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PHYTOCHEMISTRY OF ETHANOL EXTRACT OF YOUNG COCONUT FIBER AND ITS EFFECTIVENESS AS AN IRON CORROSION INHIBITOR IN SEAWATER MEDIA

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ABSTRACT

This study aims to examine the effectiveness of tannin extract as an iron corrosion inhibitor in seawater media. Tannin extract was obtained through a maceration extraction process using 96% ethanol solvent. Its properties were analysed by UV-Vis Spectrophotometry and FTIR, while the corrosion rate and inhibitor efficiency were tested using Gravimetry and Electrochemistry methods based on tannin concentration and immersion time in seawater media. The results of qualitative and quantitative analysis obtained an extract yield of 13.47% and contained active compounds including alkaloids (21.32%), saponins (9.87%), terpenoids (8.32%), condensed tannins (1.73%), phenolic compounds (1.16%), and flavonoids (0.36%), while the results of the analysis with UV-Vis Spectrophotometry showed that absorption occurred at a wavelength of 302 nm due to the $\pi \rightarrow \pi^*$ Transition from longer conjugated bonds, while the results of the FTIR Spectrophotometry analysis showed that absorption occurred at wave numbers 1714.72 cm^{-1}, 1612.48 cm^{-1} and 3390.86 cm^{-1} indicating the interaction between the C = O, C = C aromatic and -OH groups indicating the presence of polyphenol structures in tannins. The results of Gravimetry showed the formation of a protective layer on the iron surface, thereby reducing the corrosion rate significantly. The highest inhibition efficiency reached 75.83% at a concentration of 600 ppm for 168 hours (7 days), and Tannin formed a regular monolayer layer and which was in accordance with the Langmuir adsorption isotherm. This shows that Tannin has the potential as a natural inhibitor to prevent corrosion of iron in the marine environment.

Keywords: Young Coconut Fiber Extract, Phytochemistry, Iron Corrosion, Inhibitor, Seawater.

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INTRODUCTION

Metal corrosion is a process of material degradation due to chemical or electrochemical reactions with the surrounding environment. In seawater, the corrosion process occurs faster because of the high chloride ion (Cl^-) content and is aggressive to metals such as iron (Fe). Corrosion of iron not only causes structural damage but also has the potential to cause major economic losses, especially in the marine, shipping, and coastal infrastructure sectors.[1] One effective method in controlling corrosion is the use of inhibitors, namely chemical compounds that can slow the rate of corrosion by forming a protective layer on the metal surface. Although various synthetic inhibitors are available on the market, most of them have a negative impact on the environment and are toxic. Therefore, there is a need to develop environmentally friendly corrosion inhibitors, one of which is from natural materials such as tannins.[2] Active compounds from natural materials can interact with metal ions and metal surfaces through coordination bonds or adsorption, thus forming a passive layer that inhibits the transfer of ions and electrons in the corrosion process. The active compounds in young coconut Fiber (Cocos nucifera L.) range from 5.62% to 6.62%, and are higher when compared to old coconut Fiber, which is around 4.28%, both of which have the potential to be corrosion inhibitors.[3] In addition to the type and source of active compounds, the concentration of extract in solution and soaking time are two important factors that affect the effectiveness of corrosion inhibition. Optimal tannin concentration is needed to achieve maximum efficiency without causing waste of materials. Meanwhile, soaking time affects the formation and stability of the protective film on the iron surface.[4] This study examines the efficiency of the ethanol extract of young coconut Fiber as an iron corrosion inhibitor based on variations in concentration and soaking time. Metal corrosion, especially iron, is a serious problem that causes material degradation, decreased

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structural integrity, and system failure in various industrial, maritime, and construction sectors. According to 5, global economic losses due to corrosion reach billions of dollars each year. The marine environment exacerbates this condition due to the high concentration of ions such as chloride, magnesium, and sodium which accelerate electrochemical reactions on metal surfaces, especially through the aggressive role of chloride ions in accelerating corrosion formation.[6]

EXPERIMENTAL

Materials and Methods

The materials used are young coconut fiber, 96% ethanol, tissue, and seawater. The tools used are a rotary vacuum evaporator, iron metal, Erlenmeyer flask, analytical balance, desiccator, watch glass, oven, glass jars, aluminium foil, screw microammeter, 60 mesh sieve, label paper, stirring rod, filter paper, measuring cup, and tweezers.

General Procedure

Sample Preparation and Extraction[7]

Young coconut fiber samples (Cocos nucifera L.) were cleaned and shredded into small pieces and dried in the sun. The dried samples were ground using a grinding machine and sieved to obtain samples ready for extraction. The extraction process was carried out by maceration using a sample to solvent ratio of 1:10 by weight per volume (w/v) for 72 hours, after which the extract was separated from the residue with filter paper and the extract was separated from the solvent using a vacuum evaporator until a dry extract was obtained. The extract yield was calculated using the following eqn.-1:

$$\text{Yield} = \frac{\text{extract weight}}{\text{Sample weight}} \text{ x } 100\% \quad (1)$$

Ethanol extract from coconut fiber was analyzed qualitatively and quantitatively with specific solvents and also analyzed with UV-Vis Spectroscopy and FTIR.

Iron Sample Preparation[8]

Iron was obtained from a welding workshop around Palu City and prepared according to needs, cut to a size of (5 x 3 x 3) cm3, sanded, washed, and dried in a desiccator. The prepared iron was soaked in a tannin solution with the following treatments as a control (without inhibitor) and given inhibitor treatment with variations in tannin concentrations of 100ppm, 200ppm, 300ppm, 400ppm, 500ppm, and 600ppm with variations in soaking time of 1 day, 3 days, 5 days, and 7 days. The corrosion rate of iron metal in seawater media is calculated by the following eqn.-2[9]:

$$CR = \frac{K \times W}{A \times T \times \rho} \quad (2)$$

Information:

CR = Corrosion Rate (g/cm^2/day)

K = Corrosion rate constant = 8,76x 10^4

W = Mass difference before and after corrosion [($W_{beginning} - W_{end}$)(gram)]

A = Surface area (cm^2) = $2\pi r$ (r + t)

ρ = Density of iron (g/cm^3)

T = Soaking time (day)

The effectiveness of using tannin extract as an inhibitor in inhibiting iron corrosion during 7 days of iron immersion based on variations in extract concentration in seawater media is calculated as inhibition efficiency using eqn.-3 as follows:

$$\%IE = \frac{CR_1 - CR_2}{CR_1} \text{ X } 100\% \quad (3)$$

Information:

IE= Inhibitor efficiency, CR_1= Corrosion rate without inhibitor, CR_2= Corrosion rate with inhibitor

Based on the corrosion rate, it is necessary to determine the degree of surface coverage (θ), which indicates how much extract can bind to the iron surface, so that it can prevent oxidation reactions after the iron metal is soaked for 7 days. Based on the data obtained, the degree of surface coverage of the iron metal is calculated using eqn.-4 as follows[10]:

$$\theta = \frac{\%IE}{100} \quad (4)$$

The determination of the adsorption isotherm model is carried out to understand the relationship between the concentration of the adsorbed substance (adsorbate) and the amount of adsorbate bound to the adsorbent surface at equilibrium. The isotherm approaches used in this study include the Langmuir, Freundlich, and Temkin models. Each adsorption isotherm model is shown in eqns.-5, 6 and 7 below:

$$\frac{C}{\theta} = \frac{1}{K_{Ads}} + C \quad (5)$$

$$\text{Log } \theta = \log K_f + \text{n log C} \quad (6)$$

$$\theta = B \ln C + B \ln K_T \quad (7)$$

Each model is evaluated based on the correlation coefficient (R^2) value of the linear graph. The model with an R^2 value close to one (1) is considered the most appropriate to describe the adsorption system that occurs.

RESULTS AND DISCUSSION

The extraction process of young coconut fiber was carried out using the maceration method using ethanol solvent for 3 × 24 hours at room temperature. This method was chosen because it is effective in extracting secondary metabolite compounds from natural materials without involving direct heating, which can damage thermolabile compounds and produce a concentrated brown extract with a yield of 13.47% based on the comparison of extract mass to sample mass. The results of the Phytochemical screening analysis, the ethanol extract of young coconut fiber contains complex bioactive compounds as listed in Table-1 below.

Table-1: Results of Qualitative and Quantitative Analysis of Young Coconut Fiber Ethanol Extract

Coconut fiber extract	Components in the extract	Level (%)
 Yield = 13.47%	Condensed tannins	1.73
	Phenolic	1.16
	Flavonoid	0.36
	Alkaloid	21.32
	Saponin	9.87
	Terpenoid	8.32

Alkaloids are organic nitrogen compounds known to have complex properties and high reactivity to metal surfaces. The high concentration in this extract indicates that alkaloids can play a major role in the formation of a protective layer on the metal surface through chemical adsorption. The mechanism of action of alkaloids as inhibitors generally involves the provision of electron pairs from nitrogen atoms to the metal surface that has empty orbitals, forming a stable surface complex.[11] Saponins are glycoside compounds with polar and nonpolar groups that allow the formation of a physical protective layer on the metal surface. In addition, its amphiphilic nature helps reduce surface tension, which inhibits the penetration of chloride ions to the metal surface in corrosive media.[12] Terpenoids have functional groups that can interact with metal surfaces through coordination bonds or van der Waals forces. Terpenoids contribute to physical and sometimes chemical adsorption depending on their functional structure. These compounds help form a barrier film against corrosive solutions.[13] Tannins, especially condensed tannins,

are known to have phenolic groups that are active in binding metals, either through electrostatic interactions or hydrogen bonds. Although the levels are lower than alkaloids, tannins still play an important role as inhibitors, especially in multilayer adsorption on metal surfaces.[14] Tannins also have antioxidant properties. Phenolates and flavonoids are polyphenolic compounds that are rich in aromatic –OH groups. Although the levels are relatively low, these compounds still have good electron donation capabilities. The hydroxyl group in these compounds allows strong interactions with metal ions, thus strengthening the passive layer on the metal surface.[15] Flavonoids are also known as natural antioxidants and contribute to inhibiting oxidation reactions that are the beginning of the corrosion process.[16] The existence of these compounds is reinforced by the results of the Uv-Vis Spectroscopy analysis which shows that maximum absorption occurs at a wavelength of 302 nm (Fig.-1.a) this is caused by the interaction between the –OH and C = O groups in a more complex aromatic structure so that it shifts the maximum wavelength towards a longer direction (bathochromic shift). Absorption at wavelengths between 300 - 320 nm is caused by the $\pi \rightarrow \pi^*$ transition of longer conjugated bonds. Such as in flavonoids, catechins, or oxidized tannins.[17] The presence of aromatic O–H, C=O, C–O, and C=C groups in the extract, which are the main characteristics of phenolic compounds such as tannins, flavonoids, and catechins, is also supported by the FTIR spectrum seen in Fig.-1(b).

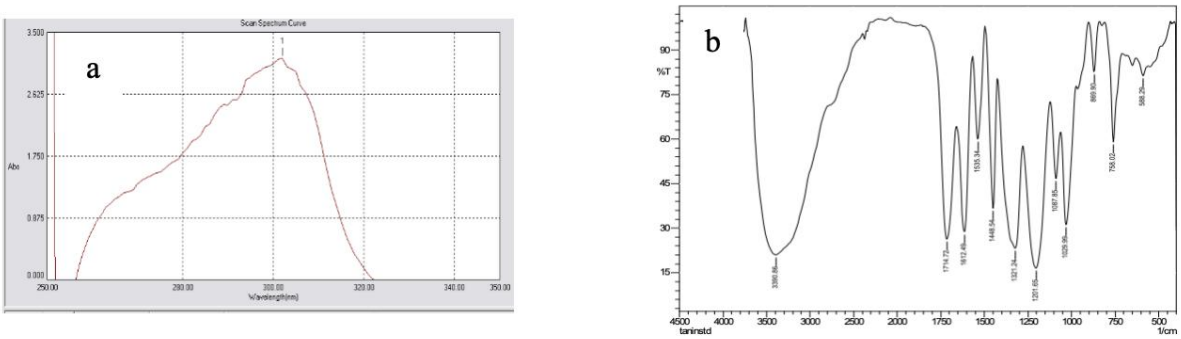


Fig.-1: Spectroscopic Spectrum of the Extract Analysis Results: (a) Uv-Vis, (b) FTIR

Table-2: Results of FTIR Spectrum Analysis of Young Coconut Fiber Ethanol Extract [18]

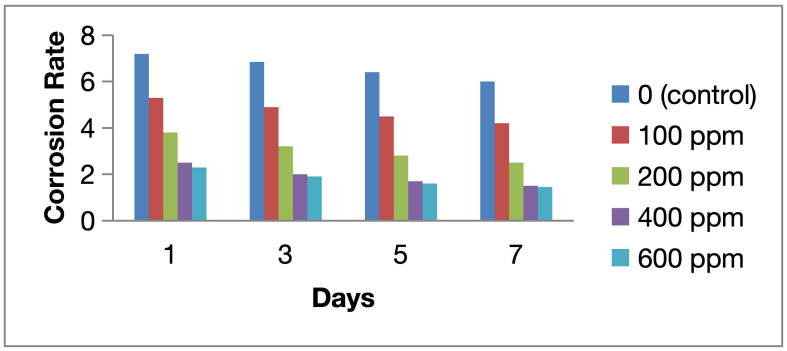
Wave Number (cm^{-1})	Types of Vibration	Functional Group	Interpretation
3288.88 cm^{-1}	Stretch O–H	Alcohol / Phenol	Indicates the presence of polyphenol compounds such as tannins, flavonoids, and catechins.
1741.72 cm^{-1}	Stretch C=O	Ester / Carboxylic Acid	The carbonyl group of an ester or phenolic acid.
1629.42 cm^{-1}	Stretch C=C aromatic	Aromatic	Indicates the presence of aromatic rings, common in flavonoids and tannins.
1525.34 cm^{-1}	Stretch C=C or C=N	Aromatic / amide	It can originate from a phenolic structure or slight protein contamination.
1445.54 cm^{-1}	Flexibility C–H	CH_2 /CH_3	Indicates the presence of hydrocarbon chains or aliphatic groups.
1373.31 cm^{-1}	Flexibility O–H / CH_3	Phenol / Alcohol	Can show free phenolic OH.
1261.45 cm^{-1}	Stretch C–O	Seconder Alcohol	Common in ether or alcohol groups.
1201.65 cm^{-1}	Stretch C–O–C	Ester / Eter	Indicates an ester or ether structure, as in

			restructured tannins.
1030.29 cm^{-1}	Stretch C–O	Alcohol, Carbohydrate	Common in glycoside compounds or bound sugars.
896.0 cm^{-1}	Aromatic deformation	C–H aromatic	Strengthens the presence of aromatic compounds.
720.03 & 528.09 cm^{-1}	Aromatic deformation	C–H aromatic	Support the presence of conjugated aromatic rings.

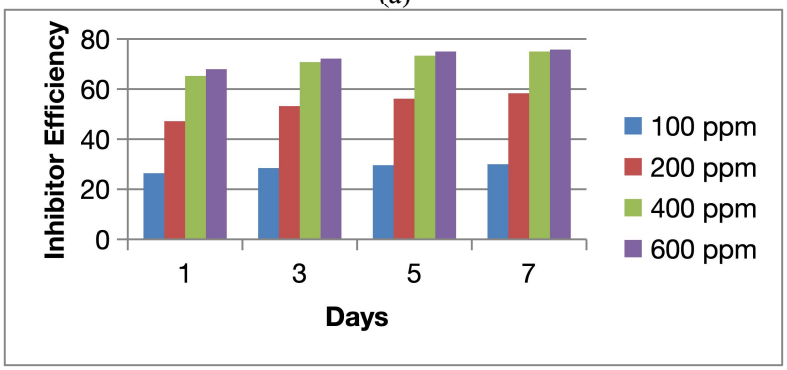
This strengthens the suspicion that the ethanol extract from young coconut Fiber contains active compounds that inhibit corrosion, which work by adsorption on metal surfaces through polar and aromatic groups.

Corrosion Rate and Inhibition Efficiency

Figure-2(a and b) shows the effect of extract concentration on corrosion rate and inhibition efficiency on iron metal. It can be seen that the highest corrosion rate is seen in the control (without extract) for all treatment groups (0, 100, 200, 400 ppm), the highest corrosion rate occurs in the treatment without the addition of inhibitor (control). In other words, without protection, corrosion occurs faster. During corrosion, iron metal easily releases electrons (has reducing properties) so that it is easily oxidized with the reaction equation $Fe \rightarrow Fe^{2+} + 2^{e-}$ in seawater media, the presence of chlorine ions (Cl^-) can increase the corrosion rate (rust formation) according to the reaction $Fe^{2+} + OH^- \rightarrow Fe(OH)_2 \rightarrow Fe_2O_3 \cdot xH_2O$ (rust).[19]



(a)



(b)

Fig.-2: (a) Corrosion Rate ($mg/cm^2/day$) b. Inhibition Efficiency (%)

Based on Fig.-2, it can be seen that increasing the concentration of extract from 0 (control) to 100, 200, 400, and 600ppm, the corrosion rate decreases, indicating that the extract is effective in inhibiting the iron oxidation process in seawater media. The most significant decrease in corrosion rate occurs from control to 200ppm, and is relatively flat until a concentration of 600ppm, which indicates a saturated or optimal effect. A consistent pattern in the four concentration variations (0, 100, 200, 400 ppm) shows that the

extract remains effective in reducing the corrosion rate as seen in Fig.-2(b). The optimal concentration is seen at 400–600 ppm, where the inhibition efficiency approaches or exceeds 75%. The addition of an extract concentration of 600ppm for 7 days of immersion can inhibit the corrosion rate with an efficiency of 75.83%; in other words, ethanol extract from coconut fiber can reduce the corrosion rate by up to 75.83% compared to an environment without an inhibitor (control). This is because the compounds in the extract have functional groups such as -OH, -COOH, and -NH_2 , which can interact with iron metal ions (Fe^{+}, $Fe^{2+,}$ and Fe^{3+}) or on the metal surface, thereby increasing adsorption efficiency. Hydroxyl groups in phenolic compounds can interact with metal surfaces through the formation of complex bonds, thereby increasing the effectiveness of adsorption against metal ions or corrosive compounds.[20] Like tannins, they have many aromatic hydroxyl groups that can form complex bonds with iron metal ions or interact with iron surfaces through hydrogen bonds and van der Waals forces. Active compounds such as tannins and flavonoids in plant extracts are known to have bond interactions that are influenced by the molecular structure, number of polar groups, and bond strength between the active compound and the adsorbent surface.[21] The interaction between functional groups in the extract and the iron metal surface can be determined based on the results of the analysis using the Langmuir, Freundlich, and Terkim linear equations shown in Fig.-3 and Table-2.

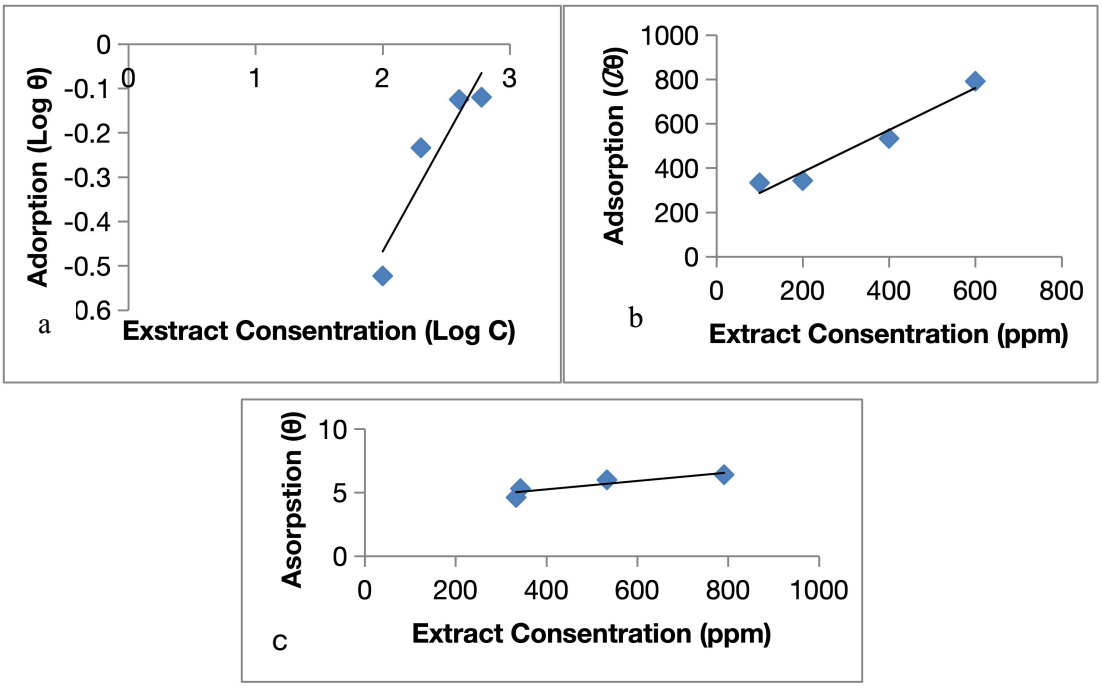


Fig.-3: Adsorption Isotherm Models a) Langmuir, b) Freunlich, c) Terkim

Table-2: Linear Equations, Determination, and Interpretation of Adsorption Isotherm Models

Model	Linear Equations	R^2	Interpretation
Langmuir	y=0.9473x+192.31	0.9565	Monolayer adsorption on homogeneous surfaces
Freundlich	y=0.5175x−1.5033	0.8779	Multilayer adsorption on heterogeneous (physical) surfaces
Temkin	y=0.0033x+3.9158	0.8137	There is interaction between inhibitor molecules

The relationship between the concentration of extract in seawater medium with the adsorption of extract absorbed on the surface of iron metal during 7 days of immersion is shown by the determination value (R^2). Based on the graph, of the three adsorption isotherm models, namely Langmuir, Freundlich and Terkim, have different determination values (R^2) and the closest to the value of 1 is the Langmuir adsorption isotherm model (R^2 = 0.9565), this indicates that the adsorption of compounds in the extract tends to follow the monolayer mechanism, where the inhibitor molecules occupy the metal surface regularly and evenly so that there is no interaction between adsorbed molecules.[22] Following the

Freundlich adsorption isotherm with a determination value (R^2 = 0.8779) indicating the presence of multilayer adsorption and non-homogeneous surfaces, possibly caused by the diversity of active compounds in the extract[23], including alkaloids (21.32%), saponins (9.87%), terpenoids (8.32%), condensed tannins (1.73%), phenolic compounds (1.16%), and flavonoids (0.36%). The lowest determination value (R^2 = 0.8137) means that around 81.37% of the variation in experimental data can be explained by the Temkin isotherm model. This shows that although there is interaction between inhibitor molecules adsorbed on the surface of iron metal, this interaction is not the main mechanism.[24] In other words, the adsorption process is more influenced by direct interaction between inhibitor molecules and the metal surface compared to interactions between inhibitor molecules themselves. Meanwhile, the Temkin model considers that the interaction between active molecules in the extract can inhibit (inhibit) the occurrence of corrosion on the metal surface.[25] So, if the data is by the Temkin model, it means that there is an interaction between inhibitor molecules that have attached to the metal surface, such as the attractive force between molecules. However, because the Temkin R^2 value is not too high, the influence of the interaction between molecules is not the main factor in the adsorption mechanism. Other factors, such as the ability of inhibitor molecules to attach directly to the surface of iron metal (as explained by the Langmuir model), are likely more dominant.[26]

CONCLUSION

Based on the extraction results, a yield of 13.47% was obtained containing alkaloid compounds (21.32%), saponins (9.87%), terpenoids (8.32%), condensed tannins (1.73%), phenolic compounds (1.16%), and flavonoids (0.36%) which have high effectiveness as iron corrosion inhibitors in seawater media. Based on the results of Gravimetry, it shows the formation of a protective layer on the iron surface is shown, thereby reducing the corrosion rate significantly. The highest inhibition efficiency reached 75.83% at a concentration of 600 ppm for 168 hours (7 days), and Tannin formed a regular monolayer layer and which is in accordance with the Langmuir adsorption isotherm. The utilization of young coconut fiber waste can provide a potential, environmentally friendly solution for corrosion control in the marine and metal construction sectors.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-9: Industry, Innovation, and Infrastructure*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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