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Syneristic effect of C. Papaya Leaves Extract-Zn^{2+} in Corrosion Inhibition of Mild Steel in Aqueous Medium

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Abstract

The corrosion inhibition of aqueous extract of C. Papaya leaves on mild steel in 60 ppm Cl^- ion containing aqueous medium was studied by using inhibition efficiency and degree of surface coverage. The most suitable inhibitor concentration was found to be 2 ml of C. Papaya leave extract with inhibition efficiency (IE) of 91% at Zn^{2+} (50 ppm) by the weight loss method. Synergism parameters have been calculated to evaluate the synergistic effect existing between C. Papaya leave extract and Zn^{2+}. The influence of immersion time and P^H has also been investigated. The protective film has been analyzed using Fourier transform infrared (FTIR) spectroscopy.

Keywords: Synergistic effect, C. Papaya, corrosion inhibition, weight loss method.

Introduction

Corrosion can be defined as the degradation of material when it comes in contact with the environment. The corrosion inhibition of metals can be achieved by the addition of inhibitors to the system that prevent corrosion from taking place on the metal surface. Inorganic compounds like chromate, phosphates, molybdates, etc., and the variety of the organic compounds containing hetero atoms like nitrogen, sulphur, and oxygen are being investigated as corrosion inhibitors[1]. But the toxicity of organic corrosion inhibitors to the environment has prompted the search for green corrosion inhibitors as they are biodegradable, renewable, and free from toxic compounds as well as heavy metals. Number of plant sources have been reported as a effective corrosion inhibitors, such as, Polyalthia Longifolia[2], Oxystelma Esculentum[3], Eclipta alba[4], Nelumbo nucifera[5], Red Onion[6], Uncariagambir[7], Ocimum gratissimum[8], etc., Like those inhibitors, many investigations are done on the corrosion inhibition of Papaya (pawpaw) of the Caricaceae family contains numerous chemical constituents which include the fermenting agent myrosin, alkaloids, rutin, resin, tannins, carpine, dehydrocarpines, pseudocarpine, flavonols, benzylglucosinolate, linalool, malic acid, methyl salicylate, chymopapain, calcium, iron, magnesium, manganese, phosphorous, potassium, zinc, beta-carotene, B-vitamins and vitamins A, C, and E, anthraquinones (bound and free), philobatinins and saponins[9]. The corrosion inhibition of Carica papaya in sulfuric acid media on mild steel was studied by using gravimetric and gasometric techniques[10]. Corrosion inhibition of C. Papaya in HCl medium on aluminium was studied, using weight loss, thermometric and hydrogen evolution techniques [11]. The corrosion inhibition of C. Papaya and azadirachta indica leaves in H_2SO_4 medium on mildsteel were compared by weight loss techniques [12]. The effect of C.papaya and C. Sinensis on the corrosion of α β (duplex) brass in 1M HNO_3 was studied by weight loss/ corrosion rate and potential measurement techniques[13]. In this work, the inhibitory action of various concentrations of c.papaya leave (CPL) extract with Zn^{2+} ions are analyzed in the presence of 60 ppm Cl^- ion containing aqueous corrosive medium which is normally present in the cooling water systems by using weight loss and surface coverage (Θ) methods.

Material and Methods

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.

Preparation of C. Papaya leaves (CPL) extract: An aqueous extract of CPL was prepared by grinding 10g of CPL, with double distilled water. The solid impurities were removed by filtration process. Then the extract was made up to 100ml[5, 14-16].

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 CPL extract in the absence and presence of Zn^{2+} for one day. The Inhibition efficiency (IE %) was calculated using the equation,

$$\text{Inhibiton efficiency, IE}(\%) = \frac{Wo-Wi}{Wo} x100$$

$$\text{Surface coverage, } (\theta) = \frac{Wo-Wi}{Wo}$$

Where W_o and W_i are the weight loss for mild steel in the absence and presence of inhibitor.

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,

$$CR = \frac{87.6 \text{ x W}}{\text{DAT}}$$

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.

Calculation of synergistic factor (S_Θ)

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

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

Results and Discussion

Weight loss method: Effects of concentration on Inhibition Efficiency: When the concentration of the plant extract increases, the fraction of surface covered by the adsorbed molecule also increases which results into an increase in the inhibition efficiency. As Shown in figure 1, the maximum inhibition efficiency of 91% is reached only for the 2ml of CPL extract – Zn^{2+} (50 ppm), above which further increase in extract concentration decreases the inhibition efficiency.

As in table 1, 2ml of CPL extract shows 32% inhibition efficiency and 50 ppm Zn^{2+} shows only 59% inhibition efficiency in 60 ppm Cl^- ion containing aqueous medium. But their combination provides 91% IE. This suggests that a synergistic effect exists between CPL extract & Zn^{2+}.

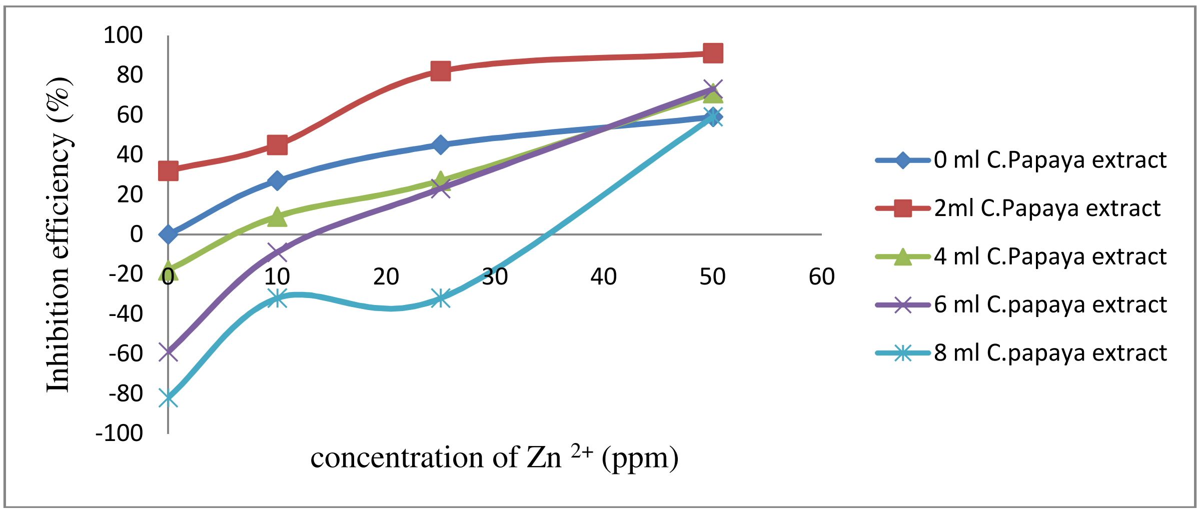

Figure-1
Concentration of Zn^{2+} on Inhibition efficiency(%)

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

S. No	Concn. of CPL extract (ml)	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	-	97.64	27	74.39	45	60.44	59	41.85
2	2	32	69.75	45	55.79	82	18.59	91	9.29
3	4	-18	120.89	9	92.99	27	74.39	71	18.59
4	6	-59	162.73	-9	111.59	23	79.04	73	27.89
5	8	-82	185.98	-32	134.84	-32	134.84	59	41.84

Immersion period: One day Inhibitor: C. Papaya leaves (CPL) extract (ml) + Zn^{2+} (ppm)

Effects of concentration on corrosion rate: As shown in figure 2, it was observed that the rate of corrosion of mild steel decreases with increase of various concentrations of CPL extract - Zn^{2+} (50 ppm), indicating that the aqueous extracts of CPL inhibited the corrosion of mild steel in aqueous medium containing 60ppm Cl^- ion.

Synergism parameter: Every inhibitor has its individual inhibition efficiency that may be high or low depends on the group of atoms present in the inhibitor molecule. If more than one, inhibitors are used for the study, which must be checked whether the synergistic behaviour is offered between the inhibitors or not[17]. Actually, many investigations concerning synergistic inhibition have been carried out[18-20]. Synergistic factor (S_Θ) is calculated for the mixture containing various concentration of CPL extract 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 CPL extracts and Zn^{2+} (50ppm).

Effect of pH on IE of CPL extracts - Zn^{2+} system: It is seen from table 3, that at pH 7, the CPL extracts (2mL) – Zn^{2+} (50 ppm) system has 91% IE. When pH is lowered to 4 the IE is decreased to 28%. When the pH is increased to 9.2, the IE is increased to 65% as in figure 3. This is due to the presence of phenolic compounds[21] such as ferulic acid, caffeic acid, chlorogenic acid found in leaves of C. Papaya[22].

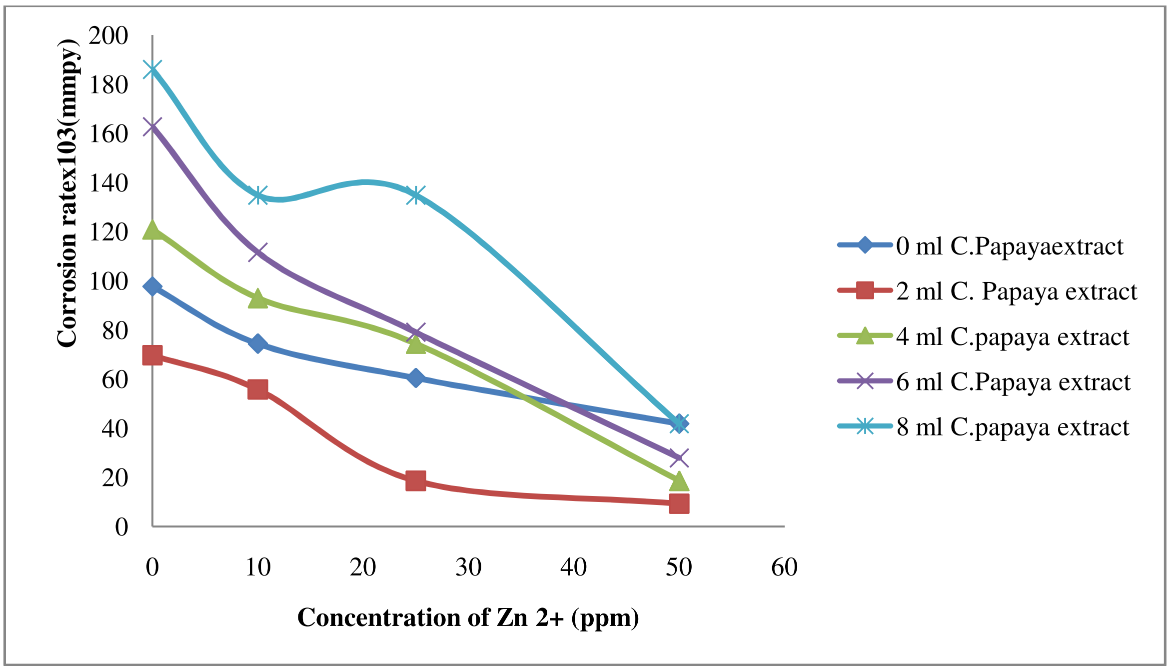

Figure-2
Concentration of Zn^{2+} on corrosion rate (mmpy)

Table-2
Synergism parameters (S_Θ) for various concentration of CPL extracts and Zn^{2+}(50 ppm)

Zn^{2+}(50ppm) Θ_B	CPL extract Θ_A	CPL extract + Zn^{2+}(50ppm) Θ_{AB}	S_Θ
0.5909	0.3182	0.9090	3.065
0.5909	-0.1818	0.8181	2.6579
0.5909	-0.5909	0.7272	2.3857
0.5909	-0.8182	0.5909	1.2588

Table-3
Effect of P^H on the CPL extract (2ml) -Zn^{2+} (50 ppm)
Immersion Time: One day

Inhibition Efficiency (%)			
P^H	**7**	**4**	**9.2**
SYSTEM: 60 ppm Cl^-+ CPL extract (2ml) –Zn^{2+} (50 ppm)	91%	28%	65%

Effect of immersion time on inhibition efficiency: From figure 4, it was clear that, the aqueous extract of CPL (2 ml) and Zn^{2+} (50ppm) have shown excellent corrosion inhibition efficiency, for up to three days. After 7 days the IE is decreased to74%. The results are clearly entered in table 4.

Table-4
Effect of Immersion time on IE of the CPL extract (2ml) - Zn^{2+} (50 ppm)

Inhibitor system	**IE%**		
	No. of days of immersion		
	1 Day	**3 Days**	**7 Days**
2ml CPL extract + 50 ppm Zn^{2+}	91%	80%	74%

Immersion Time: One day

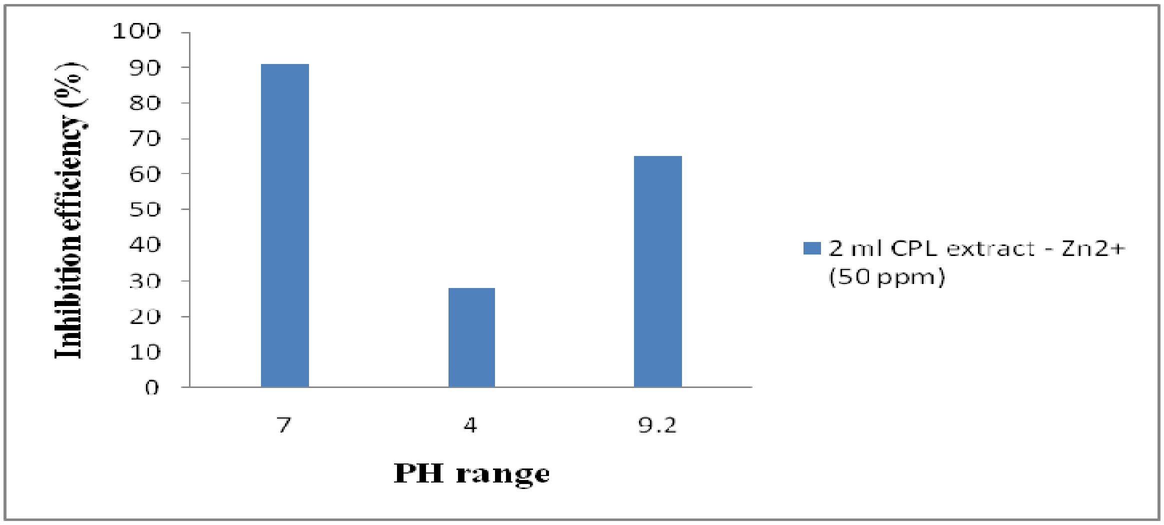

Figure-3
Influence of P^H on Inhibition efficiency

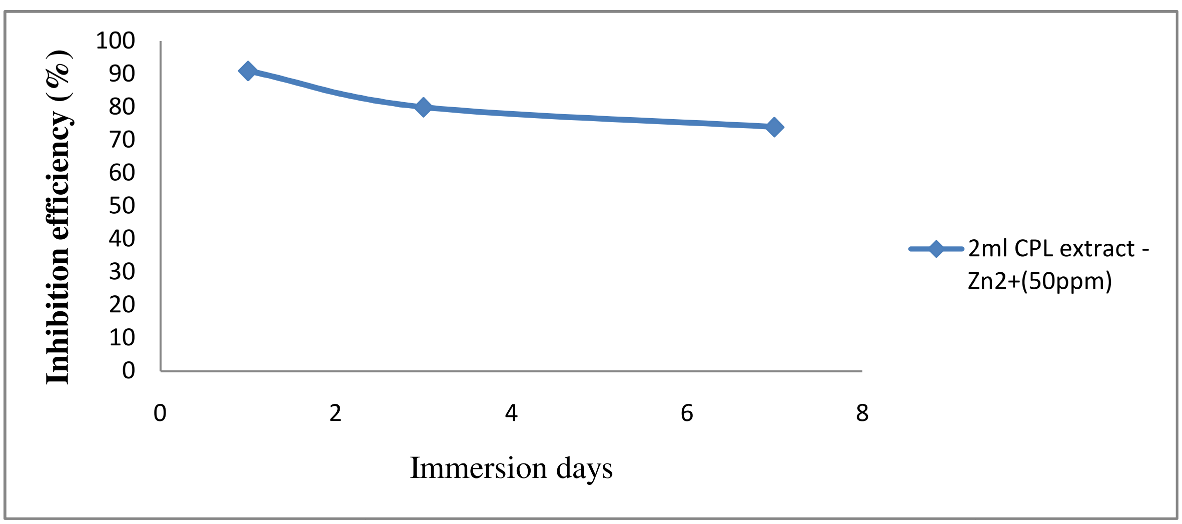

Figure-4
Effect of immersion period on Inhibition efficiency (%)

Analysis of FTIR spectra: Papaya leaf extract has gained immense popularity due to its potent therapeutic value and is now available as dietary supplement and marketed as a nutraceutical product. The nutrients in papaya leaf extract include the minerals, magnesium, potassium, iron, most amino acids and vitamins A, C, and B. Papaya leaves contains major phyto chemicals such as an alkaloid of Carpaine, Malic acid, quinic acid, a phenolic compound such as manghaslin as a anti-oxidant and also the papaya proteinase of papain.

FTIR spectra [KBr] of C.Papaya leaves and the thin film formed on the mild steel immersed in 60ppm Cl^- solution with 50ppm Zn^{2+} ion in the presence of the inhibitor formulations are shown in figure 5a and 5b.

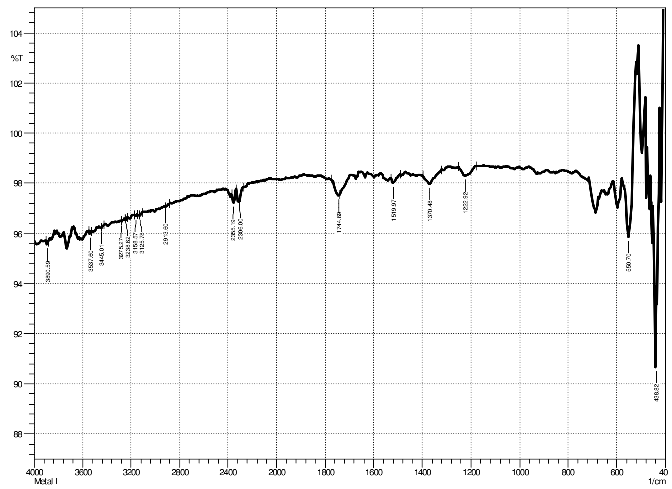

Figure-5a
Powdered C.Papaya leaves

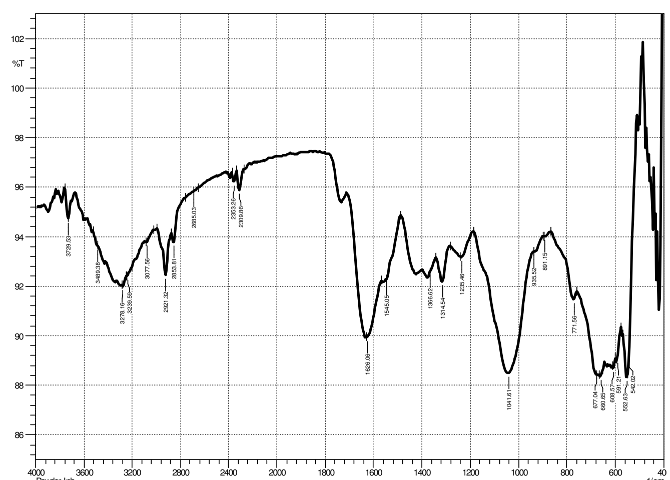

Figure-5b
Thin film formed on the mild steel

The –OH stretching in phenol has decreased from 3239cm^{-1} to 3238cm^{-1}, the -C-O strectching frequency has decreased from 1235cm^{-1} to 1222cm^{-1}, the carboxylic acid –OH stretchin frequency has decreased from 2921 to 2913cm^{-1}, the carbonyl group in amide has shifted from 1740to 1744cm^{-1}, the NH stretching frequency has decreased from 3489 to 3445cm^{-1}, the aromatic C-N stretching frequency has shifted from 1366 to 1370cm^{-1}. The peak at 1626cm^{-1} is of carbonyl group(C=Ostrectching) and ether groups (-O-stretching) peak appeared at 1041cm^{-1} (figure-5a)were due to the presence of carboxy methy cellulose of papaya. These bands are vanished from the Figure b, which is due to the interaction between the functional group and the metal. Thus these bands were clearly proved the complex of CPL extract - Zn^{2+} which is formed on the metal surface as a protective coating.

Conclusion

The present study leads to the following conclusions: i. The formulations of 2ml CPL extract and 50ppm of Zn^{2+} provide 91% inhibition efficiency to mild steel immersed in aqueous medium containing 60ppm of Cl^- ion. ii. Synergistic effect exists between CPL extract and Zn^{2+}. iii. The IE decreases, when the period of immersion increases. iv. As the value of pH is increased the corrosion inhibition efficiency also increased. v. FTIR spectra reveal that he protective film consists of Fe^{3+} - C. Papaya extract complex

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