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Effect of Concentration Variation of Cacao Leaf Extract (*Theobroma cacao.*) Inhibitor on the Corrosion Rate of ST 37 Steel in 3% HCl Solution

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Abstract

The effectiveness of cacao leaf extract (Theobroma Cacao.) used as an inhibitor on St 37 steel sample. Which cures in HCl 3 % Corrosive Medium for 144 hours, the inhibitor concentration variation added 0 %, 3%, 6 %, 9 %, and 12 %, respectively. The sample rate is measured by using the loose-weight method. The results show that the lowest sample is 1.397 mm/y of 12%, and the highest is 3.694 mm/y of 0 %. Inhibitor efficiency to the sample St 37 Stainless steel portrays adequate progress to 62.66% with 12% concentration. X-Ray Diffraction Results acquired BCC with Fe-a phase along with SEM that forms an agglomeration, cracked, and holes which result in its corrosion. In addition, EDS contains FeO Element, which indicates that stainless is still affected by corrosion and the reduced FeO content in the sample was less. Thus three samples characterized and measured show that avocado leaves effectively as an inhibitor to the sample St 37 in HCl 3% corrosive medium.

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Abstrak

Efektifitas ekstrak daun kakao (Theobroma cacao.) yang digunakan sebagai inhibitor pada sampel baja St37. Perendaman sampel baja dilakukan dalam medium korosif HCl 3 % selama 144 jam dengan variasi konsentrasi inhibitor 0%, 3%, 6%, 9%, dan 12%. Laju korosi dihitung dengan menggunakan metode kehilangan massa. Diperoleh hasil perhitungan laju korosi terendah pada sampel baja St37 dengan konsentrasi 12 % sebesar 1,379 mmpy dan laju korosi tertinggi pada sampel baja St37 dengan konsentrasi 0 % sebesar 3,694 mmpy. Efisiensi inhibitor paling optimum pada sampel baja St37 dengan inhibitor 12 % sebesar 62,66 %. Hasil karakterisasi XRD menunjukkan bahwa struktur kristal yang terbentuk merupakan BCC dengan fasa Fe-a Karakterisasi SEM menunjukkan morfologi permukaan sampel adanya gumpalan, retakan serta lubang yang merupakan produk korosi. Karakterisasi EDS pada sampel baja terdapat unsur FeO yang mengindikasikan bahwa sampel baja telah terkorosi, terlihat dari pengurangan kadar FeO dalam sampel lebih sedikit. Dari ketiga hasil karakterisasi dan perhitungan laju korosi menunjukkan bahwa ekstrak daun kakao efektif sebagai inhibitor pada baja St37 dalam medium korosif HCl 3 %.

1. Introduction

The use of steel as a material has a weakness, namely, carbon steel is not resistant to corrosion. Chemical properties such as temperature and pH also affect the corrosion rate. Corrosion (corrosion) comes from the Latin word *corrodere*, which means the destruction of metal or rust. Corrosion is a process of material degradation or loss in quality and quantity.

Several methods can be used to control and protect steel against corrosion, namely material selection based on its corrosion resistance in the working environment, coating, which limits the surface with the environment, cathodic protection, application of direct current (DC) from external sources to protect the metal from corrosion attack, and

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using inhibitors which are substances that can change the work environment both continuously and periodically (Baldenebro et al., 2015).

Using inhibitors is one of the most effective ways to prevent corrosion because the cost is relatively cheap, and the process is simple. In general, corrosion inhibitors come from synthetic chemicals, which are dangerous, relatively expensive, and not environmentally friendly (Ludiana & Handani, 2012). One of the organic materials used as a corrosion inhibitor is cocoa leaves (Apriyanto et al., 2018). Apart from being cheap and abundant in Indonesia, the high tannin content in cocoa leaves makes it potentially used to inhibit the corrosion rate of metals. The tannin content in cocoa leaves is 19.0 - 28.4% (Ratnaningrum, 2018).

Pariyanto et al. conducted research using cocoa leaves with 3% H2SO4 and 3% Na2SO4 medium. The study results showed that cocoa leaf extract inhibitors efficiently controlled the corrosion rate in a 3% H2SO4 medium of 63.89% and 56.61% of 3% Na2SO4 (Sri Pratiwi Ratnaningrum, 2018). In addition, Ludiana utilized tea leaf extract (*Camellia sinensis*) as an inhibitor against the corrosion rate of Schedule 40 Grade B ERW carbon steel using a 3% NaCl corrosive medium (Ludiana & Handani, 2012). This study found that the highest inhibition efficiency was obtained when the inhibitor concentration was 4% in immersion for three or six days.

2. Research Methods

The tools used in this study were grinding machines, rotary evaporators, spatulas, pipettes, aluminum foil, calipers, Erlenmeyer, tissues, funnels, digital balances, steel cutting tools, chainsaws, measuring cups, threads, small wood, sandpaper, small plastic, desiccator, SEM, XRD, EDS. While the materials used in this study were: carbon steel cocoa leaves St 37, hydrochloric acid (HCl), 96% ethanol, and distilled water.

The research work procedure was divided into three stages. The first was making steel samples and then carrying out experimental procedures to see the corrosion rate of the steel that had been prepared (Okafor, PC, 2008). The following is an experimental procedure to see the corrosion rate of steel prepared with cocoa leaf inhibitors, as seen in **Figure 1**.

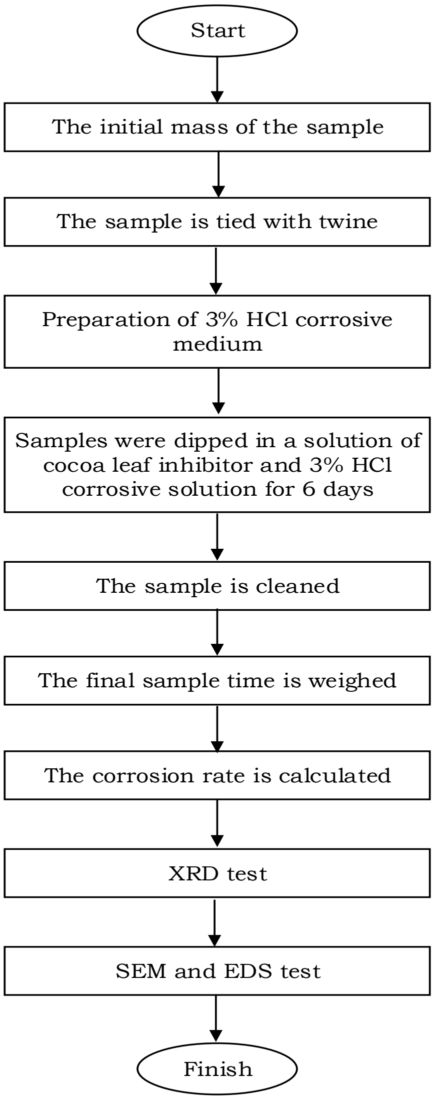

Figure 1. Research flow chart and sample characterization.

3. Results and Discussions

Effect of Inhibitor Concentration on Corrosion Rate and Efficiency

Table 1. Measurement results of St 37 carbon steel in 3% HCl corrosive medium.

Sample	*p* (cm)	*l* (cm)	*t* (cm)	*A* (cm^2)	*The Initial mass* (gr)	*The Final mass* (gr)	*Δm* (gr)
St37-6-0	2.02	2.03	1.24	18.772	30.183	29.288	0.895
St37-6-3	2.02	2.04	1.07	18.022	31.168	30.558	0.610
St37-6-6	2.12	2.02	1.02	18.040	31.982	31.408	0.574
St37-6-9	2.14	2.01	1.04	18.379	30.561	30.009	0.552
St37-6-12	2.19	2.02	1.05	18.756	31.035	30.701	0.334

From the data in **Table 1**, the corrosion rate and efficiency of low-carbon steel St 37 were calculated in a corrosive HCl environment without and with cocoa leaf inhibitors of various concentrations (Giri et al., 2017).

Corrosion Rate and Efficiency Calculation Results

Table 2 Corrosion rate of St 37 carbon steel.

Sample	corrosion rate (mmpy)
St37-6-0	3.694
St37-6-3	2.623
St37-6-6	2.465
St37-6-9	2.326
St37-6-12	1.379

Based on **Table 2**, the corrosion rate in the HCl environment without and with inhibitors is 3% (St37-6-3), 6% (St37-6-6), 9% (St37-6-9), and 12% (St37-6- 12). The greater the cocoa leaf extract inhibitor concentration used, the lower the corrosion rate in the HCl solution.

The relationship between inhibitor concentration and soaking time on the efficiency of cocoa leaf extract inhibitors is shown in **Table 3** below.

Table 3. Calculation of the inhibitor efficiency of cocoa leaf extract (*Theobroma cacao.*)

Sample	corrosion rate (mmpy)
St37-6-0	0
St37-6-3	28.99
St37-6-6	33.27
St37-6-9	37.03
St37-6-12	62.66

XRD (X-Ray Diffraction) Characterization Results

The results of the diffractogram for the two samples are shown in **Figure 4**.

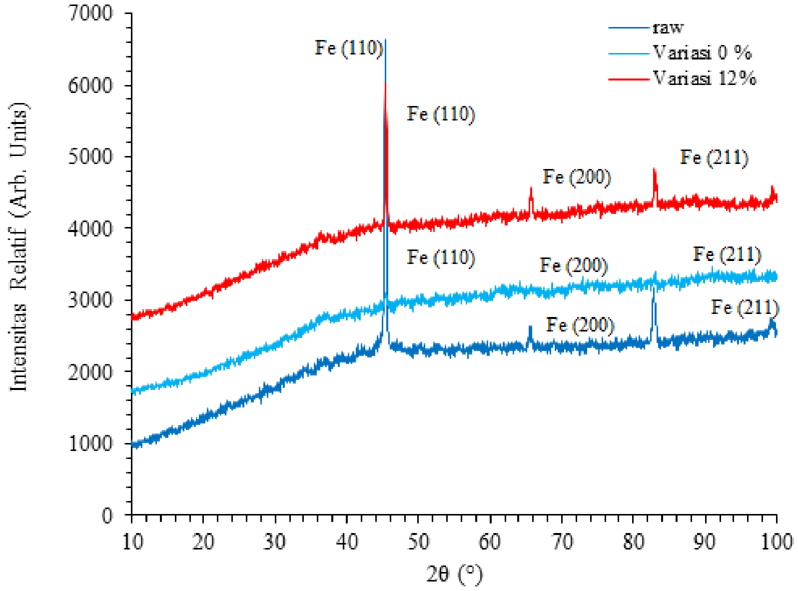

Figure 2. Results of X-ray diffraction analysis of St37 steel samples.

Figure 2 is a diffractogram for raw samples, 0% inhibitor and 12% inhibitor, with a wavelength of 1.54056 Å. From the XRD results, three sharp peaks indicate the formation of a crystalline phase.

Search match analysis results for the three samples. The Fe (iron) phase was obtained with PCPDFWIN data 06-0696. A comparison between the results of the sample study without inhibitors and the PCPDFWIN program is shown in **Table 4** and **Figure 3.**

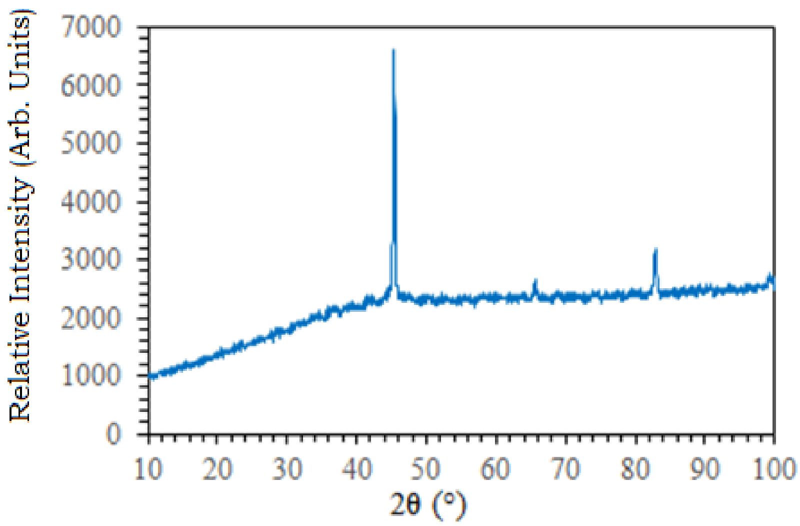

Figure 3. Diphragtogram on RAW St37 steel.

Table 4. Comparison of RAW steel research results with PCPDFWIN data

Research			PCPDFWIN's Data No 06-0696			$\Delta 2\vartheta$	Δd (Å)	Phase	Field
2ϑ	*d* (Å)	*Int* (%)	2ϑ	*d* (Å)	*Int* (%)				Hkl
45.14	2.00	100	44.67	2.02	100	0.471	0.02	Fe-α	110
65.75	1.41	13.5	65.02	1.43	20.0	0.734	0.01	Fe-α	200
83.34	1.15	24.2	82.33	1.17	30.0	1.007	0.01	Fe-α	211

In **Table 4**, there are three peaks with hkl, including (110), (200), and (211). The highest peak is at 45.145° with 100% intensity. This peak indicates the occurrence of a crystalline phase because the difference between the planes (d) and the value of 2ϑ is minimal, so it can be ascertained that this peak is the iron phase Fe-α (ferrite).

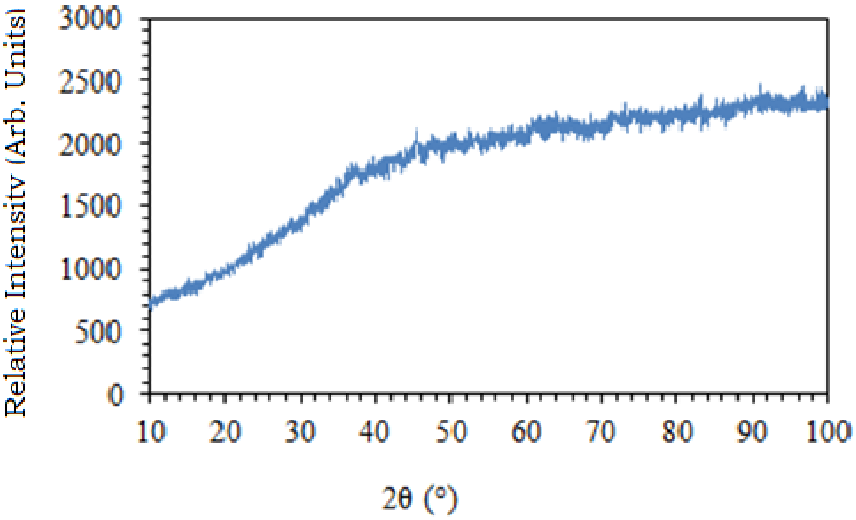

Figure 4. Diphragtogram on St37 steel with 0% inhibitor

In **Table 5**, there are three peaks with hkl, including (110), (200), and (211). The highest peak is at 45.354° with 100% intensity. This peak indicates the occurrence of a crystalline phase because the difference between the planes (d) and the value of *2θ* is minimal, so it can be ascertained that this peak is the iron phase Fe-α (ferrite).

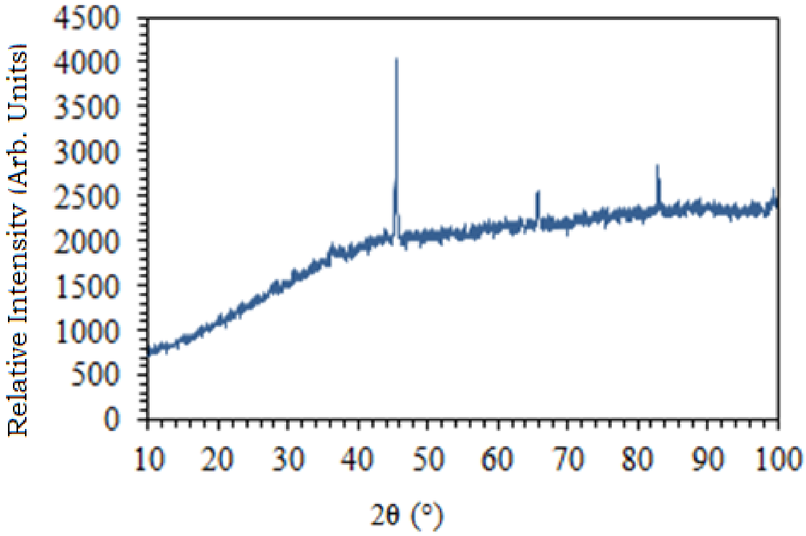

Figure 5 Diphragtogram on St 37 steel with 12% inhibitor.

Table 5. Comparison of research results with 0% inhibitors using PCPDFWIN data.

Research			PCPDFWIN's Data No 06-0696			Δ2θ	Δd (Å)	Phase	Field
2θ	*d* (Å)	*Int* (%)	*2θ*	*d* (Å)	*Int* (%)				Hkl
45.35	1.99	100	44.67	2.02	100	0.68	0.02	Fe-α	110
66.00	1.41	13.5	65.02	1.43	20.0	0.98	0.02	Fe-α	200
83.77	1.53	24.2	82.33	1.17	30.0	1.44	0.36	Fe-α	211

In **Table 6**, there are three peaks with hkl, including (110), (200), and (211). The highest peak is at 44.994° with an intensity of 100%. This peak indicates the occurrence of a crystalline phase because the difference between the planes (d) and the value of *2θ* is minimal. So that it can be ascertained that this peak is the iron phase Fe-α (ferrite). The analysis results of the two samples found that the phases formed were Fe-α (ferrite) and FeO.

Table 6. Comparison of research results with 12% inhibitor I using PCPDFWIN data

Research			PCPDFWIN's Data No 06-0696			Δ2θ	Δd (Å)	Phase	Field
2θ	d (Å)	Int (%)	2θ	d (Å)	Int (%)				Hkl
44.99	2.01	100	44.67	2.02	100	0.32	0.013	Fe-α	110
65.52	1.42	13.5	65.02	1.43	20.0	0.50	0.010	Fe-α	200
83.01	1.16	24.2	82.33	1.17	30.0	0.68	0.008	Fe-α	211

Based on crystallographic data obtained from PCPDFWIN software. From the two samples that have been tested, it was found that the phase formed is a pure Fe (iron) phase with the space group symbol lm3m (229) where the cell parameters are (a = b = c = 2.866), lattice angle (α = β = γ = 90°) and this indicates that the Fe phase has a BCC (Body Center Cubic) crystal structure.

The Fe peak with low intensity can be seen in the sample without an inhibitor. The corrosion rate is greater than the sample with the inhibitor, which is also strengthened by the corrosion rate calculation.

Results of Characterization of Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

SEM testing was conducted on samples by immersion with RAW cocoa leaf extract inhibitor concentrations, 0% and 12% in corrosive HCl media. The EDS test uses a SE (Secondary electron) detector, while the SEM test uses a BSE (Back-scattered Electron) detector aims to make the corroded steel surface visible clearly. SEM testing was carried out with a magnification of 1000x.

Tests were carried out on samples with sample code St37 raw. The purpose of doing EDS on this raw St37 sample is to reference and compare samples carried out with various treatments. Furthermore, the results of the EDS analysis on the raw St37 sample can be seen in **Figure 6**.

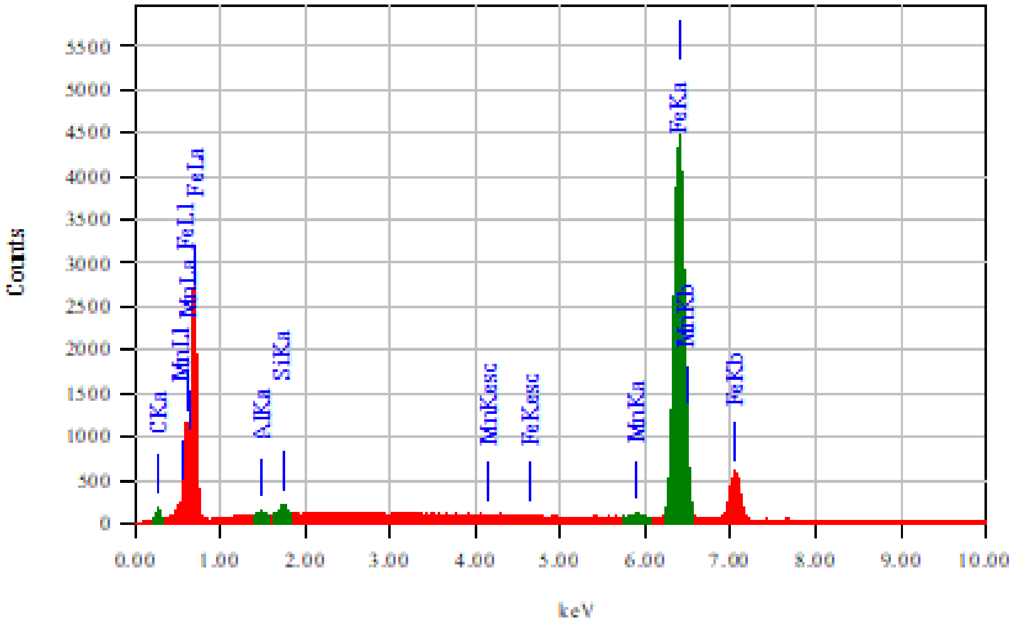

Figure 6. EDS test results of *raw* St 37 steel samples.

While the raw St37 steel sample has the main elements, as shown in **Table 7**.

Table 7. Results of EDS analysis on St 37 *raw samples.*

No.	Element	Percentage (%)	Compound	Percentage (%)
1	C	8.65	C	6.45
2	Al	0.23	Al_2O_3	0.33
3	Si	0.55	SiO_2	0.89
4	Mn	0.77	MnO	0.78
5	Fe	89.80	FeO	91.55

Table 7 shows the results of the EDS analysis on the raw St 37 sample. In this sample, the elements carbon (C), aluminum (Al), silicon (Si), manganese (Mn), and iron (Fe) were detected at 8.65% each, 0.23%, 0.55%, 0.77%, and 89.80%. It can be seen in the table that the highest compound, namely FeO, is 91.55% because this sample is a raw steel material that has not been treated, so the elemental content of iron (Fe) is still very high.

Next is the EDS analysis on the St 37 sample with an inhibitor concentration of 0%. The results of the EDS analysis on this sample can be seen in **Figure 6**. Based on **Figure 6**, the St 37 steel sample with an inhibitor concentration of 0% in HCl solution soaking for six days has the main elements shown in **Table 8**.

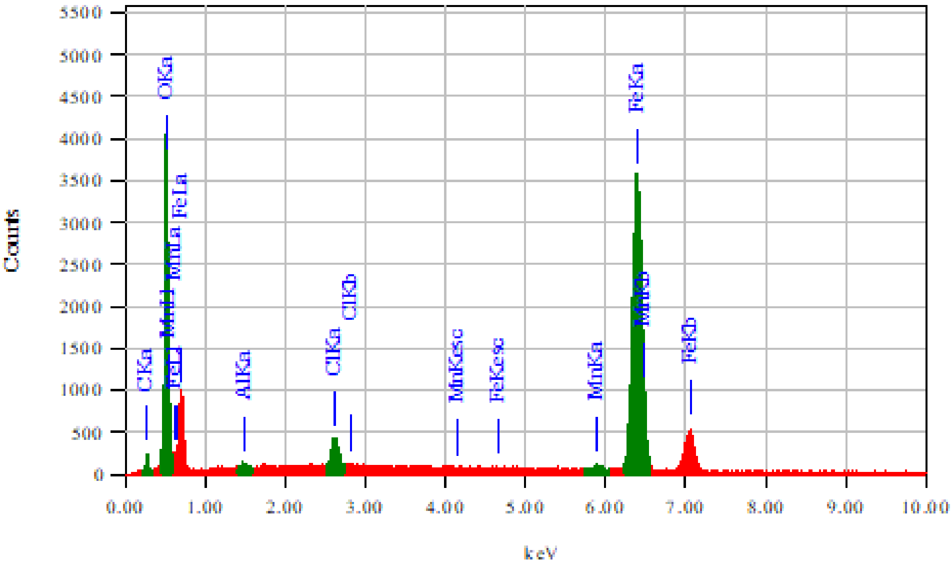

Figure 7. EDS test results of St 37 steel sample with 0% inhibitor concentration.

Table 8. Results of EDS analysis on St 37 sample with 0% inhibitor concentration.

No.	Element	Percentage (%)	Compound	Percentage (%)
1	C	10.41	C	10.41
2	O	19.68	-	-
3	Al	0.25	Al_2O_3	0.48
4	Cl	1.75	Cl	1.75
5	Mn	0.58	MnO	0.75
6	Fe	67.33	FeO	86.62

Based on **Table 8**, the main element identified is iron at 67.33% as the main component of steel. This causes the amount of iron (Fe) to be corroded to be small.

Then the EDS analysis on the St 37 sample with 12% inhibitor concentration the EDS analysis results on this sample are shown in **Figure 8**. Based on **Figure 8**, the St 37 steel sample with a 12% concentration in HCl immersion for six days has the main elements, as shown in **Table 9**.

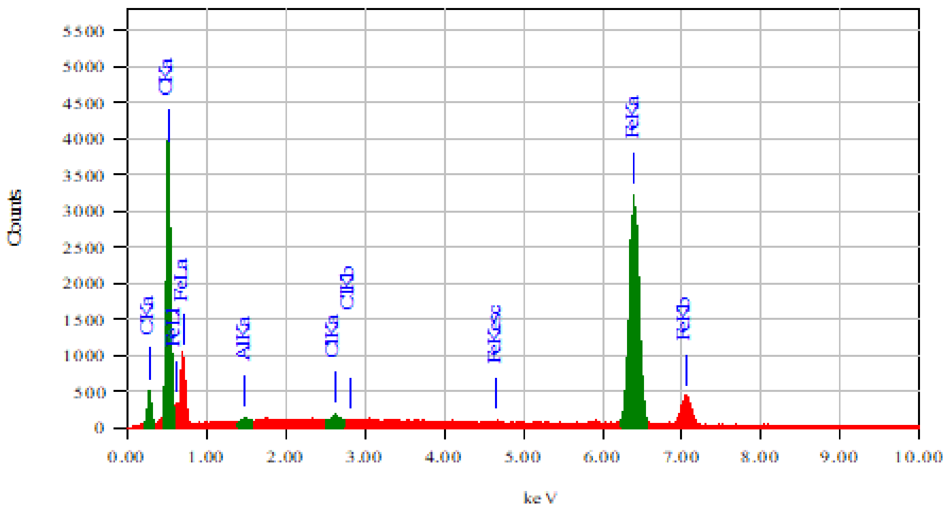

Figure 8. EDS test results for the St37 sample with 12% inhibitor concentration.

Table 9. Results of EDS analysis on St37 sample with 12% inhibitor concentration.

No.	Element	Percentage (%)	Compound	Percentage (%)
1	C	23.26	C	23.26
2	O	17.12	-	-
3	Al	0.21	Al_2O_3	0.40
4	Cl	0.30	Cl	0.30
5	Fe	59.10	FeO	76.03

Table 9 shows the results of the EDS analysis on the St37 sample with an inhibitor concentration of 12% in HCl immersion for six days. It can be seen in the table that it detected elemental iron (Fe) with a concentration of 59.10% and a FeO compound of 76.03%. This FeO content was more significant than this St 37 sample denotes a steel sample has been corroded. However, the level is less than the St 37 steel sample with 0% inhibitor concentration.

SEM characterization was carried out to see the corroded surface. Like the EDS analysis, SEM analysis was performed on five samples: St 37 raw, St 37 with 0% inhibitor concentration, and St 37 with 12% inhibitor concentration. Secondary electrons produce the topography of the object being analyzed. High surfaces are brighter than the surface low (Hermawan, Sri, 2012). While the back-scattered electrons give a difference in the molecular weight of the atoms that make up the surface, atoms with a more considerable molecular weight will have a brighter color than atoms with a lower molecular weight.

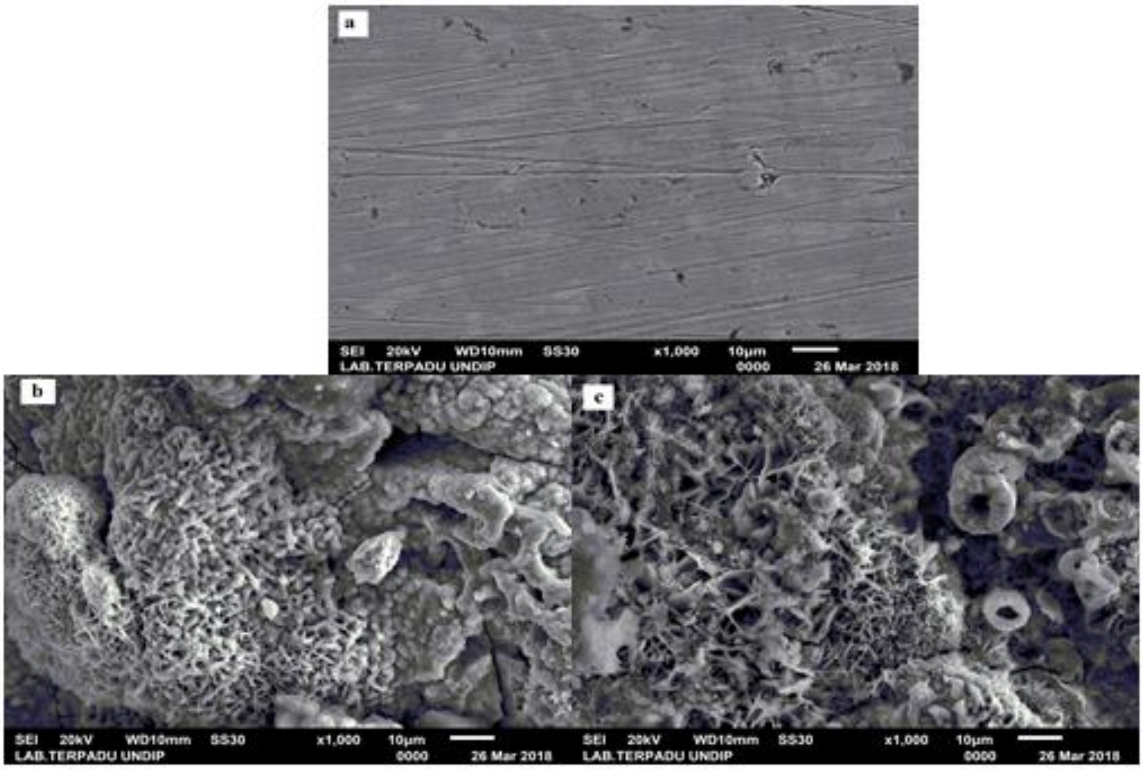

Figure 9. SEM characterization results with a magnification of 1000 ': (a) St 37 RAW sample, (b) St 37 sample with 0% inhibitor concentration, and (c) St 37 sample with 12% inhibitor concentration.

Cl elements were produced in the samples without inhibitors with a relatively high percentage of 1.24%. This indicated that the metal had been contaminated due to the interaction between hydrochloric acid and the sample (Malfinora et al., 2014).

4. Conclusion

Based on the research and discussion results, it was found that the greater the concentration of cocoa leaf extract inhibitor used, the corrosion rate will decrease, and the inhibition will increase in St 37 steel. Microstructure, the steel surface in the sample with the addition of 12% inhibitor was smoother than the steel surface in the sample with the 0% inhibitor. Showed that the elemental oxygen content was more significant, and the element Fe in the use of inhibitors was 0 % smaller than the sample with the addition of 12% inhibitor.

Maximum efficiency obtained from the cocoa leaf extract inhibitor in the XRD test in HCl 3 corrosive medium % present at 12% inhibitor concentration with an immersion time of 6 days equal to 64.35 %. The results show that the phase formed is Fe-α (ferrite) with a BCC (Body Center Cubic) crystal structure.

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