



Comparative Study of Corrosion Inhibition Efficacy of Alkaloid Extract of *Artemesia vulgaris* **and** *Solanum tuberosum* **in Mild Steel Samples in 1 M Sulphuric Acid**

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Abstract: Two different types of alkaloids are successfully extracted from two plants *Artemisia vulgaris* (AV) and *Solanum tuberosum* (ST) in the laboratory and used as corrosion inhibitors for mild steel samples. The corrosion inhibition potential of these alkaloids is determined by weight loss and potentiodynamic polarization measurement methods. Based on the weight loss measurement study of a sample immersed for 6 h in 1000 ppm inhibitor solution of AV and ST alkaloids, the corrosion inhibition efficiency is found to be 92.58% and 90.79%, respectively. The potentiodynamic polarization measurement shows 88.06% and 83.22% corrosion inhibition efficiency for AV and ST alkaloids, respectively, for the sample immersed for 1 h in 1000 ppm inhibitor solution. These promising efficiency and suitable immersion time effect can lead to the development of good green inhibitors.

Keywords: Artemisia vulgaris; Solanum tuberosum; alkaloids; inhibitor; weight loss; polarization

1. Introduction

Corrosion is a spontaneous physical or chemical attack on materials due to an interfacial reaction in an ambient environment resulting in the loss of material properties [1,2]. A severe corrosion condition may result in tremendous economic loss as well as environmental impact to some extent. Mild steels (MS) are extensively used in various industrial and manufacturing plants, including petroleum, chemical, petrochemical, construction, pulp and paper, and transportation industries, where mild steel corrosion occurs inevitably during the process of cleaning boilers, acid pickling, and de-scaling. Such industries are the major contributors to corrosion losses [3,4]. It is reported that corrosion destroys about 150 million tons of steel per year, which is one-quarter of the world's annual steel production [5,6]. In this context, it is imperative to inhibit the corrosion process and its subsequent losses. For the reduction in MS corrosion, different protective methods such as the selection of material, design of corrosion resistive material, coating, and electrical protection methods are being adopted; however, such protective methods could be insufficient to control the underlying corrosion in the cleaning processes such as acid pickling, de-scaling, and cleaning boilers [7]. The use of corrosion inhibitors in the cleansing fluid is the common approach to control MS corrosion [8]. The effectiveness of a particular corrosion inhibitor is partly dependent on the nature of metals or composition of alloys to be protected, active centers in the inhibitors, as well as the severity of the environment [9].

In the 1950s, organic chemicals operating as corrosion inhibitors were developed in the petroleum industry; however, a major problem was related to their immediate toxicity [10].



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Besides being toxic, such organic compounds are expensive, water-insoluble, not readily available, and liable to pollute the environment in relation to the process of synthesis and application [11]. In this regard, there has been growing interest in the development of corrosion inhibitors based on natural resources, which are termed green corrosion inhibitors. Natural products are excellent alternatives as a green corrosion inhibitor from the viewpoint of availability, non-toxicity, economy, and environmentally friendly [8].

Natural products are rich sources of nitrogen-containing compounds and their derivatives, sulfur-containing compounds, aldehydes, thioaldehydes, acetylenic compounds, and alkaloids [9]. These compounds are adsorbed onto the metal surface and block the site of corrosion, hence, reducing the corrosion rate. It has been observed that adsorption of organic moieties onto the metal surfaces depends mainly on certain physicochemical properties of the inhibitor group, such as functional group, electron density at the donor atom, orbital character, and the electronic structure of the molecule [12,13].

Several studies are going on in the development of natural product-based environmentally friendly corrosion inhibitors. The first evidence of natural products used as corrosion inhibitors is the extracts of *Chelidonium majus* (Celadine) used in H₂SO₄ pickling baths [9]. Later on, various plant extracts were reported in the use of corrosion inhibition. The bark extract of *Euphorbia royleana* [6], Green Tea (GTE) and Black Tea (BTE) [14], *Aegle marmelos* [15], *Juniperus* [16], *Ficus asperifolia* [17], *Solanum lasiocarpum* [18], *Lantana camara* [19], *Erigeron floribundus* [20], *Gmelina arborea* [21], *Hyptis suaveolens* [22], *Pennisetun glaucum* [23], *Azadirachta indica* [24], mango and orange peels [25], *Baphia nitida* [26], *Solanum tuberosum* [27], ginger extract [28], rubber extract [29], *Scnecio anteuphorbium* [30], Luffa cylindrical leaf extract on mild steel in an HCl acid environment [31], and *Mahonia nepalensis* plant extract as a corrosion inhibitor for mild steel in 1 M sulfuric acid [32] have been reported as green inhibitors with most promising efficiency.

Phytochemical constituents consist of various functional groups in their structure, some of which contain heteroelements. The corrosion inhibition efficacy of such phytochemicals is largely influenced by the presence of such heteroatoms and follows a general trend of O < N < S < P [6]. Alkaloids extract from *Oxandra asbeckii* as corrosion inhibitor for C38 steel in 1 M HCl medium [33], *Neolamarckia cadamba* alkaloids for mild steel in HCl solution [34], indole alkaloids of *Alstonia angustifolia* var *latifolia* as a green corrosion inhibitor for mild steel corrosion in 1 M HCl media [35], caulespin—A bis indole from the marine Alga *Caulerpa racemosa* as a green corrosion inhibitor for the corrosion of mild steel in 1 M HCl solution [36], and an alkaloid of *Rhynchostylis retusa* as green inhibitor for steel corrosion in 1 M H₂SO₄ [37], are reported as a green inhibitors. Green inhibitors are safe, low-cost, readily available, biocompatible, and renewable sources of materials as compared with organic chemicals as corrosion inhibitors [38].

For the development of greener alternatives in corrosion inhibition, alkaloid extracts from *Artemisia vulgaris* and *Solanum tubersom* were selected in this research. *Artemisia vulgaris*, commonly called *Titepati* in Nepali, is reported as a medicinal plant [39]. The fern-like leaves of AV are covered with white hairs; the stem is thin and woody and available in temperate and cold temperate zones of the world [40]. The methanol extract of leaves of AV was found to be rich in alkaloids, total flavonoids, and phenolic content [40,41]. The commonly found alkaloid in *Artemisia vulgaris* is 3-Methyl butanamide, 1-Naphthyl amine, 2-Naphthyl amine, 3-Amino biphenyl, and 4-Amino biphenyl [41,42].

The plant *Solanum tuberosum* is a shrub plant having a maximum height up to 60 cm [43]. The leafy stem of ST is a waste part that consists of various components such as carbohydrates, chlorophyll, ascorbic acid, nitrates, starch, lipids, phosphorous, flavonoids, etc. [44]. Most of the *Solanum* species are rich in the store of diverse alkaloids with the major component of glycoalkaloids (α —solanine and α —chaconine) [45]. Nitrogen, an essential constituent of alkaloids, acts as an active center for the adsorption process due to the presence of a lone pair of electrons; therefore, nitrogenous heterocyclic compounds of alkaloids.

loid solutions are predominantly responsible for the inhibition of corrosion [46]. Herein, alkaloid extracts of these two plants are used as a corrosion inhibitor for mild steel and the inhibition efficacy has been studied by weight loss measurement and potentiodynamic polarization method.

2. Experimental Methods

2.1. Preparation of Specimens

A flat mild steel sheet of thickness 0.55 cm was collected from Aakash Metal Workshop in Kathmandu, Nepal, and cut into coupons of dimension ($4 \times 4 \times 0.55$) cm³. To obtain a clean and corrosion-free surface, each coupon was polished by silicon carbide (SiC) paper of 100–1200 grits size. The dimension of each coupon was measured with a digital Vernier caliper and recorded before each experiment. The corrosion-free coupon was then washed with hexane to remove organic impurities and ultrasonicated in ethanol. Washed coupons were air-dried and stored in a desiccator. The process was repeatedly carried out for every experiment.

2.2. Extraction of Alkaloids

The leafy stems of ST were collected from Dhulikhel, Nepal, and the stems of AV were collected from Budhanilkhantha, Nepal in June/July. Collected samples were washed and shade dried. The dried sample was ground into powder form by a grinding mill. 100 g of powder of each sample was soaked in hexane for 24 h and filtered. The residue was soaked in methanol separately and kept for 15 days, followed by filtration. The filtrate was taken as methanol extract. The pH of methanol extract was first made acidic by adding 5% tartaric acid, filtered and made alkaline (pH more than 10) by adding ammonia solution in a controlled manner. The alkaloid fraction was separated using dichloromethane (DCM) in the separating funnel. A dark green slurry of alkaloids in the organic layer was collected. A small amount of Na₂SO₃ was added to the alkaloid fraction to remove traces of water. The solution was then filtered. The organic layer thus obtained was separated, concentrated by using a rotatory evaporator under reduced pressure, and evaporated (below 40 °C) up to dryness to obtain alkaloids of ST, and AV, each separately. The presence of alkaloids was ensured by Mayer's test and a Fourier transform infra-red (FTIR) test.

2.3. Test for Alkaloids

A chemical test was carried out for the alkaloid test. For this, a small amount of extract was treated with Mayer's reagent ($HgCl_2 + KI$) and the result was observed.

2.4. Physicochemical Characterization

For the analysis of the functional group, FTIR spectrum of alkaloid extract of AV and ST was recorded by FTIR spectrometer (IR Prestige 21-FTIR Spectrometer, SIMADZU, Sendai, Japan) by the ATR method in the range of 400 cm⁻¹ to 4000 cm⁻¹.

2.5. Preparation of Media

Corrosive and inhibition media were prepared by taking sulphuric acid and alkaloids in the same acid, respectively. One-gram alkaloid of each AV and ST was dissolved in 50 mL of 1 M H₂SO₄ separately, followed by adding 1 M H₂SO₄ to make a 1000 mL solution in the separate volumetric flask. Each solution in a volumetric flask was filtered to remove the un-dissolved extract and the volume was maintained at 1000 mL by adding the required quantity of 1 M sulphuric acid. The filtrate was labeled as 1000 ppm of stock solutions of each AV and ST. Alkaloid solutions of required concentrations were prepared from those stock solutions by serial dilution method.

2.6. Weight Loss Measurement

An electronic analytical balance (PHOENIX, PH2204C) was used to measure the weight of MS coupons before and after their immersion in acid and inhibitor solution. Weight loss measurement was applied in the inhibitor solution of different concentrations (200, 400, 600, 800, and 1000 ppm) to determine the rate of corrosion. Similarly, the immersion time effect was studied by immersing the coupons for 1/2, 1, 3, 6, 13, and 24 h separately.

The inhibition efficiency (IE %) was determined using the formula:

Inhibition efficiency (IE%) =
$$\frac{w_0 - w_p}{w_0} \times 100$$
 (1)

where w_0 = weight loss in the absence of inhibitors, w_p = weight loss in the presence of inhibitors

The data obtained from this weight loss experiment at different time intervals and different concentration intervals were used to calculate the inhibition efficiency of the inhibitor solutions.

2.7. Potentiodynamic Polarization

The polarization measurement method was used to evaluate the corrosion current, and corrosion inhibition efficiency. Potentiodynamic polarization measurements were carried out using Hokuto Denko potentiostat (HA-151). A three-electrode cell system was used for the polarization. The electrolytic cell was set up using a mild steel sample as a working electrode, a saturated calomel electrode (SCE) as a reference electrode, and a graphite electrode as a counter electrode. 1 M sulphuric acid, as well as inhibitor solution (concentration ranging from 200–1000 ppm) of extract solution, was used as electrolyte. The working electrode, i.e., the mild steel specimen whose small area was exposed in extract solution (inhibitor solution) as compared to that of the counter electrode, exerts uniform potential on the working electrode. A salt bridge was made to connect the working electrode to the SCE. A time interval of 25 min before polarization was given for each experiment to attain the steady-state open current potential (OCP). Then the sample was subjected to cathodic and anodic polarization in the potential window—0.8 to 0 V, i.e., ± 350 mV from OCP. Polarization measurement was carried out for steel samples in different concentrations of inhibitors as well as in acid solution in both immersed and as-immersed conditions. The inhibition efficiency of the inhibitor was calculated using Equation (2).

Inhibition efficiency (IE %) =
$$\frac{I_{corr} - I_{corr}^*}{I_{corr}} \times 100$$
 (2)

where I_{corr} = corrosion current in the absence of inhibitors, I_{corr}^* = corrosion current in the presence of inhibitors.

2.8. Surface Morphology Study

The surfaces of MS samples before and after corrosion tests were studied by taking optical images through a light polarizing microscope (Radical Scientific, Haryana, India). The optical images of MS surface before immersion and after 1 h immersion in acid (1 M H_2SO_4) as well as in the presence of inhibitor solutions (1000 ppm AV inhibitor and 1000 ppm ST inhibitor) at 25 °C were studied.

3. Results and Discussion

3.1. Test for Alkaloids

Quantitative determination of alkaloids was performed for which the yield of 1.05 and 0.94% from AV and ST, respectively, were achieved. A chemical test for extracted alkaloids was performed. For this, a small amount of extract was treated with Mayer's reagent (HgCl₂ + KI), whereby a yellow precipitate appeared, indicating the presence of alkaloids.

3.2. Fourier Transform Infra-Red (FTIR) Analysis

Functional group analysis of both AV and ST alkaloid extract was carried out from the FTIR spectrum (Figure 1). The broad absorption peak at 3200-3400 cm⁻¹ is due to O-H

stretching of the phenolic group and N-H stretching of secondary amine. The sharp peaks at 2924.09 cm⁻¹ and 2916.36 cm⁻¹ are due to C-H stretching of alkane and the splitting peaks at 2854.65 cm^{-1} and 2846.93 cm^{-1} are due to the C-H stretching of the aldehyde group. The splitting peak at 1697.35 cm⁻¹ is due to C=O stretching of the amide group and the peak at 1604.77cm⁻¹ and 1597.05 cm⁻¹ is N-H bending of amine. The medium peak at 1357.88 cm⁻¹ and 1319.31 cm⁻¹ is due to the bending vibration of O-H bending of alcohol. Similarly, the absorption peaks at 1249.87 cm^{-1} and 1203.49 cm^{-1} are due to the C-N stretching of aromatic amine and the strong peak at 1018.41 cm⁻¹ and 1049.27 cm⁻¹ is due to the C-N stretching of amine [47,48]. The intensities of the peaks in the spectra are slightly different, but the positions of the peaks are not significantly different. This implies that there is no significant difference in the functional groups present in the alkaloids from these two different plants. However, there may be some differences in the elemental composition of as-identified chemical functionalities. The presence of the -OH group or catechol can support the binding of organic molecules onto the surface of the steel. The presence of amine or amide group further supports the presence of nitrogen group in the alkaloid and avails the lone pair electrons for bonding with MS. Presence of such functional moieties in alkaloids can assist in their adsorption process and hence reduce the corrosion potency.



Figure 1. FTIR spectrum of alkaloid extract of AV and ST.

3.3. Weight Loss Measurement and Corrosion Inhibition Efficiency

In this study, weight loss of MS was studied in terms of different parameters; the effect of inhibitor concentration and the effect of immersion time. Based on the weight loss measurement, the corrosion inhibition efficiency was studied.

3.4. Effect of Inhibitor Concentration

MS surface reacts with the acid upon immersion into the acid solution resulting in the formation of corrosion products which leads to the weight loss of MS. The decrease in the weight of MS coupons is related to the nature of MS surface, temperature, and concentration of the bath solution. Keeping the rest of the environment constant, the weight loss of material is directly proportional to the concentration of the aggressive environment. If the inhibitor solution is added to the aggressive environment, weight loss depends only on the concentration of the inhibitor. The loss in weight of MS is very high in the absence of an inhibitor. Besides the nature of the inhibitor, weight loss of MS gradually decreases with an increase in the concentration of the inhibitor, as shown in Figures 2 and 3. This is because, on increasing inhibitor concentration, the number of inhibitor molecules increases and are adsorbed on the MS surface. Hence, the weight loss of MS coupon due to corrosion in 200 ppm inhibitor solution is high and that of 1000 ppm is low.



Figure 2. Variation of weight loss with different concentrations of AV alkaloids on MS in $1M H_2SO_4$ solution at 20 °C at different intervals of immersion time.



Figure 3. Variation of weight loss with different concentrations of ST alkaloid on MS in $1M H_2SO_4$ solution at 20 °C at different intervals of immersion time.

The inhibition efficiency of each type of inhibitor for MS was studied by taking different concentrations (200, 400, 600, 800, and 1000 ppm) of inhibitor in 1M H_2SO_4 at different time intervals (Figures 4 and 5). The 1000 ppm AV and ST alkaloid showed maximum inhibition efficiency of 92.58% and 90.79%, respectively, for 6 hours' immersion time. The result shows that the inhibition efficiency increases with the increase in inhibitor concentration. This could be due to the increased concentration of extract, which could easily avail the number of inhibitor molecules for the adsorption onto the MS surface. The acid molecules have to rush up towards the MS surface against the crowding of inhibitor molecules and suffer many futile attempts for corrosion.



Figure 4. The inhibition efficiency of AV alkaloid solution in 1 M H₂SO₄ for mild steel at different immersion times.



Figure 5. The inhibition efficiency of ST alkaloid solution in $1 \text{ M H}_2\text{SO}_4$ for mild steel at different immersion times.

3.5. Effect of Immersion Time

The results of the weight loss experiment for mild steel immersed in 1 M H₂SO₄ with and without inhibitor are shown in Figures 6 and 7. The weight loss measurement showed that the presence of an alkaloid inhibitor reduced the weight loss of MS in the acidic medium as compared to that in 1 M sulphuric acid solution without an alkaloid inhibitor. Experiments were performed in different time intervals, i.e., $\frac{1}{2}$, 1, 3, 6, 13, and 24 h in 1 M H₂SO₄ in both the presence and absence of an inhibitor. From the figure, it is clear that, on increasing the immersion time, the weight loss of metal was found to be increased in both cases, but the ratio of weight loss was minimum for the use of inhibitor as compared to that without inhibitor in 1 M H₂SO₄. The weight loss of the MS coupons is the highest in acid solution and lowest in 1000 ppm inhibitor solution. The reason could be as follows. The inhibitors are adsorbed on the MS surface, forming an adsorptive layer on it. This adsorptive layer acted as a barrier against acid penetration. There is a slight increase

in weight loss observed even in the presence of inhibitors. This may be due to desorption phenomena and may be due to the large size and orientation of inhibitor molecules. A longer time exposure of the MS sample to the inhibitor solution in an acidic medium showed an increased weight loss, which could be due to the desorption of molecules from the MS surface.



Figure 6. Weight loss of mild steel immersed in different concentrations of AV alkaloids at different intervals of time at 20 °C.



Figure 7. Weight loss of mild steel immersed in different concentrations of ST alkaloids at different intervals of time at 20 °C.

The corrosion inhibition efficiency of the inhibitor of different concentrations in 1 M H_2SO_4 for MS samples was measured at 20 °C in a different interval of time up to 24 h. The inhibition efficiency of the inhibitor at different immersion times and in different concentrations of inhibitors is shown in Figures 8 and 9. The inhibition of the inhibitor is very good at 1–6 h immersion time. The result showed that the inhibition efficiency of the 1000 ppm solution is the highest. For 6 h immersion of MS in 1000 ppm solution, the maximum inhibition efficiency is found to be 92.58% for AV alkaloid and 90.79% for ST alkaloid, respectively. These inhibitor solutions showed maximum inhibition efficiency

from the very beginning at 3–6 h immersion time. Corrosion inhibition is slightly lower at initial $\frac{1}{2}$ h immersion. This may be because the time of immersion is very short, so the inhibitor molecules are unable to form the complete adsorptive layer. Until 6 h of immersion, the efficiency was gradually increasing in search of complete adsorption of inhibitors on the MS surface. After 6 h of immersion, efficiency gradually decreased; this may be due to the desorption of the inhibitor over a prolonged time [49].



Figure 8. Inhibition efficiency of AV alkaloids for mild steel immersed at different intervals of time.



Figure 9. Inhibition efficiency of ST alkaloids for mild steel immersed at different intervals of time.

3.6. Potentiodynamic Polarization (as-Immersed and 1 h Immersed MS Sample)

Potentiodynamic polarization of the as-immersed MS sample was carried out in the different concentrations (200, 400, 600, 800, and 1000 ppm) of AV and ST alkaloids in 1 M H_2SO_4 solution. From polarization curves (Figures 10 and 11) of the as-immersed sample, it is found that the anodic slope is higher than the cathodic slope for the same concentration of acid and inhibitor solution. This difference in slope is in relation to the charge at anode and cathode. Even though the rate of reaction for both cases is the same, the generation of potential difference is different, indicating the flat potential at the cathode and sharp potential at the anode. The polarization curve also indicates that there is a decrease in

current density with the addition of an inhibitor. The slight shifting of potential (<50 mV) in both anodic and cathodic directions indicates that these inhibitors act as mixed types of inhibitors.



Figure 10. Potentiodynamic polarization curves for mild steel in 1 M H₂SO₄ containing different concentrations of AV alkaloids as-immersed condition.



Figure 11. Potentiodynamic polarization curves for mild steel in 1 M H₂SO₄ containing different concentrations of ST alkaloids as-immersed condition.

The inhibition efficiency of each AV alkaloid and ST alkaloid is also tabulated in Table 1. The inhibition efficiency of alkaloids increases by increasing the concentration of the inhibitor. In the presence of an inhibitor, the MS surface is covered with inhibitor molecules so that the active site (exposed site for corrosion) on MS is small. Reaction at this small area results in the small current density exhibiting high corrosion inhibition efficiency. This also indicates that the alkaloids extracted and used in this experiment can act as good inhibitors. The maximum inhibition efficiency of AV and ST alkaloids is found to be 85.29% and 80.48%, respectively, for 1000 ppm concentration of inhibitor.

Table 1. Inhibition efficiency of AV alkaloids and ST alkaloids for as-immersed MS sample by polarization method.

Inhibitor Concentration (ppm)	Corrosion Current Density (i _{corr}) in AV Alkaloid Inhibitor	Efficiency (%) of AV Alkaloids	Corrosion Current Density (i _{corr}) in ST Alkaloid Inhibitor	Efficiency (%) of ST Alkaloids
$1 \text{ M H}_2\text{SO}_4$	0.476	-	0.502	-
200	0.221	53.57	0.226	54.98
400	0.182	61.77	0.208	58.57
600	0.131	72.48	0.172	65.74
800	0.090	81.09	0.139	72.31
1000	0.070	85.29	0.098	80.48

Polarization of the experiment was carried out after immersing MS samples in different concentrations of AV and ST alkaloids solutions for 1 h. A plot of the logarithmic function of corrosion current density versus potential is plotted as shown in Figures 12 and 13. As in the as-immersed condition, there is almost no shifting of potential, indicating mixed types of inhibitors. It is found that the current density decreases in the presence of an inhibitor solution. Within this immersion time, the inhibitor molecules completely covered the MS surface so that there was the least chance of reacting with acid. In addition, the current density decreases by increasing the concentration of the alkaloid solution; therefore, the decrease in current density with the increase in the concentration of inhibitor solution suggests the retardation of corrosive reaction due to increased surface coverage by the inhibitor molecules on the MS surface. This result suggests that these alkaloids can act as effective inhibitors.



Figure 12. Potentiodynamic polarization curves for MS in 1 M H₂SO₄ containing different concentrations of AV alkaloid for 1 h immersed sample.



Figure 13. Potentiodynamic polarization curves for MS in 1 M H₂SO₄ containing different concentrations of ST alkaloid for 1 h immersed sample.

The current density and respective inhibition efficiency of AV and ST alkaloids for MS from the polarization curve are tabulated in Table 2. The current density measured in the inhibitor medium is lower than the current density in the acid medium. In the presence of an inhibitor, the rate of MS dissolution is very low. This is due to the formation of an inhibitor adsorptive layer on MS. The efficiency of the inhibitor gradually increases by increasing its concentration. The maximum efficiency for AV alkaloids is found at 88.06%, and for ST alkaloids is found at 83.22% in 1000 ppm inhibitor solution at 20 °C, respectively.

Inhibitor Concentration (ppm)	Corrosion Current Density (i _{corr}) of AV Alkaloid	Efficiency (%) of AV Alkaloid	Corrosion Current Density (i _{corr}) of ST Alkaloid	Efficiency (%) of ST Alkaloid
$1 \text{ M H}_2\text{SO}_4$	0.243	-	0.292	-
200	0.102	58.03	0.115	60.62
400	0.070	71.19	0.098	66.44
600	0.041	83.13	0.078	73.29
800	0.034	86.01	0.052	82.19
1000	0.019	92.18	0.026	91.10

Table 2. Current density and respective inhibition efficiency of AV and ST alkaloids for 1 h immersed MS sample.

3.7. Inhibition Efficiency of Alkaloid for Immersed and as-Immersed Condition

For both immersed and as-immersed samples and all the concentrations of inhibitor, polarization was carried out. The inhibition efficiency of the alkaloid is calculated from the polarization method according to Equation (2). The inhibition efficiency of the alkaloid as an inhibitor is higher in 1 h immersed condition. This is because, on immersion, inhibitor molecules can have sufficient time to become adsorbed and attain an equilibrium state. This adsorbed layer protects the MS from an aggressive environment and reduces the corrosion rate. The detail efficiency variation is shown in Figures 14 and 15.



Figure 14. Inhibition efficiency of inhibitor obtained from the polarization of both immersed and as-immersed MS sample 1 M H₂SO₄ in the presence of AV alkaloid as an inhibitor.



Figure 15. Inhibition efficiency of inhibitor obtained from the polarization of both immersed and as-immersed MS sample 1 M H₂SO₄ in the presence of ST alkaloid as an inhibitor.

Figures 14 and 15 revealed that the inhibition efficiency increases with an increase in the concentration of the inhibitor solution. It is due to the increase in the fraction of surface covered by mild steel by the adsorbed molecule, which results in the increase in inhibition efficiency on the increasing concentration of inhibitor solution.

3.8. Comparative Study of Corrosion Inhibition of AV and ST

The corrosion inhibition efficiency of alkaloid extract from AV and ST has been studied in terms of weight loss method and potentiodynamic method. For 6 h immersion of MS in 1000 ppm solution, the maximum inhibition efficiencies recorded by the weight loss method were 92.58% for AV alkaloid and 90.79% for ST alkaloid, respectively. The maximum inhibition efficiencies of 92.18% and 85.29% were found at 1000 ppm concentration of AV alkaloid inhibitor solution in 1 M H_2SO_4 on the MS sample immersed for 1 h and asimmersion, respectively, based on the potentiodynamic method. Similarly, the maximum inhibition efficiencies of 91.10% and 80.48% were found at 1000 ppm concentration of ST alkaloid inhibitor solution in 1 M H_2SO_4 on MS sample immersed for 1 h and as-immersion, respectively, based on the potentiodynamic method.

All in all, though the corrosion inhibition efficiency recorded for the weight loss measurement method and potentiodynamic measurement method were of different periods (6 h and 1 h, respectively), the AV alkaloid inhibitor was found to be better compared to that of ST alkaloid inhibitor; however, the corrosion inhibition efficiency for ST is also remarkably satisfactory. For the same alkaloid, the inhibition efficiency measured was found to be a bit different for different methods. The weight loss measurement method is manually operated and may owe some handling error, whereas the potentiodynamic method is instrumental and has less bias of handling errors.

3.9. Surface Morphological Study

The surface of MS samples before and after corrosion tests was studied by taking optical images through a light polarizing microscope (Radical Scientific, Haryana, India). The optical images of MS surface before immersion and after immersion in acid, as well as in the presence of inhibitor solutions, are in Figure 16.



Figure 16. The MS surface images (**a**) polished surface before immersion, (**b**) after 1 h dipping in acid at 25 °C, (**c**) after 1 h dipping in AV inhibitor at 25 °C, and (**d**) after 1 h dipping in ST inhibitor solution at 25 °C.

The MS surface was polished with silicon carbide paper before the immersion test to make it smooth. A significant roughness was observed on the MS surface after its immersion in the acid solution $(1 \text{ M H}_2\text{SO}_4)$ as compared to that into 1000 ppm inhibitor in 1 M H₂SO₄ solution. A large number of grooves and pits were observed on the MS surface dipped into acid for 1 h, contrary to the smooth surface observed on the MS surface immersed in the inhibitor solution. The smooth surface of MS could be due to the uniform coverage of inhibitor molecules on the surface, such that it could hinder the deep penetration of acid molecules onto the surface. Consequently, the surface coverage by the inhibitor molecules suppresses the rate of corrosion [37].

3.10. Mechanism of Green Corrosion Inhibitor

Alkaloids are phytochemicals that contain at least a nitrogen atom in their structure as an active center and play a key role in green corrosion inhibition. Elements with lone pair of electrons such as O, N, S, and P in phytochemicals serve as active centers for the adsorption on the metal surface. Green inhibitors are adsorbed on the metal surface by the electrostatic force of attraction between ions or dipoles of inhibitor molecules and electrically charged metal surfaces via the physisorption process [50,51]. It has been observed that adsorption depends mainly on certain physicochemical properties of the inhibitor group, such as the functional group, the electron density of the donor atom, π -orbital character, and the electronic structure of the molecule [6,12].

The corrosion inhibition could be due to the adsorption of the inhibitor molecules onto the metal surface, hence increasing or decreasing anodic or cathodic reaction, decreasing the diffusion rate for reactants to the surface of the metal, and formation of protective barrier film [9]. AV and ST alkaloids inhibit corrosion in the MS surface, especially via the physisorption process [51]. Besides the physical and chemical adsorption, it is also proposed that chemical compounds in plant extract may react with atoms of metal surface, forming the organometallic complex. For example, the reaction of iron metal can be shown as,

$${
m Fe}
ightarrow {
m Fe}^{2+} + 2e^-$$

 Fe^{2+} + plant extract \rightarrow [Fe - Plant extract]

These complexes are adsorbed by the metal surface by van der Waals force of attraction. Then it forms a protective layer for the retardation of corrosion. In the process, the solvent water molecule could also be adsorbed or desorbed in the metal solution. So, this adsorption can also be considered a quasi- substitution process [10]. The organic inhibitors are adsorbed on the metal surface by replacing water molecules, as shown in the equation.

Inhibitor molecule (aq.) + M-H₂O (ads) \rightarrow M-Inhibitor molecule (ads) + n H₂O (sol.) (3)

where n represents the number of molecules that are replaced to accommodate the organic molecule. The hydrocarbon part of the organic inhibitor is oil soluble and hence it repels water from the metallic surface; therefore, it provides a barrier that keeps water away and thus prevents corrosion [52].

Whatever may be the mechanism of adsorption, the density of the functional groups, polarizability, and electronegativity are the important parameters that determine the inhibition efficiency. Adsorption strength can be obtained from the adsorption isotherm, which shows the equilibrium relationship between concentrations of corrosion inhibitors on the surface and in the bulk of the solution. A schematic diagram of the inhibition mechanism is given below (Figure 17).



Figure 17. Schematic diagram for the mechanism of inhibition.

4. Conclusions and Recommendations

The methanol fraction of alkaloids was successfully extracted from two plants *Artemisia vulgaris* (AV) and *Solanum tuberosum* (ST) in the laboratory and ensured by chemical tests as well as FTIR analysis. These alkaloids were used as corrosion inhibitors for mild steel samples. The corrosion inhibition efficiency of the AV and ST alkaloids was performed using the weight-loss method and potentiodynamic polarization measurements in 1 M H₂SO₄. These AV and ST alkaloids can work up to 6 h immersion time and can act as good inhibitors with very attractive inhibition efficiency by 1000 ppm inhibitor solution. Though the inhibition efficiency is nearly 80%, these inhibitors can work up to 6 h immersion time with high inhibition potential. These inhibitors with an acid solution can be used for the cleaning processes.

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