

## Aqueous Extract of *Pulicaria Crispa* as Corrosion Inhibitor for Mild Steel -X52- in 1 M H<sub>2</sub>SO<sub>4</sub> Solutions

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**Abstract:** The corrosion and corrosion inhibition of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> by *Pulicaria crispa* leaves extracts has been studied using chemical technique (mass loss) and electrochemical techniques (electrochemical impedance spectroscopy and electrochemical polarizations and scanning electron microscopic stud). The weight loss technique results showed that the extract of *Pulicaria crispa* is excellent corrosion inhibitor. Electrochemical polarizations data revealed the mixed mode of inhibition. The results of electrochemical impedance spectroscopy shows that the change of the impedance parameters, charge transfer resistance and double layer capacitance with the change in concentration of the extract is due to the adsorption of active molecules leading to the formation of a protective layer on the surface of mild steel. Scanning electron microscopic studies provided the confirmatory evidence of improved surface condition, due to the adsorption, for the corrosion protection.

**Keywords:** Mild steel, *Pulicaria crispa*, Acid corrosion inhibitor, Electrochemical polarization, Electrochemical impedance spectroscopy, Scanning electron microscopic studies.

### Introduction

Huge amount of H<sub>2</sub>SO<sub>4</sub> is used in the chemical industry for removal of the undesired scales and rust. The addition of corrosion inhibitors effectively secures the metal against an acid attack. Many studies in this regard using organic inhibitors have been reported<sup>1-5</sup>. Most of the inhibitors are organic compounds with N, S and O heteroatoms have higher electron density making them the reaction centers.

These compounds are adsorbed on the metallic surface and block the active corrosion sites and most of them are highly toxic to both human beings and environment. Hence use of the natural products as eco-friendly and harmless corrosion inhibitors, has become popular<sup>6-14</sup>. *Pulicaria crispa*, a *Compositae* family plant is native to parts of Africa, Arabian Peninsula and India<sup>15</sup>.

Alternately arranged, oval and elliptic leaves having a very rough surface, making them look like sand paper. The leaves are used for treatment of haemostatic ophthalmia, coughs and haemorrhoid. It is also used for treating various infections and as a sand Paper for polishing woods<sup>16</sup>. However, the leaves have never been exploited as the corrosion inhibitor in acid medium. Hence, the present work was aimed at in this direction.

## Experimental

About 20 g of dried and powdered leaves of *Pulicaria crispa* was refluxed with 1 M H<sub>2</sub>SO<sub>4</sub> for about 5 h and was kept overnight to extract the basic components. The solution was filtered off and the filtrate was diluted with the appropriate quantities of the 1 M H<sub>2</sub>SO<sub>4</sub> to obtain the desired concentrations. The aggressive acid solutions used were made of AR grade of H<sub>2</sub>SO<sub>4</sub> and diluted with double distilled water. The concentration range of the powdered leaves taken was varied from 50 to 2000 ppm in 1 M H<sub>2</sub>SO<sub>4</sub>.

### *Specimen preparation*

Mild steel of the composition (MS) containing Mn (0.90-1.6), Ni(0.015 ≤), Nb (0.04 ≤), Al(0.06 ≤), Ti (0.05 ≤), Si (0.10 - 0.50), C (0.16≤), P (0.03 ≤), S (0.025 ≤), CE (0.043 ≤), (V + Nb+ Ti) (0.10 ≤), (V + Nb) P (0.07 ≤), were used for the electrochemical polarisations and impedance measurements. For the weight loss method and scanning electron microscopic (SEM) analysis specimens of 1x1 cm of same MS were used.

The surface preparation of the mechanically polished specimens were carried out using different grades of emery papers, degreased with acetone dried at room temperature and then stored in a desiccator before use.

### *Weight loss method*

The polished and pre-weighed MS specimens were suspended in 100 mL test solutions, with and without the extracts of different concentrations, for a fix period of time and were washed, dried and weighed. From the weight loss data, percent inhibition efficiency (IE%) was calculated.

### *Electrochemical and impedance measurements*

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system (Tacussel), which included a digital potentiostat model VoltaLab 80 (PGZ402 & VoltaMaster 4) computer at E<sub>corr</sub> after immersion in solution without bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential.

Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hour of exposure at 298 K. The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility.

## Results and Discussion

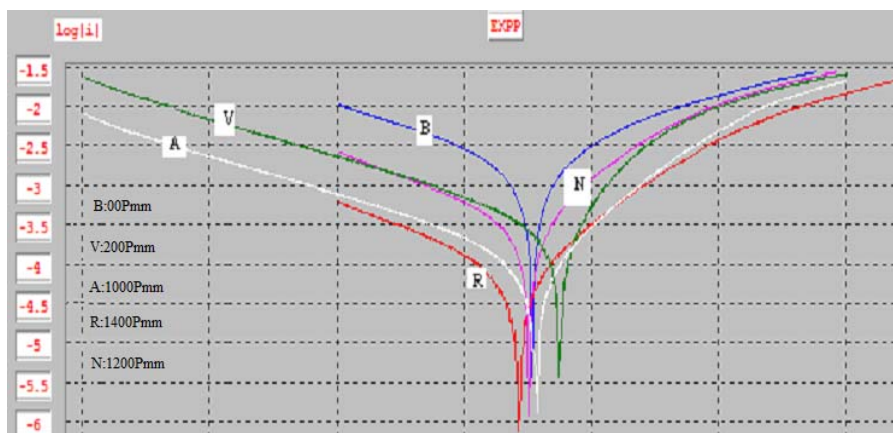
Based on the weight loss measurements, the corrosion rates (W) and the values of inhibition efficiency (IEW%) for various concentrations of *Pulicaria crispa* after 1 h of immersion at 25 °C obtained are given in Table 1.

From the Table, it is clear that the value of IEW% increases with the increase in the concentration reaching a maximum value of 96.69% at the highest concentration of 1400 ppm, suggesting that the number of molecules adsorbed were increased over the MS surface, blocking the active sites of acid attack and thereby protecting the metal from corrosion.

The potentiodynamic polarization data are shown in the Tafel plots for MS in 1 M H<sub>2</sub>SO<sub>4</sub> with the addition of various concentrations of the additive (Figure 1). The corrosion kinetic parameters such as corrosion potential (E<sub>corr</sub>), corrosion current density (I<sub>corr</sub>), anodic and cathodic Tafel slopes (ba and bc) were derived from these curves and are given in Table 2.

**Table 1.** Inhibition Efficiency of MS in 1 M H<sub>2</sub>SO<sub>4</sub> in the presence and absence of different concentrations of *Pulicaria crispa* extract

C ppm	W 10 <sup>3</sup> , g/cm <sup>2</sup> mim	W, mm/an	IE, %
50	3.3227	22.5382	6.14
200	2.2062	15.0980	37.13
400	1.8442	13.4372	44.04
600	1.5039	11.4598	52.28
800	0.8443	7.9882	66.73
1000	0.7321	4.9332	79.95
1200	0.4196	2.8238	88.22
1400	0.1286	0.8340	96.69
1600	0.1415	0.9535	96.04
1800	0.3861	1.2142	94.60
2000	0.2701	1.8200	92.45

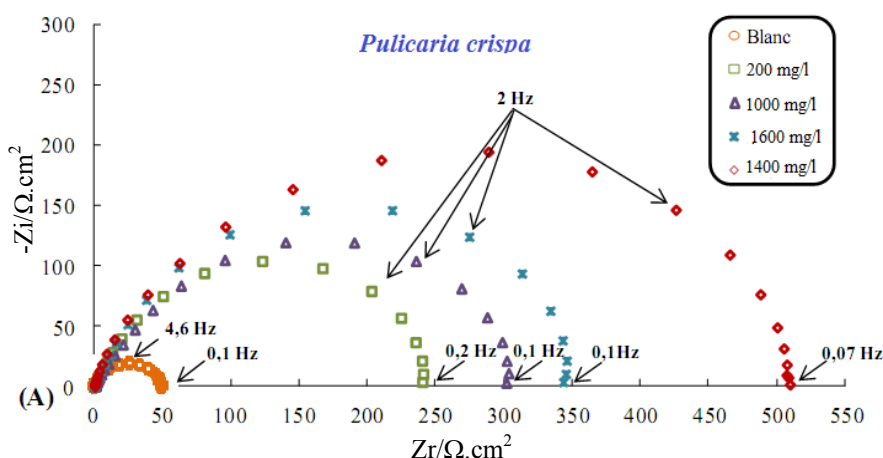
**Figure 1.** Tafel plots showing effect of *Pulicaria crispa* extracts on corrosion of MS in H<sub>2</sub>SO<sub>4</sub> medium**Table 2.** Effect of *Pulicaria crispa* extract on corrosion of MS in 1 M H<sub>2</sub>SO<sub>4</sub> solution studied by Tafel polarisation method

Concentration, ppm	RPR, kLcm <sup>2</sup>	Ba, mv/decade	Bc, mv/decade	I <sub>corr</sub> , A/cm <sup>2</sup>	E <sub>corr</sub> , mv	V <sub>corr</sub> , mm/an	IE, %
00	21.78	125.2	210.8	2.0597	508.1	24.09	-
200	36.72	83.6	176.5	0.9945	478.4	11.63	55.08
1000	89.61	27.6	52.8	0.0748	469.7	0.875	96.36
1400	193.49	46.00	81.10	0.0398	470.1	0.465	98.07
1200	80.60	63.60	88.60	0.1128	478.30	1.320	94.52

The values of inhibition efficiency (IE %) are calculated and tabulated (Table 2). From the Table, it is observed that the I<sub>corr</sub> values gradually decreased with gradual increase in the concentration of additive up to 1400 ppm leading to 98.07% of IE. Further, there was anodic shift of the E<sub>corr</sub> value of -0.35V (blank) to -0.55V at 1400 ppm indicating that the *Pulicaria crispa* extracts acted as an anodic inhibitor<sup>17</sup> for MS in 1 M H<sub>2</sub>SO<sub>4</sub> which was supported by the gradual and significant decrease of anodic Tafel slope, (ba) is 125.2 mV/

decade of blank to 46.00 mV/ decade at 200 ppm. It could be derived from this decrease that the rate of anodic dissolution was much retarded in comparison to that of cathodic hydrogen evolution. This means that the extract must have acted predominantly by blocking anodic sites and also cathodic sites to some extent and the extract contained the active molecules which behaved as mixed-type of the acid corrosion inhibitors.

The corrosion behaviour of MS in 1 M  $\text{H}_2\text{SO}_4$ , in absence and the presence of various concentrations of *Pulicaria crispera* extract were also investigated by EIS technique. The resultant Nyquist plots are shown in Figure 2. The existence of a single semicircle in each plot shows that there was only single charge transfer process during the anodic dissolution of MS and remained unaffected in the presence of inhibitive molecules of the extract added in the acid.

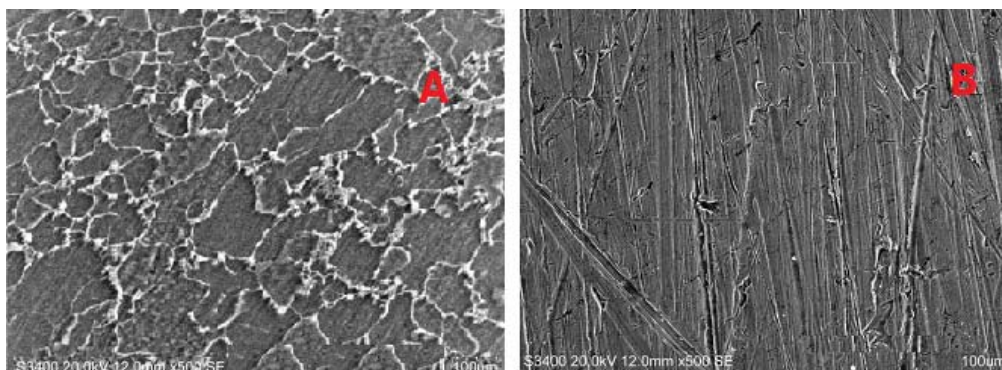


**Figure 2.** Nyquist plots showing effect of *Pulicaria crispera* extracts on corrosion of MS in  $\text{H}_2\text{SO}_4$  medium

The charge transfer resistance ( $R_{ct}$ ) and the interfacial double layer ( $C_{dl}$ ) values are derived from these curves and it is found that  $R_{ct}$  values increase with increase in the inhibitor concentration while  $C_{dl}$  values decrease which results in maximum IE (97%) at high concentration. This indicated that the inhibitive molecules of the extracts have been adsorbed on the MS surface and decreased the roughness of the MS surface.

*Pulicaria crispera* has been reported to contain many heterocyclic compounds such as alkaloids and flavonoids. The presence of such compounds enhances their adsorption on the metal surface and thereby blocking the surface and protecting the metal from corrosion. The results revealed that the acidic extract of the plant can be used as a good corrosion inhibitor for steel in acidic medium at room temperature. To obtain the maximum protection efficiency, critical plant extract concentration should be determined. Polarization studies reveal that the extracts behave as mixed type inhibitors.

This indicated that the inhibitive molecules of the extracts have been adsorbed on the MS surface and decreased the roughness of the MS surface. The SEM photograph in Figure 3(a) has shown that the surface of MS was extremely damaged in the absence of the extract while Figure 3(b) has clearly shown the formation of a film by the active *Pulicaria crispera* constituents on the MS surface which was responsible for the corrosion inhibition.



**Figure 3.** SEM images of MS (a) in 1 M H<sub>2</sub>SO<sub>4</sub> media and (b) with *Pulicaria crispa* extract (1400 ppm)

The inhibition properties of *Pulicaria crispa* must be due to the presence of nitrogenous compounds<sup>18</sup> or tannins<sup>19</sup> in the extract of leaves. However, tannins are complex astringent aromatic acidic glycosides found in various plants and their presence can be ruled out as they are made up of the polyphenols and their acidic and heterocyclic derivatives because such constituents would not have been extracted in the acid.

## Conclusion

- The active molecules present in the extract of *Pulicaria crispa* have effectively inhibited corrosion of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> at 25° C by forming a protective barrier layer. The inhibition efficiency of the extract increased gradually with increase in its concentration.
- Polarization measurements have shown that the extract of *Pulicaria crispa* has acted as a mixed- inhibitor, retarding predominantly anodic dissolution of steel in 1M H<sub>2</sub>SO<sub>4</sub>.
- The results of the weight loss, electrochemical polarisation and AC impedance spectroscopy were all in very good agreement to support the above conclusions.
- Photographs by SEM have clearly shown the formation of the protective film on the surface of mild steel.
- The acid extract of *Pulicaria crispa* can be considered as a source of relatively cheap, eco-friendly and effective acid corrosion inhibitors.

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