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Feasibility of *Azadirachta indica* as a Green Inhibitor for Corrosion: A Preliminary Study

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Abstract

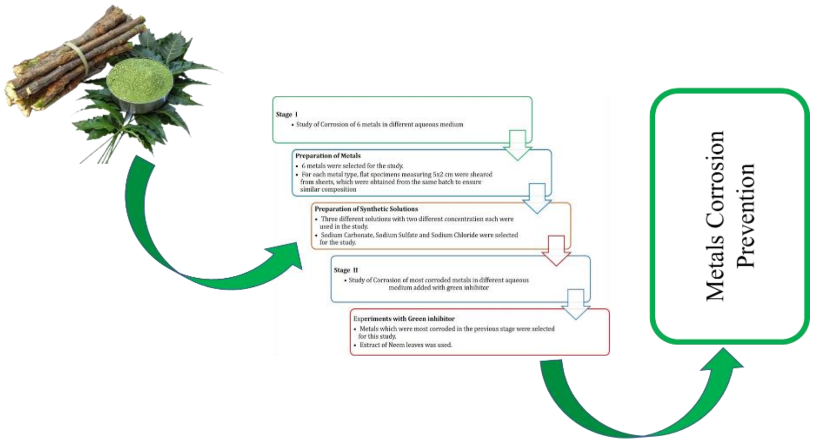
One of the principal problems faced by industries of all sorts of industries is corrosion. Several researchers have constantly been working and presenting solutions; though the methods were proved to be efficient in reducing corrosion, these are found to have adverse effects on humans. Owing to these reasons, there is an urgent need to search for green inhibitors. The present work investigates corrosion rates of six metals in different mediums like sodium chloride, sodium carbonate and sodium sulphate solutions with varying concentrations to determine the most hostile environment. Weight loss technique was adopted in which selected metal strips were immersed entirely in non-flowing media of the above-said solutions for a total exposure duration of 56 days. The most belligerent medium was observed to be 0.5M NaCl followed by 0.5M sodium sulphate, while sodium carbonate was the least with a concentration of 1.0M. In the second stage of the study, a green inhibitor (A.indica) was added to the mediums of the first stage to assess the corrosion inhibition property. The analytical measures adopted for this part of the study were gravimetric and spectrophotometric methods. Greater inhibitor efficacy attributed to the least rate of corrosion was presented at a concentration of 15ml by the inhibitor. Further, the inhibition was proportional to the increasing concentration of the inhibitor. The present study concludes that extract from neem leaves can act as an effective corrosion inhibitor.

Keywords: green inhibitor, neem leaves extract, sodium sulphate, sodium chloride, spectrophotometry.

Highlights of the study:

- Analysing three different media for corrosiveness, each at three different concentrations.
- Evaluating the inhibition potential of neem leaf extracts in three different corrosive media at three different concentrations.
- Evaluation of corrosion in terms of weight loss and corrosion products.

Graphical Abstract:



Stage I
- Study of Corrosion of 6 metals in different aqueous medium

Preparation of Metals
- 6 metals were selected for the study.
- For each metal type, flat specimens measuring 5x2 cm were sheared from sheets, which were obtained from the same batch to ensure similar composition

Preparation of Synthetic Solutions
- Three different solutions with two different concentration each were used in the study.
- Sodium Carbonate, Sodium Sulfate and Sodium Chloride were selected for the study.

Stage II
- Study of Corrosion of most corroded metals in different aqueous medium added with green inhibitor

Experiments with Green inhibitor
- Metals which were most corroded in the previous stage were selected for this study.
- Extract of Neem leaves was used.

Introduction

A natural phenomenon wherein alloys and metals effort to return to stable form by reacting with the surrounding environment. It is inevitable in almost all environments, getting aggravated in the water, oils, liquid chemicals, humidity and pollutants (Valdez-Salas et al., 2021). Inhibition of corrosion may be bought by organic and inorganic substances, which adsorb on the metals, isolating them from their surrounding media, thus reducing the process of oxidation-reduction. While organic inhibitors bring inhibition through adsorption on the metal surfaces forming a protective layer, inorganic inhibitors improve corrosion resistance by acting as anodic inhibitors. Corrosion inhibitors that have been most sought out and investigated are reported to be toxic, resulting in environmental severe hazardous limiting their use owing to environmental regulations. Hence, the search for inhibitors that are eco-friendly/green with exemplary efficiency is continuing to be an ageless area of research playing a critical role in preventing corrosion.

Natural/green inhibitors have particularly become an interest of researchers and have been studied and explored. Studies have reported that the aerial parts in precise and other plant parts can be used as corrosion inhibitors. Some of the plant parts that have been studied were leaves (Aribo et al., 2017; Benarioua et al., 2019; Joseph et al., 2017; Kasuga et al., 2017; Khadom et al., 2018; Mahmudzadeh et al., 2019; Nathiya et al., 2017; Pradipta et al., 2019; Verma et al, 2018), seeds (Patni et al., 2013; Singh et al., 2016), fruits (Patni et al., 2013; Singh et al., 2016; Singh et al., 2019), juice/extracts, pulp of fruits (Abdallah et al., 2021), plant gums (Abdallah, 2004; Peter et al., 2015), entire plant (Sulay et al., 2015; Ameh, 2015; Bammou et al., 2014; Dehghani et al., 2019; Guo et al., 2017; Khiya et al., 2019; Shalabi et al., 2019), seed husk (Aiad et al., 2018; Alaneme et al., 2016), grasses (Ataei et al., 2019), essential oil from seed (Gualdrón et al., 2013; Baran et al., 2019), flowers (Dehghani et al., 2019; Alibakhshi et al., 2019) roots (Wang et al., 2019; Nwanonenyi et al., 2017), grains (Saeed et al., 2019), fruit peels (Fernandes et al., 2019), bark (Hussin et al., 2016; Umoren et al., 2016; Haddadi et al., 2019), fruit and seed outer shell (Sanni et al., 2019; Farag et al., 2018), along with the organic waste from agriculture (McNeill et al., 2001).

Advantages of green inhibitors include their ongoing availability, enhancing metal life span, enhancing corrosion resistance by forming a protected blockade on the surface of the metal, providing more excellent corrosion resistance owing to their inherent photochemical properties, economic, possess great chemical bonding with the metal and above all does not affect the environment. In line with the above discussion, the present study has been taken up to appraise the efficacy of neem leaf extracts' potential as green inhibitors under three different aqueous mediums.

Methodology :

In Table 1 are listed some of the methods applied in the present corrosion studies.

Corrosion process rate	**Corrosive attack type and characterization of corrosion products**	**Nature of corrosion products**
Gravimetrical methods	Macroscopic method: - visual examination	Spectroscopic method (UV-Visible).

Table 1: The study has been designed and executed in two stages.

Stage – 1

Six metals were selected for the present study: Iron Steel, Copper, Brass, Aluminium,

The immersion method was adopted towards studying the rate of corrosion of these metals (table 1) by immersing in three different solutions taken in 2 different concentrations: NaCl, Na_2CO_3 and Na_2SO_4 with concentrations of 0.5M and 1.0M each (Figure – 1) (Table 2).

Metals are coded about the solutions they are immersed in: Six metals were coded as samples 1 to 6, i.e. S1 to S6.

S1	Iron	S4	Aluminium
S2	Stainless steel	S5	Brass
S3	Copper	S6	Zinc

Table 2: 0.5M Solution labelled as A and 1.0M Solution marked as B. The coding of the samples is listed down as follows:

S1ACl	Iron immersed in 0.5M NaCl solution		S2ACl	Stainless Steel immersed in 0.5M NaCl solution
S1BCl	Iron immersed in 1.0M NaCl solution		S2BCl	Stainless Steel immersed in 1.0M NaCl solution
S1ACO$_3$	Iron immersed in 0.5M Na_2CO_3 solution		S2ACO$_3$	Stainless Steel immersed in 0.5M Na_2CO_3 solution
S1BCO$_3$	Iron immersed in 1.0M Na_2CO_3 solution		S2BCO$_3$	Stainless Steel immersed in 1.0M Na_2CO_3 solution
S1ASO$_4$	Iron immersed in 0.5M Na_2SO_4 solution		S2ASO$_4$	Stainless Steel immersed in 0.5M Na_2SO_4 solution
S1BSO$_4$	Iron immersed in 1.0M Na_2SO_4 solution		S2BSO$_4$	Stainless Steel immersed in 1.0M Na_2SO_4 solution

S3ACl	Iron immersed in 0.5M NaCl solution		S4ACl	Stainless Steel immersed in 0.5M NaCl solution
S3BCl	Iron immersed in 1.0M NaCl solution		S4BCl	Stainless Steel immersed in 1.0M NaCl solution
S3ACO$_3$	Iron immersed in 0.5M Na_2CO_3 solution		S4ACO$_3$	Stainless Steel immersed in 0.5M Na_2CO_3 solution
S3BCO$_3$	Iron immersed in 1.0M Na_2CO_3 solution		S4BCO$_3$	Stainless Steel immersed in 1.0M Na_2CO_3 solution
S3ASO$_4$	Iron immersed in 0.5M Na_2SO_4 solution		S4ASO$_4$	Stainless Steel immersed in 0.5M Na_2SO_4 solution
S3BSO$_4$	Iron immersed in 1.0M Na_2SO_4 solution		S4BSO$_4$	Stainless Steel immersed in 1.0M Na_2SO_4 solution

S5ACl	Iron immersed in 0.5M NaCl solution		S6ACl	Stainless Steel immersed in 0.5M NaCl solution
S5BCl	Iron immersed in 1.0M NaCl		S6BCl	Stainless Steel immersed in

	solution			1.0M NaCl solution
$S5ACO_3$	Iron immersed in 0.5M Na_2CO_3 solution		$S6ACO_3$	Stainless Steel immersed in 0.5M Na_2CO_3 solution
$S5BCO_3$	Iron immersed in 1.0M Na_2CO_3 solution		$S6BCO_3$	Stainless Steel immersed in 1.0M Na_2CO_3 solution
$S5ASO_4$	Iron immersed in 0.5M Na_2SO_4 solution		$S6ASO_4$	Stainless Steel immersed in 0.5M Na_2SO_4 solution
$S5BSO_4$	Iron immersed in 1.0M Na_2SO_4 solution		$S6BSO_4$	Stainless Steel immersed in 1.0M Na_2SO_4 solution

Immersion Tests:

Corrosiveness was tested through the immersion method (static). Only one specimen was immersed in each beaker containing 75mL of the test solution. All metal samples were weighed for initial weights before immersion into the solutions for investigating the rate of corrosion. At regular intervals, immersed metal strips were cleansed manually using a brush to remove corrosion deposits from the metal surface, washed and dried. The equivalent changes in the weights were recorded. The weight loss was recorded every seven days for up to 56 days. An average value of three samples was recorded. At regular intervals, for every seven days, the working solutions were analyzed for the presence of corrosion products in the form of ferrous ion, copper ion and zinc, respectively, using the spectrophotometer method.[45]

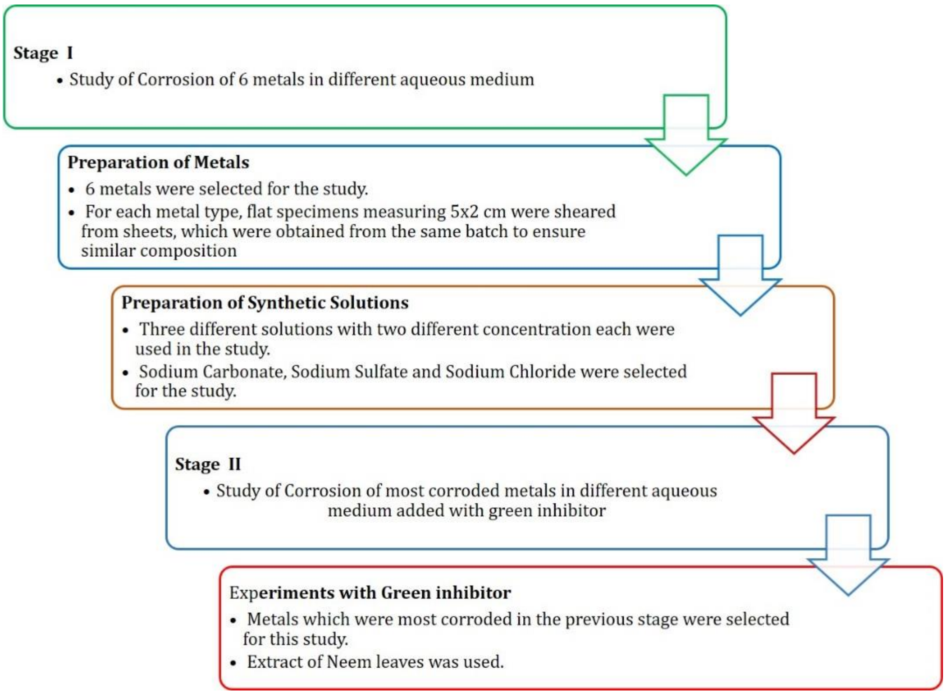


Figure 1: Flow chart of the methodology adopted.

Stage – II

Most corroded metals from stage 1 (Iron, Zinc, Copper and Brass) were selected for stage 2. A green inhibitor was added to 1.0M test solutions to understand the corrosion rates of metals and the inhibitory action of the green inhibitor. The green inhibitor selected for the study was extracted from Neem leaves.

1.1 Extraction of Inhibitor

Leaves from neem trees aged above ten years collected from the campus of GITAM (Deemed to be University) are cleaned and shade dried before storing for later use. Dried neem leaves were ground to powder form and boiled with double distilled water to extract different concentrations 5, 10 and 15%. Immersion studies were carried out similarly as in stage 1 except for only 1M solutions of NaCl, Na_2CO_3 and Na_2SO_4. The inhibitor was added in concentrations of 5ml, 10ml and 15ml, respectively. Weight loss determination and spectrophotometric determinations were carried out as said in stage – 1.

Results :

Weight Loss Studies

Sodium Chloride medium

The highest weight reduction was reported in 0.05M NaCl solution by Zinc on the 42nd day (3.02%), followed by Copper on the 56th day by 1.82%. On the contrary, the metals with the slightest reduction in weight were Steel and Brass with 0.14 and 0.23%, respectively. Copper recorded the highest weight reduction in 1.0M NaCl on the 56th day (1.79%), followed by Copper on the same day (1.36%), and the metals with the minor reduction in weight on the 56th day were Steel and Brass with 0.07 and 0.22% respectively (Figure 2).

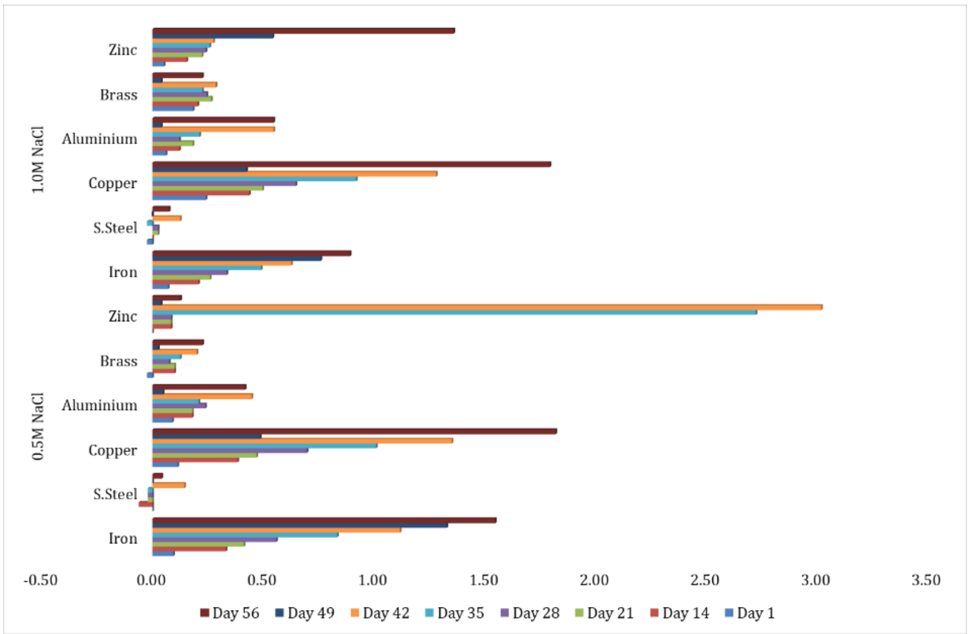


Figure 2: Weight Reduction (%) of Metals in two Concentrations of Sodium Chloride Solution.

Sodium sulphate medium :

Iron noted maximum weight reduction in 0.05M Na2SO4 on 56th day (1.02%) followed by Zinc on 56th day (0.38%). On the other hand, metals with fewer weight reductions were Copper and Steel with 0.00 and 0.02%, respectively. In the 1.0M solution, the maximum reduction in weight was seen by Iron on the 56th day (0.79%) followed by Zinc on the 56th day (0.51%), while metals with no reduction in weight were Copper and Steel (Figure 3).

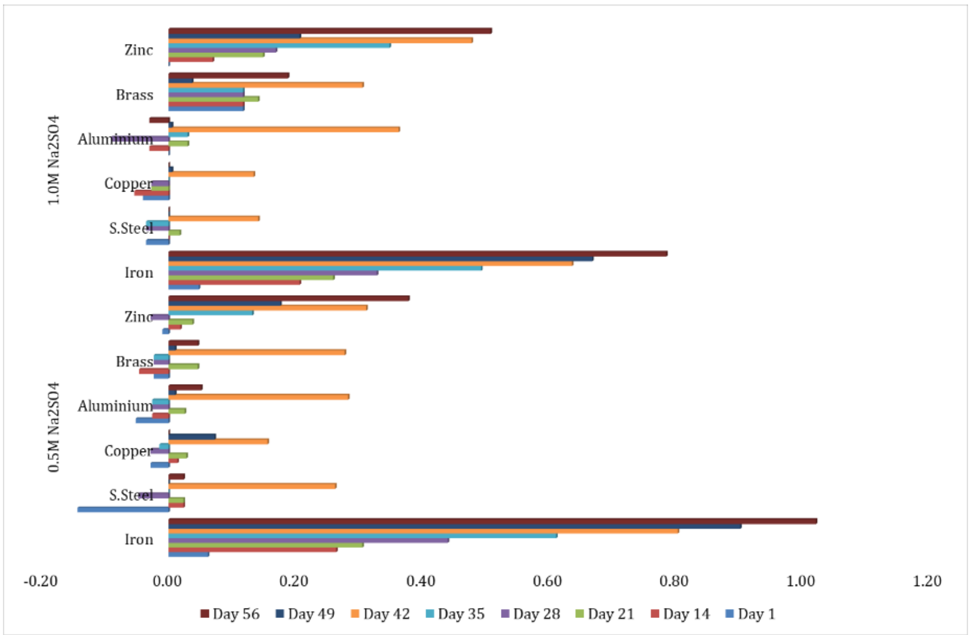


Figure 3: Weight Reduction (%) of Metals in two Concentrations of Sodium Sulphate Solution

Sodium carbonate medium

Aluminium showed the most significant weight loss by 7.49%, followed by Brass with 2.84% showing supreme weight reduction on the 56th day. Conversely, metals with minimum reduction are Iron and Steel with -0.02 and 0.04%, respectively. Similarly, for 1.0M Na_2CO_3 highest weight reduction was seen in Aluminium by 4.81% on the 56th day compared to others (Figure 4).

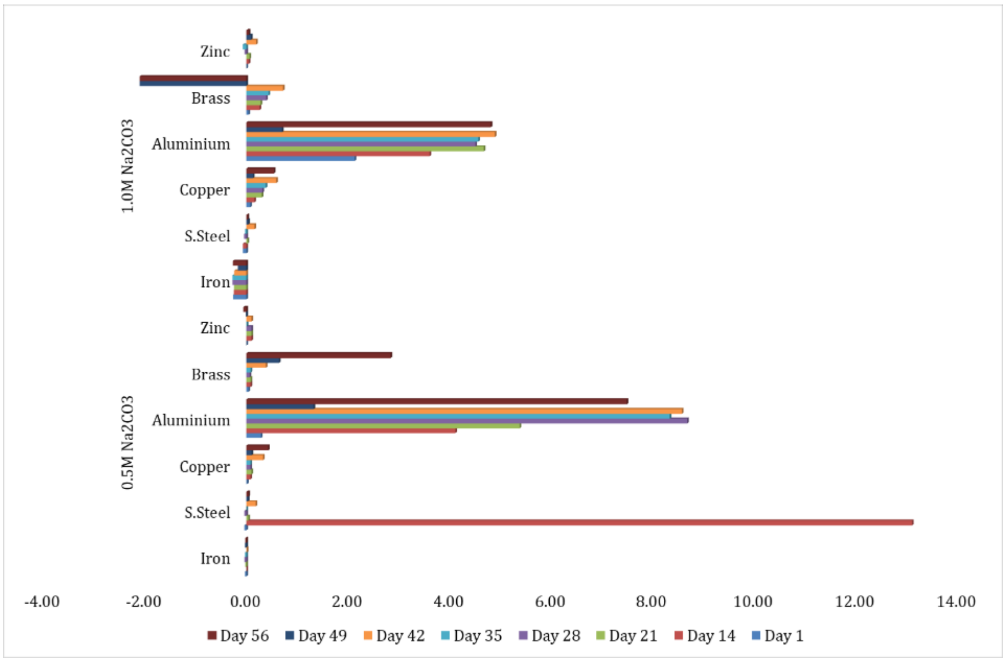


Figure 4: Weight Reduction (%) of Metals in two Concentrations of Sodium Carbonate Solution

Comparative Account of Weight Reduction of Metals in test solutions with different concentrations of green inhibitor

Sodium chloride solution :

It is observed that Iron (0.408 over 0.76%) and Copper (0.340 over 0.42) have undergone lower weight reduction with the addition of inhibitor at 15ml concentration of the inhibitor. At the same time, the weight reduction by Brass (0.199 over 0.04) and Zinc (0.625 over 0.54) was more excellent with inhibitor. Still, it showed a trend of lesser weight reduction with increasing inhibitor concentration (Figure 5).

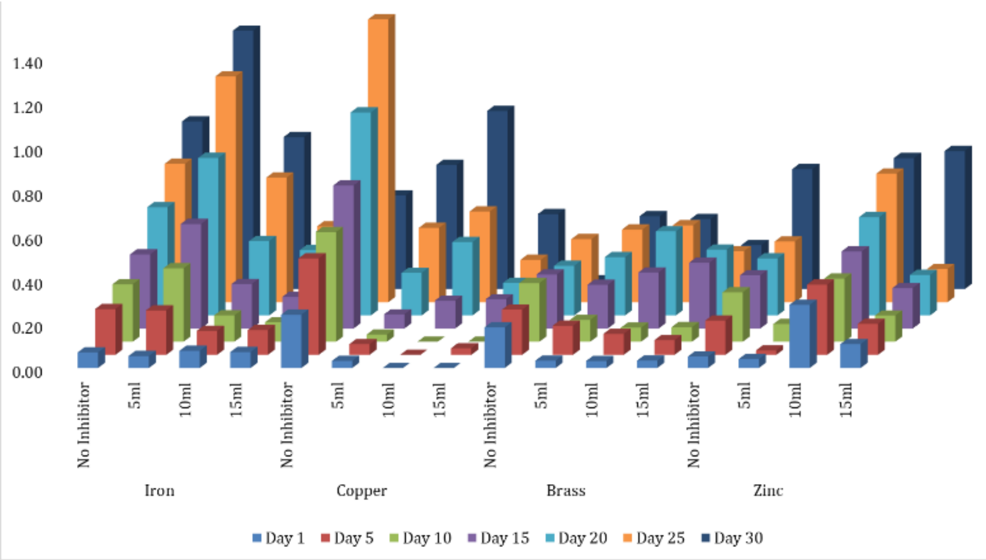


Figure 5: Comparison of Weight Reduction of metals with and without inhibitor in Sodium Chloride Solution

Sodium sulphate solution :

It is observed that Iron (0.57 over 0.67), Copper (0.01 over 0.01), and Zinc (0.168 over 0.21) have undergone lower weight reduction with the addition of inhibitor at 15ml concentration of the inhibitor. In contrast, the weight reduction by Brass (0.061 over 0.04) was more significant with inhibitor but showed a trend of lesser weight reduction with increasing concentration of the inhibitor (Figure 6).

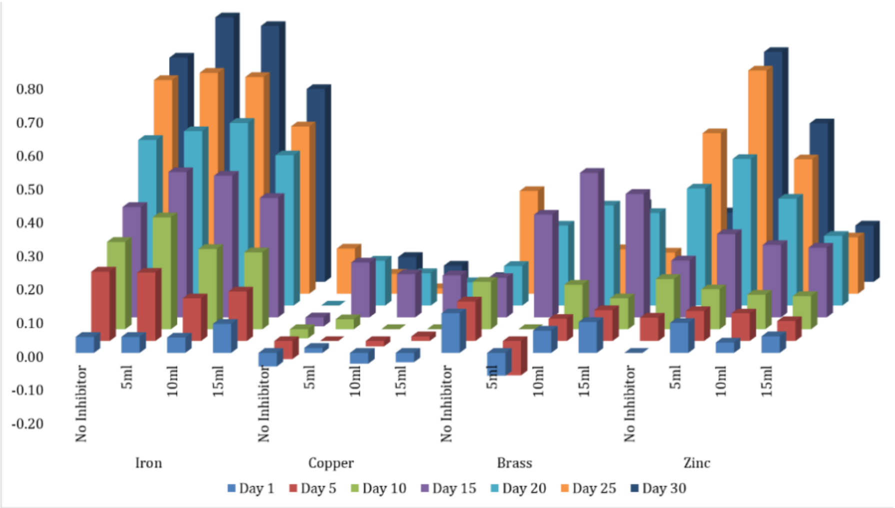


Figure 6: Comparison of Weight Reduction of metals with and without inhibitor in Sodium Sulphate Solution

Sodium carbonate solution :

Figure 7 depicts a comparative account of weight reduction by metals with and without inhibitors in sodium carbonate solution. It is observed except for Zinc (0.061 over 0.09), all three metals have undergone higher weight reduction with the addition of inhibitor (Figure – 7).

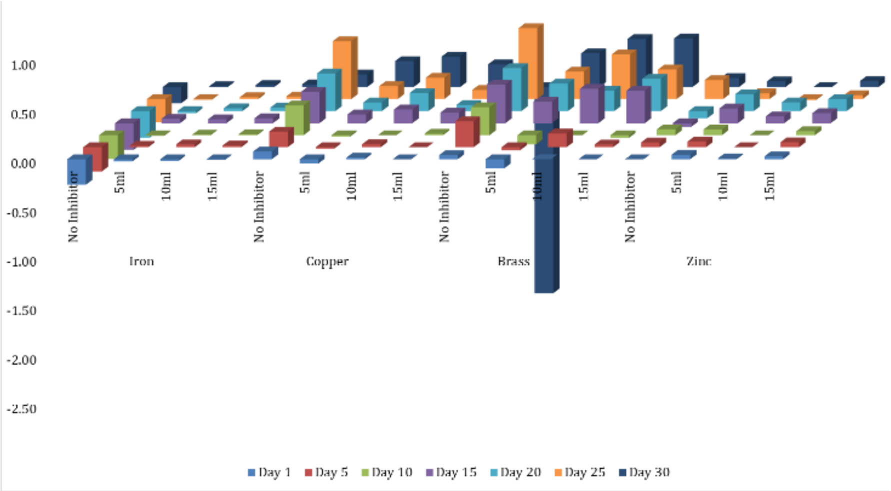


Figure 7: Comparison of Weight Reduction of metals with and without inhibitor in Sodium Carbonate Solution

Spectrophotometric results ;

Sodium chloride solution

It is observed that Iron (0.029 over -0.091) and Zinc (0.04 0ver -0.017) have recorded more concentration of corrosion products with inhibitor than without inhibitor. In contrast, the concentration of corrosion products by Copper (0.668 over 1.08) and Brass (0.631 over 0.667) was lesser with the addition of inhibitor (Figure – 8).

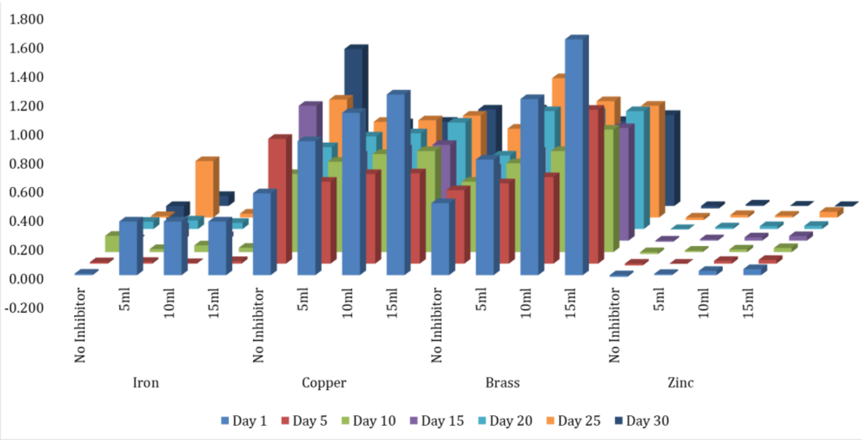


Figure 8: Comparison of corrosion products of metals with and without inhibitor in Sodium Chloride Solution

Sodium sulphate solution :

It is observed that Iron (0.056 over -0.045), Copper (0.59 0ver 0.46), and Zinc (0.024 over -0.02) have recorded more concentration of corrosion products with inhibitor than without inhibitor. In contrast, Brass's concentration of corrosion products (0.609 over 0.66) was lesser with the addition of inhibitor (Figure 9).

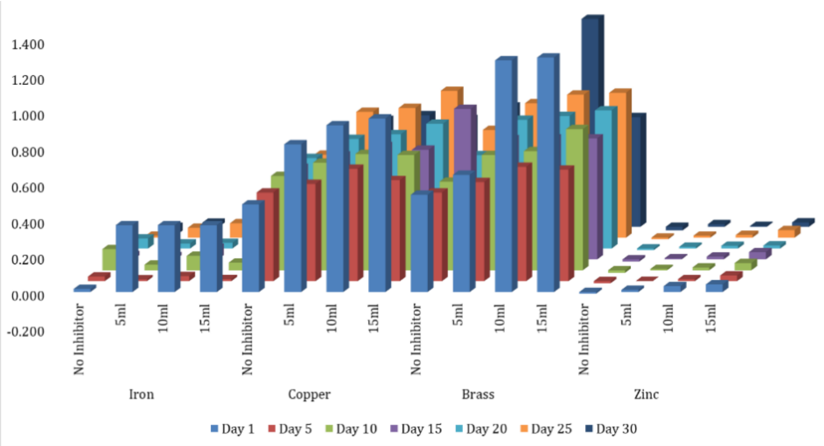


Figure 9: Comparison of corrosion products of metals with and without inhibitor in Sodium Sulphate Solution

Sodium carbonate solution :

It is observed that Iron (0.023 over -0.045) and Zinc (0.051 0ver -0.02) have recorded more concentration of corrosion products with inhibitor than without inhibitor. Whereas the concentration of corrosion products by Copper (0.636 over 0.80) and Brass (0.721 over 1.05) was lesser with the addition of inhibitor (Figure 10).

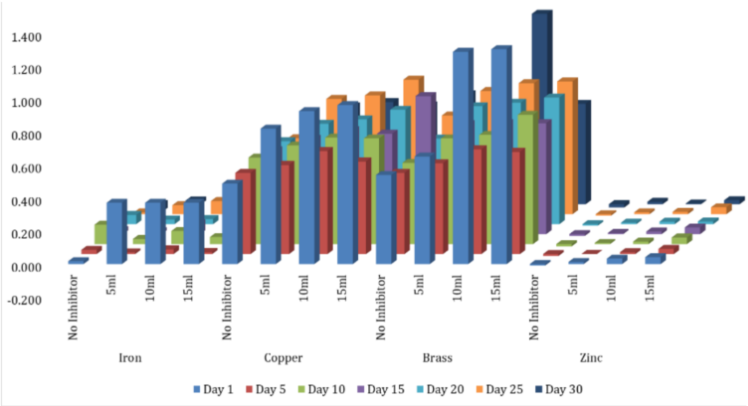


Figure 10: Comparison of corrosion products of metals with and without inhibitor in Sodium Carbonate Solution

Discussion :

Corrosion studies are needed towards reducing the difficulties of maintaining appropriate and adequate surfaces of the metal. The fact that the metals are open to the atmosphere enhances the probability and magnitude of corrosion, which demands that the studies be intensified towards searching and exploring new methods and barriers to protect metals (Valentini et al., 1985).

Stage – I

The analysis of result shows that on the whole, the metal strip immersed in distilled water had the highest corrosion rate while in terms of salt solutions; 0.5M of NaCl had the highest corrosion rate followed closely by 0.5M of Na_2SO_4 solution while the least was 0.5M solution of Na_2CO_3. Trends of corrosion rates in test solutions are attributed to the fact that the metal strips did not have any protective coating, which might have enhanced corrosion rates. 0.5M and 1.0M concentrations of NaCl solution were the first and second most corrosive media, respectively. In general, the metal corrosion rate is associated with electrons flow encompassing two reactions oxidation and reduction happening at cathodic and anodic sites of the metal surface. The availability of anodic and cathodic areas on the metal is governed by factors like microstructure, stress and segregation.

Further, it is also deduced that the higher the concentration of salts in test solutions more excellent the magnitude of corrosion (Ikechukwu et al., 2014). Sodium chloride attacks the passive protective layer and reduces oxygen concentration in the solution, leading to aggravated corrosion rates. It has been reported that an increase of 25% sulfate ion concentration resulted in 200% enhanced corrosion (Karim et al., 2010). Moreover, aerated water systems are the most common mediums improving Iron and its alloys (Barton et al., 1973).

According to Arzola-Peralta et al., 2003 corrosion mechanism attacks immersed in sulphate solutions start at lonely locations spreading laterally. The ability of sulphate ions to form soluble complexes with ferrous and ferric ions in mildly alkaline solutions. Sulphate ions tend to accelerate the active dissolution of Iron and the formed films due to the supersaturated nature of solutions containing iron salts arising probably from iron hydroxy sulfate, dissolving Iron at a high rate permitting precipitation of a non-protective film (Hasan et al., 2013). The corrosion rate of Copper in chloride dominating environments has been studied by several researchers and reported to be approximately one µmy−1 in marine environments, which is initially high and declines over time due to the build-up of the protective layer from corrosion products (Graedel et al., 2001).

Copper's corrosion products' mechanism and evolution start with the formation of cuprite (Cu_2O) that continues to grow, leading to the formation of nantokite (CuCl). The process ceases and ends with paratacamite ($Cu_2Cl(OH)_3$), which is the end product of corrosion (Krätschmer et al., 2002; Lopesino et al., 2018; Wallinder et al., 2014). Copper corrosion products in chloride dominated environments include Cu_2O, $Cu_2Cl\ (OH)_3$ and brochantite ($Cu_4SO_4(OH)_6$), while on zinc, these include zincite (ZnO), and simonkolleite ($Zn_5Cl_2(OH)_8{\cdot}H_2O$) and hydrozincite ($Zn_5(CO_3)_2(OH)_6$) (Lee et al., 1995). Resistance of Aluminium to corrosion under aqueous conditions is credited to the rapid development of strongly adherent, compact and continuous oxide film (Hamza et al., 2020; Abiola et al., 2009).

Stage – II

Green inhibitors extracted from plant sources are viewed as extremely rich in natural chemical substances that can be removed using humble procedures economically (Abdel-Gaber et al., 2008; Umoren et al., 2009; Nik et al., 2011). The principal phenomenon of corrosion inhibition in alkaline liquids is adsorption onto the metal surface. Corrosion inhibitor molecules contain heterocyclic compounds with polar functional groups and conjugated double bonds with various aromatic systems. The corrosion inhibition exhibited by neem leaves extract was very promising and is in line with the previous studies. Neem leaves have demonstrated moral inhibition in lower pH solutions (Nahlé et al., 2010; Obiukwu et al., 2013; Loto et al., 2011; Desai, 2015). Neem leaves extract proved to inhibit corrosion in zinc metal through a synergistic effect governed by the concentration of the inhibitor and temperature (Sharma et al., 2009). Abro et al., 2021 reported the potential of inhibition by neem leaves to extract due to the phenolic compounds that form a protective layer on the metal surface.

Factors governing the efficiency of corrosion inhibition by organic compounds include types and number of adsorbing groups, molecular size and structure, and interaction with the metal's surface. Further, the inhibition is bought about by the phenomenon of either physisorption or chemisorption on the metal surface. The physisorbed molecules cease corrosion through shifting of cathodic reaction on zones they attach. On the other hand, chemisorbed molecules attach at anodic zones retarding the reactivity of these zones. Apart from possessing about 100 protolimonoids, tetranortriterpenoids, exanortriterpenoids, neem leaf extract has tannins that contain polyphenolic moieties that can form tannate salts reacting with ferric ions.

These ferric tannate salts, which are highly cross-linked networks, protect the surface of the metal. More significant corrosion inhibition of neem leaves extracts is credited to the presence of tannins, triterpenes and several additional organic compounds (Vaidya et al., 2021; Feng et al., 2021). Furthermore, organic mixtures containing nitrogen, phosphorus, and oxygen possess polar functions enabling them to adsorb on the metal surface as an organic barrier layer. The dipole moment of organic molecules might form electrostatic interactions with the metal surface, leading to solid adsorption on a metal surface.

Conclusion :

Metal corrosion in three different media was tested in the first level of the study, followed by adding green inhibitor (neem leaves extract) to these media to evaluate the corrosion inhibition potential of the green inhibitor. In the first level of the study, the corrosion rate is found to be dependent on the concentration of the corroding media, which was directly proportional. 0.5M NaCl solution resulted in the highest corrosive tendency, followed by 0.5M Na_2SO_4, and the least was 0.5M Na_2CO_3. Among several efforts been made to prevent corrosion, green inhibitors are the most sought out, focussed and growing in practice. The advantages of natural or green inhibitors have been widely attributed to being acceptable environmentally, available readily, and renewable.

In the present study, Azardirachta indica (Neem) leaves extract has the potential to inhibit corrosion of metals in most test solutions, which increased with increasing extract concentration. With the highest concentration of 15ml, the inhibition efficiency was enhanced. The principal mechanism of corrosion inhibition was understood to be the physicochemical adsorption on the surface of the metal, resulting in the formation of a protective barrier. The results obtained are promising. Nevertheless, precise understanding of the corrosion inhibition mechanism, large-scale applicability, and materialized ways and means of commercializing the inhibitor.

Conflict of interest:

The authors declare no conflict of interest.

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