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A Novel Utilization of Flueggea leucopyrus- Chitosan Composite Hybrid Beads in Inhibiting the Attrition of Carbon Steel

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Abstract

A novelty based ethanolic extract of Flueggea leucopyrus Willd (FL) was used on carbon steel in acidic medium for anti-attrition efficiency analysis. The anti-corrosion efficiency of FL was determined by weight loss method, for various concentrations of the extracts with Zn^{2+} ion in 0.5M HCl medium. For the maximum concentration ratio of the inhibitor systems (FL, FL-Zn^{2+}) were encapsulated by the bio-polymer chitosan (CS) which extends the stability of the resistive film. The resistive film that protects the surface of the metal was confirmed by the electrochemical studies such as potentiodynamic polarization, AC impedance and by the spectral studies such as FT-IR, UV-Visible and fluorescence spectra. The film formation is confirmed by the surface morphologies SEM analysis and EDAX which confirms the formation of complex between the metal cation and FL-CS, FL-Zn^{2+}-CS composite beads by encapsulation method.

Keywords: Flueggea leucopyrus , Chitosan, Biocomposite, Anti-corrosion, SEM, EDAX.

1. Introduction

Metals are integral to a wide array of technological applications, industries, and household appliances. Corrosion, a natural process that leads to the deterioration of metals, can be managed but not entirely eliminated. Historically, chemical inhibitors were employed to mitigate corrosion, but their hazardous and toxic nature led to the search for safer alternatives. Consequently, eco-friendly and less toxic inhibitors became preferable. Recently, there has been a shift towards using natural, green inhibitors derived from plant materials, which offer both environmental and health benefits [1-3]. Steel is a solid composite of iron, carbon and certain other metal elements present in various ratios. The usage of steel in the society is vast in various fields. Even though there are many other metals that are used as substituent to steel but they doesn't retain as the steel does. The drawback of usage of steel based materials is rusting. The iron which is present in the composite of steel is highly reactive towards environmental oxygen and water. This reactivity nature of the iron towards oxygen leads to the formation of rust. Rusting can be prohibited by various corrosion preventing methods. Addition of inhibitor method is one of the popular preventing methods. Inhibitors are the substances that are added in minimal concentration to control the corrosion process. For the past decades organic and inorganic compounds are used as inhibitors, but they are toxic in nature. Later green chemical compounds were used and now-a-days natural products, synthetic and bio-polymers are used as corrosion controllers. The inhibitors are widely used in cooling water systems, refinery units, chemicals, oil and gas production units and boiler plants containers steel pipelines etc to control corrosion.

Generally the phyto-constituents that are present in the plants have effective hetero atoms such as oxygen, nitro-

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gen and sulphur, the lone pairs that are present in the hetero atoms are responsible for the formation of the protective layer on the metal surface by the complexation of the lone pair with the metal cation [4]. The usage of chemical inhibitors have been reduced because they are toxic to the environment and human, some of the inhibitors are expensive, disposal is difficult as they are non-biodegradable, preparation methodologies are tedious and expensive. Plants are chosen as inhibitors because they are non-toxic to the nature and human, economically cheaper, easily available, biodegradable, extraction methodologies are simple and low cost [5].

2. Experimental Methods

2.1 Metal Specimens

The carbon steel specimens with the composition (wt%) of S-0.026 , P -0.06, Mn- 0.4, C- 0.1 and balance iron are taken. The dimensions of the metal active surface are 1.2 X 4.1 X 0.2 cm which was used for weight loss measurements. The carbon steel specimens were mechanically polished, washed in double distilled water and degreased with acetone and used for the weight loss method and surface examination studies.

2.2 Extraction

The plant Flueggea leucopyrus Willd (FL) was collected from Pachaimalai hills near Trichy district located at 119^0N, $78^0$21'E of Trichy. The leaves were washed thoroughly for about seven times in the running tap water and it was taken and dried under shade. About 100g of the powder was soaked in 500ml of ethanol under cold percolation method. At regular intervals of time the extract was filtered and distillation was carried out to collect the crude extract. The extract was stored in an amper bottle and refrigerated[6].The extract is taken for phytochemical screening[7] and anti-corrosion efficiency analysis by weight loss method[8].

2.3 Synthesis of inhibitor Flueggea leucopyrus Willd (FL)-chitosan (FL-CS) composite beads

About 2.0 g of chitosan (CS) was dissolved using 2 % of acetic acid medium at 40 °C with incessant stirred up to three hours separately. Now, the above prepared inhibitor was added into the homogeneous chitosan solution and this mixture was stirred for four hours at room temperature. Once, the homogeneous inhibitor-chitosan solution was obtained it would drop into 0.1 M NaOH solution and simultaneously the honey colored EFL and white colored EFLZ composite beads were obtained [9].

2.7 Weight-Loss Method

2.7.1 Determination of Corrosion Rate

Weight loss measurements were carried out using an ACCULAB Electronic top loading balance, with readability/sensitivity of 0.1 mg in 210g range. The specimens were immersed in beaker containing 100ml acid solutions without and with different concentration of the plants chosen extract using hooks. Before it was immersed, the specimens were cleaned and the weight is recorded. After three days, the test specimens were removed and then washed with double distilled water, dried and reweighed. The average mass loss of two parallel carbon steel specimens were obtained.[10]

From the change in weight of specimens the corrosion rate was calculated using the following relationship,

$$\text{Corrosion Rate} = [87.6 \times W] / [A \times T \times D] \quad (\text{mpy})$$

Where, W is loss in weight in mg, A is surface area of the specimen (cm2), T is time in hours and D is density (7.2g/cm3). Corrosion Inhibition Efficiency (IE) was then calculated using the equation

$$IE = 100[1-(W2/W1)] \%$$

Where, W1 is corrosion rate in the absence of inhibitor and W2 is corrosion rate in the presence of inhibitor.

2.4 Potentiodynamic polarization study

Potentiodynamic polarization studies were carried out using CHI electrochemical impedance analyzer, model 660 A. The working electrode was a rectangular specimen of carbon steel with one face of the electrode (1 cm2 area) exposed and the rest shielded with red lacquer. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. The working electrode and platinum electrode were immersed in 0.5 M HCl in the absence and presence of inhibitor. Saturated calomel electrode was

connected with the test solution through a salt bridge. Potential (E) Vs log current (I) plots were then recorded. Corrosion potential (Ecorr) and Tafel slopes ba and bc were determined from E Vs log I plots.[11]

2.5 Infra-Red (IR) Spectroscopy

Infrared spectroscopy is a well-developed technique to identify chemical compounds. The specimens were suspended by means of hooks in solution having with and without inhibitor for 72 hours. After 72 hours the specimen was taken out. Then the film formed on the metal surface was scratched off and taken for FT-IR spectral study.

2.6 UV- Visible Spectroscopy

The possibility of the formation of film on the metal surface was examined by mixing the respective solution and recording their UV-visible absorption spectra using Lambda 35 UV-visible spectrophotometer which is a PC controlled single beam scanning spectrophotometer. It covers wavelength range from 200 nm to 1000 nm with a setting accuracy of ± 1 nm.

2.7 Fluorescence Spectroscopy

Fluorescence spectra of solutions and also the films formed on the metal surface were recorded using Jasco F-6300 spectrofluorometer.

2.8 SEM Analysis

The carbon steel specimen immersed in blank solution and in the inhibitor solution for a respective period of time was removed, rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology.

2.9 Energy Dispersive Analysis of X-Rays (EDAX)

Generally the carbon steel immersed in blank solution and in the inhibitor solution for respective period of time was removed, rinsed with double distilled water, dried and observed in a Energy Dispersive Analysis of X-Rays (EDAX) to examine the elements present on the carbon steel surface by using an energy dispersive X-ray analyzer (EDAX) unit attached to the SUPRA 55 Field Emission Scanning Electron Microscope (FESEM).

3. Results and Discussion

The primary metabolites such as carbohydrates, amino acids, proteins are found to be active and some of the secondary metabolites like alkaloids, terpenoids, flavonoids , saponins, phenolic compounds are also found to be present in the ethanolic extract of Flueggea leucopyrus. These active phytoconstituents are responsible for the inhibition efficiency against corrosion [13].

Determination of Corrosion Rate

The corrosion rate was determined for carbon steel in 0.5M HCl by using weight loss method. Inhibition efficiency of carbon steel with various concentration of Flueggea leucopyrus Willd (FL) ethanolic leaves extract in 0.5M HCl at room temperature are presented in the Table (5). It is clear from the table that the corrosion inhibition enhances with the inhibitor concentration. The inhibitor systems that are used to determine the corrosion rate and the inhibition efficiency were FL- CS (EFL); FL- Zn^{2+} -CS (EFLZ) composite beads. It was found that at FL-Zn^{2+} (50:25) and FL-Zn^{2+} (50:50) the inhibition efficiencies were 82 and 83% respectively for 72 hours. On further encapsulation to the inhibitor ratio of FL-Zn^{2+} (50:50) the inhibition efficiencies of EFL (0.5g for 7 days) ; EFLZ (0.1g for 7 days) composite beads were found to be 87 and 86.5% respectively.

Table-1: Inhibition efficiencies and corrosion rates of carbon steel in EFL & EFLZ in 0.5M HCl

Beaker No.	Wt. of beads (g)	Immersion Period (Days)	EFL		EFLZ	
			IE (%)	CR (mpy)	IE (%)	CR (mpy)
1	0.1	5	76	1.6	84.5	0.9
2		7	68	1.6	86.5	0.7
3	0.3	5	86	0.9	85	1.03
4		7	85	0.7	84.7	0.8
5	0.5	5	83	0.8	78	1.5
6		7	87	0.6	74	1.3

3.5 Analysis of FTIR

The FTIR spectrum of the extract and the film formed on the surface of the metal immersed in 0.5M HCl in the presence of the inhibitor were taken. FTIR spectroscopy has been used to analyze the protective film formed on the metal surface.[14-15] The FTIR spectrum of the EFL; EFLZ composite beads as inhibitors are correlated in Fig.(1). For EFL composite beads as inhibitor the band observed at 3369.64 cm-1. There is a decrease in the frequency from 3600.00 cm -1 to 3369.64 cm-1. Similar decrease pattern is observed for EFLZ composite beads, the bands were observed at 3377.15cm -1 respectively. The peak observed at 3877.91 cm-1 is due to N-H stretching in EFL composite beads as inhibitor. The peak observed at 3854.91cm-1 is due to N-H stretching in EFLZ composite beads as inhibitor.

The bands at 1629.22 cm-1 and 1234.23cm-1 which are due to the coupling of -C-O stretching and -C-O-H in-plane bending of the carboxylate anion in EFL composite beads similar bands were observed at 1629.13cm-1 and 1236.13cm-1 in EFLZ composite beads. The bands at 1023.03 cm-1 and 851.91 cm-1 (due to the ring oxygen and metal oxygen bond) are shifted to 1050.69 cm-1 and 843.53 cm-1. This reveals that due to interaction between the metal and the active constituents there is a change in the chemical nature of the active constituents [16].

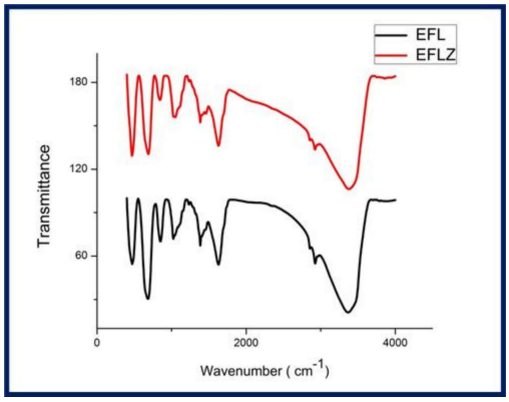
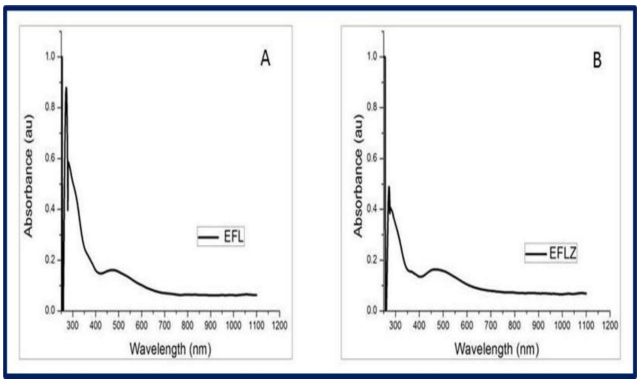


Fig.1: Correlation IR spectra of EFL and EFLZ

3.6 Analysis of UV-Visible absorption spectra

The UV-Visible absorption spectra of the solution containing EFL; EFLZ composite beads are correlated in Fig.2 . A peak appears at 271.20nm (0.8792au), 281.10 nm (0.5856au), 472.15 (0.1614 au) when FL-Zn^{2+}-CS is added a peak appears at 272.45nm (0.4898 au), 278.65 nm (0.4067 au), 467.20 nm (0.1642au) the intensity decreases on comparing with the FL and FL-Zn^{2+} systems respectively. This indicates the complexation of EFL; EFLZ composite with the metal surface[17-19].



Figs. 2. A. UV-Visible spectrum of EFL B. UV-Visible spectrum of EFLZ

3.7 Analysis of Fluorescence

Fluorescence spectrum is used to detect the presence of the inhibition complex formed on the metal surface. The λex for the emission spectrum of the EFL as inhibitor is found to be 344.67 nm (153.19), 397.71 nm (96.49), 569.24 nm (22.31) and668.25 nm (60.68) and for EFLZ the peak is obtained at 347.87 nm (93.28), 390.40 nm (65.36), 396.27 nm (65.49), 568.96 nm (18.46), 672.10nm (34.91). There is a shift in the intensity on comparing with the EFL fluorescence value indicates the formation of protective film on the surface of the metal[20-23]. The slight variation is due to the formation of Fe^{2+}-EFL and Zn (OH)2 on the metal surface.

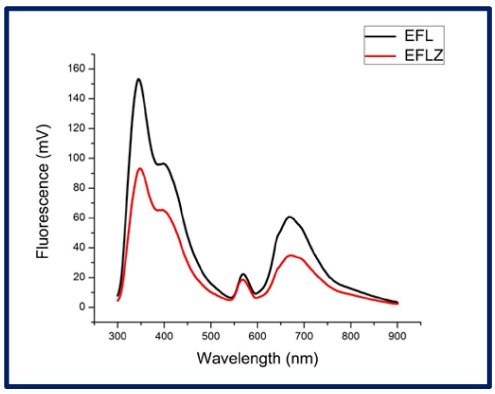


Fig.3: Correlation Fluorescence spectra of EFL & EFLZ

4. Potentiodynamic Polarization

Polarization study is an electrochemical method used to identify the formation of protective film on the metal surface. If a protective film is formed on the metal surface, the linear polarization resistance (LPR) increases and corrosion current (ICorr) decreases[24]. The polarization curves of carbon steel immersed in the presence and absence of ternary inhibitor mixture are correlated in Fig.4. The corrosion parameters such as corrosion potential (Ecorr), Tafel slopes (bc = cathodic ba = anodic) and corrosion current (Icorr) are given in Table 2.

Table-2: Corrosion parameters of carbon steel immersed in 0.5M HCl in the absence and presence of EFL and EFLZ systems determined from polarization method

System	E_{corr} mve vs SCE	b_c mV/ decade	b_a mV/ decade	I_{corr} A/cm^2	LPR ohm cm^2	Type of Protection
Blank	-495.2	134.522	104.522	8.922 ×10^{-4}	286.26	-
EFL	-502.9	159.766	112.637	7.508× 10^{-4}	382.06	Cathodic
EFLZ	-515.82	136.439	95.139	1.937× 10^{-4}	1256.53	Anodic

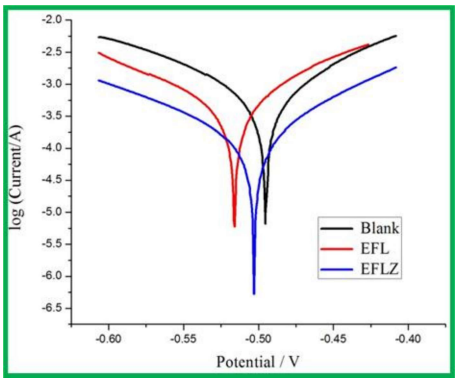


Fig.4 Polarization curve correlation of blank, EFL and EFLZ

5. Scanning Electron Microscope (SEM) Analysis

The texture and pore structure of the inhibited and uninhibited metal surface in acidic medium and their corresponding hybrid beads are shown in Figs.5 & 6. It is confirmed that the inhibitor systems has formed a dense film over the metal surface. The surface of the uninhibited metal was found to be rough. The surface of the inhibited metal was found to be smoother and the small white colored particles found on the surface are due to the biopolymer molecules (chitosan). The size of EFL hybrid beads is 848.3 µm and the surface of the bead has greater number of white colored particles (chitosan molecules), similar surface was observed in the protective film formed on the metal surface also. The size of EFLZ hybrid beads is 1639 µm and the surface of the bead has greater number of elongated thread- like needle white colored particles (chitosan molecules bonded with Zn2+), similar surface was observed in the protective film formed on the metal surface also. Thus the surface morphological interpretation of the uninhibited and inhibited metal surface confirms the protective film formed on the surface of the metal. Similar results were depicted by Sabirneeza et al for polyvinyl alcohol cysteine as corrosion inhibitor in 1M HCl [25].

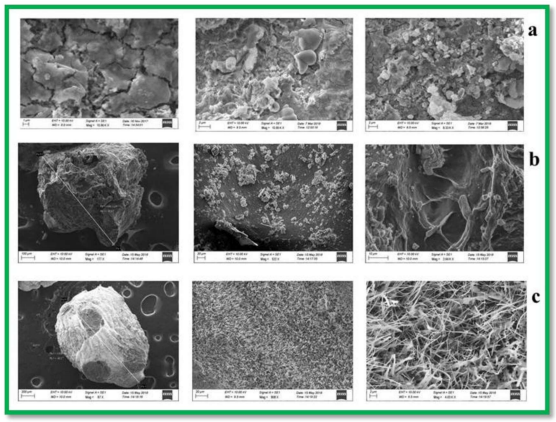


Fig.5. SEM images of a) blank b) EFL bead c) EFLZ bead

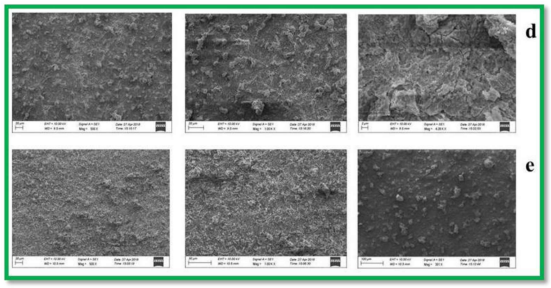
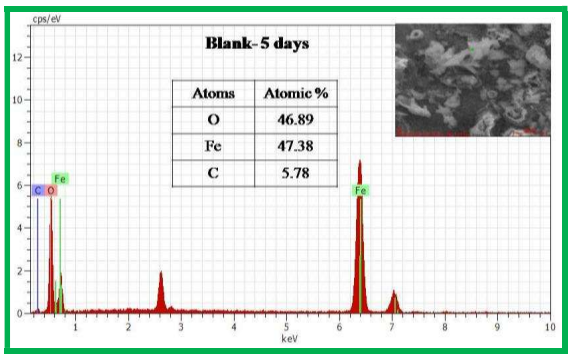


Fig.6. SEM images of d) EFL e) EFLZ

6. Energy Dispersive Analysis of X-rays (EDAX)

The EDAX spectrum of the resistive film of the inhibitor systems formed on the metal surface shows the characteristic peaks of the elements constituting such as C,O, N, P, S, Fe, and Zn atoms. The EDAX spectrum of carbon steel immersed in 0.5M HCl containing EFL and EFLZ hybrid beads are shown in Figs. 7 & 8. It shows the characteristic peak for the existence of O and Zn. Thus the presence of O, N, S and Zn atoms in the resistive film indicates the inhibition efficiency of the inhibitor systems studied. Thus the elemental analysis confirms the complexation of Fe2+-EFL and Zn2+ as Zn(OH)2.



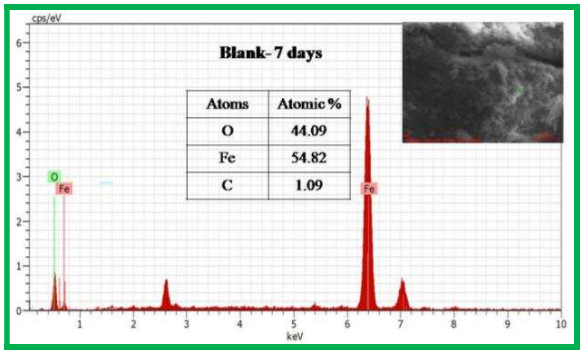


Fig.7: EDAX Spectra of blank for 5 and 7 days

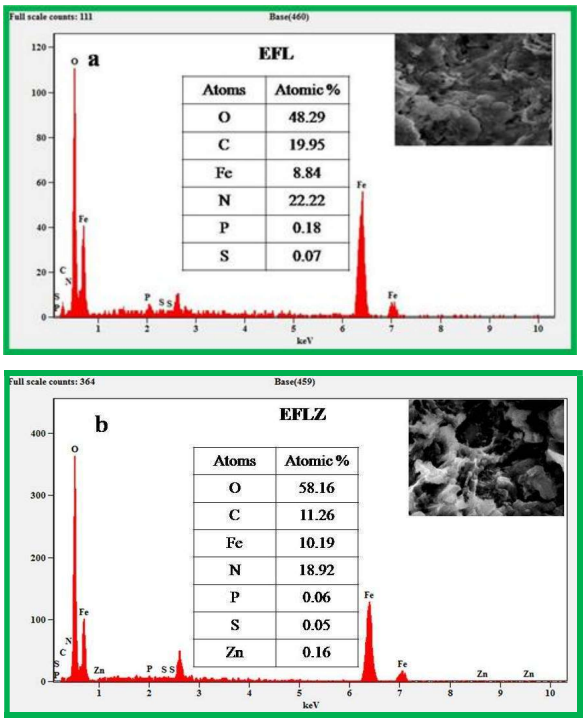


Fig. 8: EDAX Spectra of (a) EFL and (b) EFLZ

7. CONCLUSION

Flueggea leucopyrus has a good anticorrosion ability for carbon steel in 0.5 M HCl solution is due to the active phytoconstituents present in the plant. The shift in the peaks observed in FT-IR, UV-Visible spectra proves the formation of the film on the surface of the metal. The variation in the intensities observed in the fluorescence study results the formation of the film on the surface of the metal. The protective film formed on the metal surface is found to be denser by the SEM analysis. Thus, the SEM and EDAX images finally confirm the formation of the

protective film on the metal surface and the elements present in the resistive film respectively.

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