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Study of corrosion resistrance of pipeline API 5L X42 using green inhibitor bawang dayak (*Eleutherine americanna Merr.*) in 1M HCl

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Abstract. This study aimed to investigate the ability of Eleutherine americanna Merr. extract as an environment friendly inhibitor for API 5L X42 in 1M HCl. Corrosion inhibition ability of this extract was tested using tafel polarization, weight loss and electrochemical impedance spectroscopy methods. FTIR test was used to investigate *flavonoid* and antioxidant compound that play an important role to inhibit the corrosion process. In this study, the concentration of *Eleutherine americanna Merr*. extract used was 0 ppm, 100 ppm, 250 ppm, 500 ppm, and 1000 ppm. The corrosion rate decreases within the increasing of inhibitor's concentration.The highest percentage inhibition efficiency was found to be 84.5% at 1000 ppm. It can be concluded that *Eleutherine americanna Mer*. extract can be used as an alternative and environmental friendly inhibitor for API 5L X42 in 1M HCl.

1.Introduction

In oil and gas industry, corrosion can be seen on the pipe of production oil and gas or the separator machine of oil, gas, and water. The existence of aggressive ion such ion Cl^-can make a pitting corrosion [1].This type of corrosion is the most dangerous attack because we couldn't see clearly the existence of the pit because it's tiny size. On the other hand, the fluid which contained in the pipe could be the cause of erosion corrosion and H_2S corrosion.

Basically, oil and gas industry is using pipeline in which made by steel because its cheap price, whereas, the corrosion resistance of steel is low [1]. Therefore, researchers and engineers are still finding the best way to prevent the corrosion. One of the research found a chemical liquid which can prevent the corrosion called inhibitor and it doesn't cost much. Inhibitor is a chemical liquid which added to the fluid in a small concentration and has an effect to prevent the corrosion [1].The effect of inhibitor for preventing the corrosion was proven in many experiments. However, it has a side effect which can be harmful for the environment. Nowadays, researchers and engineers are developing an inhibitor which called green inhibitor which made by organic compound such as plants and fruits.

It's quite important to do some experiments to know the ability of each kind of green inhibitors to inhibit the corrosion. This experiment is based on the investigation of the ability of green inhibitor Bawang Dayak (*Eleutherine americanna Merr*.) in 1M HCl to inhibit the corrosion using weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy. The adsorption isotherm was also included.

2. Materials and Method

2.1. Preparation the Sample of Pipeline API 5L X42

The material used in this experiment is pipeline API 5L X42 which made by steel. This type of pipeline is commonly used in oil and gas industry as the pipeline for production of oil and gas. The API 5L X42 is cut into small specimens for weight loss testing, electrochemical testing, and FTIR testing.

2.1.1. Weight Loss Test. For the weight loss samples, the steel is cut using a chainsaw to be 40mm x 30mm x 5mm, then the specimens are drilled with 5mm drill bit which will be used to place the yarn when testing the weight loss. After the cut, the sample is then getting smoothed on the surface using a grinder, followed by sandpaper with grit paper 80, 120, 240, 400, 600, 800. Before the weight loss test, pickling is done in accordance with NACE RP0775-2005 standard. Then calculate the weight of the specimens.

Inhibitory Efficiency is used to know the corrosion rate that occurs with addition of inhibitor and or without addition. The efficiency can be calculated by using this equation [2]:

$$Inhibition\ Efficiency = \frac{Corr.rate\left(unhibited\right) - Corr.rate\left(inhibited\right)}{Corr.rate\left(inhibited\right)} \times 100\% \quad (1)$$

2.1.2. Electrochemical Test. Potentiodynamic polarization is a method to determine the parameters the kinetic of corrosion, such as corrosion potential and current density which are used to find the corrosion rate. The curve between Ecorr and Icorr will be given as the result. Electrodes which used in this method are working electrode, counter electrode, dan reference electrode. The inhibition efficiency is calculated using:

$$IE\left(\%\right) = \frac{icorr - i'corr}{icorr} \times 100 \quad (2)$$

where, *icorr and i'corr* are corrosion current densities (A) in the presence and absence of the inhibitors, respectively.

Electrochemical Impedance Spectroscopy (EIS) is a method to analyze the response of a corroded electrode to a potential signal. The results of EIS measurements are expressed in the Nyquist chart. The electrical resistance in the EIS is expressed in impedance (Z). The impedance itself is a measure of the ability of a circuit to resist the flow is a semicircle diagram that flow real impedance to the imaginary impedance. The inhibition efficiency is calculated from the electrochemical impedance diagrams, using:

$$IE\% = 100\left(1 - \frac{Rp}{Rp'}\right) \quad (3)$$

where, *Rp* and *Rp'* are the polarization resistance (Ω) with and without inhibitor.

In addition to weight loss samples, samples are also prepared for electrochemical testing, in example polarization and EIS tests. The sample size for the electrochemical test is 10mm x 10mm x 10mm. After the cut, the sample is getting smoothed on the surface using the sandpaper with grit paper 80 to 1000, after it is connected with copper wire using solder. Then the sample is mounted with resin. Before the test, the sample is sanded back with grit 80 to 600.

2.2. Preparation of Eleutherine americanna Merr. Extract

The green inhibitor which used in the experiments were in powder shaped and will be used in weight loss testing, electrochemical testing, FTIR testing. The extract is first mixing the green inhibitor into HCl 1M.

2.3. Preparation of HCl 1M Solution

The test solution was 350 ml 1M HCl, whichwas prepared by the dilution of technical grade 32% m/v HCl with distilled water. Inhibitors were dissolved in acid solution at required concentrations in mgL^{-1} (ppm) and the solution in the absence of inhibitor was taken as blank for comparison purposes.The concentration range of the *Eleutherine americanna Merr.* extracts varied from blank to 1000 ppm in the electrolyte solution.

3. Result and Discussion

3.1. Weight Loss Test Measurement

The effect of addition of *Eleutherine americanna Merr.* extract tested at various concentrations on the corrosion of API 5L X42 in 1M HCl solution was observed by weight loss measurements after 7 days of immersion. The values of inhibition efficiency and corrosion rate are summarized in Table 1. It is observed that the decreasing corrosion rate is associated with the increase of inhibitor's concentration which indicates, adsorption of inhibitors onto the steel surface or at the solution interface on increasing its concentration and providing wider surface coverage. The highest percentage inhibition efficiency was found to be 83% at 1000 ppm.

Table 1. *Weight Loss*

Concentration of Inhibitor	Initial weight (g)	Final weight (g)	ΔW (g)	Corr. Rate (mm/yr)	Inhibitory Efficiency
0 ppm	32,7397	31,2029	1,5368	5,8692	-
100 ppm	28,4732	27,3538	1,1194	4,2751	27,16%
250 ppm	30,1456	29,2519	0,8937	3,4131	41,84%
500 ppm	32,5805	31,9208	0,6597	2,4091	59%
1000 ppm	31,5104	31,2491	0,2613	0,9979	83%

3.2. Polarization Test Measurement

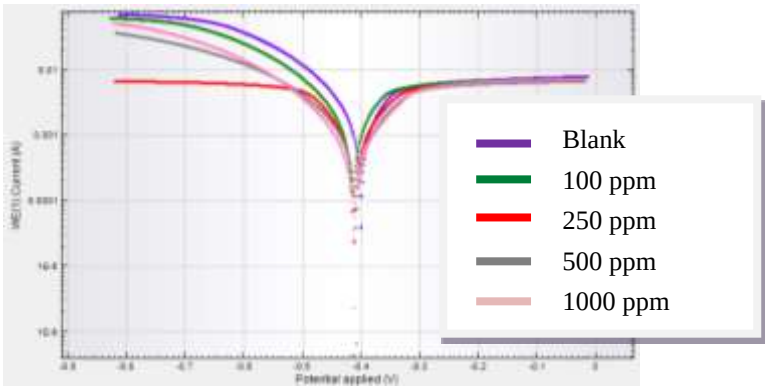

Figure 1. Polarization Tafel Curve

Figure 1 illustrates the cathodic and anodic Tafel polarization curves of sample of pipeline API 5L X42 in 1 M HCl without and with different concentrations of *Eleutherine americanna Merr.*extract. Tafel extrapolations of the anodic and cathodic lines of the polarization curves were used to determine several electrochemical parameters such as anodic slope (*ba*), cathodic slopes (*bc*), potential (E_{corr}), and current density of corrosion (i_{corr}) as given in table 2.

Table 2. Tafel Polazitation

No	Concentration	βa (mV/dec)	βc (mV/dec)	Ecorr (mV)	Icorr (µA)	Corr.rate (mm/yr)	Inhibitory Efficiency
1	Blank	35,0770	42,8020	-401,440	476,230	5,5338	-
2	100 ppm	29,2150	26,8400	-414,390	292,370	3,3973	38.6%
3	250 ppm	31,5230	26,2540	-410,540	210,320	2,4439	55,8%
4	500 ppm	15,9920	16,7930	-408.900	93,697	1,0888	80,3%
5	1000 ppm	10,2030	22,7630	-415,610	81,635	0,94859	84,5%

From table 2, we can see that the value of i_{corr}decreases with increasing inhibitors concentrations. The same condition also happens on both the cathodic and anodic current densities. Therefore, the presence of molecules from inhibitor inhibits the hydrogen evolution and the anodic dissolution processes [6]. This condition indicates that the inhibitors act as mixed type corrosion inhibitors. Moreover, the maximum displacement in E_{corr} was 12.29 mV where was not exceed 85 mV. Thus, this inhibitor is classified as mixed type inhibitors[7].According to the highest percentage inhibition efficiency was 84.5% in 1000 ppm, *Eleutherine americanna Merr*. can be used to inhibit the corrosion process of API 5L X42 in 1M HCl.

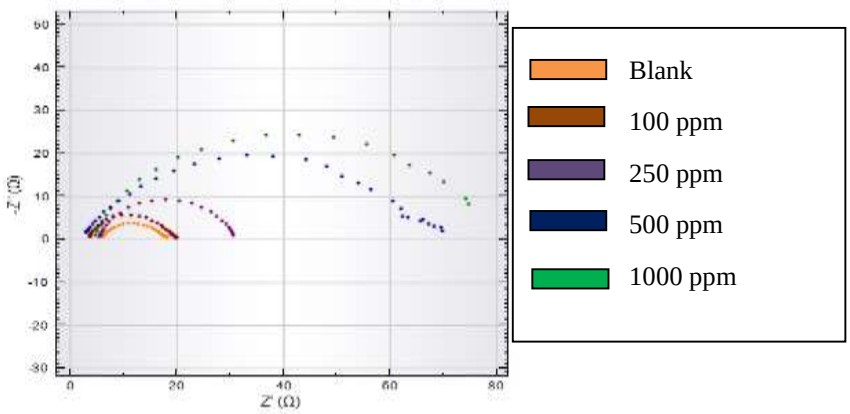

Figure 2. Graph of Electrode Impedance Spectroscopy

3.4. Electrochemical Impedance Spectroscopy (EIS) Test Measurement

In table 3, there are an increasing of Rct value and a decreasing CPE value. Punita [8], increasing of Rct value indicates the presence of a protective layer on the metal interface and solution. CPE is widely used to replace Cdl in analyzing coating phenomenon [9]. Obot [10], decreasing of CPE value indicates an increase in the thickness of the protective layer of the inhibitor molecule on the metal surface. Changes in CPE values indicate a shift between the water molecules on the metal surface. Hazwan [11], a decrease

in CPE value is the result of a decrease in surface dielectric constant followed by the addition of thickness of the double layer. The inhibition layer increases with increasing concentration of inhibitor added, where more and more molecules of inhibitor can be adsorbed on the surface of the metal.

Table 3. Result of Fitting and Simulation EIS

Concentration of Inhibitor	Rs(Ω)	Rct(Ω)	CPE (mMho)	Inhibitory Efficiency
0 ppm	5,49	12,6	1,89	-
100 ppm	3,24	16,2	1,09	22,22%
250 ppm	5,25	25,5	1,04	50,58%
500 ppm	1,84	67,3	0,729	81,27%
1000 ppm	3,92	74,8	0,723	83,15%

The following table shows that the values of CPE decrease with the increase in inhibitor concentrations due to the addition of inhibitor that increases the adsorption phenomena, which consequently may decrease the electrical capacity and/or increase in the thickness of the electrical double layer[12]. This double layer was formed by the adsorption of the inhibitor molecules at the metal-solution interface and replaced water molecules gradually [12].

4. Conclusion

Bawang Dayak extract (*Eleutherine americanna Merr*.) is classified as an eco-friendly organic inhibitor of mixed inhibitor type with flavonoid compounds that play a role in corrosion inhibitor process on API 5L X42.The highest inhibitory efficiency occurs when the addition of 1000 ppm inhibitor concentration into HCl 1M solution. Where efficiency of inhibitor from each test result, weight loss equal to 83%, tafel polarization equal to 84,5%, and EIS equal to 83,15%. Addition of inhibitor concentration of 1000 ppm Bawang Dayak is able to decrease the steel corrosion current density of API 5L X42 to 81,635 µA and increase the solution resistance to 74,8 Ω. Effective inhibitory concentrations inhibit the corrosion process in sequence is 100 ppm < 250 ppm < 500 ppm < 1000 ppm. Extract of Bawang Dayak physically inhibits the langmuir isotherm mode, which will predominantly control the charge transfer process on the API 5L X42 steel interface.

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