

CAPPARIS DECIDUA SEEDS: POTENTIAL GREEN INHIBITOR TO COMBAT ACID CORROSION OF COPPER

Prassan Singh Pratihar, Monika, P. S. Verma and Alka Sharma*

Centre of Advanced Study, Department of Chemistry, University of Rajasthan, Jaipur

*E-mail: sharma_alka21@yahoo.com

ABSTRACT

Inhibitory efficiency of Ethanolic Extract of *Capparis decidua* Seeds (EECdS) towards corrosion of Copper corrosion in 0.5 M hydrochloric acid at 303 ± 1 K was studied employing weight loss measurements, electrochemical polarization technique and electrochemical impedance spectroscopy. Maximum inhibition efficiency of *Capparis decidua* seed-extract was found to be 94.60% at 1.0426 g/L for 72 hours of immersion period. The inhibition efficiency (IE %) was found to increase with the increase in extract concentration. The adsorption of EECdS over copper coupon surface followed Langmuir adsorption isotherm at the studied temperature. The results obtained showed that the extract of EECdS can be used very effectively as an environmentally friendly, low cost inhibitor to combat corrosion of copper in 0.5 M HCl.

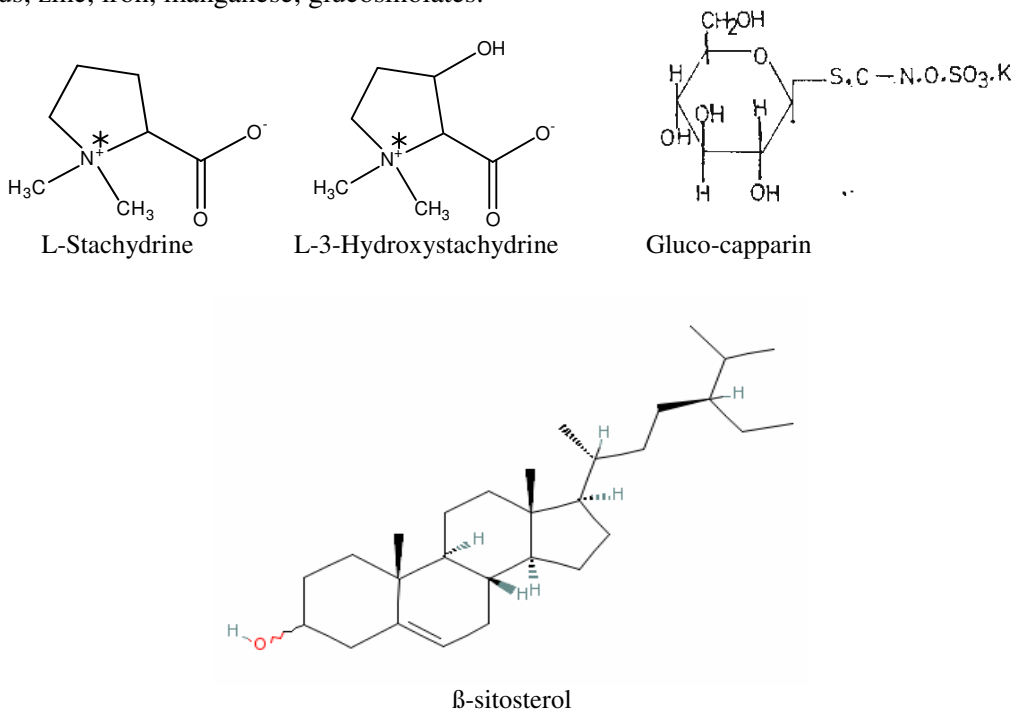
Keywords: Corrosion inhibition, *Capparis decidua*, electrochemical impedance spectroscopy, SEM

©2015 RASAYAN. All rights reserved

INTRODUCTION

Copper is a very important metal because it has a wide range of applications due to its good properties like its excellent heat conductivity and good corrosion resistance in water. Copper is an industrially important metal because it is used in electronics, for production of wires, sheets, tubes, heating and cooling systems, condensers and also to form various alloys. In heating and cooling systems, condensers, there is deposition of carbonates and oxides, which decreases the heating transmission.¹ To overcome this problem these systems should be regularly cleaned to descale. Diluted hydrochloric acid is used to clean such surfaces. Copper is resistant toward the influence of atmosphere and many chemicals, but in aggressive media it is susceptible to corrosion. In such conditions it is necessary to stop corrosion of copper. We have to use copper corrosion inhibitors because no protective passive layer is possible. To inhibit copper corrosion in such solutions small amounts of corrosion inhibitor can be used to reduce corrosion rates.² In the past various organic and inorganic corrosion inhibitors were used but these are toxic and costly. The presence of large molecules with functional groups containing of heteroatom (such as oxygen, nitrogen, sulphur, and phosphorus), triple bonds or aromatic rings in the inhibitor's chemical structure enhance the adsorption process.³ Nowadays, the research has been carried out for extraction of compounds which are non toxic, natural and environmentally friendly inhibitors such as *Prosopis juliflora*, *Rosamarinus officinalis* L., *Hibiscus Rosa-sinensis*, *Nympha fructicans*, red onion skin, *Allium cepa* and *Allium sativum*, *Vernonia amygdalina*, *punica granatum*, *vitis vinifera*, *Piper nigrum*, etc.⁴⁻¹³ Different compounds and extract have been used for inhibition of copper corrosion as *N*-phenyl-1,4-phenylenediamine, Pyridazine Derivatives, 1,3,4-Thiadiazole-2,5-Dithiol, Dithiobiurets, *Embblica Officinalis*, *Vitis vinifera*.¹⁴⁻²¹ *Capparis decidua* belongs to capparidaceae family, locally known as Kair it is found in India, Pakistan, Arabia, Egypt North and Tropical Africa. The plant is commonly known as Caper berry in English, Karira in Sanskrit, Kerada in Gujarati, Karer or Kurrel in Hindi. The plant is a large, climbing, thorny shrub, densely branched, spinous shrub or tree, up to 6 meters in height (rarely 10 meters), with a clear bole of 2.4 meters. Tender branches with waxy bloom; bark grey, rough and corky, covered with straight or recurved, 3-7 mm long, paired thorns; leaves on young branches, caduceous, linear, 1-2 cm long, apex short, stiff, pale mucro like pickle, petioles very short, stipular thorns long, sharp, straight orange yellow, seeds globose, 2-5 mm in diameter dried seeds are reniform, 4-5 mm in

length, 3-4 mm in width, 1.5- 2 mm in thickness, covered with greyish white fleshy aril.²² The flowers, fruits, and seeds contains n-pentacosane, n-triacontane,²³ n-triacontanol, L-Stachydrine, Gluco-capparin, L-3-Hydroxystachydrine 2-carboxy-1,1-dimethylpyrrolidine, 6-(1-hydroxy-non-3-enyl) tetrahydropyran-2-one, β -sitosterol, β -carotene, ascorbic acid, proteins, total carbohydrates, calcium, potassium, phosphorus, zinc, iron, manganese, glucosinolates.²⁴⁻²⁶



EXPERIMENTAL

Preparation of extract

Seeds of *Capparis decidua* in natural condition were air dried in shade. The finely powdered dried material was soaked in sufficient quantity of distilled ethyl alcohol for desired period. It was later refluxed and the concentration of EECdS per ml was evaluated as per standard procedure.¹²

Specimen preparation

The rectangular coupons of copper of dimensions (3cm \times 2.4cm \times 0.16cm) were used with a small hole of 2mm diameter near upper edge for hanging in test media. Each coupon was surface treated prior to each experiment, as per standard procedure,¹² and kept in desiccators.

Test Solution

AnalR grade HCl was used and 0.5 M solution was prepared by using doubly distilled water.

Weight loss method

In weight loss method the surface treated Cu coupons were dipped in beakers containing various concentrations of inhibitor in aggressive medium. Concentrations of inhibitor were in the range of 0.0744 to 1.0426 g/L marked as (C1, C2, C3, C4, C5 and C6). From the weight loss method, the Inhibition efficiency and Corrosion rate of copper were calculated using equations (1 and 2).

$$\%I.E. = \frac{(W_1 - W_2)}{W_1} \times 100 \quad (1)$$

$$\text{Corrosion Rate (mm}^{-1}\text{)} = 87.6 \times \Delta W / DA \quad T \quad (2)$$

where W_1 and W_2 are weight loss of copper in absence and presence of the inhibitor respectively, A is surface area in cm^2 , D (8.933 gcm^{-3}) is density of metal and T is time period in hours (h) and $\Delta W = W_1 - W_2$ (loss in weight).

Electrochemical Measurements

The electrochemical measurements – potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements were carried out employing CHI760D Electrochemical workstation Instrument, USA. Copper with an exposing surface area of 1 cm^2 to the electrolyte was used as working electrode (WE), Pt as the auxiliary electrode (CE), and saturated calomel electrode (SCE) as the reference electrode (RE).

EIS was carried out with the open circuit potential EOCV for each sample. Coupons were immersed for 30 min over a frequency range of 100 kHz to 10 m Hz with signal amplitude 5 mV and scan rate 2 mVs^{-1} . The value of R_{ct} was calculated from plot and the inhibition efficiency, IE, was calculated by the following equation (3).

$$\% \text{I.E.} = \frac{R_{ct\text{inh}} - R_{ct}}{R_{ct\text{inh}}} \times 100 \quad (3)$$

where R_{ct} and $R_{ct\text{inh}}$ refer to charge transfer resistance without and with the addition of an inhibitor. Before each measurement, the surface treatment was given to the electrode similar to weight loss experimentation.

Surface morphological analyses

Surface morphological analyses of the coupons were carried out by SEM with S-3400 Hitachi (Japan). Besides, the adsorptive propensity of the active constituents was assessed by carrying out FT-IR spectroscopy employing FTIR spectrometer (8400s Shimadzu, Japan).

RESULTS AND DISCUSSION

Weight Loss Measurements

i. Additive effect on Corrosion rate

The various corrosion parameters were evaluated from the weight loss data, viz., corrosion rate (mm^{-1}), Fractional Surface coverage (θ), Adsorption Equilibrium Constant (K_{ad}) and inhibition efficiency (%) for copper coupon immersed in different concentrations of inhibitor (EECdS) for various immersion periods in 0.5M HCl. The results have been tabulated in Table–1.

Fig-1, clearly illustrated that the corrosion rate of copper decreases in the presence of EECdS as compared to the blank (i.e. without inhibitor). In aggressive medium, without additive, it was found to rise from 0.7499 mm^{-1} to 2.3772 mm^{-1} when copper coupons were immersed for longer period (3 hours to 72 hours). The corrosion rate was found to be minimum (0.1284 mm^{-1}) in presence of additive (EECdS) (1.0396 g/L) immersed for 72 hours. Thus, clearly depicting a strong inhibitive propensity of the additive towards acid corrosion of copper.

ii. Additive-concentration on inhibition efficiency (IE %)

Table–1 and. Fig–2 clearly depicts an increase in inhibition efficiency (IE %) with increasing concentration of the EECdS. The maximum IE % (94.60 %) was observed at 1.0426 g/L of EECdS at 72 hours immersion period in 0.5 M HCl. It was also observed that IE % was high at higher concentration of EECdS for the entire range of immersion periods. Figs. 2 & 3, also illustrates that at lower immersion period and lower concentration of inhibitor, an irregular trend for IE (%) was observed; but at higher immersion period, IE (%) showed a linear relation with extract concentration. This may be due to insufficient EECdS concentration (at its lower value) to cover the active sites of the metal surface, while with an increase in EECdS concentration lead to a uniform adsorption and forms protective film over the surface of coupon. This was further endorsed by applying the experimental data on various adsorption isotherms and Langmuir Adsorption Isotherm was found to be the best fitted.

Table-1: Corrosion Parameters of acid corrosion of Copper without and with different concentrations of EECdS for various Immersion time (h) at room temperature.

Immersion period (h)	Concentration of inhibitor (g/L)	Corrosion parameters				
		Weight loss ($\times 10^{-3}$ g)	Corrosion rate (ρ_{corr}) ($\times 10^{-2}$ mmy $^{-1}$)	Inhibition efficiency (IE %)	Fractional surface coverage (θ)	Adsorption equilibrium constant (K_{ad})
3	C0 Blank	3.7	74.99	-	-	-
	C1 (0.0744)	2.9	58.78	21.62	0.2162	3.71
	C2 (0.1488)	1.8	36.48	51.35	0.5135	7.09
	C3 (0.2232)	2.5	50.67	32.43	0.3243	2.15
	C4 (0.4464)	1.5	30.4	59.46	0.5946	3.29
	C5 (0.6696)	1.2	24.32	67.57	0.6757	3.11
6	C6 (1.0426)	1	20.27	72.97	0.7297	2.59
	C0 Blank	5.6	56.75	-	-	-
	C1 (0.0744)	2.7	27.36	51.79	0.5179	14.44
	C2 (0.1488)	2.5	25.33	55.36	0.5536	8.33
	C3 (0.2232)	2.1	21.28	62.50	0.6250	7.47
	C4 (0.4464)	2	20.27	64.29	0.6429	4.03
12	C5 (0.6696)	1.8	18.24	67.86	0.6786	3.15
	C6 (1.0426)	1.2	12.16	78.57	0.7857	3.52
	C0 Blank	11.2	56.75	-	-	-
	C1 (0.0744)	4.2	21.28	62.50	0.6250	22.40
	C2 (0.1488)	4.1	20.77	63.39	0.6339	11.64
	C3 (0.2232)	5.1	25.84	54.46	0.5446	5.36
18	C4 (0.4464)	4.4	22.29	60.71	0.6071	3.46
	C5 (0.6696)	3.2	16.21	71.43	0.7143	3.73
	C6 (1.0426)	2.3	11.65	79.46	0.7946	3.71
	C0 Blank	18.2	61.48	-	-	-
	C1 (0.0744)	8.1	27.36	55.49	0.5549	16.76
	C2 (0.1488)	8	27.02	56.04	0.5604	8.57
24	C3 (0.2232)	7.5	25.33	58.79	0.5879	6.39
	C4 (0.4464)	6.2	20.94	65.93	0.6593	4.34
	C5 (0.6696)	5.3	17.9	70.88	0.7088	3.63
	C6 (1.0426)	3.5	11.82	80.77	0.8077	4.03
	C0 Blank	35.1	88.92	-	-	-
	C1 (0.0744)	19.5	49.4	44.44	0.4444	10.75
48	C2 (0.1488)	12.4	31.41	64.67	0.6467	12.30
	C3 (0.2232)	9.2	23.31	73.79	0.7379	12.61
	C4 (0.4464)	7.3	18.49	79.20	0.7920	8.53
	C5 (0.6696)	7.1	17.99	79.77	0.7977	5.89
	C6 (1.0426)	4.4	11.15	87.46	0.8746	6.69
	C0 Blank	154	195.08	-	-	-
72	C1 (0.0744)	48.2	61.06	68.70	0.6870	29.50
	C2 (0.1488)	32.9	41.68	78.64	0.7864	24.74
	C3 (0.2232)	22.4	28.37	85.45	0.8545	26.32
	C4 (0.4464)	15.2	19.25	90.13	0.9013	20.46
	C5 (0.6696)	12.1	15.33	92.14	0.9214	17.51
	C6 (1.0426)	8.4	10.64	94.55	0.9455	16.63
72	C0 Blank	281.5	237.72	-	-	-
	C1 (0.0744)	134.4	113.5	52.26	0.5226	14.71
	C2 (0.1488)	74.9	63.25	73.39	0.7339	18.54
	C3 (0.2232)	43.1	36.4	84.69	0.8469	24.78
	C4 (0.4464)	31.4	26.52	88.85	0.8885	17.84
	C5 (0.6696)	21.5	18.16	92.36	0.9236	18.06
	C6 (1.0426)	15.2	12.84	94.60	0.9460	16.80

iii. Effect of immersion period (h) on Inhibition efficiency (IE %)

The effect of immersion period (h) on inhibitive efficacy of EECdS was investigated in aggressive medium (0.5 M HCl) without and with various concentration of additive at room temperature. The stability and the adsorptive ability of the active constituents of the inhibitor were assessed at temperature at different immersion period (h). Fig.-3 depicts that inhibition efficiency increased initially up to 6 h and thereafter attaining stability, it gains maximum value (94.60 %) at 72 h.

The increase in inhibition efficiency reflects the adsorption of active constituents of the extract onto the metal surface, resulting formation of a protective layer over copper-coupon surface (as barrier at coupon-solution interface), and thus hinders the aggressive media molecules (hydrochloric acid solution) to reach the metal surface. This is an indication that the mass loss is sensitive to the concentration of the EECdS extract. The adsorption and surface coverage (θ) of the metal was also found to increase linearly with concentration of the inhibitor, it further endorse that the surface of the copper is more effectively separated from the corrosive medium in presence of additive.

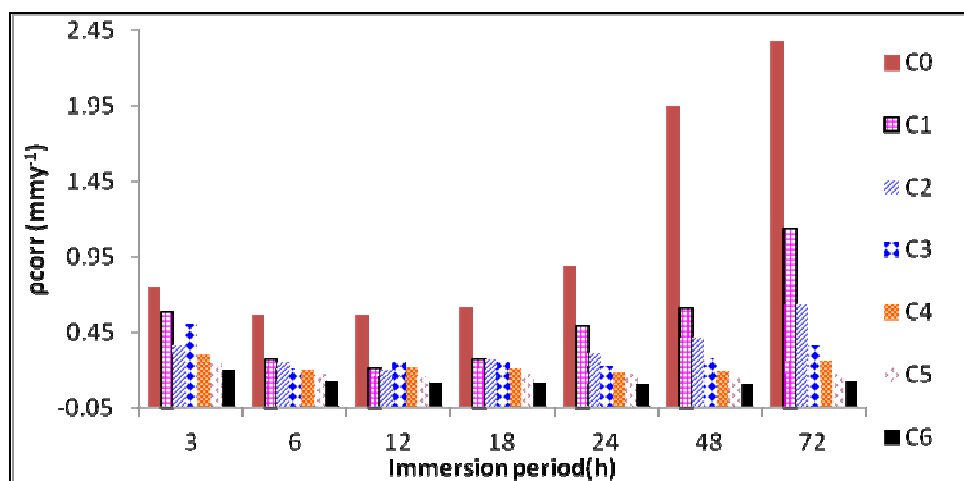


Fig.-1: Corrosion rate (ρ_{corr}) ($\text{mm}\cdot\text{y}^{-1}$) vs Immersion period (h) without and with different concentrations of EECdS

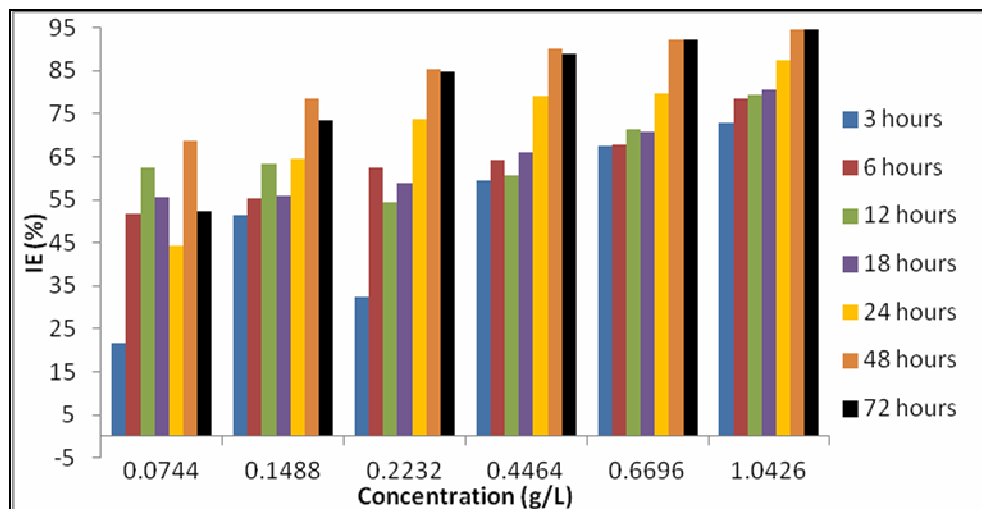


Fig.-2: Inhibition efficiency (IE %) v/s various concentrations of EECdS at different Immersion period (h)

iv. Adsorption considerations

Adsorption isotherms are usually used to describe the adsorption process. The adsorption of EECdS extract molecules was mainly due to the adsorption and the interaction between the adsorbed molecules was ignored. Various adsorption isotherms were tested to fit in the experimental data and Langmuir adsorption isotherm was observed to be the best fitted. Langmuir isotherm, expressed as:

$$C/\theta = 1/K_{\text{ads}} + C \quad (4)$$

where θ is the degree of surface coverage, C the molar inhibitor concentration in the bulk solution and K_{ads} is the equilibrium constant of the process of adsorption. The plot of C/θ versus C was linear. Plot of C/θ against C as shown in Figure-4 gave straight lines which clearly show that copper corrosion inhibition in 0.5 M HCl by EECdS at room temperature studied obeys Langmuir adsorption isotherm.

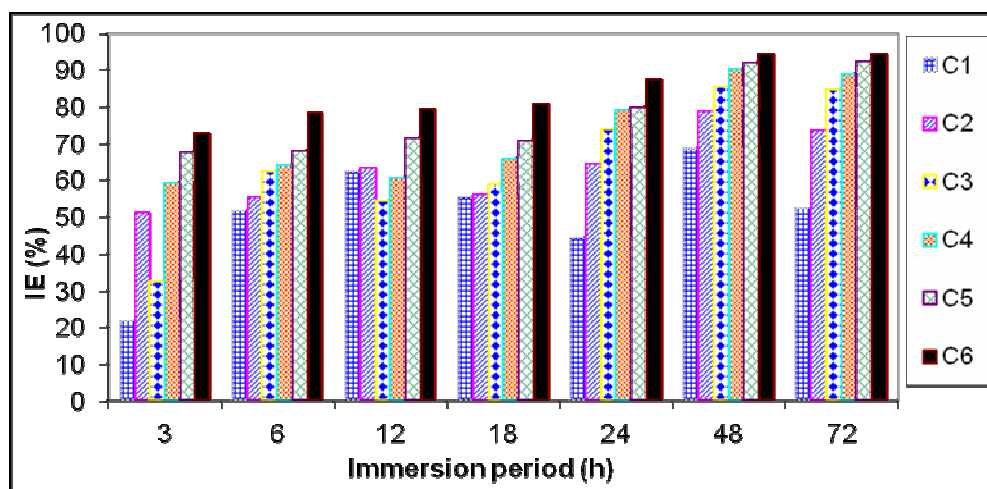


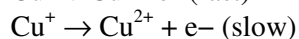
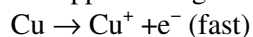
Fig.-3: Inhibition efficiency (IE %) v/s Immersion period (h) with various concentrations of EECdS

The correlation coefficient, slopes, and adsorption coefficients obtained from Langmuir isotherm plots are shown in Table-2. The free energy of adsorption, ΔG_{ads} , is associated with water adsorption equilibrium. ΔG_{ads} was calculated from the relation in equation- 5.

$$K = 1/(55.5) \exp^{(-\Delta G_{\text{ads}}/RT)} \quad (5)$$

The negative value of ΔG_{ads} , here indicate that the adsorption process on copper surface is spontaneous. The correlation coefficient (R^2) and slope obtained was nearly equal to unit. The ΔG_{ads} values were higher than -20 kJ/mole, indicating physical adsorption.

According to E.M. Sherif, Su-Moon Park,²⁶ the anodic reaction at HCl, less than 1.0 M, is the dissolution of copper through oxidation of Cu(0) to Cu^+ , then Cu^+ to Cu^{2+} :

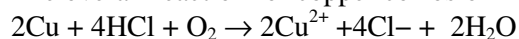


As Cu^+ reacts faster with Cl^- than Cu^{2+} forming CuCl , $[\text{Cu}^+ + \text{Cl}^- \rightarrow \text{CuCl}]$, which has poor adhesion and is unable to provide enough protection for the copper surface, thus transforms to a soluble cuprous chloride complex, CuCl_2^- $[\text{CuCl} + \text{Cl}^- \rightarrow \text{CuCl}_2^-]$.

The anodic dissolution of copper is thus controlled by both electrodisolution of copper and diffusion of CuCl_2^- to the bulk solution. Insoluble CuCl precipitates on the copper surface in the presence of Cl^- and acts as a protective barrier safeguarding copper from its further oxidation. In acidic solutions, the adsorbed CuCl layer is destroyed. It has also been reported that if this CuCl_2^- is adsorbed on the surface its dissolution will occur as follows:



The overall reaction for copper corrosion in an acidic chloride solution is represented as-



Electrochemical Measurements

i. Potentiodynamic Polarization

The potentiodynamic polarization curves of Copper in 0.5M HCl in the absence and presence of different concentrations of EECdS were recorded (figure-5). The electrochemical corrosion kinetic parameters,

corrosion potential E_{corr} , cathodic and anodic Tafel slopes (β_c and β_a) and corrosion current density I_{corr} obtained from the Tafel polarization curves and results were tabulated in Table-3. The %IE is defined as:

$$\% \text{IE} = \frac{(I_{\text{corr}}^0 - I_{\text{corr}}) \times 100}{I_{\text{corr}}} \quad (6)$$

where I_{corr}^0 and I_{corr} are the corrosion current density values without and with inhibitor, respectively. The polarization resistance (R_p) was calculated from the linear I-E plots. It can be seen from polarization results that the I_{corr} values decreases R_p increases considerably in the presence of inhibitor. The corrosion current density was calculated from Stern-Geary equation^{21, 40} (as expression – 7 below):

$$I_{\text{corr}} = \beta_a \beta_c / 2.3 R_p (\beta_a + \beta_c) \quad (7)$$

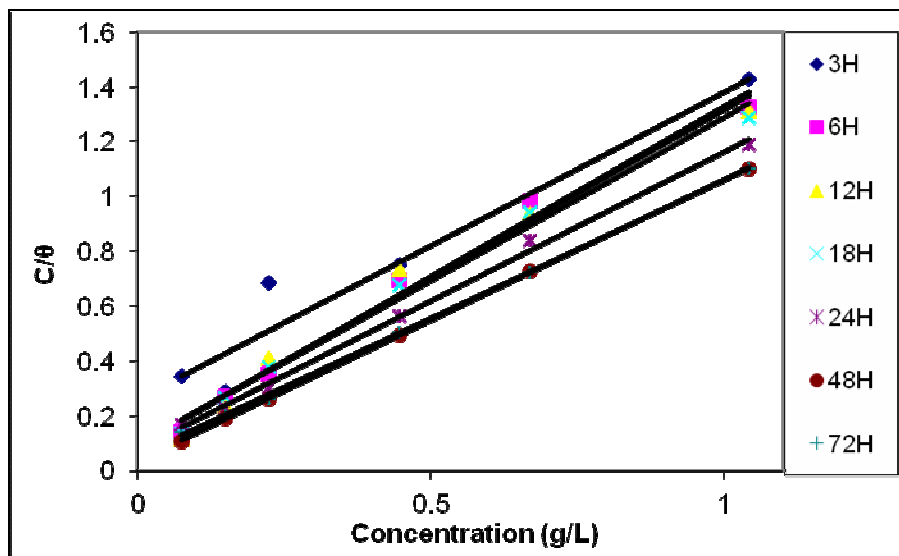


Fig. -4: Langmuir adsorption Isotherm

Table-2: Langmuir Adsorption Isotherm parameter: Correlation coefficient (R^2), slopes and ΔG_{ads}

Time (h)	Slope	R^2	K_{ad}	ΔG_{ads} (KJmol ⁻¹)
3	1.116	0.943	3.79	-13.4753
6	1.239	0.988	10.99	-16.1589
12	1.221	0.979	10.64	-16.0771
18	1.192	0.989	10.31	-15.998
24	1.086	0.997	12.99	-16.5798
48	1.027	0.999	29.41	-18.6394
72	1.002	0.999	18.52	-17.4738

Table-3 shows that Corrosion current rate decreases with increasing concentration of inhibitor EECdS. Maximum inhibition efficiency (51.11%) was observed at C6 (1.0426 g/L). From fig. 5 and table 3, it is clear that both the rate of cathodic and anodic reactions are reduced as the concentrations of inhibitor increased by reducing the current densities on both sides of the polarization curves. The illustrations in fig-5 and results of table-3 also endorse shift in polarization from negative to more positive potential with increasing concentration of inhibitor thus, indicating the inhibitor as an anodic inhibitor. Besides, the shift in the anodic Tafel slopes of the tests with different concentrations of extract is higher than the shift in the cathodic Tafel slopes, also indicate that the decrease in the oxidation rate of the metal with increasing extract concentrations corresponds to the relative drop in the corrosion rate.

ii. Electrochemical Impedance Measurements

The inhibitory effect of additive towards the copper-corrosion in 0.5 M HCl was investigated by employing EIS technique at 298 ± 1 K. Nyquist plots (fig. 6) illustrated that the impedance response of copper is significantly changed after the addition of EECdS. The charge transfer resistance (R_{ct}) and the double layer capacitance (C_{dl}) values were derived using the Nyquist plots and the Impedance parameters were tabulated in table-4. The Nyquist plots (Fig-6) shows semicircles with single capacitive loop and increasing diameter as the concentration of the plant extract increases. With an increase in the concentration of EECdS, the value of R_{ct} was observed to increase, thus indicate a charge-transfer process is controlling the corrosion of copper. The decrease in double layer capacitance (C_{dl}) values with an increase in the inhibitor concentration depict that the active constituents of extract were adsorbed over the metal surface (table-4). In the presence of inhibitor, the charge transfer resistance (R_{ct}) values were increased and the corrosion rates were reduced, thus confirming good inhibitive efficacy of EECdS towards acid corrosion of copper.

Table-3: Electrochemical and corrosion parameters for Copper without and with various concentrations EECdS in 0.5 M HCl

Concentration (g/L)	E_{corr} (-mV)	β_c (-mV/dec)	β_a (mV/dec)	R_p (Ωcm^2)	I_{corr} (mAcm^{-2}) ($\times 10^{-2}$)	%IE
C0 (blank)	152	46.02	71.42	421.36	2.88	
C2 (0.1488)	157	48.23	39.89	483.27	1.96	31.98
C4 (0.4464)	131	24.56	63.04	502.9	1.53	47.09
C6 (1.0426)	155	27.23	56.47	565.79	1.41	51.11

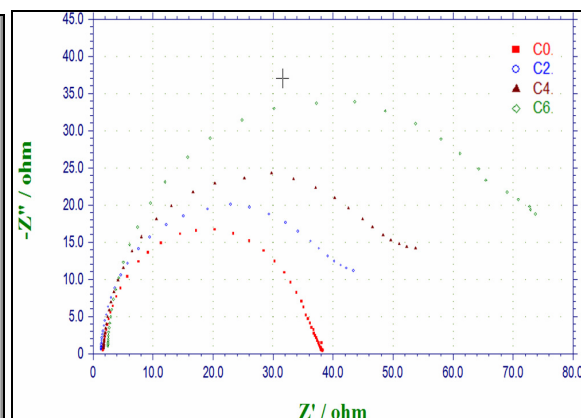
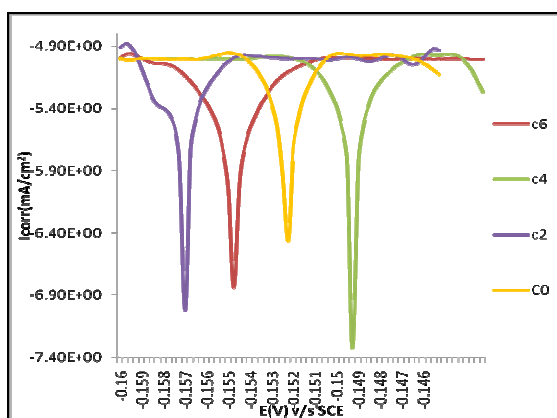


Fig-5: Polarization curves of Copper coupons
(Both Figs.- 5 and 6: in the absence and presence of different concentrations of EECdS in 0.5 M HCl)

Table-4: Impedance parameters for Copper-coupons in the absence and presence of EECdS

EECdS Concentration (g/L)	R_{ct} (Ωcm^2)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	IE_{Ret} (%)	IE_{Cdl} (%)
C0	33.82	6.89	-	-
C2	42.04	3.92	19.55	43.18
C4	52.011	3.17	34.98	54.02
C6	74.188	2.22	54.41	67.77

Surface Morphological Analyses

i. Fourier Transform Infrared Spectroscopy (FTIR)

The active functional groups of the constituents of EECdS were elucidated by carrying FTIR spectroscopy. The vacuum-dried extract and the adsorbed film formed over the coupon surface were analyzed using FTIR spectrometer.

The prominent peaks of the chemical constituents of the extract and the adsorbed film over the copper-coupon surface were tabulated (Table-5). On comparing the spectra of FTIR of extract of *Capparis decidua* seeds with that of the adsorbed layer of extract onto the copper-coupon surface in 0.5 M HCl, the shifts in peaks of the functional groups of the major constituents of additive were observed, thus illustrating its adsorption via H-bonding or weak van der Waal forces or due to the interaction between the inhibitor and metal-coupon surface via lone pair of electrons of hetero atoms, such as N, O etc. FTIR spectroscopy also support good adsorptive propensity of EECdS for copper corrosion in 0.5 M HCl. The ΔG_{ads} (KJmol^{-1}) values were also found to be nearly -20 KJ/mol, indicating physisorption.

ii. Scanning Electron Microscopic analysis

SEM of corroded and inhibited copper-coupons after 72 h immersion period in 0.5 M HCl were carried out at the magnification of 5000 (figs.-7 & 8). A large number of grooves and cracks on corroded the surface of the copper-coupon can be clearly seen in SEM micrograph (fig.-7); whereas a comparatively smooth surface was observed in the scanning electron micrograph of inhibited-copper coupons in presence of 1.0426 g/L *Capparis decidua* seeds extract (fig.-8). The inhibitor's active constituents gets adsorbed onto the copper-coupon surface, providing protection against corrosion, as proved by the absence of pits grooves and cracks on the coupon-surface (fig.-8). Scanning electron microscopic studies show that the extent of corrosion of copper decreases with the increase of concentration of the inhibitors.

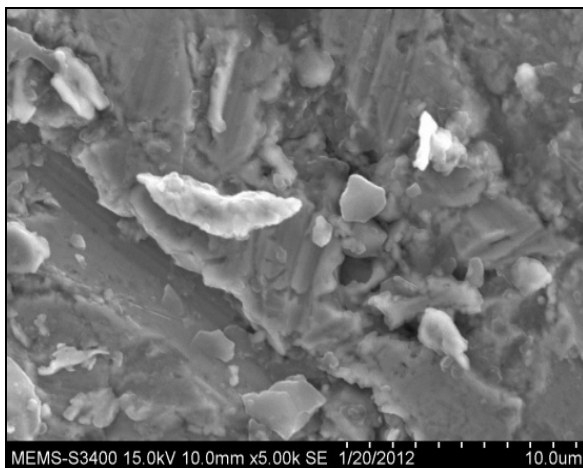


Fig.-7: SEM micrograph of corroded Cu surface

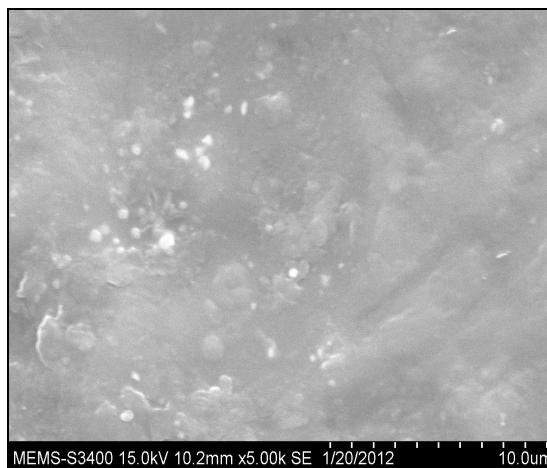


Fig.-8: SEM micrograph of inhibited Cu coupon

CONCLUSIONS

The following conclusions may be drawn from the studies:

1. Extract of *Capparis decidua* seeds (EECdS) is found to be an effective inhibitor for copper in acidic medium with a significantly high inhibition efficacy 94.60 % at its 1.0426 g/L concentration for 72 h of immersion period.
2. The IE % increases on increasing concentration of extract. *Capparis decidua* seeds depicting good inhibitor to impede copper corrosion in acidic medium.
3. The adsorption of *Capparis decidua* seeds is spontaneous, physical in nature and followed Langmuir adsorption isotherm.

4. Inhibition efficacies from the electrochemical measurements (impedance and tafel polarization) were reasonably well in agreement with the chemical measurements.
5. EIS results also show that increase in IE % and R_{ct} values and decrease in C_{dl} values confirm that the *Capparis decidua* seeds extract was adsorbed onto the copper surface.
6. The surface morphological analyses, SEM as well as FT-IR further endorse the formation of the protective film over the metal coupon surface.
7. The good inhibition efficacy of *Capparis decidua* seeds is due to the phytochemical constituents present in it. These phytochemical constituents contain multiple bonds and hetero atoms like nitrogen and oxygen which increase the adsorptive propensity of the inhibitor.
8. It can be concluded that *Capparis decidua* seeds is an effective eco-friendly corrosion inhibitor with significantly high inhibition efficacy (94.60%) for copper in 0.5 M HCl and moreover, it can be a good replacement for many chemical constituents to be used as corrosion inhibitor.

Table-5: FTIR spectral peaks of EECdS and the adsorbed film onto metal-coupon-surface

Spectral Peaks obtained for <i>Capparis decidua</i> seeds extract		Spectral Peaks obtained for adsorbed film onto copper surface	
Frequency (cm ⁻¹)	assigned group	Frequency (cm ⁻¹)	assigned group
2990-2850	Trisubstituted C-H str.-CH ₃ and CH ₂ in aliphatic compound	2940	Some of peaks disappear
2910	C-Hstr	2915	C-H str.
2850	Aliphatic and aromatic C-H str. (methyl)	2840	Aromatic CH str.
3360-3340	-NH ₂ in primary amides	3200-3400	Peaks disappear
2370	N-H str.	2380	N-H str.
1710	C=O str. Cyclic five membered aldehyd and ketone	1720	C=O Str.
1720	Aromatic C=C	1730	Shifted to 1730
1450-1460	C-H def.	1480	Benzene ring stretch in aromatic compounds
1490	-NH ₃ in amino acids	1490	Becomes weak
1510	N-H def.	1610	N-H str.

ACKNOWLEDGMENTS

Authors are highly grateful to the Head, Department of Chemistry, University of Rajasthan, Jaipur for providing necessary research facilities and to UGC for financial support of the project.

REFERENCES

1. Guddi Choudhary, Arpita Sharma, and Alka Sharma, *Int. J. Innovative Res. Sci. Eng. Tech*, **2**, 5467(2013).
2. Anees A. Khadom, Aprael S. Yaro, Abdul Amir H. Kadhum, *J. Corros. Sci. Engg.*, **12(18)**, 1466(2009).
3. Alka Sharma, 2012, *Green Corrosion Inhibitors: Status in Developing Countries*; in: Sanjay Sharma (Eds.), *Green Corrosion Chemistry and Engineering: Opportunities and Challenges*; Wiley-VCH Verlag GmbH & Co. KGaA: Germany, pp. 157-180.
4. M. M. Antonijevic, M. B. Petrovic, *Int. J. Electrochem. Sci.*, **3**, 1 (2008).
5. Rittu Chowdhary, S. P. Mathur, *J. Electrochem. Soc. India*, **54 (1)**,1(2005).
6. M. Kliskic, J. Radosevic, S. Gudic, V. Katalinic, *J. Appl. Electrochem.*, **30 (7)**, 823(2000).
7. K. O. Orbite and N. C. Ofaraka, *Mater. Lett.*, **58 (11)**, 1768(2004).
8. P. C. Okafor, U. J. Ekpe, E. E. Ebenso, E. E. Oguzie, A. N. S. Umo, A. R. Etor, *Trans. SAEST*, **41 (2)**, 82(2006).

9. A. O. Odiongenyi, S. A. Odoemelani, N. O. Eddy, *Portug. Electrochim. Acta*, **27(1)**, 33(2009).
10. P. Deepa Rani and S. Selvaraj, *J. Phytol.*, **2(11)**, 58(2010).
11. P. Deepa Rani and S. Selvaraj, *RASAYAN J. Chem.*, **3(3)**, 473(2010).
12. Rekha N. Nair, Shashi Sharma, I.K.Sharma, P.S.Verma and Alka Sharma, *RASAYAN J. Chem.*, **3(4)**, 783(2010).
13. Shashi Sharma, Prassan S. Pratihari, Rekha N. Nair, P. S. Verma and Alka Sharma, *RASAYAN J. Chem.*, **5(1)**, 16(2012).
14. P. Arora, S. Kumar, M. K. Sharma and S. P. Mathur, *E-J. Chem.*, **4(4)**, 450(2007).
15. Alka Sharma, Arpita Sharma, Guddi Choudhary, and Swati Yadav, "*Int. J. Sci. Adv. Tech.*", **2(12)**, 68(2013).
16. C. A. Loto, R.T. Loto and A.P. I. Popoola, *Int. J. Electrochem. Sci.*, **6**, 4900 (2011).
17. B. A. Abd-El-Nabey, A. M. Abdel-Gaber, M. El. Said Ali, E. Khamis, S. El-Housseiny, *Int. J. Electrochem. Sci.*, **8**, 5851(2013).
18. P. Deepa Rani and S. Selvaraj, *J. Chem. Biol. Physical Sci.*, **3(2)**, 998(2013).
19. P. Deepa Rani. S.P Selvaraj, *Indian J. Appl. Res.*, **4(5)**, 59(2014).
20. Swati Yadav and Alka Sharma, *Rev. Res.*, **2(7)**, 1(2013).
21. M. S.-Nooshabadi, F. S. Hoseiny and Y. Jafari, *Anal. Bioanal. Electrochem*, **6(3)**, 341(2014).
22. Mohsin E. Al-Dokheily, Husam. M. Kredy and Rasha N. Al-Jabery, *J. Natural Sci.*, **4(17)**, 60 (2014).
23. A. S. Fouda, K. Shalabi, A. A. Idress, *Int. J. Electrochem. Sci.*, **9**, 5126(2014).
24. T. V. Sangeetha and M. Fredimoses, *E-J. Chem.*, **8(S1)**, S1(2011).
25. G. O. Avwiri and E. Osarolube, *Scientia Africana*, **9(2)**, 51(2010).
26. E. M. Sherif and Su-Moon Park, *Electrochimica Acta*, **51**, 4665(2006).
27. A. Zarrouk, T. Chelfi, A. Dafali, B. Hammouti, S.S. Al-Deyab, I. Warad, N. Benchat and M. Zertoubi, *Int. J. Electrochem. Sci.*, **5**, 696(2010).
28. G. Vastag, E. Szöcs, A. Shaban and E. Kálmán, *Pure Appl. Chem.*, **73(12)**, 1861(2001).
29. H. Baeza, M. Guzman, P. Ortega and L. Vera, *J. Chil. Chem. Soc.*, **48(3)**, 0717(2003).
30. M. Yadav and Dipti Sharma, *Portug. Electrochim. Acta*, **28(1)**, 51(2010).
31. P. Deepa Rani, S. Selvaraj, *Arch. Appl. Sci. Res.*, **2(6)**, 140(2010).
32. M. Lashgari, M.-Reza Arshadi and Masoume Biglar, *Chem. Eng. Comm.*, **197** 1303(2010).
33. Matjaž Finšgar, Janez Kovač, Ingrid Milošev, *J. Electrochem. Soc.*, **157(2)**, C52(2010).
34. P. Singh, G. Mishra, Sangeeta, Shruti Srivastava, K. K. Jha and R. L. Khosa, *Der Pharmacia Lettr*, **3(2)**, 71(2011).
35. P. D. Verma, R.D. Dangar, K. N. Shah, D. M. Gandhi and B. N. Suhagia, *J. Appl. Pharm. Sci.*, **1(10)**, 06(2011).
36. M. U. Dahot, *J. Chem. Soc. Pak*, **15(1)**, 78(1993).
37. Durga N. Dhar; R. P Tewari, R. D. Tripathi, A. P Ahuja, *Proc. Nat. Acad. Sci., India, Sec. A: Phy. Sci*, **42(1)**, 24(1972).
38. N. Ismail, Ph. D. Thesis, H.E.J. Research Institute of Chemistry, University of Karachi (1991).
39. S. Arif, Ph.D. thesis, H.E.J. Research Institute of Chemistry, University of Karachi (1986).
40. Harish Kumar and R.S.Chaudhary, *J. Indian Chem.Soc.*, **88**, 1589(2011).

[RJC-1351/2015]