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Corrosion Inhbition Capability of L-Tryptophan and Zn^{2+} Ion on Carbon Steel in Cauvery Water

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ABSTRACT

The investigation of corrosion inhibition capability of L-Tryptophan with Zn^{2+} ion against carbon steel in Cauvery water was done using weight loss method. Along with this, the electrochemical studies such as FTIR, UV, Tafel polarization were done and the protective film formed was authenticated by SEM analysis. All these studies stand as proof for the inhibitive effect of L-Tryptophan and Zn^{2+} ion as excellent corrosion inhibitor. Complex mixture of L-Tryptophan and Zn^{2+} ion effectively inhibited the corrosion of carbon steel in Cauvery water with 70% of inhibition efficiency.

Key words: L-Tryptophan, Cauvery water, Carbon steel, FTIR, UV, Tafel polarization, SEM

1. INTRODUCTION

In the past years corrosion inhibitors have been treated against the phenomenon of corrosion in cooling water systems, to support the same to clean industrial acid, to acidify oil well and to descale because of their economical and efficient properties [(1-3)]. However the environmental destruction have been registered in the past years because of their toxicity on aquatic lies and plants. The classical inhibitors such as chromate, nitrate, polyphosphate and organic phosphate have been banned in very many countries [(4, 5)]. Hence the present scenario in the research field requires the corrosion inhibitors which are safe, non-toxic, easily biodegradable and more environmental friendly green chemicals in order to meet environmental protection requirements [(6, 18-19)].

Amino acids are non-noxious, ecologically favorable and uncomplicated in their production with purities greater than 99%. In modern times many creative accomplishments have been attained in the laboratories regarding the usage of amino acids as corrosion inhibitors [(7-12)].

Tryptophan is an essential amino acid. It plays a vital biological role which is mostly associated with metabolic pathways involved in tryptophan catabolism. Scrotinin, which is an important neuromodulator, being associated to mood, stress response, sleep and appetite control whose precursor is L-Tryptophan [(15, 17)]. Also it plays a vital role in normal functionality of the brain-gut axis and immunology [(16)]. L-Tryptophan is derived from indole. Molecular structural analysis reveals that it has potentiality to exhibit excellent corrosion inhibition. Ashassi-Sorkhabi et al.,[(11)] reported that the inhibition efficiency of L-Tryptophan is considerably more than the other amino acids such as leucine, valine, proline, and methionine. However the research work on the inhibition effect of L-Tryptophan and Zn^{2+} ion on carbon steel in cauvery water medium is rare. In this study the inhibition capability of L-Tryptophan with Zn^{2+} ion was determined by weight loss method in room temperature. Also various electrochemical studies such as FTIR, UV and Tafel polarization were done. SEM micrographs of the surface was also examined in the existence and non-existence

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of the inhibitor namely. L-Tryptophan and Zn^{2+} ion to know the characteristics of the defensive film formed on the surface.

MATERIALS AND METHODS

MATERIALS

L-Tryptophan was purchased from HPLC, Mumbai. In this study the concentration of L-Tryptophan used was 1 g in 1000 ml and the concentration of Zn^{2+} ion used was 4.4g in 1000 ml. The medium of corrosion used in this investigation was cauvery water which is elixir of life in and around Trichy and other delta villages.

THE METAL USED FOR THIS STUDY WAS CARBON STEEL WHOSE COMPOSITION WAS AS FOLLOWS, NAMELY

ELEMENT	COMPOSITION OF CARBON STEEL (%)
Carbon	0.1
Sulphur	0.026
Phosphorous	0.06
Manganese	0.4
Silicon	0.129
Chromium	0.022
Molybdenum	0.011
Nickel	0.013
Iron	Rest

WEIGHT LOSS METHOD

Carbon steels of whose dimension is $1.2\times4\times0.1\ cm^3$ were made use for weight loss methods. These carbon steel metals were polished and weighed before immersing them into the corrosive environment. Then the metals were immersed in the solutions with and without L-Tryptophan along with Zn^{2+} ion. The investigation was carried out in room temperature. The system was left undisturbed up to one day. After one day the metals were removed, rinsed thoroughly with tap water, dehydrated by drying and weighed. The rate of corrosion (W_{corr}) and the percentage of inhibition efficiency (IE_w %) over the period of one day were determined by using the formulae below.

i] $W_{corr} = \frac{87.6\times W}{ATD}$ Where,

W- Weight loss afore and after the immersion in solution
A- Surface area of the metal

T- Period of immersion
D- Density of metal

ii] $IE_w\ \% = \frac{W1-W2}{W1}\times 100$ Where,

W1 & W2 – unsuppressed and suppressed rates of corrosion respectively ($mg\ cm^{-2}\ h^{-1}$)

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ELECTROCHEMICAL STUDIES

Electrochemical studies such as FTIT, UV-Vis spectroscopy and Tafel polarization were carried out to affirm the formation of the protective film.

SURFACE ANALYSIS

To know the characteristics of the defensive film formed on the metal surface, scanning electron micrographs have been taken. This was done in the existence and non-existence of inhibitor mixture namely, L-Tryptophan and Zn^{2+} ion.

2. RESULTS AND DISCUSSION

Weight loss method

The metals were polished mechanically before immersing them into the solution. Polished metals were wiped with acetone, dehydrated by drying and placed in the desiccator. The solutions containing inhibitors were prepared, namely, Zinc sulphate solution and L-Tryptophan solutions were prepared. Then concentration of Zinc sulphate solution was 4.4 g/1000 ml and the concentration of L-tryptophan was 1 g/1000 ml. Out of these, various concentrations of solutions were prepared. The system was done in three levels, namely, first the metals were immersed in cauvery water for one day with various Zn^{2+} ion concentrations whose range is varied from 10 ppm to 60 ppm and then the metals were immersed in cauvery water for one day with various L-Tryptophan concentrations ranging from 50 ppm to 300 ppm and finally the metals were immersed in cauvery water for one day with various concentrations of L-Tryptophan ranging from 50 ppm to 300 ppm along with Zn^{2+} ion of 50 ppm concentration all through. The data obtained from these investigations are listed in the tables and drawn as pie charts below. Table 1 shows the inhibition effect of Zn^{2+} ion in cauvery water wherein at 50 ppm the maximum inhibition of 40% is obtained. Table 2 shows the inhibition effect of L-Tryptophan in cauvery water wherein at 150 ppm the maximum inhibition effect of 50% is obtained. Table 3 shows the inhibition effect of L-Tryptophan with Zn^{2+} ion wherein the maximum inhibition efficiency is obtained when the mixture ratio is at 150:50 respectively.

Zn^{2+} ION SYSTEM FOR 1 DAY

When the carbon steel metals were drowned in cauvery water in the existence of Zn^{2+} ion of varied numerous concentrations ranging from 10 ppm to 60 ppm the inhibition efficiency was found to increase as the concentration increased. At 50 ppm the maximum inhibition efficiency of 40% was obtained. These data are expressed in the table below along with the pie chart representation.

Zn^{2+} SYSTEM FOR 1 DAY

S.NO.	CONC. OF L-TRY (PPM)	CONC. OF ZN^{2+} ION (PPM)	INHIBITION EFFICIENCY (%)	CORROSION RATE (MMPY)
1	0	10	15	0.0810
2	0	20	20	0.0762
3	0	30	25	0.0715

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4	0	40	35	0.0620
5	0	50	40	0.0574
6	0	60	17.5	0.0786

TABLE NO. 1

RATE OF CORROSION AND PERCENTAGE OF INHIBITION EFFICIENCY OF ZN^{2+} ION IN CAUVERY WATER FOR 1 DAY

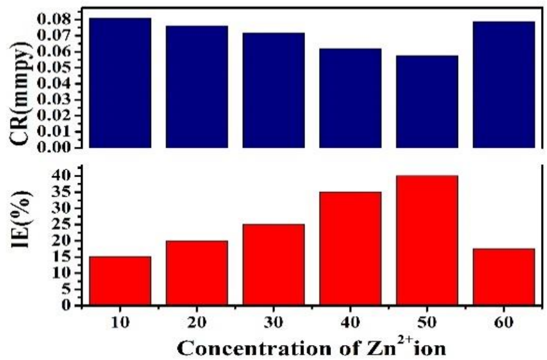

FIGURE 1

L-TRYPTOPHAN SYSTEM FOR 1 DAY

When the carbon steel metals were drowned in cauvery water in the existence of L-Tryptophan of varied numerous concentrations whose range is varied from 50 ppm to 300 ppm the inhibition efficiency of L-Tryptophan was found to increase as the concentration increased. At 150 ppm L-Tryptophan showed the maximum inhibition capability of 50%. These data are expressed in the table below along with the pie chart representation.

L-TRYPTOPHAN SYSTEM FOR 1 DAY

S.NO.	CONC. OF L-TRY(PPM)	CONC. OF ZN^{2+} ION (PPM)	INHIBITION EFFICIENCY (%)	CORROSION RATE (MMPY)
1	50	0	10	0.0858
2	100	0	25	0.0715
3	150	0	50	0.0476
4	200	0	30	0.0668
5	250	0	17.5	0.0786
6	300	0	2.5	0.0930

TABLE NO. 2

RATE OF CORROSION AND PERCENTAGE OF INHIBITION EFFICIENCY OF L-TRYPTOPHAN IN CAUVERY WATER FOR 1 DAY

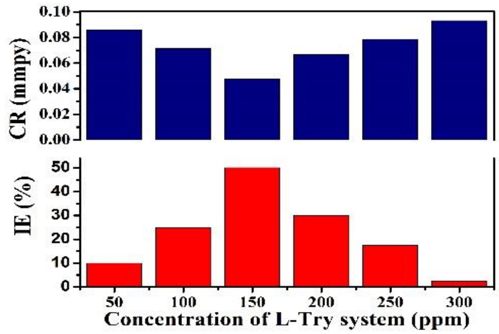

FIGURE 2

L-TRYPTOPHAN AND ZN^{2+} ION SYSTEM FOR 1 DAY

When the carbon steel metals were drowned in cauvery water in the existence of L-Tryptophan of varied numerous concentrations whose range varied from 50 ppm to 300 ppm with Zn^{2+} ion of concentration 50 ppm all through, the inhibition efficiency of the complex mixture namely, L-Tryptophan and Zn^{2+} ion, increased as the concentration of L-Tryptophan up surged. When the concentration of the complex mixture was in the ratio 150:50 ppm of L-Tryptophan and Zn^{2+} ion respectively, it exhibited maximum inhibition efficiency of 70%. These data are expressed in the table below along with the pie chart representation.

L-TRYPTOPHAN AND ZN^{2+} ION SYSTEM FOR 1 DAY

S.NO.	CONC. OF L-TRY (PPM)	CONC. OF ZN^{2+} ION (PPM)	INHIBITION EFFICIENCY (%)	CORROSION RATE (MMPY)
1	50	50	50	0.0858
2	100	50	65	0.0715
3	150	50	70	0.0476
4	200	50	65	0.0668
5	250	50	60	0.0786
6	300	50	55	0.0930

TABLE NO. 3

RATE OF CORROSION AND PERCENTAGE OF INHIBITION EFFICIENCY OF L-TRYPTOPHAN AND ZN^{2+} ION IN CAUVERY WATER FOR ONE DAY

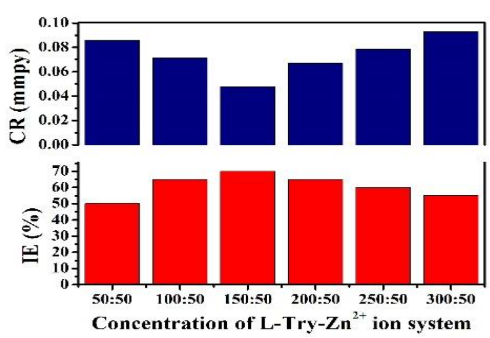

FIGURE 3

SPECTRAL ANALYSIS

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FTIR

FTIR SPECTRUM OF L-TRYPTOHAN AND L-TRYPTOHAN WITH ZN^{2+} ION

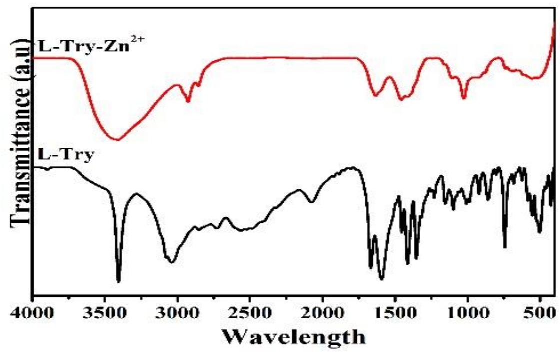

FIGURE 4

FTIR spectroscopy is a technique which is useful in identifying the functional groups that reside in the samples under investigation. FTIR spectroscopy is being used examining the defensive film formed on the metal surface(13-14). Two samples have been investigated for FTIR namely, L-Tryptophan and Zn^{2+} ion film powder and pure L-Tryptophan. On comparing these graphs the following observations were made. The peak of pure L-Tryptophan at 3405.80 cm^{-1} which was due to –NH and -OH stretching vibrations was being shifted to 3409.23 cm-1 for L-Tryptophan and Zn^{2+} ion. The peak of pure L-Tryptophan at 3040.16 cm^{-1} which was due to alkyl stretching was being shifted to 2856.54 cm^{-1} for L-Tryptophan and Zn^{2+} ion. The peak of pre L-Tryptophan at 1592.38 cm^{-1} which was due to –NH bending of $–NH_2$ group was being shifted to 1457.83 cm-1 for L-Tryptophan and Zn^{2+} ion. The peak of pure L-Tryptophan observed at 1667.41 cm^{-1} which was due to carbonyl stretching was being shifted to 1632.50 cm^{-1} for L-Tryptophan and Zn^{2+} ion. Also formation of – ZnO stretching was confirmed by the peak of L-Tryptophan and Zn2+ obtained at 1242.13 cm^{-1}.

Hence the defensive film formation on the carbon steel was confirmed with all such diagnosed groups in the complex mixture. Hence the FTIR investigation lead to the result that the defensive film consisted of Fe^{2+}-L-Tryptophan mixture and $Zn(OH)_2$ on the carbon steel metal surface.

INTERPRETATION OF THE FTIR DATA

TYPES OF VIBRATIONS	PEAKS (cm^{-1})	
	L-TRY	L-TRY + Zn^{2+}
-NH and –OH str	3405.86	3409.23
Alkyl str	3040.16	2856.54
-NH bending of –NH2	1592.38	1457.83
Carbonyl str	1667.41	1632.50
ZnO str	-	1242.13

TABLE NO. 4

UV-VISIBLE SPECTROSCOPY

UV- VISIBLE SPECTRUM OF SOLUTION AND FILM POWDER OF L-TRYPTOPHAN AND ZN^{2+} ION

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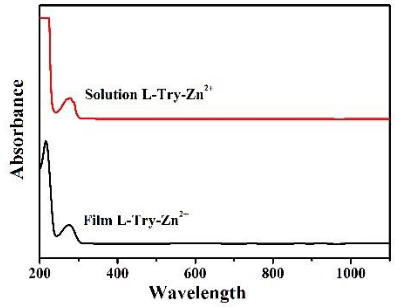

FIGURE 5

The UV-Visible absorption spectroscopy of L-Tryptophan and Zn^{2+} ion solution and the film powder of L-Tryptophan and Zn^{2+} is shown in the figure below. In case of the solution mixture, the peak was obtained at 278.6 nm (0.829a.u.). Whereas for the powder mixture, the peak was obtained at 274.9 nm (1.415 a.u.) and in this case the intensity was found decreasing. This indicates that complex formation has occurred between L-Tryptophan and Zn^{2+} ion in the defensive film formed on the surface of the metal.

INTERPRETATION OF UV-VISIBLE DATA

NAME	NO.	PEAK (NM)	PEAK(AU)
L-Try-Zn^{2+} Sol.	1	278.6	0.829
	2	287.3	0.685
L-Try-Zn2+ Film	1	274.9	1.415

TABLE NO. 5

TAFEL POLARIZATION

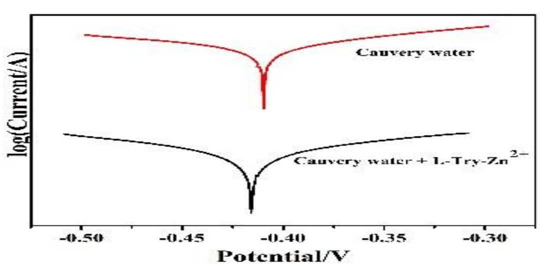

FIGURE 5

Tafel polarization curves of pure L-Tryptophan and L-Tryptophan and Zn^{2+} ion
Polarization study of carbon steel drowned in varied ambiances, namely,
i) Cauvery water
ii) Cauvery water + 150 ppm of L-Tryptophan + 50 ppm of Zn^{2+}

The potentiostatic polarization curves of carbon steel drowned in varied corrosive ambiances are presented in figure below. The corrosion statistical parameters have been presented in the table. When carbon steel got drowned in cauvery water the potential of corrosion is deciphered to be -415.653 mV Vs saturated calomel electrode (SCE). The mixture of 150 ppm L-Tryptophan and 50 ppm 0f Zn^{2+} attempts to shift the corrosion potential to -434.743 mV Vs saturated calomel electrode (SCE) which suggests that the anodic reaction was controlled

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predominantly. The same formulated mixture, namely, 150 ppm of L-Tryptophan and 50 ppm of Zn^{2+} attempts to shift the anodic slope from 251.657 mV to 113.105 mV. This gives the information that the mixture functions as anodic inhibitor controlling anodic reaction.

INTERPRETATION OF TAFEL POLARIZATION CURVES

L-Try (ppm)	Zn^{2+} (ppm)	E_{corr}	b_a	b_c	I_{corr}
0	0	-415.653	251.657	237.955	4.254
150	50	-434.743	113.105	164.454	2.706

TABLE NO. 6

SCANNING ELECTRON MICROGRAPH

SEM gives the illustrated graphical depiction of the metal surface. To know the measure of corrosion of the carbon steel and comprehend the characteristics of the surface film formed in the non-existence and existence of the inhibitor (L-Tryptophan and Zn^{2+} ion), the SEM micrographs are examined. The SEM images of Carbon steel specimen drowned in cauvery water for one day with and without inhibitor are shown below.

The SEM images in Fig (7) shows the various magnifications of carbon steel in cauvery water for one day namely, 1.64 KX, 2.50 KX, and 10.02 KX. Here in these images the carbon steel surface is found very rough which implies that the metal has been corroded to a greater extent.

SEM IMAGES OF VARIOUS MAGNIFICATIONS OF CARBON STEEL IN CAUVERY WATER FOR ONE DAY (1.64 KX, 2.50 KX, 10.02 KX)

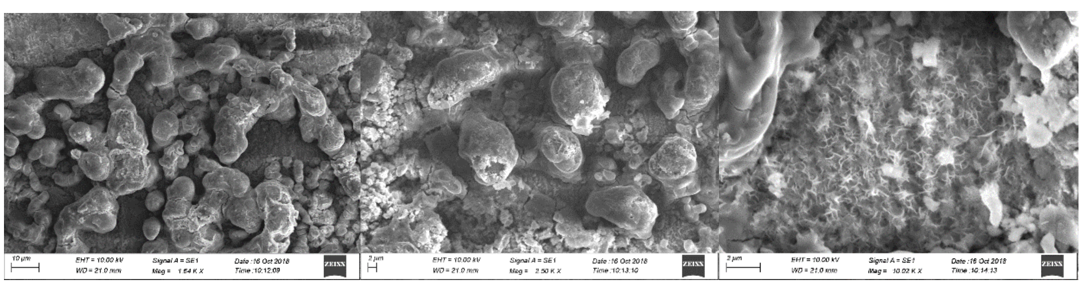

FIGURE 5

The SEM images in Fig (8) shows the various magnifications of carbon steel in cauvery water with L-Tryptophan and Zn^{2+} ion for 1 day namely, 1.64 KX, 2.50 KX, 10.02 KX. In this case the SEM images appear to be smoother which implies that the protective film has been formed. In the existence of 150 ppm of L-Tryptophan and 50 ppm of Zn^{2+} ion in cauvery water the rate of corrosion is found suppressed which is evident from the decrease in corroded areas. This is due to the insoluble metal inhibitor complex (L-Tryptophan and Zn^{2+} ion) on the metal surface which effectively controls the deterioration of carbon steel.

SEM IMAGES OF VARIOUS MAGNIFICATIONS OF CARBON STEEL IN CAUVERY WATER WITH L-TRYPTOPHAN AND ZN^{2+} ION FOR 1 DAY (546 X, 4.02 KX, AND 10.03 KX)

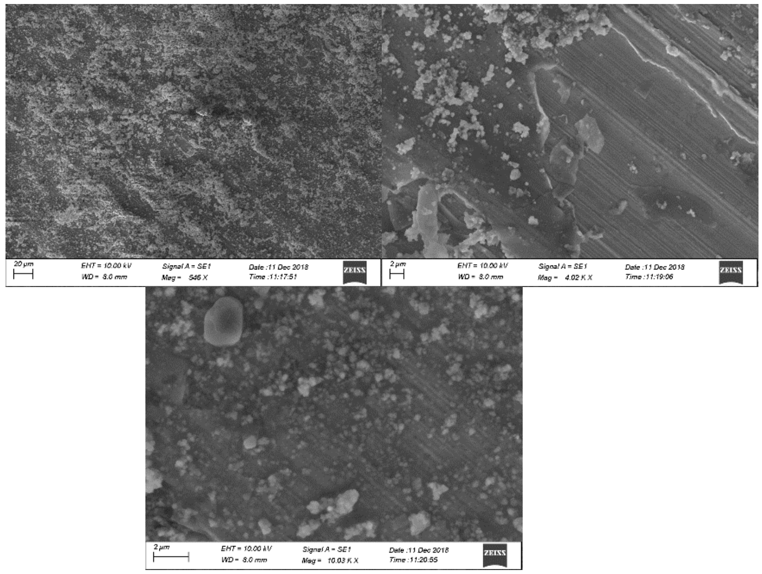

FIGURE 6

3. CONCLUSION

In this investigation, chemical and electrochemical investigations have been carried out to probe into the corrosion inhibition efficiency of L-Tryptophan and Zn^{2+} ion on carbon steel in cauvery water The findings of the study is being summarized as follows.

- Though L-Tryptophan has been asserted to exhibit appreciable inhibition capability in itself, when it was mixed with Zn^{2+} ion a very goof synergistic effect occurred between them due to which the inhibition efficiency has increased considerably.
- Tafel measurement showed that the mixture of L-Tryptophan and Zn^{2+} ions acted as anodic inhibitor.
- Formation of insoluble metal inhibitor complex (L-Try & Zn^{2+}) has been confirmed by scanning electron microscopy.
- Complex mixture of L-Tryptophan (150 ppm) and Zn^{2+} ion 50 (ppm) was proved to inhibit the corrosion of carbon steel in Cauvery water with the inhibition capability of 70%.

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