

## Study of Corrosion Inhibitory Effects of Alcoholic Extracts of *Tinospora Cordifolia* on Metal Tin in Acidic Media HCl with and without Additive (KCl)

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### Abstract

The corrosion inhibitory efficiency of *Tinospora Cordifolia* stem and leaf extract in different concentrations of HCl acid (0.5, 1, 2, and 3N) was examined using weight loss and thermometric methods in the absence and presence of an additive (KCl). According to the findings of this investigation, inhibition efficiency ( $\eta\%$ ) rises with increasing inhibitor concentration as well as acid strength, and additional improvement in inhibition efficiency was found with the addition of additives (KCl) owing to a synergistic effect. According to the findings, stem extract is a better corrosion inhibitor than leaf extract. The maximum inhibition efficiency was observed for stem and leaf extracts (95.76 and 92.47 %) at their maximum concentrations (0.8 %) in the absence of an additive in the maximum strength of HCl acid (3N), while it was observed at 98.58 and 95.29 % in the presence of additive (3N KCl) of maximum strength.

**Keywords:** Corrosion; Additives; Inhibitors; Metals; Synergistic effect; Inhibition efficiency.

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### 1. Introduction

Corrosion is a naturally destructive process, in which a metal surface is destructed or deteriorated gradually by chemical or electrochemical reactions with its surrounding environment [1-3]. Corrosion is an unfavorable process that adversely affects metal surfaces and alloys [4]. Metals usually oxidize in acidic environments, and hydrogen gas is liberated during the process [5,6]. The natural degrading process of metals and alloys caused by the attack of air gases, moisture, and other substances is known as corrosion. [7,8]. The majority of metals are impacted by this destructive process which is not ideal. For more than a thousand years, tin and its alloys have been used to create tools and weapons. Its highly popular alloy, *bronze*, is well-known to us and is used to make coins, sculptures, musical instruments, medals, ship components, and other car parts. Tin and its alloys are employed as solders in the electrical sector, as well as in the manufacture of cans and foils [9,10]. Due to a persistent oxide layer on its surface, tin typically does not

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corrode in the presence of water or moisture, but in the presence of acidic media like HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub> it severely corrodes [11,12].

Metal and alloy utilization is a major pillar of the industry. The most common issue in industries is metal corrosion; therefore, the simplest and cheapest way to prevent corrosion is to utilize corrosion inhibitors. The corrosion rate is reduced by these inhibitors, which helps to avoid monetary loss [13]. Numerous chemical compounds with heteroatoms are effective inhibitors and have anticorrosive properties, but they are also very toxic, expensive, and hazardous for both the environment and living things [14]. Many studies have been conducted to investigate the use of inexpensive, non-toxic, renewable, and environmentally friendly natural products or plant materials as efficient corrosion inhibitors [15,16].

Due to the presence of heteroatoms like N, O, S, and P as well as their increased basicity and electron density, natural compounds isolated from plants are shown to be effective and efficient corrosion inhibitors [17,18]. These organic items or plant extracts are affordable, environmentally friendly, non-toxic, and non-polluting [19,20]. They are also biodegradable and non-toxic. The current investigation study examines the effectiveness of *Tinospora Cordifolia* plant extract (stem and leaves) in inhibiting the oxidation of tin metal at various HCl concentrations (0.5, 1, 2, and 3N).

## 2. Plant Description

### Classification of *Tinosporacordifolia*

Kingdom	: Plantae
Sub-Kingdom	: Tracheobionta
Division	: Magnoliophyta
Class	: Magnoliopsida
Sub-class	: Ranunculidae
Order	: Ranunculales
Family	: Menispermaceae
Genus	: <i>Tinospora</i>
Species	: <i>Cordifolia</i>

A member of the Menispermaceae family, *Tinospora Cordifolia* is a climbing shrub. In every season, it is easily accessible. All across India, as well as in Sri Lanka, Bangladesh, Myanmar, China, Southern Eastern Asia, Africa, and Australia, it is widespread. It is sometimes referred to as "Amrita" or "Guduchi." Its name is "Giloy" in Hindi. Because of its extensive therapeutic powers, Giloy is referred to in Sanskrit as "Amrita," which means the root of immortality. It is used to treat a variety of conditions, including intermittent and chronic fevers, burning sensations, gout, inflammations, cough, asthma, diabetes, urinary infections, jaundice, leprosy, anemia, cardiac debility, skin conditions, chronic diarrhea, and dysentery. Alkaloids, diterpenoid lactones, glycosides, steroids,

sesquiterpenoids, aliphatic chemicals, and polysaccharides are only a few of its many constituents [21-23].



Fig. 1. *Tinospora Cordifolia* plant.

### 3. Experimental

#### 3.1. Weight loss method

Square specimens of metal tin with dimensions of  $2.5 \times 2.5 \text{ cm}^2$  and a tiny hole nearing 2 mm in diameter at the top edge were collected for corrosion analysis. The samples were cut from a sheet, polished to a flawless finish, and then degreased. HCl solutions of various concentrations were made using double-distilled water. Each specimen was placed in a glass beaker with 50 mL of the test solution at room temperature and suspended using a V-shaped glass hook constructed of fine capillaries. For each example, the length of time that the specimens were exposed to the test solution was different. After receiving enough exposure, specimens were removed, cleaned under running water, and then dried under hot air. Each experiment was repeated twice, and weight loss ( $\Delta W$ ) was computed. The percentage inhibition efficiencies of inhibitors were calculated as [24]:

$$\eta\% = \left[ \frac{(\Delta W_u - \Delta W_i)}{\Delta W_u} \right] \times 100$$

Where  $\Delta W_u$  and  $\Delta W_i$  are the weight loss of the metal in the uninhibited and inhibited solution, respectively.

The corrosion rate (CR) in mm/yr (mm per year) was expressed as [25] :

$$\text{Corrosion rate (mm/yr.)} = \frac{(\Delta W \times 87.6)}{(A \times T \times d)}$$

Where  $\Delta W$  is the weight loss of the specimen in mg, A is the area of exposure of the specimen in square  $\text{cm}^2$ , T is the time of exposure in hours and d is the density of the specimen in  $\text{g/cm}^3$ .

The degree of surface coverage ( $\theta$ ) was calculated as [26]:

$$\theta = \left[ \frac{(\Delta W_u - \Delta W_i)}{\Delta W_u} \right]$$

Where  $\Delta W_u$  and  $\Delta W_i$  are the weight loss of the metal in the uninhibited and inhibited solution, respectively.

Additionally, the thermometric approach was used to calculate inhibition efficiency. In this procedure, a single specimen is submerged in a reaction chamber with insulation that contains 50 mL of a solution that is initially at room temperature. A thermometer with a precision of 0.01 °C, was used to measure temperature changes at regular intervals. The temperature increased gradually at first, then quickly reached a peak, and then started to fall. It was recorded at whatever the maximum temperature was.

The percentage inhibition efficiency was calculated as [27]:

$$\eta\% = \frac{(RN_f - RN_i)}{RN_f} \times 100$$

Where  $RN_f$ =Reaction Number in uninhibited solution.

$RN_i$ = Reaction Number in the inhibited solution.

Reaction Number, RN ( $Kmin^{-1}$ ) is given as [28]:

$$RN = \frac{T_m - T_i}{t}$$

Where  $T_m$ = Maximum temperature of the solution.

$T_i$  = Initial temperature of the solution.

$t$ = time required (in minutes) to attain maximum temperature.

## 4. Results and Discussion

### 4.1. Weight loss method

Tables 1-4, and Tables 5-8 include information on weight loss ( $\Delta W$ ), percentage inhibition efficiency ( $\eta\%$ ), corrosion rate (mm/yr), surface coverage ( $\theta$ ), and  $\log(\theta/1-\theta)$  for various concentrations of HCl and inhibitors (0.2, 0.4, 0.6, and 0.8%) in both the absence and presence of additives.

Table 1. Weight loss ( $\Delta w$ ), percentage inhibition efficiency ( $\eta\%$ ) for tin in 0.5N HCl with the inhibitor of stem and leaves extract.

Inhibitors concentration	$\Delta w$	Surface coverage ( $\theta$ )	Corrosion rate (mm/yr)	I.E. ( $\eta\%$ )	$\log\left(\frac{\theta}{1-\theta}\right)$
Stem					
Uninhibited	0.415		0.00212		
0.2	0.080	0.8072	0.00040	80.72	0.62187
0.4	0.070	0.8313	0.00035	83.13	0.69264
0.6	0.060	0.8554	0.00030	85.54	0.77200
0.8	0.051	0.8771	0.00026	87.71	0.85349
Leaves					
0.2	0.105	0.7469	0.00053	74.69	0.46997
0.4	0.093	0.7759	0.00047	77.59	0.53936
0.6	0.081	0.8048	0.00041	80.48	0.61520
0.8	0.068	0.8361	0.00034	83.61	0.70767

Temperature : 301K  $\pm$  0.1 K, Area of Specimen : 13 cm<sup>2</sup>, Time of Exposure : 180 h

Table 2. Weight loss ( $\Delta w$ ), percentage inhibition efficiency ( $\eta\%$ ) for tin in 1N HCl with the inhibitor of stem and leaves extract.

Inhibitors concentration	$\Delta w$	Surface coverage ( $\theta$ )	Corrosion rate (mm/yr)	I.E. ( $\eta\%$ )	$\log\left(\frac{\theta}{1-\theta}\right)$
Stem					
Uninhibited	0.422		0.00277		
0.2	0.070	0.8341	0.00046	83.41	0.70137
0.4	0.061	0.8554	0.00040	85.54	0.77200
0.6	0.054	0.8720	0.00035	87.20	0.83330
0.8	0.044	0.8957	0.00028	89.57	0.93387
Leaves					
0.2	0.090	0.7867	0.00059	78.67	0.56681
0.4	0.082	0.8056	0.00053	80.56	0.61742
0.6	0.069	0.8364	0.00045	83.64	0.70863
0.8	0.056	0.8672	0.00036	86.72	0.81492

Temperature: 301 K  $\pm$  0.1 K, Area of specimen: 13 cm<sup>2</sup>, Time of exposure : 140 h

Table 3. Weight loss ( $\Delta w$ ), percentage inhibition efficiency ( $\eta\%$ ) for tin in 2N HCl with the inhibitor of stem and leaves extract.

Inhibitors concentration	$\Delta w$	Surface coverage ( $\theta$ )	Corrosion rate (mm/yr)	I.E. ( $\eta\%$ )	$\log\left(\frac{\theta}{1-\theta}\right)$
Stem					
Uninhibited	0.430		0.00412		
0.2	0.055	0.8720	0.00052	87.20	0.83330
0.4	0.045	0.8953	0.00043	89.53	0.93202
0.6	0.036	0.9162	0.00034	91.62	1.03874
0.8	0.031	0.9279	0.00029	92.79	1.10956
Leaves					
0.2	0.079	0.8162	0.00075	81.62	0.64745
0.4	0.068	0.8418	0.00065	84.18	0.72600
0.6	0.054	0.8744	0.00051	87.44	0.84272
0.8	0.045	0.8953	0.00043	89.53	0.93202

Temperature: 301 K  $\pm$  0.1 K; Area of specimen: 13 cm<sup>2</sup>; Time of exposure: 96 h

Table 4. Weight Loss ( $\Delta w$ ), Percentage inhibition efficiency ( $\eta\%$ ) for tin in 3N HCl with the inhibitor of stem and leaves extract.

Inhibitors concentration	$\Delta w$	Surface coverage ( $\theta$ )	Corrosion rate (mm/yr)	I.E. ( $\eta\%$ )	$\log\left(\frac{\theta}{1-\theta}\right)$
Stem					
Uninhibited	0.425		0.00783		
0.2	0.039	0.9082	0.00071	90.82	0.99533
0.4	0.033	0.9223	0.00060	92.23	1.10375
0.6	0.025	0.9418	0.00046	94.18	1.20903
0.8	0.018	0.9576	0.00033	95.76	1.35381
Leaves					
0.2	0.062	0.8541	0.00114	85.41	0.76745
0.4	0.052	0.8776	0.00095	87.76	0.85552
0.6	0.042	0.9018	0.00077	90.18	0.96299
0.8	0.032	0.9247	0.00058	92.47	1.08920

Temperature: 301 K  $\pm$  0.1 K; Area of specimen: 13 cm<sup>2</sup>; Time of exposure: 50 h

The data from Tables (1-4) demonstrate that the value of  $\Delta W$  decreases and the inhibitor's inhibition efficiency ( $\eta$  %) increases with increasing inhibitor concentration, from 0.2 to 0.8 %, as well as with increasing acid concentration (0.5, 1, 2, and 3N HCl), with the highest inhibitor efficiency seen at the highest acid concentration (i.e., 3N). The corrosion rate rises as acid concentration without an inhibitor increases, and it falls as inhibitor concentration rises in an acid environment.

Surface coverage also increases as inhibitor concentration rises (from 0.2 to 0.8 %), peaking at 0.8 % inhibitor concentration in 3N HCl solution, the highest possible concentration of acid. In comparison, 0.8 % leaf extract inhibitor solution in 3N HCl had an exhibition efficiency of 92.47 % whereas 0.8 % stem extract inhibitor solution in 3N HCl had a maximum inhibitor efficiency of 95.76 %. The outcome demonstrates that at various concentrations of HCl, stem extract is a more effective corrosion inhibitor than leaf extract. The values of  $\log(\theta/1-\theta)$  appear to rise linearly with increasing inhibitor concentrations and reveal that it follows chemisorption.

Table 5. Weight loss ( $\Delta w$ ) and percentage inhibition efficiency ( $\eta\%$ ) for tin in 0.5N HCl with the inhibitor of stem and leaves extract in presence of additive (KCl).

Inhibitors concentration	$\Delta w$	Surface coverage ( $\theta$ )	Corrosion rate (mm/yr)	I.E. ( $\eta\%$ )	$\log\left(\frac{\theta}{1-\theta}\right)$
Stem					
Uninhibited	0.415		0.00212		
0.2	0.065	0.8433	0.00033	84.33	0.730913
0.4	0.052	0.8746	0.00026	87.46	0.843511
0.6	0.040	0.9036	0.00020	90.36	0.971899
0.8	0.026	0.9373	0.00013	93.73	1.174611
Leaves					
0.2	0.089	0.7855	0.00045	78.55	0.563718
0.4	0.073	0.8240	0.00037	82.40	0.670414
0.6	0.061	0.8530	0.00031	85.30	0.763631
0.8	0.049	0.8819	0.00025	88.19	0.873169

Temperature: 301 K  $\pm$  0.1 K; Area of specimen: 13 cm<sup>2</sup>; Time of exposure: 180 h; Additive: 0.5N KCl.

Table 6. Weight Loss ( $\Delta w$ ) and Percentage inhibition efficiency ( $\eta\%$ ) for tin in 1N HCl with the inhibitor of stem and leaves extract in presence of additive (KCl).

Inhibitors concentration	$\Delta w$	Surface coverage ( $\theta$ )	Corrosion rate (mm/yr)	I.E. ( $\eta\%$ )	$\log\left(\frac{\theta}{1-\theta}\right)$
Stem					
Uninhibited	0.422		0.00277		
0.2	0.058	0.8625	0.00038	86.25	0.787456
0.4	0.045	0.8933	0.00029	89.33	0.922832
0.6	0.031	0.9265	0.00020	92.65	1.100558
0.8	0.020	0.9526	0.00013	95.26	1.303132
Leaves					
0.2	0.073	0.8270	0.00048	82.70	0.679459
0.4	0.065	0.8459	0.00042	84.59	0.739516
0.6	0.052	0.8767	0.00034	87.67	0.851887
0.8	0.041	0.9028	0.00026	90.28	0.967925

Temperature: 301 K  $\pm$  0.1 K; Area of specimen: 13 cm<sup>2</sup>; Time of exposure: 140 h; Additive: 1N KCl.

Table 7. Weight loss ( $\Delta w$ ) and percentage inhibition efficiency ( $\eta\%$ ) for tin in 2N HCl with the inhibitor of stem and leaves extract in presence of additive (KCl).

Inhibitors concentration	$\Delta w$	Surface coverage ( $\theta$ )	Corrosion rate (mm/yr)	I.E. ( $\eta\%$ )	$\log\left(\frac{\theta}{1-\theta}\right)$
Stem					
Uninhibited	0.430		0.00412		
0.2	0.044	0.8976	0.00042	89.76	0.942782
0.4	0.031	0.9279	0.00029	92.79	1.109565
0.6	0.024	0.9441	0.00023	94.41	1.227606
0.8	0.011	0.9744	0.00020	97.44	1.580497
Leaves					
0.2	0.066	0.8465	0.00063	84.65	0.741518
0.4	0.056	0.8697	0.00053	86.97	0.824425
0.6	0.045	0.8953	0.00043	89.53	0.932021
0.8	0.032	0.9255	0.00030	92.55	1.094220

Temperature: 301 K  $\pm$  0.1 K; Area of specimen: 13 cm<sup>2</sup>; Time of exposure: 96 h; Additive: 2N KCl.

Table 8. Weight loss ( $\Delta w$ ) and percentage inhibition efficiency ( $\eta\%$ ) for tin in 3N HCl of stem and leaves extract in presence of additive (KCl).

Inhibitors concentration	$\Delta w$	Surface coverage ( $\theta$ )	Corrosion rate (mm/yr)	I.E. ( $\eta\%$ )	$\log\left(\frac{\theta}{1-\theta}\right)$
Stem					
Uninhibited	0.425		0.00783		
0.2	0.032	0.9247	0.00058	92.47	1.089205
0.4	0.020	0.9529	0.00036	95.29	1.306026
0.6	0.012	0.9717	0.00022	97.17	1.535740
0.8	0.006	0.9858	0.00011	98.58	1.841500
Leaves					
0.2	0.052	0.8776	0.00095	87.76	0.855515
0.4	0.046	0.8917	0.00084	89.17	0.915590
0.6	0.031	0.9270	0.00057	92.70	1.103756
0.8	0.020	0.9529	0.00036	95.29	1.306026

Temperature: 301 K  $\pm$  0.1 K; Area of specimen: 13 cm<sup>2</sup>; Time of exposure: 50 h; Additive: 3N KCl.

Tables (5-8) show weight loss ( $\Delta W$ ), inhibitor efficiency ( $\eta\%$ ), surface coverage ( $\theta$ ), corrosion rate for various acid concentrations, and inhibitor presence with varying concentrations of additive (KCl). With increasing levels of inhibition efficiencies, the Table data exhibits the same trend as that seen in HCl alone. As acid and additive concentrations rise, the effectiveness of the inhibition rises (KCl).

At the maximum concentration of acid (3N HCl), the inhibitor's effectiveness increases (3N KCl). The highest levels of inhibitory effectiveness for stem and leaf extract at a concentration of 0.8 % were found to be 98.58 and 95.29 % respectively, in 3N HCl in the presence of additive 3N KCl. Surface coverage also rises with rising acid concentrations, and measurements display maxima at concentrations of 3N HCl and 3N KCl. It appears that the values of  $\log(\theta/(1-\theta))$  grow linearly with increasing inhibitor concentrations, indicating that they follow the chemisorption process.

The results of the current investigation show that the inhibitors (stem/leaf) were more effective in inhibiting the metal Tin in HCl acid solution when additive (KCl) was present than when the inhibitors (stem/leaf) were present alone. Synergistic effects are to blame for this. The combined effect of the two chemicals on a metal surface is larger than the combined effects of the two chemicals acting separately or concurrently.

#### 4.2. Thermometric method

The thermometric approach was also used to investigate inhibition efficiency. Temperature variations were observed for test solutions in various acid concentrations (1, 2, and 3N HCl) both in the presence and absence of the additive (KCl). However, there were no substantial temperature changes recorded for 0.5N HCl. The results summarized in Table 9 for HCl and Table 10 for HCl in the presence of additive (KCl) indicate good agreement with the weight loss technique results.

Table 9. Reaction number (RN) and inhibition efficiency ( $\eta\%$ ) for tin in 1, 2, and 3N HCl with the inhibitor of stem and leaves extract.

Inhibitor Concentration	3N HCl		2N HCl		1N HCl	
	RN	I.E.( $\eta\%$ )	RN	I.E.( $\eta\%$ )	RN	I.E.( $\eta\%$ )
Stem						
Uninhibited	0.5546		0.3526		0.1542	
0.2	0.1832	65.88	0.1326	62.39	0.0636	58.75
0.4	0.1745	68.53	0.1190	66.25	0.0603	60.89
0.6	0.1535	72.32	0.1115	68.37	0.0556	63.94
0.8	0.1374	75.22	0.1010	71.35	0.0496	67.83
Leaves						
0.2	0.2021	63.55	0.1425	59.58	0.0684	55.64
0.4	0.1860	66.46	0.1345	61.85	0.0634	58.88
0.6	0.1690	69.52	0.1210	65.68	0.0575	62.71
0.8	0.1532	72.37	0.1120	68.23	0.0526	65.88

Temperature: 301 K  $\pm$  0.1 K; Area of specimen: 13 cm<sup>2</sup>.

Table 10. Reaction number (RN) and inhibition efficiency ( $\eta\%$ ) for tin in 1, 2, and 3N HCl with the inhibitor of stem and leaves extract in presence of the additive.

Inhibitor concentration	3N HCl + 3N KCl		2N HCl + 2N KCl		1N HCl + 1N KCl	
	RN	I.E.( $\eta\%$ )	RN	I.E.( $\eta\%$ )	RN	I.E.( $\eta\%$ )
Stem						
Uninhibited	0.5546		0.3526		0.1542	
0.2	0.1744	68.55	0.1215	65.54	0.0598	61.21
0.4	0.1482	73.27	0.1110	68.51	0.0562	63.55
0.6	0.1366	75.36	0.1006	71.46	0.0515	66.60
0.8	0.1096	80.23	0.0875	75.18	0.0442	71.33
Leaves						
0.2	0.1910	65.56	0.1348	61.76	0.0651	57.78
0.4	0.1759	68.28	0.1242	64.77	0.0602	60.95
0.6	0.1518	72.62	0.1152	67.32	0.0533	65.43
0.8	0.1258	77.31	0.1010	71.35	0.0475	69.19

Temperature: 301 K  $\pm$  0.1 K; Area of specimen: 13 cm<sup>2</sup>.



The maximum inhibition efficiencies for stem and leaf extract at their highest concentrations of 0.8 % in the highest concentration of acid (3N HCl) in the absence of additive were 75.22 and 72.37 %, respectively, whereas the maximum inhibition efficiencies for stem and leaf extract in the presence of additive KCl were 80.22 and 77.30 %. Data from Tables (9 and 10) reveal a linear relationship between reaction number and inhibitor concentration, indicating that reaction number (RN) declines as inhibitor concentrations increase.

Normally, organic molecules with heteroatoms like N, O, or S readily adsorb on metal surfaces and impede the corrosion process. Chemicals present in inhibitors (stem/leaf) having heteroatoms adsorb easily on the metal surface and form a monolayer, thus inhibiting corrosion and decreasing the corrosion rate. The molecular structure of inhibitors having such groups exerts a positive mesomeric effect, which increases electron density at the hetero atoms. This increased electron density help inhibitor to adsorb more easily on corroding sites/active sites of the metal.

The inhibition efficiency of the inhibitor is higher at a maximum acid concentration (3N HCl). This may be due to the faster ionization of inhibitor molecules in a higher concentration of acids. Therefore, inhibitors show better inhibitor efficiencies at a higher strength of acids. The inhibition efficiencies increased in the presence of additives due to a synergistic effect—the combined action of two chemicals on a metal surface, which was larger than the sum of their separate effects. Only the synergism of the chloride ion may explain the increase in inhibitory efficiencies in the presence of an additive (KCl).

## 5. Conclusion

The study of stem and leaf extract of *Tinospora Cordifolia* has found them to be efficient corrosion inhibitors in different strengths of Hydrochloric acid, on the metal tin in the absence and presence of additive (KCl). Both weight loss and thermometric methods have shown that the inhibition efficiency of stem and leaf inhibitors increases with the increasing inhibitor concentrations from 0.2 to 0.8 % and also with the increasing acid strength from 0.5 to 3N for HCl. Stem and leaf extracts were shown to have the highest levels of inhibition (95.76 and 92.47 %, respectively) at their highest concentrations of 0.8 % and in the presence of the highest concentration of acid (3N HCl). Similarly, maximal inhibitory efficiency was determined to be 98.58 and 95.29 % for stem and leaf extract at their highest concentrations of 0.8 % and 3N HCl at their maximum concentrations in the presence of additives (KCl). According to the findings of this investigation, stem extract is a superior corrosion inhibitor in HCl than leaf extract. The results of both weight loss and thermometric approaches are in good agreement.

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