

Evaluation of *Daucus Carota* Aerial Extract as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Medium

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Abstract- The influence of *Daucus carota* aerial part extract (DCA) on the corrosion inhibition of mild steel in 1N hydrochloric acid solution was studied by weight loss measurement and theoretical analysis. Characterization of DCA was carried out using HPLC and phytochemical screening. Maximum inhibition efficiency of 95.72% was achieved with 2% of DCA extract at 5h of immersion at 30°C. DCA adsorbed on the mild steel surface follows Temkin adsorption isotherms. The inhibition efficiency increases with increase in concentration of the inhibitor and time of immersion. The composition of DCA was identified and quantified by HPLC analysis and with phytochemical screening. Theoretical analysis with quantum chemical method results revealed that β -carotene possess corrosion inhibition property on surface of mild steel by adsorption process. Weight loss measurements and phytochemical screening showed that DCA acts as mixed type inhibitor and adsorb on the metal surface to protect against corrosion.

Index Terms- *Daucus carota*, Corrosion inhibition, HPLC, Theoretical analysis, β -carotene.

1. INTRODUCTION

Corrosion is a natural phenomenon that causes a total loss of billions of dollars to many industries. To overcome corrosion problem many methods are available such as inhibitors, anodic protections, cathodic protections and coatings. Corrosion inhibitors are substances which when added in small concentrations to the corrosive environment will reduce the rate of corrosion [Riggs, 1973]. Application of corrosion inhibitor is quite popular method to control corrosion issues.

Hydrochloric acid is a very commonly used acid in pickling process in industries but it is one of the most difficult acids to handle due to its very corrosive nature even in dilute forms [Noor, 2008].

The use of non-hazardous inhibitors or eco-friendly inhibitors is one of the solutions possible to control the corrosion of the materials. The extracts, oils or pure compounds from natural plants play major role to keep the environment secure. Among the various natural products, such as the *Lawsonia* extract [El-Etre *et al.* 2005], Black pepper [Bothi *et al.* 2008], *Musa acuminata* flower extract [Gunavathy and Murugavel, 2012], *Aquilaria Crassna* leaves extracts [Helen, *et al.* 2013], *Phyllanthus amarus* extract [Okafor *et al.* 2008], Fenugreek extracts [Noor *et al.* 2008], *Tectona grandis* seed extract [Rexin *et al.*

2014], *Azadiracta indica* [Oguzie *et al.* 2008], *Garcinia kola* extract [Oguzie *et al.* 2006], *Cucurbita maxima* plant extract [Anbarasi and Vasudha, 2014], *Hibiscus sabdariffa* extract [Oguzie *et al.* 2008], Eucalyptus oil [Gong *et al.* 2006], Thymus oil [Bammou *et al.* 2010], *Nypa fruticans* Wurmb [Orubite *et al.* 2004]. *Chamaemelum mixtum*, *Cymbopogon proximus*, *Nigella sativa*, *Phaseolus vulgaris* have been established for anti-corrosion properties [Abdel-Gaber *et al.* 2006].

The studies on corrosion control have been reported to be good inhibitors for metals in acidic solutions. Natural compounds containing sulphur, oxygen and nitrogen atoms are more effective as corrosion inhibitors in acid media [Muralidharan *et al.* 1995]. Sribharathy *et al.* (2011) reported aqueous extract of the leaves of DCA as corrosion inhibitor of mild steel in sea water.

This work is also aimed to find a better green corrosion inhibitor from natural source through extract of DCA.

The assessments of the corrosion behavior were studied using phytochemical analysis, HPLC analysis, weight loss measurement and theoretical analysis of the plant extract.

2. MATERIALS AND METHODS

2.1. Plant Material

The *Daucus Carota* plants were collected from local market, Coimbatore. The aerial parts of the plant were cut into small pieces and shade dried at room temperature for few weeks, and powdered in electrical blender and stored in airtight containers.

2.2. Phytochemical Screening

Phytochemical screening was carried out on the DCA extracts by standard procedure [Harborne, 1998]. The plant extracts were screened for reducing sugar, alkaloids, protein, phenols, flavonoids, amino acids, tannin, steroids, glycosides and saponins.

2.3. Analysis of plant extract

HPLC analysis was performed for plant extract using HPLC Waters system, equipped with 515 HPLC pump and waters 2998 photodiode array detector. The compounds were identified by comparing retention time and reference compounds.

2.4. Preparation of the extract

25g of the powdered DCA was weighed and added to 500ml of 1N HCl. This mixture was refluxed for three hours and kept overnight. The following day, it was filtered and residue was repeatedly washed with small amount of 1N HCl and the filtrate was made up to 500 mL. The prepared extract with 1N HCl was taken as the stock solution. The required concentrations were prepared by diluting the stock solution.

2.5. Sample Preparation

The mild steel samples obtained from a locally available industry with a chemical composition of carbon 0.071%, manganese 0.49%, silicon 0.03%, phosphorus 0.008%, sulphur 0.002%, chromium 0.017%, nickel 0.018% and iron 99.09% identified at SiTarc, Coimbatore was utilized for the present study. The mild steel samples, with an active surface of 1cm x 5cm with 2mm thickness, a hole drilled at one end of coupons for suspension in the solution were cut from the large sheet. These steel pieces were mechanically polished to remove any rust on it. The metal pieces were then degreased with acetone washed with distilled water and edges were polished

with fine grade of emery papers, cleaned, dried and stored in desiccators.

2.6. Weight loss measurements

Metal coupons were weighed using electronic balance. Weighed mild steel coupons were immersed in 100mL of 1N HCl with different concentrations of plant extract (0.05, 0.10, 0.50, 1.0, 1.5, and 2.0 % v/v) and without plant extract (Blank). After various immersions period, the coupons were removed from the test solution washed, dried and weighed. From the initial and final mass of the specimens, the loss of weights were calculated, and the corrosion rate (in mpy) was computed from the following equation (Bhat and Alva, 2009, Abdallah *et al.* 2012).

$$\text{Corrosion rate, CR} = \frac{87.5 W}{DAT} \quad (1)$$

Where W is the weight loss (mg) of the coupons, D is the density of the coupon (7.8 g/cm^3), A is the surface area of coupon (cm^2), and T is the immersion time (h). Inhibition efficiency of the mild steel was then calculated (Osarolube *et al.* 2008).

2.7. Effect of temperature

The polished and pre-weighed coupons were suspended in 100 mL of the test solution without and with different concentrations of the DCA extract for 1h in the temperature range of 30-80°C using thermostat. After the immersion phase, the coupons were washed with distilled water, dried and weighed. From the weight loss, the inhibition efficiency (IE %) of the inhibitor was calculated.

2.8. Theoretical analysis

The Quantum chemical calculations were done using semi-empirical method - Parametrized Model 3 (PM3) [Stewart, 1989]. This method is suitable for analyzing closely resembling molecules that are subject of our correlation studies. The output of MOPAC program reports values such as ionization potential, Eigen values, dipole moment etc. The quantum chemical parameters were generated to evaluate the theoretical inhibition efficiency of the β -carotene molecule.

3. RESULTS AND DISCUSSIONS

3.1. Phytochemical analysis

It is recommended fact that the adsorption properties of the plant extract is directly attributed to the presence of various chemical constituents. Therefore during scrutinizing the plant extract for their adsorption properties, the determination of chemical composition is very essential. The phytochemical screening proved that the plant extract is rich in protein, phenol, amino acids and tannins. These compounds contain oxygen and nitrogen atoms which are the centre of adsorption. The DCA extracts establish their inhibitive action through adsorption of phytochemical component molecules on the metal surface. The results of phytochemical screening are shown in Table no. 1.

Table No. 1- Quantitative analysis on phytochemical screening of *Daucus carota* aerial extract

“++” active compound copiously present,
 “+” active compound present,
 “-” active compound absent

3.2. HPLC analysis

β -carotene is the predominant compound in *Daucus carota* pulp and leaf [Almeida-Muradian *et al.* 1997]. The analysis was performed to quantify and

identify the β -carotene in DCA. The phenolic compounds were eluted with 89% acetonitrile and 11% dichloromethane as mobile phase at flow rate of 1 mL/min with injection volume 10 μ L/min using detection wavelength at 254 nm. The HPLC fingerprint chromatogram of DCA produced 13 peaks in phenolic compounds. Peaks of Phenolic compounds were identified by comparison of retention times with those of authentic reference compounds. β -carotene appeared at 3.687 min in the chromatogram.

S. No.	Phytochemical	DCA
1.	Reducing sugar	+
2.	Alkaloids	+
3.	Protein	++
4.	Phenols	++
5.	Flavonoids	+
6.	Amino acids	++
7.	Tannin	++
8.	Steroids	-
9.	Glycosides	+
10.	Saponins	-

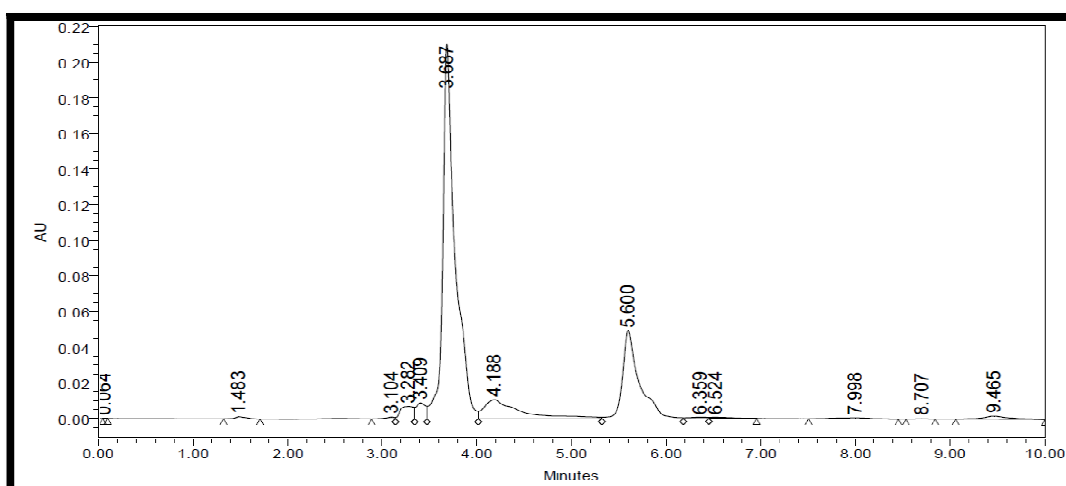


Figure 1: HPLC chromatogram of DCA

The plant extract propose inhibition on mild steel due to presence of effective organic molecules as functional groups. Phenolic compounds also contribute for the inhibition efficiency of DCA extract. The composition of β -carotene was quantified in DCA extract and found to be 4.26 mg/100 g.

3.3. Gravimetric Measurements

Table no. 2 gives values of the inhibition efficiency obtained from the weight loss measurements of mild steel for various concentrations of DCA in 1 N HCl at 30°C after different hours of immersion.

Table No.2- Inhibition efficiency (IE) of DCA extract in 1N HCl against mild steel at various concentrations and different immersion period

Conc. of extract in v/v %	Percentage Inhibition Efficiency (IE %)				
	Immersion time in hours				
	1	3	5	7	24
0.05	61.29	69.19	72.70	71.38	63.45
0.10	77.42	79.46	81.91	80.34	70.13
0.50	79.03	81.08	85.53	83.79	72.65
1.00	83.87	85.95	88.49	85.86	76.90
1.50	87.10	88.65	92.11	87.93	80.05
2.00	88.71	92.97	95.72	88.28	81.59

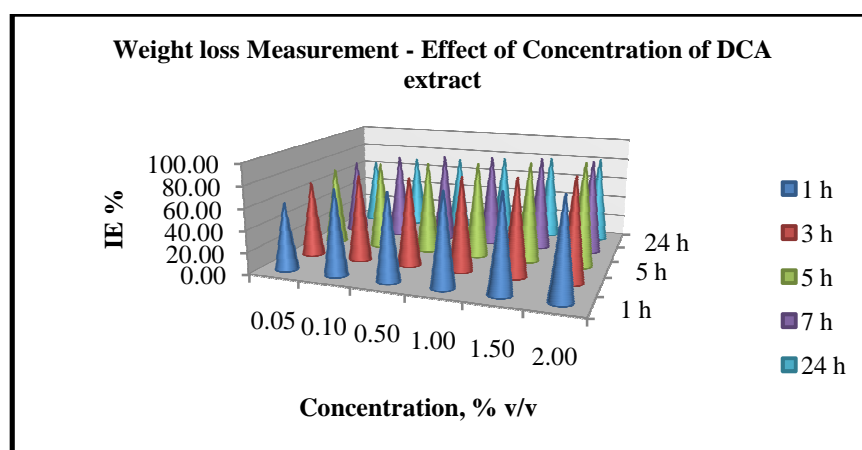


Figure 2 (a): Effect of concentration on Inhibition efficiency of mild steel with various concentrations of DCA extract in 1 N HCl.

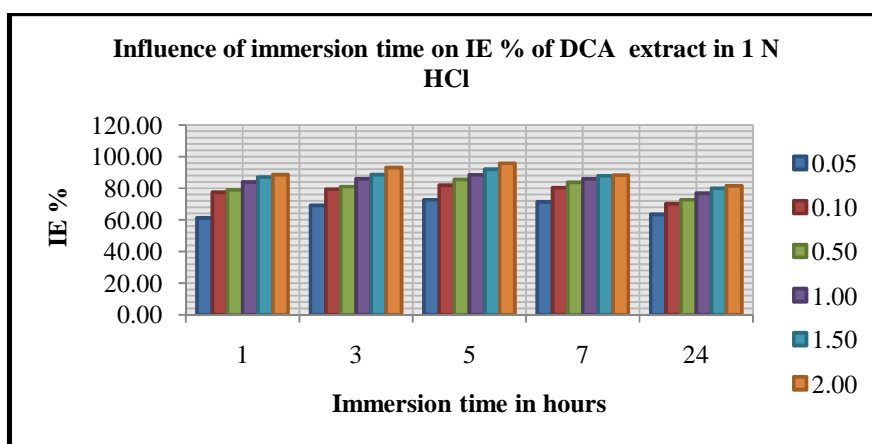


Figure 2 (b): Influence of immersion time on Inhibition efficiency of mild steel with various concentrations of DCA extract in 1 N HCl.

The inhibition efficiency was calculated using the formula [Akpan, 2012, Shylesha *et al.* 2011]

$$IE\% = \frac{W_1 - W_2}{W_1} \times 100 \quad (2)$$

Where W_1 and W_2 are the values of weight loss of mild steel after immersion in solutions with out and with inhibitor respectively.

As the concentration of inhibitor increases, the rate of corrosion decreases because the inhibitor molecules prevent the dissolution of mild steel by effective adsorption phytonutrients of plant extract on the metal surface area. The adsorbed organic molecules prevent the further interaction of the acid with metal. The activity of the extract in 1N HCl produced maximum efficiency of 95.72% was achieved with 2% of DCA extract at 5h of immersion at 30°C. At

1h and 3h, the maximum inhibition efficiency of 88.71% and 92.97% were obtained for DCA extract shown in Table no. 2 and Figure 2 (a) & 2 (b).

3.4. Effect of Temperature

Table No. 3- Inhibition efficiency of DCA extract in 1N HCl against mild steel at different temperature

Conc. v/v %	Inhibition Efficiency %				
	303 K	313 K	323 K	333 K	343 K
0.05	61.29	68.16	73.64	75.81	67.47
0.10	67.74	74.30	80.62	85.54	73.49
0.50	77.42	83.24	85.66	89.59	80.72
1.00	79.03	83.80	87.21	92.30	81.50
1.50	80.65	85.47	89.15	93.11	84.34
2.00	83.87	89.94	92.64	95.14	88.98

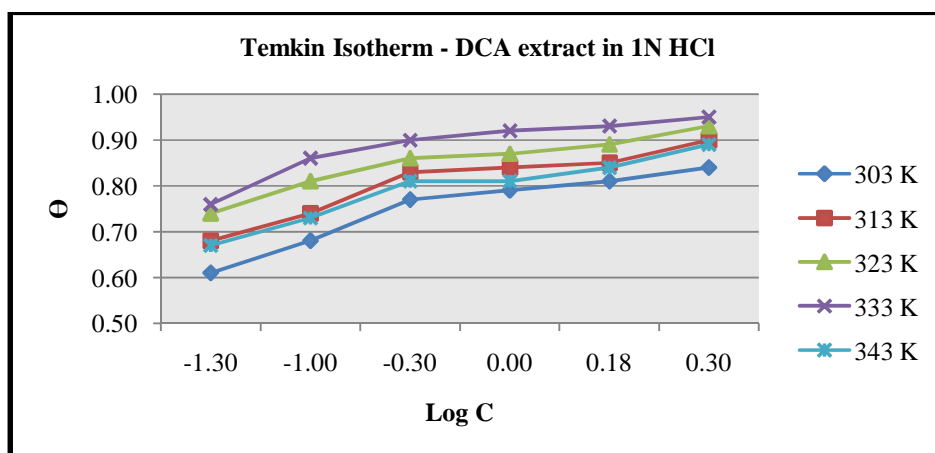


Figure 3. Temkin adsorption isotherm plot for adsorption of different concentrations of DCA on mild steel in 1 N HCl at different temperatures

The maximum efficiency of 95.14% was achieved with 2% of DCA extract at 333K. At 313K and 323K, the maximum inhibition efficiency of 89.94% and 92.64% were obtained for DCA extract shown in Table no. 3.

Data were tested graphically by fitting Temkin isotherms. From the linear plots of θ versus $\log C$, it can be seen that the inhibitor obeys Temkin isotherm (Figure 3) indicating that the main process of inhibition involves the adsorption of the inhibitor on mild steel [Karthikai selvi *et al.* 2009].

Adsorption isotherms are very important in determining the mechanism of organic electrochemical reactions. The adsorption of organic compounds under study obeys the Temkin adsorption isotherm. The effect of temperature on inhibition reaction is highly complex, because changes may occur on the metal due to rapid etching, rupture, desorption of inhibitor, decomposition and rearrangement of inhibitor [Shamitha *et al.* 2010].

The effect of temperature on the rate of corrosion was studied in the absence and presence of DCA extract.

The inhibitive action of organic compounds depends on their structure and functional groups, nature of the metal and aggressive medium [Chitra *et al.* 2010, Saliyan and Adhikari, 2009].

3.5. Theoretical analysis

The major constituent of *Daucus carota* is carotenoids and predominant being β -carotene (Figure 4(a)). HPLC analysis report shows that the composition of β -carotene in DCA was 4.26 mg/100g. β -carotene was subjected to quantum chemical studies to get insight in the corrosion inhibition efficiency of the compound on mild steel. Theoretical calculations and parameters were generated using MOPAC 2007 which is a freely available electronic structure code [Olivella, 1984].

Quantum chemical parameters are obtained from the theoretical calculations which are responsible for the inhibition efficiency of β -carotene on mild steel such as HOMO, LUMO, energy gap, dipole moment (μ), electronegativity (χ), electron affinity (A), global

hardness (η), softness (S), ionization energy (I) and the electrophilicity (ω) are collected (Table no. 4). The low ionization energy 7.753 (eV) of β -carotene indicates the good inhibition efficiency.

Absolute hardness and softness are important properties to measure the molecular stability and reactivity. A hard molecule has a large energy gap and a soft molecule has a small energy gap [Obi-Egbedi *et al.* 2011]. For the simplest transfer of electron, adsorption could occur at the part of the molecule where softness(S), which is a local property, has a highest value [Hasanov *et al.* 2007]. β -carotene with the softness value of 0.284 has the agreeable inhibition efficiency.

β -carotene with hardness value 3.520 (eV) have a low energy gap. The frontier molecular orbitals of the compound are shown in Figure 4(b).

Table No.4 - Quantum chemical parameters of the β -carotene of *Daucus carota*

S.No	Chemical Parameters	β -carotene
1.	E HOMO (eV)	-7.753
2.	E LUMO (eV)	-0.713
3.	ENERGY GAP (ΔE)	7.040
4.	EA (eV)	0.713
5.	IE (eV)	7.753
6.	χ (eV)	4.233
7.	η (eV)	3.520
8.	S	0.284
9.	μ	-4.233
10.	ω	2.545

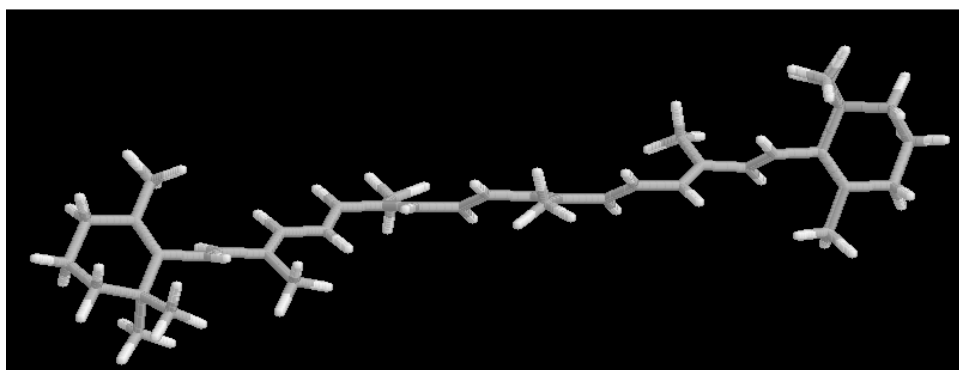


Figure 4: (a). Structure of β -carotene

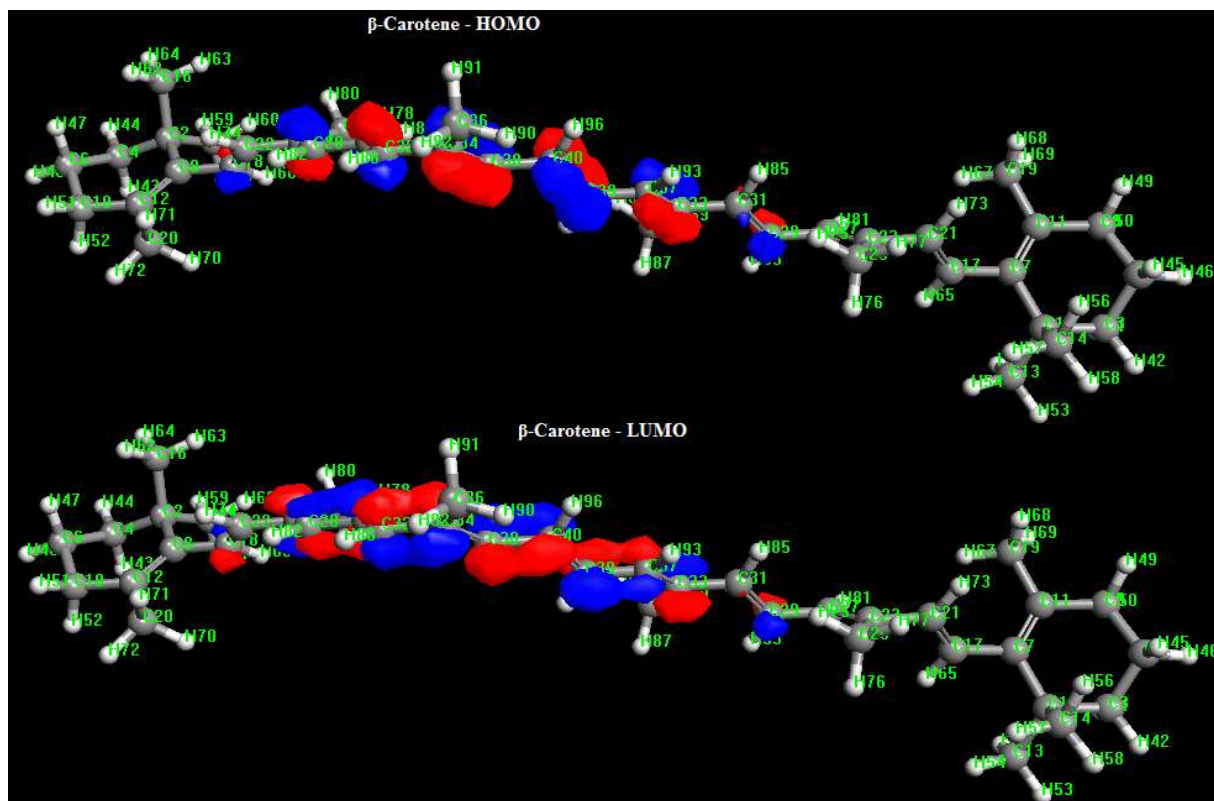


Figure 4: (b). Frontier molecular orbital of β -carotene

The energy of the highest occupied molecular orbital (EHOMO) measures the tendency of molecule to donate electrons. Therefore, higher values of EHOMO indicate good tendency towards the contribution of electron, enhance the adsorption of the inhibitor on mild steel and demonstrate better inhibition efficiency.

4. CONCLUSION

Based on the above results, the following conclusion can be drawn,

- DCA extract of plant was found to be an effective inhibitor for the corrosion of mild steel in HCl medium. Inhibition efficiency increased with an increase in DCA extract content.
- The weight loss measurements, phytochemical screening and theoretical analysis, confirmed the inhibitive nature of the DCA in HCl medium.
- The composition of β -carotene in DCA was 4.26 mg/100g reported using HPLC analysis. Theoretical analysis on β -carotene using

MOPAC showed that the compound shows interaction with metal surface which was proved with the quantum chemical parameters.

- The corrosion inhibitive process is effective by adsorption of the DCA extract on the mild steel surface follows Temkin adsorption isotherm. This indicates that the inhibition effect of the extract is due to adsorption of phytochemical constituents of DCA extract.
- Thus the extract was proved to be an effective eco friendly green inhibitor with cost efficient to be applied in the industries.

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