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A Study of Potato Peel Extract (Solanum Tuberosum L) as a Green Corrosion Inhibitor on Low Carbon Steel in a 3.5% NaCl Environment

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Abstract

Wide application in the oil and gas industry made carbon steel suffer annual losses due to corrosion. The corrosion protection utilizes inhibitor have drawbacks expensive and harmful to the environment. Potato peel extract (solanum tuberosum L) and its main constituents, such as flavonoids, alkaloids, and tannins, have been investigated as a green corrosion inhibitor for low-carbon steel in a 3.5% NaCl solution. The inhibitor's effectiveness and corrosion rate monitoring were measured using weight loss. Potentiodynamic polarization was used to investigate the type of corrosion inhibition and adsorption of plant extract on the surface. Fourier transform infrared spectroscopy (FTIR) was utilized to observe the presence of functional groups, natural compounds, and the type of bonding for adsorbed organic inhibitors on the surface. The results of the Tafel polarization analysis indicated that the potato peel extract acts as a mixed-type inhibitor. The inhibition efficiency increased with the concentration of the inhibitor extract. The optimal inhibition efficiency of 73.33% ~~is~~ was achieved with 6 ml of potato peel extract and 216 hours of immersion time. The inhibitive effect is due to the adsorption of inhibitor molecules on the steel surface, following the Langmuir adsorption isotherm.

Keywords: Solanum Tuberosum L, Corrosion Inhibition, Weight Loss, Polarization, Adsorption.

1. Introduction

Low-carbon steel is widely used in the marine and oil and gas industries, for example in ship structures and pipeline construction. This is due to its availability, mechanical properties, and reasonable price. However, low-carbon steel is highly susceptible to corrosion. The corrosion rate of the marine environment to which low-carbon steel is exposed is high. One of the most practical methods of protecting metals from corrosion is using inhibitors. Traditional inhibitors have been widely used in the oil and gas industry to mitigate the corrosion problem due to CO_2, H_2S, etc [1]. However, the main problem associated with the common inhibitor is not economically and environmentally friendly. In addition, the plant extract green inhibitor as a replacement for the traditional corrosion inhibitors has gained significant attention due to its environmentally and economically friendly nature and application in various fields. Therefore, this paper focuses on the corrosion performance of novel green corrosion inhibitors to develop a practical implementation to reduce the metal corrosion process.

Plant extracts are increasingly important in the scientific study of corrosion inhibitors. This is due to the advantages of low-cost and green properties. For example, Barbouchi et al. [2], Lebrini et al. [3], Dent and Fuchs-Godec [4], Fekri et al. [5], Benzidia et al. [6], used several plant extracts as corrosion inhibitors in NaCl medium. Barbouchi et al. [2] found 86.4% inhibitor efficiency at 3000 ppm of essential oils obtained from twigs, leaves, and fruits of Terebinth. It is stated by Lebrini et al. [3] that the plant extract of Bagassa guianensis produces 97% at 100 ppm for zinc corrosion. Meanwhile, potentiodynamic polarization by Dent and Fuchs-Godec [4] reported that the sage extract inhibition

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efficiency of up to 82.5%. Additionally, Fekri et al. [5] confirmed that Turnip peel extract generates almost 92% of inhibitor efficiency. The experiment of Benzidia et al. [6] concluded that the Aloe Saporia Tannin extract compound acts as a cathodic type inhibitor with an efficiency of 90% at 150 ppm.

Furthermore, the study of corrosion inhibition with different plant ex- tracts in various mediums, i.e., acid solution, was also carried out by Liao et al. [7], Hjouji et al. [8], Shanmugapriya et al. [9] and Ganash et al. [10] In addition, Chowdury et al. [11] and [12] concluded that the tulsi extract produced better inhibitory efficacy than the green tea extract in alkaline and acidic media. Fuchs-Godec [13] found that the inhibition efficiency reached more than 99% after a 1-hour immersion test and remained the same after five days on ferritic stainless steel with surface modification. In addition, according to Vorobyova and Skiba [14], pomace extract at an immersion time of 48 hours promotes inhibition capacity. Furthermore, increasing the im- mersion time increases the inhibition efficiency to 98% after 48 hours. This is in line with the compilation of plant extract by Miralrio and Vasquez [15] in which the corrosion inhibition efficiency is around 80-90%. Accordingly, the inhibition efficiency at different natural extract concentrations is a valuable index for selecting an extract for a specific purpose. Although there is no standard for the classification of corrosion inhibitor efficiency, some reviews concerning corrosion inhibitor efficiency have been carried out. For instance, a review by Fazal et al. [16] summarized that the performance of green corrosion inhibitors for CO_2 corrosion in many cases has met the inhibition rate of 0.1 mm/y required by corrosion engineers. In corrosive media, Zakeri et al. [17] found that the GCI's performance is around 85.11% – 99.6%. Furthermore, in the oil and gas industry, Hossain et al. [18] stated that the corrosion inhibitors efficiency of plant extract is between 86% – 98.96%.

Al-Shaikhan et al. [19] reported that the antioxidant activity was evenly distributed throughout the tuber. At the same time, the highest content was found in the peel, where the most increased antioxidant activity was found in the skin tissue. In addition, potato peel contains flavonoids, alkaloids, and tannins, which are known to be used to produce environmentally friendly inhibitors. Potato peel, a waste product from processed potato foods, is an organic waste, giving it a distinct economic advantage in its use as a source of environmentally friendly inhibitors. Potato peels contain potent antioxidants, i.e., chlorogenic acid and quercetin. Potato (Solanum Tuberosum L.) is a vegetable belonging to the Solanaceae genus. It is commonly used as a food ingredient and is typically grown in tropical countries. In this study, we investigated the use of potato peel extract, which is typically discarded as waste, as a green and eco-friendly corrosion inhibitor for low-carbon steel in a 3.5% NaCl solution. The corrosion inhibition, corrosion behavior, and adsorption thermodynamics of potato peel extract on low-carbon steel are evaluated by weight loss measurement, potentiodynamic polarization measurement, and Fourier transfer infrared spectroscopy (FTIR).

2. Methods

2.1 Material Preparation and Solution

The study used low-carbon steel API-5L obtained from the Department of Metallurgy and Material FTUI. Carbon steel API 5L is commonly used for oil and gas transmission. API 5L has two manufacturing products: seamless and welded steel pipe. These include plain-end, threaded-end, and bell-end pipes for use in petroleum and natural gas pipelines. The chemical composition is presented in Table 1. The specimen was machined to dimensions of 10 mm in length, 10 mm in width, and 3mm in depth. Prior to the experiment, the surface was cleaned with distilled water and polished using 80 and 120 mesh sandpaper.

Table 1. The Chemical Composition of Low-Carbon Steel

C (%)	Si (%)	Mn (%)	P (%)	S (%)	Cr (%)	Mo (%)
0.211	0.247	0.429	0.021	0.009	0.008	< 0.005 ∗ ∗
Ni (%)	Al (%)	Cu (%)	Nb (%)	Ti (%)	V (%)	Fe (%)
0.01	0.008	< 0.002	< 0.002	< 0.002	< 0.002	bal.

A 3.5% NaCl solution was prepared by dissolving 35 grams of common salt in 1000 ml of distilled water. A stirrer was used to expedite the process. Solutions with varying concentrations of potato peel extract inhibitor were prepared by adding 2, 4, 6, and 8 mL of the inhibitor to the 3.5% NaCl solution. Furthermore, a 3.5% NaCl solution without an inhibitor was also prepared.

2.2 Extract Inhibitor Preparation

Potato peels were collected from the restaurants around the UI campus, as shown in Figure 1. These were dried in the sun for 4-5 days. The dried peels were blended, weighed, and mixed with ethanol to extract the organic compounds from the potato peels. The dried peels were blended and sifted into small chips and weighed using a digital balance of ± 0.0001 g accuracy. The percentage of water/ethanol (30/70) solvents were employed to prepare the extract. The mixture was left to settle for a day before being filtered using paper to obtain the extract. The solution was filtered through a Whatman no. 4 filter paper.

Figure 1. Potato Peels

2.3 Weight Loss Measurement

Standard Practice for Laboratory Immersion Corrosion Testing of Metals ASTM G31 – 71 is utilized as a reference for the weight loss measurement low-carbon steel specimens were weighed using a digital balance before being immersed in a prepared solution to investigate the effect of corrosion inhibition. The immersion lasted for 3, 6, 9, and 12 days in a 3.5% NaCl solution. Afterward, the specimens were cleaned with distilled water, dried, and weighed to determine weight loss. The corrosion rate (*CR*) equation for weight-loss measurement is as follows:

$$CR = \frac{87.6.W}{D.A.T} \quad (1)$$

where, W = Weight Loss, D = Density of low-carbon steel, A = Area of the specimen, T = Exposure Time. The effectiveness of corrosion is given with the following equation.

$$\eta = \frac{W - W_{inh}}{D.A.T} \quad (2)$$

where, η (%) = efficiency, W = weight loss without inhibitor, W_{inh} = weight loss with inhibitor.

2.4 Electrochemical Measurement

The present study conducted inhibitor measurement polarization tests to evaluate inhibition performance. The electrochemical measurement used ASTM G5 – 94, a standard reference test method for making potentiostatic and potentiodynamic anodic polarization measurements. The polarization measurements employed three electrodes: a low-carbon steel sample as the working electrode, a carbon rod as the counter electrode, and a silver/silver chloride (Ag/AgCl) electrode as the reference electrode. The working electrode had a side area of 1 cm^2. Prior to the polarization process, the open circuit

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potential (OCP) is measured by immersing the working electrode in the test solution for 30 minutes. The polarization process is then carried out in the cathodic potential range from -0.1 V to E_{corr}, followed by an anodic potential of 0.1 V to E_{corr}, at a scan rate of 0.25 mVs^{-1}. Finally, the obtained polarization curve is plotted.

After completing the polarization process, the inhibition efficiency η (%) is calculated to continue the process. The inhibition efficiency is determined by

$$\eta = \frac{i_{corr} - i_{corr(inh)}}{i_{corr}} \quad (3)$$

where i_{corr} and $i_{corr(inh)}$ are values without and with potato peel extract, respectively.

2.5 *Fourier Transform Infrared Spectroscopy*

FTIR aims to determine the nature of the organic inhibitor bonds and the bonds formed between the organic inhibitors adsorbed on the surface metal. FTIR testing was carried out using a Perkin Elmer Spectrum Two FTIR spectrometer. Three test samples were used for comparison, consisting of a) potato peel extract and b) low carbon steel immersed for 48 hours in a 3.5% NaCl solution with the addition of 6 mL of potato peel extract. Each sample is expected to give a spectrum of low-carbon steel, a spectrum of functional groups from pure potato peel extract, and a spectrum of functional groups from the extract adsorbed on the metal surface. The results were used to determine whether potato peel extract adsorbs to metal surfaces to act as a protective layer between the metal surface and the environment.

3. Result and Discussion

3.1 *Characterization of Potato Peel Extract*

Figure 2 shows the FT-IR spectrum of potato peel extract. The observations indicate the presence of O-H, C=C, C-H, and C-O groups, suggesting that the active compound group in potato peel is a phenolic compound, precisely a type of flavonoid. Phenolic compounds are characterized by oxygen atoms surrounding the entire aromatic ring.

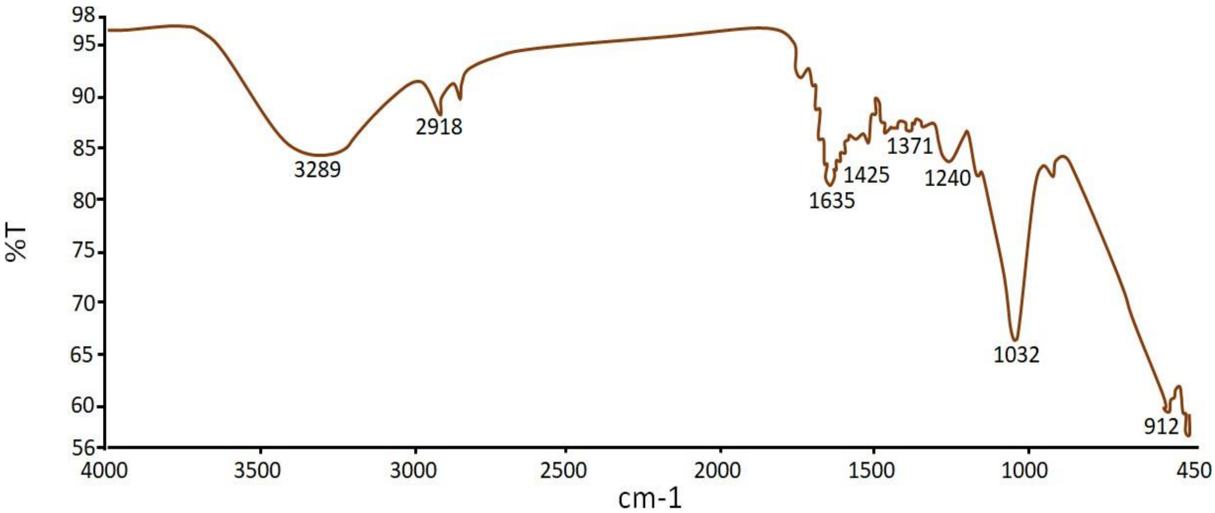

Figure 2. FTIR Spectra of Potato Extract

Figure 3 shows the FTIR spectrum of the adsorption layer on the surface of low-carbon steel after immersion for 48 hours in a 3.5% NaCl solution with the addition of 6 mL of potato peel extract as an inhibitor. Comparison the FTIR spectrum of potato peel extract and extract adsorbed on the surface of low-carbon steel, the frequency of the O-H stretching phenolic group changes from 3289 cm^{-1} to 3327 cm^{-1}. The C-O frequency changes from 1240 cm^{-1} to 1114 cm^{-1}. The C=C stretching frequency has changed from 1635 cm^{-1} to 1656 cm^{-1}. This may be caused by forming a quercetin-Fe^{2+} complex adsorbed on the surface of low-carbon steel. The changes may be due to the adsorption of potato peel extract on the surface of low-carbon steel. Competition between inhibitors to reach the low-carbon steel surface results in other inhibitors not reaching the low-carbon steel surface or due to the flat monolayer

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condition on the surface, indicating that only a few inhibitor molecules inhibit the low carbon steel surface and there is no inhibitory activity from the remaining inhibitor molecules in the solution.

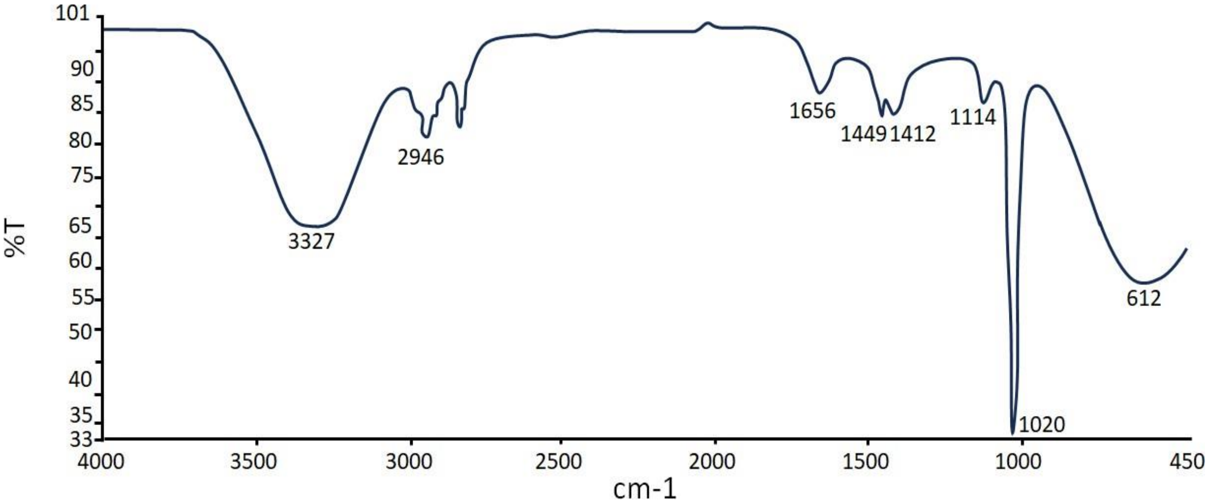

Figure 3. FTIR Spectrum of the Adsorption Layer on the Surface of Low Carbon Steel after Immersion for 48 Hours in a 3.5% NaCl Solution with the Addition of 6 mL of Potato Peel Extract as an Inhibitor

These results are consistent with the previous findings of Chen et al. [20] regarding the calculated slope of the adsorption isotherm. This indicates the formation of a monolayer of inhibitor molecules on the metal surface, with no interaction between the adsorbed molecules. Furthermore, the chemical bond formed and the interaction between the inhibitor and low-carbon steel is related to the adsorption of corrosion inhibitor molecules on the metal surface. There are several adsorption isotherm models describing the adsorption mechanism of organic inhibitors on the metal surface, e.g., Langmuir, Temkin, and Frumkin. In this study, the Langmuir isotherm is the best model that fits extracts as corrosion inhibitors on metals. Adsorption equilibrium constant K_{ads} is correlated to Gibbs adsorption energy ΔG°_{ads}, on the following equation.

$$\Delta G^{\circ}_{ads} = 55.5RTlnK_{ads} \quad (4)$$

where R is the universal gas constant, T is the temperature, K_{ads} is the adsorption equilibrium constant, and 55.5 is the concentration of water solution in mol/L units. The negative sign of ΔG°_{ads} indicates the spontaneous adsorption of the corrosion inhibitor molecules on the metal surface. Values below 40 kJ/mol are related to chemisorption, with intervals from 40 to 20 kJ/mol to mixed physisorption–chemisorption regime and above 20 kJ/mol to physisorption. The calculation shows the price value of ΔG°_{ads} is -7.717 kJ/mol. The negative sign indicates that the absorption of potato peel extract on the metal surface occurs spontaneously, but the negative sign also explains the stability. The value of ΔG°_{ads} is smaller than -20 kJ/mol, indicating that physical adsorption explains the interaction of electrostatic interaction between the molecular charge and the metal charge, while if it is greater than -40 kJ/mol, it indicates chemical adsorption, which explains the charge sharing or transfer of the inhibitor molecules to the surface. A small K value indicates the interaction of the absorbed inhibitor molecules with the metal surface, causing the inhibitor molecules to be easily detached from the metal surface. This suggests that inhibitors that work by Physical adsorption mechanism will have their adsorption strength weakened with increasing temperature, by analogy to the increase in corrosion activation energy in the presence of inhibitor molecules compared to conditions without inhibitors, often interpreted as the formation of a physisorption adsorbed film. The greater the K value or the negative ΔG°_{ads}value, the higher the adsorption energy. This is related to the immediacy of the adsorption process of potato peel extract to the metal surface and the stability of the adsorbed layer on the adsorbent surface. Where phenolic compounds are adsorbed to the surface through free electron pairs on oxygen and nitrogen atoms, a layer isolates the surface of low-carbon steel. The arrangement of oxygen and nitrogen atoms is opposite in the phenolic structure. The arrangement of these atoms indicates that the phenolic molecules are horizontally adsorbed to the carbon steel surface.

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3.2 Weight Loss Measurement

Figure 4 illustrates that corrosion rates decrease as inhibitor concentration increases. This is due to the higher absorption of inhibitor molecules at the carbon steel-solution interface. The optimum corrosion rate is achieved at a concentration of 6 mL and an immersion time of 216 hours. Moreover, due to the potato peel extract inhibitor molecules, the corrosion rate in-creases beyond the optimal inhibitor concentration of 6 mL. These molecules are absorbed onto the carbon steel surface and reach their ideal concentration before returning to solubility. When the concentration approaches or falls below the critical concentration, it may cause damage to the protective layer. Adsorption corrosion affects the corrosion rate in two ways. Firstly, it reduces the reaction area between the environment and the low-carbon steel surface. Secondly, it adjusts the activation energy of cathodic and/or anodic reactions during the corrosion inhibition.

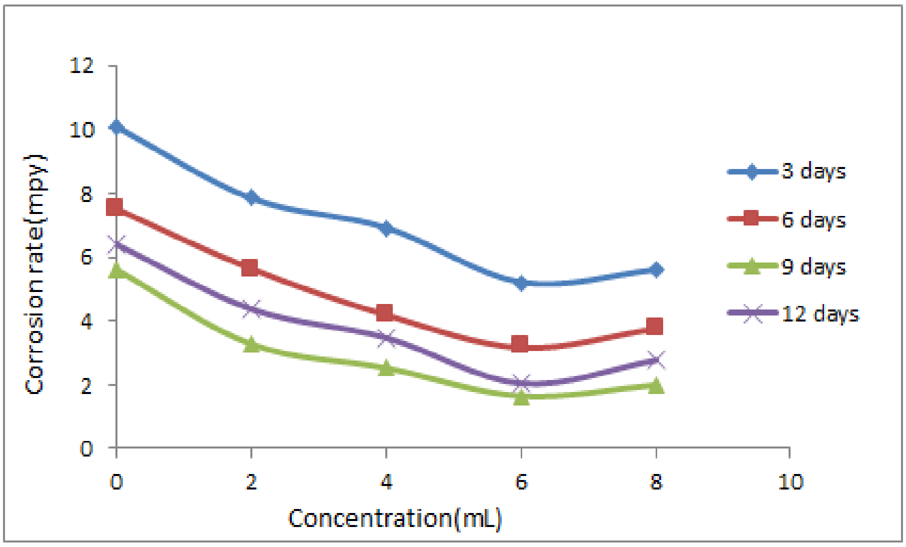

Figure 4. Corrosion Rate Plot of Low-Carbon Steel Without and With Different Concentrations of Potato Peel Extract and Immersion Period

Figure 5 shows that during the immersion periods of 3, 6, 9, and 12 days, the inhibition efficiency improves with increasing inhibitor concentration but falls after passing the critical concentration. The inhibitor's effectiveness was enhanced by adding potato peel extract at doses of 2, 4, and 6 mL while adding 8 mL reduced efficiency. During the three and 6-day immersion periods, the inhibitory efficiency value was lowest at a 2 mL inhibitor concentration, gradually increasing to the optimum at 6 mL.

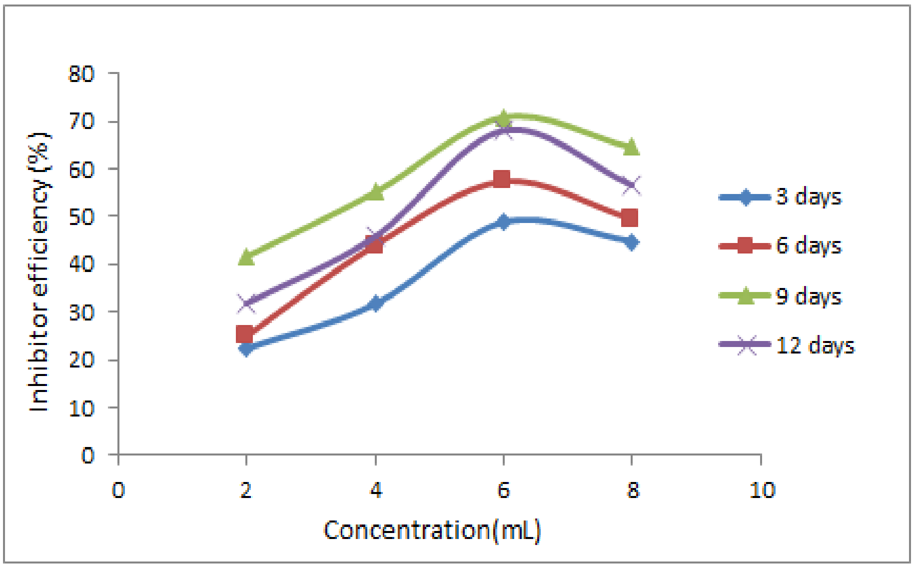

Figure 5. Inhibitor Efficiency Plot of Low-Carbon Steel Without and With Different Concentrations of Potato Peel Extract and Immersion Period

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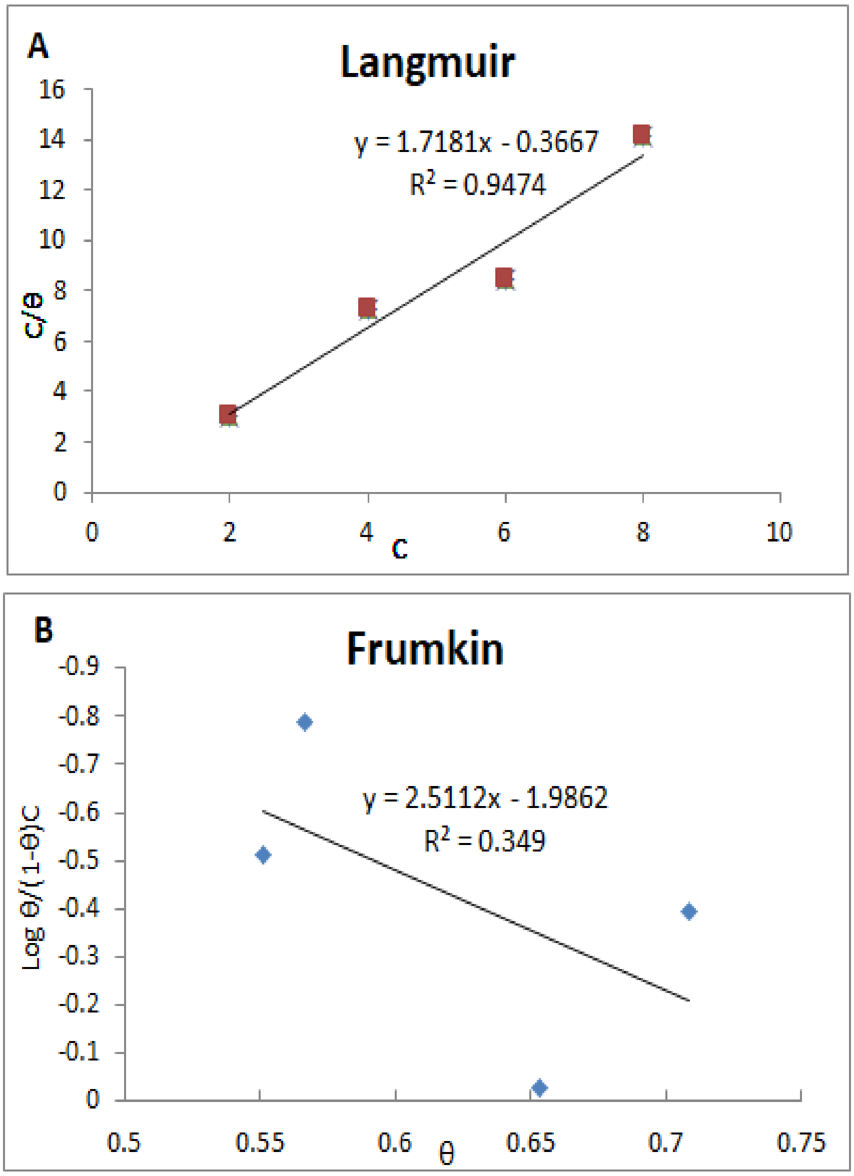
Inhibition efficiency is more significant when excellent surface coverage (θ) of inhibitor molecules adsorbed on the surface of low-carbon steel and rising inhibitor concentration. This is due to the various organic molecules in potato peel extract that metal surfaces can absorb, including oxygen and nitrogen. The chemicals are absorbed by the surface of the carbon steel, which reduces the area targeted by hostile ions from the 3.5% NaCl solution. The comparison results and previous study is added in the following sentences: "In addition, Quraishi et al. [21] found that the adsorption of an organic adsorbate on the metal-solution interface was donated by a substitutional adsorption process between the organic molecules in the aqueous solution Org(sol) and the water molecules on the metal surface H_2O(ads).

$$Org_{(sol)} + xH_2O_{(ads)} \rightleftarrows Org_{(ads)} + xH_2O_{(sol)} \tag{5}$$

where Org(sol) and Org(ads) are the subsequent organic molecules in the aqueous solutions and adsorbed on the metal surface, H_2O(ads) are the water molecules on the metal surface, and x is the size ratio representing the number of water molecules replaced by one molecule of organic adsorbate.

3.3 Adsorption Isotherm

According to the adsorption isotherm approach, i.e., Langmuir, Frumkin, and Temkin, as shown in Figure 6. The r^2 value for the Langmuir isotherm is 0.947, the Frumkin isotherm is 0.349, and the Temkin isotherm is 0.127.



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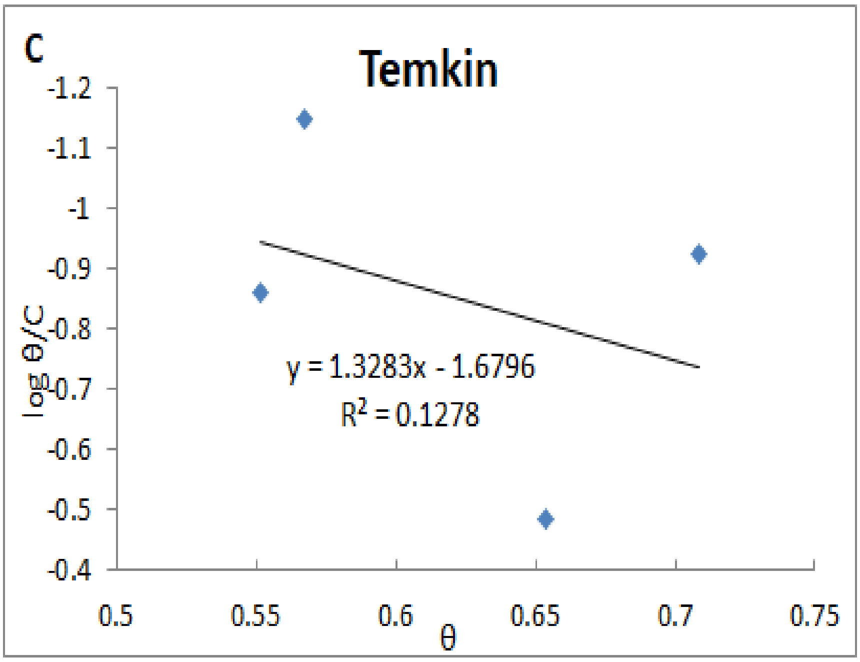

Figure 6. (a) Langmuir, (b)Frumkin, and (c) Temkin, Isotherm for Adsorption of Potato Peel Extract on the Low-Carbon Steel

The Langmuir isotherm correlates best with the experimental data from these results. Furthermore, the Langmuir isotherm at different immersion periods is presented in Figure 7. Organic compounds are responsible for the inhibition observed on the metal surface. The adsorption mechanism follows Langmuir, indicating the formation of a monolayer of the inhibitor on the surface of the low-carbon steel. The Langmuir isotherm assumes that the adsorption area on the low-carbon steel surface is evenly distributed equally, and the maximum number of inhibitor molecules per area is one, which indicates monolayer adsorption. The study Singh et al. [22] revealed that inhibitor molecules do not interact with each other. Additionally, the results demonstrated that potato peel extract decreased the dissolution of low-carbon steel by absorbing active components on the metal surface. The effectiveness of this process increased with higher inhibitor concentrations.

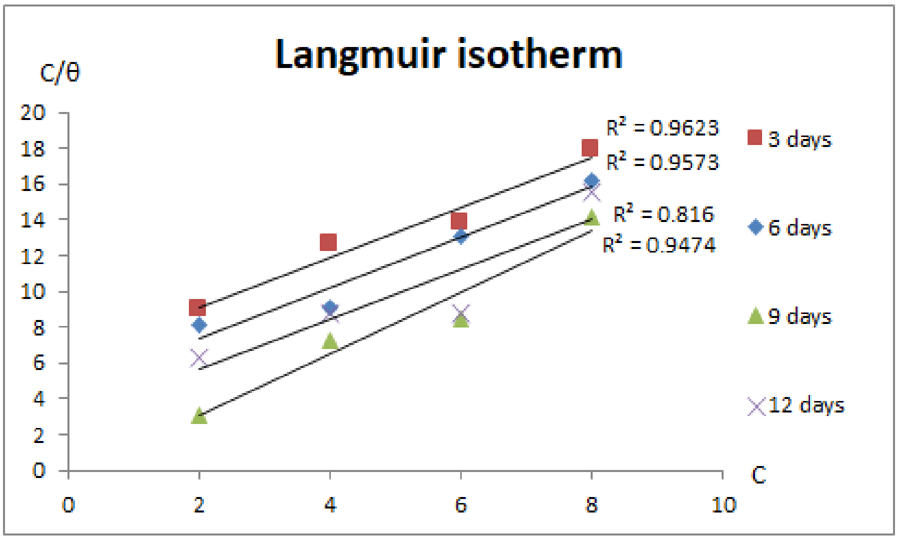

Figure 7. Langmuir Isotherm for Adsorption of Potato Peel Extract Inhibitor on Low-Carbon Steel Surface in 3.5% NaCl Solution

The efficiency of the inhibitor is directly proportional to the surface coverage on low-carbon steel resulting from the absorption of potato peel extract as an inhibitor. The Langmuir isotherm parameter can be used to describe the relationship between concentration and surface coverage. In potato skins, monolayer adsorption occurs, and there is no interaction between inhibitor molecules. The negative ΔG

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value indicates the reaction's spontaneity, as Vorobyova and Skiba concluded [23]. Positioning oxygen atoms around the aromatic ring in phenolic compounds results in the compulsory sorption of these compounds onto the surface of low-carbon steel. This mechanism increases the protection area against interaction with the corrosive environment, with only a few molecules being adsorbed onto the surface of the low-carbon steel.

3.4 Potentiodynamic Polarization

Polarization tests were carried out to determine the type of corrosion inhibition provided by the potato peel extract. Tests were carried out on a blank solution (NaCl 3.5%) and a 3.5% NaCl solution to which 6 mL of potato peel extract was added. Figure 8 shows the polarization curves of low-carbon steel with and without adding potato peel extract concentration in a 3.5% NaCl environment.

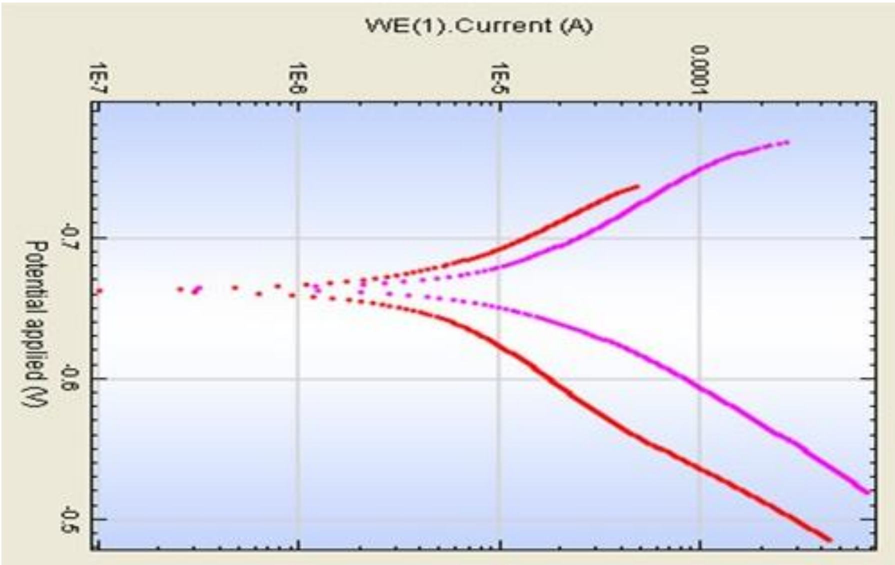

Figure 8. Polarization curve, blank (purple) and optimum (red)

The corrosion potential of carbon steel immersed in a 3.5% NaCl environment is approximately -664.29 mV, referred to as the Ag/AgCl electrode. Adding 6 mL of the potato peel concentration causes the corrosion potential to shift towards the anodic direction, resulting in a higher potential of -662.84 mV. The change in E_{corr} is less than 85 mV, classifying the inhibitor as a mixed type as it is neither anodic nor cathodic. The shift toward positive potential indicates that the inhibitor predominantly controls the anodic reaction. In the anodic region, potato peel extract controls the anodic reaction by forming complex compounds on the surface of the low-carbon steel. In the cathodic region, complexes are formed on the surface of the low-carbon steel, controlling the cathodic reaction.

Table 2. Polarization Parameters on Low-Carbon Steel in Blank and Optimal Conditions in 3.5% NaCl Environment

Inhibitor (mL)	E_{corr} (mV)	I_{corr} (μA/cm^2)	βa (mV/dec)	βc (mV/dec)	CR (mpy)
0	-664.29	9.79	83.33	80.42	0.11
6	-662.84	3.27	98.65	66.50	0.04

Table 2 shows that the presence of an inhibitor reduces the corrosion current density (I_{corr}) on both the anodic and cathodic curves compared to the solution without an inhibitor. This indicates a reduction in the corro- sion reaction and, consequently, in the corrosion rate. The corrosion current density (I_{corr}) decreases with increasing inhibitor concentration due to the adsorption process of potato peel extract at the interface of low-carbon steel or 3.5% NaCl solution, which inhibits both anodic and cathodic reactions.

Changes in βa and βc values were observed as the concentration of potato peel extract increased, indicating an adsorption process of inhibitor molecules in both the anodic and cathodic regions. This

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blocks the reaction of the corrosive environment with the surface of the low-carbon steel. Changes in both the anodic and cathodic regions also indicate a mixed inhibitor. The highest inhibition efficiency value was achieved with the addition of 6 mL concentration, resulting in a value of 73.33%.

4. Conclusion

This study examines the effectiveness of potato peel extract, a commonly discarded waste product, as a green and eco-friendly corrosion inhibitor for low-carbon steel in a neutral environment containing 3.5% NaCl. The corrosion rates and inhibition efficiency were evaluated using weight loss, while potentiodynamic polarization was used to investigate the adsorption of the organic inhibitor compound on the metal surface and the type of corrosion inhibition. Fourier transform infrared spectroscopy (FTIR) was used to detect the presence of functional groups, natural organic compounds, and the bonding type of adsorbed organic inhibitors on the surface. The results are presented below:

1. Weight loss testing revealed that the lowest corrosion rate was 1.59 mpy, with the highest inhibition efficiency of 73% achieved at an optimal concentration of 6 mL and an immersion period of 9 days.
2. Polarization testing demonstrated that the addition of potato peel ex- tract decreased the corrosion current density (I_{corr}) of low-carbon steel in a 3.5% NaCl solution from 9.79 µA.cm^{-2} to 3.27 µA.cm^{-2} at the optimal concentration of 6 mL. The results suggest that potato peel extract acts as a mixed-type inhibitor, as evidenced by the potential change from the blank condition to the optimal condition of 6 mL, which did not exceed 85 mV.
3. Additionally, the extract is a natural antioxidant with a high concentration of quercetin. Weight loss and polarization tests demonstrate that the extract effectively inhibits the corrosion process of carbon steel in a 3.5% NaCl environment.
4. The FTIR test compares the wave numbers of potato peel extract and low-carbon steel surface adsorbed by potato peel extract. The comparison shows that the film layer adsorbed on the surface of low-carbon steel is potato peel extract, which contains phenolic oxygen groups C=C and C-O, indicating the adsorption of potato peel extract on the surface of low-carbon steel.
5. According to the adsorption isotherms, the potato peel extract ad- sorption process on the surface of low-carbon steel follows Langmuir isothermal adsorption. The layer formed on the surface is a monolayer, and the adsorption of potato peel extract is evenly distributed on the surface. The adsorbed molecules are concentrated or immobile on the metal surface, and there is no interaction between inhibitor molecules.

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