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Soybean and Glycine as Potential Corrosion Inhibitors for Steel in Hydrochloric Acid: Electrochemical and Morphological Studies

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ABSTRACT

The potential of soybean and glycine as organic corrosion inhibitors for steel in acid solution was examined through weight loss tests and potentiodynamic polarization. Both soybean and glycine were characterized via FTIR and UV-visible. The result shows that the soybean and glycine contain isoflavone and nitrogen bonds respectively as a beneficial element in inhibiting the corrosion of steel. Corrosion tests were performed with and without the presence of soybean and glycine for 3 days of immersion in the acidic medium. Corrosion inhibition efficiency measured via electrochemical test found that both soybean and glycine give an excellent corrosion inhibition efficiency at 1.5 g/L in 0.5 M HCl up to 96% and 94% respectively. Tafel analysis reveals both inhibitors perform mixed types inhibitors which predominantly anodic inhibition. Pseudo-passivation was observed in the Tafel curve indicating the capabilities of both inhibitors to passivate the corrosion at anodic potential. Observation of the steel samples through an optical microscope shows that the corrosion of the steel surface was inhibited in the addition of soybean and glycine in HCl. The roughness of the steel surface affected by the combination of uniform and pitting corrosion was also reduced. In overall, soybean and glycine exhibit excellent anticorrosive properties due to the presence of significant chemical structures and active functional groups. Analysis of the inhibition mechanism through isotherm showed that soybean and glycine followed Langmuir isotherm, indicating the adsorption type for both inhibitors is chemisorption. The results obtained *from this study could be a good reference in diversifying the study of amino acids as metal corrosion inhibitors to benefit metal-based industries.*

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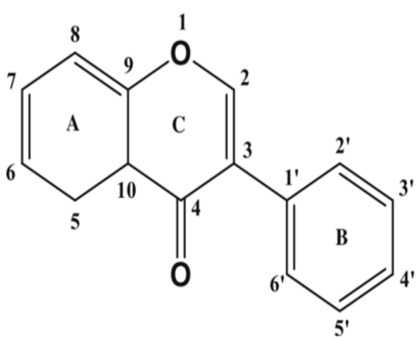
Keywords: Corrosion; Stainless Steel; Soybean; Potentiodynamic Polarization; Adsorption

INTRODUCTION

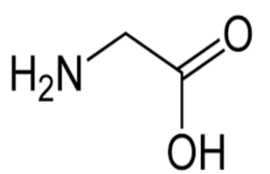
The utilization of metal-based materials especially steel and its alloy are the norm in industrialized nations. Steel is exploited in a wide range of applications, including residential and commercial constructions, bridges and trusses, automobiles, engines, pipelines and gas processing plants. Several protection and control methods have been performed extensively to sustain the steel integrity, however, it depends on the environmental condition, types of alloys and practicality [1]. Corrosion is a natural occurrence that is always being degraded whenever in contact with an aggressive environment. Corrosion may also cause the metal to lose some crucial qualities. When steel being rusts, for example, it loses its toughness, and the rusty iron crumbles readily [2]. Corrosion of ferrous metal in acid should be controlled to avoid loss of plant efficiency, reduce failure, improve safety, expand product quality and reduce lifetime cost.

Corrosion inhibitors which are a substance used to control the metal degradation, when added in small quantities reduce the rate of corrosion of a metal in an environment. Nowadays, organic corrosion inhibitors in acidic environments become popular in industrial usage [3-6]. This preference was due to the significant impact on the environment, less toxic, eco-friendly, and more biodegradable. The use of natural resources, especially plants, to produce valuable organic chemicals has drawn a lot of interest [7]. Plant extract [3], [8], polymeric and ionic liquid [9], [10], drugs [11], macrocycles, gums, carbohydrates [12] and amino acid [13], have been reported as a good corrosion inhibitors in acid medium.

Amino acids are molecules that must possess at least one carboxyl (-COOH) group and one amino (-NH2) group usually bonded to the same carbon atom [13]. The capability of amino acid to inhibit corrosion of metal has a wide range which is strongly dependent on the corrosion system studied. The use of green and organic chemical sources was more desirable in formulating a corrosion inhibitor. Soybean, rich with amino acids is seen to be an alternative corrosion inhibitor as it contains a high percentage of protein as well as carbohydrates. Macromolecules such as protein and polysaccharides play an important role in the inhibitory action towards mild steel acid corrosion [14]. Soybean has high potential as an organic corrosion inhibitor as it is a compound containing oxygen, nitrogen and sulfur which reported to be a good corrosion inhibitors [15]. Soybeans are the main source of isoflavones, a subclass of polyphenols with a high added value isoflavone of flavonoids that has a diphenylpropane structure (C6–C3–C6) (Figure 1(a)). The main structural difference between isoflavone and flavone is at carbon of the C-ring and the B-ring is located in the flavonoid skeleton [16]. Glycine is another compound that may act as a corrosion inhibitor due to its important active groups in the structure. Glycine (Figure 1(b)) is an aliphatic and nonpolar structure of amino acid classes. The significant functional group such as NH_2, CH_2 and COOH can coordinate with metals through the nitrogen atom and oxygen atom of the carboxyl group. It has been reported that glycine gives below 60% corrosion inhibition for cooper in nitric and hydrochloric acid [17].



(a)



(b)

Figure 1: Chemical structure of (a) isoflavone and (b) glycine

A comparative study between soybean and glycine has never been comprehensively reported. This study is important to ensure that the natural sources of amino acid from soybean plant was fully utilized in any area of industries. To investigate the soybean and glycine effectiveness as corrosion inhibitors for steel, corrosion inhibition will be measured through corrosion analysis. Chemical characterization of both soybean and glycine was carried out by FTIR and UV-visible to identify the presence of active functional groups for corrosion inhibitory properties. The corrosion inhibition efficiency by soybean extract and glycine as corrosion inhibitors for SUS304 were evaluated at different concentrations of hydrochloric acid through immersion test and potentiodynamic polarization test. Adsorption study was performed for the selected corrosive medium. Surface morphology was done to investigate the corrosion effect with and without soybean and glycine in an acidic medium.

METHODOLOGY

Preparation of metal coupon and corrosion inhibitor

A metal of stainless steel SUS304 samples was cut into the size of 21mm x 21mm x 3mm. The chemical composition of the steel is C:0.042 %, Si:0.470 %, Mn:0.970 %, P:0.029 %, S:0.004 %, Ni:8.090 %, Cr: 18.060 %, N:0.058 %, Cu:0.020 % and Fe:72.260 %. The sample was then cleaned and polished by using a polishing machine. The samples were then dipped in acetone and distilled water to clean the impurities on the steel and then washed using distilled water [18]. Hydrochloric acid was used as a corrosive medium. The acid solution was prepared at the concentrations of 0.25M, 0.5M and 1.0M. The corrosion inhibitor was prepared by dissolving the soybean powder and glycine in an ethanol solution. Both corrosion inhibitor solutions were prepared in different concentrations in the range of 0.5 to 2.5 g/L. The characterization of corrosion inhibitors was done through FTIR and UV-Vis to identify the appearance of functional groups.

Immersion test

Immersion test or formally known as weight loss test was performed by determining the loss of weight before and after an immersion in a corrosive medium. The final weight of the metal specimen was measured as soon as the metal coupon had been dried after being withdrawn from the corrosive medium and inhibitor. The data obtained were then used to calculate the corrosion rate (Eq. 1) and inhibition efficiency (Eq. 2) in every corrosion inhibitor concentration used in this study. The test methods performed in this study were based on the ASTM G31-72 standard [19].

$$\text{Corrosion rate (mm/y)} = \frac{K \times W}{D \times A \times T} \tag{1}$$

where,
K = 8.76×10^4
W = weight loss (g)
D = density of metal (g cm^{-3})
A = area of metal (cm^2)
T = time of exposure (hours)

$$\text{Inhibition efficiency, IE\%} = \frac{CR_o - CR_f}{CR_o} \times 100 \tag{2}$$

where,
CR_0 = corrosion rate of uninhibited metal (g)
CR_f = corrosion rate of inhibited metal (g)

Potentiodynamic polarization studies

In potentiodynamic polarization measurements, three-electrode systems were used. The SUS304 steel specimen was used as a working electrode. A platinum mesh and a conventional Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The metal specimens were then placed in an electrochemical cell containing 0.25M, 0.5M and 1.0M HCl in the presence of glycine and soybean extract. The potentiodynamic polarization experiments were performed in the applied potential range from ±250 mV with different scan rate of 1 mV s^{-1} by using a potentiostat-galvanostat, equipped with NOVA 1.0 software. The test methods performed followed the ASTM G59-97 standard method [20].

Surface Analysis

Surface analysis particularly morphology and surface structure were performed by using a light microscope Olympus SZ51. Surface analysis was done to examine and observe the effect of the corrosion on the metal specimen. The sample chosen for morphology analysis was taken after completing the immersion test (72 h immersion). The sample was cleaned and dried before being analyzed under a microscope.

RESULT AND DISCUSSION

Characterization of soybean and glycine

Infrared spectrum analysis is a useful tool for interpreting chemical bonds and obtaining information on the molecular structure of a produced substance. In this study, the purpose of FTIR analysis is to identify the functional group present in both soybean and glycine.

Table 1 shows the FTIR wavenumber and vibrational character for soybean extract and glycine. Soybean spectra lies within the range of 4000 cm^{-1} - 600 cm^{-1}. It was detected that a peak at 3280.31 cm^{-1} indicates an N-H stretch which is an amide. Whereas C-H stretch can be seen at the 2925.19 cm^{-1} and 2856.96 cm^{-1}. The C=O stretch is shown at wavenumber 1743.15 cm^{-1}. A peak at 1637.88 cm^{-1} was possibly shows a C-O and C-N stretch. A functional group of C-N stretching and N-H bending was found at 1541.60 cm^{-1}. Whereas at the 1399.83 cm^{-1}, a CH_3 bending and COO- symmetrical stretching are detected. The peak at 1241.09 represents amide III assignment which typically occurs around 1200-1300 cm^{-1} and arises from the combination of N-H bending and C-N stretching vibrations in proteins. The vibration wavelength at 1047.19 cm^{-1} signifies the C-O stretch. While at 698.23 cm^{-1} a bond of O-C-O bending is present [21].

The NH_3^+ stretching vibrations in glycine are liable for the wide band in the higher energy area between 3100 – 2699.57 cm^{-1}. The asymmetrical

NH_3^+ bending vibration and the NH_3^+ group's torsional oscillation may be responsible for the band at 2173.4 cm^{-1}. The COO group's asymmetric and symmetric stretching modes were attributed to two overlapping bands at roughly 1571.12 and 1483.74 cm^{-1}. The CH_2 bending, CH_2 twisting, and COO bending was found at the peaks around 1388.99, 1324.2, and 681.24 cm^{-1} respectively. The varieties of functional groups presence in soybean and glycine exhibits the capability of both substances to have an anticorrosion properties.

Table 1: Frequencies and assignment vibrations of soybean and glycine via FTIR analysis

Soybean		Glycine	
Wavenumber (cm^{-1})	**Assignment of Vibration**	**Wavenumber (cm^{-1})**	**Assignment of Vibration**
3280.31	N-H stretch	3091.797	NH_3^+ stretch
2925.19	C-H stretch	2173.4	NH^+ bending
2856.96	C-H stretch	1571.12	COO- asymmetric stretching
1743.15	C=O stretch	1483.74	COO- symmetric stretching
1637.88	C-O, C-N stretch	1388.99	COO- symmetric stretching
1541.60	C-N stretching, N-H bending	1324.2	CH_2 twisting
1399.83	CH_3 bending, COO- stretching (sym)	1125.10	NH_3^+ rocking
1241.09	N-H bending, C-N stretching	1043	CCN symmetric stretching
1047.19	C-O stretch	924	CH_2 rocking
698.23	O-C-O bending	891.07	CCN symmetric stretching
-	-	681.24	COO- bending

UV-Vis Analysis

Observing the corrosion inhibitors absorption of ultraviolet (UV) light is one of the most used techniques for examining a compound properties and purity in solution. The UV spectroscopy provides the specific information of molecules based on quantum mechanics. When molecules absorb UV radiation, their electrons that make up the pi-bond or conjugation form (chromophore) are excited. Table 2 represents the wavelength of soybean and glycine detected via UV-visible analysis. Our result shows the soybean wavelength was detected at 340, 290 260 and 205 nm. Meanwhile Glycine shows several vibrations at the wavelength 262, 267 and 270 nm. Soybean extracted in ethanol will dissolve a phenolic compound namely isoflavone [22]. The UV absorption peak of soy isoflavone was reported to be appeared at 245 to 270 nm. The shoulder peak of soy isoflavone is at 310 to 330 nm [16].

According to a review by Jung et al. [16], most of the flavonoid scaffolds have two main UV absorption spectra: cinnamoyl system (B-ring) located around 300–380 nm and benzoyl system (A- ring) positioned at 240 –280 nm in a flavonoid structure. From our result, it is suggested that the soybean extract shows the presence of isoflavone. These properties show a good indication for a corrosion inhibitory action. The existence of an aromatic compound in corrosion inhibitors molecules will enhance the efficiency of corrosion inhibition.

Table 2: Wavelength of soybean and glycine detected via UV-visible

Soybean (nm)	Glycine (nm)
340	-
290	270
260	267
205	262

Immersion Test

Figure 2 shows the corrosion rate of SUS304 in different concentration of hydrochloric acid, HCl. The highest corrosion rate at 5.38 mm/y was observed in the 1.0 M HCl solution, whereas the lowest one was in 0.25 M

HCl with only 3.48 mm/y. It can be deduced that the higher the concentration of acid, the greater the corrosion rates value. This is accordance to the high dissolution rate of steel once contact in the high concentration of acid solution. It should be noted that the oxidation of metals in acid solution involves the steel dissolution. Meanwhile, the reduction processes involved hydrogen evolution. In our study, the corrosion systems were let to be exposed to an atmosphere. The reduction processes involved in the corrosion reaction would be also an oxygen reduction. However, the environment was not at the high amount of dissolved oxygen. Therefore, hydrogen evolution was the main reduction process in this corrosion reaction.

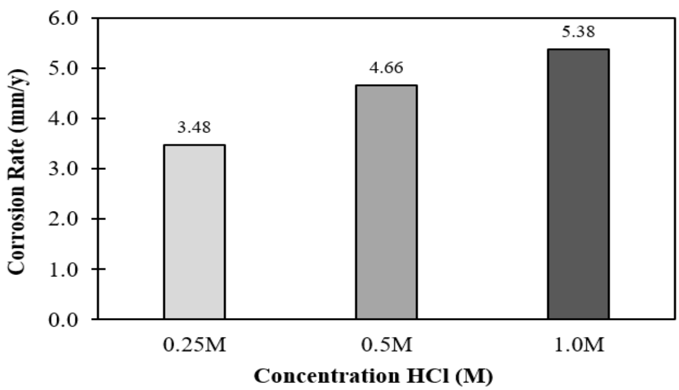


Figure 2: Corrosion rate of SUS304 in different concentration of hydrochloric acid

Immersion test through weight loss method was performed to determine the effect of soybean and glycine addition in inhibiting corrosion of stainless steel in hydrochloric acid. Figure 3 shows the result for the weight loss test which presented the inhibition efficiency of various concentration of soybean and glycine in different concentration of acid.

Soybean and glycine have shown the highest inhibition at 1.5 g/L in 0.5 M HCl with moderate efficiency up to 73 % and 69 % respectively. The lowest inhibition was shown in both inhibitors at all concentrations studied in 1.0 M HCl. It can be observed that by increasing the concentration of inhibitors up to 2.5 g/L, the capability of soybean to inhibit steel corrosion was reduced by showing the IE value at 22 % to 30 % in all of the acid concentrations. A similar trend is also shown by glycine, however the inhibition efficiency is much better than soybean which is in the range of 28 % to 48 %. High concentration of inhibitors may destruct the adsorption process. This will be happened through mutual attractive and repulsive force that might weaken the inhibitor film adsorbed on the steel surface. This effect was more clearly observed for soybean inhibitors which have a large molecule structure and tend to cause steric hindrance effect. Unlike the simple structure of glycine, the occurrence of competitive interaction in the solution/metal interfaces may be lesser than in soybean.

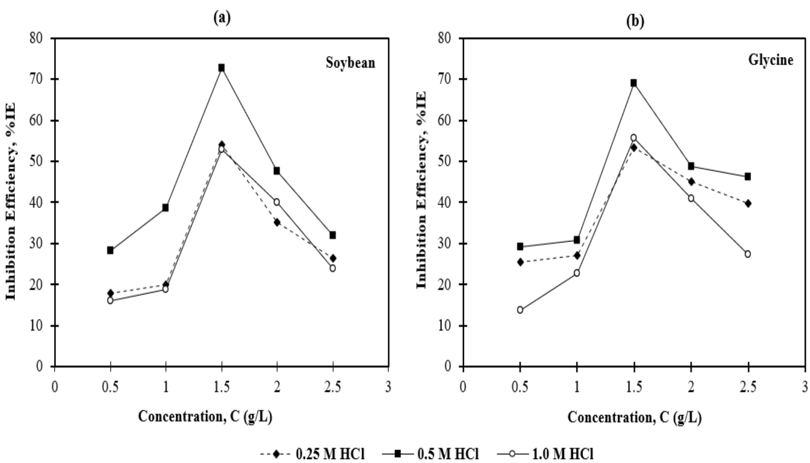


Figure 3: Corrosion inhibition efficiency (%IE) of SUS304 in different concentration of hydrochloric acid in the presence of (a) soybean and (b) glycine via weight loss method at room temperature ±25 ºC.

Potentiodynamic Polarization

Potentiodynamic polarization test was performed to determine the electrochemical parameter and the corrosion kinetic. Table 3 shows the result obtained from the potentiodynamic polarization test performed in 0.5 M HCl with and without soybean. The concentration of soybean at 1.5 g/L gives the highest inhibition at 96 % with the corrosion rate values 0.47 mm/y indicating an excellent performance in the studied system. The shift in corrosion potential to a more positive potential and the decrease in current density was observed in the Tafel curve (Figure 4).

Table 3: Electrochemical parameters of SUS304 with and without soybean in 0.5M HCl

Concentration Soybean g/L	E_{corr} (mV)	I_{corr} (μ A/cm²)	Corrosion Rate (mm/y)	Inhibition Efficiency (%)
0.0	-438.050	910.080	10.575	-
0.5	-397.700	427.230	4.964	53
1.5	-363.010	40.782	0.474	96
2.5	-377.580	47.932	0.557	95

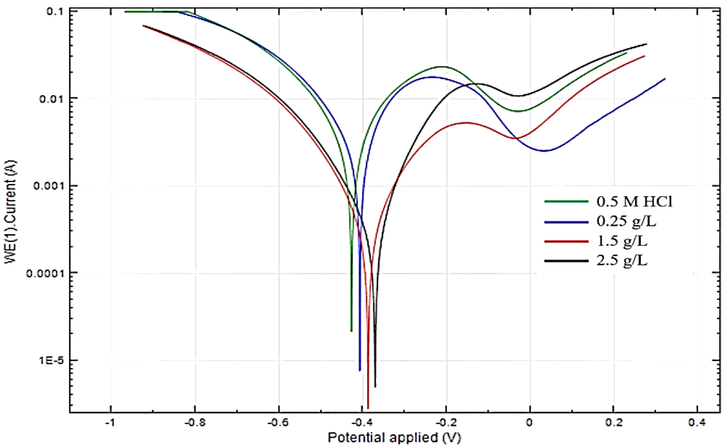


Figure 4: Tafel polarization curve of SUS304 in 0.5 M HCl and with soybean at different concentration

The lowest inhibition efficiency was showed at 0.5 g/L soybean with only 53 %. This could be happened due to the very low concentration of soybean extract to hinder the aggressive acid from attacking the steel surfaces. The addition of soybean up to 2.5 g/L gives insignificant changes in IE value as compared to 1.5 g/L. It is suggested that at the concentration (2.5 g/L), there may be steric hindrance when a large molecule attempts to fit onto a surface that already partially occupied with the molecules previously. In consequence at the highest concentration, the complete coverage of soybean molecules on the metal surface is difficult to achieve, thus the inhibition was reduced. These occurrences always happen in a large molecule of corrosion inhibitors [2]. From the Tafel curve, it can be observed there is a shift in potential value to a more positive potential. However, by considering the value of E_{corr} which is within the range of ±85mv for all of the concentrations studied with respect to the blank HCl, the soybean has behaved as mixed types corrosion inhibitor. This signifies that the soybean molecules have retard the corrosion by affecting both the anodic and cathodic redox reaction. Nevertheless, the inhibition was predominantly anodic effectiveness [23]. The potentiodynamic polarization in glycine also has been done and the result follows the similar trend as in soybean extract.

Table 4 shows the electrochemical parameter for SUS304 in glycine at 1.5 g/L in different concentration of HCl. The I_{corr} value shows significant changes, whereby the highest I_{corr} was recorded for glycine in 1.0 M HCl. This result was corresponded to the high corrosion rates and low IE values. The progress in current density for the whole potential in the polarization test was shown in Figure 5. It also can be seen that in the 0.5 M HCl, the low corrosion rate at 0.635 mm/y results in the highest IE which has reduced in I_{corr} value. All these results shows that the glycine also was capable to react as good corrosion inhibitors for SUS304 steel in 0.5 M HCl. The chloride ion was suggested to facilitate the inhibition efficiency as it can provide the co-operative adsorption on the steel surface rather than enhance the dissolution of surface. The protonated inhibitor (glycine) can electrostatically adsorb onto the halide-covered surface through its hydrogen ion. Thus, the presence of chloride has increased the efficiency of an organic inhibitor and reduce the corrosion rate.

Table 4: Electrochemical parameters of SUS304 in the presence of 1.5g/L glycine in different concentration of HCl

Concentration HCl (M)	E_{corr} (mV)	I_{corr} (µ A/cm^2)	Corrosion Rate (mm/y	Inhibition Efficiency (%IE)
0.25	-304.210	206.060	2.394	72
0.5	-356.930	154.600	0.635	94
1.0	-369.140	372.540	4.329	67

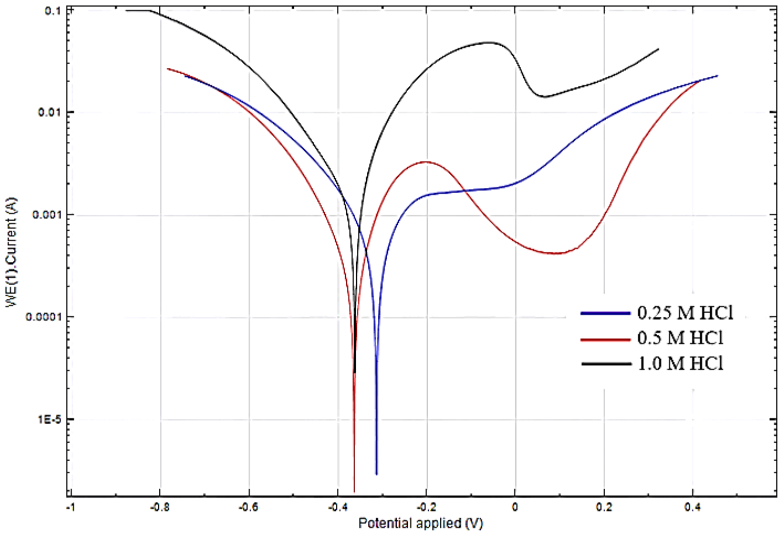


Figure 5: Tafel polarization curve of SUS304 in 1.5 g/L glycine in different concentrations of HCl

In this study, both corrosion inhibitors (soybean and glycine) were showed a good inhibition efficiency in 0.5 M HCl, but moderate efficiency in 0.25 M and 1.0 M. This could be happened due to the effect of chloride concentration. It should be noted that the presence of chloride in corrosion inhibitors systems could be either benefit or detriment the corrosion inhibition [2]. Chloride ion may assist in inhibition by having a cooperative adsorption between the organic molecules and metal surfaces. In other side, the chloride ion may also enhance the corrosion by attacking the metal surface. In this study the presence of chloride concentration in 0.5 M HCl gives an advantage to the glycine (as well as soybean extract) to perform an efficient corrosion inhibitor. Meanwhile, the high concentration of chloride ion in 1.0 M HCl results in the low efficiency of inhibition. The moderate efficiency also was shown at 0.25 M HCl even though the chloride ion was in minimum concentration. It is suggested that, at the system of 0.5 M HCl in the presence of 1.5 g/L glycine (and soybean), a maximum inhibition efficiency was achieved due to the interaction of inhibitors in both redox reaction (inhibit cathodic and anodic reaction) and with the assistance of chloride ions.

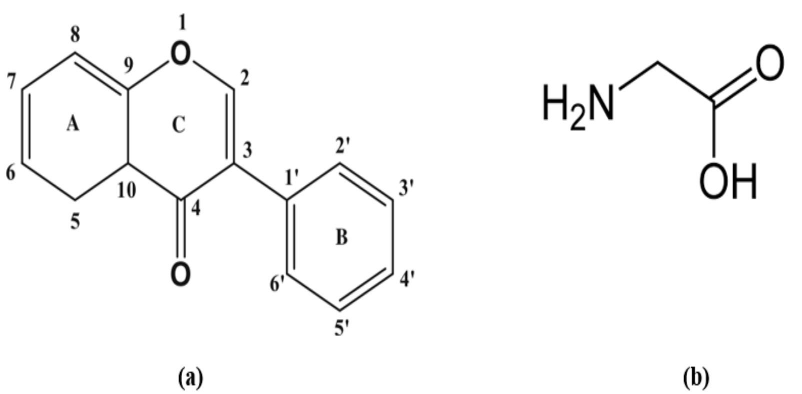
From the Tafel curve in both Figure 4 and Figure 5, the stainless steel in the presence of 1.5 g/L inhibitors shows the phenomenon of passivation. This situation indicated by the shouldered curve along the positive potential polarization. There is a sudden decreased in current density results in the form of sharp peak (or shoulder) at the more positive potential. This signifies the oxidation process at the anode was affected by the presence of inhibitors which might form a protective barrier on the steel surfaces. The pseudo-passivation was observed for almost all of the system studied indicating the passivation has occurred at a very short time. The formed protective barrier was unable to maintain the protectivity roles, in consequences, the current density was increased up and the steel was said to be transpassive. The mechanism of oxide growth is explained by applying the concepts of passivity of metals to the corrosion system [24]. Passivity is defined as the decrease in chemical or electrochemical activity of a metal as a result of the metal's reaction with its surroundings to develop a protective layer on the metal surface [2], [24].

The results obtained in weight loss test was agreed with those obtained in the potentiodynamic polarization test. However, it should be emphasized that the immersion test, which employs a more real time experimental technique than the electrochemical method, yields more trustworthy results. Due to these variations, it is therefore expected that the results from the two tests shows a few minor deviations. Nevertheless, both approaches produced results that were quite similar and are trustworthy methods to evaluate corrosion inhibition.

Surface Morphology

Figure 6 shows the morphology surfaces of stainless steel SUS304 in 0.5 M HCl in the presence of 1.5 g/L soybean and glycine. In this study, the coupon metal which involved in the surface analysis was obtained from the immersion test. The steel surfaces in the blank solution (Figure 6(a)) shows the appearance of oxide scattered on the entire of the surface indicated the formation of oxide as well as corrosion product due to the corrosion process. The formation of corrosion product precipitation around the pits resulting from the aggressive attack to the stainless steel by chloride ions [25].

studied. The use of green and organic chemical sources was more desirable in formulating a corrosion inhibitor. Soybean, rich with amino acids is seen to be an alternative corrosion inhibitor as it contains a high percentage of protein as well as carbohydrates. Macromolecules such as protein and polysaccharides play an important role in the inhibitory action towards mild steel acid corrosion [14]. Soybean has high potential as an organic corrosion inhibitor as it is a compound containing oxygen, nitrogen and sulfur which reported to be a good corrosion inhibitors [15]. Soybeans are the main source of isoflavones, a subclass of polyphenols with a high added value isoflavone of flavonoids that has a diphenylpropane structure (C6–C3–C6) (Figure 1(a)). The main structural difference between isoflavone and flavone is at carbon of the C-ring and the B-ring is located in the flavonoid skeleton [16]. Glycine is another compound that may act as a corrosion inhibitor due to its important active groups in the structure. Glycine (Figure 1(b)) is an aliphatic and nonpolar structure of amino acid classes. The significant functional group such as NH_2, CH_2 and COOH can coordinate with metals through the nitrogen atom and oxygen atom of the carboxyl group. It has been reported that glycine gives below 60% corrosion inhibition for cooper in nitric and hydrochloric acid [17].



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Soybean		Glycine	
Wavenumber (cm^{-1})	**Assignment of Vibration**	**Wavenumber (cm^{-1})**	**Assignment of Vibration**
3280.31	N-H stretch	3091.797	NH_3^+ stretch
2925.19	C-H stretch	2173.4	NH^+ bending
2856.96	C-H stretch	1571.12	COO- asymmetric stretching
1743.15	C=O stretch	1483.74	COO- symmetric stretching
1637.88	C-O, C-N stretch	1388.99	COO- symmetric stretching
1541.60	C-N stretching, N-H bending	1324.2	CH_2 twisting
1399.83	CH_3 bending, COO- stretching (sym)	1125.10	NH_3^+ rocking
1241.09	N-H bending, C-N stretching	1043	CCN symmetric stretching
1047.19	C-O stretch	924	CH_2 rocking
698.23	O-C-O bending	891.07	CCN symmetric stretching
-	-	681.24	COO- bending

UV-Vis Analysis

Observing the corrosion inhibitors absorption of ultraviolet (UV) light is one of the most used techniques for examining a compound properties and purity in solution. The UV spectroscopy provides the specific information of molecules based on quantum mechanics. When molecules absorb UV radiation, their electrons that make up the pi-bond or conjugation form (chromophore) are excited. Table 2 represents the wavelength of soybean and glycine detected via UV-visible analysis. Our result shows the soybean wavelength was detected at 340, 290 260 and 205 nm. Meanwhile Glycine shows several vibrations at the wavelength 262, 267 and 270 nm. Soybean extracted in ethanol will dissolve a phenolic compound namely isoflavone [22]. The UV absorption peak of soy isoflavone was reported to be appeared at 245 to 270 nm. The shoulder peak of soy isoflavone is at 310 to 330 nm [16].

According to a review by Jung et al. [16], most of the flavonoid scaffolds have two main UV absorption spectra: cinnamoyl system (B-ring) located around 300–380 nm and benzoyl system (A- ring) positioned at 240 –280 nm in a flavonoid structure. From our result, it is suggested that the soybean extract shows the presence of isoflavone. These properties show a good indication for a corrosion inhibitory action. The existence of an aromatic compound in corrosion inhibitors molecules will enhance the efficiency of corrosion inhibition.

Table 2: Wavelength of soybean and glycine detected via UV-visible

Soybean (nm)	Glycine (nm)
340	-
290	270
260	267
205	262

Immersion Test

Figure 2 shows the corrosion rate of SUS304 in different concentration of hydrochloric acid, HCl. The highest corrosion rate at 5.38 mm/y was observed in the 1.0 M HCl solution, whereas the lowest one was in 0.25 M

HCl with only 3.48 mm/y. It can be deduced that the higher the concentration of acid, the greater the corrosion rates value. This is accordance to the high dissolution rate of steel once contact in the high concentration of acid solution. It should be noted that the oxidation of metals in acid solution involves the steel dissolution. Meanwhile, the reduction processes involved hydrogen evolution. In our study, the corrosion systems were let to be exposed to an atmosphere. The reduction processes involved in the corrosion reaction would be also an oxygen reduction. However, the environment was not at the high amount of dissolved oxygen. Therefore, hydrogen evolution was the main reduction process in this corrosion reaction.

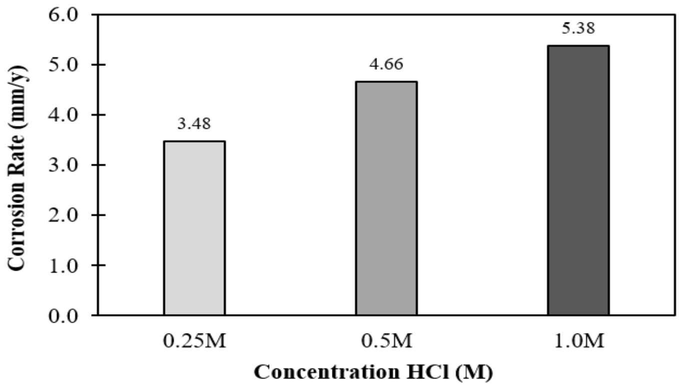

Figure 2: Corrosion rate of SUS304 in different concentration of hydrochloric acid

Immersion test through weight loss method was performed to determine the effect of soybean and glycine addition in inhibiting corrosion of stainless steel in hydrochloric acid. Figure 3 shows the result for the weight loss test which presented the inhibition efficiency of various concentration of soybean and glycine in different concentration of acid.

Soybean and glycine have shown the highest inhibition at 1.5 g/L in 0.5 M HCl with moderate efficiency up to 73 % and 69 % respectively. The lowest inhibition was shown in both inhibitors at all concentrations studied in 1.0 M HCl. It can be observed that by increasing the concentration of inhibitors up to 2.5 g/L, the capability of soybean to inhibit steel corrosion was reduced by showing the IE value at 22 % to 30 % in all of the acid concentrations. A similar trend is also shown by glycine, however the inhibition efficiency is much better than soybean which is in the range of 28 % to 48 %. High concentration of inhibitors may destruct the adsorption process. This will be happened through mutual attractive and repulsive force that might weaken the inhibitor film adsorbed on the steel surface. This effect was more clearly observed for soybean inhibitors which have a large molecule structure and tend to cause steric hindrance effect. Unlike the simple structure of glycine, the occurrence of competitive interaction in the solution/metal interfaces may be lesser than in soybean.

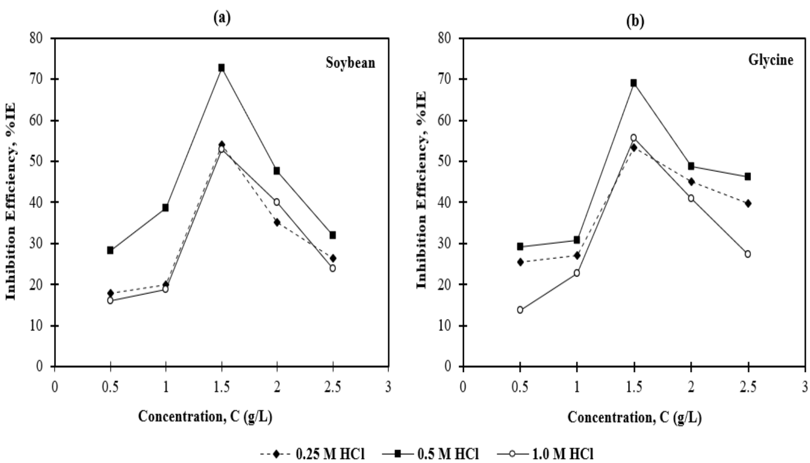

Figure 3: Corrosion inhibition efficiency (%IE) of SUS304 in different concentration of hydrochloric acid in the presence of (a) soybean and (b) glycine via weight loss method at room temperature ±25 °C.

Potentiodynamic Polarization

Potentiodynamic polarization test was performed to determine the electrochemical parameter and the corrosion kinetic. Table 3 shows the result obtained from the potentiodynamic polarization test performed in 0.5 M HCl with and without soybean. The concentration of soybean at 1.5 g/L gives the highest inhibition at 96 % with the corrosion rate values 0.47 mm/y indicating an excellent performance in the studied system. The shift in corrosion potential to a more positive potential and the decrease in current density was observed in the Tafel curve (Figure 4).

Table 3: Electrochemical parameters of SUS304 with and without soybean in 0.5M HCl

Concentration Soybean g/L	E_{corr} (mV)	I_{corr} (μ A/cm²)	Corrosion Rate (mm/y)	Inhibition Efficiency (%)
0.0	-438.050	910.080	10.575	-
0.5	-397.700	427.230	4.964	53
1.5	-363.010	40.782	0.474	96
2.5	-377.580	47.932	0.557	95

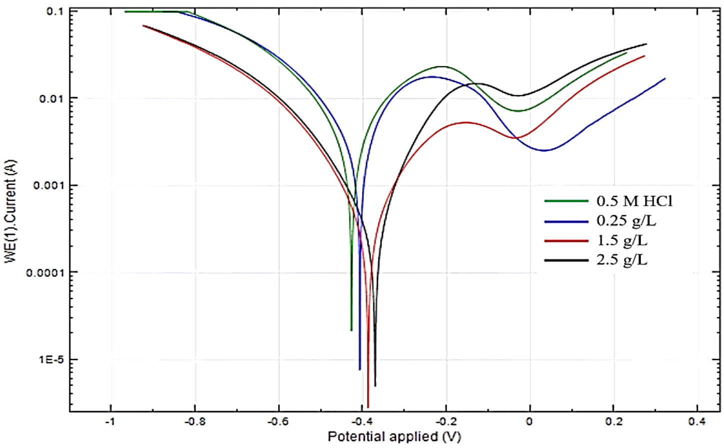

Figure 4: Tafel polarization curve of SUS304 in 0.5 M HCl and with soybean at different concentration

The lowest inhibition efficiency was showed at 0.5 g/L soybean with only 53 %. This could be happened due to the very low concentration of soybean extract to hinder the aggressive acid from attacking the steel surfaces. The addition of soybean up to 2.5 g/L gives insignificant changes in IE value as compared to 1.5 g/L. It is suggested that at the concentration (2.5 g/L), there may be steric hindrance when a large molecule attempts to fit onto a surface that already partially occupied with the molecules previously. In consequence at the highest concentration, the complete coverage of soybean molecules on the metal surface is difficult to achieve, thus the inhibition was reduced. These occurrences always happen in a large molecule of corrosion inhibitors [2]. From the Tafel curve, it can be observed there is a shift in potential value to a more positive potential. However, by considering the value of E_{corr} which is within the range of ±85mv for all of the concentrations studied with respect to the blank HCl, the soybean has behaved as mixed types corrosion inhibitor. This signifies that the soybean molecules have retard the corrosion by affecting both the anodic and cathodic redox reaction. Nevertheless, the inhibition was predominantly anodic effectiveness [23]. The potentiodynamic polarization in glycine also has been done and the result follows the similar trend as in soybean extract.

Table 4 shows the electrochemical parameter for SUS304 in glycine at 1.5 g/L in different concentration of HCl. The I_{corr} value shows significant changes, whereby the highest I_{corr} was recorded for glycine in 1.0 M HCl. This result was corresponded to the high corrosion rates and low IE values. The progress in current density for the whole potential in the polarization test was shown in Figure 5. It also can be seen that in the 0.5 M HCl, the low corrosion rate at 0.635 mm/y results in the highest IE which has reduced in I_{corr} value. All these results shows that the glycine also was capable to react as good corrosion inhibitors for SUS304 steel in 0.5 M HCl. The chloride ion was suggested to facilitate the inhibition efficiency as it can provide the co-operative adsorption on the steel surface rather than enhance the dissolution of surface. The protonated inhibitor (glycine) can electrostatically adsorb onto the halide-covered surface through its hydrogen ion. Thus, the presence of chloride has increased the efficiency of an organic inhibitor and reduce the corrosion rate.

Table 4: Electrochemical parameters of SUS304 in the presence of 1.5g/L glycine in different concentration of HCl

Concentration HCl (M)	E_{corr} (mV)	I_{corr} (μ A/cm^2)	Corrosion Rate (mm/y	Inhibition Efficiency (%IE)
0.25	-304.210	206.060	2.394	72
0.5	-356.930	154.600	0.635	94
1.0	-369.140	372.540	4.329	67

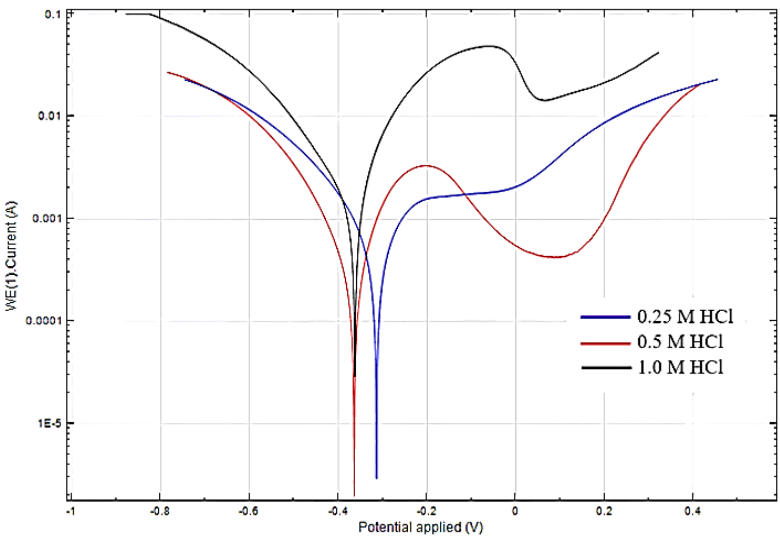

Figure 5: Tafel polarization curve of SUS304 in 1.5 g/L glycine in different concentrations of HCl

In this study, both corrosion inhibitors (soybean and glycine) were showed a good inhibition efficiency in 0.5 M HCl, but moderate efficiency in 0.25 M and 1.0 M. This could be happened due to the effect of chloride concentration. It should be noted that the presence of chloride in corrosion inhibitors systems could be either benefit or detriment the corrosion inhibition [2]. Chloride ion may assist in inhibition by having a cooperative adsorption between the organic molecules and metal surfaces. In other side, the chloride ion may also enhance the corrosion by attacking the metal surface. In this study the presence of chloride concentration in 0.5 M HCl gives an advantage to the glycine (as well as soybean extract) to perform an efficient corrosion inhibitor. Meanwhile, the high concentration of chloride ion in 1.0 M HCl results in the low efficiency of inhibition. The moderate efficiency also was shown at 0.25 M HCl even though the chloride ion was in minimum concentration. It is suggested that, at the system of 0.5 M HCl in the presence of 1.5 g/L glycine (and soybean), a maximum inhibition efficiency was achieved due to the interaction of inhibitors in both redox reaction (inhibit cathodic and anodic reaction) and with the assistance of chloride ions.

From the Tafel curve in both Figure 4 and Figure 5, the stainless steel

The coupon treated with inhibitors shows a rough and coarse structure affected entirely of the metal surfaces, but none of corrosion products was observed. The addition of the corrosion inhibitors has reduced the corrosion effect and avoid the adherent of strong corrosion products. This has been proven by the inhibition efficiency data or value obtained through the weight loss analysis. The lost of coupon weight signified the reduction in corrosion effect, thus the integrity of metal is conserved. Our result also shows the formation of pitting corrosion was extended to uniform corrosion. From our observation physically, the severity of roughness for both coupon in soybean and glycine inhibitor reveals significant different as compared to the coupon in blank solution. The amount of corrosion product also reduced with addition of inhibitors. This result shows the good impact in using both soybean and glycine in the HCl medium.

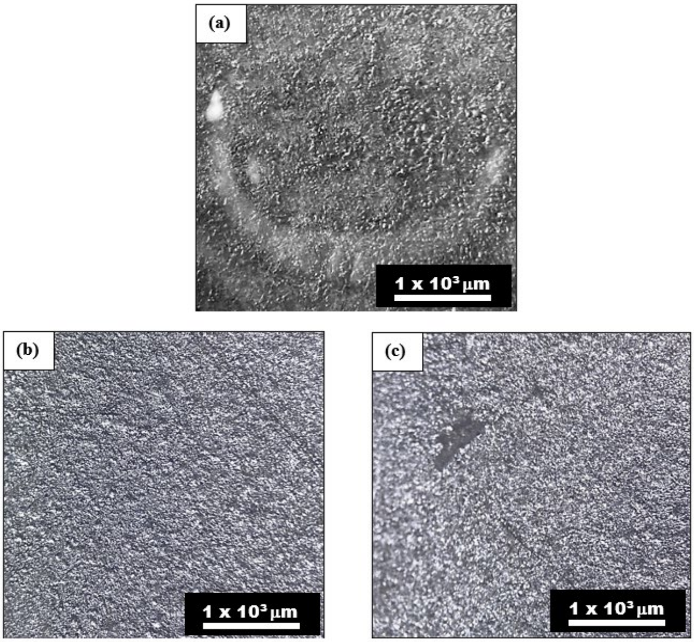

Figure 6: Optical image of stainless steel SUS304 after immersion test in (a) 0.5 M HCl and with addition of corrosion inhibitors (b) 1.5 g/L soybean (c) 1.5 g/L glycine

Adsorption isotherm

Adsorption isotherm study was performed to understand the mechanism of corrosion inhibition which explain the nature of metal-inhibitor interaction. In this presence study, the highest concentration of HCl which is 1 M HCl has been fitted to Langmuir isotherms. The highest concentration has been chosen for this analysis rather than 0.25 M and 0.5 M because an identification capability of inhibition through an adsorption at high acid concentration is more interesting to be studied. Since at low and moderate acid concentration will gives good inhibition, thus the capability of inhibitors at high concentration gains attractive queries. To investigate the capability of corrosion inhibition through adsorption isotherm analysis, an experiment has been performed at 30, 40, 50 and 60 ºC.

Figure 7 shows a plot of Langmuir isotherm for the adsorption of soybean and glycine on the surface of stainless steel in 1 M HCl at various temperature. The linear regression, R^2 value that close to 1 signifies the organic molecules of corrosion inhibitor behave as Langmuir postulation [27-30]. Langmuir postulations describes that, molecule adsorb on homogenous surface site, no interaction between adsorbed molecules, and only one layer of molecules formed on the surface site. From the result obtained, it can be suggested that the soybean and glycine behave as Langmuir postulation at the temperature of 60 ºC and 50 ºC respectively. These results give a good indication of corrosion inhibition capability of both inhibitors even in at high temperature. The molecules of soybean and glycine were arranged in monolayer form on the homogeneous surface of stainless steel. The inhibitors molecules were steadily oriented without having any attractive and repulsive force among the adsorb molecules. Generally, the adsorption isotherm analysis that follows the Langmuir isotherm corresponds to the chemisorption type.

In this result also, the R^2 values for the studied system at 40 ºC was not close to 1, ascribes the adsorption of both inhibitors molecules was unfavorable at the temperature. It is believed that at 40 ºC, the stainless steel surface was start to have a rough structure due to the steel dissolution in acidic solution.

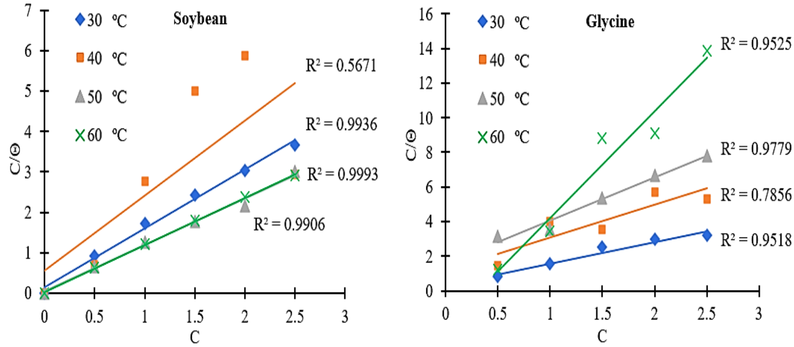

Figure 7: Langmuir adsorption isotherms for the soybean and glycine adsorbed on the stainless steel surface in 1 M HCl solution at different temperature

This has results in the heterogeneities of the steel surfaces. The rise in temperature up to 50 and 60 ºC contributes to the homogeneous surface after the steel dissolution has affected uniformly on the entire of steel surface. Thus, at 40 ºC the steel surface was uneven, so the inhibitors molecules of soybean and glycine were not led to an adsorption as compared to uniform surfaces structure at high temperature. The uneven metal surface has disrupted the inhibitors molecules from being oriented and adsorbed to perform corrosion inhibition.

Corrosion inhibition mechanism

In this presence study, the use of soybean and glycine as an organic corrosion inhibitor was suggested to inhibit the corrosion of steel by an adsorption process. A main factor in favoring the corrosion inhibition process in acid solution in this study are the concentration of acid and a molecular structure of inhibitors which may determine the types of adsorptions. The effectiveness of organic compounds as corrosion inhibitors can be ascribed to the adsorption of molecules of the inhibitors through their polar functions on the metal surface [31].

The adsorption process can occur through the replacement of solvent molecules (eg: H_2O) from the metal surface by ions (eg: H^+ and Cl^-) and molecules (inhibitors) oriented in the vicinity of the metal/solution interface [2]. Ions can accumulate at the metal/solution interface in excess of those required to balance the charge on the metal at the operating potential. The anions (eg: Cl^-) are adsorbed when the metal surface (eg: SUS304 steel) has an excess positive charge in an amount greater than that required to balance the charge corresponding to the applied potential [24]. The amount of anion was related to the concentration of acid solution. This will contribute to the occurrences of specific adsorption. This phenomenon describes the physical adsorption which related to electrostatic types interaction [2].

The involvement of aromatic compounds (eg: in isoflavone) typically associated with strong adsorption on electrode surfaces. The inhibitor's unpaired and π-electrons can effectively interact with the metal atoms' d-orbitals and initiate the formation of a protective film through donor–acceptor interaction. The exact nature of the interactions between a metal surface and an aromatic molecule depends on the relative coordinating strength toward the given metal of the particular groups present.

Both inhibitors may inhibit steel corrosion through several ways; formation of protective film through adsorption, passivating the steel surface by producing an oxide layer, minimizing the acidity of HCl since it is an amphoteric compound (for glycine) and chelating with Fe ion to form a Fe-glycine complexes [2, 32].

Through an electrochemical measurement, it is clear that both soybean and glycine were a mixed types corrosion inhibitor. The inhibitors have retard both anodic and cathodic reaction in the acidic environment. The predominant inhibition was suggested undergoes anodic inhibition since there was a formation of passive layer on the steel surface. These results indicating that the corrosion inhibition by soybean and glycine was combination of physical and chemical adsorption at room temperature. A study in different temperature of medium shows that the soybean and glycine performed chemisorption types for inhibition mechanism revealed from Langmuir isotherm analysis.

CONCLUSION

In conclusion, soybean and glycine are able to give high corrosion inhibition efficiency for SUS304 in hydrochloric acid. The presence of significant functional groups and molecular structure in both inhibitors have made soybean and glycine a substantial class of green corrosion inhibitors. The mixed type corrosion inhibitor devotes the practical inhibition types as both redox reactions can be inhibited in the particular studied system.

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