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Inhibition Effect of Some Plant Extracts on The Corrosion of Mild Steel in H_2SO_4 Medium

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The inhibitive effect of extracts of *Cotula cinerae, Retama retam* and *Artemisia herba alba* plants on the corrosion of X52 mild steel in aqueous 20 % (2.3 M) sulfuric acid was investigated. Weight-loss determinations and electrochemical measurements were performed. Polarization curves indicated that the plant extracts behave as mixed-type inhibitors. The corrosion rates of steel and the inhibition efficiencies of the extracts were calculated. The results reveal that the extract solutions of the plants could serve as effective inhibitors for the corrosion of steel in sulphuric acid media. Inhibition rate was found to increase with increasing concentration of the plants extract up to an optimum concentration.

Key Words: Plant extract, Corrosion inhibition, Acidic media.

INTRODUCTION

Corrosion has always been regarded as costly problem to mitigate in any manufacturing, production and processing industries because of its pervasive nature. Use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions to prevent metal dissolution and acid consumption. The known toxic effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. Organic compounds containing nitrogen, sulfur and oxygen have been found to function as very effective corrosion inhibitors. The efficiency of these compounds as corrosion inhibitors can be attributed to the number of mobile electron pair present, the orbital character of free electrons and electron density around these atoms. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. Several investigations have been reported using such plant extracts.

The inhibitive action of the aqueous extract of the root of Shirsh El zallouh (*Ferula harmonis*) toward the corrosion of carbon-steel in HCl solution was investigated. The inhibition efficiency was measured using weight loss and potentiostatic polarization techniques. The electrochemical behaviour of the extract was investigated using cyclic voltammetry. It was found that the addition of the extract reduces the corrosion rate of carbon-steel[1].

The study of the inhibitive action of leaves, seeds and a combination of leaves and seeds extracts of *Phyllanthus amarus* on mild steel corrosion in HCl and H_2SO_4 solutions was carried out. The results indicate that the extracts functioned as a good inhibitor in both environments and inhibition efficiency increased with extracts concentration[2]. Raja *et al.*[3] investigated the corrosion inhibitive effect of the extract of black pepper on mild steel in 1 M H_2SO_4 media. The results revealed a good effectiveness against corrosion. The inhibition effect of *Zenthoxylum alatum* extract on the corrosion of mild steel in 5 and 15 % aqueous hydrochloric acid solution has been investigated by weight loss and electrochemical impedance spectroscopy. The corrosion inhibition efficiency increases on increasing plant extract concentration till 2400 ppm[4].

The inhibition efficiency of ethanolic extract of different parts of *Capparis decidua* on the corrosion of aluminium in acidic medium has been evaluated by mass loss and thermometric methods. Values of inhibition efficiency obtained from the two methods are in good agreement and are dependent upon the concentration of inhibitor and acid[5]. The effect of extracts of chamomile (*Chamaemelum mixtum* L.), halfabar (*Cymbopogon proximus*), black cumin (*Nigella sativa* L.) and kidney bean (*Phaseolus vulgaris* L.) plants on the corrosion of steel in aqueous 1 M sulphuric acid have been reported using electrochemical impedance spectroscopy and potentiodynamic polarization techniques[6]. The inhibitive effect of the extract of khillah (*Ammi visnaga*) seeds on the corrosion of SX 316 steel in HCl solution was determined using weight loss measurements as well as potentiostatic technique[7]. It was found that the presence of the extract reduces markedly the corrosion rate of steel in the acid solution. The inhibition efficiency increases as the extract concentration is increased.

In the present work, corrosion, inhibition of mild steel in 20 % H_2SO_4 by extracts of *Cotula cinerae* and *Retama retam* was evaluated using weight-loss determinations and electrochemical measurements methods.

EXPERIMENTAL

Plant extraction: 1 Kg of each plant material in natural condition was air dried for 10 days in shade. Then grained and powdered. 30 g of finely powdered dried material was taken in a 100 mL of double distilled water. The solution was left 48 h and then filtered. The concentration of the solution was determined by evaporating 10 mL of the filtrate under vacuum and weighing the residue.

Another solution containing 0.28 g of the plant extract dissolved in 100 mL of acidic solution (2800 ppm) was prepared and used to prepare other solution of different concentrations.

Preparation of specimens: Mild steel coupons having per cent composition of 0.971 Mn, 0.126 Si, 0.002S, < 0.002 P, 0.103 C, < 0.010 Cr, < 0.005 Mo and remaining Fe were used. The specimens were metallographically polished, degreased with trichloroethylene and washed with distilled water before experiment.

Electrolyte: The solutions were made using analytical reagent-grade H_2SO_4. Appropriate concentration of acid was prepared by using double distilled water. The concentration range of inhibitor (plant extract) employed was varied from 800 to 2800 ppm and the electrolyte used was 200 mL.

Weight loss method: Weight loss of rectangular steel specimens of size 1 cm × 5 cm × 2 cm immersed in 200 mL of electrolyte with and without the addition of different concentrations of plant extract was determined after 1 h at room temperature. The results of mass loss experiments are the mean of three runs, each with fresh electrolyte and fresh metal sheet.

The corrosion rate in mmpy (millimeter per year) can be obtained by:

$$\text{Corrosion rate (mmpy)} = (\text{Mass loss} \times 87.6) / (\text{Area} \times \text{Time} \times \text{Metal density})$$

where mass loss is expressed in mg, area is expressed in cm^2 of exposed metal surface, time is expressed in hours of exposure, metal density is expressed in g/cm^3 and 87.6 is a conversion factor.

The percentage inhibition efficiency (IE) was calculated from the equation:

$$\text{IE (\%)} = [(CR_i - CR_f) / CR_i] \times 100$$

where CR_i and CR_f are corrosion rates of steel in uninhibited and inhibited solutions.

Electrochemical method: Electrochemical tests and polarization curve measurements were achieved using a potentiostat/galvanostat PGP201. Metal electrodes were polished with different grades of emery papers, degreased with acetone and rinsed by distilled water before being immersed in the test solution.

A three-compartment cell, with a saturated calomel reference electrode (SCE) and a platinum foil auxiliary electrode, was used. The inhibition efficiency was in the same way as above.

RESULTS AND DISCUSSION

The inhibition efficiency (%) calculated from the corrosion rates in sulphuric acid without and with inhibitors are given in Tables 2-4. It is observed that the inhibition efficiency increases with increasing inhibitor concentration up to an optimum. Each plant extract has shown the maximum efficiency in the chosen concentration range. *Cotula cinerae* extract shows minimum 41.74 % inhibition efficiency at 800 ppm and maximum 94.65 % at 1600 ppm. *Retama reatam* extract shows minimum 78.14 % inhibition efficiency at 800 ppm and maximum 93.24 % at 2000 ppm. *Artemisia herba alba* extract shows minimum 80.59 % inhibition efficiency at 800 ppm and maximum 88.37 % at 2400. *Rosmarinus officinalis* extract shows inhibition efficiency minimum 65.02 % at 800 ppm and maximum 92.62 % at 1600 ppm. The *Cotula cinerae* extract has showed the best corrosion inhibition with respect to the other extracts.

Similar curves were also obtained for the remaining two extracts and they are not shown here because they all have the same general feature. Fig. 1 indicates that both anodic and cathodic potentials increase slightly at the low values of applied current density. At this stage, both cathodic and anodic reactions are established.

TABLE-1
CORROSION RATES (CR), mmpy AND INHIBITION EFFICIENCIES FOR THE TESTED EXTRACTS AS REVEALED FROM WEIGHT LOSS MEASUREMENTS
CORROSION RATE WITHOUT INHIBITOR CR_i = 33,5611 mmpy

Concentration (ppm)	*Cotula cinerae*		*Retama reatam*		*Artemisia herba alba*	
	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)
800	7.2384	78.43	7.3344	78.14	6.5112	80.59
1200	4.5214	86.52	7.2326	78.44	5.7266	82.93
1600	1.7928	94.65	6.0377	79.78	4.9837	85.15
2000	4.8975	85.40	2.2686	93.24	4.2317	87.39
2400	5.2130	84.46	3.8636	88.48	3.9003	88.37
2800	7.1358	78.73	3.8748	88.45	5.3469	84.06

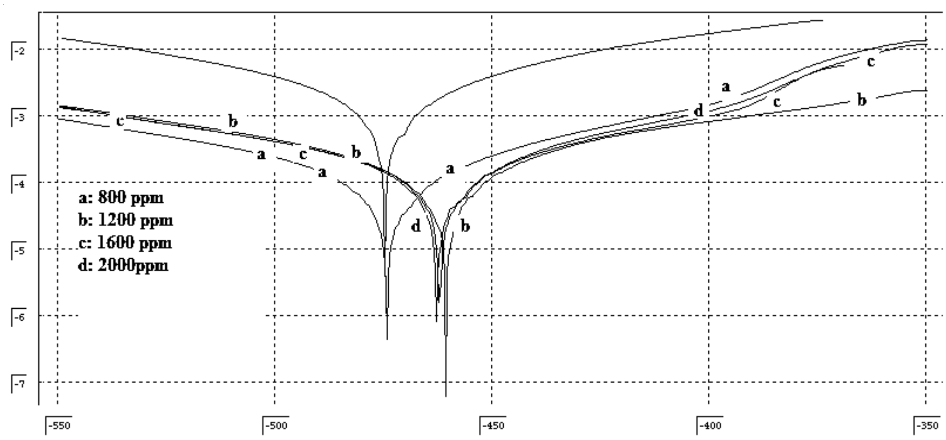

Fig. 1. Represents the anodic and cathodic polarization curves of carbon-steel X52 in 20 % sulfuric acid solutions devoid of and containing different concentrations of *Cotula cinerae* extract

This region of the polarization curve is known as the pre-Tafel region. As the applied anodic or cathodic current is increased further, one of the two reactions becomes predominant and the variation of potential becomes higher and thus the Tafel region is obtained.

A number of conclusions could be drawn on reading the data of the above tables. The corrosion potential is shifted toward less active values as the added concentration of plant extract is increased. On the other hand, the corrosion current decreases as the added extract concentration is increased. The calculated inhibition efficiencies are more or less comparable to those obtained by weight loss experiments. Moreover, the addition of plant extracts changes slightly both the anodic and cathodic Tafel constants. However, in few cases the Tafel constants are remarkdly changed. This results indicate that plant extract acts as mixed corrosion inhibitor. It could also be concluded that the presence of plant extract does not change the corrosion mechanism in most tested cases.

TABLE-2
ELECTROCHEMICAL PARAMETERS OF CARBON-STEEL CORROSION WITH *Cotula cinerae* EXTRACT

Concentration (ppm)	E_{corr} (mV)	I_{corr} (mA/cm^2)	Ba (mV)	Bc (mV)	CR (mmpy)	EI (%)
000	-473.6	2.8963	99.1	-89.0	33.880	00.00
800	-459.3	0.2192	109.7	-97.5	2.565	92.42
1200	-461.5	0.1390	67.6	-94.7	1.626	95.20
1600	-472.9	0.1275	70.8	-90.2	1.492	95.59
2000	-460.9	0.1411	74.5	-94.4	1.651	95.12

TABLE-3
ELECTROCHEMICAL PARAMETERS OF CARBON-STEEL CORROSION WITH *Retama* EXTRACT

Concentration (ppm)	E_{corr} (mV)	I_{corr} (mA/cm^2)	Ba (mV)	Bc (mV)	CR (mmpy)	EI (%)
000	-473.6	2.8963	99.1	-89.0	33.880	00.00
800	-443.7	0.1757	54.6	-105.9	2.056	93.93
1200	-468.3	0.1477	83.3	-95.4	1.728	94.89
1600	-472.1	0.1366	110.5	-101.6	1.598	95.28
2000	-476.0	0.1338	93.9	-88.0	1.565	95.38

TABLE-4
ELECTROCHEMICAL PARAMETERS OF CARBON-STEEL CORROSION WITH *Artemisia* EXTRACT

Concentration (ppm)	E_{corr} (mV)	I_{corr} (mA/cm^2)	Ba (mV)	Bc (mV)	CR (mmpy)	EI (%)
000	-473.6	2.8963	99.1	-89.0	33.880	00.00
800	-484.6	0.2129	117.4	-344.5	4.954	85.37
1200	-420.3	0.0832	34.4	-49.5	1.936	94.20
1600	-447.3	0.1324	74.2	-108.4	1.567	95.37
2000	-434.1	0.0486	50.4	-54.7	0.576	98.29

Conclusion

The plant extracts of *Cotula cinerae*, *Retama retam* and *Artemisia herba alba* can be used as excellent corrosion inhibitors for steel in acidic medium at room temperature. To obtain the maximum protection efficiency, critical plant extract concentration should be determined. The inhibition mechanism depends on the formation of a stable plant extract-complex on the steel surface. Polarization studies reveal that the extracts behave as mixed type inhibitors.

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