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INFLUENCE OF *MURRAYA KOENIGII* (CURRY LEAVES) EXTRACT ON THE CORROSION INHIBITION OF CARBON STEEL IN HCl SOLUTION

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ABSTRACT

The inhibitive action of extract of curry leaves (*Murraya koenigii*) on carbon steel in 1N HCl has been studied using weight loss, gasometric studies and electrochemical polarization and AC impedance measurements. The effect of temperature on the corrosion behaviour of carbon steel in 1N HCl with optimum concentration of inhibitors was studied in the temperature ranging from 30 -80˚C. The protective film formed on the surface of carbon steel by the adsorption of extracts in 1N HCl solution was confirmed by SEM studies.
Keywords: Corrosion inhibition, *Murraya koenigii,* carbon steel, HCl.

INTRODUCTION

Several researchers are trying to make use of natural products as corrosion inhibitors. Plant scientists have already established the active principles present in most of the plant materials. The active principles form protective films on metal surfaces by coordinating with metal ions through O, S or N atoms of the functional groups present in the active principles. When the active principles are extracted with acids or organic solvents or with water, usually a mixture of several compounds is obtained. It is very difficult and tedious to isolate and purify them.

Before the 1960s inorganic inhibitors such as zinc, chromate, polyphosphate and nitrite were used as inhibitors. However, discharge of such materials has become unacceptable, due to environmental hazards. The recent trend is towards environment – friendly inhibitors. Most of the natural products are non-toxic, biodegradable and readily available in plenty. Various parts of plants – seeds, fruits, leaves, flowers, etc – have been used as corrosion inhibitors[1].

Increasing awareness of health and ecological risks drawn attention to find more suitable inhibitors, which are non-toxic. Accordingly greater research efforts have been directed towards formulating environmentally acceptable inhibitors. The cost of using green inhibitors is very less when compared to that of organic inhibitors which takes lot of chemicals and also time for its preparation. Hence in the present work, the extract of curry leaves are collected and evaluated for its corrosion inhibition performance such as Weight loss, gasometric, potentiodynamic polarization, impedance studies and hydrogen permeation studies and a suitable mechanism regarding the mode of inhibition is also to be proposed.

EXPERIMENTAL

Material preparation

Carbon steel strips of size 4.5cm × 2cm × 0.2cm 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 hydrogen permeation studies. For electrochemical studies, carbon steel strips of the same composition coated with lacquer with an exposed area of 1 cm^2 were used. Carbon steel strips were polished mechanically with emery papers of 1/0 to 4/0 grades. They were subsequently degreased with trichloroethylene before use. Analytical reagent grade HCl (Merck) and double distilled water were used for preparing test solutions for all experiments[2].

Preparation of natural product extract

The curry leaves *(Murraya koenigii) were* taken and cut into small pieces and they were dried in air oven at 80ºC for 2 hrs. They were ground well into powder. From this, 10g of the sample were refluxed in 100mL-distilled water for 1hour. The refluxed solution was then filtered carefully and the filtrate volume was made up to 100 mL using double distilled water. The concentration of the stock solution is expressed in term of %(v/v) [3,4].

RESULTS AND DISCUSSION

The extract of curry leaves (Murraya koenigii) on the corrosion inhibition of the carbon steel in 1N HCl solution under various operating conditions are given and discussed.

Weight loss measurements

Various corrosion parameters such as corrosion rate (CR), inhibition efficiency (IE) and surface coverage (θ) were obtained from weight loss measurements for different concentrations of curry leaves extract i.e. 2 % (v/v), 4 % (v/v), 6 % (v/v), 8 % (v/v), and 10 % (v/v), for the corrosion of carbon steel in 1N HCl for 3hr duration at 30°C are given in *Table-1***.** The corrosion rate decreased upto 4 % (v/v) concentration and the maximum inhibition efficiency obtained was 84.6 at 4 %(v/v). Further increase in the concentration of inhibitor from 4 to 10 0 (v/v) decreases the inhibition efficiency. Hence, the optimum concentration required to achieve maximum inhibition was 4 % (v/v).

Gasometric method

The results of the gasometric method to evaluate the corrosion inhibition efficiencies of curry leaves extract in 1N HCl are given in *Table-2* The result shows the same trend in inhibition efficiency as observed in weight loss method. From gasometric studies, it can be concluded that there is no interaction between inhibitor and hydrogen gas evolved from the metal is negligible, since the inhibition efficiency calculated by weight loss method and gasometric method are in good agreement with each other.

Table- 1:Corrosion parameters obtained from weight loss measurements for carbon steel in 1N HCl containing different concentrations of curry leaves extract

Conc. of Extract (% in v/v)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)	Surface Coverage (θ)
Blank	30.67	----	----
2.0	5.58	81.8	0.82
4.0	4.50	84.6	0.88
6.0	4.54	83.2	0.85
8.0	5.60	81.7	0.82
10.0	6.01	80.4	0.80

Effect of immersion time at 30°C

The effect of immersion time on corrosion rate and inhibition efficiency of Curry leaves extract with an optimum concentration at 30°C are given in **Table .3 Fig. 1** shows that the inhibition efficiency of the extract slightly decreased with the increase of immersion time from 3 to 24h.

Potentiodynamic polarization measurements

Electrochemical corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), anodic and cathodic Tafel slopes (b_a and b_c) and percentage inhibition efficiency (IE) for the corrosion of carbon steel in 1N HCl at 30°C in the absence and presence of different concentrations of extract are given in *Table-4* and its corresponding polarization curves are shown in Fig. 2 The addition of extract in 1N HCl solution does not show any significant change in E_{corr} suggesting that the prepared extract control the corrosion by controlling both anodic and cathodic reactions by blocking active anodic and cathodic sites on the metal surface. This indicates that the inhibition of corrosion of carbon steel in 1N HCl for the

extract is under mixed control i.e promoting retardation of both the anodic and the cathodic reactions. The corrosion current (I_{corr}) decreased with inhibitor concentration.The decrease of corrosion current may be explained by the action of inhibitor on both cathodic and anodic reactions[5]. The maximum inhibition efficiency obtained at an optimum concentration of extract was found to be 88.5%. Inhibition efficiencies obtained from I_{corr} values follow the same trend as already observed in the weight loss measurements.

Table- 2:Inhibition efficiency obtained from gasometric measurements for carbon steel in 1N HCl containing different concentrations of curry leaves extract

Conc. of Extract % (v/v)	Volume of Hydrogen Gas evolved at 30°± 1° C	Inhibition Efficiency (%)
Blank	7.0	--
2.0	1.3	81.4
4.0	1.0	84.2
6.0	1.2	82.8
8.0	1.4	80.0
10.0	1.5	78.6

Table -3:Effect of immersion time on percentage inhibition efficiency of mild steel in 1N HCl at 30°C in the presence of an optimum concentration of inhibitor

Name of the Natural inhibitor	Inhibition Efficiency (%)							
	Time (h)							
	3	6	9	12	15	18	21	24
Curry leaves	84.6	84.4	84.3	84.1	84.0	83.7	83.5	83.2

A.C. Impedance measurements

Impedance diagrams obtained for the frequency range of 100 kHz to 10mHz at the open circuit potential in the absence and presence of different concentrations of curry leaves extract at 30°C are shown in Fig. 3 The impedance diagrams obtained having a semicircular appearance show that the corrosion of carbon steel is mainly controlled by a charge transfer process. The impedance spectra (Nyquist plots) were analyzed by fitting the experimental data to a simple equivalent circuit model as previously reported[6,7, 8, 9]. The R_{ct} value is a measure of electron transfer across the surface and is inversely proportional to corrosion current. It is apparent from these plots that the impedance response of carbon steel in uninhibited HCl has significantly changed after the addition of extract. The corrosion kinetic parameters such as charge resistance (R_t) and double layer capacitance (C_{dl}) were derived from the Nyquist plots and percentage inhibition efficiency (IE) are given in **Table. 5** The charge transfer resistance (R_t) values were calculated from the difference in impedance at low and high frequencies. Double layer capacitance (C_{dl}) were obtained at the frequency f_{max} at which the imaginary component of the impedance is maximum ($-Z''_{max}$) by the following equation-

$$f(-Z''_{max}) = \frac{1}{2\pi C_{dl} R_t}$$

The maximum R_t value of 69.8 was observed for curry leaves in 1N HCl. The capacitance value of double layer (C_{dl}) decreased with concentration indicating the adsorption of inhibitor molecules on the metal surface. In the case of curry leaves, the maximum decrease in C_{dl} was obtaine at 4% (v/v). Decrease in C_{dl} may be due to a decrease in local dielectric constant and an increase in the thickness of the electrical double layer. Values of inhibition efficiency obtained from R_t values for different concentrations of curry leaves extract follow the same trend as those obtained from weight loss and potentiodynamic polarization measurements.

Table-4:Potentiodynamic polarization parameters for carbon steel in 1N HCl containing different concentrations of curry leaves extract at 30°C

Conc. of Extract % (v/v)	E_{corr} (V)	I_{corr} (mA/cm^2)	Tafel Slope mV/decade		Inhibition Efficiency (%)
			b_a	b_c	
Blank	-0.507	3.57	78	122	—
2.0	-0.490	0.55	78	124	84.5
4.0	-0.490	0.40	76	122	88.5
6.0	-0.487	0.47	74	120	86.8
8.0	-0.490	0.59	76	122	83.5
10.0	-0.487	0.67	78	124	81.2

Table -5:Impedance parameters for the corrosion of carbon steel in 1N HCl in the absence and presence of different concentrations of curry leaves extract at 30^{0}C

Conc. of Extract % (v/v)	R_t (Ω cm^2)	C_{dl} (μF/cm^2)	Inhibition Efficiency (%)
Blank	7.5	285.3	—
2.0	48.7	50.1	84.6
4.0	69.8	31.0	89.1
6.0	60.1	36.0	87.4
8.0	48.3	44.7	84.3
10.0	40.6	53.4	81.3

Adsorption isotherm

The surface coverage (θ) for different concentrations of curry leaves extract in 1N HCl solution was evaluated from weight loss measurements is given in *Table-1* The data was tested graphically by fitting various isotherms including Frumkin, Langmuir and Temkin. A plot of C/θ vs log C was found to be linear is shown in Fig. 4. This figure indicates that the adsorption of the extract on carbon steel in 1N HCl solution obeys the Langmuir adsorption isotherm.

Surface examination studies

Surface examination studies through scanning electron microscopy at a magnification of 1000X for the metal specimens dipped in 1N HCl at 30°C for 3h in the absence and presence of an optimum concentration of extract are shown in Fig. 5 and 6 In the absence of extract, the corroded metal surface with etched grain boundaries and corrosion products are clearly seen in Fig. 5 But in the presence of

inhibitor there is a formation of adsorbed layer of inhibitor on the metal surface without any corrosion products as seen in Fig.6.

Mechanism of inhibition

The obtained results indicate that natural product extract perform good inhibition for the corrosion of carbon steel. Curry leaves extract shows inhibition efficiency due to its main components such as monoterpene hydrocarbons (pinene, camphene, myrcene, and limonene) and monoterpene-derived alcohols (linalool, terpinene-4-ol, nerol, and geraniol, also their acetates. Most of the bio-extracts are compounds with at least one functional polar group which facilitates their physical adsorption /chemisorption on metal surface.

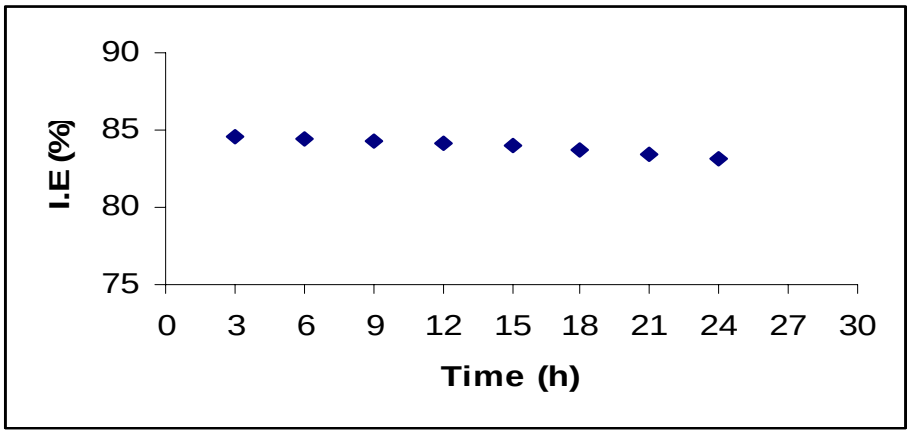

Fig.-1: Inhibition efficiency vs Time plot for carbon steel in 1N HCl solution containing an optimum concentration of Curry leaves (4% v/v) extract

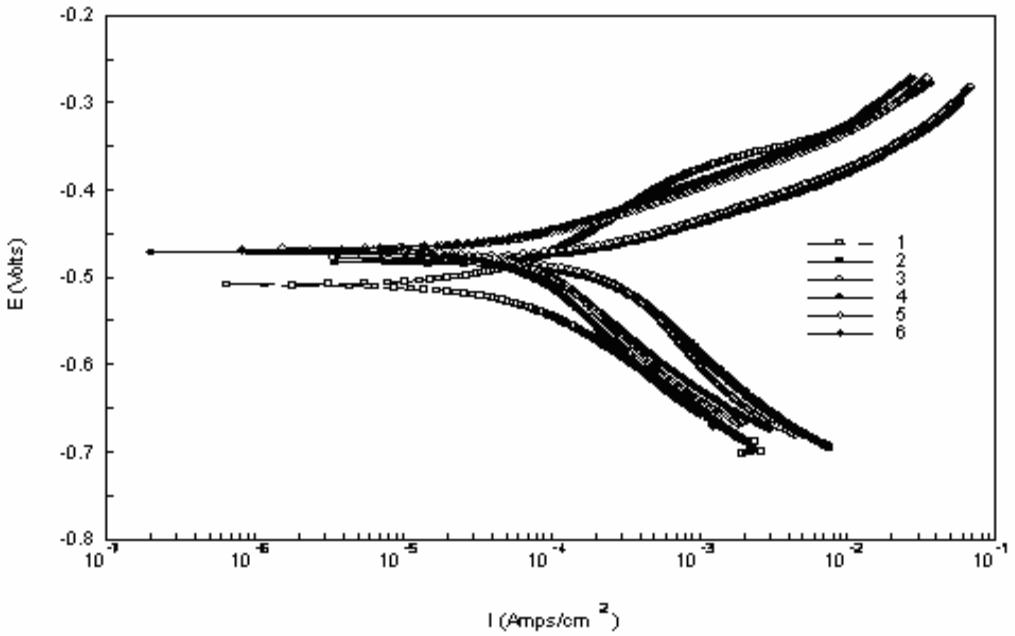

Fig.-2: Potentiodynamic polarization curves for carbon steel in 1N HCl solution in the absence and presence of different concentrations of curry leaves extract
(1)Blank (2) 2.0 (%v/v) (3) 4.0 (% v/v) (4) 6.0 (% v/v) (5) 8.0 (% v/v) (6) 10.0 (%v/v)

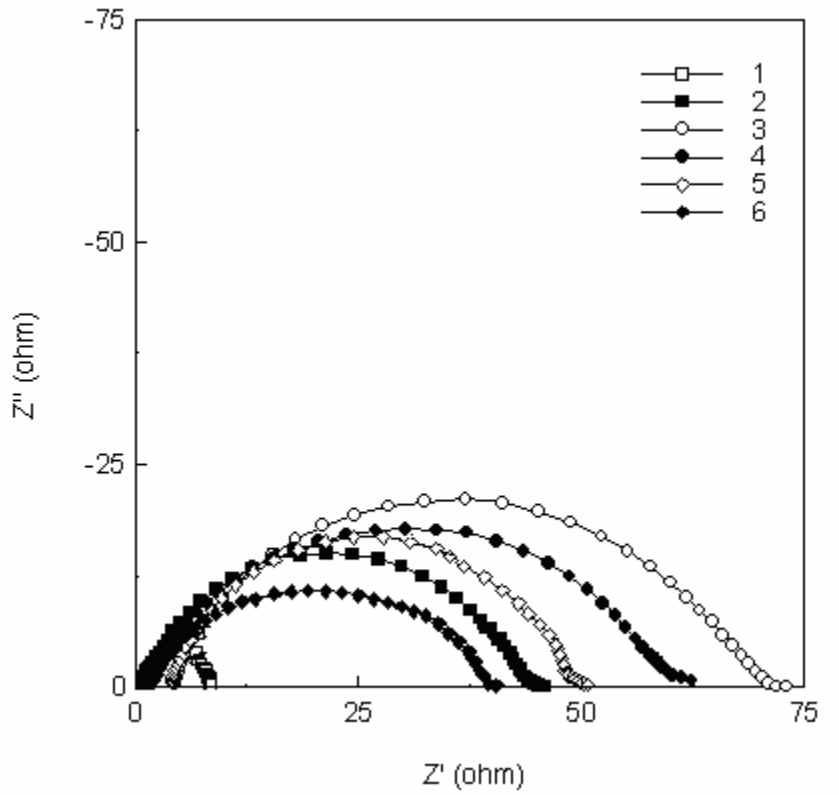

Fig.-3: Impedance diagrams for carbon steel in 1N HCl solution in the absence and presence of different concentrations of curry leaves extract
(1) Blank (2) 2.0 (% in v/v) (3) 4.0 (% in v/v) (4) 6.0 (% v/v)(5) 8.0 (% in v/v) (6) 10.0 (% in v/v)

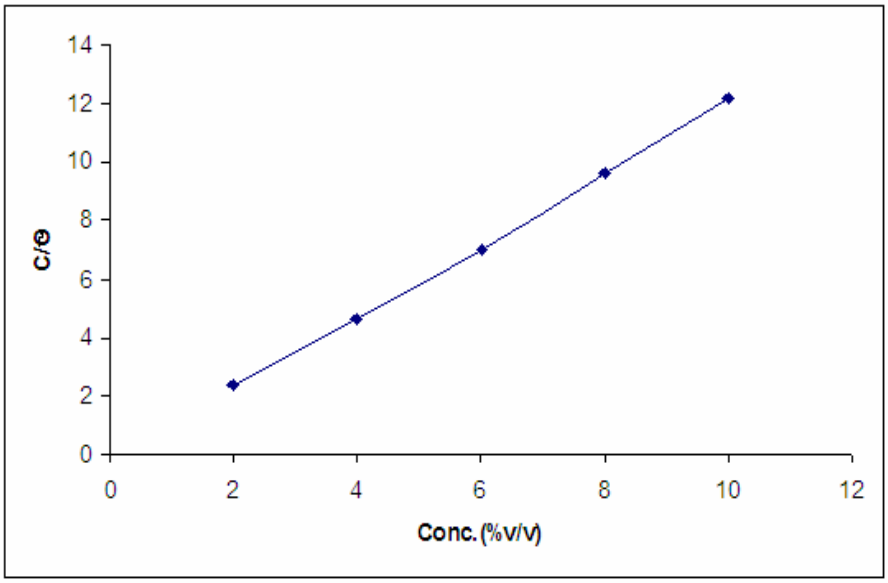

Fig .-4: Langmuir adsorption isotherm plot for the adsorption of different concentrations of curry leaves extract on the surface of carbon steel
in 1N HCl solution

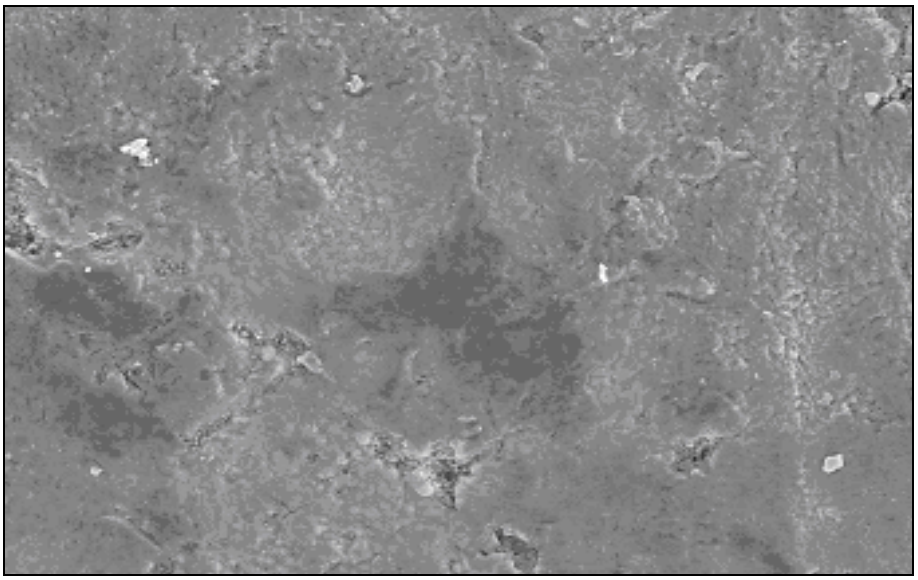

Fig.-5: SEM Photograph of carbon steel immersed in 1N HCl solution

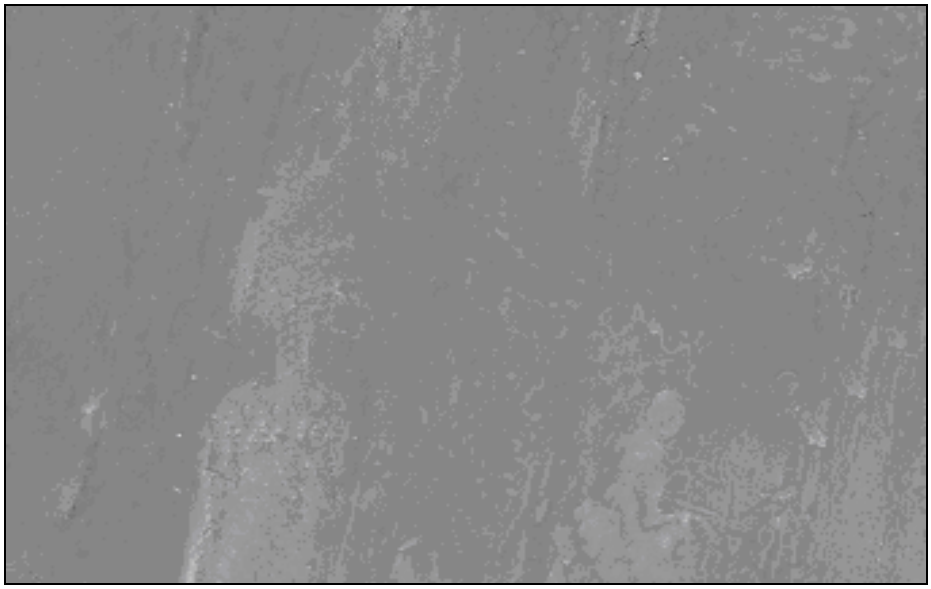

Fig.-6: SEM Photograph of carbon steel immersed in 1N HCl solution containing an optimum concentration (4.0 % v/v) of curry leaves extract

CONCLUSION

Curry leaves extract acts efficient corrosion inhibitor on carbon steel in 1N Hydrochloric acid solution. The use of curry leaves extract, as corrosion inhibitor is environmentally safe, less toxic, eco-friendly, cost effective and easily available. The maximum inhibition efficiency was found to be 84.6% at an optimum concentration of 4% in v/v of the extract. The extract of curry leaves showed maximum efficiency of 83.2 % at the optimum Concentration at 24 hrs of immersion time at 30^{o}C. Potentiodynamic polarization studies indicated that the studied curry leaves extract affected both anodic and cathodic reactions by blocking the active sites of steel surface and are inhibitors of mixed type. Results obtained in non- electrochemical methods (weight loss method) have good agreement with the

electrochemical methods such as potentiodynamic polarization and Impedance method. The adsorption of different concentrations of curry leaves extract on the surface of mild steel in 1N Hydrochloric acid follows Langmuir adsorption isotherm.

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