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Frabication of an eco-friendly corrosion inhibitor from Terminalia catappa leaf concrete reinforcement in seawater

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Abstract— *Metal corrosion is one of the most challenging problems facing industries. Using corrosion inhibitors is one reasonable approach to protecting metal surfaces. Due to the toxicity of industrial corrosion inhibitors, researchers are continuously searching for green, economical, and friendly alternatives. The present study focuses on the application of Terminalia catappa leaf extract to mitigate the corrosion of concrete reinforcing steel in a simulated seawater environment. The dry product from the Terminalia catappa leaf extraction process was determined to have amino functional groups in polyphenols. Polarization results demonstrate that the corrosion current density decreases from 8.87 A/cm^2 (for samples soaked in blank solution) to 5.12 µA/cm^2 when adding the optimal concentration of 0.004% of Terminalia catappa leaf extract. 3.5% NaCl solution. Electrochemical impedance spectroscopy (EIS) analysis showed that the inhibition efficiency reached over 90% at this concentration after 24 hours of soaking.*

Keywords— ***extraction, Terminalia catappa, corrosion inhibitor, concrete reinforcement, seawater.***

I. INTRODUCTION

The marine and coastal atmospheres often contain high concentrations of aggressive substances and changes in wet and dry conditions due to rain and monsoons. The influence of the marine and coastal atmospheres on metallic materials is mainly shown through the aggressive nature of chloride ions in the air and the specific conditions of the coastal climate of each region. The steel corrosion rate in seawater increased significantly with temperature and aeration; the rate decreased with increased carbon content and with a change from dry blasting to wet blasting. Field tests in tropical seawater were carried out at 2 and 12 m depths. No significant difference in corrosion rate was found at these two depths. Average corrosion rates of 0.53 and 0.35 mm/year were measured for exposure periods of 2 and 12 months, respectively.[1-7]

Reinforced concrete was invented and applied in the mid-19th century. However, it was only in the late 19th and early 20th centuries that it was used to construct marine structures. Reinforced concrete structures can work sustainably in a non-aggressive environment for over 100 years. Meanwhile, in aggressive coastal environments, steel reinforcement and concrete corrosion lead to cracking and destruction of concrete and reinforced concrete structures, which can appear after 10 to 30 years of use. The durability of reinforced concrete structures depends on environmental aggression and the quality of the materials used.[2, 8-11]

Currently, many measures have been researched and applied to minimize the effects of metal corrosion. Among the anti-corrosion measures, environmentally friendly corrosion inhibitors are among the most influential and economical methods. Limiting the corrosion process can be achieved by increasing anodic or cathodic polarization, reducing the movement or diffusion of ions onto the metal surface, increasing the resistance of the metal surface, etc. According to theory, the organic inhibitors used need to be well adsorbed on the metal surface for good inhibition. Typically, aromatic compounds containing heteroelements such as O, N, S, and P will interest research because these heteroelements are electron-rich elements and are readily adsorbed on metal surfaces. Through the process of creating electron-accepting bonds with metal atoms. In addition to heteroatoms, the aromatic ring is an essential factor that enhances the adsorption process. The pi-electron system will increase the electrostatic interaction between the inhibitors and the metal surface.[10, 12-16] In this paper, the extraction of *Terminalia catappa* leaf and the corrosion inhibition effect of concrete reinforcement in seawater were studied.

II. EXPERIMENTS

Chemicals

Macklin Company (China) provided the gallic acid (98.5%) and Folin-Ciocalteu's phenol reagent (2N). Xilong Company (China) provided the ethanol (96%), sodium chloride (99.5%), and sodium carbonate (99.5%).

Preparation of Terminalia catappa leaf extract

Leaves of *Terminalia catappa* are harvested in the morning. After being cleaned, the leaves were dried till the mass didn't alter. Ultimately, a fine powder is made from the dried leaves. Using ultrasonic diffusion, the dried *Terminalia catappa* was mixed with ethanol at a 5 g/100 ml ratio for 60 minutes. For two hours, the polyphenols were extracted at 60 ^oC. Via vacuum filtration, the *Terminalia catappa* extract was gathered.

Using gallic acid as the standard reagent, the Folin-Ciocalteu technique was used to determine the polyphenol concentration17-20. The solution was then tested at a wavelength of 713 nm using UV-vis spectroscopy. The following formula can be used to calculate the extract's polyphenol content:

C = 25.302 * Abs - 0.3903 (R^2 = 0,9916)

The infrared spectrum of polyphenols extracted from *Terminalia catappa* leaf in the range of 4000–400 cm^{-1} demonstrates the presence of characteristic functional groups.

Weight loss method

Prepare eight small CB300 steel samples with a cross-section of 1 cm^2 and a thickness of about 5-8 mm, then grind the surfaces and calculate the total area of the samples. Prepare samples soaked in 100 ml of mixture with different extract ratios of 0%, 0.002%, 0.004%, 0.006%, 0.008%, and 0.01% with 3.5% NaCl. Mark and soak CB300 steel samples in different concentrations. Measure the amount of corrosion every day. Calculate the corrosion rate according to the following formula:

$$\rho = \frac{m_0 - m_t}{S \times t} = \frac{\Delta m}{S \times t}$$

In there:

- ρ: corrosion rate;
- m_0: weight of the metal sample before testing (g) or (mg);
- m: weight of the metal sample after the experiment (g) or (mg);
- S: metal surface area (cm^2);
- t: time (hour) or (day, night) or year.

Polarization curve method

The CB300 steel electrode sample had its surface smoothed and then soaked in a 3.5% NaCl solution with a ratio of 0.002% to 0.04% almond leaf extract for 30 minutes before measurement to create a surface coating. All electrochemical measurements were performed on an Autolab PGSTAT12/30/302 at room temperature in a three-electrode system consisting of a reference electrode (RE) of Ag/AgCl, an auxiliary electrode (CE) of Pt metal plate, and a CB300 steel electrode sample prepared as the working electrode (WE) as shown in Figure 1.[21-24]

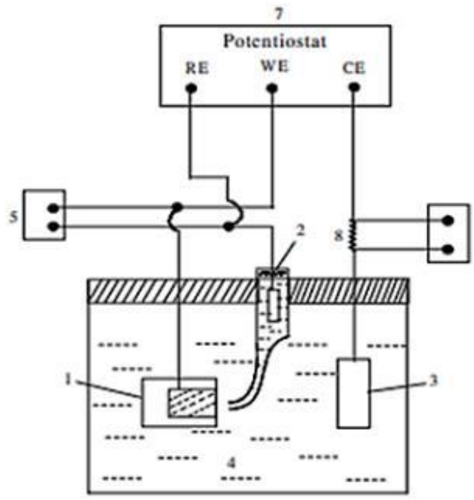

Fig. 1: Diagram of the electrochemical measurement method.

1. Working electrode (WE); 2. Reference electrode (RE) - Ag/AgCl electrode; 3. Auxiliary electrode (CE) made of Pt; 4. Electrolyte solution (3.5% NaCl solution); 5, 6. Carmilivol; 7. Potentionstat; 8. The sample resistance has a known value

Electrochemical impedance spectroscopy method

The steel electrode sample has a smooth surface. Electrochemical impedance spectroscopy (EIS) analysis was performed at OCP in the frequency range of 100 kHz ÷ 0.1 Hz. The EIS spectra were fitted using Nova 2.1.5

software. Before measuring the total resistance, the electrode surface was coated with a varnish solution and soaked in a mixture of 3.5% + 0.002% to 0.01% NaCl solution. Experiments were repeated three times for each extract concentration. All impedance measurements were performed on an Autolab PGSTAT12/30/302 at room temperature in a three-electrode system consisting of an Ag/AgCl reference (RE) electrode, a Pt auxiliary (CE) electrode, and a steel reinforcement sample as the working electrode (WE). The standard circuit model is shown in Figure 2.[25-28]

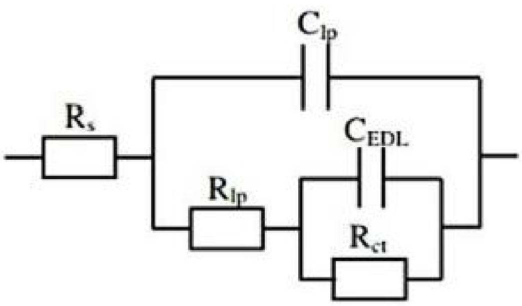

Fig. 2: The equivalent circuit is used to fit the EIS spectrum.

III. RESULTS AND DISCUSSION

Characterization of Terminalia catappa leaf extract

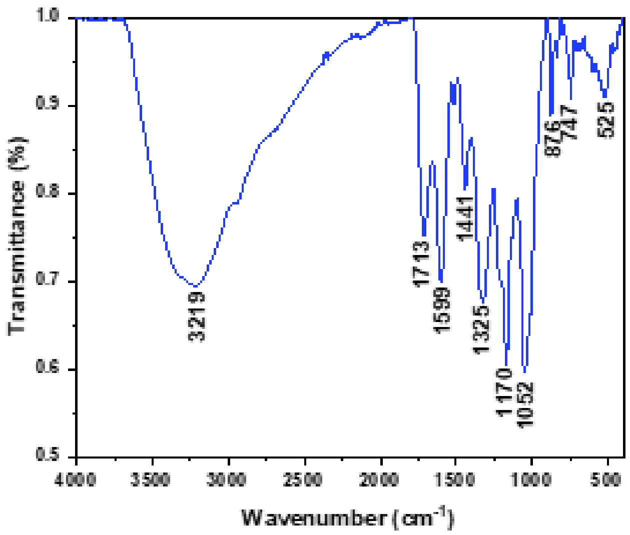

Fig. 3: FTIR spectroscopy of dried extract of Terminalia catappa leaf.

Figure 3 displays the FTIR spectroscopy of a dried extract from *Terminalia catappa*, demonstrating the presence of unique functional groups. In the wavenumber range, an oblique peak of significant prominence is observed at 3219 cm^{-1}. Polyphenolic compounds are characterized by the symmetric and asymmetric relaxation vibrations of the polymer hydroxyl group (O–H), also known as H-bond relaxation, which are represented by the range 3400–3200 cm^{-1}. There may be a link between the -C=O group and the six-carbon aromatic ring, as shown by a vibration that may be detected at 1713 cm^{-1}. The wavenumber at 1599 cm^{-1} is in the range of 1550 - 1650 cm^{-1}, representing strong in-plane NH_2 scissor absorption. Additional proof of the existence of the -CH- group of methylene on aromatic rings stretching is provided by the C-H linkage-related deformation variations at wave-numbers 1441 cm^{-1} in the ranges 1430–1470 cm^{-1}. The wavenumber at 1170 cm^{-1} is in the range of 1000-1250 cm^{-1} assigned to the vibration of the C-N bond in the aliphatic amine functional group. The region between 1000 and 1100 cm^{-1} is sometimes referred to as the fingerprint zone because it contains a large number of unique low-intensity single bands that are associated with specific functional groupings. A vibration at 1052 cm^{-1} is linked to the stretching of -C-O-C-. Finally, the wavenumber at 747 cm^{-1} is responsible for the C-H bond of the phenyl radical.

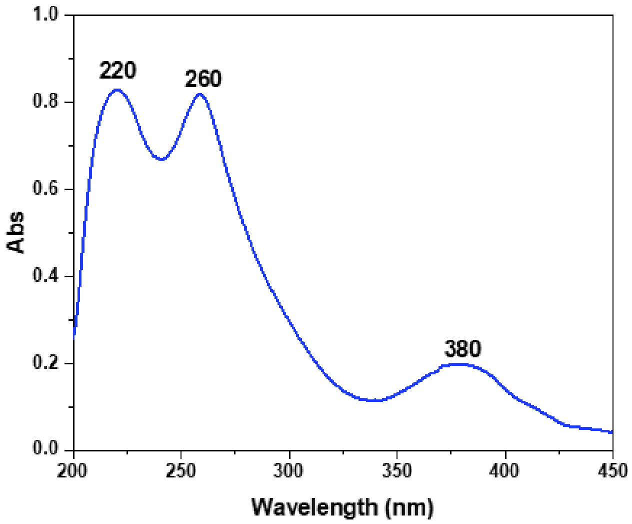

Fig. 4: UV-Vis spectroscopy of dried extract of Terminalia catappa leaf.

Figure 4 displays the UV-Vis photometric spectrum of the leaf extract from Terminalia catappa. Two nearby peaks on the spectrum, located at 220 and 260 nm, are thought to represent the polyphenols found in Terminalia catappa leaves. Furthermore, a smaller peak was also detected at 380 nm. The equation used to quantify the polyphenol content in the Terminalia catappa extract was used to compute the polyphenol concentration using the UV-Vis photometric technique. The extract of *Terminalia catappa* showed a polyphenol content of 24,291 mg/L.

Weight loss method

The weight loss method was used to preliminarily evaluate the corrosion inhibition of the extract on CB300 steel reinforcement in 3.5% NaCl solution. Experiments were conducted with different concentrations of *Terminalia* *catappa* leaf extract after different time periods. The results are recorded in Figure 5 and Table 1.

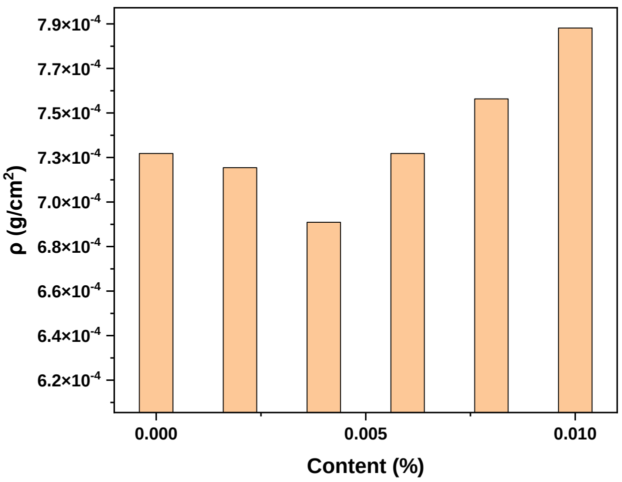

Fig. 5: Graph of the effect of Terminalia catappa leaf extract concentration on steel corrosion rate.

Within the survey, steel samples were immersed in a simulated seawater environment with a concentration of 0.004% Terminalia catappa leaf extract for the best corrosion resistance. The reason may be that the polyphenol component in Terminalia catappa leaf extract is acidic, so, at high concentrations, it will increase the possibility of corrosion from 0.006% to 0.01% of the extract.

Table 1. Time-dependent weight loss results with different extract contents.

Time, days	2	7	9	13	16	21	23	28	30
Content, %	Weight loss (mg)								
0.00%	0.65	0.48	0.45	0.50	0.60	0.56	0.45	0.52	0.30
0.00%	0.60	0.38	0.40	0.43	0.47	0.38	0.35	0.32	0.35
0.00%	0.35	0.34	0.55	0.33	0.33	0.40	0.45	0.38	0.25
0.01%	0.65	0.48	0.30	0.48	0.33	0.44	0.40	0.52	0.50
0.01%	0.65	0.42	0.35	0.40	0.43	0.46	0.60	0.34	0.30
0.01%	0.35	0.48	0.40	0.27	0.40	0.40	0.35	0.34	0.30
0.02%	0.75	0.38	0.45	0.45	0.27	0.56	0.45	0.40	0.50
0.04%	0.05	0.50	0.25	0.37	0.47	0.34	0.50	0.36	0.45

Polarization curve method

Figure 6 and Table 2 show that the adsorption of the extract changes the anode dissolution process as well as the development of hydrogen at the cathode, clearly the addition of *Terminalia catappa* leaf extract from 0.002% to 0.006% has reduced the corrosion current density, corrosion speed, corrosion voltage increase. On the contrary, with the addition of extract from 0.008% to 0.04%, the corrosion potential increased by increasing icorr, corrosion rate and decreasing E_{corr}. This can be explained that *Terminalia catappa* leaf extract is acidic, and when added at high concentrations, it will increase the corrosion ability of steel reinforcement. This finding suggests that *Terminalia catappa* leaf extract can be classified as a type of mixed inhibitor in seawater solution.

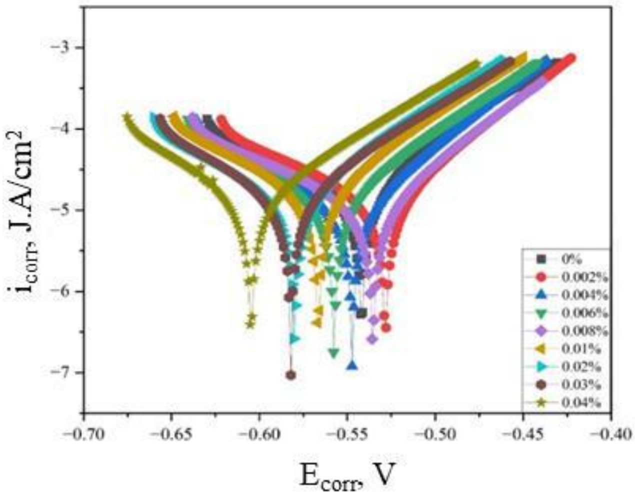

Fig. 6: Potentiodynamic polarization curves recorded in 3.5 wt.% NaCl solution for the steel at different Terminalia catappa leaf extract contents.

Table 2. Corrosion potential (E_{corr}), corrosion current density (i_{corr}), corrosion rate (v_{corr}), and inhibition effect (H_{in}).

Contents (%)	0%	0,002%	**0,004%**	0,006%	0,008%	0,01%	0,02%	0,03%	0,04%
E_{corr} (V)	-0,543	-0,530	**-0,548**	-0,559	-0,537	-0,568	-0,581	-0,583	-0,606
i_{corr} (A/cm²)	8,87	6,76	**5,12**	7,18	7,75	7,77	8,34	9,22	10,5
v_{corr} (mm/năm)	0,1031	0,0786	**0,0594**	0,0834	0,0901	0,0903	0,0969	0,1071	0,1220
H_{in} (%)	0	23,76	**42,39**	19,11	12,61	12,42	6,01	-3,88	-18,33

Electrochemical impedance spectroscopy

From Figure 7, we see that the EIS curve of the sample containing a concentration of 0.004% of the *Terminalia catappa* leaf extract has the shape of the largest radius and is almost a perfect circle. This shows that the varnish layer containing 0.004% extract has very poor electrical conductivity and high corrosion resistance in NaCl solution. The EIS curve of varnish-coated steel reinforcement samples with a concentration of 0.006% to 0.01% extract will have a gradually smaller radius shape and be deformed compared to samples without extract. It has been shown that at high concentrations, the varnish layer is affected by the presence of *Terminalia catappa* leaf extract, reducing the electrical conductivity and corrosion resistance of the original varnish layer. The explanation for the interaction between the composition of the *Terminalia catappa* leaf extract and the varnish layer becomes stronger as the concentration of the extract increases, based on the concave characteristic of the Nyquist graph. Ion diffusion becomes stronger the higher the concentration of *Terminalia catappa* leaf extract because *Terminalia catappa* leaf contain active ingredients such as polyphenols, flavonoids, and tannins, which can form complexes with metal ions in the varnish layer. Thus, we can conclude that the impedance response of the metal increases with the inhibitor concentration, from 0.002% to 0.004%, and decreases when the inhibitor concentration ranges from 0.006% to 0.01%.

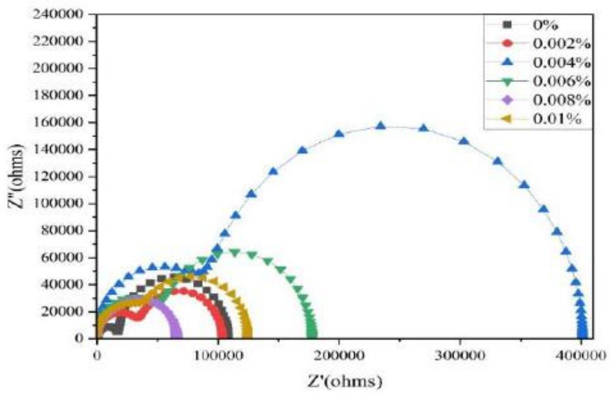

Fig. 7: Electrochemical impedance spectroscopy recorded in 3.5 wt.% NaCl solution for the steel at different Terminalia catappa leaf extract contents.

IV. CONCLUSION

The research results on Terminalia catappa leaf extract to minimize concrete reinforcement corrosion in simulated seawater environments are positive. Corrosion current density decreased from 8.87 A/cm^2 (for samples soaked in a 3.5% blank NaCl solution) to 5.12 µA/cm^2 when adding 0.004% *Terminalia catappa* leaf extract. Electrochemical impedance spectroscopy (EIS) shows that the inhibition efficiency is over 90% at the same concentration after 24 hours of soaking. *Terminalia catappa* leaf extract contains many polyphenols, which inhibit the corrosion process of concrete reinforcement in a seawater environment.

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