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Research Article

A Comparative Study of the Inhibitory Effect of the Extracts of *Ocimum sanctum*, *Aegle marmelos*, and *Solanum trilobatum* on the Corrosion of Mild Steel in Hydrochloric Acid Medium

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A comparative study of the inhibitory effect of plant extracts, *Ocimum sanctum, Aegle marmelos*, and *Solanum trilobatum*, on the corrosion of mild steel in 1N HCl medium was investigated using weightloss method, electrochemical methods, and hydrogen permeation method. Polarization method indicates plant extracts behave as mixed-type inhibitor. The impedance method reveals that charge-transfer process mainly controls the corrosion of mild steel. On comparison, maximum inhibition efficiency was found in *Ocimum sanctum* with 99.6% inhibition efficiency at 6.0% v/v concentration of the extract. The plant extracts obey Langmuir adsorption isotherm. The SEM morphology of the adsorbed protective film on the mild steel surface has confirmed the high performance of inhibitive effect of the plant extracts. From hydrogen permeation method, all the plant extracts were able to reduce the permeation current. The reason for the reduced permeation currents in presence of the inhibitors may be attributed to the slow discharge step followed by fast electrolytic desorption step. Results obtained in all three methods were very much in good agreement in the order *Ocimum sanctum* > *Aegle marmelos* > *Solanum trilobatum*.

1. Introduction

Mild steel is a structural material widely used in automobiles, pipes and used in most of the chemical industries. Mild steel suffers from severe corrosion in aggressive medium of acids and pickling processes. Hydrochloric acid is widely used for pickling, descaling, and chemical cleaning processes of mild steel. 90% of pickling problems can be solved by introducing appropriate pickling inhibitor to the medium. Generally, organic compounds containing O, N, and S atoms are normally used as inhibitors to reduce the corrosion of mild steel in hydrochloric acid medium [1, 2]. Environmental concerns worldwide are increasing and are likely to influence the choice of corrosion inhibitors in the present and in future. Environmental requirements are still being developed, but some elements have been established. One of the methods to protect metals against corrosion is addition of species to the solution in contact with the surface in order to inhibit the corrosion rate. Unfortunately, many of the inhibitors used are inorganic salts or organic compounds with toxic properties or limited solubility. Increasing awareness of health and ecological risks has drawn attention to find more suitable inhibitors which are nontoxic. Accordingly, greater research efforts have been directed towards formulating environmentally acceptable inhibitors.

Due to the diversity of their structures, many extracts of common plants have been used as corrosion inhibitors for materials in pickling and cleaning processes. Plant materials contain proteins, polysaccharides, polycarboxylic acids, tannin, alkaloids, and so forth. These compounds are potential acid corrosion inhibitors for many metals [3]. The cost of using green inhibitors is very low when compared to that of organic inhibitors which require a lot of chemicals and also time for its preparation. Chemical inhibitors are more expensive and cause more hazard effects. Nowadays due to strict environmental legislation, emphasis is being focused on usage of natural products that are corrosion inhibitor. The recent and growing trend is using plant extracts as corrosion inhibitor. Recently, many plant extracts have been reported as effective corrosion inhibitors within India and outside India [4–20]. In this study, leaf extracts of three medicinal plants, namely, *Ocimum sanctum* (Tulasi), *Aegle marmelos* (Vilvam), and *Solanum trilobatum* (Thuthuvalai), have been selected to study the inhibition effect on the corrosion of mild steel in 1N hydrochloric acid medium using weight loss method, the potentiodynamic polarization method, electrochemical impedance method, and hydrogen permeation method.

2. Experimental Procedure

2.1. Preparation of Mild Steel Specimen. Mild steel strips were mechanically cut into strips of size 4.5 cm × 2 cm × 0.2 cm containing the composition of 0.14% C, 0.35% Mn, 0.17% Si, 0.025% S, 0.03% P, and the remainder Fe and provided with a hole of uniform diameter to facilitate suspension of the strips in the test solution for weight loss method. For electrochemical studies, mild steel strips of the same composition but with an exposed area of 1 cm^2 were used. Mild steel strips were polished mechanically with emery papers of 1/0 to 4/0 grades, subsequently degreased with trichloroethylene or acetone and finally with deionised water, and stored in the desiccator. Accurate weight of the samples was taken using electronic balance.

2.2. Preparation of the Plant Extract. The leaves of the plants *Ocimum sanctum, Aegle marmelos*, and *Solanum trilobatum* were taken and cut into small pieces, and they were dried in an air oven at 80°C for 2 h and ground well into powder. From this, 10 g of the sample was refluxed in 100 mL distilled water for 1 h. The refluxed solution was then filtered carefully, the filtrate volume was made up to 100 mL using double distilled water which is the stock solution, and the concentration of the stock solution is expressed in terms of % (v/v). From the stock solution, 2–10% concentration of the extract was prepared using 1N hydrochloric acid. Similar kind of preparation has been reported in studies using aqueous plant extracts in the recent years [21–30].

2.3. Weight Loss Method. The pretreated specimens' initial weights were noted and were immersed in the experimental solution with the help of glass hooks at 30°C for a period of 3h. The experimental solution used was 1N HCl in the absence and presence of various concentrations of the inhibitors. After three hours, the specimens were taken out, washed thoroughly with distilled water, and dried completely, and their final weights were noted. From the initial and final weights of the specimen, the loss in weight was calculated and tabulated. From the weight loss, the corrosion rate (mmpy), inhibition efficiency (%), and surface coverage (θ) of plant extracts were calculated using the formula

$$\text{Corrosion rate (mmpy)} = \frac{KW}{AtD}, \tag{1}$$

where $K = 8.76 \times 10^4$ (constant), W is weight loss in g, A is area in cmm^2, t is time in hours, and D is density in gm/cmm^3 (7.86):

$$\begin{aligned} \text{Inhibition efficiency (\%)} &= \frac{(\text{CR}_B - \text{CR}_I)}{\text{CR}_B} \times 100, \\ \text{Surface coverage } (\theta) &= \frac{\text{CR}_B - \text{CR}_I}{\text{CR}_B}, \end{aligned} \tag{2}$$

where CR_B and CR_I are corrosion rates in the absence and presence of the inhibitors.

2.4. Potentiodynamic Polarization Method. Potentiodynamic polarization measurements were carried out using electrochemical analyzer. The polarization measurements were made to evaluate the corrosion current, corrosion potential, and Tafel slopes. Experiments were carried out in a conventional three-electrode cell assembly with working electrode as mild steel specimen of 1 sq. cm area which was exposed and the rest being covered with red lacquer, a rectangular Pt foil as the counter electrode, and the reference electrode as SCE. Instead of salt bridge, a luggin capillary arrangement was used to keep SCE close to the working electrode to avoid the ohmic contribution. A time interval of 10–15 minutes was given for each experiment to attain the steady state open circuit potential. The polarization was carried from a cathodic potential of −800 mV (vs SCE) to an anodic potential of −200 mV (vs SCE) at a sweep rate of 1 mV per second. From the polarization curves, Tafel slopes, corrosion potential, and corrosion current were calculated. The inhibitor efficiency was calculated using the formula

$$\boxed{\text{IE (\%)} = \frac{I_{\text{Corr}} - I_{\text{Corr}}^{*}}{I_{\text{Corr}}} \times 100,} \tag{3}$$

where I_{Corr} and I_{Corr}^{*} are corrosion current in the absence and presence of inhibitors.

2.5. Electrochemical Impedance Method. The electrochemical AC-impedance measurements were also performed using electrochemical analyzer. Experiments were carried out in a conventional three-electrode cell assembly as that used for potentiodynamic polarization studies. A sine wave with amplitude of 10 mV was superimposed on the steady open circuit potential. The real part (Z') and the imaginary part (Z'') were measured at various frequencies in the range of 100 KHz to 10 MHz. A plot of Z' versus Z'' was made. From the plot, the charge transfer resistance (R_t) was calculated, and the double layer capacitance was then calculated using

$$C_{\text{dl}} = \frac{1}{2\pi f_{\max} R_t}, \tag{4}$$

where R_t is charge transfer resistance, and C_{dl} is double layer capacitance. The experiments were carried out in the absence and presence of different concentrations of inhibitors. The percentage of inhibition efficiency was calculated using

Table 1: Corrosion parameters obtained from weight loss measurements for mild steel in 1N HCl containing various concentrations of the plant extracts.

Name of the plant extract	Conc. of the extract (% in v/v)	Corrosion rate (mmpy)	Inhibition efficiency (%)	Surface coverage (θ)
Ocimum sanctum	Blank	30.67	—	—
	2.0	2.39	92.2	0.9221
	4.0	1.10	96.4	0.9641
	6.0	0.12	99.6	0.9961
	8.0	1.08	96.5	0.9648
	10.0	1.32	95.7	0.9570
Aegle marmelos	Blank	30.67	—	—
	2.0	3.81	87.6	0.8758
	4.0	3.03	90.1	0.9012
	6.0	2.02	93.4	0.9341
	8.0	0.76	97.5	0.9752
	10.0	0.76	97.5	0.9752
Solanum trilobatum	Blank	30.67	—	—
	2.0	12.75	58.4	0.5843
	4.0	8.42	72.5	0.7255
	6.0	6.59	78.5	0.7851
	8.0	5.21	83.0	0.8301
	10.0	3.00	90.2	0.9022

$$\boxed{\mathrm{IE}\ (\%) = \frac{R_t^* - R_t}{R_t^*} \times 100,} \qquad (5)$$

where R_t^* and R_t are the charge transfer resistance in the presence and absence of inhibitors.

2.6. Hydrogen Permeation Method. When metals are in contact with acids, atomic hydrogen is produced. Before they combine to produce hydrogen molecules, a fraction may diffuse into the metal. Inside the metal, the hydrogen atoms may combine to form molecular hydrogen. Thus, a very high internal pressure is built up. This leads to heavy damage of the metal. This is known as "hydrogen embrittlement". This phenomenon of hydrogen entry into the metals can occur in industrial processes like pickling, plating, phosphating, and so forth. An inhibitor can be considered as completely effective only if it simultaneously inhibits metal dissolution and hydrogen penetration into the metal [31]. Hydrogen permeation study has been taken up with an idea of screening the inhibitors with regard to their effectiveness on the reduction of hydrogen uptake. Hence, the hydrogen permeation study was carried out using an adaptation of the modified Devanathan-Stachurski two-compartment cell assembly [32, 33] in 1N HCl medium in the absence and presence of optimum concentration of the extracts. Similar kind of study is reported in the works of Quraishi and Rawat [34].

2.7. Surface Examination Studies. Surface examination of mild steel specimens in the absence and presence of the optimum concentration of the extracts immersed for 3 h at 30°C was studied using JEOL-Scanning electron microscope (SEM) with the magnification of 1000x specimens.

3. Results and Discussion

3.1. Weight Loss Studies. The weight loss studies were done in 1N hydrochloric acid in the absence and presence of various concentrations of the plant extracts ranging from 2% to 10% v/v. Using the weight loss data, the corrosion rate, inhibition efficiency, surface coverage, and the optimum concentration of the extract have been calculated. The corrosion parameters obtained in the weight loss method are listed in Table 1.

From Table 1, it was found that with the addition of the plant extract to 1N hydrochloric acid, the weight loss of mild steel decreased, the corrosion rate also decreased, while the inhibition efficiency increased. The optimum concentration for *Ocimum sanctum* was found to be 6% v/v with maximum inhibition efficiency of 99.6%, *Aegle marmelos* at 8% v/v with maximum inhibition efficiency of 97.5%, and *Solanum trilobatum* at 10% v/v with maximum inhibition efficiency of 90.2% for a period of 3 hours of immersion time. This result indicated that the plant extracts could act as effective corrosion inhibitors for mild steel in 1N HCl. The effect of immersion time studied for a period of 3 h to 24 h as given in Table 2 reveals that the plant extracts showed maximum efficiency at 3 h of immersion time which is sufficient for pickling process. The order of inhibition effect among the three plant extracts on mild steel in 1N HCl is found to be *Ocimum sanctum* > *Aegle marmelos* > *Solanum trilobatum*.

3.2. Potentiodynamic Polarization Studies. The potentiodynamic polarization parameters for different concentrations of the plant extracts are given in Table 3, and the polarization curves are given in Figure 1. Potentiodynamic polarization studies revealed that the corrosion current density (I_{corr})

Table 2: Effect of immersion time on percentage inhibition efficiency of mild steel in 1N HCl at 30°C in the presence of optimum concentration of the plant extracts.

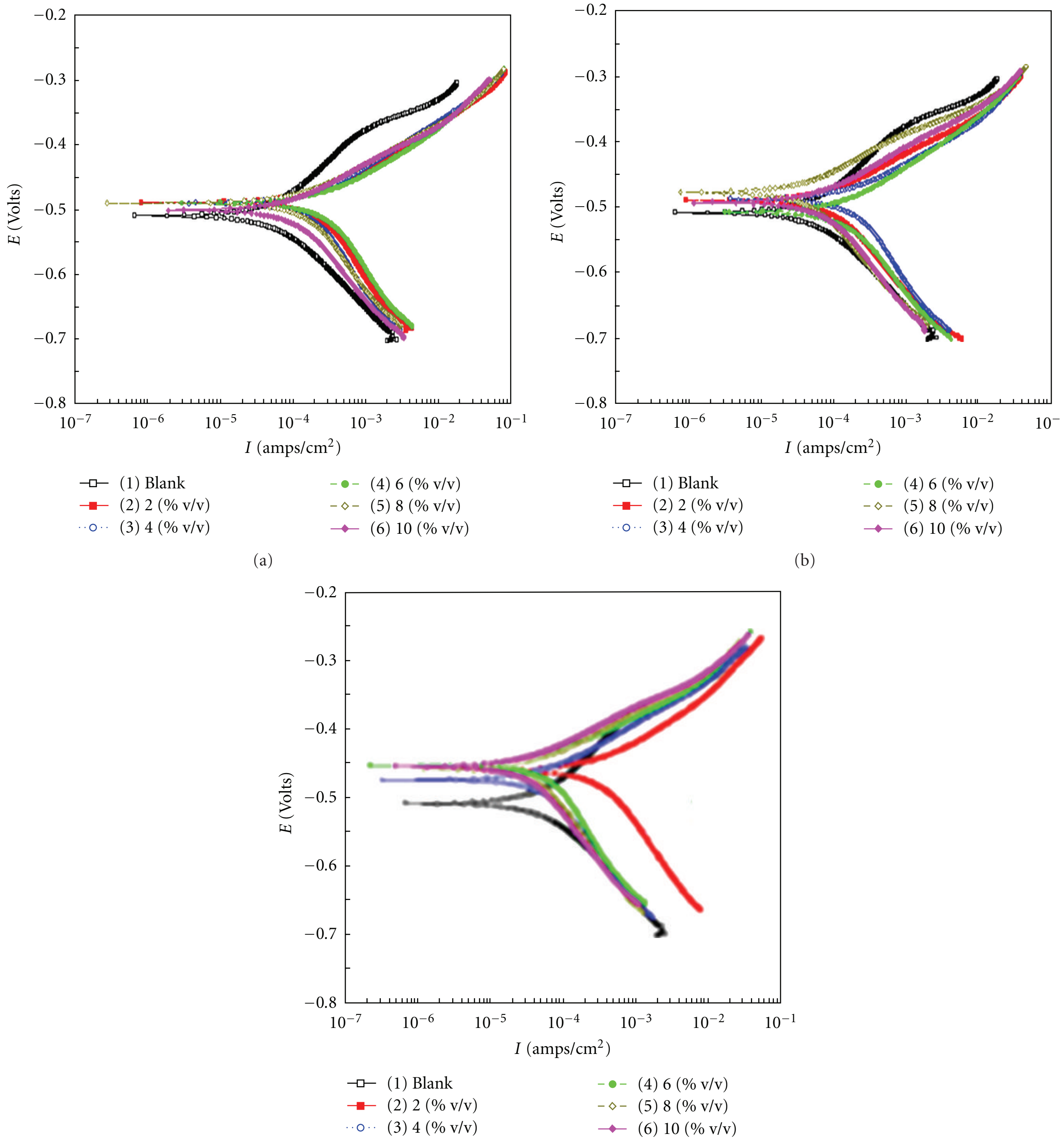
Name of the plant extract with optimum conc.	Inhibition efficiency (%) Time (h)							
	3	6	9	12	15	18	21	24
6% v/v of *Ocimum sanctum*	99.6	98.5	98.0	97.3	96.5	96.0	95.3	94.8
8% v/v of *Aegle marmelos*	97.5	96.7	95.6	95.0	94.2	93.0	92.6	90.8
10% v/v of *Solanum trilobatum*	90.2	89.5	89.4	88.6	88.0	87.5	87.0	86.2

Table 3: Potentiodynamic polarization parameters for mild steel in 1N HCl containing various concentrations of the plant extracts.

Name of the plant extract	Conc. of extract (% in v/v)	E_{corr} (V)	I_{corr} (mA/cm^2)	Tafel slope mV/decade		Inhibition efficiency (%)
				b_a	b_c	
Blank	—	−0.510	3.57	78	122	—
Ocimum sanctum	2.0	−0.515	0.24	74	126	93.3
	4.0	−0.498	0.12	76	124	96.6
	6.0	−0.496	0.01	74	124	99.7
	8.0	−0.499	0.09	74	122	97.5
	10.0	−0.500	0.12	76	124	96.6
Aegle marmelos	2.0	−0.493	0.40	78	126	88.5
	4.0	−0.492	0.31	76	124	91.3
	6.0	−0.497	0.21	74	122	94.1
	8.0	−0.483	0.09	74	122	97.5
	10.0	−0.492	0.09	76	124	97.5
Solanum trilobatum	2.0	−0.490	1.45	74	126	59.4
	4.0	−0.480	0.97	76	128	72.8
	6.0	−0.462	0.75	74	126	79.0
	8.0	−0.459	0.56	78	130	84.3
	10.0	−0.460	0.33	76	128	90.8

Table 4: Impedance parameters for the corrosion of mild steel in 1N HCl in the absence and presence of various concentrations of the plant extracts at 30°C.

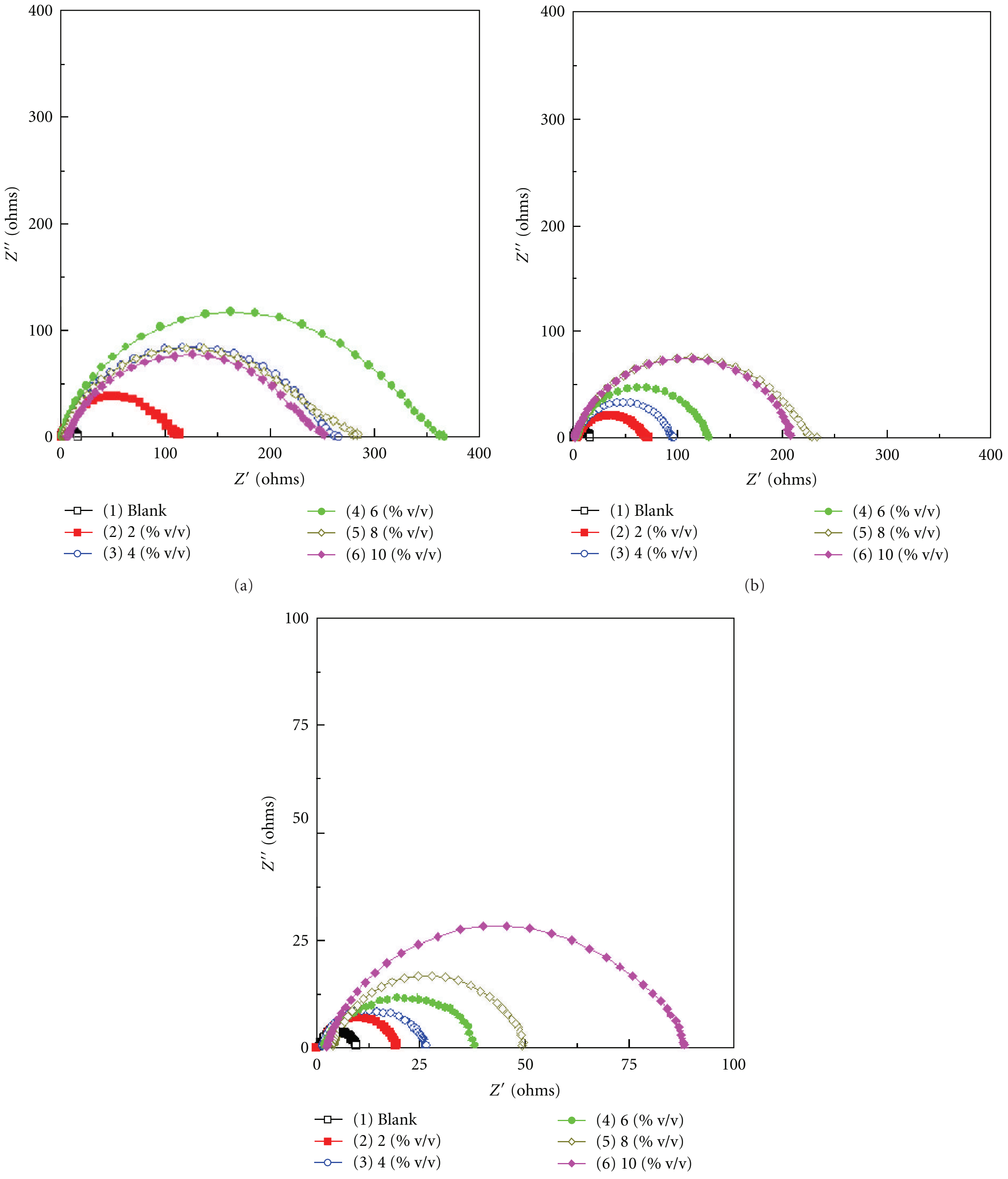
Name of the plant extract	Conc. of extract (% in v/v)	R_t (Ω cm^2)	C_{dl} (μF/cm^2)	Inhibition efficiency (%)
Blank	—	7.58	285.34	
Ocimum sanctum	2.0	110.91	19.34	93.2
	4.0	253.86	8.44	97.0
	6.0	358.80	6.00	97.9
	8.0	274.99	7.95	97.2
	10.0	239.25	9.02	96.8
Aegle marmelos	2.0	69.85	31.09	89.1
	4.0	88.41	24.52	91.4
	6.0	136.49	15.86	94.4
	8.0	224.80	9.62	96.6
	10.0	208.34	10.25	96.4
Solanum trilobatum	2.0	18.62	116.02	59.3
	4.0	27.34	79.00	72.3
	6.0	37.12	58.35	79.6
	8.0	48.31	44.72	84.3
	10.0	87.86	24.52	91.4



(a) (b) (c)

Figure 1: Potentiodynamic polarization curves for mild steel in 1N HCl solution in the absence and presence of various concentrations of the plant extracts (a) *Ocimum sanctum*, (b) *Aegle marmelos*, and (c) *Solanum trilobatum*.

markedly decreased with the addition of the extract and the corrosion potential shifts to less negative values upon addition of the plant extract. Moreover, the values of anodic and cathodic Tafel slopes (b_a and b_c) are slightly changed indicating that this behavior reflects the plant extracts' ability to inhibit the corrosion of mild steel in 1N HCl solution via the adsorption of its molecules on both anodic and cathodic sites, and, consequently, the extracts act through mixed mode of inhibition [15, 16]. It was observed that with increase in concentration of the plant extract from 2% to 10%, the maximum inhibition efficiency of 99.7% was observed for *Ocimum sanctum* extract at 6% v/v, for *Aegle marmelos* with 97.5% at 8% v/v, and for *Solanum trilobatum* with 90.8% at 10% v/v of the extract.



(a)

(b)

(c)

Figure 2: Impedance diagrams for mild steel in 1N HCl solution in the absence and presence of various concentrations of the plant extract (a) *Ocimum sanctum*, (b) *Aegle marmelos*, and (c) *Solanum trilobatum*.

3.3. Electrochemical Impedance Studies. Impedance measurements were studied to evaluate the charge transfer resistance (R_t) and double layer capacitance (C_{dl}), and through these parameters, the inhibition efficiency was calculated. Figure 2 shows the impedance diagrams for mild steel in 1N HCl with different concentrations of the plant extract, and the impedance parameters derived from these investigations are given in Table 4.

As noticed from Figure 2, the obtained impedance diagrams are almost in a semicircular appearance, indicating

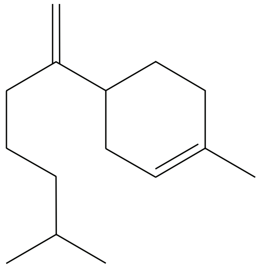


Figure 3: Structure of α-bisabolene.

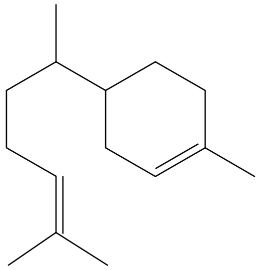


Figure 4: Structure of β-bisabolene.

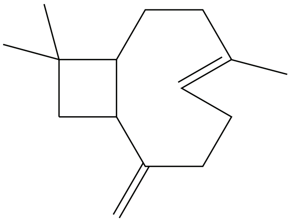


Figure 5: Structure of β-caryophyllene.

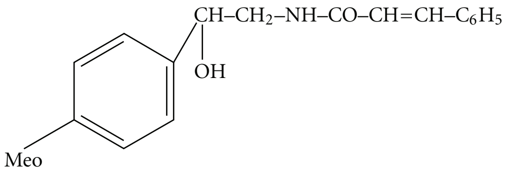


Figure 6: Structure of aegelin.

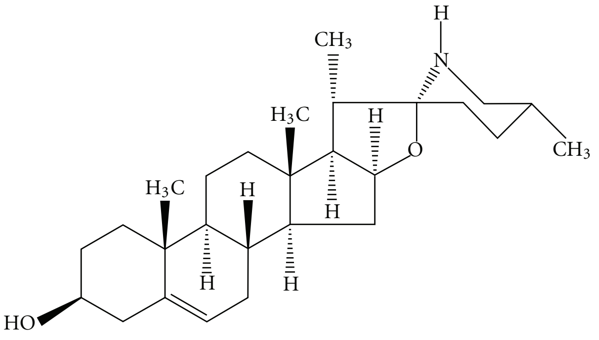


Figure 7: Structure of solasodine.

that the charge-transfer process mainly controls the corrosion of mild steel. Deviations of perfect circular shape are often referred to the frequency dispersion of interfacial impedance. This anomalous phenomenon may be attributed to the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena. In fact, in the presence of the plant extracts, the values of R_t have enhanced and the values of double-layer capacitance are also brought down to the maximum extent. The decrease in C_{dl} shows that the adsorption of the inhibitors takes place on the metal surface in acidic solution.

For *Ocimum sanctum* extract, the maximum R_t value of $358.80\,\Omega\,\mathrm{cm}^2$ and minimum C_{dl} value of $6.00\,\mu\mathrm{F/cm}^2$ are obtained at an optimum concentration of 6% in v/v with a maximum inhibition efficiency of 97.9%. For *Aegle marmelos* extract, the maximum R_t value of $224.80\,\Omega\,\mathrm{cm}^2$ and minimum C_{dl} value of $9.62\,\mu\mathrm{F/cm}^2$ are obtained at an optimum concentration of 8% in v/v with a maximum inhibition efficiency of 96.6%. For *Solanum trilobatum* extract, the maximum R_t value of $87.86\,\Omega\,\mathrm{cm}^2$ and minimum C_{dl} value of $24.52\,\mu\mathrm{F/cm}^2$ are obtained at an optimum concentration of 10% in v/v with a maximum inhibition efficiency of 91.4%. A good agreement is observed between the results of weight loss method and electrochemical methods (potentiodynamic polarization method and impedance method).

3.4. Kinetics and Reason for the Corrosion Inhibition. The major phytochemical constituents present in *Ocimum sanctum* are β-bisabolene (7.6–15.4%), α-bisabolene (9.4–19.6%), and eugenol (24.2–38.2%) as given in Figures 3, 4, and 5, and the other phytochemical constituents present are 1,8-cineole (5.6–11%), E-β-ocimene (4.0–4.7%), β-Caryophyllene (1.4–2.5%), α-humulene (2.0–3.5%), methylchavicol (11.6–14.%), and germacrene-D (2.4–4.5%). The major phytochemical constituent present in *Aegle marmelos* is Aegelin (Figure 6), and the major phytochemical constituent present in *Solanum trilobatum* is Solasodine as shown in Figure 7 [35–37].

Inspection of the chemical structures of the phytochemical constituents reveals that these compounds are easily hydrolysable and the compounds can adsorb on the metal surface via the lone pair of electrons present on their oxygen atoms and make a barrier for charge and mass transfer leading to decrease the interaction of the metal with the corrosive environment. As a result, the corrosion rate of the metal was decreased. The formation of film layer essentially blocks discharge of H^+ and dissolution of metal ions. Acid pickling inhibitors containing organic N, S, and OH groups behave similarly to inhibit corrosion [38, 39].

It follows that inhibition efficiency (IE) is directly proportional to the fraction of the surface covered by the adsorbed molecules (θ). Therefore, (θ) with the extract concentration specifies the adsorption isotherm that describes the system. Adsorption isotherm gives the relationship between the coverage of an interface with the adsorbed species and the concentration of species in solution. The use of adsorption isotherms provides useful insight into the corrosion inhibition mechanism. The values of the degree

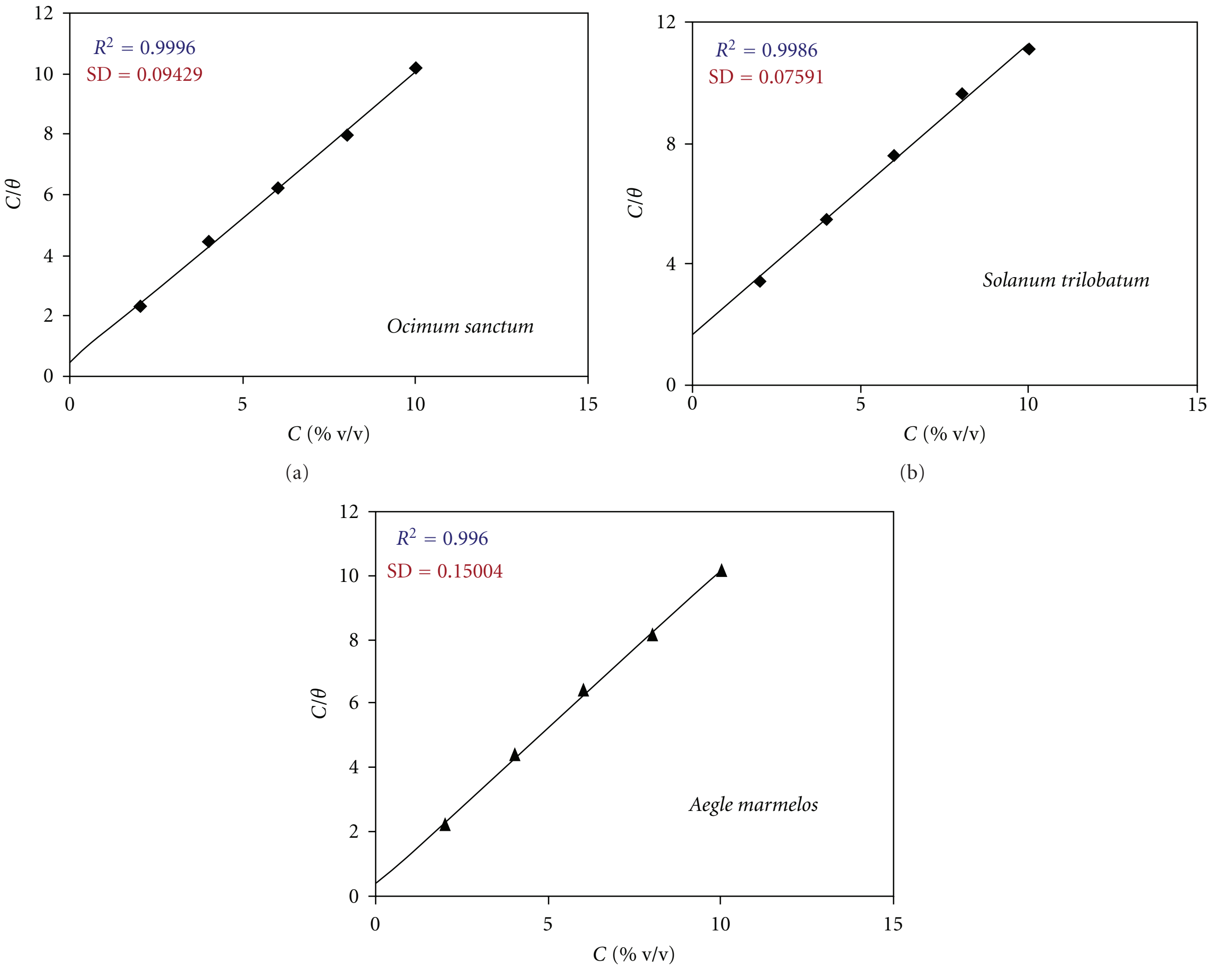


FIGURE 8: Langmuir adsorption isotherm plot for the adsorption of various concentrations of the plant extracts on the surface of mild steel in 1N HCl solution.

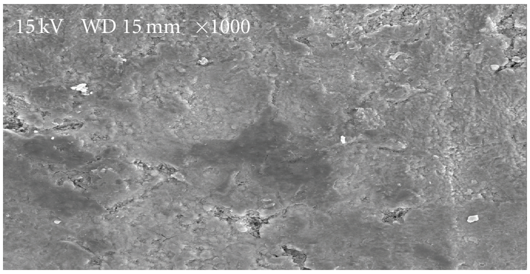


FIGURE 9: SEM Photograph of mild steel immersed in 1N HCl solution (blank).

of surface coverage (θ) were evaluated at different concentrations of the inhibitors in 1N HCl solution. Attempts were made to fit θ values to various adsorption isotherm. An inhibitor is found to obey Langmuir, if a plot of log $\theta/1-\theta$ versus $\log C$ is linear. Similarly, for Temkin plot θ versus $\log C$, for BDM plot ($\log C - \log \theta/1-\theta$) versus $\theta^{3/2}$, and for Frumkin plot log $\theta/(1-\theta)$C versus θ will be linear. On examining, the adsorption of different concentrations of *Ocimum sanctum, Aegle marmelos*, and *Solanum trilobatum* extracts on the surface of mild steel in 1N hydrochloric acid was found to obey Langmuir adsorption isotherm. The Langmuir adsorption isotherm plot for the adsorption of various concentrations of the plant extracts is given in Figure 8.

3.5. Surface Examination Studies. Surface examination of the mild steel specimens was made using JEOL-Scanning electron microscope (SEM) with the magnification of 1000x. The mild steel specimens after immersion in 1N HCl solution for three hours at 30°C in the absence and presence of optimum concentration of the plant extracts were taken out, dried, and kept in a dessicator. The SEM images of mild steel immersed in 1N HCl in the absence and presence of the optimum concentration of the plant extracts are shown in Figures 9, 10, 11, and 12. The protective film formed on the surface of the mild steel was confirmed by SEM studies. From the SEM images, it was found that more grains were found in

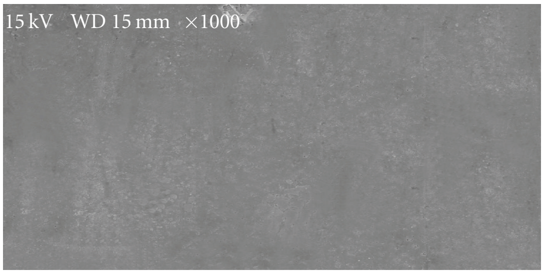


Figure 10: SEM Photograph of mild steel immersed in 1N HCl solution containing an optimum conc. (6% v/v) of *Ocimum sanctum*.

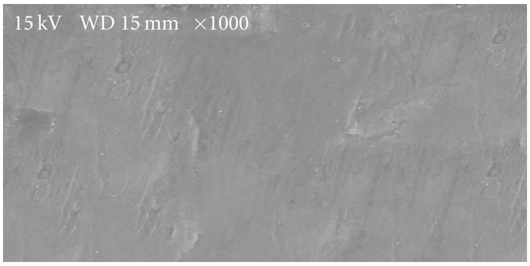


Figure 11: SEM Photograph of mild steel immersed in 1N HCl solution containing an optimum conc. (8% v/v) of *Aegle marmelos*.

SEM image of mild steel immersed in 1N HCl solution in the absence of the inhibitor, whereas no grains were found in the SEM image of mild steel immersed in 1N HCl solution in the presence of the plant extracts, which shows the presence of a protective film over the surface of the mild steel in the presence of the inhibitors, and the protective film is uniform in the order: *Ocimum sanctum* > *Aegle marmelos* > *Solanum trilobatum*. The SEM morphology of the adsorbed protective film on the mild steel surface has confirmed the high performance of inhibitive effect of the plant extracts.

3.6. Hydrogen Permeation Studies. The behaviour of the inhibitors with regard to hydrogen permeation can be understood by measuring the permeation current with and without inhibitors. Those inhibitors which reduce the permeation current are good at inhibiting the entry of hydrogen into the metal concerned [31]. There are basically two reaction schemes. Common to both schemes, the first step is the diffusion of few hydrogen atoms that get onto the electrode surface. Hydrated protons are reduced to form neutral hydrogen atoms upon those areas of the surface, which are unoccupied. One can say protons are discharged on to free sites on the electrode to form adsorbed hydrogen atoms

$$\mathrm{M(e)} + \mathrm{H_3O^+} \longrightarrow \mathrm{MH_{ads}} + \mathrm{H_2O}, \qquad (6)$$

where M is the cathodic metal surface. The second step is the desorption step. The two basic reaction paths are

(i) discharge D, followed by chemical desorption, CD,

$$\mathrm{MH_{ads}} + \mathrm{MH_{ads}} \longrightarrow 2\mathrm{M} + \mathrm{H_2} \uparrow \qquad (7)$$

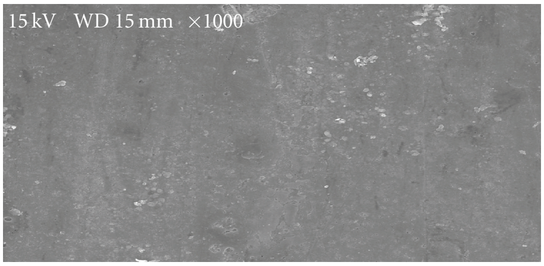


Figure 12: SEM Photograph of mild steel immersed in 1N HCl solution containing an optimum conc. (10% v/v) of *Solanum trilobatum*.

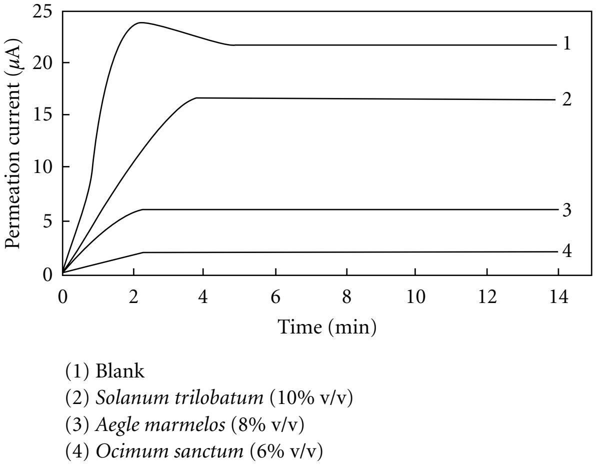


Figure 13: Hydrogen permeation current versus time plots for mild steel in 1N HCl solution in the absence and presence of an optimum concentration of the inhibitors.

(ii) discharge D, followed by electrolytic desorption, ED,

$$\mathrm{MH_{ads}} + \mathrm{H_3O^+} + \mathrm{M(e)} \longrightarrow 2\mathrm{M} + \mathrm{H_2O} + \mathrm{H_2} \uparrow . \qquad (8)$$

For transition metals, it has been reported that the electrolytic desorption is the rate determining step. A part of the atomic hydrogen liberated during these processes enters the metal, when the remainder is evolved as hydrogen gas [40]. Permeation current versus time curves for mild steel in 1N HCl in the absence and presence of inhibitors are shown in Figure 13, and their corresponding permeation are given in Table 5.

From the hydrogen permeation studies on mild steel in 1N HCl in the absence and presence of inhibitors, it was observed that all the prepared extracts were able to reduce the permeation current compared to the control. The decrease in the permeation current follows the order *Ocimum sanctum* > *Aegle marmelos* > *Solanum trilobatum*. The reason for the reduced permeation currents in presence of the inhibitors can be attributed to the slow discharge step followed by fast electrolytic desorption step

$$\begin{gathered}\mathrm{M(e)} + \mathrm{H_3O^+} \xrightarrow{\text{slow}} \mathrm{MH_{ads}} + \mathrm{H_2O}, \\ \mathrm{MH} + \mathrm{H_3O^+} + \mathrm{M(e)} \xrightarrow{\text{fast}} 2\mathrm{M} + \mathrm{H_2O} + \mathrm{H_2}.\end{gathered} \qquad (9)$$

Table 5: Values of hydrogen permeation current for the corrosion of mild steel in 1N HCl alone and in the presence of inhibitors.

Inhibitor	Conc. of the extract (% in v/v)	Permeation current (μA)	Reduction in permeation current (%)
Blank	—	23.0	—
Ocimum sanctum	6.0	2.2	90.43
Aegle marmelos	8.0	6.0	73.91
Solanum trilobatum	10.0	17.3	24.78

The reduction of hydrogen uptake could be attributed to adsorption of the phytochemical constituents present in the plant extracts on the mild steel surface, which prevented permeation of hydrogen into metal.

4. Conclusion

- (i) The leaf extracts of *Ocimum sanctum*, *Aegle marmelos*, and *Solanum trilobatum* act as good and efficient inhibitors for corrosion of mild steel in 1N hydrochloric acid.
- (ii) Potentiodynamic polarization studies revealed that the extracts act through mixed mode of inhibition.
- (iii) The Nyquist diagrams obtained in impedance method revealed that charge-transfer process mainly controls the corrosion of mild steel.
- (iv) The mechanism involved in this study is the phytochemical constituents in the plant extracts that have adsorbed on the mild steel surface forming a protective thin film layer preventing the discharge of H^+ ions and dissolution of metal ions and has prevented the small corrosion on the surface of the metal.
- (v) The plant extracts obey Langmuir adsorption isotherm.
- (vi) The SEM morphology of the adsorbed protective film on the mild steel surface has confirmed the high performance of inhibitive effect of the plant extracts.
- (vii) From hydrogen permeation method, it was observed that all the plant extracts were able to reduce the permeation current compared to the control.
- (viii) The reduction of hydrogen uptake in hydrogen permeation method could be attributed to adsorption of the phytochemical constituents present in the plant extracts on the mild steel surface, which prevented permeation of hydrogen into metal.
- (ix) Results obtained in weight loss method were very much in good agreement with the electrochemical methods (potentiodynamic polarization method and impedance method) and hydrogen permeation method in the order *Ocimum sanctum* > *Aegle marmelos* > *Solanum trilobatum*.
- (x) Among the three plant extracts studied, the maximum inhibition efficiency was found in *Ocimum sanctum* which showed 99.6% inhibition efficiency at 6.0% v/v concentration of the extract.

References

[1] M. Ajmal, A. S. Mideen, and M. A. Quraishi, "2-hydrazino-6-methyl-benzothiazole as an effective inhibitor for the corrosion of mild steel in acidic solutions," *Corrosion Science*, vol. 36, no. 1, pp. 79–84, 1994.

[2] A. A. Hosary, R. M. Saleh, and A. M. S. Eldin, "Corrosion inhibition by naturally occurring substances-1. The effect of *Hibiscus subdariffa* (Karkade) extract on the dissolution of Al and Zn," *Corrosion Science*, vol. 12, pp. 897–904, 1972.

[3] S. A. Verma and M. N. Mehta, "Effects of acid extracts of powered seeds of *Eugenia Jambolans* on corrosion of mild steel in HCl-study by DC polarisation techniques," *Transactions of the Society for Advancement of Electrochemical Science and Technology*, vol. 32, no. 4, pp. 89–93, 1997.

[4] I. B. Obot, S. A. Umoren, and N. O. Obi-Egbedi, "Corrosion inhibition and adsorption behaviour for aluminuim by extract of Aningeria robusta in HCl solution: synergistic effect of iodide ions," *Journal of Materials and Environmental Science*, vol. 2, no. 1, pp. 60–71, 2011.

[5] H. Al-Sehaibani, "Evaluation of Henna leaves as environmentally friendly corrosion inhibitors for metals," *Materialwissenschaft und Werkstofftechnik*, vol. 31, no. 2, pp. 1060–1063, 2000.

[6] M. Lebrini, F. Robert, and C. Roos, "Inhibition effect of alkaloids extract from *Annona squamosa* plant on the corrosion of C38 steel in normal hydrochloric acid medium," *International Journal of Electrochemical Science*, vol. 5, no. 11, pp. 1698–1712, 2010.

[7] C. A. Loto and A. I. Mohammed, "The effect of *Anacardium Occidentale* (cashew) juice extract on the corrosion of mild steel in hydrochloric acid," *Corrosion Prevention and Control*, vol. 47, no. 2, pp. 5056–5063, 2000.

[8] G. D. Davis, "The use of extracts of tobacco plants as corrosion inhibitors," DACCO SCI, Inc., Columbia, Md, USA, 2000.

[9] O. K. Abiola, "The inhibition of mild steel corrosion in an acidic medium by fruit juice of *citrus paradisi*," *Journal of Corrosion Science and Engineering*, vol. 5, no. 10, 2006.

[10] A. O. James and E. O. Ekpe, "Inhibition of corrosion of mild steel in 2 M hydrochloric acid by *Aloe Vera*," *International Journal of Pure and Applied Chemistry*, vol. 35, no. 10, 2002.

[11] M. Lebrini, F. Robert, and C. Roos, "Alkaloids extract from *Palicourea guianensis* plant as corrosion inhibitor for C38 steel in 1 M hydrochloric acid medium," *International Journal of Electrochemical Science*, vol. 6, no. 3, pp. 847–859, 2011.

[12] J. Bruneton, *Pharmacognosie-Phytochimie, Plantes Médicinales*, revue et ugmenté, Tec&Doc-Edition, Médicinales Internationales, Paris, France, 4th edition, 2009.

[13] E. E. Ebenso, N. O. Eddy, and A. O. Odiongenyi, "Corrosion inhibitive properties and adsorption behaviour of ethanol extract of *Piper guinensis* as a green corrosion inhibitor for mild steel in H_2SO_4," *African Journal of Pure and Applied Chemistry*, vol. 2, no. 11, pp. 107–115, 2008.

[14] I. M. Mejeha, A. A. Uroh, K. B. Okeoma, and G. A. Alozie, "The inhibitive effect of *Solanum melongena* L. leaf extract on the corrosion of aluminium in tetraoxosulphate (VI) acid," *African Journal of Pure and Applied Chemistry*, vol. 4, no. 8, pp. 158–165, 2010.

[15] A. Y. El-Etre, "Inhibition of aluminum corrosion using *Opuntia extract*," *Corrosion Science*, vol. 45, no. 11, pp. 2485–2495, 2003.

[16] A. Y. El-Etre, M. Abdallah, and Z. E. El-Tantawy, "Corrosion inhibition of some metals using *lawsonia* extract," *Corrosion Science*, vol. 47, no. 2, pp. 385–395, 2005.

[17] E. E. Oguzie, "Studies on the inhibitive effect of *Occimum viridis* extract on the acid corrosion of mild steel," *Materials Chemistry and Physics*, vol. 99, no. 2-3, pp. 441–446, 2006.

[18] G. Gunasekaran and L. R. Chauhan, "Eco friendly inhibitor for corrosion inhibition of mild steel in phosphoric acid medium," *Electrochimica Acta*, vol. 49, no. 25, pp. 4387–4395, 2004.

[19] K. O. Orubite and N. C. Oforka, "Inhibition of the corrosion of mild steel in hydrochloric acid solutions by the extracts of leaves of *Nypa fruticans Wurmb*," *Materials Letters*, vol. 58, no. 11, pp. 1768–1772, 2004.

[20] Y. Li, P. Zhao, Q. Liang, and B. Hou, "*Berberine* as a natural source inhibitor for mild steel in 1 M H_2SO_4," *Applied Surface Science*, vol. 252, no. 5, pp. 1245–1253, 2005.

[21] M. A. Quraishi and D. K. Yadav, "Corrosion and its control' by some green inhibitors," in *Proceedings of the 14th National Congress on Corrosion Control*, 2008.

[22] A. Y. El-Etre, "Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves," *Journal of Colloid and Interface Science*, vol. 314, no. 2, pp. 578–583, 2007.

[23] A. M. Abdel-Gaber, B. A. Abd-El-Nabey, I. M. Sidahmed, A. M. El-Zayady, and M. Saadawy, "Inhibitive action of some plant extracts on the corrosion of steel in acidic media," *Corrosion Science*, vol. 48, no. 9, pp. 2765–2779, 2006.

[24] A. M. Abdel-Gaber, B. A. Abd-El-Nabey, and M. Saadawy, "The role of acid anion on the inhibition of the acidic corrosion of steel by lupine extract," *Corrosion Science*, vol. 51, no. 5, pp. 1038–1042, 2009.

[25] B. Anand and V. Balasubramanian, "Corrosion behaviour of mild steel in acidic medium in presence of aqueous extract of *Allamanda blanchetii*," *E-Journal of Chemistry*, vol. 8, no. 1, pp. 226–230, 2011.

[26] M. H. Hussin and M. J. Kassim, "Electrochemical studies of mild steel corrosion inhibition in aqueous solution by *uncaria gambir* extract," *Journal of Physical Sciences*, vol. 21, pp. 1–13, 2010.

[27] A. M. Al-Turkustani, "*Aloe* plant extract as environmentally friendly inhibitor on the corrosion of aluminum in hydrochloric acid in absence and presence of iodide ions," *Modern Applied Science*, vol. 4, pp. 105–124, 2010.

[28] S. Rajendran, M. Agasta, R. B. Devi, B. S. Devi, K. Rajam, and J. Jeyasundari, "Corrosion inhibition by an aqueous extract of Henna leaves (Lawsonia Inermis L)," *Zaštita Materijala*, vol. 50, pp. 77–84, 2009.

[29] J. A. Selvi, S. Rajendran, V. G. Sri, A. J. Amalraj, and B. Narayanasamy, "Corrosion Inhibition by Beet root extract," *Portugaliae Electrochimica Acta*, vol. 27, pp. 1–11, 2009.

[30] G. Ilayaraja, A. R. Sasieekhumar, and P. Dhanakodi, "Inhibition of mild steel corrosion in acidic medium by aqueous extract of *tridax procumbens* L.," *E-Journal of Chemistry*, vol. 8, no. 2, pp. 685–688, 2011.

[31] M. A. V. Devanathan and Z. Stachurski, "The Adsorption and diffusion of electrolytic hydrogen in palladium," *Proceedings of Royal Society*, vol. 270, no. 1340, pp. 90–102, 1962.

[32] J. O. M. Bockris, J. McBreen, and L. Nanis, "The hydrogen evolution kinetics and hydrogen entry into a-iron," *Journal of The Electrochemical Society*, vol. 112, no. 10, pp. 1025–1031, 1965.

[33] M. J. Danielson, "Use of the Devanathan-Stachurski cell to measure hydrogen permeation in aluminum alloys," *Corrosion Science*, vol. 44, no. 4, pp. 829–840, 2002.

[34] M. A. Quraishi and J. Rawat, "Influence of iodide ions on inhibitive performance of tetraphenyl-dithia-octaaza-cyclotetradeca-hexaene (PTAT) during pickling of mild steel in hot sulfuric acid," *Materials Chemistry and Physics*, vol. 70, no. 1, pp. 95–99, 2001.

[35] http://www.himalayahealthcare.com/herbfinder.

[36] K. K. Bhargava, "Himalaya herbal monograph," *Indian Journal of Chemistry*, vol. 8, p. 664, 1970.

[37] P. S. Latha and K. Kannabiran, "Antimicrobial activity and phytochemicals of *Solanum trilobatum* Linn," *African Journal of Biotechnology*, vol. 5, no. 23, pp. 2402–2404, 2006.

[38] M. J. Sanghvi, S. K. Shukla, and A. N. Misra, "Inhibition of hydrochloric acid corrosion of mild steel by aid extracts of *Embilica officianalis, Terminalia bellirica* and *Terminalia chebula*," *Bulletin of Electrochemistry*, vol. 13, no. 8-9, pp. 358–361, 1997.

[39] S. J. Zakvi and G. N. Mehta, "Inhibition of corrosion of mild steel in acid extracts of *Mahasudarshana Churna*," *Journal of the Electrochemical Society of India*, vol. 37, no. 3, pp. 237–239, 1988.

[40] K. N. Srinivasan, M. Selvam, and S. V. K. Iyer, "Hydrogen permeation during zinc-manganese alloy plating," *Journal of Applied Electrochemistry*, vol. 23, no. 4, pp. 358–363, 1993.