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Duplex Stainless Steel 2101 corrosion inhibition in an acidic environment using Solanum tuberosum leaves and roots extract

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Abstract

The effectiveness of *Solanum tuberosum* (Potato) leaves (STPL) extract and *Solanum tuberosum* (Potato) roots (STPR) extract as corrosion inhibitor on Duplex Stainless Steel 2101(DSS2101) in 0.5M Hydrogen tetra oxo sulphate (IV) acid (H_2SO_4) solution were studied by weight loss, electrochemical potentiodynamic polarization and Fourier Transform Infrared Spectroscopy (FTIR) techniques. The increase in inhibition efficiency (IE) as the inhibitor dose increases show the effectiveness of inhibition. The FTIR spectrums of DSS2101 showed compounds of the extract that act as the inhibitor. The adsorption processes were calculated and discussed. The STPL and STPR isotherm adsorption behaviour on the surface of DSS2101 is known with isotherm adsorption of Langmuir and involves physical adsorption. The adsorption and protective thin layer formation cause an improvement in surface condition of the steel. The polarization curve results and thermodynamic parameters revealed that STPL and STPR provided inhibition in the H_2SO_4 acid environment.

Keywords: Duplex Stainless Steel 2101, Solanum tuberosum, potentiodynamic polarization, Langmuir isotherm

1. Introduction

Duplex stainless steels 2101 (DSS 2101) composition is of equivalent fractional of austenite (γ) and ferrite (α) phase and has very strong resistance to corrosion and deformation. Therefore, it has many applications such as in natural gas and petroleum transportation pipelines, condenser, desalinator, heat exchanger, construction industry, etc. [1- 4]. DSS 2101 due to its microstructure and high nitrogen content has a high mechanical strength, with resistance to pitting and crevice corrosion [1]. Moreover, DSS 2101 application in petroleum industry show stress corrosion cracking resistance and this has make it to be superior to that of standard austenitic grades [5]. Unfortunately, in the corrosive environmental conditions, DSS 2101 is susceptible to corrosion when in service. Therefore, the corrosion phase on the surface of DSS 2101 must be removed by pickling by the use of inorganic acids. However, the inorganic acid during pickling remove oxidation products of DSS 2101 surface thereby causing erosion of the DSS 2101 substrate itself, hence lead to the corrosion of the steel [6].

The application of corrosion inhibitor on metals to prevent corrosion has recently been found to be a good method of metal protection against corrosion [7]. Corrosion inhibitors have a reactive group and aromatic rings that are attached to hydrocarbon with functional group like −OH, −COOH, NH_2, etc. These reactive groups bond with the surface of the metal, while the hydrocarbon molecular part is in contact with the environment [8; 9]. The adsorption of the molecules, which are characterized by lone paired electrons on the metal surface, makes inhibitory effective [10]. However, some corrosion inhibitors are very expensive and can bring negative impact to the environment due to their toxicity [11; 12]. Organic corrosion inhibitors of plant origin in recent studies

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show that they are friendly to the ecosystem. Natural plants extracts like henna leaf and mangrove wood contain saponins, tannins and flavonoid monomer which are potential inhibitors [13; 14]. An important number of publications have been done to develop "green" corrosion inhibitors such as Mucuna pruriens seed extract [15]; Griffonia simplicifolia extract [16] and Asparagus racemosus extract [17]. *Mounir et al*., [18] investigated *Malus domestica* vinegar inhibitive effect on API5L steel in an acidic environment.

Study on cocoa peel extract inhibitive effect was reported to have maximum inhibition efficiency at 2.5%v/v extract concentration when in 1.5M HCl and NaCl solution [19]. Investigation on plant extracts as naturally occurring corrosion inhibitors substances have shown to be environmentally friendly, readily available and source of renewable corrosion prevention materials [20]. However, natural antioxidants with phenolic acids and phenolic compounds are good corrosion inhibitors and can generate as waste from food-processing by-product [21]. Rehman *et al* [22] reported that petroleum ether of potato extract provides a strong antioxidant. The extraction and utilization of phenols in potato peels has been studied [23].

In view of this, the inhibitive effect of *Solanum* tuberosum (Potato) leaves (STPL) and roots (STPR) extract on DSS 2101in H_2SO_4 acid media was investigated by weight loss, thermodynamic parameters and potentiodynamic polarization. The active components of the inhibitor were investigated using FT- IR.

2. Experimental

2.1. Materials and solutions preparation

The analytical grade Hydrogen tetraoxosulphate (VI) acid (H_2SO_4) bought from the Sigma-Aldrich and 0.5M solution of the acid was prepared using deionized water. Test solutions 0, 100ppm, 200ppm and 300ppm of STPL and STPR were prepared in the volumetric flask. Duplex Stainless Steel 2101 electrodes were made in the laboratory. Then, the Duplex Stainless Steel 2101 blocks faces were carefully polish on 400 mesh sandpaper homogeneity. The Duplex Stainless Steel 2101 block was inserted into 2 cm diameter white PVC pipe connected by copper wire, and then covered with epoxy resin leaving the working surface uncovered. The Duplex Stainless Steel 2101 samples were characterised using SEM.

2.2. Inhibitor

Solanum tuberosum (Potato) leaves (STPL) and *Solanum tuberosum* (Potato) roots (STPR) were obtained from Aponmu farm in Akure, Ondo State, Nigeria. The leaves and roots were harvested and washed with deionized water, then latter dried at 22^0C for 21 days and then pulverized using electric herb grinder and the powder was kept until required.

2.3. Preparation of the extracts

2.3.1. Organic extracts

The leaves and root powder in separate beakers were mixed with 750ml ethanol for extraction. The mixtures were kept for 72 hours in an air tight container, and then filtered. The filtrates were heated at 60°C in a steam bath to remove all the ethanol and the extracts were kept for the research. The concentrations of STPL and STPR extract used for this work ranged from 0 to 300ppm.

2.4. Characterization of Extracts

2.4.1. FTIR characterization of Solanum tuberosum (Potato) leaves and roots extract

The STPL and STPR extracts were characterized by FTIR and the spectra measurements were carried out on FTIR830 spectrophotometer using the KBr pellets.

2.5. Potentiodynamic polarization measurements

The study was done using a computerized AUTOLAB potentiostat PGSTAT204 as reported by Olaseinde *et al.,* [24]. The testing set-up procedure was in accordance with ASTM G59-97 [25].

The I.E % was determined by equation;

$$I.E\,(\%) = \frac{C_{blank} - C_{inhibitor}}{C_{blank}} \times 100 \quad (1)$$

I.E is the inhibition efficiency, C_{blank} is the corrosion rate in the absence of inhibitor and $C_{inhibitor}$ is the corrosion rate in the presence of inhibitor.

2.6. Adsorption Study

Surface coverage $[\theta]$ values were evaluated from the electrochemical potentiodynamic polarization test and best isotherm data were obtained.

$$\text{Surface coverage } \theta = 1 - \frac{Wi}{Wb} \quad (2)$$

Where W_b is the weight loss per unit time without inhibitor and W_i is the weight loss per unit time with inhibitor.

The adsorption isotherm was determined using expression in equation (3):

$$\frac{C}{\theta} = \frac{1}{Kads} + C \quad (3)$$

C is the concentration of inhibitor, $Kads$ is the adsorption equilibrium constant and θ is the surface coverage.

2.7. Corrosion rate (Gravimetric method)

The Corrosion test was done by immersing the Duplex Stainless Steel 2101 in of 0.5 M Hydrogen tetraoxosulphate (VI) acid (H_2SO_4) corrosive medium with and without extract. While the corrosion rate value was calculated for exposure time 48, 96, 192, 384 and 768 hours. The varying concentration of the extract ranging from blank, 100ppm, 200ppm and 300ppm was immersed directly to the H_2SO_4 acid medium. The sample was removed from the corrosion medium after the corrosion process at a specified time. Then, deionized water and soft brush was used to wash the sample and acetone was latter used to rinsed the sample and air dried at 22^0C

The rate of corrosion was determined using the expression in equation (4) [26]

$$Cr = \frac{87.6 \text{ x } (W_{blank} - W_{inhibitor})}{\rho St} \quad (4)$$

Where ρ=steel density (g cm^{-3}), S = surface area of the metal that is exposed (cm^2), and t= immersion time (h). W_{blank} and $W_{inhibitor}$ are the loss in weight (g) for Duplex Stainless Steel 2101 with inhibitor and without inhibitor in H_2SO_4 acid environment respectively.

3. Results and Discussion

3.1. Duplex Stainless Steel 2101 Spectrometric Analysis

The DSS2101 composition (in wt. %) used for this study consist of C = 0.03, Si = 0.45, Mo= 0.5, P = 0.023, Cu = 0.001, N = 0.22, Ni = 1.5, Cr =21.5, Mn= 4.80, Fe=balance.

3.2. Characterization of Solanum tuberosum (Potato) leaves and roots

The functional groups of STPL and STPR extracts components were identified by FTIR [27]. The FTIR spectrum of STPL and STPR extracts (Figures 1a and 1b) shows that some chemical functional groups are present. For STPL (Figure 1a), the absorption vibration band at 3441.12 cm^{-1} agreed with hydroxyl (O-H) stretching mode [28]. Another peak was obtained at 1649.19 cm^{-1} agreed with the (C=C) aromatic alkenes group stretching mode. While at 1128.39 cm^{-1} C-O or C-N stretching vibration appears.

In FTIR spectrum peaks of the STPR extract solution (fig 1b), the absorption mode at 3404.47 cm^{-1} is attached to the hydroxyl (O-H) and amide (N-H) group stretching mode [29]. The absorption vibration mode at 2929.97cm^{-1} corresponds to O–H stretching, which indicates that the inhibitor contains organic acid group.

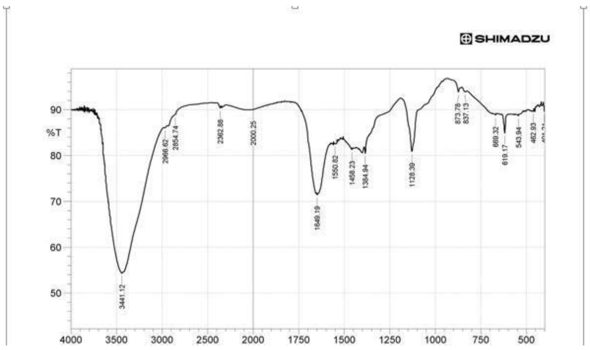

Figure 1a: Spectrum peaks of the *Solanum* tuberosum leaves extract solution measured by FT-IR

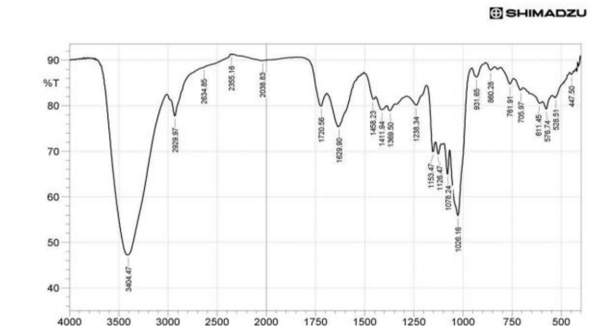

Figure 1b: Spectrum peaks of the *Solanum tuberosum* root extract solution measured by FT-IR.

While the spectrum peak at 1629.90cm^{-1} corresponds to aromatic alkenes group stretching (C=C) and the strong band at 1720.56$cm^{-1}$is C=O stretching mode (ketone) [30]. This shows that the extracts contain aromatic ring and some functional groups like Oxygen and Nitrogen atoms.

3.3. Phytochemical analysis of plant extracts

Phytochemical screening of the STPL and STPR extract was carried out to identify their chemical composition, the summary is displayed in Table1.

Table1: Phytochemical analysis and percentage phytochemical of plant extracts

S/N	Phytochemical	Tests	Inference		Percentage of Phytochemical in the Plant Extracts (%)	
			Leaf	Root	Leaf	Root
1	Saponins	Froth	++	+	1.10	1.15
2	Tannins	Ferric chloride	+	+	2.12	2.04
3	Flavonoids	Shinoda	+	+	12.08	11.96
4	Alkaloids	Dragendorff	+	+	4.32	4.11
5	Phenols	Pyridine -$FeCl_3$	+	+	2.12	2.02

Where (+) means the presence of the chemical constituent and (++) means the presence of more chemical constituent.

The summary of the phytochemical analysis of the STPL and STPR extract, show that the plant extract contains phytochemicals that are corrosion resistance organic agents (e.g. saponin, tannins, steroid and flavonoids). Besides, the presences of these phenolic and antioxidant in STPL and STPR extract show the effectiveness as corrosion inhibitor. Tannin compound as organic agents' forms complexes with Fe (III) on metal surface [19]. The presences of saponin and flavonoid on metal form complex affinity that is effective for corrosion inhibitor performance. This shows that the phenolic compounds present on the surface of DSS2101 metal provided strong adsorption molecules of the STPL and STPR extract film. Hence, it contributed to the IE of the inhibitors because of cyclic compounds that are present [31].

3.4. Weight loss measurement

The effectiveness of corrosion inhibitor STPL and STPR extract solution on DSS2101 metal in 0.5M H_2SO_4 medium can be proven with increase in the STPL and STPR concentration. The result is shown in figure 2.

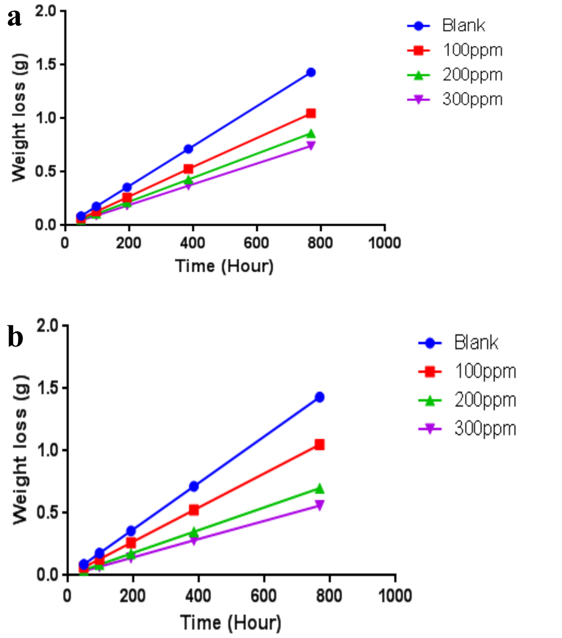

Figure 2: Weight loss variation with exposure time for 2101duplex stainless sample immersed in 0.5M H_2SO_4 with various Solanum tuberosum (Potato) (a) leaves; (b) roots extract concentrations.

Figure 2 shows that the STPR extract produce better corrosion inhibition than STPL extract. Comparative results between extracts of root, stem and leaf of plants have been reported for the coffee extract [32] as well as Artemisia pallens [33]. Figure 2 clearly shows a loss in weight of the DSS2101 coupons in the absence of STPL and STPR extract compared to when extract is added. It also shows that corrosion depend on time, because the rate of corrosion is directly proportional to time, also there is an increase at a specified condition which agreed with the findings of Eddy and Ebenso [34].

3.5. Potentiodynamic Polarization analysis

The use of polarization resistance technique for corrosion investigation is intended to observe the changes in 2101duplex stainless resistance to oxidation when there is any external potential. Figure 3 show the superimposed electrochemical polarization curves of DSS2101 in 0.5 M H_2SO_4 with STPL and STPR extract, and without STPL and STPR extract at 298 K.

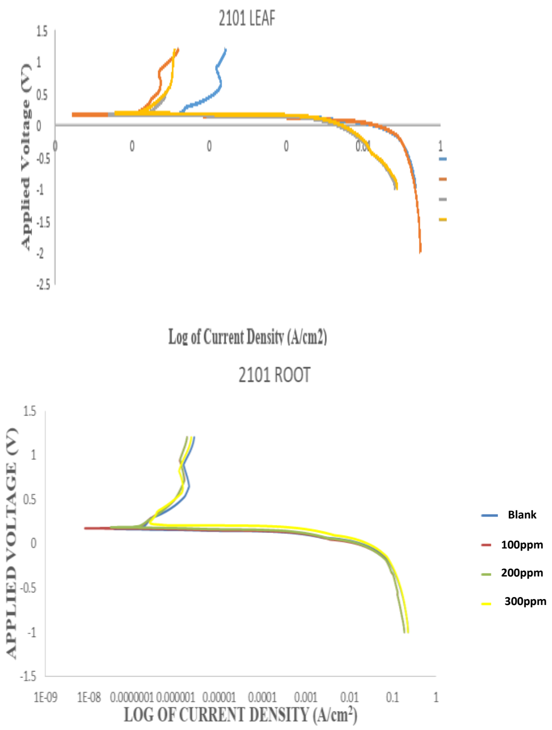

Figure 3: The electrochemical Polarization curves for DSS2101 immersed in 0.5 M H_2SO_4 with STPL and STPR extract, and without STPL and STPR extract at 298 K.

The electrochemical parameters values at different concentrations of ethanol extracts of STPL and STPR are given in the Table 3.

The corrosion current density (*Icorr*) decreases for STPL and STPR extract by increasing their concentration and in the process increasing the inhibition efficiency as shown in Table 2. The presence of STPL extract shifted corrosion potential (*Ecorr*) toward positive values between 0.16827V and 0.19325V. While the presence of STPR extract shifted *Ecorr* values between 0.17407V and 0.21520V. Comparing the blank and the anodic and cathodic polarization curves there are modification.

Table 2: The parameters electrochemical polarization for DSS2101 immersed in the solution of 0.5M H_2SO_4 acid at different STPL and STPR extract concentrations.

	LEAF				ROOT			
Samples concentration (ppm)	Ecorr (V)	Icorr (A/cm^2)	Corrosion Rate (mm/yr)	Inhibitor Efficiency	Ecorr (V)	Icorr (A/cm^2)	Corrosion Rate (mm/yr)	Inhibitor Efficiency
Blank	0.168	1.772E-07	2.059	-	0.168	1.772E-07	2.058	-
100	0.168	2.295E-08	1.505	26.915%	0.174	1.299E-07	1.509	26.701%
200	0.169	1.679E-08	1.240	39.754%	0.186	8.670E-08	1.008	51.061%
300	0.193	1.544E-08	1.079	47.570%	0.215	2.790E-07	0.807	60.806%

Also, there is an increase in IE as the concentration of inhibitor increases, these means that the inhibitor concentration enhances corrosion inhibition [35]. And this also indicated that the adsorption and inhibitor coverage on DSS 2101 metal surface increases as the inhibitor concentration increases. Then, at 300ppm, the maximum IE is 47.570 % for STPL extracts and 60.806 % for STPR extracts, which means that there are moderate corrosion inhibitors for DSS2101 metal. Figure 3 also shows that the IE value of STPR extract is greater than STPL extracts value. Hence from the values of the results obtained in this study different STPL and STPR extract behave as mixed-type inhibitor.

Inhibition efficiency was at maximum of 47.570 % when 300ppm of STPL extract was used. But least inhibition efficiency of 26.915% was shown by 100ppm STPL extract inhibitor concentration. The corrosion rate (CR) equally decreases from 2.05870mm yr^{-1} to 0.80687mm yr^{-1}. When 100ppm STPR extract was used, there was lowest IE of 26.701%. While maximum IE of 60.806% was attained at 300ppm STPR extract concentration. The CR decreases from 2.05870mm yr^{-1} to 1.07937mm yr^{-1}. This also agreed with earlier works on inhibition by Tridax Procumbens L Leaves Extract [36] and Cinnamon Plant Extract [37].

3.6. Adsorption Behaviour

The variation of surface coverage (θ) and *C/*θ with STPL and STPR extract concentration in 0.5M H_2SO_4 is shown in Table 3.

The *C/*θ was plotted against *C* for the STPL and STPR extract based on the polarization resistance results. The result agreed with the previous observation from weight loss behaviour. Inhibitor reduces metal corrosion by metal/solution interface adsorption, while the adsorption isotherm shows the effect of the inhibitor on the metal-surface interaction [38].

The plot of *C/*θ against C is a linear graph at all extract on DSS2101 metal as shown in figure 4.

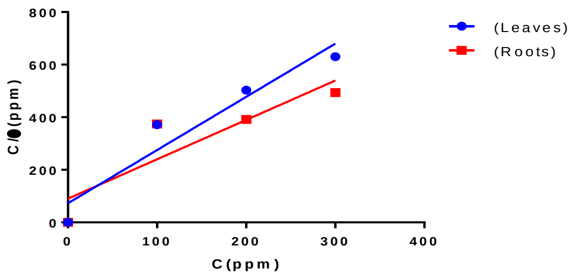

Figure 4: Langmuir plot for STPL and STPR extract on DSS2101 metal in 0.5M H2SO4 at different concentration.

The correlation coefficients curves are almost equal to 1 (r2 > 0.92). It can be inferred that the inhibitor adsorption on the surface of is DSS2101 in the 0.5 M H_2SO_4 acid is Langmuir isotherm. That is the inhibitor constituent of inhibition is absorbed on specific adsorption site of the metal/solution, hence preventing the corrosion caused by corrosion medium [39]. The adsorption isotherm shows the interaction between STPL and STPR extract and the surface of the DSS2101 metal. The (θ) for the extract concentrations obtained from Potentiodynamic polarization was evaluated, while the correlation coefficient (r^2) was used to choose the most suitable isotherm [40]

However, the adsorption free (ΔG^o_{ads}) was determined using equation (5)

$$\Delta G^o_{ads} = -RT\ln(10^6 K_{ads}) \quad (5)$$

Where ΔG^o_{ads} is the standard free energy (kJ mol^{-1}) and the equilibrium constant is K_{ads}. Table 4 show the ΔG^o_{ads} of the process.

Table 3: Variation of Surface Coverage with *Solanum* tuberosum (Potato) leaves and roots extract concentration in 0.5M H_2SO_4

Concentration (C) (ppm)	*Solanum tuberosum* (Potato) leaves Extract in 0.5M H_2SO_4		*Solanum tuberosum* (Potato) Roots Extract in 0.5M H_2SO_4	
	Surface Coverage (***θ***)	C/***θ*** (ppm)	Surface Coverage (***θ***)	C/***θ*** (ppm)
0	0	0	0	0
100	0.26915	371.54003	0.26701	374.51780
200	0.39753	503.10668	0.51061	391.68837
300	0.47570	630.64956	0.60806	493.37236

Table 4: Values of surface coverage, free energy with respect to inhibitor concentration and the adsorption equilibrium constant.

	Solanum tuberosum (Potato) leaves(STPL)			*Solanum tuberosum* (Potato) roots(STPR)		
Samples concentration (ppm)	surface coverage (θ)	Equilibrium constant of adsorption (K)	Gibbs free energy, ΔG (kJ/Mol)	surface coverage (θ)	Equilibrium constant of adsorption (K)	Gibbs free energy, ΔG (kJ/Mol)
Blank	0	0	0	0	0	0
100	0.26915	0.00368	-20.479	0.26701	0.00364	-20.451
200	0.39753	0.00329	-20.199	0.51061	0.00521	-21.346
300	0.47570	0.00302	-19.986	0.60806	0.00517	-21.326

The -ΔGoads negative sign suggests spontaneous organic extracts onto the surface of the DSS2101. The well accepted physical adsorption values for $-\Delta G^o_{ads}$ is lesser or equal to −20 kJ mol^{-1}, while at greater or equal to −40 kJ mol^{-1} indicate that electrons are been shared or transfered across the co-ordinate [41; 42]. The value of $-\Delta G^o_{ads}$ obtained proposes a physical adsorption of ethanol extract of STPL and STPR in H_2SO_4 acid media. This adsorption covered large surface area with a very small amount of adsorbed molecules. At low concentrations of the extract, high inhibition efficiency could be achieved. The increase in the extract concentration above a certain value has slight effect on the IE.

4. Conclusion

This research work focused on investigating the efficiency of *Solanum tuberosum* (Potato) leaves and roots extract solution on DSS2101 metal in 0.5M H_2SO_4 acid solution by increasing the *Solanum tuberosum* (Potato) leaves and roots extract concentration. The parts of the plant explored (leaf and root) were subjected to characterization by using FTIR to determine the organic corrosion inhibition agents present. The stretching vibration of hydroxyl (O-H), amide (N-H), aromatic alkenes (C-C) and sulfano (S=O) groups observed show the presence of organic anti corrosion agent saponin, tannins, steroid and flavonoid. The weight loss measurement proved that as the concentration of inhibitor increases, the weight loss of DSS2101 reduced. It shows that extract has very good IE for 0.5 M H_2SO_4 at 60.806%. In other words, the extract solution of *Solanum tuberosum* (Potato) leaves and roots is considering to be a very good corrosion inhibitor that can slow down the corrosion rate of DSS2101 metal in H_2SO_4 acid environment. The polarization curves show better inhibition of *Solanum tuberosum* (Potato) leaves and roots extract on the 2101 duplex stainless steel by at the same environment at room temperature. The extract corrosion inhibition is by a spontaneous physical adsorption process. *Solanum tuberosum* (Potato) leaves and roots extract obey Langmuir isotherm from the experimental data and values of ΔG^o_{ads} are negative suggesting that the *Solanum tuberosum* (Potato) leaves and roots extract strongly adsorbed on the 2101 duplex stainless steel and the values also support the physical adsorption mechanism.

5. Acknowledgments

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