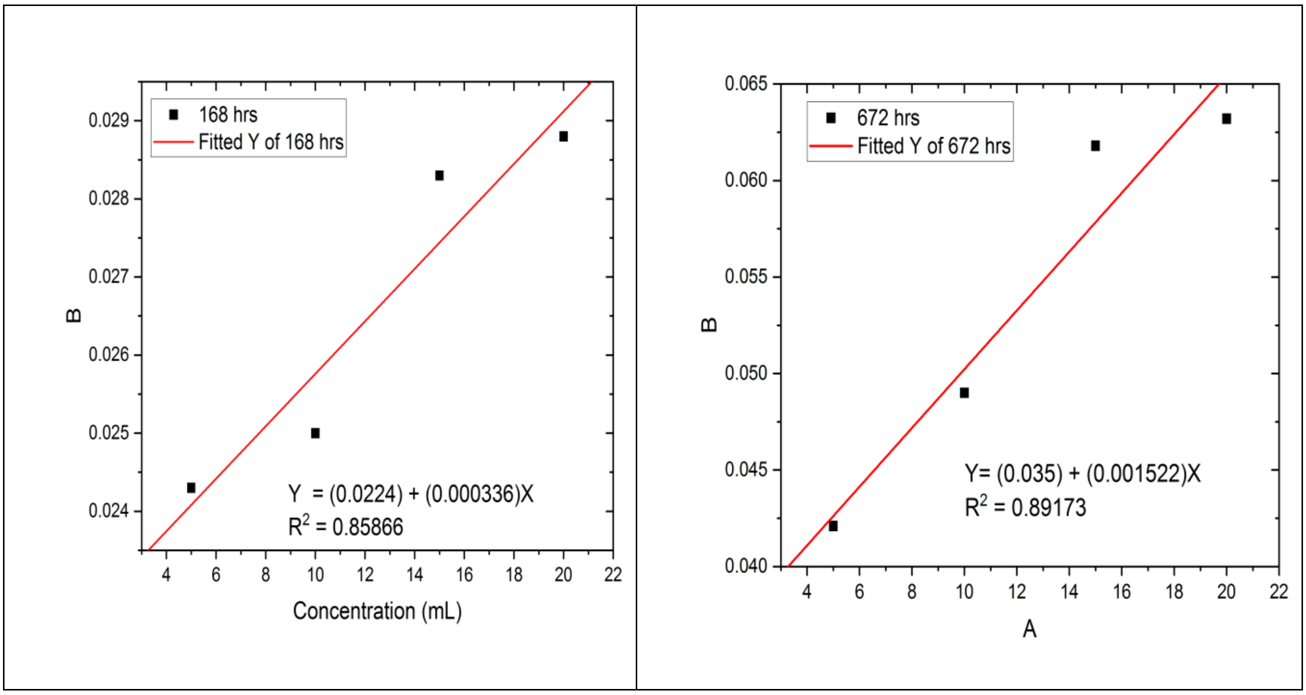

Fig 12: The Langmuir adsorption isotherms for *Cnidoscolus aconitifolius* in 1.0 M NaCl solution at 168 and 672 hours exposure times

DISCUSSION

Corrosion Penetration Rate

Figures 1–4 represent the corrosion penetration rate profiles for the extract of *Cnidoscolus aconotofolius* in the various corrosion media. It is quite evident that the curves obtained are parabolic in nature. The parabolic nature of these curves is a key characteristic observed in the corrosion processes for materials that undergo diffusion-controlled corrosion mechanisms like oxidation or high-temperature corrosion. In this instance, the former case obtains – oxidation (Fontana, 1986; Callister, 1997; Schweitzer, 2010). It is believed that in diffusion-controlled corrosion processes, the rate of corrosion is influenced by the diffusion of ions or atoms through protective films or scales formed on the metal's surface. This occurs when the metal reacts with the environment, generating a protective layer that, over time, can impede the diffusion of reactants to the metal surface (Askeland, 1985; Uhlig and Revie, 2008). This layer acts as a barrier between the metal and the corrosive elements, slowing down the corrosion process. As time progresses, defects or discontinuities in this protective layer permit the diffusion of corrosive agents to the metal surface (Roberge, 2008; Talbot and Eyre, 1997).

Previous works have established that the parabolic shape is due to the relationship between the thickness of the protective layer and the rate of diffusion of corrosive agents through the layer. Initially, as the protective layer forms, the rate of corrosion is relatively low, resulting in a slow and controlled metal loss. However, as defects develop in the protective film, the rate of diffusion of corrosive agents increases, leading to an accelerated metal loss, hence the curvature in the CPR curve (Sedriks, 1996; Papavinasam, 2013; Finšgar and Jackson, 2014).

Inhibition Efficiency

The plots of the inhibition efficiencies of the extract of *Cnidoscolus aconotofolius* in the various corrosion environments are depicted in Figures 5 – 8. A cursory look at the plots shows that there is an increasing linear relationship between the inhibition efficiency and concentration, which tends to increase over time. Inhibition efficiency is a crucial concept in corrosion studies, particularly when assessing the effectiveness of corrosion inhibitors. Usually, when a material is exposed to a corrosive environment, it undergoes degradation due to chemical or electrochemical reactions with its surroundings. Corrosion inhibitors are therefore substances designed to mitigate or prevent this degradation by either slowing down or entirely stopping the corrosion process (Ahmad, 2006; Fontana, 1986). The significance of inhibition efficiency lies it its ability to: assess inhibitor performance; optimize inhibitor concentration; select suitable inhibitors for specific applications; and assist in the economic considerations of the utilization of such inhibitors. Specifically, understanding inhibition efficiency assists in cost-effectively utilizing inhibitors as it helps in determining the most efficient concentration that balances effectiveness with economical use (Landolt 2007; Marcus and Mansfed, 2002). In general, inhibition efficiency studies contribute significantly to the development and application of corrosion inhibitors across various industries, including oil and gas, automotive, aerospace, and infrastructure, ultimately prolonging the lifespan of materials and reducing maintenance costs (Adhikari, 2013; Groysman, 2010; Schweitzer, 1996).

Therefore, a plot of inhibition efficiency, as in this case, helps determine the optimal concentration of the inhibitor, illustrating how effective the inhibitor is at various concentrations. It allows researchers to identify the point at which the inhibitor's efficiency plateaus or reaches its maximum effectiveness, thereby aiding in the selection of the most suitable concentration for practical applications. Here again, it can be seen that the 20ml extract concentration depicts the best relative to this study when viewed on the premise of exposure time. However, the increasing inhibition efficiency with increasing extract concentration as seen in this study suggests that the optimum concentration at which the inhibitor's effectiveness is at its maximum is yet to be reached (Schweitzer, 2013; Bradford, 2009; Schweitzer, 2007).

Langmuir Adsorption Isotherms

Figures 9 – 12 represent the Langmuir adsorption isotherms for the initial 168 hours exposure time and the terminal 672 hours exposure time of the inhibition behavior of the extract of *Cnidoscolus aconitifolius* in the various corrosion media.

The plots depict the relationship between the reciprocal of the Langmuir constant (K), 1/K with concentration (C). The reciprocal 1/K signifies the ratio of desorption to adsorption rates, providing insights into the reversibility of the adsorption process. A linear relationship, as in this case indicates that the adsorption follows the Langmuir model, showcasing a consistent equilibrium between adsorbed molecules and the available surface sites (Patiha *et al*., 2016; Alafnan *et al*., 2021). This simply interpreted means that there are no extraneous factors to distort the system's chemical equilibrium, such that the adhesion bonds holding the adsorbent molecules to the metal surface is very strong and do not allow the adsorbates to flake off. The gradients of the lines are generally steep, indicating that adsorption capacity or maximum adsorption at equilibrium for the adsorbate (mild steel) - adsorbent (*Cnidoscolus aconitifolius* extract) system is high and hence the probability of the protective film collapse is extremely low (Ayawei *et al*., 2017; Mustapha *et al*., 2019). The intercepts of the lines are seen to cut majorly along the *x – axis*, except for 0.5 M H_2SO_4 at 168 hours and 0.5 M NaCl at 168 hours. That the intercept is on the x-axis indicates a very high adsorption affinity, suggesting a strong interaction between the adsorbate and the adsorbent (Chang *et al*., 2019; Kalam *et al*., 2021). For the two cases where the intercept is on the y-axis, it only implies an initial weak adsorption, which progressively became stronger as the exposure time increased. Factors like surface heterogeneity (e.g. ribs, contours or other manufacturing defects) and the chemical conditions (e.g. the presence of grease and other extraneous impurities) of the metal surface can contribute to this behavior (Desta, 2013).

CONCLUSION

The inhibition potentialities of *Cnidoscolus aconitifolius* in both tetraoxosulphate (vi) acid and sodium chloride solution (brine) has been established. The inhibition efficiencies in each of the corrosion media are quite appreciable, reaching 72.56% in 1.0 M H_2SO_4 and 84.21% in 1.0 M NaCl solution. The Langmuir adsorption isotherm model was obeyed with the most fitted R^2 values of 0.83903 in 1.0 M H_2SO_4 at 168 hours exposure time and 0.89173 in 1.0 M NaCl solution at 672 hours exposure time; while the least fitted values of were observed for H_2SO_4 at 0.52552 in 0.5 M at 168 hours and for NaCl solution at 0.63754 at 168 hours respectively. On the whole, this study has proven that there are boundless possibilities of the utilization of *Cnidoscolus* *aconitifolius* as a veritable green corrosion inhibitor in the manufacturing sector, more specifically in oil and gas.

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