SYNERGISTIC EFFECT OF WATER HYACINTH LEAVES – ZN^{2+} SYSTEM IN CORROSION INHIBITION OF MILD STEEL IN AQUEOUS MEDIUM

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Abstract

An aqueous extract of Water Hyacinth (Eichorrnia Crassipes) leaves extract has been used as a corrosion inhibitor in controlling corrosion of mild steel immersed into 60ppm Cl^- ion containing aqueous medium. The inhibitive action of this plant extract was explained using inhibition efficiency and degree of surface coverage. The most suitable inhibitor concentration was found to be 0.1% with inhibition efficiency (IE) of 87% at Zn^{2+} (50 ppm) by the weight loss method. Influence of surfactants CTAB, Sodium sulphite, some synergists TSC, Sodium Gluconate, immersion period on the inhibition efficiency on the metal surface has also been investigated.

Keywords synergistic effect, Water Hyacinth, corrosion inhibition, weight loss method.

1. INTRODUCTION

Corrosion is the deterioration of the useful properties of materials caused by the environment. A substantial portion of the government and industrial funds are being spent all over the world for combating corrosion losses. One of the best ways of controlling corrosion is selecting a suitable corrosion inhibitor. According to NACE, an inhibitor is "a substance which retards corrosion when added to an environment in small concentration" [1]. Almost all organic molecules containing hetero atoms such as nitrogen, sulphur, phosphorus, and oxygen show significant inhibition efficiency. But most of them are toxic, non-biodegradable and thus causing environmental problems. Hence these deficiencies have prompted the search for their replacement. The reason for use of plant extracts and their products as corrosion inhibitors are due to their abundant availability, cost effective and harmless to environment.

Many plant extracts has been widely reported as efficient corrosion inhibitors in several corrosive medium [2-8].In recent times, many studies have been carried out on Water Hyacinth (Eichorrnia Crassipes), of abundant noxious fresh water weed [9] and found that the presence of anti oxidants of chlorophylls, carotenoids, phenols, alkaloids, and terpenoids in their extracts showed corrosion inhibition efficiency on magnesium alloy [10]. The corrosion inhibitive effect of leaves (ELT) and roots (ERT) extracts of Eichorrnia Crassipes on mild steel in HCl solutions has been explained using gasometric technique and Quantum chemical calculations [11]. The corrosion inhibition of Eichorrnia Crassipes leaves extract in marine environment for AISI 1030 steel was examined using weight loss and electrode potentials techniques [12]. Thus in this research work, the corrosion inhibition due to synergistic effect of Eichorrnia Crassipes leaves extract-Zn^{2+} in aqueous medium containing 60ppm Cl^- ion environment which is normally present in the cooling water system is analyzed by using weight loss and surface coverage (Θ) methods provides additional insight into the mechanism of inhibitory action.

2.METHODS AND MATERIALS

2.1 Preparation of Specimen

Mild steel specimens of size 1.0 cm ×4.0 cm ×0.2 cm and chemical composition 0.026 % sulphur,0.06 % phosphorous, 0.4 % manganese, 0.1% carbon and the rest iron were polished to a mirror finish and degreased with acetone and used for the weight loss method and surface examination studies.

2.2 Extraction of plant materials

The WH Leaves are collected, shade dried and powdered. Plant materials are dried in shade so as to enrich the active principles in them, by reducing their moisture content. The extract was prepared by refluxing 25 g of powdered dry leaves in 500 ml dd water for 5 hr and kept overnight. Then it was filtered and the volume of the filtrate was made up to 500 ml using the same water and this was taken as stock solution [13-15].

2.3 Weight – loss method

Mild steel specimens were immersed in 100 ml of the aqueous medium containing 60 ppm Cl^- ions in various Concentrations of the inhibitor in the absence and presence of Zn^{2+} for one day. The Inhibition efficiency (IE %) was calculated using the equation,

$$\text{Inhibition Efficiency (IE \%)} = (1-W_1/W_2) \times 100$$

$$\text{Surface coverage } (\Theta) = (1-W_1/W_2)$$

Where W_1 and W_2 are the weight loss for mild steel in the presence and absence of inhibitor.

2.4 Determination of corrosion Rate

The corrosion rate (CR) is directly proportional to the weight loss / cm^2 in a specified time and was calculated by the formula.

$$CR = (87.6 \times W)/ DAT$$

Where, W = weight loss in mg.
D = density of mild steel (7.86 g / cm^2 for mild steel),
A = Area in cm^2,
T = Exposure time in hours
Trends of CR and IE are graphically evaluated.

2.5 Calculation of synergistic factor (S_Θ)

$$S_\Theta = (1-\Theta_A-\Theta_B + \Theta_A\, \Theta_B)/ (1- \Theta_A\, \Theta_B)$$

Where Θ_A and Θ_B are the surface coverage of compounds A and B respectively, acting alone and Θ_{AB} is the experimentally observed combined surface coverage of the solution containing both A and B.

3.RESULTS AND DISCUSSION

3.1WEIGHT LOSS METHOD

a) Effects of concentration on corrosion rate

The variation of corrosion rate of mild steel in 60 ppm Cl^- in the absence & presence of various concentrations of aqueous extracts of WHL-Zn^{2+} was shown in figure1. The result showed that the corrosion rate of mild steel in 60ppm Cl^- ion containing aqueous medium decreases with increase in the concentration of the extracts indicating that aqueous extracts of WHL inhibited the corrosion of mild steel in aqueous medium containing 60ppm Cl^-ion. This result was tabulated in Table 1.

b)Effects of concentration on Inhibition Efficiency:

As seen in fig 2, the inhibition efficiency of the WHL extracts -Zn^{2+} on the mild steel increases with increasing the concentration of WHL- Zn^{2+}.

This may be due to the concentration of the WHL extract -Zn^{2+} increases, the fraction of the surface covered by the adsorbed molecule also increases which results in to an increase in the inhibition efficiency. The maximum inhibition efficiency of 87% was obtained even at 0.1 % (v/v) of WHL extract and 50 ppm of Zn^{2+}, above which, further increase in extract concentration did not cause any significant change in the performance of the extracts.

A synergistic effect exists between WHL extract and Zn^{2+}. For example, 0.1% (v/v) of WHL extract shows 60% IE and 50 ppm Zn^{2+} shows 41% IE. But their combination has 87% IE. This suggests that a synergistic effect exists below WHL extract & Zn^{2+}.

c) Calculation of synergistic factor (S_Θ)

Synergistic inhibition is an effective means used to improve the inhibition efficiency of an inhibitor in order to decrease the amount of usage and to diversify the application of inhibitor. Thus, it is necessary for corrosion scientists to discover, explore and use synergism in the complicated corrosive media. Actually, many investigations concerning synergistic inhibition have been carried out [16 - 18]. Synergistic factor (S_Θ) is calculated for the mixture containing plant inhibitor WHL extract 0.1 % (v/v) as A & Zn^{2+}(50ppm) as B.

$$S\Theta = \frac{(1 - \Theta A - \Theta B + \Theta A \Theta B)}{(1 - \Theta AB)}$$

Where Θ_A and Θ_B are the surface coverage of compounds A & B respectively, acting alone and Θ_{AB} is the experimentally observed combined surface coverage of the solution containing both, A and B. If inhibitors, A and B have no effect on each other & adsorb at metal –solutions interface independently, then the value of synergistic factor, S_Θ=1. When the value of S_Θ >1, shows synergistic effect and S<1 shows antagonistic effect between the inhibitors. From the table 2, it was cleared that the synergistic factor S_Θ > 1. Thus a good synergistic effect was exhibit between various concentrations of WHL extracts and Zn^{2+} (50ppm).

3.2 Effect of Immersion Time

The WHL extract of concentration 0.1% (v/v) and Zn^{2+} (50ppm) has shown a excellent corrosion inhibition efficiency, for a longer period. After 30 days only the IE is decreased. The results are clearly entered in Table 3.

3.3 Effect of Surfactant

Corrosion inhibition has complex mechanisms and depends on the formation of mono (or) multi-dimensional protective layers on the metal surface. The protective nature of the surface layer depends on many factors: 1) Interaction between inhibitor and substrate, 2) Incorporation of inhibitor in the surface layer, 3) Chemical reactions, 4) Electrode potential, 5) Concentration of inhibitor, 6) Temperature, 7) Properties of the corroding surface, etc,

The corrosion by surfactant molecules are related to the surfactant's ability to aggregate at interfaces & in solution. The effectiveness of surfactant inhibitor can be studied on the basis of their miscellar properties in a particular medium. The most well known inhibitors are surfactants containing long chain of C-atoms and hetero atoms like,-N,-S, and-O atoms.

a) Influence of cetyl Tri methyl ammonium bromide (CTAB):

The cationic inhibitor of CTAB is a biocide and it can control the corrosion caused by bacteria [19]. The inhibition efficiency of WHL (0.1% (v/v)) and Zn^{2+} (50ppm) is not changed by increasing the concentration of CTAB, But the addition of CTAB may provide a excellent biocidal efficiency [20]. This result is shown in table 3.

From the figure3, it is clear that only 20ppm of CTAB shows 83% inhibition efficiency, after that when the concentration of CTAB increases there is a constant IE% would be exists.

b) Influence of Sodium sulphite

The inhibition efficiency of Sodium sulphite (Na_2SO_3), non-ionic surfactant is given in table5. The use of Na_2SO_3 for metallic protection is due to its oxygen scavenging tendency. A reaction of typical scavenger is indicated by the equation as,

$$2\ Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

In the figure 4,when the non-ionic surfactant sodium sulphite concentration increases the formulations of WHL extract of 0.1% (v/v) and 50 ppm Zn^{2+} does not change its inhibition efficiency as in CTAB. Since Water Hyacinth has the anti-oxidant activities [10] due to the presence of chlorophylls, carotenoids, phenols, alkaloids and terpenoids, the presence of sodium sulphite not very much influence the inhibition efficiency of WHL extract on mild steel.

3.4 Effects of synergist

The corrosion Inhibition of WHL - Zn^{2+} has been further analyzed by the addition of various concentrations of synergists using Tri sodium citrate as well as sodium gluconate and the results are in the tables 6& 7.

a) Influence of Tri sodium Citrate

As the concentration of TSC increases for the stable composition of WHL (0.1 % (v/v)) +Zn^{2+} (50ppm) mixtures, the inhibition efficiency is first increased to 88% for 10 ppm of TSC, after that the further increase in concentration of TSC decreases the inhibition efficiency of the system which is plotted in figure 5.

b) Influence of Sodium gluconate

Sodium gluconate concentration when increases the corrosion inhibition of WHL extract (0.1 % (v/v)) + Zn^{2+} (50ppm) is decreased first & then increase from the Concentration of 50 to 100ppm of sodium gluconate. The inhibition efficiency of 83% is obtained for 50 to 100ppm of sodium gluconate concentration which is shown in the figure 6.

4. CONCULSION

The following conclusion were made from the following studies

1) The inhibition efficiency increases with the increase of inhibitors concentration and thus increases the protective action of the inhibitor on mild steel
2) The inhibitor showed maximum inhibition efficiency of 87% at 0.1%v/v inhibitor concentration
3) The formulation of WHL 0.1%(v/v)+Zn^{2+} (50ppm)protective coating can with stand for a long period of time and to prevent corrosion.
4) Synergistic effect exists between WHL extract and Zn^{2+}.
5) The presence of anti-oxidants in WHL extract act as good oxygen scavengers and thus it can prevent well the oxidative corrosion than by using anti-oxidants like sodium sulphite.
6) Addition of 10ppm of TSC slightly increases the IE to 88%, further increase in concentration of TSC decreases the IE.
7) The presence of biocide CTAB and synergists like sodium gluconate does not change the excellent inhibition efficiency of the WHL extract – Zn^{2+} system.

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Table.1. Corrosion rate (CR) and Inhibition efficiency (IE) of mild steel immersed in 60ppm Cl^- containing aqueous medium by weight loss method

Immersion period: One day, Inhibitor: WHL extract %(v/v) + Zn^{2+} (ppm)

S. No	IE %	Zn^{2+}ppm							
		0		10		25		50	
		%IE	Corr. rate×10^3 mmpy	%IE	Corr. rate×10^3 mmpy	%IE	Corr. rate×10^3 mmpy	%IE	Corr. rate×10^3 mmpy
1	0	0	139.490	40	83.694	43	79.044	50	69.745
2	0.05	37	88.343	67	46.496	80	27.898	83	23.248
3	0.1	60	55.796	60	41.847	70	23.248	87	18.598
4	0.2	47	74.394	67	46.496	82	25.732	83	23.248

5	0.3	40	83.694	58	58.121	76	32.547	80	27.898
6	0.4	37	88.343	53	65.095	75	34.872	76	32.547
7	0.5	33	92.993	53	65.095	65	48.821	75	34.872
8	0.6	30	120.891	50	69.745	58	58.121	71	39.522

Table:2. Synergism parameters (S_Θ) for various concentration of WHL extracts in the presence and absence of inhibitor

Zn^{2+}(50ppm) Θ_B	WHL extract Θ_A	WHL extract + Zn^{2+}(50ppm) Θ_{AB}	S_Θ
0.5000	0.3667	0.8333	1.8995
0.5000	0.6000	0.8667	1.5001
0.5000	0.4667	0.8333	1.5996
0.5000	0.4000	0.8000	1.5000
0.5000	0.3667	0.7667	1.3572
0.5000	0.3333	0.7500	1.3334
0.5000	0.3000	0.7167	1.2354

Table3. Influence of immersion time on IE of WHL extract (0.1 % V/V) –Zn^{2+} (50ppm)

Immersion period(3days)	1	3	5	7	9	15	30
CR×10^3 System:WHL0%(v/v)+ Zn^{2+}(0ppm)+60ppm Cl^-	139.49	292.93	539.36	613.75	1032.2	3012.99	5853.94
CR×10^3 System:WHL0.1%(v/v)+ Zn^{2+}(50ppm)+60ppm Cl^-	18.598	65.095	69.74	111.59	209.24	999.68	2455.03
% IE	87	78	87	82	80	67	50

Table.4. Influence of concentrations of CTAB on 0.1% (v/v) WHL extract + 50 ppm Zn^{2+} in 60 ppm Cl^- ion in aqueous medium Immersion period: one day

S No	Concentration of WHL extract % (v/v)	Concentration of Zn^{2+} ppm	Concentration of CTAB (ppm)	Weight loss(g)	Corr.rate×10^3 mmpy	Θ	% IE
1	0.1	50	0	0.0004	18.598	0.8667	87
2	0.1	50	10	0.0006	27.898	0.8000	80
3	0.1	50	20	0.0005	23.248	0.8333	83

4	0.1	50	30	0.00065	30.222	0.7833	78
5	0.1	50	40	0.0006	27.898	0.8000	80
6	0.1	50	50	0.0006	27.898	0.8000	80

Table 5. Influence of concentrations of Sodium sulphite on 0.1% (v/v) WHL extract + 50 ppm Zn^{2+} in 60 ppm Cl^- ion in aqueous mediuImmersion period: one day

S No	Concentration of WHL extract % (v/v)	Concentration of Zn^{2+} ppm	Concentration of Sodium sulphite (ppm)	Weight loss(g)	Corr.rate×10^3 mmpy	Θ	% IE
1	0.1	50	0	0.0004	18.598	0.8667	87
2	0.1	50	10	0.0006	27.898	0.8000	80
3	0.1	50	20	0.0005	23.248	0.8333	83
4	0.1	50	30	0.00065	30.222	0.7833	78
5	0.1	50	40	0.0006	27.898	0.8000	80
6	0.1	50	50	0.0006	27.898	0.8000	80

Table 6. Influence of Tri sodium citrate on Inhibition efficiency (%IE) Immersion period: One day

S. No	Concentration of WHLextract % (v/v)	Concentration of Zn^{2+} (ppm)	TSC (ppm)	Weight loss (g)	Corrosion rate ×10^3 mmpy	Θ	% IE
1	0.1	50	0	0.0004	18.598	0.8667	87
2	0.1	50	10	0.00035	16.273	0.8833	88
3	0.1	50	20	0.0004	18.598	0.8571	86
4	0.1	50	30	0.0004	18.598	0.8571	86
5	0.1	50	40	0.00045	20.923	0.8500	85
6	0.1	50	50	0.0005	23.248	0.8333	83

Table 7. Influence of Tri sodium gluconate in 0.1% inhibition +50ppm Zn^{2+} Immersion period: One day

S.No	Concentration of WHL extract % (v/v)	Concentration of Zn^{2+} ppm	SG ppm	Weight loss (g)	Corrosion Rate×10^3 mmpy	Θ	% IE
1	0.1	50	0	0.0004	18.598	0.8667	87
2	0.1	50	10	0.0009	41.847	0.7000	70
3	0.1	50	20	0.0007	32.547	0.7660	77
4	0.1	50	40	0.0006	27.898	0.8000	80
5	0.1	50	50	0.0005	23.248	0.8333	83
6	0.1	50	75	0.0005	23.248	0.8333	83
7	0.1	50	100	0.0005	23.248	0.8333	83

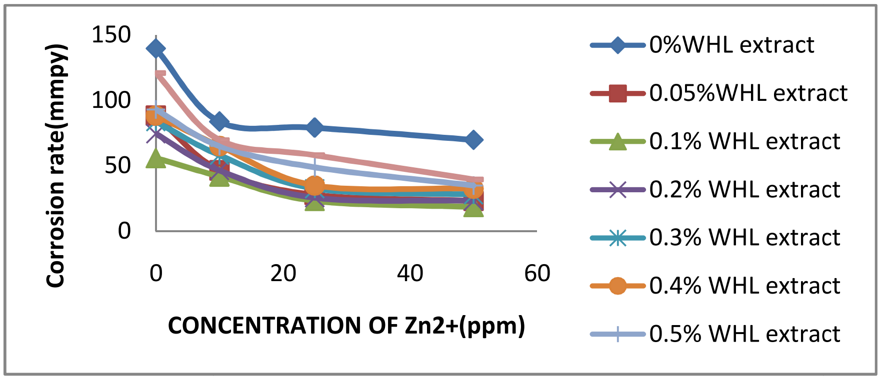

Figure 1. Concentration of Zn^{2+} on Corrosion rate

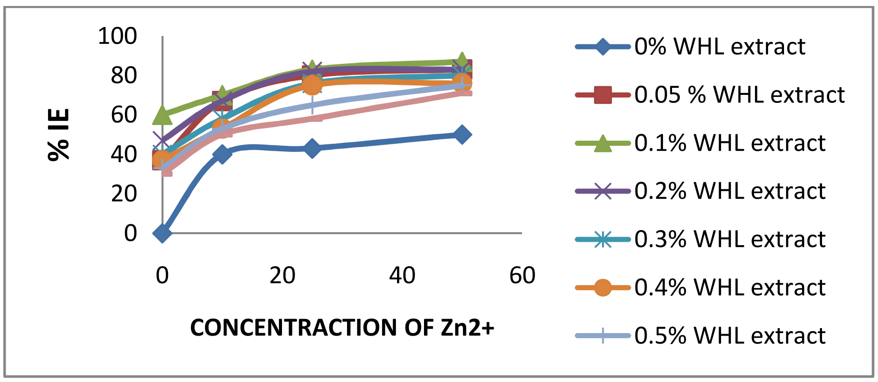

Figure:2. Concentration of Zn^{2+} on percentage of Inhibition efficiency

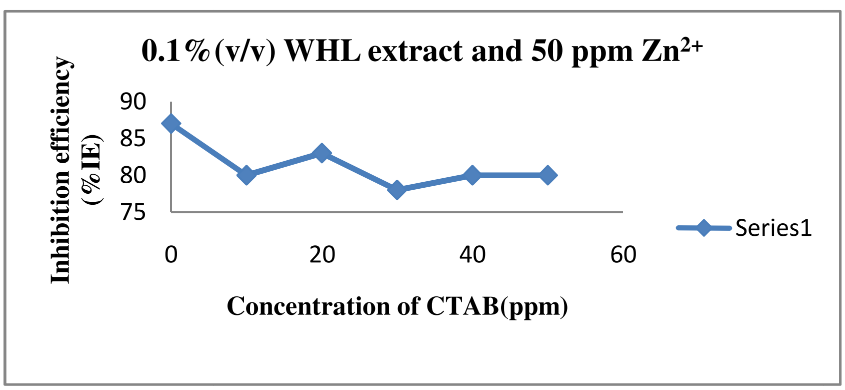

Figure3. Concentration of CTAB Vs inhibition efficiency

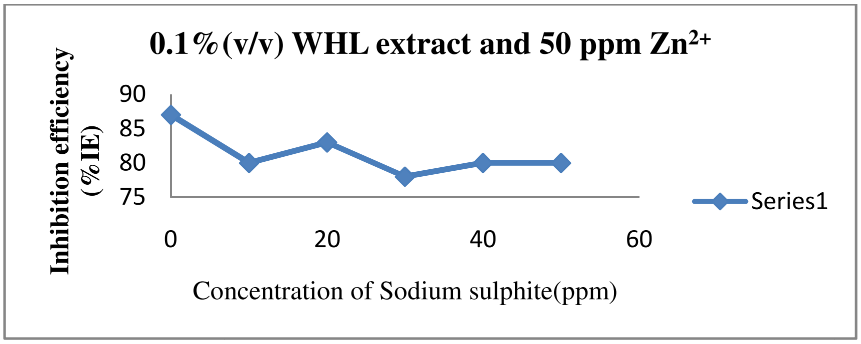

Figure 4. Concentration of Sodium sulphite Vs inhibition efficiency

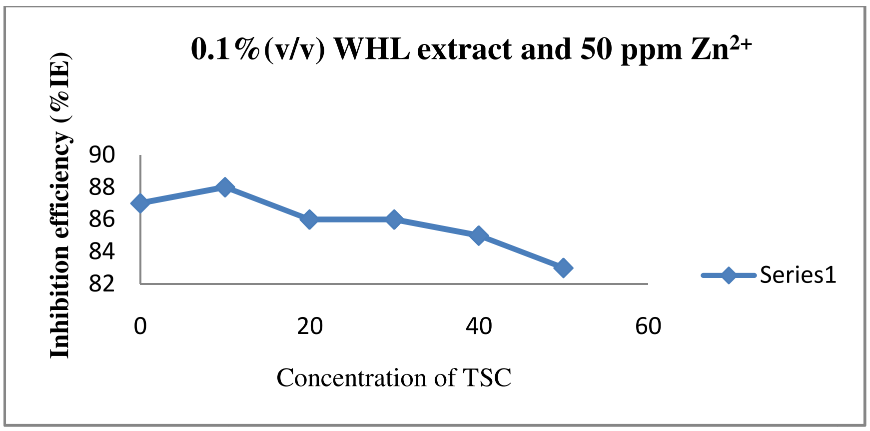

Figure: 5 Concentration of Tri sodium citrate V_S inhibition efficiency.

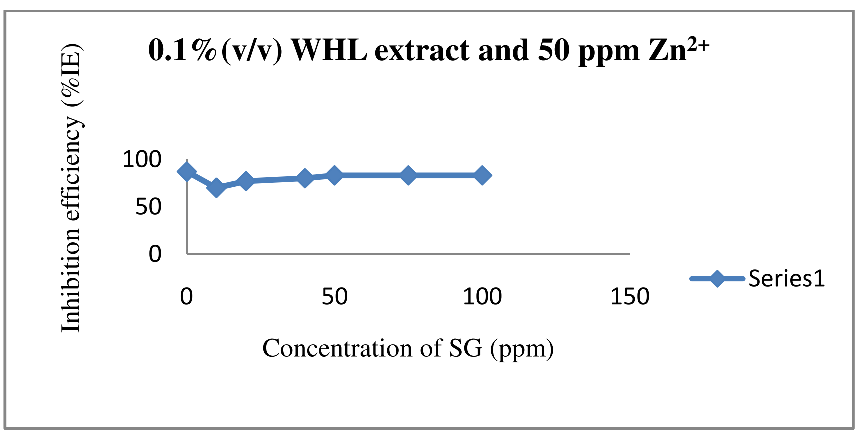

Figure 6.Concentration of sodium gluconate vs inhibition efficiency