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Corrosion Inhibition Effect of *Centella asiatica* (Vallarai) on Mild Steel in Hydrochloric Acid

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Corrosion of oil and gas well equipment during acidization process causes severe problem in oil and gas well industries. This problem can be prevented to a maximum extent by the application of corrosion inhibitors. Present work involves the study of aqueous extract of *Centella asiatica* as corrosion inhibitor on mild steel in 1 N hydrochloric acid and has been investigated by weight loss method, gasometric method, potentiodynamic polarization method and AC impedance method. *Centella asiatica* yields maximum inhibition efficiency of 85-86 % in presence of an optimum concentration of 10 % v/v of the extract. The inhibition efficiency was found to vary with its concentration, temperature, immersion time. Potentiodynamic polarization studies show that *Centella asiatica* is a mixed type inhibitor. It inhibits mild steel corrosion by blocking the active sites of metal. Results obtained in non electrochemical methods (weight loss method and gasometric method) have good agreement with the electrochemical methods (potentiodynamic polarization method and impedance method). The adsorption of *Centella asiatica* follows Langmuir adsorption isotherm. The inhibition action is due to the presence of *Asiaticoside*, a triterpene glycoside present in the leaves of *Centella asiatica*.

Key Words: Corrosion inhibition, *Centella asiatica*, Mild steel, Impedance, Asiaticoside, Langmuir adsorption isotherm, Polarization curves.

INTRODUCTION

Hydrochloric and sulphuric acids are widely used for removal of undesirable scale and rust by pickling in several industrial processes. Use of inhibitors is one of the most practical methods to prevent metal dissolution and reduce acid consumption during pickling process. Generally organic compounds containing oxygen, sulphur and nitrogen are normally used to reduce corrosion of mild steel in HCl medium. Extracts of some plants have nitrogen and sulphur as constituent atoms and hence can be a useful source of biodegradable inhibitor for such applications[1-8]. Nevertheless, the known hazard effects of the most synthetic inhibitors and the need to develop environment friendly processes, researches are focused on the use of natural products. Near their environmental and acceptable ecological properties, naturally occurring antioxidants are cheap and readily available and renewable sources of materials[9]. In this study, the leaves of *Centella asiatica* has been chosen as corrosion inhibitor. Centella asiatica is otherwise called as 'Vallarai' which is a creeping herb with leaves which are kidney shaped. The major active constituent present in *Centella asiatica* is Asiaticoside, a triterpene glycoside. In this study the corrosion inhibition effect of *Centella asiatica* (Vallarai) on mild steel in hydrochloric acid has been investigated using weight loss method, gasometric method, potentiodynamic polarization method and AC impedance method.

EXPERIMENTAL

Material preparation: Mild steel strips of size 4.5 cm × 2 cm × 0.2 cm containing 0.14 % C, 0.35 % Mn, 0.17 % Si, 0.025 % S, 0.03 % P and the remainder Fe were used for weight loss and gasometric method. For electrochemical studies, mild steel strips of the same composition coated with lacquer 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 and subsequently degreased with trichloroethylene before use. Analytical reagent grade HCl (Merck) and double distilled water were used for preparing test solutions for all experiments.

Solution preparation: The leaves of *Centella asiatica* was taken and cut into small pieces and they were dried in an air oven at 80 ºC for 2 h and ground into powder. From this 10 g sample was refluxed in 100 mL distilled water for 1 h, filtered carefully and made up to 100 mL using double distilled water. The concentration of the stock solution is expressed in terms of % (v/v). From the stock solution 2 to 10 % concentration v/v of the extract was prepared for the study.

Detection method

Weight loss method: The experimental solution, 1 N HCl with different concentrations of inhibitors was used. The pretreated specimens were immersed in the experimental solution with the help of glass hooks. The volume of solution used was 100 mL. The initial weight of the specimens was noted and it was immersed completely into the experimental solution at 30 ºC for 3 h. After 3 h, the specimens were taken out, washed thoroughly with distilled water, 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. The corrosion rate (mmpy) and the efficiency of inhibitors can be calculated using the formula,

$$\text{Corrosion rate (mmpy)} = KW/ATD \quad (1)$$

where $K = 8.76 \times 10^4$ (constant), W = weight loss in g, A = area in sq.cm, T = time in hours and D = density in g/c.c. (7.86).

$$\text{Inhibition efficiency (\%)} = (W_B - W_I)/W_B \times 100 \quad (2)$$

where W_B and W_I are weight loss per unit time in the absence and presence of inhibitors. The degree of surface coverage (θ) was calculated from the weight loss measurement results using the formula,

$$\text{Surface coverage } (\theta) = (W_B - W_I) / W_B \quad (3)$$

where, W_B and W_I is the weight loss in the absence and presence of inhibitor.

Gasometric method: This technique gives accurate results compared to that of conventional weight loss method provided, the inhibitor does not react with hydrogen and the hydrogen penetration into the metal is small compared to the total volume of hydrogen gas. The gasometric studies were carried out as described earlier[1]. The inhibition efficiency was calculated using the formula,

$$\text{Inhibition efficiency (\%)} = (V_0 - V_1)/V_0 \times 100 \quad (4)$$

where, V_0 is the volume of hydrogen evolved in the absence of inhibitor, V_1 is the volume of hydrogen evolved in the presence of inhibitor.

Potentiodynamic polarization studies: Potentiodynamic polarization measurements were carried out using Solartron Electrochemical analyzer (Model-1280). Experiments were carried out in a conventional three-electrode cell assembly. The working electrode was mild steel specimen of 1 sq cm area which was exposed and the rest being covered with red lacquer. A rectangular Pt foil was used as the counter electrode. To exert uniform potential on the working electrode, it is designed in such a way that the counter electrode is much larger in area compared to the working electrode. The reference electrode used was 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 min 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:

$$IE\,(\%) = \frac{I_{corr} - I^*_{corr}}{I_{corr}} \times 100 \quad (5)$$

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

Impedance measurements: The electrochemical AC-impedance measurements were performed using Solatron-Electrochemical analyzer (Model 1280). Experiments were carried out in a conventional three-electrode cell assembly as that used for potentiodynamic polarization studies. The working electrode was mild steel specimen of 1 sq cm area which is exposed and the rest being covered with red lacquer. A rectangular Pt foil is used as the counter electrode. 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' *vs.* Z'' was made. From the plot, the charge transfer resistance (R_t) were calculated and the double layer capacitance was then calculated using the equation:

$$C_{dl} = 1/2\pi f_{max} R_t \quad (6)$$

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 the equation:

$$\text{IE (\%)} = \frac{R_t^* - R_t}{R_t^*} \times 100 \quad (7)$$

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

RESULTS AND DISCUSSION

Weight loss method: The weight loss method was done with concentrations ranging from 2 to 10 % v/v. The weight loss data are listed in Table-1. It was found that with the rise in concentration of the *Centella asiatica* extract from 2.0 to 10 % in v/v, the weight loss of mild steel decreased, the corrosion rate also decreased while the inhibition efficiency increased. At the optimum concentration of 10 % in v/v, *Centella asiatica* has a highest inhibition efficiency of about 85.3 %. This result indicated that extracts of *Centella asiatica* could act as corrosion pickling inhibitor at the optimum concentration of 10 % in v/v for an immersion period of 3 h.

TABLE-1
CORROSION PARAMETERS OBTAINED FROM WEIGHT LOSS MEASUREMENTS FOR MILD STEEL IN 1N HCl CONTAINING DIFFERENT CONCENTRATIONS OF *Centella asiatica* EXTRACT

Concentration of extract (% in v/v)	Corrosion rate (mmpy)	Inhibition efficiency (%)	Surface coverage (θ)
Blank	30.67	–	–
2.0	12.82	58.2	0.58
4.0	10.79	64.8	0.65
6.0	8.55	72.1	0.72
8.0	6.56	78.6	0.79
10.0	4.50	85.3	0.85

Gasometric method: The results obtained in gasometric method reveals that the hydrogen penetration into the metal decreased as the concentration of the inhibitor increased from 2.0 to 10 % in v/v and showed maximum inhibition efficiency of 84.3 % at 10 % v/v concentration of the extract *Centella asiatica* (Table-2). This technique gives accurate result compared to the conventional weight loss method.

TABLE-2
GASOMETRIC MEASUREMENTS FOR MILD STEEL IN 1 N HCl CONTAINING DIFFERENT CONCENTRATIONS OF *Centella asiatica* EXTRACT

Concentration of extract (% in v/v)	Volume of hydrogen gas (mL) evolved at 30 ± 1 ºC	Inhibition efficiency (%)
Blank	7.0	–
2.0	3.0	57.1
4.0	2.5	64.3
6.0	2.0	71.4
8.0	1.5	78.6
10.0	1.1	84.3

Potentiodynamic polarization method: The potentiondynamic polarization parameters for mild steel in 1 N HCl containing different concentrations of *Centella asiatica* extract are given in Table-3 and the polarization curves are given in Fig. 1. Inspection of the figure revealed that the polarization curves shift towards less negative potential and lower current density values upon the addition of extract. This behaviour reflects the inhibitive action of *Centella asiatica* extract. Table-3 shows that the corrosion potential shifts to less negative values as the concentration of added extract is increased. On the other hand, the corrosion current density is markedly decreased upon addition of the extract. The extent of its decrease, increased with increase in extract concentration. Moreover, the numerical values of both anodic and cathodic Tafel constants decreased as the concentration of extract was increased. It was observed that with increase in concentration of *Centella asiatica* extract from 2 to 10 %, the maximum inhibition efficiency of 85.7 % was observed at an optimum concentration of 10 % in v/v.

TABLE-3
POTENTIODYNAMIC POLARIZATION PARAMETERS FOR MILD STEEL IN 1 N HCl CONTAINING DIFFERENT CONCENTRATIONS OF *Centella asiatica* EXTRACT

Concentration of extract (% in v/v)	E_{corr} (V)	I_{corr} (mA/cm^2)	Tafel slope (mV/decade)		Inhibition efficiency (%)
			b_a	b_c	
Blank	-0.5226	3.57	78	122	–
2.0	-0.4879	1.47	76	128	58.8
4.0	-0.4861	1.22	78	126	65.8
6.0	-0.4803	0.97	80	122	72.8
8.0	-0.4669	0.74	74	126	79.3
10.0	-0.4914	0.51	76	124	85.7

Impedance measurements: 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. Fig. 2 shows the impedance diagrams for mild steel in 1N HCl with different concentrations of *Centella asiatica* extract and the impedance parameters derived from these investigations are given in Table-4. As noticed from Fig. 2, the obtained impedance diagrams are almost in a semi-circular appearance, indicating 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, the presence of *Centella asiatica* extract enhanced the values of R_t in acidic solution. Values of double layer capacitance are also brought down to the maximum extent in the presence of inhibitor and the decrease in values of C_{dl} follows the order similar to that obtained for I_{corr} in this study. The decrease in C_{dl} shows that the adsorption of this inhibitor takes place on the metal surface in acidic solution.

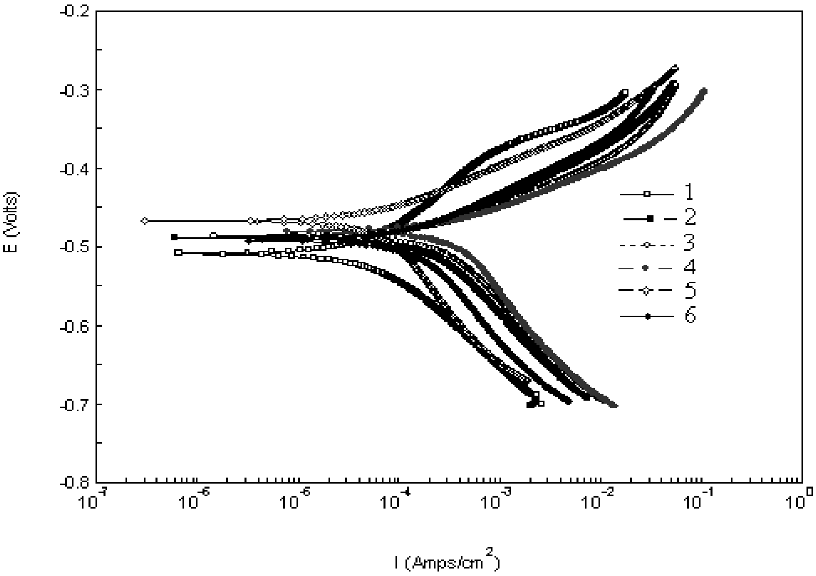


Fig. 1. Potentiodynamic polarization curves for mild steel in 1 N HCl solution in the absence and presence of different concentrations of *Centella asiatica* extract
(1) Blank (2) 2.0 (%v/v) (3) 4.0 (% v/v) (4) 6.0 (% v/v) (5) 8.0 (% v/v) (6) 10.0 (%v/v)

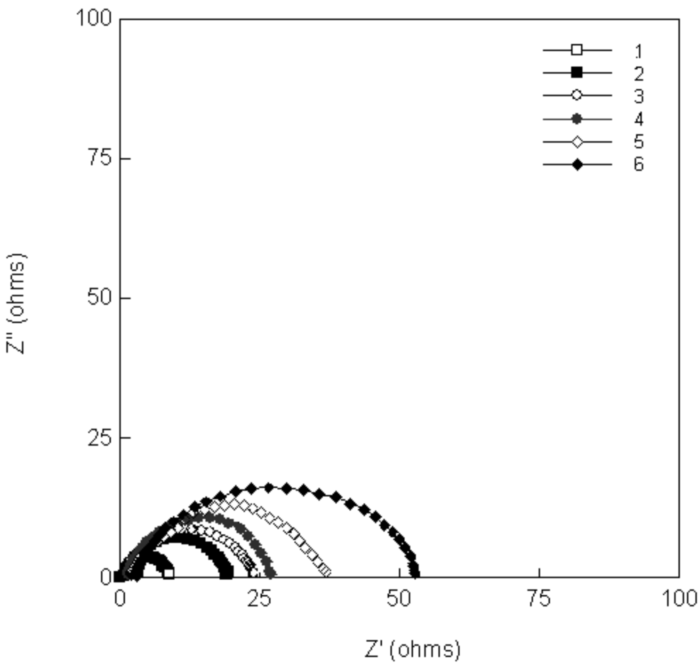


Fig. 2. Impedance diagrams for mild steel in 1 N HCl solution in the absence and presence of different concentrations of *Centella asiatica* extract; (1) Blank 2) 2.0 (% in v/v) (3) 4.0 (% in v/v) (4) 6.0 (% v/v) (5) 8.0 (% in v/v) (6) 10.0 (% in v/v)

TABLE-4
IMPEDANCE PARAMETERS FOR THE CORROSION OF MILD STEEL IN 1 N HCl IN THE ABSENCE AND PRESENCE OF DIFFERENT CONCENTRATIONS OF *Centella asiatica* EXTRACT AT 30 ºC

Concentration of extract (% in v/v)	R_t (Ω cm^2)	C_{dl} (μF/cm^2)	Inhibition efficiency (%)
Blank	7.58	285.34	–
2.0	18.32	118.02	58.6
4.0	22.35	96.61	66.1
6.0	27.54	78.50	72.5
8.0	35.12	61.51	78.4
10.0	54.32	39.88	86.0

Moreover, the increase in the value of R_t with the inhibitor concentration leading to the increase in inhibition efficiency. The R_t value without inhibitor (blank) was found to be 7.58 Ω cm^2 and C_{dl} value was 285.34 μF/cm^2. At the optimum concentration of 10 % in v/v the R_t value of 54.32 Ω cm^2 and minimum C_{dl} value of 39.88 μF/cm^2 was obtained with a maximum inhibition efficiency of 86 %. A good agreement is observed between the results obtained in non-electrochemical method (weight loss and gasometric method) and electrochemical methods (potentiodynamic polarization method and impedance method).

Kinetics and reason for the corrosion inhibition: The corrosion of mild steel in HCl solution is a heterogenous one, composed of anodic and cathodic reactions. Based on this, the kinetic analyses of the data were considered. The Arrehenius plot for mild steel immersed in 1 N HCl solution in the absence and presence of optimum concentration (10 % v/v) of *Centella asiatica* extract is given in Fig. 3. The use of

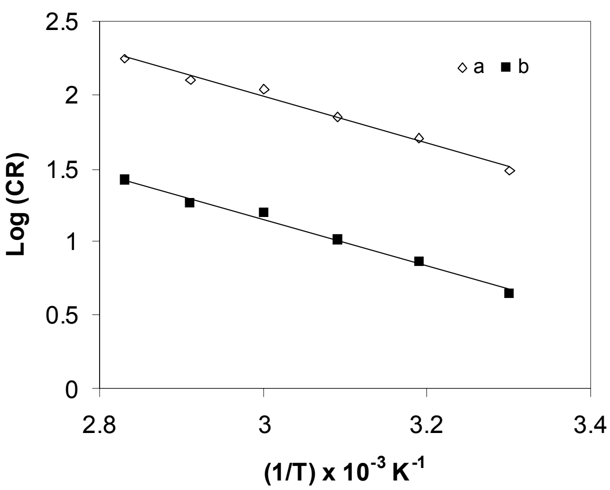


Fig. 3. Arrhenius plots for mild steel immersed in 1 N HCl solution in the absence and presence of optimum concentration (10.0 % v/v) of *Centella asiatica* extract (a) Blank (b) *Centella asiatica*

adsorption isotherms provides useful insight into the corrosion inhibition mechanism. The adsorption of different concentrations of *Centella asiatica* extract on the surface of mild steel in 1 N hydrochloric acid follows Langmuir adsorption isotherm (Fig. 4).

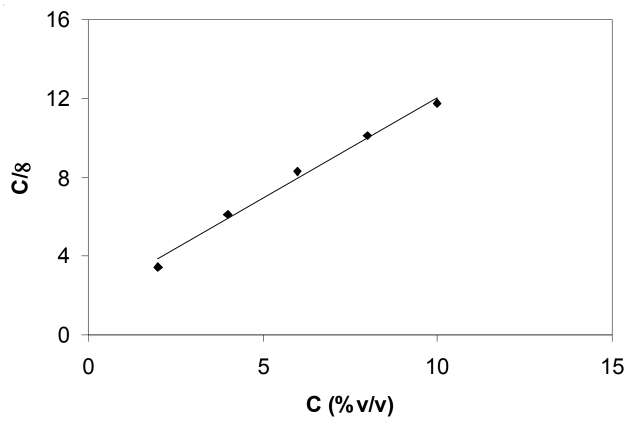
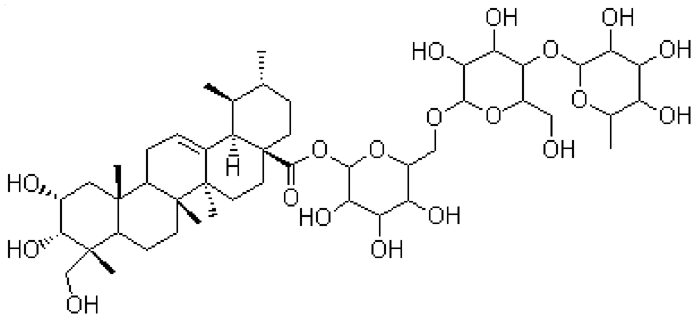


Fig. 4. Langmuir adsorption isotherm plot for the adsorption of different concentrations of *Centella asiatica* extract on the surface of mild steel in 1 N HCl solution

From literature survey it reveals that the inhibition action may be due to the presence of *Asiaticoside*, a triterpene glycoside present in the leaves of *Centella asiatica*[10].

Name: Asiaticoside; Synonyms: [6-[[3,4-Dihydroxy-6-(hydroxymethyl)-5-(3,4,5-trihydroxy-6-methyl-oxan-2-yl)oxy-oxan-2-yl]oxymethyl]-3,4,5-trihydroxy-oxan-2-yl](1S,2R,4aS,6aS,6bR,9S,10R,11R,12aS,14bR)-10,11-dihydroxy-9-(hydroxymethyl)-1,2,6a,6b,9,12a-hexamethyl-2,3,4,5,6,6a,7,8,8a,10,11,12,13,14b-tetradecahydro-1*H*-picene-4a-carboxylate

Molecular structure:



Molecular formula: $C_{48}H_{78}O_{19}$; Molecular weight: 959.12.

Inspection of the chemical structure of *Asiaticoside* reveals that the compound can adsorb on the metal surface *via* the lone pair of electrons present on their oxygen atoms. The adsorption of such compounds on the metal surface 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[1-8].

Conclusion

1. *Centella asiatica* (Vallarai) acts as efficient corrosion pickling inhibitor on mild steel in 1 N HCl. 2. The use of *Centella asiatica* as corrosion inhibitor is environmentally safe, less toxic, ecofriendly, cost effective and easily available. 3. The maximum inhibition efficiency was found to be 85.3 % at an optimum concentration of 10 % in v/v of the extract at 3 h of immersion time. 4. Results obtained in non-electrochemical methods (weight loss and gasometric method) have good agreement with the electrochemical methods (potentiodynamic polarization method and impedance method). 5. The corrosion inhibition action is due to the presence of the *Asiaticoside*, a triterpene glycoside present in the leaves of *Centella asiatica*. 6. The adsorption of different concentrations of *Centella asiatica* extract on the surface of mild steel in 1 N hydrochloric acid follows Langmuir adsorption isotherm.

REFERENCES

1. K.O. Orubite and N.C. Oforka, *Mater. Lett.*, **58**, 1768 (2004).
2. Y. Li, P. Zhao, Q. Liang and B. Hou, *Appl. Surface Sci.*, **252**, 1245 (2005).
3. A.Y. El-Etre, M. Abdullah and Z.E El-Tantawy, *Corrosion Sci.*, **47**, 385 (2005).
4. E. Emeka and Oguzie, *Mater. Chem. Phys.*, **99**, 441 (2005).
5. G. Gunasekaran and L.R. Chauhan, *Electrochim. Acta*, **49**, 4387 (2004).
6. P. Bommersbach, C. Alemany-Dumont, J.P. Millet and B. Normand, *Electochim. Acta*, **51**, 1076 (2005).
7. A. Bouyanzer, B. Hammouti and L. Majidi, *Mater. Lett.*, **60**, 2840 (2006).
8. L.Valek and S. Martinez, *Mater. Lett.*, **61**, 148 (2007).
9. A.M. Abdel-Gaber, B.A. Abd-El-Nabey, I.M. Sidahmed, A.M. El-Zayady and M. Saadawy, *Corrosion Sci.*, **48**, 2765 (2006).
10. http: //www.chemblink.com/products/16830-15-2.htm

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