

Green approach in anti-corrosion coating by using *Andrographis paniculata* leaves extract as additives of stainless steel 316L in seawater

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Abstract

The analysis of anticorrosion coating by using *Andrographis paniculata* (kalmegh) leaves extract (KLE) as an additive to protect stainless steel 316L that immersed in seawater environment was successfully carried out. The anti-corrosive coating is the combination of selected binder, pigment, solvent, and additive. *Andrographis paniculata* leaves extract was selected as an additive due to excellent antioxidant properties. There are five types of coating with different concentration which are C1 (0 wt.%), C2 (3 wt.%), C3 (6 wt.%), C4 (9 wt.%) and C5 (12 wt.%). The coated substrate the immersed in seawater for 30 days and taken out for each subsequent 10 days for analysis. The analysis involves optical, electrochemical, and morphology studies. A few techniques involve including of Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-Vis), electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PP) and scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM/EDS). The result of FTIR shows several functional group presence in the KLE that can enhance anti-oxidation properties such as phenol, carboxylic acid, carbonyl, and amide. The presence of andrographolide compound obtained from UV-vis analysis at peak absorption spectrum 229 nm. Electrochemical analysis result from EIS, the most efficiency coating was predicted at C3. Hence, it has higher R_{ct} value and low C_{dl} value. The result in EIS is corresponding to PP; hence the result of corrosion rate at C3 is the lowest value, which is 0.00211 mm/year at 30th day immersion. The observation on the surface morphology of the coating also shows that C3 that has a smooth surface with less pitting, cracks, and salt precipitate when compared to another coating. The addition of KLE increases the efficiency of anticorrosion coating with optimum concentration, which is 6 wt.%.

Key words: corrosion, coating, stainless steel, seawater, *Andrographis paniculata*.

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1. Introduction

Corrosion is the external disintegration of metals or alloys in particular condition. Several metals evidence a great corrosion resistance than others and this can be ascribed to a few particular points such as their chemical elements, the environment of electrochemical reactions itself and others [1, 2]. The problem that causes by corrosion not only intrude the economic, but it might also disturb the social environment and the safety and health of the people, that live nearby corrosion environment or working in the industries. One of the most industries that influenced by corrosion problem is the oil industry such as in Mexico due to this phenomenon bring to bear its consequence from every second of oil extraction on, creates a continuous fight opposed to it [3]. Corrosion cannot be stopped but can be slow down. The structure that undergoes marine corrosion tends to experience crevice corrosion, pitting corrosion, and microbial corrosion [4]. Corrosion can cause failure to metallic structure in the industry thus increase the monetary problem, for example, marine industry in the United States has reported that \$785 million out of \$810 million used for the maintenance and repairs and \$1.12 billion spend for new construction [5].

Austenitic AISI or stainless steel 316L (SS316L) is stainless steel that commonly used in marine industries due to its properties that have substantial resistant towards the marine environment. Regularly, a failure that happens in SS316L in the marine environment is hazardous, which is localized corrosion [6]. SS316L chemical constituent consists of carbon, manganese, silicon, chromium, nickel, molybdenum, phosphorus, sulphur, nitrogen, and iron [7]. As for this research, the coating is a suitable method. Several ways have believed can prevent corrosion and also can increase the lifetime of the metallic and alloy structure [8]. There are five basic things in corrosion control practice, which are design, inhibitor, cathodic protection, material selection, and coating [9–11]. As for this research, the coating is a suitable method. Coating historically can give excellent protection to the metals against corrosion from the aggressive environment [12]. There are two types of coating which are an organic and inorganic coating. An organic coating is believed to give great protection towards the coated metal, especially when the coated metal exposed in the marine environment that rich with chloride ions [13].

The coating system consists of four main components, which are binders, pigments, additives, and solvent. Each component has its specialty and function in the coating. In the coating system, binder refers to substances that hold the particles of pigment together in paint and a major component presence in the paint. Pigment plays the main role in contributing colours and also act as filler in the coating or paint [14, 15]. Solvent plays a role as a carrier that allows the paint to be coated on the surface of the steel. Solvents are used to control the viscosity of the coatings for an acceptable application. Solvents give effect to the flow and levelling, drying time, gloss, *etc.* [16]. The additive is a special

substance that gives a huge impact on paints with a small quantity added in the paints. The uses of additive with the right time, order, and proportion will help the improvement in the coating system. The improvement that additive can help maybe in the form of appearance paint durability or flow of the paints. In this research, WW Gum Rosin acts as a binder due to its strong adhesion and anticorrosive properties [17]. There are two pigments consist of the coating, which is, zinc oxide (ZnO) and calcium carbonate (CaCO₃). From previous research, CaCO₃ and ZnO improved the coating properties such as corrosion resistance, UV resistance, and mechanical strength such as scratch and scraped area [18]. Besides, CaCO₃ also has been chosen as a pigment in the coating due to its low cost and easily get [19]. Methyl-isobutyl ketone (MIBK) was chosen as a solvent in the coating component due to the price, solubility, and evaporation rates. MIBK also environmentally friendly compared to another usual solvent such as xylene and toluene, which affect the consumers when they start to evaporate [20].

Corrosion additive plays a very important role in protecting engineering materials, and in recent years, many new corrosion additives are developed [21]. The toxicity of the environment caused by synthetic additive become an attraction to the researcher nowadays. To overcome this problem, the usage of a natural additive such as plant have been concerned. The usage of plant as an additive can reduce the toxicity of the environment that cause by the synthetic additive. This is because plant extract is environmentally friendly, biodegradable, and do not contain heavy metal. Other than that, the plant is inexpensive, readily available, and renewable [22, 23]. *Andrographis paniculata* (Burm. F) Nees, commonly known as the “king of bitters”, is an herbaceous plant belonging to Acanthaceae and mostly discovered for tropical and subtropical Asia, Southeast Asia, and also India [24, 25]. In India, *Andrographis paniculata* has been known as “Kalmegh”; over China it may be known as “Chuan-Xin-Lian”; to Thailand it may be known as “Fah Tha Lai”; Previously, Malaysia it may be known as “Hempedu Bumi”; to Japan it is known as “Senshinren”; and in Scandinavian nations it is known as “green chiretta” [26, 27]. Andrographolide is the main constituent, and it also the active principle of the plant [28]. The previous study showed that the anti-oxidant effect elucidated by aqueous *Andrographis paniculata* is due to its ability to activate the anti-oxidant enzyme that catalyzes the reactions of oxidants [29]. Thus the evaluation of plant extract as additives is believed to become an excellent anticorrosion coating to overcome corrosion problem.

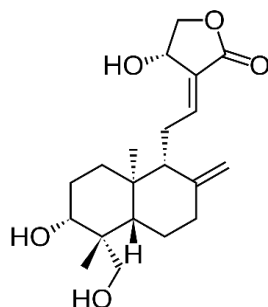


Figure 1. Andrographolide compound [30].

2. Experimental

2.1 Sample preparation

Stainless steel 316L was cut into $25 \times 25 \times 2$ mm. Then, the substrate mechanically polished using 800, 1000, and 1200 emery paper is lubricated with distilled water to remove the oxide layer. After that, the substrate was clean by using acetone and wash again using distilled water before dry it at room temperature. The substrate was then stored in a dry box until used.

2.2 Extract preparation

Kalmegh leaves powder was weighed and soaked with 80% of ethanol with ratio 1:10. The mixture then shook using a shaker with 200 rpm speed for 24 hours. The mixture then filtered using vacuum pump before evaporated using a rotary evaporator at 40°C water bath and cooling compressor 10°C to get the crude extract [31]. Crude extract obtained the stored in the chiller until used.

2.3 Coating formulation

The coating was a mixture with binder, pigment, solvent, and additive. The coating was prepared by combining binder (WW Rosin) and pigments (ZnO and CaCO_3) first then followed by solvent (MIBK) and an additive which is kalmegh leaves extract (KLE) [32]. Five types of the coating were produced by using different weight percentage of KLE, which are C1 (0 wt.%), C2 (3 wt.%), C3 (6 wt.%), C4 (9 wt.%) and C5 (12 wt.%).

2.4 Optical studies

Optical studies of extract and coating involve two characterizations which are Fourier Transform Infrared and Ultraviolet-visible Spectroscopy (UV-Vis) The FTIR spectrometer was used to identify the functional groups of Kalmegh leaves extract by observing at the vibrational motion of bonds in the molecule. The absorbance of the extract solution was measured by using Lambda 256 Perkin Elmer UV/VIS spectrometer. UV-Vis Spectroscopy is an instrument that usually used to analyze the absorption of the polymer and dyes. The data obtained from FTIR and UV-Vis, measurement then plotted using Origin Pro 8.

2.5 Immersion test

The tests are carried out for 30 days on the open site. Samples will be left hanging on a frame underwater and taken out for each subsequent 10 days for analysis. The substrates were immersed at Merang, Setiu. The immersion site is located at $5^\circ 32' 17.7''$ N, $102^\circ 56' 44.9''$ E.

2.6 Electrochemical studies

Electrochemical studies involve Electrochemical Impedance (EIS) and Potentiodynamic Polarization (PP). EIS was used to study the impedance characteristic as well as capacitance behavior of the substrate in the presence and absence of KLE. Impedance measurement was carried out using AUTO LAB PGSTAT302N controlled by software NOVA 10.1 with parameter frequency range 100 kHz to 10 kHz. Potentiodynamic polarization (PP) is the most common polarization method used for measuring corrosion resistant. The characterization was to study the anodic and cathodic polarization of the coated and uncoated samples that involves several parameters such as i_{corr} , E_{corr} , and corrosion rate.

2.7 Morphology studies

The morphology of coated and uncoated substrates was observed using JSM-6390LA Scanning Electron Microscope (SEM) to investigate the interaction of the surface of coated steels with seawater. The samples were dried before coated with fine gold spray using fine coater machine. The surface condition was examined with x100 magnification and 15 kV of accelerated voltage. The elemental characterization also conducted using Energy Dispersive X-Ray (EDX) that performed along with SEM.

3. Results and discussion

3.1 Optical studies

Figure 2 shows the peak on the graph that show the functional group that detected in kalmegh leaves extract by using FTIR Spectroscopy. The functional groups that were observed include alcohol, carboxylic acid, alkynes, nitriles, amide, nitro, and carbonyl. At wavenumber 3352.28 cm^{-1} , a strong and broad peak observed which represent the alcohol or phenolic group (O–H) stretching vibration was detected. Strong appearance of carboxylic acid (O–H) was observed at wavelength 2918.3 cm^{-1} . The weak and spectrum were obtained at wavelength 2324.22 cm^{-1} and 2227.78 cm^{-1} , which represent alkynes (C=C) and nitriles (C≡N). Amide (C=O) group was represented at the wavenumber 1678.07 cm^{-1} . According to the peak value of 1406.11 cm^{-1} , the peak present nitro asymmetric stretch (NO₂) with strong appearance while at wavelength 1033.85 cm^{-1} was determined to be a strong vibration of the carbonyl group (C=O) [1].

A functional group such as phenol, carboxylic acids, carbonyl, and amide is expected to provide antioxidant properties because they contain heteroatoms. That functional group is believed to donate the lone pair electron to the empty orbital and help the metal to achieve a stable state. This also will increase the adhesive property of the coating matrix [33].

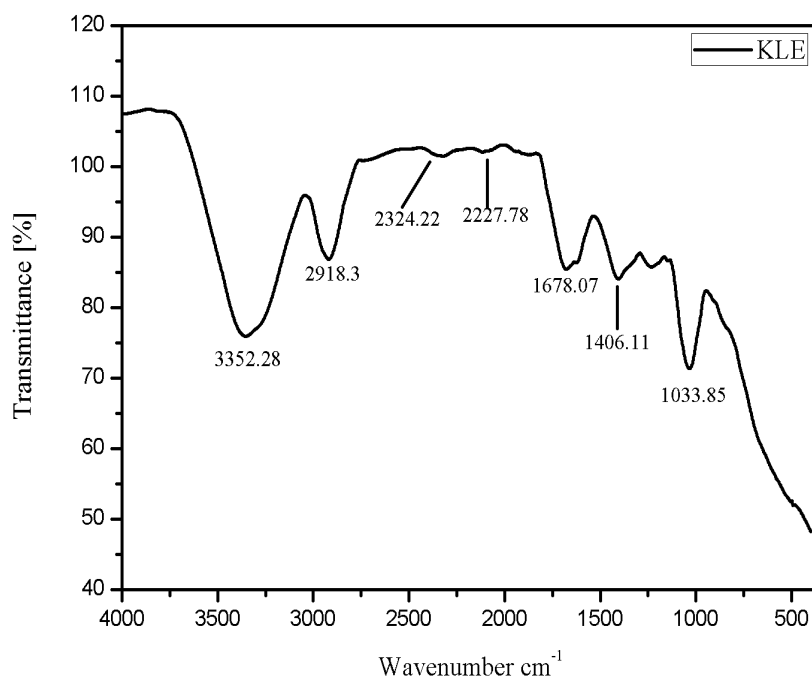


Figure 2. FTIR spectrum for kalmegh leaves extract.

UV-Vis spectrometer was used to measure the amount of light absorbance by the compounds of kalmegh leaves extract at a certain wavelength. The range of the wavelength used was between 200 to 800 nm. Since most plant compound usually falls in this region. Figure 3 shows the UV-Vis absorption spectrum detected in KLE. Based on the graph shown below, it was found that absorption observed at 229 nm show the presence of andrographolide compound [34].

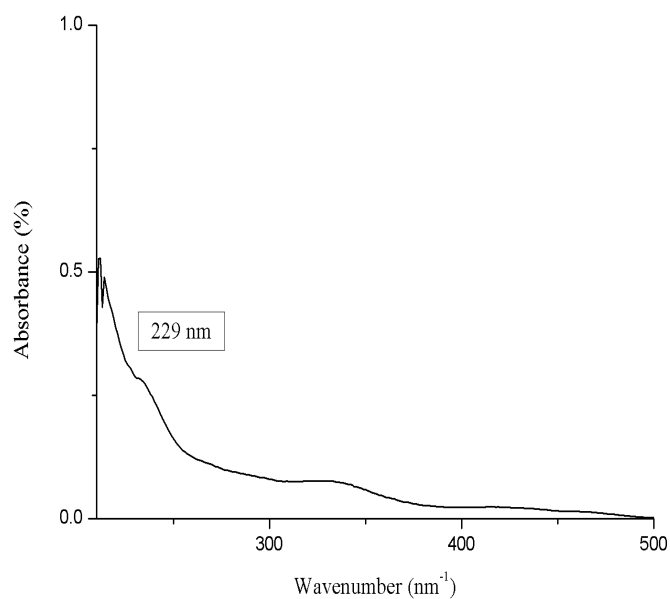


Figure 3. UV-Vis spectrum of kalmegh leaves extract.

3.2 Electrochemical Impedance Spectroscopy (EIS)

EIS is a common technique to measure and analyze the behavior of coating or metal after being exposed to a harsh medium. The method used equivalent circuits to represent the phenomenon of corrosion where parameters involve are charge transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}). R_{ct} is to measure the susceptibility of metal to corrosion while C_{dl} measure amount of water absorb by coating. The Nyquist plot shows the impedance behaviour of uncoated and coated stainless steel 316L that immersed in seawater for 10 days, 20 days and 30 days.

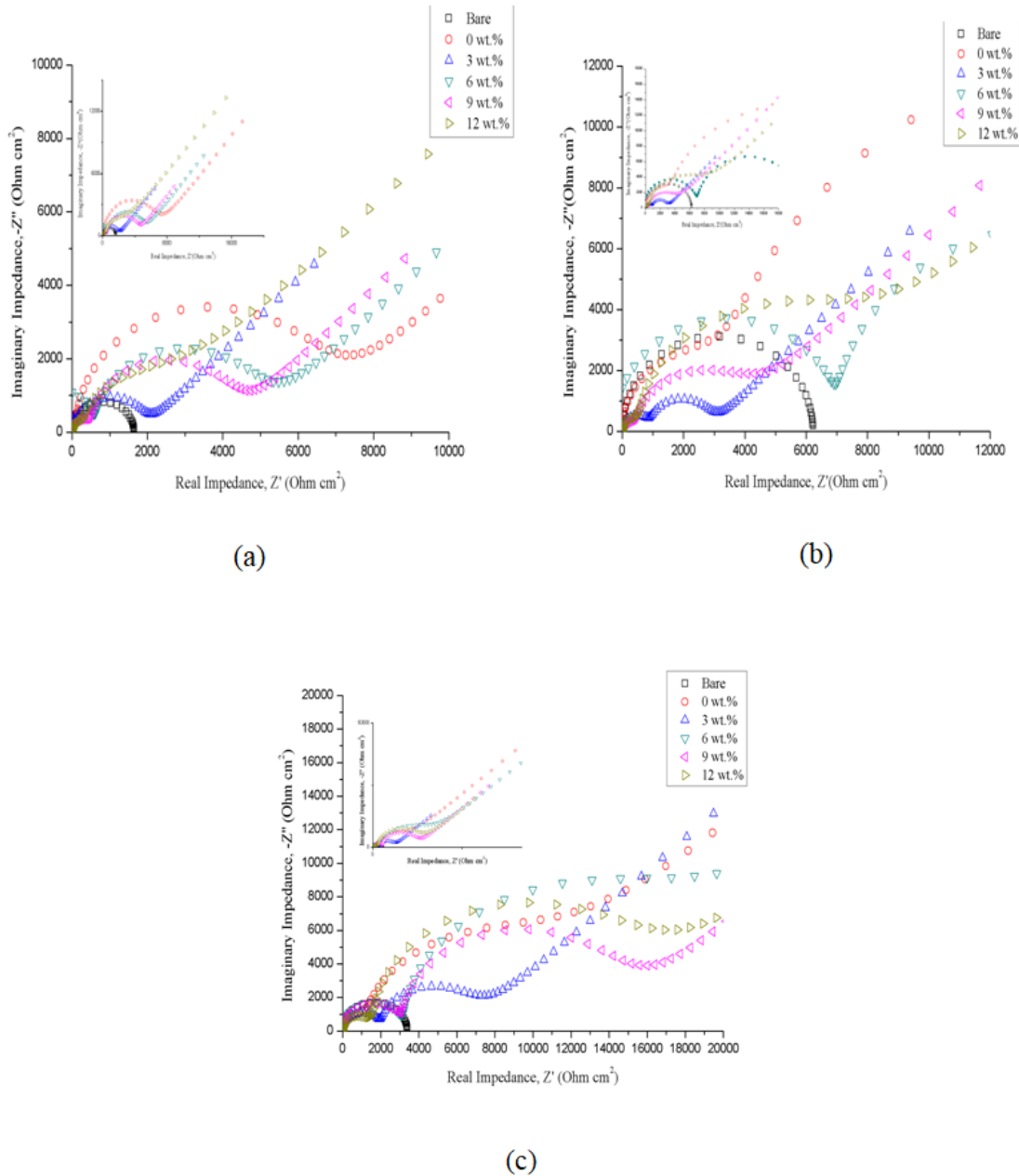


Figure 4. Nyquist plot for a) 10 days, b) 20 days, and c) 30 days immersion.

Figure 4 represents the Nyquist plots for (a) 10 days (b) 20 days and (c) 30 days. The value of R_{ct} and C_{dl} of all immersion period was recorded in Table 1. From the tabulated data of R_{ct} value, the highest R_{ct} value for 10 days immersion was at the coating that has 6 wt.% of KLE. Same goes to the samples that immersed for 20 days and 30 days. The highest value of R_{ct} also at C3, which is a coating that added with 6 wt.% of KLE. Hence, the optimum value of KLE based on the resistance data obtained signifies that 6 wt.% of KLE is the best concentration for the coating system.

As for the double-layer capacitance (C_{dl}), the value during the period of immersion seems not consistent. The increase C_{dl} value generalized the increasing value of water uptake by the coating as the time increase. Based on Table 1, the lowest value of C_{dl} for 10 days immersion is at C5, which is 1.18 μ F. As for 20 days and 30 days immersion, the lowest value of C_{dl} obtained both is at C3, which is coating with 6 wt.% KLE. Contrarily, based on Table 1, the values of C_{dl} for C3 displayed a typical trend where it exhibited an almost constant reading during the 20th to 30th days.

Table 1. Impedance parameters.

Days	Coating	R_{ct} ($\Omega \cdot \text{cm}^2$)	C_{dl} (F)
10	Bare	1.65 k	37.6 μ
	C1 (0%)	6.32 k	3.35 μ
	C2 (3%)	1.75 k	2.38 μ
	C3 (6%)	48.2 k	4.32 μ
	C4 (9%)	3.15 k	8.11 μ
	C5 (12%)	2.02 k	1.18 μ
20	Bare	6.23 k	79.2 μ
	C1 (0%)	12.3 k	578 n
	C2 (3%)	1.82 k	2.57 μ
	C3 (6%)	16.3 k	925 n
	C4 (9%)	3.15 k	4.31 μ
	C5 (12%)	6.36 k	5.16 μ
30	Bare	3.40 k	85.5 μ
	C1 (0%)	8.17 k	1.55 μ
	C2 (3%)	4.57 k	4.20 μ
	C3 (6%)	14.0 k	512 n
	C4 (9%)	11.0 k	1.34 μ
	C5 (12%)	13.4 k	5.08 μ

3.3 Tafel polarization

The Tafel plot in Figure 5 shows the polarization of anodic and cathodic behavior of corrosion of sample that immersed in seawater for (a) 10 days, (b) 20 days and (c) 30 days. The parameter involves in this characterization are corrosion potential (E_{corr}), corrosion density (i_{corr}), and corrosion rate (CR). The data collected for this characterization tabulated in Table 2. By referring the Tafel plots in Figure 5, the anodic and cathodic slope changes with the different addition of KLE in the coating. This is because of retardation process occurs in both section that corresponding to adsorption of inhibitor molecule [35].

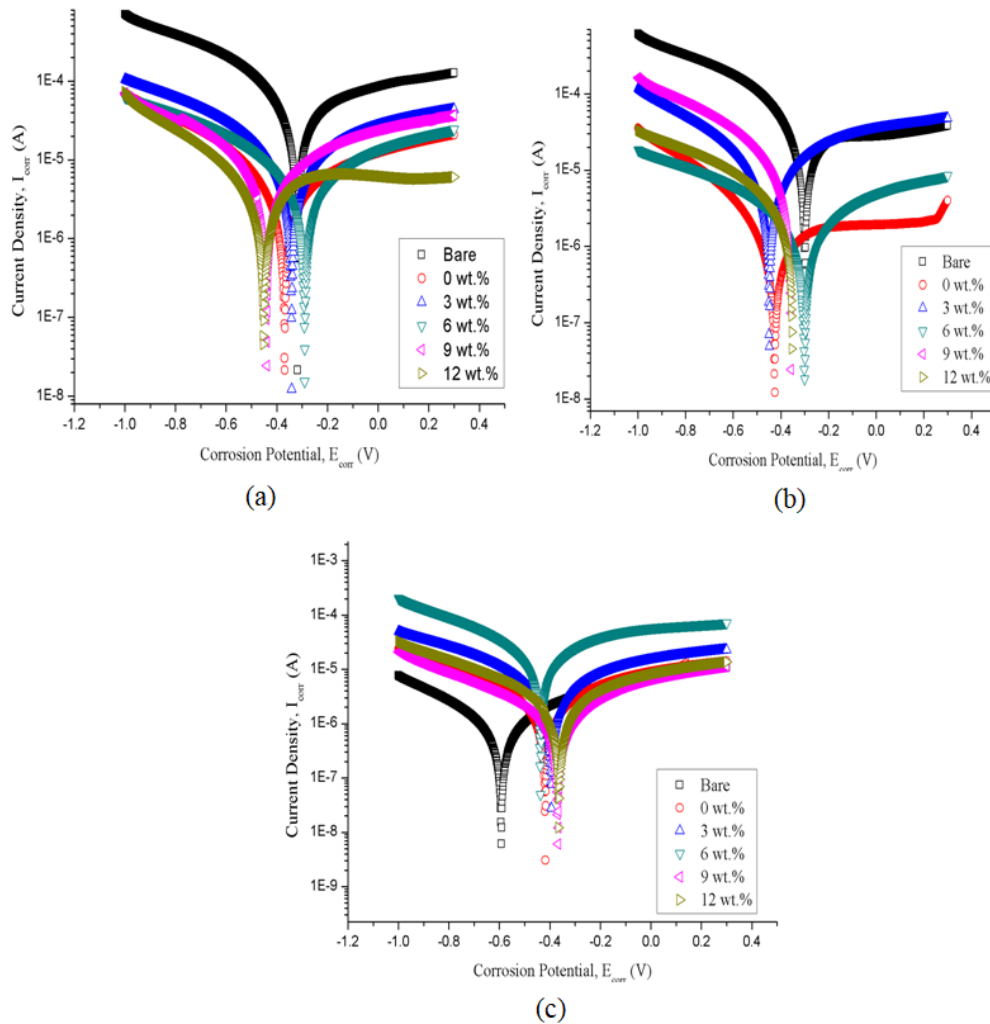


Figure 5. Tafel plot for a) 10 days, b) 20 days, and c) 30 days immersion.

Corrosion current density (i_{corr}) denotes the corrosion progress and acts as the indicator for the type of inhibitive action. As the i_{corr} increase, corrosion progress is faster. From Table 2, the lowest i_{corr} value for 10 days immersion is at C3 which is $3.15 \cdot 10^{-5} \text{ A} \cdot \text{cm}^2$ that corresponding to the value of corrosion rate 0.052661 mm/year that also the lowest value compared to others coating. As for samples that immersed for

20 days and 30 days, the excellent coating behavior also at C3 due to the lowest value of i_{corr} and corrosion rate. The value of i_{corr} and corrosion rate for 20 days immersion is $1.5494 \cdot 10^{-6} \text{ A} \cdot \text{cm}^2$ and 0.35689 mm/year while for 30 days immersion is $1.26 \cdot 10^{-6} \text{ A} \cdot \text{cm}^2$ and 0.00211 mm/year. The lowest E_{corr} value for all immersion duration was identified at C3 explained the limitation of the absorption of KLE into coating formulation; hence, it can be assigned as the optimum value of KLE needed in the coating. The performance of the coating decrease when it reaches a certain amount of extract concentration [36].

Table 2. Tafel polarization data.

Days	Coating	Corrosion potential, E_{corr} (V)	Corrosion current density, i_{corr} ($\text{A} \cdot \text{cm}^2$)	Corrosion Rate (mm/year)
10	Bare	-0.31864	0.000472	0.7888
	C1 (0%)	-0.39639	$5.20 \cdot 10^{-5}$	0.086937
	C2 (3%)	-0.34222	$5.53 \cdot 10^{-5}$	0.092358
	C3 (6%)	-0.29054	$3.15 \cdot 10^{-5}$	0.052661
	C4 (9%)	-0.43894	$5.60 \cdot 10^{-5}$	0.093588
	C5 (12%)	-0.45413	$6.17 \cdot 10^{-5}$	0.10316
20	Bare	-0.29883	0.000191	0.00103
	C1 (0%)	-0.42648	$6.1915 \cdot 10^{-6}$	0.56925
	C2 (3%)	-0.44935	$3.26 \cdot 10^{-5}$	1.017
	C3 (6%)	-0.30136	$1.5494 \cdot 10^{-6}$	0.35689
	C4 (9%)	-0.35681	$7.4371 \cdot 10^{-5}$	1.1175
	C5 (12%)	-0.35269	$6.8958 \cdot 10^{-6}$	0.75241
30	Bare	-0.41104	0.000227	0.37863
	C1 (0%)	-0.37406	$4.92 \cdot 10^{-6}$	0.057119
	C2 (3%)	-0.39497	$4.64 \cdot 10^{-5}$	0.077517
	C3 (6%)	-0.32123	$1.26 \cdot 10^{-6}$	0.00211
	C4 (9%)	-0.36738	$6.61 \cdot 10^{-6}$	0.011047
	C5 (12%)	-0.36613	$2.29 \cdot 10^{-5}$	0.038247

3.4 Morphology study

SEM/EDS is one of the common techniques to observe the surface condition of the material. In this study, the coated and uncoated stainless steel 316L that immersed in seawater for 30 days was observed to know the surface condition after exposed to an aggressive environment. Figure 6(a) shows the surface condition of bare stainless steel

316L. From the image observed, the surface of the bare metal was deposited with salt as we can see the white precipitate that presence on the surface of the specimen. Figure 6(b) is the substrate that coated with the coating without the addition of leaves extract. The surface of the coating was severely damaged with the presence of cracks and pitting. The condition of coating with 3 wt.%, in Figure 6(c) also undergoes damages on the surface due to the pitting occurs on the surface of the coating and a lot of salt deposited. For coating that contains 6 wt.% of leaves extract in Figure 6(d), the surface of the coating is smooth with no pitting or holes shows while for Figure 6(e) and (f) the surface of the coating with 9 wt.% and 12 wt.% of leaves extract have a rough surface when compared with Figure 6(d).

From the observation, coating with 6 wt.% shows the surface that smooth and fewer damages compared to other coating. The excellent of the surface condition of coating is due to the presence of an optimum concentration of leaves extract. The presence of leaves extract can enhance the properties of the coating when the extract will create a strong carbon chain and increase the adhesion properties of coating, thus prevent the coating from degrading. The pitting or cracks that occur on the coating surface will lead to degradation of coating because it will enhance the water enters the coating.

The element composition that observed under EDX measurement showed in Table 3. From the Table 3, the composition of the chromium element on the surface of the coating with 6 wt.% (C3) is the lowest compared to C1, C2, and bare metal. This is because the coating can prevent the oxidation of stainless steel 316L to happen. The oxidation of stainless steel 316L will release chromium ions that harmful toward a few species of aquatics life by affecting the organ of the fish such as gills, kidney, and liver [37].

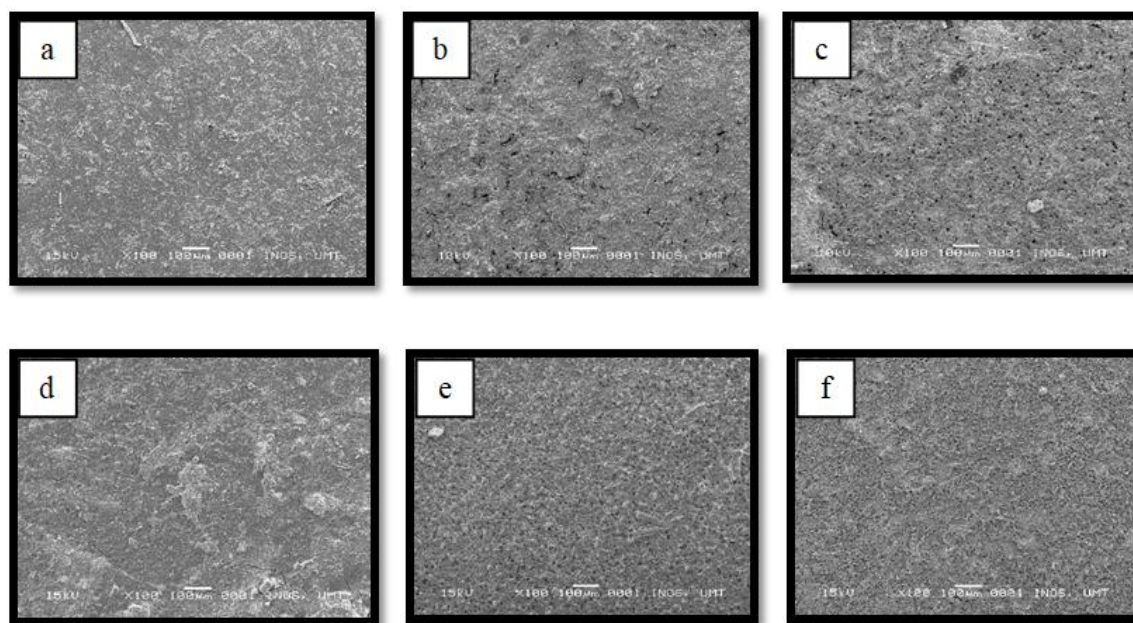


Figure 6. SEM image for sample immersed for 30 days a) bare metal, b) C1, c) C2, d) C3, e) C4, and f) C5.

Table 3. Element composition of metals that immersed for 30 days.

Element	Mass (%)			
	Bare	C1 (0 wt.%)	C2 (3 wt.%)	C3 (6 wt.%)
Na	2.18	38.78	47.21	53.37
Cl	0.94	33.10	43.63	27.71
Cr	58.79	5.28	5.02	4.99
Ni	38.09	22.85	4.13	13.93
Total	100.00	100.00	100.00	100.00

Conclusion

From this research conducted, it is concluded that:

1. The coating with the addition of *Andrographis paniculata* leaves extract proved that is successful and able to slow down the corrosion process in seawater.
2. FTIR analysis shows the functional group such as carbonyl and phenol, inhibit the mechanism of corrosion.
3. The electrochemical studies indicate that the efficiency of coating with leaves extract as an additive increase until certain concentration achieve.
4. From observation under SEM/EDX measurement, the surface condition of coating contains an optimum concentration of leaves extract to improve the capability of the surface condition.
5. The addition of LLE into the coating matrix decreased the corrosion rate when the extract was used up to 6 wt.% (C2) and further increase yields in higher corrosion rate.

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