Effect of a mixture of paint and *Rhizophora mucronata* leaves extract as a natural inhibitor of marine steel in 3.5% NaCl solution

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Abstract

Marine steel is steel used in marine environments, such as steel for offshore construction and ships. Marine steel is easily corroded. To increase the corrosion resistance of marine steel, paints can be mixed with natural inhibitors, such as *Rhizophora mucronata* leaves extract. This study aimed at determining the effect of a mixture of paint and *Rhizophora mucronata* leaves extract as a corrosion inhibitor on marine steel. The GC-MS test was performed to determine the content of chemical compounds in *Rhizophora mucronata* leaves extract. Emission spectroscopy testing was carried out to determine marine steel elements. The corrosion inhibitor was prepared by making a mixture of paint and concentrated *Rhizophora mucronata* leaves extract with concentrations of 10, 20, 30, and 40% by volume. A potentiostat/galvanostat (PGSTAT101) was utilized to acquire anodic and cathodic polarization curves for marine steel in 3.5% NaCl solution. Based on GC-MS test results, *Rhizophora mucronata* leaves extract contain chemical compounds that can coat and inhibit the surface oxidation process of marine steel. Based on emission spectroscopy, marine steel specimen contained 98.56% Fe, 0.316% C, 0.26 Si and 0.655 Mn. The paint mixture with *Rhizophora mucronata* leaves extract could reduce the corrosion rate to 0.000112485 mm/year in 3.5% NaCl solution. The paint-coated specimens with all the concentrations of *Rhizophora mucronata* leaf extract had almost the same percentage increase in inhibitor efficiency (%IE), 97.86–98.96%. Therefore, the use of a mixture of the paint with 20% *Rhizophora mucronata* leaves extract was taken as the optimal composition.

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1. Introduction

Steel is most widely used in the construction sector, around 50%, the transportation sector, such as cars, planes, and other vehicles, and 14% in industrial machinery [1]. Steel is also widely used in marine environments. It is known as marine steel, for example, steel used in

onshore and offshore buildings, ships, oil and gas facilities [2]. Much marine steel is used in docks, and ships. Various other types of steel are used in marine environments in archipelagic countries, such as Indonesia. Marine steel is easily corroded, so it needs to be given a corrosion-protective coating such as paint. The use of paint in coating marine steel for a long period can produce toxic agents [3]. To increase the corrosion resistance and reduce the release of toxins, paints can be mixed with natural inhibitors.

The “green chemistry” movement is attempting to ensure the environment and human wellbeing, including discovering inhibitors that are effectively biodegradable, harmless to the ecosystem, and simple to renew [4]. Natural inhibitors can be obtained especially from plants [5].

Rhizophora mucronata is a species of plant that is commonly found in mangrove forests. *Rhizophora mucronata* leaves contain phenolic compounds [6] which may function as natural inhibitors. *Rhizophora* leaves are good candidates for natural inhibitors because it is easy to renew, harmless to the ecosystem and biodegradable. This research aimed to determine the effect of a mixture of paint and *Rhizophora mucronata* leaves extract as a corrosion inhibitor on marine steel.

2. Materials and Methods

2.1. *Rhizophora mucronata* leaves extract

Mangrove (*Rhizophora mucronata*) leaves utilized in this research were taken from Balikpapan mangrove forests. The mangrove leaves are dried at room temperature for a month. Air-dried mangrove leaves have a 15.06% moisture content. 500 grams of mangrove leaves were cut into small pieces and put into a glass beaker. 500 ml of 96% ethanol was added to the beaker. The beaker was covered and stored at room temperature for 48 hours. The extract was filtered and concentrated to 100 ml.

The GC-MS test was performed using 10 ml of the concentrated extract. The GC-MS test aims to determine the content of chemical compounds in the extract. 90 ml of concentrated extract was used as a natural inhibitor to be mixed with a paint (natural oil, white organic pigment, and thinner) to coat marine steel for corrosion testing.

2.2. Marine steel plates

Emission spectroscopy testing was carried out to determine the marine steel elements.

2.3. Polarisation study

The corrosion inhibitor was prepared by making a mixture of paint and *Rhizophora mucronata* leaves concentrated extract. Mixture with concentrations of 10, 20, 30, and 40% by volume were made. Marine steel was cut into 10×10×2 mm coupons. One of the marine steel surfaces was covered with a resin so the corrosion test was focused on one surface. A mixture of the paint with concentrated mangrove extract was applied to the uncovered surface of the marine steel and left to dry for 24.

A potentiostat/galvanostat (PGSTAT101) was utilized to record anodic and cathodic polarization curves [7] for marine steel with various concentrations of the paint and *Rhizophora mucronata* leaves concentrated extract in 3.5% NaCl solution. 3.5% NaCl was used on a lab scale to replace seawater [8]. Research was done by recording marine steel corrosion rate curves and polarization curves.

Figure 1. Corrosion test specimens.

2.4. Marine steel surface microscopic structure

The microscopic structure was determined to characterize the corroded marine steel surface after the polarisation study.

3. Results and Discussion

3.1. *Rhizophora mucronata* extract characteristics

The GC-MS test results of *Rhizophora mucronata* leaves extract are presented in Figure 1 and Table 1.

A natural corrosion inhibitor may contain aromatic rings, N-, S-, O-, P- and heterocyclic moieties [9]. Based on GC-MS test result from Table 1, the *Rhizophora mucronata* leaves extract contains 11 chemical compounds which had cyclic structures and O-structures, such as 1,2-benzendiol, 2 chemical compounds which had a heterocyclic structure and O-structure, such as α -D-Glucopyranose, 4,6-O-ethylidene, and 1 chemical compound which had a cyclic structure, O-structure, and N-structure, *i.e.*, *N,N*-dimethyl-*L*-homoserine lactone. Chemical compounds with these functional groups can coat and inhibit the surface oxidation process of marine steel.

Figure 2. The GC-MS test results of *Rhizophora mucronata* leaves extract.

Table 1. Chemical composition based on GC-MS test results of *Rhizophora mucronata* leaves extract.

Peak	Ret.Time (minutes)	Conc. (%)	Chemical name	Chemical structure	Functional chemical structure
1	4.438	8.37	Cyclopentyl 4-ethylbenzoate (4-Ethylbenzoic acid, cyclopentyl ester)		Cyclic structure O-structure
2	5.066	2.69	2-Oxepanone		Cyclic structure O-structure
3	6.740	1.61	2H-Pyran-2,6(3H)dione		Cyclic structure O-structure

Peak	Ret.Time (minutes)	Conc. (%)	Chemical name	Chemical structure	Functional chemical structure
4	8.023	2.41	Cyclotrisiloxane		Cyclic structure O-structure
5	8.331	2.13	<i>N,N</i> -Dimethyl- <i>L</i> -homoserine lactone		Cyclic structure O-structure N-structure
6	9.270	2.03	Alletone		Cyclic structure O-structure
7	10.900	2.11	Pyranone		Cyclic structure O-structure
8	12.698	15.79	1,2-Benzendiols		Cyclic structure O-structure
9	12.997	2.87	Guaiacol		Cyclic structure O-structure

Peak	Ret.Time (minutes)	Conc. (%)	Chemical name	Chemical structure	Functional chemical structure
10	18.814	3.29	4- <i>t</i> -Pentylcyclohexene		Cyclic structure
11	21.034	2.01	3-Methyl-4-methylene-2-hexanone		O-structure
12	21.223	2.17	Neoclovene		Heterocyclic structure
13	22.193	1.75	Megastigmatrienone		Cyclic structure O-structure
14	25.484	2.58	2,3-Bis(1-methylallyl)pyrrolidine		Cyclic structure N-structure

Peak	Ret.Time (minutes)	Conc. (%)	Chemical name	Chemical structure	Functional chemical structure
15	30.190	3.24	Dimethyl 4- <i>O</i> -methylhexopyranosiduronate		Cyclic structure O-structure
16	30.275	2.89	4,6- <i>O</i> -Ethylidene- α - <i>D</i> -glucopyranose		Heterocyclic structure O-structure
17	30.370	14.04	3- <i>O</i> -Methyl- <i>D</i> -glucose		O-structure
18	30.405	4.55	4- <i>O</i> -Methylmannose		Cyclic structure O-structure
19	30.443	22.04	2- <i>O</i> -Methyl- <i>D</i> -mannopyranosa		O-structure

Peak	Ret.Time (minutes)	Conc. (%)	Chemical name	Chemical structure	Functional chemical structure
20	36.072	1.44	Isosteviol methyl ester		Heterocyclic structure O-structure

3.2. Marine steel Plates Characteristics

The marine steel elements determined by emission spectroscopy are listed in Table 2.

Table 2. Elemental composition of marine steel plates.

Elements	Percentage (%)
Fe	98.56
Si	0.260
C	0.316
Al	0.035
Mn	0.655
Mo	0.038
P	0.024
V	0.044

1040 steel for marine use contains 98.58% Fe, 0.40% C, 0.23% Si and 0.65% Mn [10]. A steel with high carbon content will be easily corroded [11]. The corrosion resistance of steel tends to increase due to silicon [12] and manganese [13].

3.3. Polarisation study

Based on the observations, the paint mixture with *Rhizophora mucronata* leaves extract can completely coat the surface of the marine steel. A good inhibitor can coat and prevent corrosion on marine steel surface perfectly [14]. The effect of *Rhizophora mucronata* leaves extract mixed with paint as a corrosion inhibitor on marine steel in 3.5% NaCl solution can be seen in the following Tafel plot.

Figure 3. Tafel plot corrosion test of *Rhizophora* leaves extract mixed with paint in 3.5% NaCl solution.

The Tafel plot of marine steel coated with paint only is on the right, while the Tafel plot of marine steel coated with a mixture of paint and *Rhizophora* leaves extract tends to approach the anodic side or lower current density. A lower current density indicates that the corrosion reaction is smaller [15], which means the inhibitor successfully prevents corrosion. Marine steel surfaces coated with inhibitors have a lower polarization curve compared to uncoated marine steel inhibitors [16].

The values of E_{corr} , I_{corr} , and %IE from the test specimens coated with a mixture of paint and *Rhizophora mucronata* leaves extract are shown in Table 4.

Table 4. Effect of paint mixture with *Rhizophora mucronata* leaves extract at various concentrations.

Inhibitor concentration (%)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{corr} (mV)	Corr. rate (mm/year)	%IE
0	1.4073	−704	10.84×10^{-3}	0.00
10	0.0301	−677	0.23×10^{-3}	97.86
20	0.0259	−712	0.20×10^{-3}	98.16
30	0.0217	−709	0.17×10^{-3}	98.46
40	0.0146	−750	0.11×10^{-3}	98.96

Marine steel without being coated with an inhibitor had a corrosion rate of 10.84×10^{-3} mm/year in a 3.5% NaCl solution. In comparison, steel without a coating immersed in seawater has a corrosion rate of 0.07 ± 0.02 mm/year [17]. Marine steel is easily corroded because it is used in marine waters with a high corrosion rate, so it is necessary to apply a coating comprising a corrosion inhibitor.

Marine steel was coated with a mixture of paint with *Rhizophora* leaves extract, and the corrosion inhibitor reduced the corrosion rate from 0.23×10^{-3} to 0.11×10^{-3} mm/year in 3.5% NaCl solution. The paint mixture with henna extract as a natural inhibitor has a corrosion rate of aluminum at 0.003846 to 0.001767 mm/year [18]. The addition of *Rhizophora* leaves extract concentrate to the paint mixture decreased the corrosion rate of marine steel and increased the inhibitor efficiency.

The corrosion potential (E_{corr}) of plates coated with a mixture of paint with *Rhizophora* leaves extract is almost unchanged compared to those that are not coated. This shows that the mixture of paint with *Rhizophora* leaves extract protects the plate against corrosion attack. I_{corr} values were found to decrease on the surface of the tested plates. %IE increases with increasing mangrove extract concentration. The paint-coated specimens with all various concentrations of *Rhizophora mucronata* leaves extract had almost the same percentage increase in inhibitor efficiency (%IE), 97.86–98.96%. Therefore, the use of a mixture of paint with 20% *Rhizophora mucronata* leaves extract was taken as the optimal concentration.

3.4. Marine steel surface microscopic structure

Microscopic pictures of the marine steel specimen surface after the corrosion testing can be seen in Figure 4, where “0% test specimen” means a specimen coated with the paint with no corrosion inhibitor and “10% test specimen” means a specimen coated with 90% paint + 10% mangrove extract.

Figure 4. (a). Microscopic picture of 0% test specimen after polarisation study.
(b). Microscopic picture of 10% test specimen after polarisation study.

Corrosion on metal surfaces can be seen using an optical microscope [19]. Based on Figure 4, the 0% test specimen showed a corroded steel surface. Corroded steel is marked with a brownish colour [20], which is due to the iron element being oxidized [21]. While the 10% test specimen, the steel surface is coated with inhibitors, so the mixture of paint with *Rhizophora* leaves extract can minimize corrosion. A steel surface covered with an inhibitor can prevent corrosion [22].

Conclusion

Based on the GC-MS test result, *Rhizophora mucronata* leaves extract as natural corrosion inhibitor contains 11 chemical compounds which had cyclic structure and O-structure, 2 chemical compounds which had heterocyclic structure and O-structure, and 1 chemical compound which had cyclic structure, O-structure, and N-structure. Based on emission spectroscopy, marine steel contain 98.56% Fe, 0.316% C, 0.26 Si and 0.655 Mn. The paint mixture with *Rhizophora mucronata* leaves extract can completely coat the surface of the marine steel. On marine steel coated with a mixture of paint with *Rhizophora mucronata* leaves extract, and corrosion inhibitor reduced the corrosion rate 0.23×10^{-3} to 0.11×10^{-3} mm/year in 3.5% NaCl solution. The paint-coated specimens with all concentrations of *Rhizophora mucronata* leaf extract had almost the same percentage increase in inhibitor efficiency (%IE), 97.86–98.96%. Therefore, the use of a mixture of the paint with 20% *Rhizophora mucronata* leaves extract was taken as the optimal concentration.

References

1. OECD. Perspectives on steel by steel-using industries, DSTI/SU/SC, 2010, 4 68th Steel Committee Meeting, Paris, 6–7 May 2010.
2. M. Abbas and M. Shafiee, An overview of maintenance management strategies for corroded steel structures in extreme marine environments, *Mar. Struct.*, 2020, **71** (March 2019), 102718. doi: [10.1016/j.marstruc.2020.102718](https://doi.org/10.1016/j.marstruc.2020.102718)
3. E.M.E. Mansour, A.M. Abdel-Gaber, B.A.Abd-El Nabey, N. Khalil, E. Khamis, A. Tadros, H. Aglan and A. Ludwick, Developing and testing of a new anti-corrosive coating containing algae as a natural inhibitor for preventing marine corrosion of steel, *Corrosion*, 2003, **59**, no. 3, 242–249. doi: [10.5006/1.3277557](https://doi.org/10.5006/1.3277557)
4. S. Marzorati, L. Verotta and SP. Trasatti, Green Corrosion Inhibitors from natural sources and biomass waste, *Molecules*, 2019, **24**, 48.
5. A. Salhi, A. Bouyanzer, A. Chetouani, E.El Ouariachi, A. Zarrouk, B. Hammouti, J.M. Desjobert and J. Costa, Chemical Composition, Antioxidant and Corrosion Activities of *Mentha suaveolens*, *JMES*, 2017, **8**, no. 5, 1718–1728.
6. N.A.Z. Abidin, N.H.A. Halim and R. Me, Basic study of chemical constituents in *Rhizophora* species, *The open conference proceedings journal*, 2013, **4** (Supl-2, M7), 27–28.

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7. O.S.I. Fayomi, A.P.I. Popoola, L.R. Kanyane and T. Monyai, Development of Reinforced in-situ anti-corrosion and Wear Zn-TiO₂/ZnTiB₂ Coatings on Mild Steel, *Results Phys.*, 2017, **7**, 644–650.
 8. J. Xu, S. Du, X. Yang, Y. Hao and X. Wang, Molecular dynamics simulation of the effects of different salts on methane hydrate formation: An analysis of NaCl, KCl and CaCl₂, *IOP Conf. Ser.: Earth Environ. Sci.*, 2021, **675**, no. 1. doi: [10.1088/1755-1315/675/1/012180](https://doi.org/10.1088/1755-1315/675/1/012180)
 9. J.A. Rodríguez, J. Cruz-Borbolla, P.A. Arizpe-Carreón and E. Gutiérrez, Mathematical models generated for the prediction of corrosion inhibition using different theoretical chemistry simulations, *Materials*, 2020, **13**, no. 24, 1–34. doi: [10.3390/ma13245656](https://doi.org/10.3390/ma13245656)
 10. A. Çalik, Effect of cooling rate on hardness and microstructure of AISI 1020, AISI 1040, and AISI 1060 Steels, *Int. J. Phys. Sci.*, 2009, **4**, no. 9, 514–518.
 11. M.A. Hafeez, A. Inam and A. Farooq, Mechanical and corrosion properties of medium carbon low alloy steel after cyclic quenching and tempering heat-treatments, *Mater. Res. Express*, 2020, **7**, no. 1, 0–12. doi: [10.1088/2053-1591/ab6581](https://doi.org/10.1088/2053-1591/ab6581)
 12. H.E. Townsend, Effects of alloying elements on the corrosion of steel in industrial atmospheres, *Corrosion*, 2001, **57**, no. 6, 497–501. doi: [10.5006/1.3290374](https://doi.org/10.5006/1.3290374)
 13. Y. Hyun, and H. Kim, Effects of alloying elements (Cr, Mn) on corrosion properties of carbon steel in synthetic seawater, *J. Korean Inst. Metals Mater.*, 2016, **54**, no. 2, 68–78. doi: [10.3365/KJMM.2016.54.2.68](https://doi.org/10.3365/KJMM.2016.54.2.68)
 14. M. Taghavikish, N.K. Dutta and N.R. Choudhury, Emerging Corrosion Inhibitors for Interfacial Coating, *Coatings*, 2017, **7**, no. 12, 217. doi: [10.3390/coatings7120217](https://doi.org/10.3390/coatings7120217)
 15. B.N. Popov, Electrochemical Kinetics of Corrosion, *Corrosion Engineering*, Ch. 3, 2015. doi: [10.1016/b978-0-444-62722-3.00003-3](https://doi.org/10.1016/b978-0-444-62722-3.00003-3)
 16. O. Gomez, H. Aponte, E. Vera and Y. Pineda, Evaluation of Corrosion inhibitor simulating Conditions of Operation, *J. Phys. Conf. Ser.*, 2017, **935**. doi: [10.1088/1742-6596/935/1/012060](https://doi.org/10.1088/1742-6596/935/1/012060)
 17. P. Refait, A.M. Grolleau, M. Jeannin, C. Rémazeilles and R. Sabot, Corrosion of Carbon Steel in Marine Environments: Role of the Corrosion Product Layer, *Corros. Mater. Degrad.*, 2020, **1**, no. 1, 198–218. doi: [10.3390/cmd1010010](https://doi.org/10.3390/cmd1010010)
 18. W.B. Wan Nik, H.M. Hajar, M.J. Suriani, M.G.M. Sabri and M.J. Ghazali, Development of anti-corrosive paint incorporated with henna extract as a natural inhibitor, *J. Mech. Eng. Sci.*, 2017, **11**, no. 4, 3179–3188. doi: [10.15282/jmes.11.4.2017.20.0286](https://doi.org/10.15282/jmes.11.4.2017.20.0286)
 19. O. Oudbashi, S.M. Emami, H. Ahmadi and P. Davami, Micro-stratigraphical investigation on corrosion layers in ancient Bronze artefacts by scanning electron microscopy energy dispersive spectrometry and optical microscopy, *Heritage Sci.*, 2013, **1**, no. 1, 1–10. doi: [10.1186/2050-7445-1-21](https://doi.org/10.1186/2050-7445-1-21)
 20. X. Yan, W. Di, T. Yingfeng, H. Minqiu and S. Hai, Experimental studies on mechanical properties of corroded steel bars after elevated temperature, *Procedia Eng.*, 2017, **210**, 622–629. doi: [10.1016/j.proeng.2017.11.122](https://doi.org/10.1016/j.proeng.2017.11.122)

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21. S. Karthick, S. Muralidharan and V. Saraswathy, Corrosion performance of mild steel and galvanized iron in clay soil environment, *Arabian J. Chem.*, 2020, **13**, no. 1, 3301–3318. doi: [10.1016/j.arabjc.2018.11.005](https://doi.org/10.1016/j.arabjc.2018.11.005)
 22. K. Tamalmani and H. Husin, Review on corrosion inhibitors for oil and gas corrosion issues, *Appl. Sci.*, 2020, **10**, no. 10. doi: [10.3390/APP10103389](https://doi.org/10.3390/APP10103389)