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Corrosion inhibition of mild steel by ethanolic extracts of *Ricinus communis* leaves

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Extracts of *Ricinus communis* leaves were tested for corrosion inhibitory effects towards mild steel in 100 ppm sodium chloride solution. The anticorrosion efficiency of plant extracts was studied by means of weight loss, electrochemical polarization and impedance measurements. It was found from weight loss measurements that the corrosion inhibition efficiency was about 84% in 300 ppm of the plant extract. Polarization measurements indicated that the plant extract acted as anodic inhibitor. Electrochemical impedance results also showed that the plant extract increased the corrosion resistance of mild steel and the formations of iron-organic complex reduced the corrosion of mild steel in neutral system.

Keywords: *Ricinus communis,* corrosion inhibitor, mild steel, electrochemical impedance
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Most of the industrial cooling water systems in refineries, chemical processing plants, petrochemical and fertilizer industries use ground water for cooling purposes. Even though the inhibition properties of ATMP and HEDP along with zinc have been widely studied[1], it is now being phased out because of its carcinogenic properties. Hence, a need exists for finding the environmentally and eco-friendly formulations for the control of corrosion.

The corrosion inhibitive properties of *Cordia latifolia* and *Carcuniun*[2] were studied on mild steel. The inhibitive effects against aqueous extract of *Eucalyptus*, *Hibiscus* flowers and *Agaricus*[3] were studied against the corrosion of mild steel in tap water. The biocidal and inhibitive effects of aqueous extract of *Azadirachta indica* were reported by Mohanan *et al*.[4], in fresh water environment. *Swertia anrustifolia* was used as inhibitor in acid environment for mild steel[5]. The effect of *Acacia arabica*[6] on acid corrosion of mild steel suggested that with the increase in the concentration of additive, the inhibition also increased. Hence, in the present work it has been aimed to investigate the corrosion inhibition efficiency of *Ricinus communis* leaf extracts on mild steel. The corrosion inhibition property of the extract was evaluated by electrochemical studies and weight loss technique.

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Experimental Procedure

Preparation of specimens

The commercially available mild steel was used for the experiment. The elemental composition of mild steel is as follows: carbon 1-2, manganese 0.1-0.2, phosphorus 0.40-0.50, sulphur 0.02-0.03% and iron (reminder). For preparing the mild steel coupons, a cylindrical steel bar was cut into pieces having dimensions of 5 × 2 × 0.1 cm. The coupons were polished to mirror finish by using emery paper 1/0 to 4/0 and used for weight loss experiments. In addition, some specimens were mounted in araldite resin of the size of 1 cm^2 which were used for potential, polarization and impedance measurements.

Preparation of plant extracts

The leaves of *Ricinus communis* were collected and dried at room temperature. Air dried leaves were extracted with ethanol for 6 h. The extract was filtered and distilled at 70 – 80 °C, to remove ethanol. The concentrate thus obtained was used as the inhibiting agent. Concentration of the ethanolic extract and consequently cooling in the ice-chest deposited a small quantity of reddish brown coloured solid which was stored in refrigerator[7] for further use.

Preparation of test media

200 mL of 100 ppm sodium chloride solution was measured into four different beakers. The extract

solution of *Ricinus communis* leaves in concentrations of 100, 300 and 500 ppm was put separately in the first three beakers. Plant extract was not added to the fourth beaker, which was used as blank.

Weight loss method

Mild steel specimens of 5× 2× 0.1 cm dimensions were mechanically polished and degreased with trichloroethylene. Weighed coupons were fully immersed in each of the beakers containing 100 ppm sodium chloride solution with and without plant extract. Weight loss measurements were made after the immersion period of 4 days. The test specimens were taken out and washed with distilled water, rinsed with trichloroethylene, dried and reweighed. The percentage of inhibition efficiency *E* was calculated[8].

Electrochemical study

Potential measurements

Potential measurements were carried out, after the electrode had been immersed in the test solution. The basic solution had 100 ppm Cl^- to which the extracts were added in varying concentrations (100, 300 and 500 ppm) and potentials were measured. The potential[9,10] was recorded at four days interval using digital voltmeter and saturated calomel electrode as the reference electrode. The curves of variation of potential versus SCE against exposure time for the data obtained are given in Fig. 1.

Polarization measurements

The surface of the mild steel specimens (area, 1 cm^2) was mechanically polished and degreased with trichloroethylene. The working electrode was mild steel specimen (1 cm^2), the saturated calomel electrode and the platinum foil were used as reference and counter electrode, respectively. The basic solution consisted of 100 ppm Cl^- to which the extracts were added in varying concentrations as mentioned above and potential dynamic polarization curves were plotted using potential BAS-IM6 Electrochemical Analyzer USA Instrument with scanning rate of 1 mV versus SCE. Anodic and cathodic branches of polarization curves were recorded[4].

Impedance measurements

Impedance measurements[4] were carried out at open circuit potential (OCP) after the immersion of electrode in the test solution for 1 h. The frequency range studied was 10 kHz to 100 mHz using the BAS-IM6 Electrochemical Analyzer USA Instrument.

Results

Weight loss study

The results obtained for the variation of weight loss with exposure time for the steel specimens immersed in 100 ppm NaCl with the addition of varied concentrations of plant extract (100, 300 and 500 ppm) are presented in Table 1. The Table 1 shows that the corrosion rate with *Ricinus communis* extract, is in the range between 0.0100 and 0.0056 mmpy. On increasing the concentration of *Ricinus communis* extract to 300 ppm, the corrosion rate decreases to 0.0042 mmpy, the inhibition efficiency is 84%. In presence of 100 ppm of *Ricinus communis* extract, the corrosion rate is about 0.0100 mmpy and the inhibition efficiency is 62%, whereas 500 ppm concentration has given 78% of inhibition efficiency with the corrosion rate of 0.0056mmpy. The lower corrosion rate values are shown in 100 and 500 ppm solutions. So, the optimum concentration for this plant was found to be 300 ppm.

Table 1 — Corrosion rate and inhibition efficiency of mild steel in 100ppm NaCl in the presence of various plant extracts evaluated by weight loss methods

S.No.	System	Concentration of plant extract (ppm)	Corrosion-rate (mmpy)	Inhibition efficiency (%)
1	Control	------	0.0261	------
		100	0.0100	62
2	*Ricinus communis* leaves extract	300	0.0042	84
		500	0.0056	78

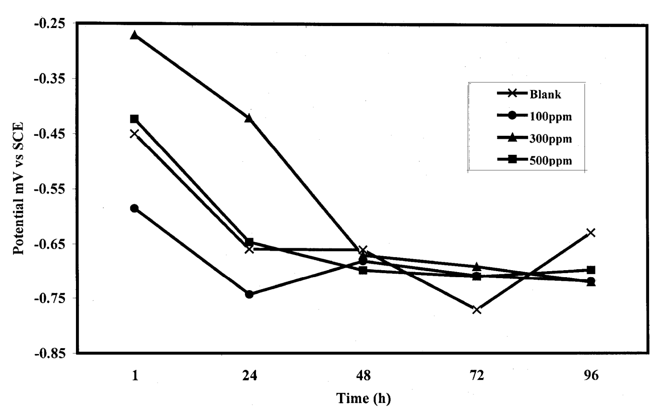

Fig. 1—Potential time behaviour of mild steel with *Ricinus communis* leaves extract and control system

Potential measurements

The potential behavior of mild steel in the presence and absence of plant extract is given in Fig. 1. The concentration used might be insufficient to create a stable passive film to inhibit corrosion of the mild steel in the test environment. All the curves show better performance in terms of potential values than the test without the plant extract addition, which has more negative potential values that range from -300 to -780 mV. In control system in presence of 100 ppm of NaCl, the initial potential was about –450 mV at the time of immersion and it shifted to –659, -660, -771 and -628 mV on the first, second, third and fourth days, respectively. In presence of plant extracts at 100 ppm concentration, the initial potential shifted from –585 to –715 mV up to 4 days. At 300 and 500 ppm concentrations the initial potential shifted from –271 to -720 mV and from –423 to –697 mV, respectively. The potential results indicated that the formation of film on the metal surface shift the potential to cathodic side with time, at various concentrations. The cathodic shift was due to the nature of adsorbed film on the metal surface. Regarding potential measurements, at 1 h the potential of control was about –471 mV versus SCE. But in presence of plant extract, the potential was shifted to positive about 100 mV versus SCE in the initial period.

Potentiodynamic polarization measurements

The potentiodynamic polarization measured in the presence and absence of inhibitor is shown in Figs 2 and 3(Table 2). In the presence of plant extract,

Table 2 — Anodic and cathodic current density, anodic and cathodic Tafel slope of mild steel in 100ppm NaCl in presence of various concentrations of plant extract evaluated by anodic polarization techniques

System	concentration (ppm)	Anodic potential (mV vs SCE)	Anodic current density (μA/ cm^2)	Anodic b_c (mV/dec)	Cathodic potential (mV vs SCE)	Cathodic current density (μA/ cm^2)	Cathodic b_c (mV/dec)
Control		-477	3.580	85	-490	2.670	71
Ricinus communis	100	-476	1.640	38	-466	1.450	41
	300	-355	0.166	20	-334	0.529	45
Leaves exract	500	-280	0.322	30	-301	0.834	58

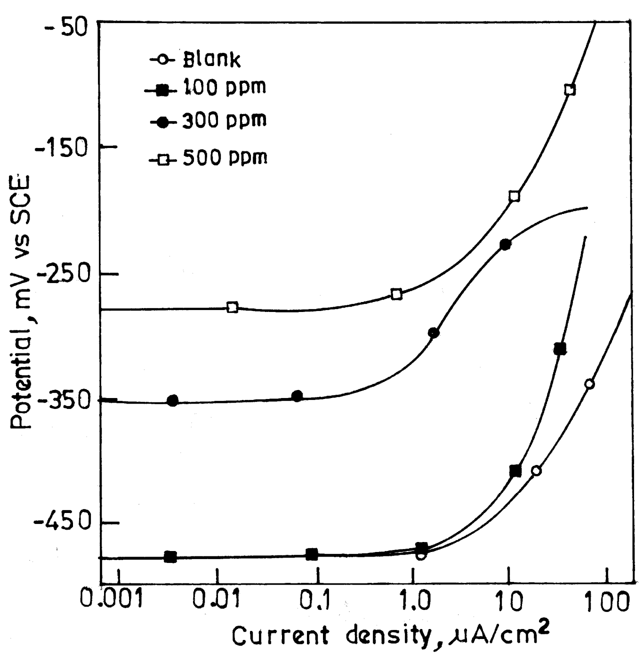

Fig. 2— Anodic potentiostatic polarization of mild steel in 100ppm sodium chloride containing various concentrations of *Ricinus communis* on 1st day

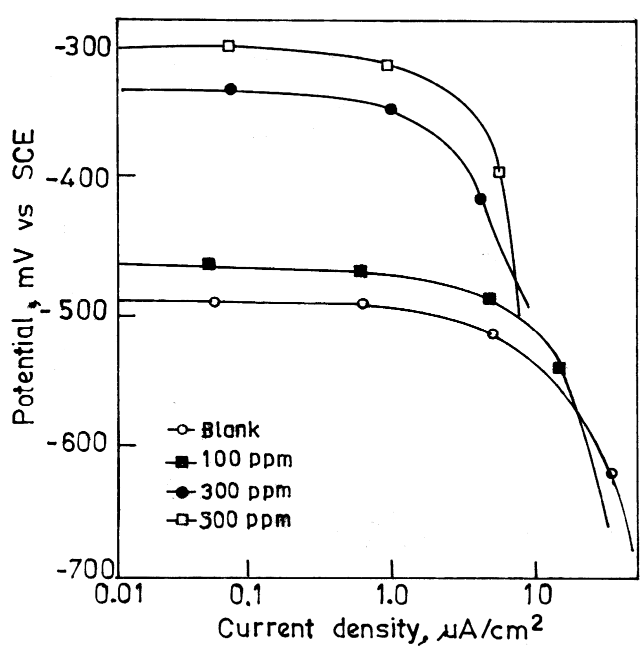

Fig. 3— Cathodic potentiostatic polarization of mild steel in 100ppm sodium chloride containing various concentrations of *Ricinus communis* leaves extract on 1st day

the curves have shifted to the low current region, thereby indicating that the extracts are corrosion inhibitive in nature. It can be seen from the Figs 2 and 3 that with the increase of inhibitor concentration the inhibition efficiency increases. The values of E_{corr} for extracts are shifted to the more negative direction, clearly indicating that the inhibition by *Ricinus communis,* in control, is anodic predominantly. Anodic curve reveals that the significant reduction of anodic current might be due to the adsorption of anodic inhibitors. In control system, the anodic current density was about 3.580 μA/cm^2 and cathodic current density was about 2.670 μA/cm^2. The anodic current density in 100 and 500 ppm was 0.322 A/cm^2 and 1.640 μA/cm^2, at 300 ppm the anodic current density was lower (0.166 μA/cm^2) when compared with other concentrations. The cathodic current density was 1.450 μA/cm^2 in 100 ppm, 0.529 μA/cm^2 in 300 ppm and 0.834 μA/cm^2 in 500 ppm. The cathodic current density was also lower at 300 ppm. The b_a and b_c values were also decreased by adsorption of inhibitor when compared to control. It reveals that the adsorbed species influence the electrochemical behaviour of mild steel in the initial stage polarization. It also reveals that plant extracts act as anodic as well as cathodic inhibitor. It is well known that plants have carbon, nitrogen, oxygen and phosphorus based organic compounds with calcium, magnesium and traces of metals like zinc, iron etc[7]. From Figs 2 and 3 it is clear that inhibitor acts as a mixed one, because its decreases both, anodic and cathodic current. The decrease in anodic reaction is likely to be related to adsorption of inhibitor on the surface of metal while decrease in cathodic current is likely to be related to the control of cathodic reaction in the solution. Because the plant extract is adsorbed on the metal surface and prevents the anodic reaction.

Impedance measurements

The results of impedance measurements are presented in Fig. 4 (Table 3). In 100 ppm and 300 ppm concentrations, the corrosion resistance values were 1.79 and 6.023 kohm.cm^2, respectively. However, plant extract offered good corrosion resistance value (4.069 kohm.cm^2) in 500ppm. The Cdl values for the 100, 300 and 500 ppm concentration of the plant extract of *Ricinus communis* were 140×10^{-5}, 7.8 × 10^{-5} and 6.9 × 10^{-5} μF, respectively. The surface coverage was noticed to be 0.56 for 500 ppm and 0.51 for 300 ppm. High resistance value of 6.023 kohm.cm^2 was observed in the presence of 300 ppm concentration of *Ricinus communis* extract system. The impedance curve reveals that the formation of film increases the resistance which is influenced by activation control.

Inhibitor efficiency

Results presented in the figures were obtained for the inhibitor efficiency of the plant extracts of different concentrations used. The inhibitor efficiency of 500 ppm concentrations of the leaves extract is very low. But 300 ppm of plant extract shows the higher inhibition efficiency. This is due to the availability of the plant extract, and also the induced

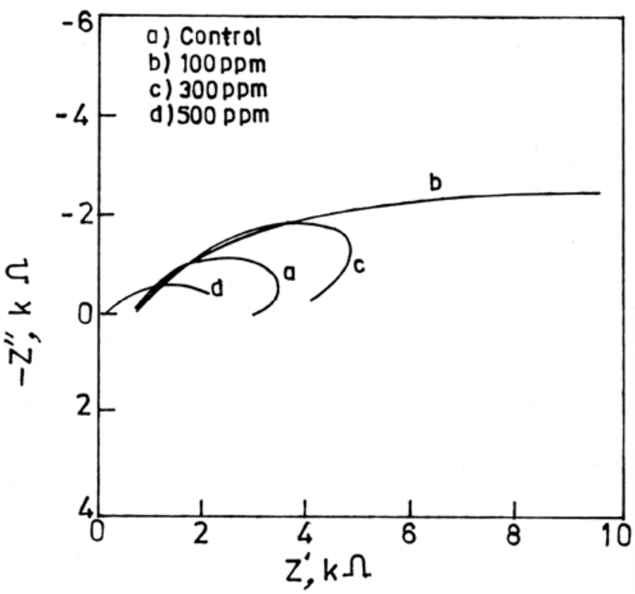

Fig. 4 —Nyquist plot of mild steel in 100ppm sodium chloride containing various concentrations of *Ricinus communis* leaves extract on 1st day.

Table 3 — Corrosion resistance and surface coverage of mild steel in 100ppm NaCl in presence of various plant extracts evaluated by impedance studies

System	Concentration ppm	R_t (Kohm.cm^2)	Cdl (μF/ cm^{-2}) 10^{-4}	Surface coverage θ
Control		2.750	16.0	---
	100	1.790	140.0	
Ricinus communis leaves extract	300	6.023	7.8	0.51
	500	4.069	6.9	0.56

component present in the plant extract, so that in 500 ppm concentration it gave lower corrosion efficiency.

Discussion

Polyphosphonates, phosphono carboxylic acid and polymers are used as inhibitors in neutral system. Zinc is also added with the phosphonate based inhibitors. However, the environmental pollution hazards and the risk of workers' safety have limited the use of the above mentioned inhibitors. Hence, non-toxic and easily degradable good inhibitors are needed for cooling water systems. The present study has been carried out to investigate the corrosion inhibition behaviour of non-toxic plant *Ricinus communis* on mild steel. The shifting of potential to negative side indicates the presence of cathodic inhibitor on mild steel coupons. At 300 ppm, the initial potential was in positive side when compared to control. It is also indicated that in the initial stage the absorbed film may act as anodic inhibitor. While increasing the concentration, the plant extract of *Ricinus communis* was found to give good inhibition efficiency. The inhibition efficiency of plant extract was found to be optimum in 300 ppm, concentration. The results obtained by weight loss study support the finding of Farrooqi *et al.*[12], who noticed that the inhibition efficiency of the inhibitors increased with increase in their concentration until maximum inhibition efficiency was obtained. *Pongamia glabra* was also found to give good inhibition efficiency at optimum concentration of 300 ppm[13]. Besides, Minhaj *et al.*[14], showed that the inhibition efficiency of all the extracts increased with the increase in extract concentration until optimum efficiency was obtained. An increase in the concentration of extract beyond optimum concentration reduced the inhibition efficiency, probably due to the solubility of already formed film. Polarization studies reveal that the anodic control is higher as compared to cathodic at various concentrations. So, it can be assumed that though plant extract acts as mixed inhibitor, anodic control is dominant. Since many plants have phosphorus, nitrogen with organic compounds, it suppresses the anodic reaction as well as cathodic reaction[7]. Farroqi *et al.*[2], discussed the potentiodynamic measurements and revealed that *Jasmium auriculatam* was anodic, while the extract of *Cardoa latifolia* was found to be cathodic. El-Etre and Abdulla[15] reported on the basis of potentiostatic techniques, that, natural honey changed the mechanism of cathodic reaction and did not affect the anodic dissolution mechanism for the corrosion of C-steel A 106. Further, they have suggested that the adsorption of natural honey on the steel surface was high in saline solution and obeyed Langmuir's adsorption isotherm. But in the present study the absorption of film on a specific area explains the chemisorption theory. Impedance curves reveal that the corrosion resistance of mild steel was higher in 300 ppm, which supports the observation made in the polarization studies and weight loss. The nature of the curve also indicated that activation control and followed by an inductive loop formation which was due to the adsorption of plant extract on the metal surface which behaved like a capacitance.

Conclusion

The maximum inhibition efficiency was obtained (85%) with in 300 ppm concentration of inhibitor. The inhibitive action of *Ricinus communis* leaves extract is due to the strong chemisorption of the phytochemical constituent of the extract, especially heterocyclic ingredients on the surface of the mild steel. From the electrochemical studies, it is evident that this eco-friendly biodegradable inhibitor acts through mixed mode of inhibition. Polarization curves show the anodic shift and impedance curves show the inductive loop. Hence, it can be concluded that the studied leaf extract of *Ricinus communis* possesses inhibitive property for the protection of mild steel in aqueous system.

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