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Mild Steel Corrosion Inhibition by *Cucurbitamaxima* Plant Extract in Hydrochloric Acid Solution

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Abstract

The inhibitive action of PCM (peel of Cucurbita maxima) on mild steel corrosion in 1N HCl was studied using weight loss method and FT IR techniques. The calculated results of corrosion rates of steel and the inhibition efficiency of plant extract show that the extract functions as a good corrosion inhibitor and IE increased with extract concentration. Maximum IE of 93 % was obtained at 2 % v/v concentration of the plant extract. Temperature studies revealed an increase in IE with rise in temperature. The adsorption of PCM extract was found to follow Langmuir's adsorption model at all concentrations and temperatures studied.

***Keywords**: Adsorption; Corrosion inhibition; Corrosion rate; Cucurbita maxima; Mild steel.*

1. INTRODUCTION

Mild steel is extensively used in different industries by virtue of its good structure, properties, mechanical workability and low cost. Dilute acid solutions are widely used in several industrial processes such as pickling, cleaning and descaling to remove the undesirable scales and rusts on the steel surface (Wang *et al.* 2012). Hydrochloric acid is widely used for pickling of metals and alloys, oil well acidification, power and in the petrochemical processes. The dissolution of steel in acidic environments and its inhibition is an important field of study. Most of the well known acid inhibitors are organic compounds containing heteroatoms such as O, N and S. Nevertheless, most of these compounds are not only expensive but also toxic for human health and environment. The known hazardous effect of most synthetic corrosion inhibitors are the motivation for the use of some natural products. Plant extracts are an incredibly rich source of natural chemical compounds that can be extracted by simple procedure with low cost and are biodegradable in nature. The natural plants extract contain a variety of organic compounds, for example amino acids, alkaloids, steroids, flavonoids, proteins and tannins as a green alternative for toxic and hazardous compounds. The use of natural products as corrosion inhibitors have been widely reported by several authors. (Saleh *et al.*1982; Gunavathy and Murugavel, 2013; Jothi and Ravichandran, 2013) reported that *Opuntia extract*, Aloevera leaves, orange and mango peels give adequate protection to steel in 5% and 10% HCl at 25 ° C and 40 ° C. (Srivatsava *et al.* 1981) found that tobacco, black pepper, castor oil seeds, Acacia gum and lignin can be good inhibitors for steel in acid medium. Ethanolic extract of *Ricimus communis* leaves was studied for the corrosion inhibition of mild steel in acid media. The anti corrosion activity has also been studied for the extracts of Eucalyptus leaves, *Pongamia glabra*, *Phyllanthus amarus*, *Acacia Arabica*, *Punica granatum*peel and *Occimum viridis*for steel in acid media. ***Cucurbita***

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maxima (Pumpkin) is a plant that belongs to the family cucurbitaceae and is widely distributed in tropical and subtropical countries. Cucurbita species is found to contain tocopherol, carotenoids, β sitosterol, saponins, carbohydrates, amino acids and fatty acids. The peel extract of C maxima contains numerous organic compounds, which may be utilized as green corrosion inhibitor (Udaya Prakash *et al*. 2013). The present study investigate the inhibiting effect of peel extract of ***Cucurbita maxima*** (PCM) on mild steel corrosion in hydrochloric acid medium using the weight loss method and FTIR techniques.

2. EXPERIMENTAL

2.1 Materials

The mild steel (0.047 % C; 0.22 % Mn; 0.015 % Ni; 0.002 % S; 0.026 % Al; 0.002 % P; 0.001 % Mo; Fe balance) specimens of dimension 5.0 cm × 2.0 cm × 0.15 cm were used for weight loss measurements. The mild steel specimens were polished with 400 and 600 grades of emery papers, degreased with acetone, rinsed with distilled water and finally dried before each experiment. The blank corrodent 1N HCl is prepared by dilution of AR grade HCl with distilled water. The dried peels of Cucurbita maxima were powdered. The 5% peel extract solution is prepared by mixing 25 gms of peel powder with 500 ml of 1N HCl solution and refluxed for 3 hr. The refluxed solution was allowed to for 8 hr, filtered and stored. The filtrate is diluted with appropriate quantity of 1N HCl to obtain inhibitor test solutions from 0.01 %, 0.05 %, 0.1 %, 0.3 %, 0.5 %, 0.8 %, 1 %, 1.5 % and 2 % v/v concentrations.

2.2 Methods

The previously weighed mild steel specimens were immersed in the test solutions with and without the PCM extract for 1, 3, 5, 7, 18 and 24 h at room temperature. After the specified immersion period the specimens were then removed, rinsed in water and acetone, finally dried and stored in a desiccator. The dried specimens were reweighed and the weight loss was determined on an analytical balance. The corrosion rate (CR) was calculated from the following equation (Hussin *et al*. 2011):

$$\mathrm{CR\ (mpy)} = 534W/\rho At \qquad (1)$$

Where W is the weight loss in mg, ñ is the density of mild steel (7.8 g/ cm^3), A is the area of specimen (4.7244 in^2) and t is the time of immersion. The inhibition efficiency (IE) was calculated as follows (Satapathy *et al*. 2009):

$$\mathrm{IE}\ \% = (W_o - W_i/W_o) \times 100 \qquad (2)$$

Where W_o and W_i are the weight loss values in absence and in presence of the inhibitor respectively.

The effect of temperature on the corrosion rate of mild steel coupons in 1N HCl solution at 303, 313, 323, 333 and 343K was also studied with same concentrations of the extract for immersion period of 1 hr. The 5% peel extract was characterized by Fourier transform infrared spectroscopy (FTIR). FTIR spectrum was recorded in Shimadzu spectrophotometer, in the spectral range from 4000 to 500 cm^{-1}.

3. RESULTS & DISCUSSION

3.1 Weight loss measurements

The weight loss method of monitoring corrosion rate and inhibition efficiency is useful because of its simple application and high reliability (Deng *et al*. 2012). The calculated CR and IE values at different immersion periods are given in Table 1. The weight loss measurements showed that the corrosion rate (CR) of mild steel decreased on increasing PCM concentration at room temperature. It can be observed that there is a marked reduction in the corrosion rate of mild steel even for a small concentration of 0.01% of PCM. There is also a decrease in corrosion rate with increase in immersion period up to 7 hr. With prolonged immersion periods there is first increase and then decrease of corrosion rate. It indicates that PCM acts as a good corrosion inhibitor for mild steel. The inhibition efficiency (IE) increases with increase in concentration of inhibitor and reach the maximum value of 93% for 2% concentration of PCM. The above observations indicate that corrosion inhibition is due to adsorption of inhibitor constituents at metal/ solution interface. The increase in inhibition efficiency and decrease in corrosion rate may be due to adsorption and desorption phenomena. The corrosion rate of mild steel and inhibition efficiency of various inhibitor concentrations at different immersion periods at room temperature is given in the Fig.1.

Fig. 2 shows variations of the IE of PCM with immersion periods. The effect of temperature on CR and IE was studied in the temperature range from 303 to 343 K. The values of CR and IE obtained from the weight loss measurement at different temperatures are listed in Table 2. From Ttable 2, it can be noted that CR increases with rise in temperature. The increase in CR can be attributed to an appreciable desorption of the inhibitor from the mild steel surface with increase in temperature.

Due to more desorption of inhibitor molecules at higher temperatures, the greater surface area of mild steel comes in contact with acid environment, resulting in increase extracts d corrosion rates with increase in temperature. The IE values are tabulated inTable 2 shows that the inhibitor PCM extracts is not only effective for room temperature but also effective in a wider temperature range. Effect of temperature on corrosion rate of mild steel with various concentrations of PCM is shown in Fig. 3. Effect of temperature on inhibition efficiency of PCM with various concentrations is shown in Fig. 4.

Table 1. CR & IE of PCM on mild steel in 1N HCl at different immersion periods

S. No	Conc.of PCM (v/v %)	1 Hr		3Hrs		5 Hrs		7Hrs		18 Hrs		24 Hrs	
		CR (mpy)	IE %	CR (mpy)	IE %	CR (mpy)	IE %	CR (mp)	IE %	CR (mpy)	IE %	CR (mpy)	IE%
1	Blank	1204		1151		1240		1093		1209		1156	
2	0.01	427	65	243	79	202	83	151	86	248	79	176	85
3	0.05	314	74	163	85	112	90	90	92	105	91	72	92
4	0.1	249	79	137	88	92	92	69	93	80	93	69	93
5	0.3	166	86	100	91	65	94	45	95	46	96	41	95
6	0.5	157	87	80	93	56	95	42	96	38	97	39	96
7	0.8	140	88	68	94	40	96	32	97	34	97	33	97
8	1	122	90	57	95	39	96	31	97	33	97	29	97
9	1.5	87	92	48	96	39	96	29	97	31	97	29	97
10	2	83	93	46	96	31	97	20	98	27	98	23	98

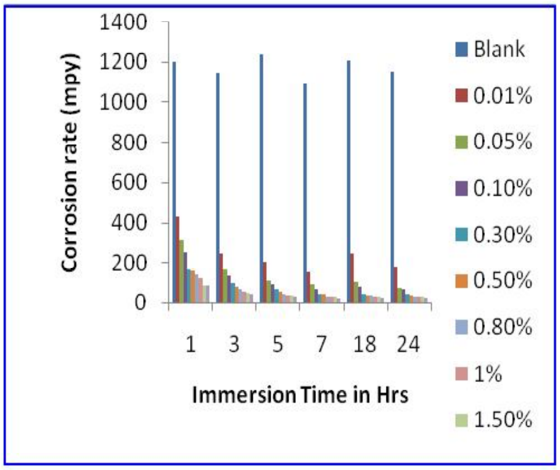


Fig. 1 : Corrosion rate of mild steel with different concentrations of PCM at different immersion periods

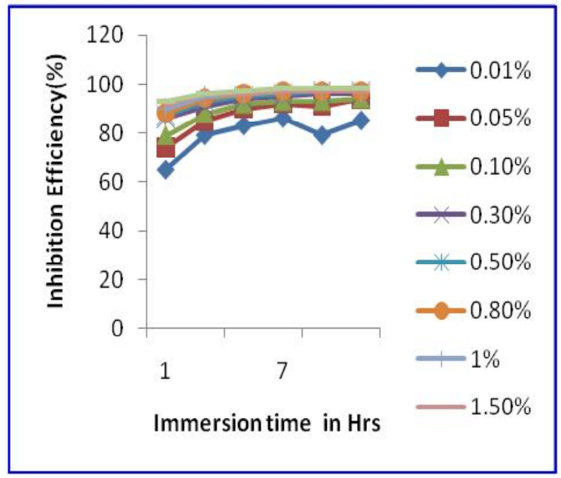


Fig. 2: Inhibition efficiency of different conc. of PCM at different immersion periods

Table 2. CR of mild steel and IE of PCM at different temperatures

S.No	Conc. Of PCM (v/v%)	303 K		313 K		323 K		333 K		343 K	
		CR (mpy)	IE%	CR (mpy)	IE%	CR (mpy)	IE%	CR (mpy)	IE%	CR (mpy)	IE%
1	Blank	1204		2228		3428		3916		4453	
2	0.01	427	65	602	73	911	73	1042	73	1705	62
3	0.05	314	74	362	84	541	84	759	81	1138	74
4	0.1	249	79	301	86	401	88	423	89	715	84
5	0.3	166	86	205	91	253	93	222	94	331	93
6	0.5	157	87	157	93	205	94	170	95	253	94
7	0.8	140	88	126	94	153	95	144	96	196	95
8	1	122	90	118	95	140	96	135	97	174	96
9	1.5	87	92	109	95	118	97	118	97	157	96
10	2	83	93	96	96	100	97	118	97	144	97

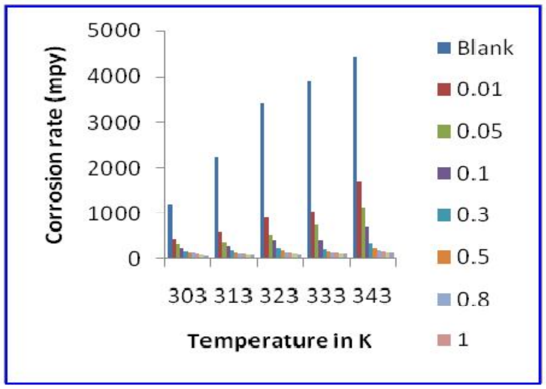
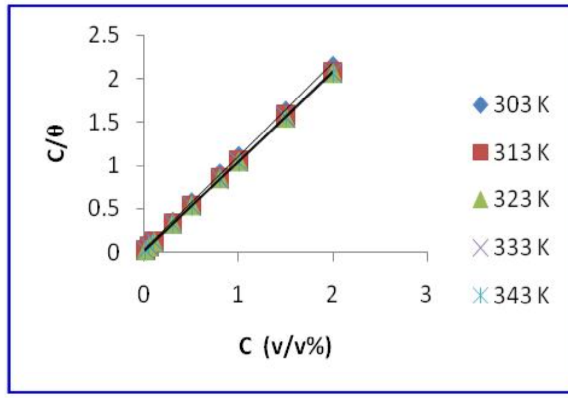


Fig. 3: Effect of temperature on corrosion rate of mild steel with various concentrations



5: Langmuir's adsorption plots for mild in 1N HCl containing different concentrations of PCM

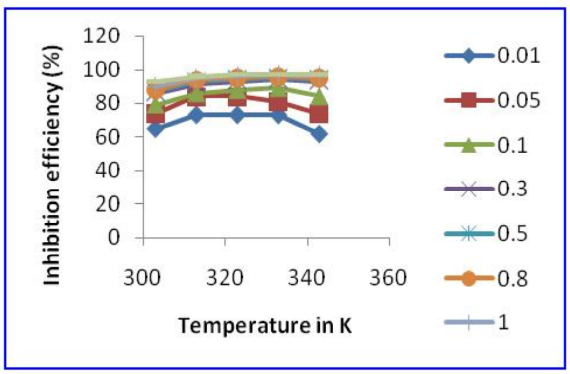


Fig. 4: Effect of temperature on inhibition efficiency steel of PCM with various concentrations of PCM.

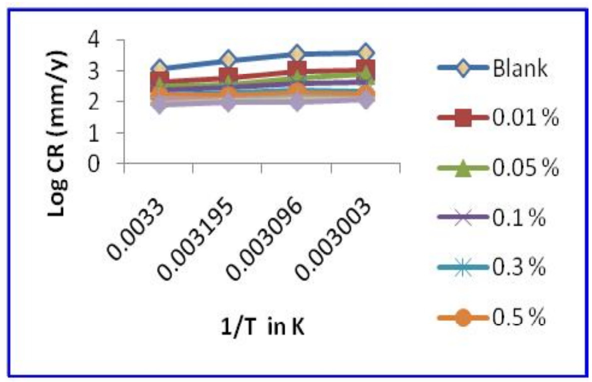


Fig. 6: Arrhenius plots of mild steel in 1N HCl solution without and with different concentrations of PCM

Table 3. Activation parameters of the adsorption of PCM in 1N HCl

Temperature (K)	ΔGads (KJ/mol)	ΔH ads (KJ/mol)	Δ Sads (J/mol/K)	E_a (KJ/mol)
303	-23.25	403.4	-4.56	27.87
313	-21.14	417.7	-4.80	28.64
323	-20.01	432.7	-5.24	28.50
333	-19.59	442.4	-5.48	21.04
343	-18.21	456.4	-6.54	12.60

3.2 Adsorption behavior of inhibitor

The plot of C/θ versus C yielded a straight line with a slope near to1 and a regression coefficient (R^2) of 0.99 as shown in Fig. 5. This suggests that the adsorption of the PCM inhibitor on mild steel surface in 1N HCl solution obeys the Langmuir adsorption isotherm. The calculated activation parameters are shown in the table.3. The negative values of ΔGads means that the adsorption of PCM on mild steel surface is a spontaneous process and furthermore the negative values of ΔGads also shows the strong interaction of the inhibitor molecule on to the mild steel surface**.** The positive values of ΔH° shows that the adsorption of the inhibitor is endothermic process and also shows the entropy of activation is negative. The Arrhenius plot of log CR versus 1/T gave the activation energies (E_a) of the corrosion process is shown in the Fig.6.

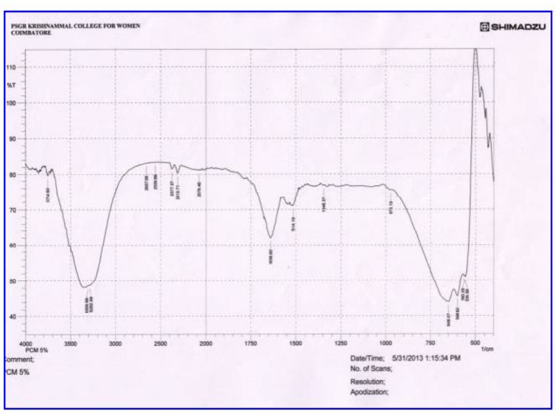


Fig. 7: FTIR Spectra of 5 % PCM extract

3.3 FTIR Analysis

FTIR spectroscopy allows us to examine the molecular structure and conformation of biological macro molecules because it measures the absorption energy, which produces an increase in the vibrational or rotational energy of atoms or groups of atoms within the molecule. FTIR spectrum of 5% PCM extract is displayed in Fig. 7. The broad band at about 3309.99 cm^{-1} can be assigned to the presence of intermolecular hydrogen bond, stretching mode of an O-H or N-H. The peak at 1514 cm^{-1} attributed to the stretching mode of aromatic substituted C=N or aromatic ring(C=C). A sharp band at 2377.33 cm^{-1} indicates the presence of primary amines (N-H). The peak at 1638.60 cm^{-1} indicates the existence of C=O and N-H bonds in primary amides. The absorption bands below 1000 cm^{-1} correspond to alkenes, aliphatic and aromatic C-H group and organic halogen compounds (C-X). This result indicates that PCM extract contains oxygen and nitrogen atoms in functional groups (O-H, N-H, C=C, C-N, C-X) and aromatic ring which meets the general consideration of typical corrosion inhibition. And also the peel extract contains mixture of compounds ie. Steroids, amino acids and fatty acids etc, and it is evident that the extracted organic compounds are stable in 1N HCl solution.

4. CONCLUSIONS

The Peel of ***Cucurbita maxima*** (PCM) extract acts as inhibitor for mild steel corrosion in hydrochloric acid solution. The maximum inhibition efficiency of 93% was observed at 2% v/v concentration at various immersion periods. Maximum Inhibition efficiency of 97% was obtained at 2% of PCM concentration at different temperatures, which suggesting chemical adsorption. The corrosion inhibition in the presence of the extract is by a spontaneous physisorption process. The adsorption of inhibitor obeys Langmuir adsorption isotherm. FTIR technique reveals that the extracted organic compounds are stable in 1N HCl.

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