

***Parthenium hysterophorus* Plant Extract as an Efficient Green Corrosion Inhibitor for Mild Steel in Acidic Environment**

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Asteraceae family - *Parthenium hysterophorus* plant leaves extract is reported as corrosion inhibitor of mild steel in HCl. Weight loss measurements, Tafel polarization and electrochemical impedance spectroscopy techniques are employed to analyze the effect on steel corrosion. A significant decrease in corrosion rate is observed using water extract of *Parthenium hysterophorus* plant as inhibitor. The maximum potential of the extract was obtained at 1100 mg L⁻¹ with 84% efficiency. It was found that adsorption of *Parthenium hysterophorus* extract follows Langmuir isotherm model. Mechanism of corrosion inhibition is explored with the help of UV-vis spectra and SEM images.

Keywords: Plant extract; Green inhibitor; Acid corrosion; Mild steel; *Parthenium hysterophorus*

1. INTRODUCTION

Mild steel is one of the most frequently used materials in many engineering applications like parts of machines, pipe lines, boilers and in chemical storage. It has natural tendency to corrode whenever it comes in contact with corrosive or reactive environments [1, 2]. Normally metals corrode at slow rate in air but when acid interacts with the metals, corrosion rate becomes very high [3,4]. Several methods are used to protect metals and alloys from corrosion but the use of inhibitors to protect the metals in the corrosive environment is one of the most common methods. Organic compounds which have different hetero atoms such as N, O, S and aromatic rings in their structure are reported as effective inhibitors [5-9]. Nowadays, researchers are focusing on the search for low cost

natural products as corrosion inhibitors rather than the very high cost synthetic organic compounds. In consideration of the naturally abundant corrosion inhibitors various plant extracts and oils are found very effective. Plant extracts have been explored as corrosion inhibitors in recent years, due to their bio-degradability, non toxicity, environment friendly nature and easy availability [10-12]. However, mainly medicinal and eatable herbs, well known plants and seeds extracts are used for this application. Inhibition efficiency of these extracts were mainly due to the presence of aromatic and heterocyclic compounds like alkaloids, flavonoids, saponins and other non- alkaloids compounds[13].

In the present work, aqueous extract of *Parthenium hysterophorus* plant leaves is reported for the corrosion inhibition of mild steel in 1 M HCl solution. This plant is well known for its anti-bacterial property which is found more effective than some famous antibiotics [14]. It is also found useful for its antitumor effects and possess antimalarial activity [15,16]. It has also been investigated as a reducing agent for the synthesis of silver nanoparticles and the synthesized nanoparticles very useful in the production of value added products for biomedical and nanotechnology based industries.[17] In Cuba, *Parthenium hysterophorus* plant has been used for treatment of several diseases since classical times However, Parthenin, a toxin, is reported as a major component of this plant [18]. This plant is abundant in the Indian environment and generally treated as waste plant. Careful selection of solvent (water) can decrease the toxicity of the plant extract as reported in the case of *Argemone maxicana* which is also a toxic plant but aqueous extract of the plant leaves was not found to be toxic [13]. Our efforts in this regard are also strengthened due to some work reported earlier on *Parthenium hysterophorus* plant [19] in which aqueous extract of leaves was found to contain least amount of parthenin. The reason may be poor solubility of active substances in water due to which they are present in water extract but in low concentrations [14]. So we have tried to avoid this toxin in the extract and found very interesting to analyze the effect of aqueous extract of *Parthenium hysterophorus* plant leaves for corrosion inhibition. Mild steel corrosion was investigated using weight loss measurement, electrochemical impedance spectroscopy and Tafel polarization techniques. Mechanism for the adsorption is also proposed and supported by the various techniques. This low cost, natural extract of a waste plant showed potential corrosion inhibitor of steel in acidic environment.

2. EXPERIMENTAL

2.1 Plant Extract

Plant leaves of *Parthenium hysterophorus* (100 g) were washed thoroughly and dried on tissue paper. It was crushed in the grinder properly and 100 mL of water was added. After preparing the solution it was kept constantly stirred for 48 hours. Extract was filtered and residue was again suspended in the double distilled water. The procedure was repeated three times for exhausted extraction. All the filtrates were pooled and dried in rotatory evaporator. Selection of plant leaves and water as extracting solvent was adopted in order to reduce the content of toxic Parthenin. Relatively less quantity of Parthenin in leaves and its poor solubility in water helped us to reduce the

concentration of this toxin in extract. Filtration followed by drying and re-suspension in water helped to reduce Parthenin significantly in final extract.

2.2 Preparation of Test Specimen

Weight loss and electrochemical experiments were conducted on mild steel specimens of dimension $1 \times 5 \times 0.09 \text{ cm}^3$ (exposure area 10 cm^2) and $1 \times 1 \times 0.09 \text{ cm}^3$ (exposure area 1 cm^2) respectively. Specimens for measurements were prepared by abrading mild steel samples with emery papers of grade 1/0 to 4/0 successively. Furthermore, acetone (AR grade) was used for cleaning and degreasing of the specimen to ensure good surface finish. After immersion time, specimens were drawn out and washed with double distilled water followed by drying in vacuum oven for half an hour. Composition of the steel used was (wt %) C (0.13), Si (0.20), Mn (0.48), S (0.03), P (0.05) and remainder Fe.

2.3 Corrosion study

2.3.1. Weight Loss Measurements

For weight loss experiments, mild steel specimens were immersed in 1 M HCl solution (100 mL) for optimized time period (5 hours). Effect was observed and analyzed by comparing the data obtained without and with different concentrations of *Parthenium hysterophorus* extract. Corrosion rate (CR) is directly proportional to the weight loss/ cm^2 in a specified time and was calculated (mmpy) by the formula:

$$CR = \frac{87.6 \times W}{A \cdot t} \quad (1)$$

where, W = weight loss in mg, ρ = density (7.85 g/cm^3 for mild steel) of material used, A = area in cm^2 and t = exposure time in hours.

Measurements were taken at room temperature ($27 \pm 1^\circ\text{C}$) for 5 hrs in triplicate (three set for one concentration) to ensure reproducibility of the results. The inhibition efficiency (IE %) and surface coverage (θ) was determined by using the following equations reported in literature.[8]

$$I.E.(%) = \frac{W_o - W_i}{W_o} \times 100 \quad (2)$$

$$\theta = \frac{W_o - W_i}{W_o} \quad (3)$$

Where, W_o and W_i is the weight loss value in absence and in presence of inhibitor.

2.3.2 Electrochemical Impedance Spectroscopy

Electrochemical Work Station, CHI 7041C (CH Instrument, USA) was used to analyze electrochemical aspects of mild steel corrosion with the help of a three electrode cell assembly with mild steel coupons (exposure area 1 cm^2) as working electrode, Ag/AgCl as reference electrode and a large area platinum mesh as counter electrode. All electrochemical experiments were conducted at room temperature ($27 \pm 1^\circ\text{C}$) using 1 M HCl (100 mL) as a corrosive medium. Electrochemical impedance spectroscopy was carried out at open circuit potential (ocp) (constant ocp to achieve accuracy) at frequency range of 10 MHz to 100 kHz at amplitude of 5 mV. The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values using the following equation:

$$\mu_{R_t} (\%) = \frac{R_t^i - R_t^o}{R_t^i} \times 100 \quad (4)$$

Where, R_t^o and R_t^i are the charge transfer resistance in absence and in presence of inhibitor.

2.3.3 Potentiodynamic Tafel Polarization Technique

This test was conducted to collect the information regarding corrosion potential and corrosion current which is directly proportional to the corrosion rate. In this study polarization was carried out from cathodic potential of -250 mV vs. Ag/AgCl to an anodic potential of + 250 mV vs. Ag/AgCl with respect to the ocp at a scan rate 0.5 mVs^{-1} to study the effect of inhibitor on mild steel corrosion. Corrosion current densities (I_{corr}) were obtained by extrapolating the linear segments of anodic and cathodic polarization curves to corrosion potential (E_{corr}) at different concentration of inhibitor [13]. The corrosion inhibition efficiency (μ_p %) was evaluated using the relationship –

$$\mu_p (\%) = \frac{I_{\text{corr}}^o - I_{\text{corr}}^i}{I_{\text{corr}}^o} \times 100 \quad (5)$$

where, I_{corr}^o and I_{corr}^i are the corrosion current densities in absence and in presence of various concentration of the inhibitor.

2.4 Surface Morphology

To see the influence of inhibitor on mild steel corrosion, surface morphology of the specimens were taken using scanning electron microscope Supra 40, Carl Zeiss, Germany. Test specimens of 1 cm^2 area were immersed in 1 M HCl with and without inhibitor and effect was observed only for

optimum concentration of inhibitor. After 5 hours exposure, images were taken and surface morphology was compared.

2.5 UV-visible Spectroscopy

UV-visible spectrum of the plant extract was analyzed in order to know the adsorption behavior of the organic molecules present in the plant extract for mild steel surface. For this experiment, mild steel specimen was immersed in a beaker having extract for 5 hours. After immersion it was dip washed 3-4 times in distilled water. Again specimen was dipped in double distilled water for half an hour followed by sonication and rubbing the surface of steel specimen. This water solution was examined for UV-visible spectrum and compared with the UV-visible spectrum of the pure plant extract.

3. RESULTS AND DISCUSSION

Mild steel corrosion behavior in 1 M HCl was investigated in the absence and presence of *Parthenium hysterophorus* plant extract with the help of weight loss and electrochemical techniques. It was seen that mild steel dissolution rate was very high in 1 M HCl alone but presence of inhibitor significantly decreased the corrosion rate of mild steel.

3.1 Weight Loss Measurements

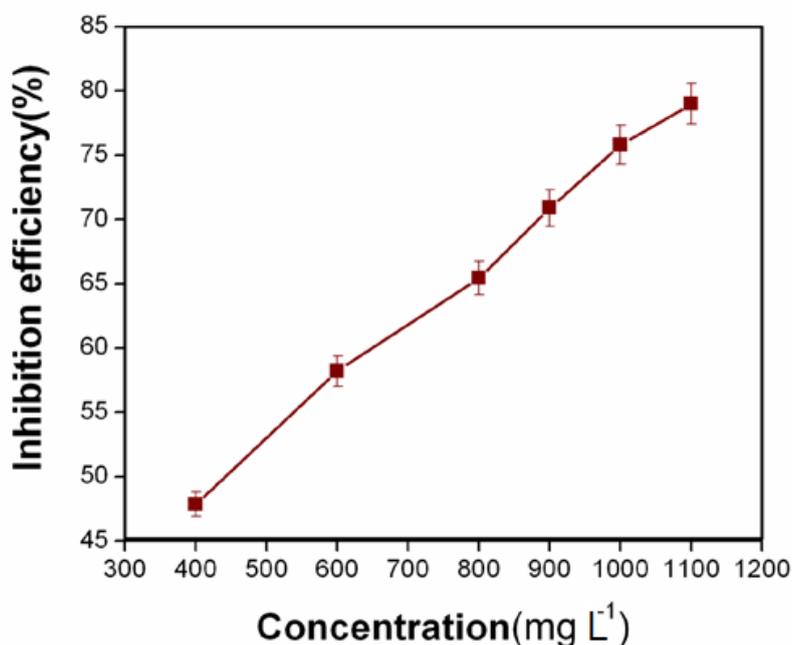


Figure 1. Effect of different concentrations of *Parthenium hysterophorus* plant extract on inhibition efficiency in 1M HCl solution

Weight loss of the samples of dimension $1 \times 5 \times 0.09 \text{ cm}^3$ was found significant (around 150 mg) in blank solution but on increasing the concentration of plant extract to 1100 mg L^{-1} it was found to be retarded (30 mg) showing maximum efficiency of nearly 79 %. Figure 1 shows the influence of inhibitor concentration on inhibition efficiency. From inspection of figure 1 it is evident that inhibition efficiency increased with increase in inhibitor concentration. Further analysis of table 1 provided that corrosion rate was retarded with addition of inhibitor. Reason for increased resistance of mild steel in acid can be attributed to molecular adsorption of inhibitor which results in increased value of surface coverage.

Table 1. Corrosion parameters for mild steel in 1 M HCl in absence and presence of different concentrations of *Parthenium hysterophorus* extract obtained from weight loss measurements at $27 \pm 1^\circ \text{C}$ for 5h.

Concentration of inhibitor mg L^{-1}	Weight loss (mg)	Inhibition efficiency %	Corrosion rate (mm/y)	Surface coverage Θ	C / θ
Blank	153.8	-	34.3	-	-
400	79.12	47.87	17.72	0.4787	835.59
600	64.31	58.21	14.40	0.5821	1030.75
800	57.14	62.18	12.79	0.6218	1286.58
900	44.41	70.90	9.94	0.709	1269.39
1000	37.18	75.81	8.32	0.7581	1319.08
1100	32.30	78.99	7.23	0.7899	1392.58

3.1.1 Adsorption Isotherm

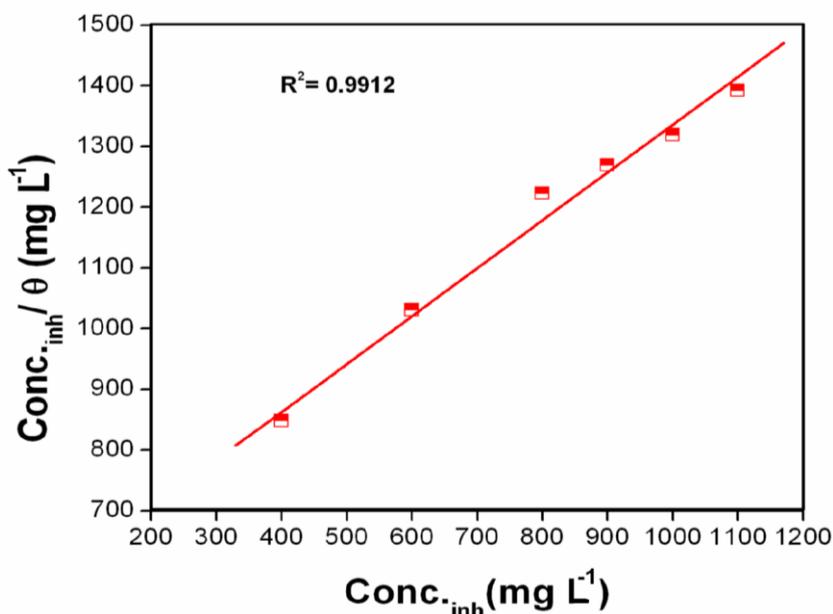


Figure 2. Langmuir adsorption isotherm Plot for *Parthenium hysterophorus* plant extract.

Adsorption isotherm study was carried out to know the behavior of inhibitor molecules with metal surface and type of adsorption. There are many isotherm models to describe the inhibitor/metal interaction like Langmuir, Frumkin, Temkin etc. but in our case Langmuir isotherm model was found to provide the best description of the adsorption behavior with the regression coefficient R^2 almost unity (0.99) as shown in Figure 2.

3.2 Tafel polarization Study

The Tafel plot shows the effect of inhibitor on the anodic reactions and hydrogen evolution. Electrochemical corrosion kinetic parameters such as E_{corr} , I_{corr} , cathodic and anodic slopes (b_c and b_a) were calculated and listed in Table 2. From figure 3 it was observed that addition of inhibitor caused shift in corrosion potential (E_{corr}) and reduced the corrosion current (I_{corr}).

Table 2. Tafel polarization parameters obtained at different concentrations of *Parthenium hysterophorus* plant extract

Concentration (mg L ⁻¹)	-E _{corr} (mV, Ag-AgCl)	I _{corr} (μA cm ⁻²)	b _a (mV dec ⁻¹)	b _c (mV dec ⁻¹)	μ _p %
Blank	500	1220	60.21	54.74	-
900	506	463	122.0	83.8	62.04
1000	526	290.12	109.3	69.45	76.22
1100	531	197.40	125.5	67.22	83.85

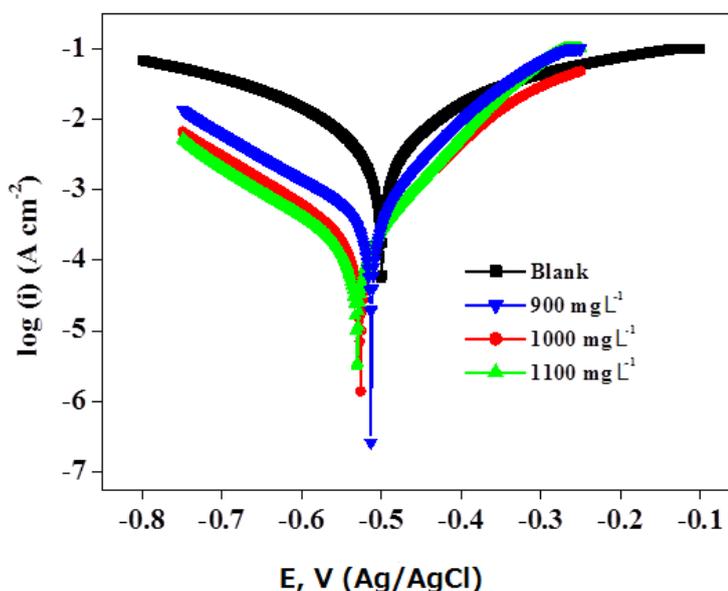


Figure 3. Tafel plot of mild steel with different concentrations of *Parthenium hysterophorus* plant extract in 1M HCl solution

Corrosion rate is directly proportional to the corrosion current which was found to decrease with increasing concentration of inhibitor. Change in the anodic segment of Tafel curve was also observed with the increasing amount of inhibitor. Probably, organic molecules were adsorbed on the mild steel surface and reduced the corrosion rate. Hydrogen evolution during the corrosion affected the cathodic segment of Tafel curve which can be clearly seen in the Figure 3. The displacement in the corrosion potential was around 30 mV, which showed a mixed type inhibitor property as also reported by Ferreira *et.al.*[20] and Li *et.al.*[21].

3.3. Electrochemical Impedance Spectroscopy

Corrosion behaviour of mild steel without and with different concentrations of *Parthenium hysterophorus* extract were also studied using impedance spectroscopy technique. Nyquist plots showed the effect of inhibitor concentration on charge transfer resistance of the system as shown in Figure 4. In the Nyquist plot, charge transfer resistance was obtained in the form of semicircle and the diameter of semicircle (charge transfer resistance) was found increasing with the increase in concentration of the inhibitor. However, it was not in the form of perfect semicircle (depressed at the centre under real axis) probably due to the sample surface heterogeneity, surface roughness, cracks, dislocations and distribution of the active sites or even adsorption of inhibitor molecules [22-24]. An equivalent circuit was introduced (*cf.* Figure 5) to analyze the spectra. This circuit was generally used to describe the interactions occurring at iron/acid interface [25] where R_s is solution resistance, R_t is polarization resistance and CPE is constant phase element. The impedance function of the CPE was achieved by following equation:

$$Z_{CPE} = Y^{-1}(j\omega)^{-n} \quad (6)$$

where, Y is the magnitude of the CPE, ω is the angular frequency and n is an important parameter representing deviation from ideal capacitor behavior. Generally n is used to describe the surface property. Low value of n indicates surface roughness and irregularity which deflect the ideal capacitor behavior whereas high value of n shows surface homogeneity and smoothness. From equation (6) we can see that for $n=0$, Z_{CPE} corresponds to a resistance with $R=Y^{-1}$; $n=-1$ an inductance with $L=Y^{-1}$ and $n=1$ an ideal capacitor condition with $C=Y$ [26]. Generally, in iron / acid interface systems, ideal capacitor behavior is not recognized due to the irregularity or asymmetric distributions of current on the electrode surface which causes frequency dispersion [23, 27, 28].

The electrochemical parameters include R_s , R_t , Y_o and n , which were obtained from fitting the recorded data with the help of ZSimDemo software using the equivalent circuit of Figure 5 and listed in Table 3. C_{dl} values listed in Table 3 were derived from CPE parameters using the following equation [29]:

$$C_{dl} = (Y_o \cdot R_t^{1-n})^{1/n} \quad (7)$$

From Table 3, it is evident that the R_t values increased with the increase in *parthenium* extract concentration. The increase in R_t value can be attributed to the formation of protective film on metal/solution interface. The increase in the value of n for the inhibited samples in comparison with uninhibited samples was observed due to the adsorption of the inhibitor on the most active adsorption sites [30]. The values of double layer capacitance (C_{dl})

Table 3. Impedance parameters for mild steel in 1.0 M HCl in the absence and presence of different concentrations of *Parthenium hysterophorus* plant extract.

Concentration (mg L ⁻¹)	R_s (Ω cm ²)	R_t (Ω cm ²)	n	Y_0 ($10^{-6}\Omega^{-1}\text{cm}^{-2}$)	C_{dl} ($\mu\text{F cm}^{-2}$)	μ_{Rt} %
Blank	1.23	30	0.802	147	41.7	-
900	0.68	55	0.804	132	39.0	45.31
1000	1.95	113	0.811	90	31.0	73.54
1100	0.44	165	0.818	72	26.0	81.86

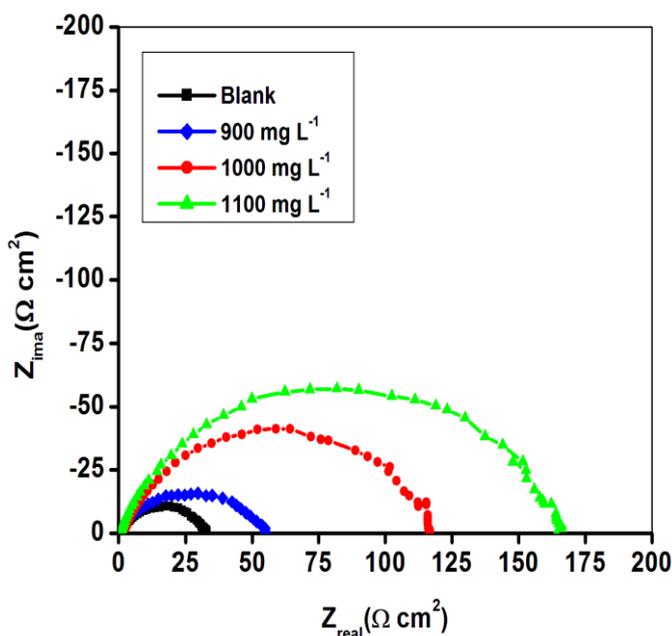


Figure 4. Nyquist plot at different concentrations of *Parthenium hysterophorus* plant extract in 1M HCl solution.

decreased with increasing *Parthenium hysterophorus* extract concentration which supported that the thickness of the protective layer was also increasing with increase of inhibitor concentration (cf. formula 8). [31]

$$C_{dl} = \frac{\epsilon \epsilon_o}{d} \tag{8}$$

where, ϵ is the dielectric constant of the protective layer and ϵ_0 is the permittivity of the free space and d is the thickness of the protective layer.

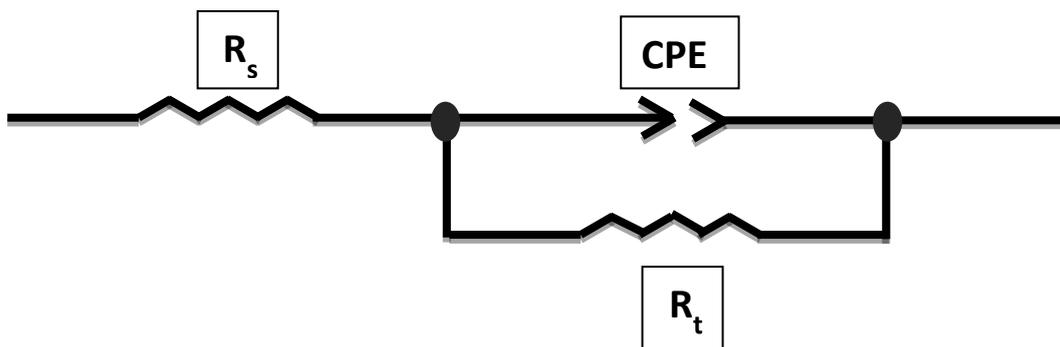
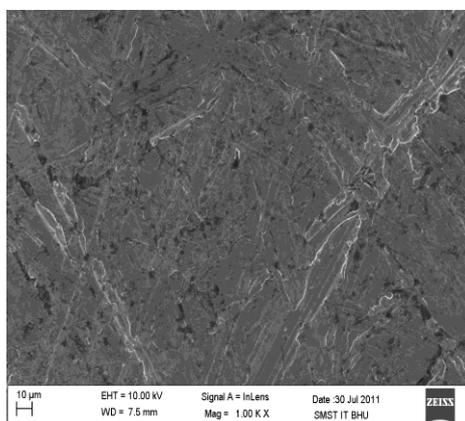
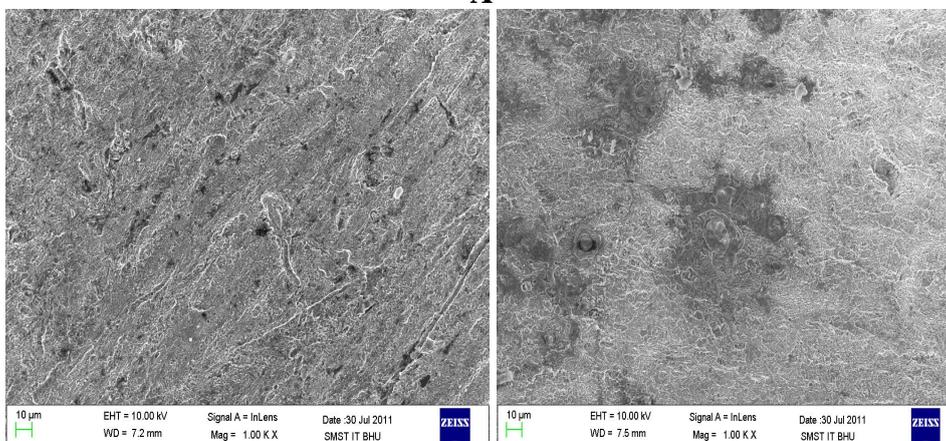


Figure 5. Electrochemical equivalent circuit used to fit the impedance plots.

3.4 Surface morphology



A



B

C

Figure 6. SEM image for surface morphology of (a) polished MS sample (b) after corrosion in 1M HCl and (c) in presence of *Parthenium hysterophorus* plant extract (1100 mg L⁻¹) in 1M HCl.

Surface morphology of the mild steel samples immersed in HCl with and without inhibitor is shown in Figure 6. When steel was exposed to the blank HCl solution, metal dissolution rate became high which caused formation of stress raisers and more active sites available for corrosion (*cf.* Figure 6 b) in comparison to the surface of pure steel (*cf.* Figure 6 a). When inhibitor was introduced to the system (1100 mg L^{-1}), a protective layer was formed which decreased the mild steel dissolution in HCl and less corrosion can be seen from the SEM image (*cf.* Figure 6 c). On the basis of surface morphology obtained it can be concluded that inhibitor covered the metal surface forming a layer through adsorption which protected it in acidic environment.

3.5 Adsorption Behavior and Corrosion Inhibition

Corrosion inhibition of mild steel in hydrochloric acid solution by *Parthenium hysterophorus* extract can be explained on the basis of molecular adsorption. *Parthenium hysterophorus* plant contains many organic components as per information provided in literature. It is quite complex to separate every compound present in the extract.

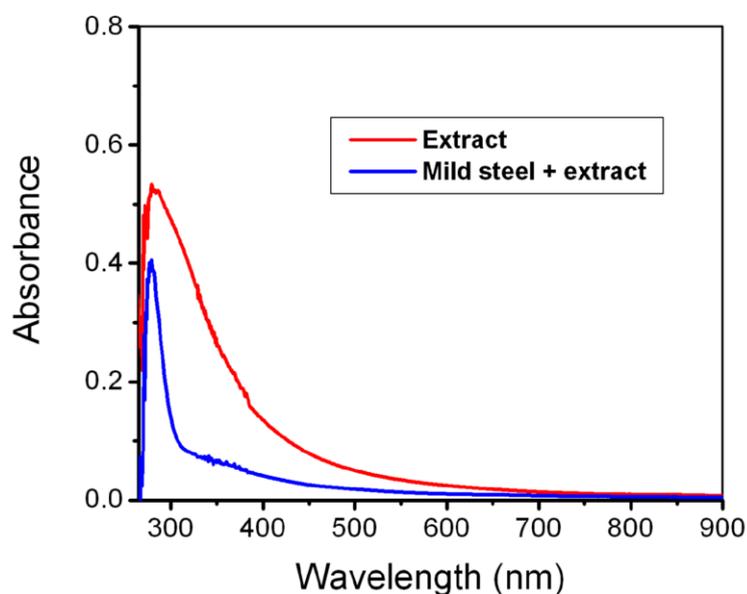


Figure 7. UV-visible spectra of the *Parthenium hysterophorus* extract and the washings of the mild steel specimen incubated in *Parthenium hysterophorus* extract.

So we used crude plant extract for the study. When inhibitor was introduced, water soluble organic components dissolved in the solution interacted with the negatively charged mild steel surface. It caused adsorption of inhibitor molecules at metal/solution interface as supported by UV-visible spectroscopy (*cf.* Figure 7). It was also observed that the plant extract and the solution, which was containing washing of mild steel sample (as explained under sub heading 2.5), followed the same pattern. On the basis of this fact, it can be concluded that the organic compounds present in the

Parthenium hysterophorus extract were adsorbed on the mild steel surface. From weight loss study we also noticed the increase in surface coverage ($\theta=0.79$), which further confirmed the molecular adsorption of inhibitor molecules over mild steel surface. Impedance spectroscopy of the inhibited samples provided clear evidence that inhibition efficiency was increased with the additional amount of inhibitor and a greater polarization resistance was achieved up to optimum concentration (1100 mg L^{-1}). In case of Tafel study, inhibitive effect was observed due to decreasing corrosion current accompanying retarded corrosion rate. Inhibitor molecules affected the corrosion of mild steel by controlling both cathodic and anodic reactions in HCl. Organic compounds present in the *Parthenium* plant extract have strong affinity towards metal surface and in acidic environment protonation of organic moieties showed better adsorption over the metal surface. Protonated species adsorbed on the cathodic sites of the mild steel and decreased the evolution of hydrogen. The adsorption on anodic sites occurred through long π -electrons of aromatic rings and lone pair of electrons of hetero atoms, which decreased anodic dissolution of mild steel.[32] We did not however study the effects of the individual organic compound present in the extract, but cooperative effect can be observed clearly in this study.

4. CONCLUSION

Parthenium hysterophorus plant extract has been used as low cost, effective and less-toxic inhibitor and retarded the corrosion rate of mild steel in HCl environment. The toxicity of the extract was reduced by reducing the concentration of the major toxin Parthenin in the extract by using plant leaves and water extraction. Low solubility of Parthenin helped in reducing its concentration by several times re-dissolving and extracting the organic compounds extracted from the plant leaves. Though it also affected the amount of other organic molecules present in the final extract but good inhibition efficiency ($\sim 84\%$) was achieved using 1100 mg L^{-1} concentration. Langmuir adsorption and UV-vis studies showed that *Parthenium hysterophorus* extract inhibited the mild steel corrosion through adsorption mechanism. It was found to act as a mixed inhibitor which was supported by Tafel polarization and impedance studies.

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