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DEVELOPMENT OF ENVIRONMENTAL FRIENDLY CORROSION INHIBITOR FROM THE EXTRACT OF ARECA FLOWER FOR MILD STEEL IN ACIDIC MEDIA

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Однією з галузей, що відіграють важливу роль у підтримці розвитку країни, є нафтогазова промисловість. Крім того, ця галузь впливає на економіку країни, тому вона повинна працювати якомога ефективніше, щоб не викликати істотних витрат і не відбиватися на економіці країни. Нафтогазова промисловість оснащена хорошим допоміжним обладнанням, яке відіграє важливу роль в успіху виробничого процесу. Найважливішим обладнанням для забезпечення безперервності виробництва є трубопроводи. Як правило, такі трубопроводи виготовляються з м'якої сталі, а матеріалом, який зазвичай використовується для труб в нафтогазовій промисловості, є API 5L. Однією з проблем, що виникають в трубопроводах для нафтогазової промисловості є корозія. Це відбувається через агресивні іони, такі як Cl^-, а також рідину, що міститься в трубі. Агресивні іони можуть викликати корозію у вигляді точкової корозії. Корозію, що виникає в трубопроводах для нафтогазової промисловості, необхідно усувати якомога ефективніше. Одним з рішень, які можуть забезпечити ефективні результати в зниженні швидкості корозії є використання інгібіторів. При додаванні належної концентрації інгібітора швидкість корозії можна знизити на 99 % або більше. Як правило, часто використовувані інгібітори являють собою неорганічні інгібітори, що містять хімічні сполуки, які шкідливі для навколишнього середовища і здоров'я. Так, в даний час існує багато розроблених екологічно чистих інгібіторів, а саме інгібіторів, одержуваних з рослин і плодів. Екологічно чисті інгібітори не мають забруднюючого впливу на навколишнє середовище, оскільки матеріал цих інгібіторів володіє органічними властивостями. До теперішнього часу було проведено багато досліджень екологічно чистих інгібіторів на сталі API 5L. Однак дослідження інгібіторів, отриманих з екстракту квіток ареки, в якості екологічно чистих інгібіторів не проводилися. Таким чином, дане дослідження спрямоване на визначення впливу екологічно чистих інгібіторів на корозійні властивості сталевих труб API 5L в агресивних середовищах, а саме в середовищі HCl. З використанням лінійної поляризації і електрохімічної імпедансної спектроскопії (ЕІС), проведено дослідження екстракту квіток ареки в якості зеленого інгібітора корозії на сталі API 5L класу B в 1 M кислотному розчині HCl. Додавання 4 мл, 8 мл, 12 мл, 16 мл і 20 мл інгібіторів корозії призводить до підвищення ефективності інгібіторів. За результатами електрохімічної імпедансної спектроскопії (ЕІС), оптимальна ефективність інгібування 96,6 % досягається при додаванні в концентрації 20 мл. Поліфенольні і флавоноїдні сполуки, що містяться в квітці ареки, інгібують корозію шляхом фізичної адсорбції з утворенням моношару, який здатний пригнічувати корозію. Адсорбція відбувається мимовільно відповідно до ізотермічної адсорбції Ленгмюра. Як показала поляризація, екстракт квіток ареки діє за допомогою інгібування змішаного типу. Величина вільної енергії адсорбції –7.026 кДж/моль вказує на те, що адсорбція молекул інгібітору була типовою для фізичної адсорбції

Ключові слова: зелені інгібітори, квітка ареки, ЕІС, потенціодинамічна поляризація, втрата ваги

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1. Introduction

In the oil and gas industry, the piping system is the supporting equipment used in the distribution of oil and natural gas. Failures often occurring in pipes are internal corrosion due to corrosive fluid [1]. Corrosion process can be managed and one of the main factors causing corrosion is the media, including the presence of oxygen, chemical composition, and temperature. Acids such as HCl (hydrochloric acid), which can accelerate the corrosion rate are often used for industrial applications: cleaning, acid pickling and oil refining [2]. Therefore, a corrosion rate controlling method is required in the internal pipe, corrosion inhibitor is one method of internal corrosion protection of the pipe. Organic inhibitors are more widely used than inorganic inhibitors because organic inhibitors are non-toxic, inexpensive, readily available in nature, easily renewable and not harmful to the environment. Most of the effective inhibitors used contain heteroatom such as nitrogen, oxygen, sulfur, hydrogen, and multiple chemical bonds in their molecules that they are adsorbed on the metal surface [3].

Some literature has recorded studies of plant extracts from the leaves, stems, fruits or roots of plants, which have corrosion inhibition properties. Research on the use of green inhibitors on steel materials such as green inhibitors from a mixture of piper betle plants with green tea [4], *Pluchea Indica Less* [5] plant *Purple Sweet Potato* [6], *morinda citrifolia* [7], *Pennisetum Purpureum* [8], *Musa Paradisica* [9], *Andrographis paniculata* [10], *Pomegranate* [11], *Starfruit Leaf* [12] have shown promising results with inhibition efficiency above 80 %.

Furthermore, the issue of the use of environmentally friendly and biodegradable materials as corrosion inhibitors continues to grow in Indonesia. Therefore, the researchers began to explore natural ingredients of plants as a potential substance inhibitor of metal corrosion. Areca is a monoceous plant with a unisexual flower where the male and female flowers are in one inflorescence. This plant grows and spreads in India, Malaysia, Taiwan, Indonesia, and other Asian countries, both individually and in population [13]. Part of areca other than the fruit is the flower, which contains polyphenols, flavonoids as antioxidants [14]. In addition, plants containing polyphenol compounds have the effect of inhibiting the low corrosion rate of carbon steel, especially in the brotowali, mangrove and gambier plants [15]. Flavonoids act as antioxidants by donating their hydrogen atoms or by their ability to attach to metals, in the form of glucosides (containing glucose side chains) or in free form called aglycons [16]. So it is necessary to do further research on the use of areca flower as an organic inhibitor.

2. Literature review and problem statement

An inhibitor is a chemical that when added in small concentrations to the environment will effectively reduce the corrosion rate. One of the unique advantages of adding inhibitors is that inhibitors can be applied without interfering or being interrupted by the ongoing process. Corrosion inhibitors generally consist of organic and inorganic compounds. Organic compounds such as amines, heterocyclic nitrogen (hypoethers, thioalcohols, thioamides, thiourea, and hydrazine), sulfur and mixtures of these compounds are commonly used [17]. However, the presence of harmful substances that are reactive and not environmentally friendly, such as chromate, nitrite, and benzoate, cause inhibitors to have less environmental effects [18]. Therefore, organic inhibitors are developed, which are environmentally friendly inhibitors, which are currently being studied. Organic inhibitors generally work through the surface adsorption process and the formation of layers. These inhibitors form a layer of hydrophobic protective film that absorbs molecules in the metal surface, which will form a barrier of metal dissolution in the electrolyte [19]. Organic inhibitors will cause the potentiostatic polarization curve of the metal to also change.

Plants or fruit that can be categorized as green inhibitors are plants that contain alkaloid compounds, flavonoids, and other natural products contained in these plants [20]. Several studies have been conducted to develop environmentally friendly inhibitors today. Plants that have reported to have inhibitory properties are *Tridax Procumbens and Chromolaena Adorata* [21], *mango peel and citrus peel [*22], *Punica Granatum* leaf [23], *Curcuma Longa L* (*Turmeric*) [24], Camapu Leaf [25].

Caesalpinia Sappan contains various kinds of chemical compounds such as chlorogenic acid, elaidic acid, citric acid, malic acid, tannin, cryptoxanthine, fiasalin, saponins, terpenoids, flavonoids, polyphenols, alkaloids, and steroids [26]. Flavonoid compounds contained in caesalpinia sappan are antioxidant compounds that are good because they have two hydroxyl groups, namely ortho and para [27].

Several previous studies have been conducted to determine the content of active compounds in *Caesalpinia Sappan* [28], extracts from *Caesalpinia Sappan* contain five active compounds of flavonoid type that function as antioxidants. [29] identified active compounds contained in the ethanol extract of *Caesalpinia sappan*, namely brazilin, brazilein, 3′-O-methylbrazilin, sappanone, chalcone, sappancalchone and other common components such as: amino acids and carbohydrates. [30] identified that the active compound contained in the genus *Caesalpiniaceae* contained sapanchalcone. Sapanchalcone is the initial compound that forms the compound brazilin [31]. This is reinforced by *Caesalpinia sappan* research conducted by [32], which found that chalcone can be a corrosion inhibitor of steel in 1 M HCl environments.

Based on research by the areca flower contains polyphenols and flavonoids, which have antioxidative properties [33]. Phenol compounds can be chemically defined by the presence of an aromatic ring carrying one (phenol) or more (polyphenols) hydroxyl substitution, including its functional characteristics. Polyphenols are a group of chemicals found in plants. This substance has a distinctive sign that it has many phenol groups in its molecule. Polyphenols have a broad spectrum with solubility in a different solvent. This is caused by the hydroxyl groups in these compounds, which have different quantities and positions. Polyphenol derivatives as antioxidants can stabilize free radicals by completing the lack of electrons possessed by free radicals. Polyphenols are the components responsible for antioxidant activity in fruits and vegetables [34]. A study of *cryptostegia grandiflora* as a corrosion inhibitor for mild steel in 1 M H_2SO_4 solution with based on UHPLC analysis to analyze the content contained in cryptostegia grandiflora, it is found that there are polyphenol contents including routine, vanillin, resveratrol, carcinogen, formononetin, biochanin A, *p*-hydroxybenzoic acid, naringin, trans-cinnamic acid, catechin, and hesperetin. Weight loss method was obtained that the highest efficiency was 87.54 % and for potentiodynamic polarization testing the highest efficiency was 83.54 % at a 500 ppm inhibitor concentration. The diameter of the Nyquist plot increases with increasing concentration of the inhibitor indicating the formation of a protective layer on the surface of the metal steel. Adsorption of cryptostegia grandiflora extracts on metal surfaces according to Temkin and Frumkin adsorption isotherms [35].

Flavonoids are one of the most common groups of secondary metabolic compounds found in plant tissues. Flavonoids are included in the group of phenolic compounds with the chemical structure of C6-C3-C6. Various types of compounds, content and antioxidant activity of flavonoids as a group of natural antioxidants are found in cereals, vegetables and fruit. Flavonoids act as antioxidants by donating hydrogen atoms or through their ability to attach to metals, in the form of glucosides (containing glucose side chains) or in a free form called aglycones A study of palm leaves as corrosion inhibitors on SS-304 steel in H_2SO_4 solution found that the photochemical test results showed that the methanol extract of *nipah leaves* contained flavonoids [36]. The higher the concentration of the extract, the higher the efficiency of inhibition. Based on their molecular structure, flavonoids have lone pairs and double bonds as a means of inhibitors interacting with metals [37].

Generally, organic inhibitors such as areca flower will inhibit the metal surface by forming a hydrophobic layer on the metal surface. The layer is formed due to adsorption of active antioxidants molecules contained in the inhibitor. The active compound contained in the extract of areca flower is expected to be inhibited by the mechanism of adsorption.

This research is focused on the study of areca flower extract as an alternative inhibitor that is environmentally friendly. In this research, we will find out the bioactive compounds that play a role in inhibiting, the performance in inhibiting and inhibiting mechanisms of bioactive compounds from the extract of areca flower.

3. The aim and objectives of the study

The aim of the study is to determine the corrosion rate of mild steel in hydrochloric solution without inhibitor and with inhibitor of areca flower extract, to assess the efficiency of inhibition and the protection mechanism of inhibitors of areca flower extract in hydrochloric solution. To achieve this aim, the test processes are carried out by varying the concentration of areca flower extract solution used. It is expected to determine the optimum efficiency of inhibition.

To achieve this aim, the following objectives are accomplished:

– characterization of areca flower extract using FTIR to find the antioxidant ingredient of inhibitor;

– weight loss corrosion test using in 1 M HCl solution to find the optimum inhibition concentration for variations of immersion time 24–72 hours;

– determining the electrochemical behavior of the surface of the sample given with the addition of inhibitor using the method of Linear Polarization Resistance and Electrochemical Impedance Spectroscopy (EIS);

– determining the adsorption mechanism wherein the inhibitor extract of the areca flower will form a monolayer on the steel surface of API 5L and in addition, the layer will be a barrier between the steel surface and the environment so that the steel surface does not directly interact with the acidic environment.

4. Materials and method for investigation of weight loss test, electrochemical testing and FTIR

4. 1. Steel materials used in the experiment

The steel materials used for this research is pipe material, that is mild steel material, namely API 5L grade B. The metal is cut with an area of 1 cm^2. Samples are soldered and connected by copper wire so they can be used in linear polarization and EIS tests. Steel samples are mounted using epoxy resin. Then the sample is sanding to grit 1.000 to remove the oxide and the rest of the paint that sticks to the sample surface and get a flat surface.

The chemical composition of steel material will be tested by Optical Emission Spectroscopy prior to the test started.

4. 2. Test solutions

The steps involved in making a 1 M HCl solution are preceded by calculating to obtain 1,000 ml 1 M of HCl with a concentration of 30 % (calculations are attached). Next, prepare a measuring flask that has been cleaned and fill with 800 ml of distilled water. Then pour 105 ml (calculation results) 30 % HCl into the measuring flask that already contains distilled water and stir it evenly. Pour the distilled water back into the measuring flask until it reaches a volume of 1,000 ml. And 1 M HCl solution is ready to use. All processes of making a 1 M HCl solution are carried out in a fume hood. 1 M HCl solution is used to create a corrosive environment to API 5L Gr B in linear polarization testing and Electrochemical Impedance Spectroscopy (EIS) testing because this solution can represent the environment around the pipeline in the oil and gas industry.

4. 3. Making the extract inhibitors

In this study, the organic inhibitor used was areca flower extract. The extraction process is done by digestion (involving heating). Making areca flower extract begins with washing areca flower with distilled water then drying at room temperature. Areca flower that has been dried was ground in a way in a blender to become powder. 100 grams of areca flower powder were extracted with ethanol for 2 days. The result was subsequently filtered by using filter paper and heated at a temperature of 50 °C until 3 hours most of the ethanol evaporated. The inhibition extract was put directly in 1 M HCl variation of the extract concentration of 4 ml, 8 ml, 12 ml, 16 ml and 20 ml.

4. 4. Weight loss testing

Testing weight loss is carried out for 3 days. Before weight loss testing is done, sample preparation is done first by sanding the sample from 80 to 1,000 grits. The sample will be immersed in a solution of HCl 1 M with different levels of inhibitor concentration (0 ml, 4 ml, 8 ml, 12 ml, 16 ml, 20 ml). These tests compare the corrosion rate of each of these inhibitor concentration levels to be able to see the efficiency of each level. Data measurement of sample weight before and after immersion as well as corrosion rate and inhibitor efficiency is done after the immersion process.

4. 5. Linear polarization measurements and electrochemical impedance spectroscopy (EIS)

Linear polarization measurements were carried out using an Autolab Potentiostat Galvanostat (PGSTAT 302 N) with NOVA 1.11 software. Linear polarization measurements were made using a three-electrode cell assembly at room temperature. API 5L Gr B of 1 cm^2 was the working electrode, platinum electrode was used as ~~an~~ counter electrode, and Ag/AgCl was used as a reference electrode. The working electrode API 5L Gr B employed for the examination was carefully polished with emery papers (grade: 400–1,200) in order to remove the corrosion products and dust on the electrode surface. Tafel curves were obtained by changing the electrode potential automatically from –200 to +200 mV versus corrosion potential (E_{corr}) at a scan rate of 0.01 v/s. Linear travel segments of anodic and cathodic curves were extrapolated to the corrosion potential to obtain corrosion current densities (I_{corr}). Inhibition efficiency of the inhibitor has been found out from the measured I_{corr} values using the following relationship:

$$EI(\%) = \frac{i_{corr(absence\ of\ inhibitor)} - i_{corr(presence\ of\ inhibitor)}}{i_{corr(absence\ of\ inhibitor)}} \times 100. \quad (1)$$

Electrochemical impedance spectroscopy (EIS) measurements were carried out using Gamry Potensiostat/Galvanostat (Gamry REF 600) with Echem Analyst 6.33 software. It consists of three electrode systems; working electrode (API 5L Gr B), carbon as the counter electrode and Ag/AgCl as the reference electrode. The EIS measurement frequency range was between 10 kHz to 0.2 Hz with an alternative (AC) amplitude 0.01 V. The polarization resistance values were obtained from the diameter of the semicircles of the Nyquist plots. The inhibition efficiency of the inhibitor has been found out from the polarization resistance values using the following equation:

$$EI(\%)=\frac{R_{p(presence\ of\ inhibitor)}-R_{p(absence\ of\ inhibitor)}}{R_{p(presence\ of\ inhibitor)}}\times 100. \quad (2)$$

The attendance of functional groups in the areca flower extract molecules was confirmed by the Fourier Transform Infrared spectroscopy (FT-IR) method. FTIR spectra were recorded using a spectrometer, which wavelength extended from 4,000 to 400 cm^{-1}. And chemical composition examination of API 5L Grade B steel was performed using Optical Emission Spectroscopy.

4. 6. FTIR testing

FTIR testing was carried out using the Perkin-Elmer 1.430 tool with a wavelength range of 4,000–400 cm^{-1}. For FTIR testing, the extract sample is the sample used in the weight loss test. FTIR testing aims to determine the functional groups of active compounds in areca flowers where the test results are in the form of a spectrum of wave numbers. The spectroscopic method used in the FTIR test is an adsorption method where the method is based on the difference of infrared radiation absorption. The infrared spectrum results from the transmission of light passing through the sample, measuring the intensity of the light by the detector and comparing it to the intensity without the sample as a function of wavelength. From these wavelengths, functional groups that can be determined in accordance with the wavelength recorded in each sample can be determined. By doing FTIR testing, it will produce peak or wave curves with different intensities from the peak differences, so the functional groups can be determined so that the content (type of compound) contained in each sample is known.

5. Results of inhibitor behaviour investigation

5. 1. Optical emission spectroscopy

The chemical composition of API 5L Grade B is shown in Table 1. The carbon steel of API 5L Grade B is a type of low carbon steel used as the pipeline material. The specification of this steel is found in the API 5L Specification for Pipe Line Standard. From the test results in accordance with Table 1, the dominant element obtained from API 5L Gr. B is Carbon 0.146 % wt, Silicon 0.193 % wt, Manganese 0.811 % wt and Chromium 0.123 % wt.

5. 2. Weight loss test result

The results of the Weight loss test are shown in Table 2. The highest corrosion rate is 23,903 mm/year in the absence (blank) of inhibitor and the lowest corrosion rate is 2.8705 in the inhibitor concentration of 20 ml.

Table 2

Weight loss test results

Inhibitor Concentration (ml)	Initial Weight (gr)	Final Weight (gr)	ΔWeight (gr)	Corrosion Rate (mm/year)	Efficiency (%)
Blank	8.2159	7.7801	0.4358	23,903	0
4	9.2927	7.5167	1.7760	9.8342	63.09
8	9.2927	8.8725	0.4202	4.6535	81.64
12	9.2927	9.0397	0.2530	3.7358	84.15
16	9.2927	9.1446	0.1481	3.2802	85.63
20	9.2927	9.2279	0.0648	2.8705	87.99

5. 3. Results of FTIR

The Areca Flower extract was characterized by FTIR (Fourier Transform Infra Red) testing to identify the functional groups contained in areca flower. The spectrum obtained from the FTIR test is in the form of bands, where the position of the band in the IR spectrum is expressed as the wave number (cm^{-1}), and the intensity of the band is expressed as Transmission (*T*). The results of the FTIR Areca Flower characterization test can be seen in Table 3 below. From Table 3 above, it can be seen that there are peaks that have wavelengths and their intensity is known. Wave number 3.326,58 cm^{-1} indicates O–H stretching vibrations belonging to alcohol and polyphenol compounds, according to the correlation of wave numbers 3,200–3,600 cm^{-1}.

Table 3

Interpretation of FTIR areca flower extract

Wavelength (cm^{-1})	Functional groups
3326.58	Stretching vibrations O–H
2973.96	Stretching vibrations C–H:CH_2 asymmetric
2927.89	Stretching vibrations C–H:CH_2 asymmetric
2884.2	Stretching vibrations C–H:CH_2 symmetric
1655.4	Stretching vibrations C=O
1454.56	Stretching vibrations C=C aromatic
1417.18	Stretching vibrations C=C aromatic
1380.21	Stretching vibrations C–H:CH_3 symmetric
1327.93	Stretching vibrations C–H:CH_3 symmetric
1274.41	Stretching vibrations N–H
1087.72	Stretching vibrations C–O
1045.65	Stretching vibrations C–O
879.84	Buckling C–H
803.27	Buckling C–H
618.95	Buckling C–H

Table 1

Results of chemical composition OES, % weight

C (%)	Si (%)	Mn (%)	P (%)	S (%)	Cr (%)	Mo (%)	Ni (%)	Al (%)	Co (%)	Cu (%)
0.146	0.193	0.811	0.0078	0.0037	0.123	0.0671	0.0732	0.0016	0.0109	0.244
Nb (%)	Ti (%)	V (%)	W (%)	Pb (%)	Sn (%)	B (%)	Ca (%)	Zr (%)	As (%)	Bi (%)
<0.002	<0.002	<0.002	<0.015	<0.025	0.01	<0.001	0.0002	0.0021	0.0187	<0.03

The results of FTIR submersion testing of the API 5L steel surface are shown in Fig. 1. The Areca flower extract is adsorbed on the metal surface and forms a thin layer that can protect the metal surface from corrosion.

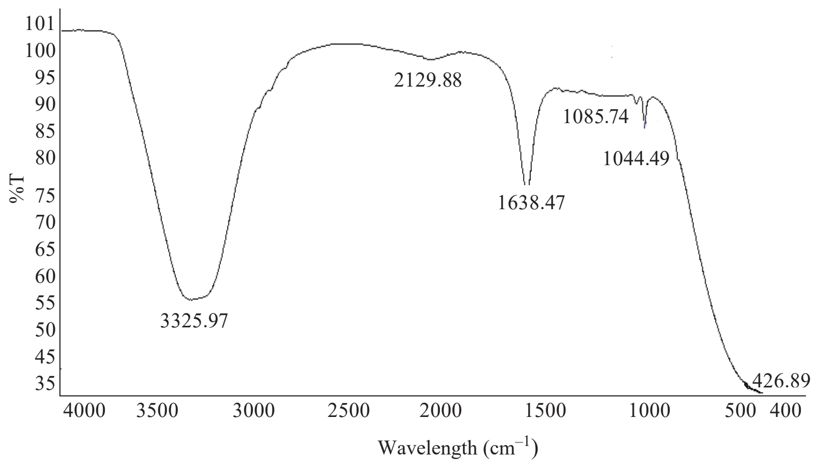

Fig. 1. Results of FTIR submersion of areca flower extract

The sample was soaked for 3 days to ensure that the Areca Flower extract was completely adsorbed on the metal surface, then the FTIR test was performed to determine the functional groups that were adopted on the sample surface. Furthermore, some of the detected groups have been adsorbed onto the metal surface (Fig. 1) in accordance with the groups contained in the areca flower compound (Table 3). Therefore, it is thought that the groups detected on the metal surface are areca flower compounds.

5. 4. Result of linear polarization testing

In this study, polarization testing was carried out with Areca Flower concentration variables, namely 4 ml, 8 ml, 12 ml, 16 ml, and 20 ml in 150 ml of 1 M HCl solution. The concentration of the inhibitor affects the performance or ability of the inhibitor to protect or inhibit metal surfaces. Corrosion rate calculation is obtained from the polarization curve. Through the polarization curve, an i_{corr} value is obtained, which will be calculated to obtain the value of the corrosion rate based on the increase in the concentration of the inhibitor.

Polarization curves obtained on API 5L Grade B steel that have been mixed with various volumes of Areca Flower extract inhibitors (0 ml, 4 ml, 8 ml, 12 ml, 16 ml, and 20 ml) in a 1 M HCl medium can be seen in Fig. 2.

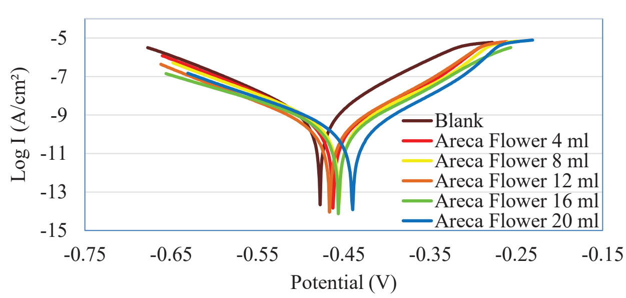

Fig. 2. API 5L steel polarization curves Gr. Be in 1 M HCl media with various volumes of areca flower extract

Based on the polarization curve, the value of i_{corr} at a concentration of 0 ml (Blank) in 1 M HCl of 196.3 µA and the value of the corrosion rate of 2,281 mm/year were obtained. At a concentration of 4 ml of areca flower, the i_{corr} value was 65.569 µA, and the corrosion rate was 0.762 mm/year. At a concentration of 8 ml of areca flower, the i_{corr} value was 57,483 µA, so the corrosion rate was 0.668 mm/year. For a concentration of 12 ml of areca flower, the i_{corr} value was 54,231 µA, and the corrosion rate was 0.630 mm/year. At a concentration of 16 ml areca flower, the i_{corr} value was 41,193 µA and the corrosion rate was 0.512 mm/year. And for a concentration of 20 ml of areca flower, the i_{corr} value was 21.31 µA and a corrosion rate value of 0.248 mm/year was obtained.

The data were obtained from linear polarization testing in the form of Tafel log (I) VS E curve that displays data, such as the tilt value of anodic and cathodic Tafel (β_a and β_c), corrosion potential (E_{corr}), current density (i_{corr}) and corrosion rate values (CR) and can be seen in Table 4.

Table 4

Calculation of corrosion rate and inhibitor efficiency (EI)

Inhibitor Concentration	β_a (mV/dec)	β_c (mV/dec)	E_{corr} (mV)	i_{corr} (µA)	Corrosion Rate (mm/year)	EI (%)
Blank	132.05	138.4	–492.91	196.3	2,281	–
4 ml	104.39	125.08	–453.62	65.569	0.762	66.60
8 ml	102.76	116.94	–454.28	57.483	0.668	70.72
12 ml	96.207	136.03	–460.79	54.231	0.630	72.37
16 ml	94.372	104.57	–455.89	41.193	0.512	79.02
20 ml	60.568	61.159	–441.26	21.31	0.247	89.14

From Table 4, it can be seen that the corrosion potential value (E_{corr}) when API 5L Gr B steel is immersed in a 1 M HCl (Blank) environment is –492.91 mV. When the areca flower extract is added with a concentration of 4 ml, the corrosion potential changes towards the anodic region of –453.62 mV. Likewise with the addition of areca flower extracts with concentrations of 16 ml and 20 ml, the corrosion potential was still in the anodic area with each value of –455.89 mv and –441.26 mV.

5. 5. Result of electrochemical impedance spectroscopy (EIS) testing

The purpose of EIS testing is to represent electrochemical phenomena that occur on metal surfaces. From the EIS test results, we will get the Nyquist curve and the bode curve, which are related to one another. The Nyquist curve states the comparison between real impedance (Zreal) and imaginary impedance (–Zimag). From the Nyquist curve we can see the effect of corrosion behavior on API 5L Gr steel. B when adding the concentration of areca flower extract in 1 M HCl acid solution. Fig. 3 is a Nyquist graph from the results of test studies with variations in the concentration of areca flower extract inhibitors.

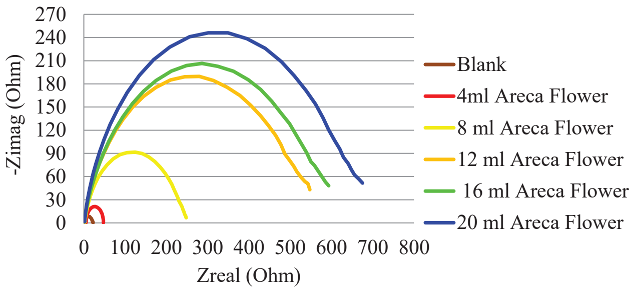

Fig. 3. Nyquist curves in several variations of the inhibitor volume

The resulting Nyquist curve in Fig. 3 forms a semicircle caused by the transfer of charge between the inhibitor and the metal layer, where the diameter of the curve describes the value of the load resistance of the system, the larger the diameter of the curve obtained, the polarization resistance value generated by the system will be even greater.

Fig. 4 described the Bode Modulus for several variations of inhibitor concentration. The curve of the inhibitor volume of 20 ml shows the highest impedance and the volume of 4 ml shows the lowest impedance.

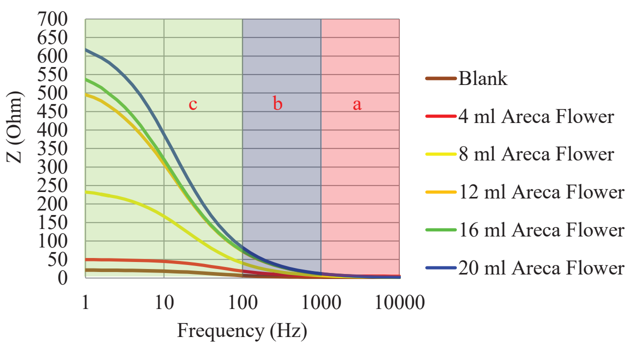

Fig. 4. Bode modulus for several variations of inhibitor volume

The results of electrical element parameters in EIS testing on several variations of inhibitor concentration are described in Table 5. The increase in the value of the resistance of variation (*Rp*) explains the decreased corrosion rate due to the formation of an inhibitory layer due to adsorption of inhibitor molecules on the metal surface.

Table 5

Values of electrical element parameters in EIS testing on several variations of inhibitor concentration

Inhibitor Volume	R_u (Ω.Cm^2)	R_p (Ω.cm^2)	C_f (μF.cm^2)	Circuit	*EI* (%)
Blank	1,748	18.59	250.2	Randles	–
4 ml	5,189	42.25	89	Randles	56.0
8 ml	2,806	209.1	37.75	Randles	91.11
12 ml	1,456	421.4	20.09	Randles	95.59
16 ml	1,447	450.9	19.91	Randles	95.9
20 ml	2,052	548.9	18.04	Randles	96.6

6. Discussion of results of inhibitor behaviour characterisation

6. 1. Chemical composition of steel material

In accordance with the API standard 5L specification literature, it can be concluded that the test material still fits within the range of API 5L Grade B. The composition of API 5L Grade B steel is included in the low carbon steel category because it has an element C content of less than 2 %. Alloy elements such as Cr, Ni, Mo, P, Al and Cu have an influence on the corrosion properties of carbon steel. It has been known that with the increase in Cr content, the corrosion resistance of carbon steel will increase, as well as the addition of Ni elements which increases, resulting in better corrosion resistance of steel W [38]. However, seeing from the results of the OES test, the content of Cr and Ni elements is relatively small so that API 5L Grade B steel is still quite susceptible to corrosion attack [39].

6. 2. Inhibitor efficiency from weight loss test

The highest efficiency of the inhibitor is 87.99 % after 3 days immersion, it showed that the green inhibition work in the acid solution. The results of the weight loss test showed that the addition of the Areca Flower extract could reduce the corrosion rate. Where there was a linear decrease directly proportional with the addition of areca flower extract. At a concentration of 4 ml, the corrosion rate is 9.8342 mm/year and gradually decreases up to 2.8705 mm/year at a concentration of 20 ml areca flower. This can occur because inhibitors can be adsorbed to the surface well and provide good inhibitory effects on API 5L steel.

6. 3. Discussion of results of FTIR of areca flower extract

Wave number 3326.58 cm^{-1} indicates O–H stretching vibrations belonging to alcohol and polyphenol compounds, according to the correlation of wave numbers 3,200–3,600 cm^{-1}. Wave number 2.973,96 cm^{-1}, 2.927,89 cm^{-1} indicates the existence of stretching vibrations of C-H indicating asymmetric CH_2 groups and 2884.2 cm^{-1} indicating symmetric CH_2 groups belonging to alkane compounds, according to the correlation of wave numbers 2,800–3,000 cm^{-1}. Wave number 1.655,4 shows stretching vibrations C=O, according to the correlation number 1,650–1,800 cm^{-1}. Wave number 1.454,56 cm^{-1}, 1.417,18 cm^{-1} shows the aromatic vibration stretching C=C. Wave number 1.380,21 cm^{-1}, 1.327,93 cm^{-1} indicates the existence of C–H stretching vibrations indicating symmetrical CH_3 groups. Wave number 1.274,41 cm^{-1} indicates N–H stretching vibrations. At wave number 1.087,72 cm^{-1} and the strongest intensity is 1.045,65 cm^{-1} where the strongest absorption of IR indicates that the bond is polar, the two wave numbers indicate the C-O stretching vibration in accordance with the correlation of wave numbers 1,000–1,300 cm^{-1}. And for wave numbers 879.84 cm^{-1}, 803.27 cm^{-1} and 618.95 cm^{-1}, act on the buckling of C-H [40].

Based on Table 2, the results of the interpretation of FTIR test, it can be concluded that the extract of the Areca Flower solution has an alkaloid functional group due to the discovery of the N-H group. Most natural organic compounds are aromatic compounds. This compound contains an aromatic carbon ring consisting of carbon atoms. These aromatic carbon rings are usually subsidized by one or more hydroxyl groups or other groups, therefore they are often called polyphenol compounds. And the alkane spectrum as evidenced by the FTIR test on Areca Flower extract indicates the presence of flavonoid compounds. From the results of the FTIR test of the Areca Flower extract, it can be concluded that it has the structure of polyphenols, alkaloids and flavonoids in accordance with the literature that forms organic inhibitors. Based on the results of the FTIR test, the wave number 3.325,97 cm^{-1} indicates O-H stretching vibrations belonging to the alcohol and phenol compounds, based on the wave number correlation of 3,200–3,600 cm^{-1}. Wave number 1.638,47 cm^{-1} indicates stretching vibration C=O aromatic. Whereas wave numbers 1.085,74 cm^{-1} and 1.044,49 cm^{-1} indicate stretching vibrations of C–O from alcohol and phenol compounds. With the presence of alcoholic compounds, phenols and aromatics which indicate that the type of polyphenol and flavonoid compound groups. It is known that areca flower contains many polyphenol and flavonoid compounds, which can function as antioxidants inhibiting the rate of corrosion in carbon steel. The structure obtained explains that the OH group has anti-oxidant properties (the ability to bind oxygen to the environment), while the free electrons in the O atom contained in the C=O and CO groups will interact and form bonds (adsorption) with electrons on the steel surface, where the type of adsorption that occurs is physical adsorption according to the value of ΔG_{ads} obtained –7.026 kJ/mol. This is supported by research conducted by Kassim (2007) on several plants that contain polyphenol compounds, such as brotowali, mangrove, and gambier plants, which can be used as organic inhibitors because they form an inhibitory coating on metal surfaces due to molecules of adsorbed polyphenol compounds to the metal surface by physical adsorption. Where the three plants that contain the highest polyphenol compounds are mangrove plants. And the optimum efficiency is obtained from the 1,000 ppm mangrove extract inhibitor content of 83.5 %. Research of Solanum Melongena plant, which contains a mixture of complex organic compounds, namely flavonoids and some polyphenol compounds. Where these compounds show antioxidant activity. From the tests carried out, it is known that adding Solanum Melongena extract will reduce the rate of corrosion when in an acidic environment. Due to the presence of molecules from Solanum Melongena extracts, which are adsorbed on the metal surface, protecting the metal surface from corrosion. Increasing the concentration of the inhibitor will expand the Surface Coverage on the metal surface, the more the surface area of the metal that is protected as a result of increased adsorption of extract molecules, the higher the protection against corrosion provided by the inhibitor [41]. Henna contains a constituent of Lawsone, which consists of phenol and benzene units, which can be used as organic inhibitors. The weight loss testing to determine the efficiency of henna inhibitors explains that the more inhibitors used, the efficiency of the inhibitor will increase, but the longer period of immersion is done, it can reduce the efficiency of the inhibitor because the film layer formed is damaged so that it is no longer able to withstand attacks from Cl-ions [42]. The properties of alkaloid content are quickly eluted when dissolved into acetone, besides the alkaloid content is easily ionized under acidic conditions that are polar [43].

6. 4. Discussion of results of linear polarization testing

The addition of areca flower extract concentrations of 4 ml, 16 ml and 20 ml of corrosion potential values (E_{corr}) experienced anodic changes, thus indicating that areca flower extracts controlled the reaction in anodic direction by forming complex compounds in the anodic region of the surface of API 5L Gr B steel. Whereas when adding 8 ml and 12 ml areca flower extract concentrations, the corrosion potential (E_{corr}) experienced a change in the cathodic direction with values of –454.28 mV and –460.79 mV, which showed increased metal energy, due to potential shifts towards a more negative direction. Changes in corrosion potential (E_{corr}) occur because cathodic reactions are also controlled by the formation of complex compounds in the cathodic area on the surface of API 5L Gr B. As per FTIR test results, the major complex compounds found on the surface are O–H stretching vibrations belonging to alcohol and polyphenol compounds and C–H groups belonging to alkane compounds. The polyphenol compounds have hydrophilic characteristics, which absorbed in the metal surface and alkane compounds tend to be hydrophobic, which barrier cathodic site from further corrosion process. So that due to the potential corrosion value (E_{corr}) with the addition of areca flower extract concentration changes in anodic and cathodic directions, it can be concluded that the Areca Flower extract inhibitors have a mixed (dominant) type inhibitor with anodic dominant direction [44].

From the Tafel plot in Fig. 2, it was found that the addition of inhibitor concentration can reduce the value of the corrosion current density (i_{corr}) compared to without the inhibitor. This states that the corrosion reaction has decreased, resulting in a decreased corrosion rate. This is due to the adsorption process of inhibitors on API 5L Gr B steel interfaces or in 1 M HCl solution, so that anodic and cathodic reactions undergo inhibition. The inhibition process increases with the addition of the inhibitor concentration. The decrease in i_{corr} value can be seen in conditions without inhibitors of 196.3 µA, after an increase in the concentration of 4 ml inhibitors experienced a significant decrease in the i_{corr} value to 65.57 µA. So that the corrosion rate decreased without 2,281 mm/year inhibitor to 0.761 mm/year, which is still classified as mild corrosion resistance. As shown in Fig. 5, at a volume of 20 ml i_{corr} 21.31 µA with a corrosion rate of 0.247 mm/year.

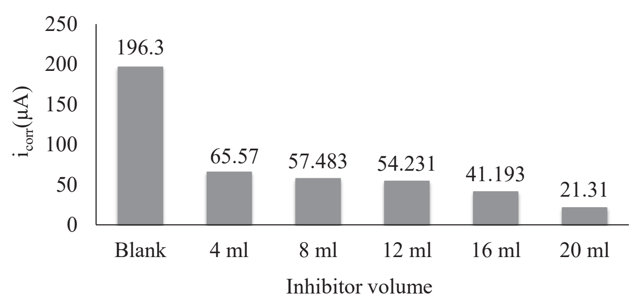

Fig. 5. Corrosion current density (i_{corr}) in the variation volume of areca flower extract

Changes in the value of i_{corr} affect the value of the corrosion rate by increasing the concentration of the inhibitor. Based on Fig. 6 below, the decrease in corrosion rate decreases with increasing concentration of the inhibitor. The lowest corrosion rate of 0.762 mm/year was obtained at a concentration of 4 ml, and the highest corrosion rate of 0.247 mm/year was obtained at a concentration of 20 ml inhibitor. With the decrease in corrosion rate, areca flower can function as an organic inhibitor.

Changes in the values of β_a and β_c can indicate that the process of adsorption of areca flower extract can change the mechanism of anodic solubility or the evolution of hydrogen in cathodics. In addition, changes in the values of β_a and β_c

when the concentration of areca flower extract is added indicate that inhibitory molecules undergo adsorption in anodic and cathodic regions [44]. Anodic reactions are controlled by the formation of layers of metal surfaces due to the adsorption of inhibitor molecules. While the cathodic reaction is controlled by the formation of oxides on metal surfaces, thus preventing the diffusion of oxygen to the metal surface.

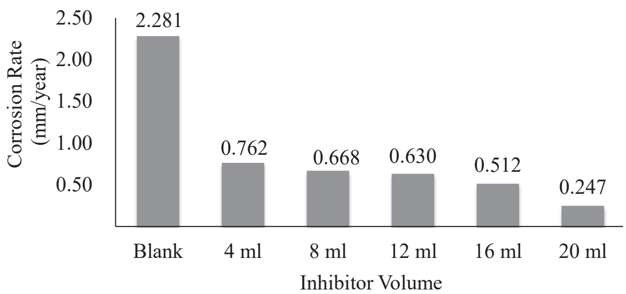

Fig. 6. Areca flower corrosion rate of linear polarization test results

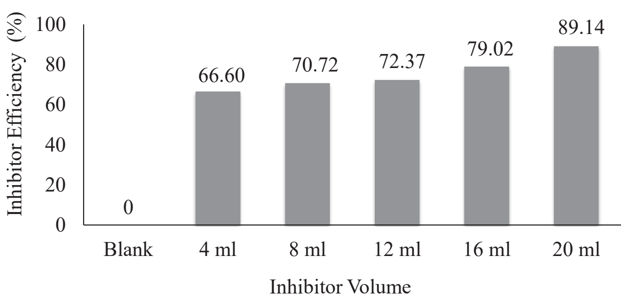

Fig. 7. Efficiency of the areca flower inhibitor for linear polarization testing

Efficiency values describe the ability of inhibitors to absorb the surface of the metal so that the metal is protected by reducing the rate of corrosion [45]. The value of the inhibitor efficiency increases with increasing concentration of the inhibitor. In Fig. 7, it is described that the lowest efficiency value of 66.6 % was obtained at a concentration of 4 ml and the optimum efficiency value of 89.14 % was obtained at a concentration of 20 ml. Raghavendra (2007), which deals with areca flowers in acidic environments, areca flowers have an efficiency of 94.4 % based on weight loss testing and 88.69 % based on polarization testing.

6. 5. Results of electrochemical impedance spectroscopy (EIS) testing

Changes in the shape of the curve indicate that there has been a change in impedance by increasing the concentration of the inhibitor. The data obtained from the EIS test included the value of solution resistance (*Ru*), polarization resistance value (*Rp*), and multiple layer resistance (*Cf*). Then the Nyquist graph is difitting to obtain electrical element and circuit data, which aims to verify the mechanistic model and calculate numerical values related to the chemical or physical properties of the electrochemical system.

In interpreting the obtained bode modulus curve in Fig. 4, we can divide the curve into three in the area *a*, *b* and *c*. Where the first region of high frequency (*a*) is an area that has a frequency range above 1 kHz, this region represents the nature of the solution/electrolyte, which represents the value of the solution resistance (*Ru*). The second area of medium frequency (*b*) is the region that shows the nature of the film/inhibitor layer. The nature of the layer as a dielectric layer that has a capacitance value of impedance. This property is simulated by the inhibitory layer capacitance, which is parallel to the value of the inhibitory layer. And the third low frequency area (*c*) describes the surface properties of the inhibitor layer with a steel substrate, which is represented by the value of the double layer capacitance (*Cf*) and polarization resistance (*Rp*). Where at low frequencies, the higher impedance value indicates the passivity of the metal surface coated by areca flower inhibitor molecules. This can be seen by the increasing concentration of the inhibitor, the polarization resistance value will increase.

The value of the resistance of the solution (*Ru*) is stable or there is no significant increase or decrease in value. It can be said that the HCl environment is in a stable state. The polarization resistance value (*Rp*) has increased significantly and has an effect on the decrease in the value of the double layer capacitance (*Cf*), due to the adsorption of inhibitor molecules on the metal surface.

The decrease in the value of the dual layer capacitance (*Cf*) as seen in Fig. 8 is caused by the adsorption of inhibitor molecules (low dielectric constants) on metal surfaces, which expel water molecules (high dielectric constants) from metal surfaces [46].

Inhibitor molecules on the metal surface will affect the electrical double layer caused by changes in the dielectric properties of the water molecules in the electric double layer [47]. A decrease in the value of the dielectric constant and/or an increase in thickness of the electrical double layer will cause a decrease in the value of the double layer capacitance (*Cf*) caused by changes in the direction of the water molecular dipole [48].

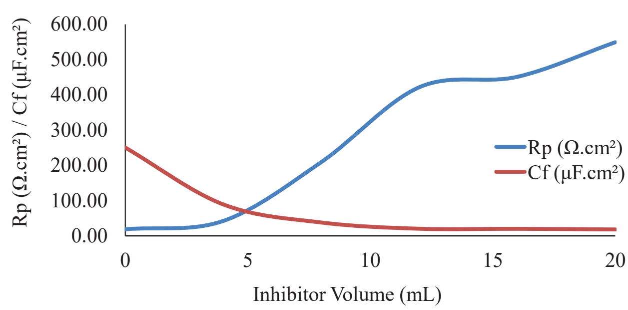

Fig. 8. Load transfer resistance values (*Rp*) and multiple layer capacitance (*Cf*) for each concentration variable

Decreased double layer capacitance (*Cf*) in Fig. 8 explains that a protective layer on the metal surface has formed [49]. With this, the results obtained from the EIS test are comparable to the results obtained by linear polarization testing, where adding the concentration of the areca flower extract inhibitor can reduce the rate of corrosion because the metal has been protected from the corrosion process.

As shown in Fig. 9, the inhibitor efficiency increases when 4 ml areca flower concentration efficiency is obtained 56 %, 8 ml concentration efficiency is obtained 91.11 %, for the addition of 12 ml concentration efficiency is 95.59 %, 16 ml areca flower concentration is 95.9 % efficiency and optimum efficiency is obtained when adding inhibitor concentration areca flower extract 20 ml, which is equal to 96.6 %. Every addition of areca flower concentration after testing has the same equivalent circuit, Randles.

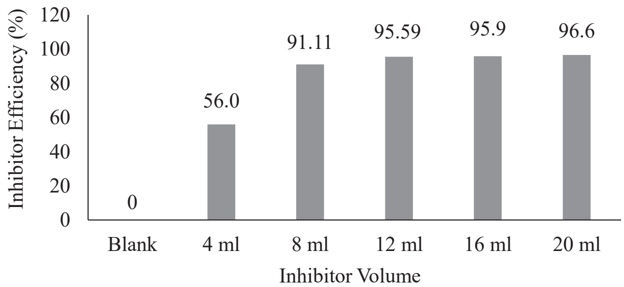

Fig. 9. Value of efficiency of inhibitors results from EIS testing

6. 6. Discussion of adsorption mechanism of inhibitor molecules

Isothermal adsorption is used to determine the adsorption and adsorption mechanism of inhibitor molecules. Thermodynamically, the process of adsorption on a molecule can be observed using isothermal adsorption. Isothermal adsorption provides basic information about the interactions that occur between the inhibitor molecule and the metal surface of the steel.

The adsorption process can be determined using the Surface Coverage value (Θ). Surface Coverage value (Θ) can be calculated using inhibitor efficiency values. Efficiency values can be obtained based on linear polarization and EIS test results. However, in this study the value of Surface Coverage (Θ) will be calculated based on the value of the inhibitor efficiency of the EIS test as in Table 6.

Table 6

Surface coverage (Θ) value on the variation of inhibitor concentration

Inhibitor Volume	Inhibitor Efficiency (%)	Surface Coverage (Θ)
Blank	–	–
4 ml	56	0.56
8 ml	91.11	0.911
12 ml	95.59	0.956
16 ml	95.9	0.959
20 ml	96.6	0.966

Determination of isothermal adsorption is done by making a graph in accordance with the variables contained in the column verification plot of Table 7. With a graph that produces the highest linear correlation coefficient, it is considered to be the most appropriate adsorption on the inhibitor molecule tested. This research will try several methods of isotermal adsorption ranging from Langmuir, Temkin, Frumkin, Bockris Swinkels, and Virial Parson.

Judging from several isothermal adsorption methods (Temkin, Langmuir, Frumkin, Bockris Swinkels, and Virial Parson) as shown below, it is found that the Langmuir isothermal adsorption method has the highest correlation coefficient value (0.977). So it can be concluded that the adsorption molecules of areca flower extract inhibitors will undergo an adsorption process in accordance with the Langmuir method.

Langmuir isothermal adsorption assumes that organic molecules are adsorbed as monolayers on metal surfaces that do not interact with other adsorbed molecules and molecules that are adsorbed only in one area (site) only [50]. Thus, the areca flower inhibitor molecule is expected to be adsorbed on a metal surface to form a single inhibitory layer (monolayer).

Table 7

Linear equations (y) and linear regression (r^2) of the isotherm adsorption method

Isothermal Adsorption Method	Linear Equation (y)	Linear Regression (r^2)
Langmuir	$y=4.576x-3.253$	0.977
Temkin	$y=-0.243x-0.101$	0.792
Bockris Swinkels	$y=-0.0151x+0.0864$	0.0068
Frumkin	$y=-1.051x+0.023$	0.974
Virial Parson	$y=-0.604x+0.054$	0.938

Thermodynamic parameters in the adsorption process can be used to predict the adsorption process that occurs. Types of adsorption are divided into two types, namely: physical adsorption or chemical adsorption [51]. From the Langmuir isothermal adsorption model to obtain the value of ΔG_{ads} we must first find the K_{ads} value (the adsorption equilibrium constant). The K_{ads} value (adsorption equilibrium constant) represents the interaction between the adsorbed molecule and the metal surface. The K_{ads} value is the opposite of the intersection point of the Y axis in the Langmuir isothermal adsorption graph line equation at concentration 0 (the intersection point on the y axis).

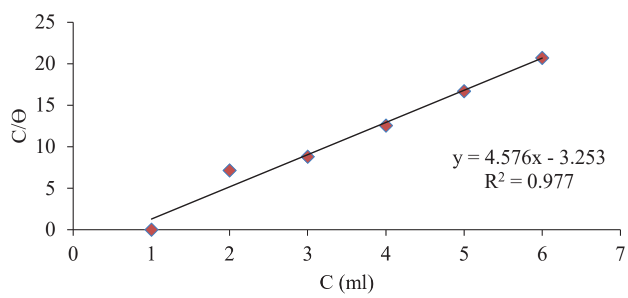

Fig. 10. Langmuir isotermal adsoption

Based on the Langmuir isothermal adsorption graph (Fig. 10), the Langmuir line equation, $y=4.576x-3.253$ is obtained. So the K_{ads} value can be obtained from the equation at 0.307. The efficiency of the inhibitor is basically a function of the magnitude of the adsorption equilibrium constant (K_{ads}). In addition to the K_{ads} value, we can get the magnitude of the coefficient value y. The coefficient value of y expresses the number of inhibitor molecules adsorbed to occupy one active site. From the line equation $y=4.576x-3.253$, the coefficient of y value of 4.576 is obtained, so that the inhibitor molecules needed to coat or cover one active site are 4,576.

Table 8

Standard Gibbs energy (ΔG_{ads}) from experimental results

Equation	K_{ads}	ΔG_{ads} (kJ/mol)
$y=4.576x-3.253$	0.307	–7.026

The value of changes in adsorption free energy (ΔG_{ads}) can explain the tendency of adsorption on inhibitor molecules. And after the calculation as per Table 8, the ΔG_{ads} value of –7.026 kJ/mol is obtained. The value of free energy changes (ΔG_{ads}) is negative, stating that the adsorption process of the areca flower inhibitor molecule takes place spontaneously. Meanwhile, to determine the type of adsorption whether chemically or physically influenced by the magnitude of the change in adsorption free energy (ΔG_{ads}). If the change in the value of the adsorption free energy (ΔG_{ads}) is greater than –20 kJ.mol, then it is stated as physical adsorption, while the value of the change of free energy adsorption equal to or less than –40 kJ/mol is expressed as chemical adsorption [52]. If the ΔG_{ads} value is in the range of –20 to –40 kJ/mol, the inhibitor is classified as a mixture of adsorption types, either physical or chemical. The type of adsorption on the areca flower inhibitor molecule is expressed as physical adsorption because the free energy value of adsorption is –7.026 kJ/mol. So it can be stated that the adsorption process between the inhibitor molecule and the metal layer that occurs is caused by the interaction between the electrostatic inhibitor molecule and the metal surface layer. Areca flower inhibitors containing polyphenol compounds and flavonoids will have a negative charge due to the arrival of O free electrons from polyphenol compounds and flavonoids. While the metal surface will have a positive charge. The difference in charge between the inhibitor molecule and the metal surface will result in electrostatic interactions that stimulate physical adsorption. Therefore, the adsorption process occurs due to electrostatic interaction, not because of the use of shared electrons or the formation of complex bonds. As a consequence, plants containing polyphenol and flavonoid compounds undergo physical adsorption processes on metal surfaces that will form inhibitory layers [53].

7. Conclusions

1. Areca flower extract can be used as an alternative environmentally friendly inhibitor for API 5L Gr B steel in 1 M HCl environment.

2. The corrosion rate of API 5L Gr B steel in 1 M HCl environment will decrease with increasing concentration of areca flower extract inhibitors, the optimum efficiency of linear polarization testing of 89.14 % is obtained by adding 20 ml of areca flower extract concentration and the optimum efficiency of EIS testing of 96.6 % is obtained on the addition of a concentration of 20 ml areca flower extract.

3. Environmentally friendly inhibitors of areca flower extract will be adsorbed onto the metal surface following the Langmuir isothermal adsorption model and the type of adsorption that occurs is physical adsorption (physisorption).

4. The adsorption mechanism is determined wherein the inhibitor extract of the areca flower will form a monolayer layer on the steel surface of API 5L and in addition, the layer will be a barrier between the steel surface and the environment so that the steel surface does not directly interact with the acidic environment.

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