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Aqueous Plant extract of Henna leaves (Lawsone inermis) as green corrosion inhibitors: A prescreening investigation for mild steel in a simulated environment

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Abstract: In oil and gas industries pipelines are the most cost-effective means of transporting oil and gas in both onshore and offshore production. During drilling operations, acidic fluids' flow and the crude oil which contains sulfur and hydrogen sulfide can induce corrosion in these pipelines. Carbon steels are still the materials used for the construction of these pipelines. Structural stresses and the high or low temperature are also the contributing factors for corroding the steel. Corrosion inhibitors play an important role in prevention of corrosion in pipelines from internal corrosion. With the advent of green chemistry and concern for the marine environment has prompted the researchers to develop the environment friendly inhibitors. In this regard many medicinal plants have been used as corrosion inhibitors for carbon steel. In this paper we describe the investigations on the pre-screening of aqueous extracts of Henna leaves for the corrosion prevention of mild steel in a simulated environment using synthetic sea water by weight loss studies in the presence and absence of H_2S. The plant extract (PE) exhibits good corrosion efficiency, biodegradable, non-toxic and has low bioaccumulation.

Keywords: Natural products, green corrosion inhibitors, bioaccumulation, Biodegradation, mild steel

1. INTRODUCTION

Corrosion inhibition is one the most explored areas of research in the last two decades. [1] A number of corrosion prevention chemicals have been developed in the recent pat. Development of green chemistry principles have made this more interesting wherein the idea of low environmental impact but highly efficient corrosion inhibitors are being developed based on plant materials.[2,3] Several geographical or country specific regulations have been imposed for the development of these environment friendly inhibitors. Some important regulations being North Sea regulations comprising of UK, Norway, Denmark and the Netherlands, eastern Canada and US-Gulf coast etc. While developing the inhibitors key aspects are covered are biodegradation, bioaccumulation, toxicity and corrosion efficiency which should comply with the norms of these area-specific regulations.

In continuation of our work on corrosion inhibitors [4], in the present study the inhibitor is developed for the application in Indian oil and gas industry for mild steel used in the pipelines for transporting oil and natural gas. Aqueous extract of the plant material was prepared and investigated for different parameters. An overview of the investigations has been reported in the study with respect to corrosion inhibition and also its environmental impact.

India is rich in its biodiversity with medicinal plants being foremost part of this biodiversity. India is known for its parallel medicine practice in the form of Ayurveda, Unani and homeopathic medicinal practices which date back to very ancient times. Some of these medicinal plants such as carica papaya, hibiscus aloe vera gel etc have been reported to be good corrosion inhibitors in different environments like acidic media, basic media and simulated environments [5-9]. Indian oil and gas industry follows the guidelines imposed by the Petroleum and natural gas regulatory board Schedule-1E Corrosion Control, the environmental policy rules and regulations proposed by the ministry of Petroleum and natural gas, Government of India and UNEP guidelines with respect to corrosion prevention. Corrosion poses a huge threat to the marine biodiversity. Corrosion of pipelines can lead to oil spillage and the consequences will have an everlasting impact for the aquatic life. It is essential that the corrosion of pipeline both internal and external should be addressed to prevent any oil spillage accident.

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2. EXPERIMENTAL

In most of cases, Studying Inhibition Efficiency is carried out by weight loss method. Same method has been employed in our study for evaluating the corrosion efficiency.

2.1 Pre-treatment of the coupons

Commercial grade mild steel sheets (IS 513 CRCA DD of composition-0.1% C, 0.45% Mn, 0.035% S, 0.035% P) cut into rectangular coupons of the dimension (4 cm x 1cm x 0.05 cm thickness). These coupons were polished with emery paper and degreased with acetone. These were later, dipped in pickling solution (2g zinc dust and 20g of NaOH in 100 cm3 of water) [10] as per ASTM G1-90 [11], to clean the surface at 90 ºC for 30 minutes. The coupons were removed, washed with distilled water, and dried. These were polished with emery paper (grade 600) till the products are removed to get a shiny surface. Then the coupons were dipped in ethyl alcohol to remove the dust, dried and stored in desiccator till they were used.

2.2. Plant extract preparation:

4 g of the plant material (leaves of henna plant) was refluxed with 100 cm^3 of distilled water for 1 hour. The extract was filtered to remove the suspended particles and the filtrate was made up to 100 ml. A series of solutions ranging from 10 ppm to 500 ppm concentration were obtained by adding suitable aliquots to the corrosion medium synthetic sea water). Synthetic sea water was prepared by dissolving suitable salts in distilled water as per ASTM standard [12].

2.3. Henna plant : Lawsonia Inermis L. (Lythracaea) is an important branched shrub that grows in Rajasthan, Gujarat states of our country. Henna plant's scientific name is Lawsone inermis. It mostly contains, contains 2-hydroxy-1,4-naphthoquinone and other terpenes. [13]. It is used in various cosmetics preparations such as Sunscreen, tanning lotion, colouring agent. It is also used as a coagulant for open wounds and a poultice to sooth burns and eczema, antiseptic for fungal or bacterial skin infections [14].

2.4. Weight loss measurements

To study the corrosion performance of the Plant extract, the MS coupons were immersed in of Synthetic sea water / 5% NaCl at room temperature (25□2 ºC) for 24 hrs with and without plant extract. Different concentrations of the PE were maintained in ppm level, 2 cm2 area of the coupons were exposed to the medium. Acculab model ALC 210.4 Analytical balance was used for weighing. All chemicals used were AR grade.

Corrosion inhibition efficiency (IE) was calculated from

$$IE = \frac{Wo - W) \times 100}{Wo}$$

Where, Wo corrosion rates for coupon in absence of inhibitor, in mpy.

W corrosion rates for coupon in presence of inhibitor, in mpy.

Weight loss measurements were evaluated both in the presence and absence of H_2S. The generation of Hydrogen sulphide was carried out insitu by adding 1700g/L of Acetic acid and 3530 mg/L of fresh sodium sulphide (Na_2S $x.H_2O$) to the 5% NaCl [15].

2.5. Cleaning of coupons after exposure:

In the absence of Hydrogen sulphide, the coupons were removed from medium washed in distilled water thoroughly cleaned with tissue paper. Then dipped in alcohol and dried, the weight was taken.

In the presence of Hydrogen sulphide, the coupons were removed from medium washed in distilled water thoroughly, cleaned with paper. Then dipped in alcohol and dried. To remove the corrosion products, the coupons were dipped in 0.01 N HCl. Then again the coupons were dipped in distilled water, thoroughly washed, dried, and weights taken.

Corrosion rate (CR) was expressed in 'mills per year' (mpy), was determined by [16].

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$$CR = \frac{K \times W}{A \times T \times D}$$

Where, K=a constant, depends on the unit desired. = (3.45 x106)
T=time of exposure in hours= (24)
A=area in cm2= (2)
D=density in g/cm3 = (7.86)
W=weight loss in g

2.6. Bioaccumulation studies [17]

Partition coefficient Po/w is defined as the ratio of the concentration of the PE present in the octanol phase to the concentration present in aqueous phase. To evaluate the bioaccumulation absorbance values were recorded on ELICO SL-159 UV-Visible spectrophotometer. Bioaccumulation determined by measuring the partition coefficient of the PE in octanol and water, by measuring the absorbance in two steps. BE is the absorbance measured for the Octanol layer separated from mixture of PE + Octanol. After measuring BE, to the PE + Octanol mixture aqueous phosphate buffer was added, shaken well on a vortex mixer, allowed to stand overnight (nearly for 24 hrs). n-Octanol was separated and its absorbance was measured as AE.

$$P_{o/w} = \frac{C\ octanol}{Caq} = \frac{BE}{BE-AE}$$

Different compositions of the inhibitor (PE), n-Octanol and buffer were prepared to evaluate the bioaccumulation as shown in **Table 2**.

Table 2: Composition of n-Octanol + plant extract (inhibitor) + buffer

Conc. no.	Volume of n-Octanol (cm^3)	Volume of inhibitor (cm^3)	Volume of Buffer (cm^3)
1	5	2	5
2	5.8	2.2	4
3	6.6	2.4	3
4	7.2	2.6	2
5	8.4	2.8	1

2.7. Determination of Toxicity of corrosion inhibitor

Toxicity [18] of the Plant Extracts (PE) used as inhibitors was determined using seawater. Species used was Brine shrimp also known as sea monkey () for the toxicity study of corrosion inhibitor. These have been used in the toxicity investigations of several consumer products. Two parameters were evaluated – EC 50 and LC 50. EC 50 is defined as the effective concentration of a chemical substance necessary to distress the 50 % of the aquatic organism population, and LC 50 is the effective concentration of a chemical substance required to kill 50 % of the population of the organism under study. Brine shrimp are marine invertebrates of about 1mm size. Freeze dried cysts were obtained from the in aquarium stores of Cubbon park aquarium, Bangalore. These were hatched in sea water in suitable conditions and used for the toxicity studies. Toxicity studies were carried out at different concentrations of plant extract in sea water (at ppm level). **Table 3** gives the dosage of inhibitor added for Toxicity studies. The volume of the sea water and plant extract mixture was maintained at 5 cm^3. The time of addition of corrosion inhibitor was noted. The tubes were kept in the same condition for few days till the 50 % of the shrimp died and the number of days was noted. Regularly the behaviour of the shrimp was monitored and recorded. The results are shown in **Table 13**.

Table 3: Dosage of inhibitor added to sea water for toxicity studies

Sl. no.	DOSAGE	Concentration (ppm)
1	1 cm^3 of sea water (control)	0.0
2	1 cm^3 of 1 ppm	0.2
3	0.25 cm^3 of 10 ppm + 0.75 cm^3 of SW	0.5
4	1 cm^3 of 10 ppm	2
5	0.25 cm^3 of 10 ppm + 0.75 cm^3 of SW	5
6	1 cm^3 of 100 ppm	20
7	0.25 cm^3 of 10 ppm + 0.75 cm^3 of SW	50
8	1 cm^3 of 1000 ppm	200
9	0.25 cm^3 of 10 ppm + 0.75 cm^3 of SW	500
10	1 cm^3 of 10000 ppm	2000

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11	0.5 cm^3 of 40,000 ppm + 0.75 cm^3 of SW	4000
12	1 cm^3 of 40,000 ppm + 0.75 cm^3 of SW	8000

2.8. Biodegradation

The third parameter evaluated for the green properties of the inhibitor is biodegradation which is measured as per OECD 306 test guidelines [19]. It is measured by determining the time for which the substance stays in the environment (seawater). Biodegradation is the ratio of the Biological Oxygen Demand (BOD) to Biological Oxygen Demand (COD) in the marine environment [20-21]. The test is carried out for a gap of 28 days, during which the compound should be rapidly biodegradable. The substance must be degradable by 60 % or more in these 28 days from the day of start of test. BOD and COD are determined as per the standard procedures available in the literature.[25-27] Large Differences in the values of COD and BOD of the sample indicates the presence of non-biodegradable substances. Hence a smaller variation is expected for the inhibitors.

Biodegradation (BD) = $\frac{\text{BOD X 100}}{\text{COD}}$

Biodegradation should be >60% for a sample to be a good biodegradable corrosion inhibitor.

3. RESULTS AND DISCUSSION

3.1. Corrosion inhibition

Effect of Inhibitor concentration on percentage inhibition efficiency (% IE) was studied by varying the concentration of the Plant Extract (PE) in the range of 10-500 ppm at room temperature for 24 Hrs period. From the weight loss measurements for Blank (medium only) with and without H2S, it is found that in the absence of plant extracts the corrosion rate is more (13.49 and 11.20 mpy) as shown in **Tables 4** and **5**.

Table 4. Calculation Of Corrosion Rate For Blank/ Medium-Without (in the absence of Plant extract)

Trial no.	Weight of coupon before immersion (g)	Weight of coupon after immersion(g)	Weight loss (g)	CR (mpy)	Average CR (mpy)
1	0.4758	0.4743	0.0015	13.72	13.49
2	0.5091	0.5077	0.0014	12.80	
3	0.4938	0.4931	0.0017	15.55	
4	0.4695	0.4682	0.0013	11.89	

Table 5: Calculation Of Corrosion Rate For Blank/ Medium- With H_2S (in the absence of PE)

Trial no.	**Weight of coupon before immersion (g)**	**Weight of Coupon after immersion(g)**	**Weight loss (g)**	**CR (mpy)**	**Average CR (mpy)**
1	0.4696	0.4685	0.0012	10.97	11.20
2	0.5051	0.5041	0.0010	9.14	
3	0.4631	0.4617	0.0014	12.80	
4	0.4278	0.4265	0.0013	11.89	

Table 6 and **7** gives the data for the inhibition efficiency of the plant extract of henna leaves in the absence and presence of H_2S.Summary is given in Table 8 and Figure 1 gives the plot of % IE with and without H_2S. From this table we can see that maximum inhibition is seen at 200 ppm of plant extract in absence of H_2S and at 100 ppm in presence of H_2S. Fig. 1 is the graphical representation of this data.

TABLE 6: Corrosion Inhibition Efficiency of Plant Extract of Henna leaves to MS-in the absence of H_2S-Immersion period of 24hrs

Sl no.	**Conc (ppm)**	**Weight before**	**Weight after**	**Weight loss**	**CR mpy**	**IE (%)**
1	10	0.5257	0.5030	0.0005	4.57	0
2	20	0.4777	0.4771	0.0006	5.49	0
3	30	0.4541	0.4537	0.0004	3.66	20
4	40	0.4617	0.4613	0.0004	3.66	20
5	50	0.4478	0.4475	0.0003	2.74	40

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6	100	0.4332	0.4329	0.0003	2.74	40
7	150	0.5014	0.5010	0.0004	3.66	20
8	200	0.5013	0.5011	0.0002	1.83	60
9	300	0.4806	0.4802	0.0004	3.66	20
10	400	0.4625	0.4623	0.0002	1.83	60
11	500	0.4718	0.4715	0.0003	2.74	40

TABLE 7: Corrosion Inhibition Efficiency of Plant Extract of Henna leaves to MS-in the presence of H_2S-Immersion period of 24hrs

Sl no	Conc (ppm)	Weight before	Weight after	Weight loss	CR mpy	IE (%)
1	10	0.4554	0.4552	0.0002	1.83	50
2	20	0.4875	0.4873	0.0002	1.83	50
3	30	0.4303	0.4301	0.0002	1.83	50
4	40	0.4775	0.4771	0.0004	3.66	0
5	50	0.4324	0.4322	0.0002	1.83	50
6	100	0.4402	0.4401	0.0001	0.92	75
7	150	0.4392	0.4390	0.0002	1.83	50
8	200	0.4184	0.4183	0.0001	0.92	75
9	300	0.4951	0.4950	0.0001	0.92	75
10	400	0.4831	0.4830	0.0001	0.92	75
11	500	0.4210	0.4209	0.0001	0.92	75

TABLE 8: Summary of IE (%) for plant extract of Henna leaves

Conc. ppm	IE (%) without H_2S	IE (%) with H_2S
10	50	0
20	50	0
30	50	20
40	0	20
0	50	40
100	75	40
150	50	20
200	75	60
300	75	20
400	75	60
500	75	40

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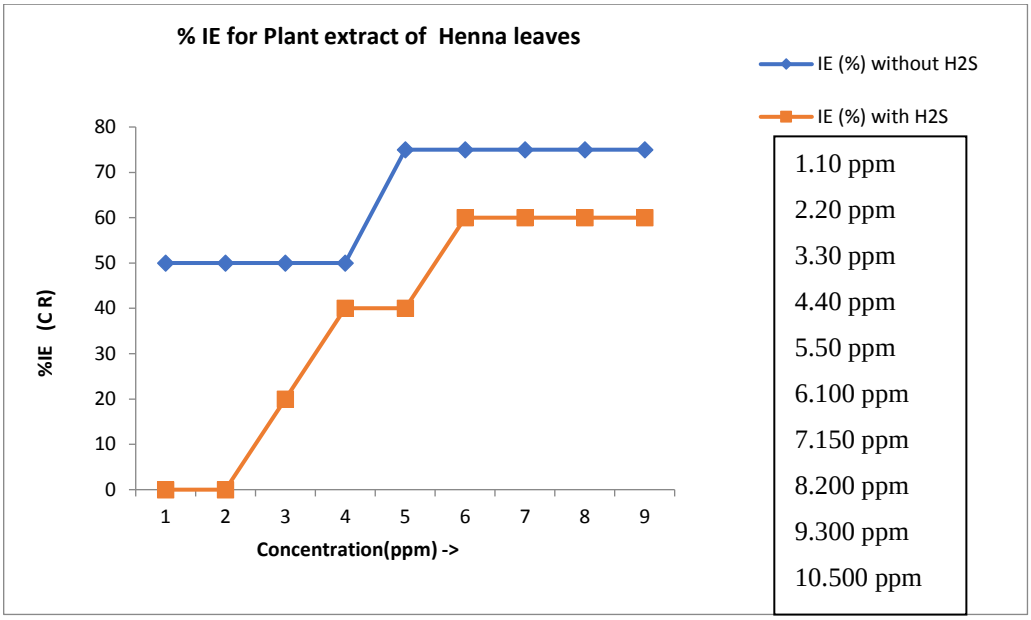

FIG. 1: Plot showing the %IE with and without H_2S for plant extract of Henna leaves

CR-Corrosion Rate, (mills per year), IE-Inhibition Efficiency

Environmental impact

The experimental data with respect to Green properties for plant extract of Henna leaves with respect to bioaccumulation, biodegradation and toxicity are given in **Tables 9, 10,** and **11**.

TABLE 9: Bioaccumulation values for the plant extract of Henna leaves

Conc.	BE	AE	$P=\frac{BE}{BE-AE}$	Log P	
C-1	2.242	0.278	1.1415	0.057	<3
C-2	2.242	0.312	1.1617	0.065	<3
C-3	2.242	0.389	1.2099	0.083	<3
C-4	2.095	0.679	1.4795	0.170	<3
C-5	2.037	1.166	2.3387	0.368	<3

Wavelength taken at 297 nm for BE and AE

Biodegradation

TABLE 10: Data and results of biodegradation for plant extract of Henna leaves

Sl. no	Sample	BOD Sample mg/ml	COD mg/ml	B.D= $\frac{BOD \times 100}{COD}$ (%)	B.D %
1	Henna leaves extract	12.22	19.76	(12.22*100)/19.76=61.8	61.8

Where,

SW-Sea water, DW-Distilled water

Toxicity

Findings of the toxicity studies are shown in **Table 13**. A graph of the concentration as x-axis, was plotted for the data of percentage of survival. It gives the time graph of percent of survival from this the 50% survival point is taken which corresponds to a value of concentration. As we can see the survival rate is higher at the higher concentration of plant extract which indicates that the extract may be acting as a feed.

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TABLE 11: Data for the toxicity studies of the plant extract of henna leaves

Sl no	DOSAGE	Conc. ppm	No. of shrimp before	No. of shrimp after 30 mins	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
1	1ml of sea water (control)	0.0	10	10	9	5	5	4	0	0	0
2	1 ml of 1 ppm	0.2	10	10	9	6	4	3	1	0	0
3	0.25ml of 10 ppm + 0.75 ml of SW	0.5	10	10	8	6	4	3	1	0	0
4	1 ml of 10 ppm	2	10	10	9	4	3	2	2	0	0
5	0.25 ml of 10 ppm + 0.75 ml of SW	5	10	10	6	4	2	0	0	0	0
6	1 ml of 100 ppm	20	10	10	6	2	2	0	0	0	0
7	0.25 ml of 10 ppm + 0.75 ml of SW	50	10	10	6	3	3	1	1	1	0
8	1 ml of 1000 ppm	200	10	10	5	3	3	1	1	1	0
9	0.25 ml of 10 ppm + 0.75 ml of SW	500	10	10	5	4	2	1	1	1	0
10	1 ml of 10000 ppm	2000	10	10	5	4	3	2	2	0	0
11	0.5 ml of 40,000 ppm + 0.75 ml of SW	4000	10	10	8	7	3	3	2	0	0
12	1 ml of 40,000 ppm + 0.75 ml of SW	8000	10	10	10	6	3	3	2	0	0

Where, SW-Seawater

Competing Interests

The author would like to declare that there are no competing interests regarding the publication of this paper.

CONCLUSION

As the data on preliminary screening investigations indicate, the plant extract of Henna leaves was found to be of low toxicity, easily biodegradable and also has good corrosion inhibition in the simulated environment for mild steel. Corrosion inhibition is observed in presence and absence of H_2S (Table 8). Bioaccumulation is <3 (Table 9), Biodegradation is >60% (Table 10) and toxicity is low (Table 13). Plausible mechanism for the inhibition property can be envisaged to be the adsorption of inhibitor on the surface of the mild steel s\and preventing the corrosive medium form coming in contact with the metal. It is concluded from the data gathered that the corrosion inhibition can be done using this plant extract where environment pollution is reduced.

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