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Corrosion Inhibition Effect of the Essential Oil of Dried and Fresh Crystal Seedless Guava Leaves (*Psidium guajava*) in Acid Medium

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Abstract

This research studied the corrosion inhibition activities of the essential oil of crystal seedless guava leaves (*Psidium guajava*) in an acid medium. The essential oil (EO) was extracted from the different treatments of raw materials (fresh and dried leaves) using the microwave hydrodistillation method with a power of 600 Watt. Water was used as the solvent, with the ratio of feed to solvent (w/v) 1:7. The extraction duration was over 3 hours. The extraction process was done at atmospheric pressure and 100°C. Different raw material treatments result in different yields, where the highest yield was obtained from the dried leave, with the value reaching 1.08%. The essential oil chemical compound was determined by GC-MS analysis. The main component obtained were caryophyllene (44.98%) and Caryophyllene oxide (14.96%). The essential oil was applied as a corrosion inhibitor for carbon steel in a 1 M Hydrochloric acid (HCl) medium. The inhibition efficiency (IE) was 67% at a concentration of 0.3g/L, while the fresh leaves essential oil was only 63%. The dried leave EO performs a higher anti-corrosion effect than the fresh leaves EO. These results show crystal seedless guava leaves' essential oil has anti-corrosion activities on carbon steel in an acid medium.

Keywords: *Psidium guajava*, essential oil, extraction, microwave hydrodistillation, corrosion inhibitor

1. Introduction

Carbon steel is widely used in industry due to its low cost and mechanical strength. Carbon steel has a high carbon content of about 0.2–2.1%, manganese (1.65%), copper (0.6%), and silicon (0.6%). [1]. However, carbon steel is highly reactive and undergoes corrosion when exposed to an acidic environment [2].

Corrosion is the metal degradation because of the electrochemical reaction between the metal and the environtment[3]. Corrosion is a spontaneous process that happens naturally. Many efforts have been made to prevent carbon steel corrosion due to acid environments. One of them is by adding corrosion inhibitors. Corrosion inhibitors are compounds that, when added in small concentrations to a corrosive media, decrease or prevent the reaction of the metal with the media [4]. Important corrosion inhibitors addition applications are acid pickling, industrial acid cleaning, acid descaling, and oil well acidizing [5]. Most corrosion inhibitors contain toxic components that are dangerous to the environment [1], so organic corrosion inhibitors become interesting to be investigated due to their environmental friendly.

On the other hand, the essential oil is an excellent and eco-friendly inhibitor under diverse corrosive environments and biofilms for most metals. Essential oils are liquids extracted from plants consisting of volatile aroma compounds. Some techniques to extract the oil from the plants are distillation, solvent extraction, oil extraction, etc. Previous research has studied the comparison of some essential oil extraction techniques. Ranging from convention methods of hydrodistillation (HD), steam distillation (SD), turbohydrodistillation (THD) to innovative techniques, such as ultrasound-assisted extraction (US-SD) and microwave-assisted extraction techniques. The result found that the best result was the microwave hydro diffusion and gravity (MHG) method[6]. The same result was investigated by Moradi et.al. They found that the Microwave hydrodistillation was superior in saving energy and extraction time to traditional distillation[7].

The application of essential oils from many sources as corrosion inhibitors has been investigated. *Artemisia herba alba* has an inhibitor efficiency of 74% when applied on steel in 0.5 M H_2SO_4 medium[8], *Atlas cedar* essential oil inhibits the corrosion of steel in 1 M HCl with an efficiency of 88% [9], *Salvia aucheri mesatlantica* showed the inhibitor efficiency 86.12% for the corrosion of steel in 0.5 M H_2SO_4[10], *Eucalyptus globulus* essential oil has been applied for C38 steel in 0.5 M Sulfuric Acid Solution and gave inhibition efficiency 81% [11], Application *Mentha Spicata* essential oil on the Corrosion of Steel in 1 M Hydrochloric Acid found the inhibition efficiency reach 97%[12].

Essential oil from *Psidium guajava's* leaves is one potential resource for corrosion inhibitors. It is because crystal guava plants are easy to grow in tropical areas. Indonesia has many Crystal guava plantations. So far, people take advantage only of the fruit, while the crystal guava leaves are only utilized as functional food, such as tea and diarrhea medicine. Generally, the leaves are discarded and do not utilize optimally.

The composition of oil contained in guava leaves include iso-caryophyllene (33.53%), veridiflorene (13.00%), farnesene (11.65%), dlimonene (9.84%), decadinene (1.75%), a-copaene (2.80%), a-humulene (3.74%), and scadinol (0.08%) [13]

Previous investigations about the potential use of the Crystal guava's leave for corrosion inhibitors have been done by Hartanto et al. (2018). The extraction process was done by using the maceration technique. The *Psidium guajava* leaves extract was applied as a corrosion inhibitor for stainless steel in a 3% NaCl medium. The inhibition efficiency obtained was 37.93% by inhibitor concentration of 1000 ppm[14].

Since the chemical composition of *Psidium guajava* leaves essential oil has potential use as a corrosion inhibitor, this research aims to extract the essential oil of *Psidium guajava* leaves and study its potential as a corrosion inhibitor for carbon steel in dilute Hydrochloric Acid solution.

2. Material and Method

2.1. Material

The raw material used in this study was crystal guava leaves obtained from Prambon District, Sidoarjo, East Java. The leaves were taken from the waste of cutting stalk. The raw material was prepared in two conditions: fresh and dried leaves. The Fresh leaves are leaves that have just been cut from the tree, while the dried leaves are leaves that have been dried. The drying process was done using a box dryer at 50 ^oC for 4 hours. Crystal seedless guava leaves (fresh and dried) are then reduced to ± 1 cm in size. Another material used in this experiment is demineralized water as the solvent.

The specimen for corrosion rate analysis was carbon steel with iron and carbon composition. A specimen was cut at 10×10×3 mm. One side of this specimen was connected to a copper wire covered with a plastic tube to avoid contact with the environment. The specimens were polished using emery paper of grades 1000. Then, specimens were washed with demineralized water and acetone. An aggressive solution of 1 M HCl was prepared by diluting 98% HCl using demineralized water.

2.2. Equipment

The main equipment used in this study was a microwave as a heater equipped with a *clevenger-type* apparatus. The additional equipment parts are a condenser, regulator, and temperature indicator. The main tools consist of a 100 ml distiller flask and a microwave that has been installed with a power regulator (the lowest microwave power is 150 Watt and the highest power is 600 Watt). It has a 2450 MHz frequency. The microwave is equipped with a time controller. The supporting equipment includes (1)Clevenger, (2) reflux condenser, (3)condenser, (4)temperature regulator and indicator, and (5)essential oil product reservoir. The design of this research tool is adopted from previous research tools conducted by Pujiastuti et al., as shown in figure 1 [15]

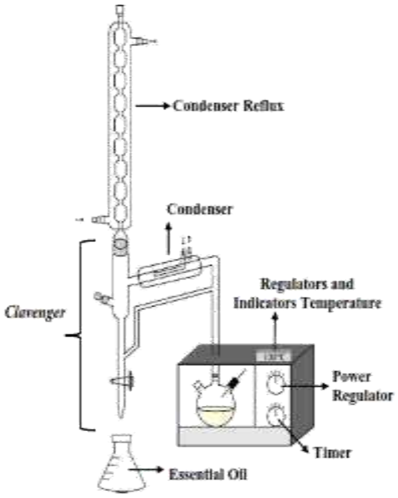

Figure 1 Schematic of the Research Tool for Extracting Essential Oil from Crystal Seedless Guava Leaves Using the Microwave Hydrodistillation Method

2.3. Research Methods

Psidium guajava leave extraction

The method in this research is essential oil extraction using the microwave hydrodistillation (MHD) process. Firstly, weighted 50-gram crystal seedless guava leaves that have been prepared before and put into a flask. Secondly, add the demineralized water into the flask with a ratio of feed to solvent (w/v) 1:7. The next step is to put the flask into a microwave equipped with a thermocouple and temperature control. Turn on the microwave to start the extraction process for 3 hours. The operating condition was set at atmospheric pressure and temperature of ± 100 ^{o}C, with a microwave power of 600 Watt.

A condenser was used to condense the vapour phase into a liquid phase. At the same time, clavenger recycled water condensates into the distillation flask to keep the ratio of the material to the solvent. It prevents the distillation flask run out of solvent. After 3 hours, the distillate was taken and separated between the solvent and the extracted oil. The oil is then stored in sealed glass vials at 4^{o}C for later analysis. This method was based on the best condition from the previous study by Erliyanti et al. [16]

Physical properties Analysis

The essential oils have been analyzed in the yield, density and refractive index. To determine the yield, firstly weighed the *Psidium guajava* leave before extraction m_a. Secondly, weighted the essential oil that was obtained from the extraction process m_b. Thirdly calculate the yield by using the following equation

$$\text{yield} = \frac{\text{weight of collected oil}}{\text{dry weight initial leave}} \text{x}100\%$$

The Refractive index was measured by using a refractometer. Calibrate the refractometer by using demineralized water. The water temperature should be no more than 20^{o}C. Put the oil in the sample area and wait until the oil temperature is stable. The reading was done by seeing the scale from the eyepiece part of the refractometer

The essential oil density has been determined using a 5 ml pycnometer at 25^{o}C. the density calculate simply using the equation

$$\rho = \frac{m_{picno+oil} - m_{picno}}{V_{picno}}$$

Where, $m = mass\ (gram), V = volume\ (ml)$

Chemical properties Analysis

GC-MS analysis was carried out in an ISQ 7000 mass spectrometer (Thermo Scientific, USA) with AEI (advance electron ionization) source. The samples were prepared by dissolving 50 µL in a 1 mL final volume of methanol, then injected 1 µL of solution into a column (TG-SQC GC, 15 m x 0.25 mm x 0.25 µm) with AS 1310 autosampler injection system (Thermo Scientific, USA). Helium gas was used as the carrier at a 1 mL/min constant flow rate. The injector temperature and MS transfer line temperature were 200 ^{o}C. The GC-MS analysys was taken at Instrument laboratory, University of Pembangunan Nasional Veteran jawa Timur.

Electrochemical Measurement

Electrochemical measurement was used to determine the corrosion rate of the steel before and after adding the inhibitor. The electrochemical measurements were carried out using a three-electrode setup comprised of an electrode (graphite rod), a working electrode (carbon steel), and a reference electrode (saturated calomel electrode). The Working electrode (carbon stell specimen) surface area was prepared as described in the material and method section.

The sample surface area was covered by resin on the backside. Then, it was dipped in the corrosion solution. The scan rate was applied at 0.1mV/s for testing polarization. The time limit for reaching equilibrium potential before the electrochemical measurement was 30 minutes.

3. Results and Discussion

3.1 Physical Properties Study

The current investigation extracted essential oil from Psidium Guajava leaves from fresh and dried leaves. The microwave hydrodistillation process was chosen to extract the essential oil from Psidium guajava leaves for high-yield purposes. The microwave power was set at 600 watts, and the extraction duration was three hours. The ratio of raw material to the solvent was 1:7 (w/v). The essential oil extract from both fresh and dried *Psidium guajava* leaves was determined by their physical properties, such as density and refractive index—the result is shown in table 1.

Table 1 The physical properties of essential oil from fresh and dried *Psidium guajava* leaves

Treatment of leaves	Yield (%)	Density (gram/ml)	Refractive index
Fresh	0.89	0.763	1.47268
Dried	1.08	0.949	1.49862

Data in table 1 show that the different raw material conditions significantly differ the yield. The dried leaves resulted in a higher yield than the fresh leaves. The drying process of the raw materials helped the essential oil gland open easily because of the heat from the oven. It made the essential oil extracted more rapidly than the fresh leaves [17]. The power of the microwave of 600 watts helped the extraction process effectively. The high power of microwave increases the extraction temperature and increases the evaporation rate, so the essenteial oil's solvent evaporates and separates from the oil. The microwave's high power also transfers the high energy to the material and converts it to the high temperatur, resulting in a higher yield of the essential oil. The less solvent in the essential oil from the Psidium guajava leaves increases the oil's density. The product was also denser and more clear. The higher the evaporation rate, the essential the oil component to be extracted and the higher the molecular weight of the essential oil. The essential oil molecular weight influences their density. The higher the molecular weight of the essential oil, the higher the density [18]

The raw material condition did not significantly influence the refractive index of the extracted essential oil. The refractive index of the essential oil is in the range of 1,8-1,5. From our research, the best yield, the density and the refractive index value obtained during the extraction process of the dried seedless guava, i.e., 1,085, 0.949 gr/ml, and 1.498, respectively.

3.2 Chemical Study

The effect of the *Psidium guajava* leaves raw material condition before extraction to the chemical compound of the essential oil determined by *Gas Chromatography-Mass Spectroscopy)* GC-MS analysis. The chemical compound analysis was done by MS quantitative method. The raw material condition, both the fresh and dried leaves, are presented in table 2.

Table 2 Chemical composition of fresh and dried crystal seedless guava leaves essential oils

NO	compound	Essential oil `(%)	
		Fresh leave	Dried leave
1	Copaene	2.91	3.83
2	Caryophyllene	19.62	44.98
3	Caryophyllene oxide	-	14.96
4	Caryophylla-4(12),8(13)-dien-5a-ol	13.95	-
5	Aromandrendene	-	3.97
6	Isoaromadendrene epoxide	4.66	-
7	Humulene	-	5.10
8	Tumerone	5.22	-
9	1,3,6,10-Dodecatetraene, 3,7,11-trimethyl-, (Z,E)	-	9.16
10	(-)-Globulol	16.49	-

Table 2 shows that the raw material condition influenced the chemical compound of the essential oil. The dried leaves resulted in the *caryophyllene* more than the fresh leaves. *Caryophyllene* is the essential oil compound in the essential oil from *Psidium guajava* leaves. The dried leaves contain 44,98% Caryophyllene, higher than that contained in the essential oil from the fresh leaves. The highest Caryophyllene compound resulted from the extraction of the dried Psidium Guajava leaves at the power of 600 watts, and the ratio of the leaves to the solvent is 1:7 (w/v). it has a good agreement with the previous research that was done by Weli et al. in 2019, where the extraction of the essential oil from Psidium guajava leaves with the conventional method resulted in the essential oil with the compound of Caryophyllene 33,53% [19]

3.3 Electrochemical Study

The efficiency of the guava leaves essential oil as a corrosion inhibitor was evaluated by the polarization curve technique. The anodic and cathodic polarization curve of the carbon steel electrode in an acid medium with the presence of different raw material treatments (fresh leave and dried leave) at 25°C was shown in Fig. 2

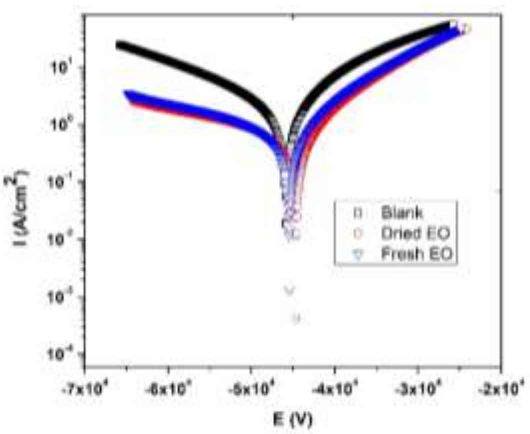

Figure 2 polarization plots of carbon steel in 1M HCl in absence and presence the esential oil from different raw material treatment (fresh and dried psidium guajava leave)

The polarization curves are extrapolated to find the intersection point between potential anodic and potential cathodic. From the intersection curve resulting ordinate corrosion current, I_{corr}, corrosion potential, E_{corr}, Tafel constant anodic (b_a) and Tafel's constant cathodic (b_c). The anodic constant (b_a) value is attributed to metal dissolution and adsorption of the inhibitor at anodic potentials, whereas the cathodic constant (b_c) is related to hydrogen evolution at cathodic potentials [20]. I_{corr} data were used to calculate the inhibition efficiency (IE) by using the following equations

$$EI\ (\%) = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}} x100 \qquad (1)$$

where I_{corr} is the corrosion current at a particular essential oil concentration in the solution, and I^0_{corr} the corrosion current density in the absence of an inhibitor.

The value of corrosion potential (E_{corr}), cathodic Tafel slope (b_c), anodic Tafel slope (b_a), Corrosion Rate (CR) and inhibition efficiency (IE(%)) are shown in Table 3.

Table 3 Electrochemical parameters and the corresponding corrosion inhibition efficiencies for the corrosion of carbon steel in 1 M HCl containing psidium guajava leave essential oil

	$-E_{corr}$	b_c (mV)	b_a (mV)	I_{corr} (A/cm^2)	CR (mm/y)	EI (%)
Blank	0.45847	231.28	149.33	3.094×10^{-5}	0.359	
Dried leave EO	0.44646	586.41	117.29	1.007×10^{-5}	0.117	0.67
Fresh leave EO	0.45445	446.58	121.73	1.105×10^{-5}	0.128	0.64

From the result shown in Table 3, we can deduce that after adding the essential oil to the 1 M HCl solution, the carbon steel electrode was inhibited both in cathodic and anodic. It is seen in the decrease of the corrosion rate from 0.359 mm/y to 0.117 mm/y for dried leave EO and 0.128 mm/y for fresh leave EO. The EO protected the carbon steel from corrosion by adsorption its chemical constituent on the carbon steel surface [21]. The presence of essential oil in the solution reduces the hydrogen ion at the cathode and the dissolution reaction at the anode (carbon steel) [22]. The EO from dried leave also showed a slightly more efficient than the fresh leave EO. It may seem because of the different physical properties, where the dried leave EO has a higher density than the fresh leave EO. This result also showed that the *Psidium guajava* essential oil has a higher inhibitory effect than their extract, which was only 37.93%[14]

4. Conclusions

This research concluded that the treatment of raw materials Psidium guajava leaves significantly affects the yield and density of essential oils but did not significantly affect the refractive index. The dried leaves showed better physical properties performance than the fresh leave. The essential oils obtained from both raw material treatments can be applied as a corrosion inhibitor for carbon steel in an HCl 1 M medium. The inhibition efficiency for dried leave EO and fresh leave EO is 67% and 64%, respectively.

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References

[1] N. I. H. Salleh dan A. Abdullah, "Corrosion Inhibition of Carbon Steel Using Palm Oil Leaves Extract," *Indones. J. Chem.*

[2] C. Verma, A. M. Kumar, M. A. J. Mazumder, dan M. A. Quraishi, "Chitosan-Based Green and Sustainable Corrosion Inhibitors for Carbon Steel," *Chitin-Chitosan - Myriad Funct. Sci. Technol.*, 2018, doi: 10.5772/intechopen.74989.

[3] D. Priest, "Measuring corrosion rates fast," *Chem. Eng.*, vol. 99, no. 11, hal. 169, 1992.

[4] K. El Mouaden *dkk.*, "Chitosan polymer as a green corrosion inhibitor for copper in sulfide-containing synthetic seawater," *Int. J. Biol. Macromol.*, vol. 119, hal. 1311–1323, 2018.

[5] K. F. Khaled dan N. Hackerman, "Investigation of the inhibitive effect of ortho-substituted anilines on corrosion of iron in 1 M HCl solutions," *Electrochim. Acta*, vol. 48, no. 19, hal. 2715–2723, 2003, doi: 10.1016/S0013-4686(03)00318-9.

[6] S. Périno-Issartier, C. Ginies, G. Cravotto, dan F. Chemat, "A comparison of essential oils obtained from lavandin via different extraction processes: Ultrasound, microwave, turbohydrodistillation, steam and hydrodistillation," *J. Chromatogr. A*, vol. 1305, hal. 41–47, 2013, doi: 10.1016/j.chroma.2013.07.024.

[7] S. Moradi, A. Fazlali, dan H. Hamedi, "Microwave-assisted hydro-distillation of essential oil from rosemary: Comparison with traditional distillation," *Avicenna J. Med. Biotechnol.*, vol. 10, no. 1, hal. 22, 2018.

[8] O. Ouachikh *dkk.*, "Application of essential oil of Artemisia herba alba as green corrosion inhibitor for steel in 0.5 M H2SO4," *Surf. Rev. Lett.*, vol. 16, no. 1, hal. 49–54, 2009, doi: 10.1142/S0218625X09012287.

[9] R. Idouhli, A. Oukhrib, Y. Koumya, A. Abouelfida, A. Benyaich, dan A. Benharref, "Inhibitory effect of Atlas cedar essential oil on the corrosion of steel in 1 m HCl," *Corros. Rev.*, vol. 36, no. 4, hal. 373–384, 2018, doi: 10.1515/correv-2017-0076.

[10] M. Znini *dkk.*, "Essential oil of Salvia aucheri mesatlantica as a green inhibitor for the corrosion of steel in 0.5M H 2SO 4," *Arab. J. Chem.*, vol. 5, no. 4, hal. 467–474, 2012, doi: 10.1016/j.arabjc.2010.09.017.

[11] S. Rekkab *dkk.*, "Green corrosion inhibitor from essential oil of eucalyptus globulus (Myrtaceae) for C38 steel in sulfuric acid solution,"*J. Mater. Environ. Sci.*, vol. 3, no. 4, hal. 613–627, 2012.

[12] M. Znini *dkk.*, "Chemical composition and inhibitory effect of Mentha spicata essential oil on the corrosion of steel in molar hydrochloric acid," *Int. J. Electrochem. Sci.*, vol. 6, no. 3, hal. 691–704, 2011.

[13] A. Weli, A. Al-Kaabi, J. Al-Sabahi, S. Said, M. A. Hossain, dan S. Al-Riyami, "Chemical composition and biological activities of the essential oils of Psidium guajava leaf," *J. King Saud Univ.*, vol. 31, no. 4, hal. 993–998, 2019.

[14] S. Hartanto, "Ekstrak Daun Jambu Biji (Psidium guajava, Linn.) Sebagai Inhibitor Korosi Pada Baja Dalam Media 3% NaCl.," *J. Tek. Mesin ITI*, vol. 2, no. 1, hal. 7–11, 2018, doi: 10.31543/jtm.v2i1.60.

[15] C. Pujiastuti, N. K. Erliyanti, dan A. D. Priyanto, "Effect of Power and Feed to Solvent Ratio Toward Yield of Essential Oil from Crystal Guava Leaves (Psidium guajava) Using Microwave Hydroditillation," *Nusant. Sci. Technol. Proc.*, hal. 358–363, 2018.

[16] A. D. Priyanto, N. K. Erliyanti, dan C. Pujiastuti, "The effect of microwave power and feed to solvent ratio on antioxidant activity and volatile compounds profile of crystal seedless guava leaves essential oils extracted using microwave-assisted hydrodistillation," *IOP Conf. Ser. Earth Environ. Sci.*, vol. 733, no. 1, 2021, doi: 10.1088/1755-1315/733/1/012097.

[17] N. K. Erliyanti, A. D. Priyanto, dan C. Pujiastuti, "Karakteristik Densitas Dan Indeks Bias Minyak Atsiri Daun Jambu

Kristal (Psidium Guajava) Menggunakan Metode Microwave Hydrodistillation Dengan Variabel Daya Dan Rasio Bahan: Pelarut," *Rekayasa Mesin*, vol. 11, no. 2, hal. 247–255, 2020.

[18] L. Pratiwi, M. S. Rachman, dan N. Hidayati, "Ektraksi minyak atsiri dari bunga cengkeh dengan pelarut etanol dan N-Heksana," 2016.

[19] A. Weli, A. Al-Kaabi, J. Al-Sabahi, S. Said, M. A. Hossain, dan S. Al-Riyami, "Chemical composition and biological activities of the essential oils of Psidium guajava leaf," *J. King Saud Univ. - Sci.*, vol. 31, no. 4, hal. 993–998, 2019, doi: 10.1016/j.jksus.2018.07.021.

[20] G. Ji, S. K. Shukla, P. Dwivedi, S. Sundaram, E. E. Ebenso, dan R. Prakash, "Green Capsicum annuum fruit extract for inhibition of mild steel corrosion in hydrochloric acid solution," *Int. J. Electrochem. Sci.*, vol. 7, no. 12, hal. 12146–12158, 2012.

[21] H. E. Megahed, M. Sobhi, dan S. Nour, "Celery (Apium graveolens) Extract as Corrosion Inhibitor for carbon steel in 1 M HCl," *J. Basic Environ. Sci.*, vol. 4, hal. 170–177, 2017, [Daring]. Tersedia pada: http://jbesci.org/published/4.2.6.pdf.

[22] R. T. Loto, E. H. Mbah, dan J. I. Ugada, "Corrosion inhibition effect of citrus sinensis essential oil extract on plain carbon steel in dilute acid media," *South African J. Chem. Eng.*, vol. 35, no. August 2020, hal. 159–164, 2021, doi: 10.1016/j.sajce.2020.08.004.