Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2013, 2 (5):1216-1223

(International Peer Reviewed Journal)

Benincasa hispida (Ash gourd) Seed Extract- As Corrosion Inhibitor For Mild Steel In Acid Medium

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Received on 17th July, Revised on 3rd August and finalized on 19th August 2013.

ABSTRACT

Seed extract of Benincasa hispida was evaluated for its corrosion inhibitive effect on mild steel in 1M H_2SO_4 *using weight loss and electrochemical measurement techniques. The results reflect that the inhibition efficiency increases with increase of extract concentration. Maximum inhibition efficiency in 1M* H_2SO_4 *was found to be 94.7% for a period of 6h with 0.5% concentration of the inhibitor. Experimental results were fitted in to Langmuir and Temkin adsorption isotherm to study the process of inhibition. Potentiodynamic polarization results reveal that the seed extract behaved like mixed type inhibitor.*

Keywords: *Benincasa hispida* seed, Mild steel, Corrosion inhibition, H_2SO_4 medium.

INTRODUCTION

The vast repercussion of corrosion has attracted a lot of investigations in inhibition of metal in recent years[1-4]. Corrosion inhibitors are of great practical importance as they minimize the base metal loss to a greater extent and are easier to use. Most of the well known inhibitors that are being utilized in industries are organic in nature and there is great need to find a non toxic replacement that is compatible with current industrial technologies. Naturally occurring substances are gaining importance in recent years due to their non toxic nature and easy availability. Increasing awareness on environmental issues have prompted researchers to focus on a more viable, eco-friendly alternatives and numerous naturally occurring substances have been successfully tried as corrosion inhibitors [5-7].Our research team successfully tested the utilization of Sprouted seeds of *Phaseolus aureus* [8] *Cyamopsis tetragonaloba* [9], *Ervatamia coronaria* [10], *Cocos nucifera* [11], *Cassia alata* [12] as corrosion inhibitors for mild steel and in our ongoing efforts in this direction, an attempt has been made to study the influence of seed extract of *Benincasa hispida* on the corrosion rate of mild steel in 1M H_2SO_4 medium.

MATERIALS AND METHODS

Extract preparation: The seeds were collected from a nearby field site in Coimbatore region. They were shade dried and powdered using a blender. The extract was prepared by refluxing 25g of *Benincasa hispida* powdered seed in 250ml of 1M H_2SO_4 for three hours and kept overnight for cooling. The cooled extract was filtered and made up to 500ml with 1M H_2SO_4 acid to get 5% extract of the inhibitor.

Gravimetric measurement: Mild steel specimens of the following chemical composition in wt %- Mn (0.27), P (0.035), C (0.14), Si (0.04), S (0.03), Ni (0.006), Cr (0.002), Mo (0.001) and Fe 99.476% were chosen for the present study. Weight loss and electrochemical studies were carried out for assessing the efficiency of the inhibitor. For weight loss study, MS specimens of size 1*5 cm^2 were used. The specimens were mechanically polished, degreased, dried and stored in a desiccator. Weighed samples are immersed in 100ml of the acid (1M H_2SO_4) without and with different concentrations of the inhibitor for various intervals of time. They are then taken out and then washed thoroughly with tap water, rinsed with distilled water, dried, stored in desiccators and reweighed. Immersion time and temperature variation are as given below

1. Time: 1/2h, 1h, 3h, 6h, 12h, 24h.
2. Concentration of the inhibitor: 0.05%- 0.5%.
3. Temperature: 313K- 353K.

Electrochemical measurements

Potentiodynamic polarization measurement: Potentiodynamic polarization studies were carried out using Solatron 1280 B. 100ml of 1M H_2SO_4 without and with different concentrations of the inhibitor was taken in an electrochemical cell. The polished electrode was then introduced. MS specimens with the exposed area of 1cm^2 were used for electrochemical study. The electrode was placed at 0.8 mV to its open circuit potential. Thus the potential was scanned at -0.2 mV sec^{-1} towards the anodic direction in Tafel extrapolation. Applied potential vs. current was plotted and on extrapolation of linear portion to the corrosion potential gives the corrosion current. In anodic and cathodic plot, the slope of the linear portion gives Tafel constants b_a and b_c respectively.

Impedance studies: Impedance measurements were carried out at various corrosion potentials. An ac sine wave of 10mV amplitude was applied to the electrode. The frequency which is varied from 10 KHz to 100MHz was superimposed at the open circuit potential. The results are presented in the form of Nyquist plots. All the measurements were presented in the corrosion potential. In impedance method, the charge transfer resistance (R_{ct}) is obtained from the plots of Z' Vs Z" (real part Vs imaginary part: Nyquist plot). The value (R_p + R_s) corresponds to Z axis to the point where the semicircle cuts the Z axis at high frequency.

Surface Examination: The mild steel specimens were immersed in various test solutions for a period of 3hrs. The specimens were taken out and dried. Optical microscope (Nikon- model EPI-plot) was used for this investigation.

RESULTS AND DISCUSSION

Effect of concentration and immersion time: The variation of inhibition efficiency and corrosion rate for different concentration and time of immersion in the presence and absence of seed extract of *Benincasa hispida* is listed in table 1. From the values, it is very clear that the corrosion rate decreases continuously with increasing additive concentration. Maximum inhibition efficiency for 1M H_2SO_4 was found to be 94% at 6 hrs with 0.5% concentration of the inhibitor.

Table 1: Inhibition efficiency as a function of immersion time and concentration of BH extract on mild steel in 1M H_2SO_4

Conc of BH Extract (%)	**Immersion period (h)**											
	½		**1**		**3**		**6**		**12**		**24**	
	CR (mpy)	**IE (%)**	**CR (mpy)**	**IE (%)**	**CR (mpy)**	**IE (%)**	**CR (mpy)**	**IE (%)**	**CR (mpy)**	**IE (%)**	**CR (mpy)**	**IE (%)**
Blank	1402	-	2450	-	1855	-	1835	-	1638	-	1272	-
0.05	279	80.1	341	86.0	182	90.1	180	90.1	169	89.6	192	84.8
0.1	266	81.0	271	88.9	168	90.9	157	91.4	164	89.9	157	87.6
0.15	253	81.9	266	89.1	153	91.7	155	91.5	143	91.2	127	89.9
0.2	243	82.6	261	89.3	141	92.4	138	92.4	118	92.7	117	90.7
0.25	241	82.8	257	89.5	138	92.5	131	92.8	114	93.0	112	91.1
0.3	279	80.0	240	90.1	131	92.8	124	93.2	113	93.0	113	91.0
0.35	233	83.3	239	90.2	126	93.1	120	93.4	107	93.4	100	92.0
0.4	231	83.4	237	90.3	121	93.4	116	93.6	104	93.6	100	92.1
0.45	211	84.8	205	91.6	117	93.6	99	94.5	103	93.6	90	92.8
0.5	187	86.6	206	91.5	115	93.7	97	94.7	101	93.8	86	93.1

This behavior may be attributed to the increase of the surface coverage by the extract, which retards the corrosion of mild steel. From the table, it can also be inferred the inhibition efficiency increases with increase in immersion time up to 6 h and after that there is slight decrease in the inhibition efficiency at 12 and 24 h. It may be explained as follows. At the initial time of immersion, concentration of the extract will be more so the rate of adsorption will be prominent. This is the reason for the enhancement of IE during first few hours (up to 6h) .With prolonged time of immersion IE decreases slightly. This may be due to the increase in cathodic or hydrogen evolution kinetic and also due to the increase in the real surface area with time [13]. However at higher concentration the IE was stabilized furnishing 93% at 24 h .This result highlighted the stability of adsorbed layer of BH seed extract on mild steel surface.

Influence of Temperature: Temperature can modify the interaction between iron electrode and acid in the presence / absence of inhibitor. The influence of temperature on the corrosion behavior of MS in acid medium in the presence of various concentrations of BH seed extract are investigated by weight loss trends in the temperature range 303 – 353K during 1/2h immersion.

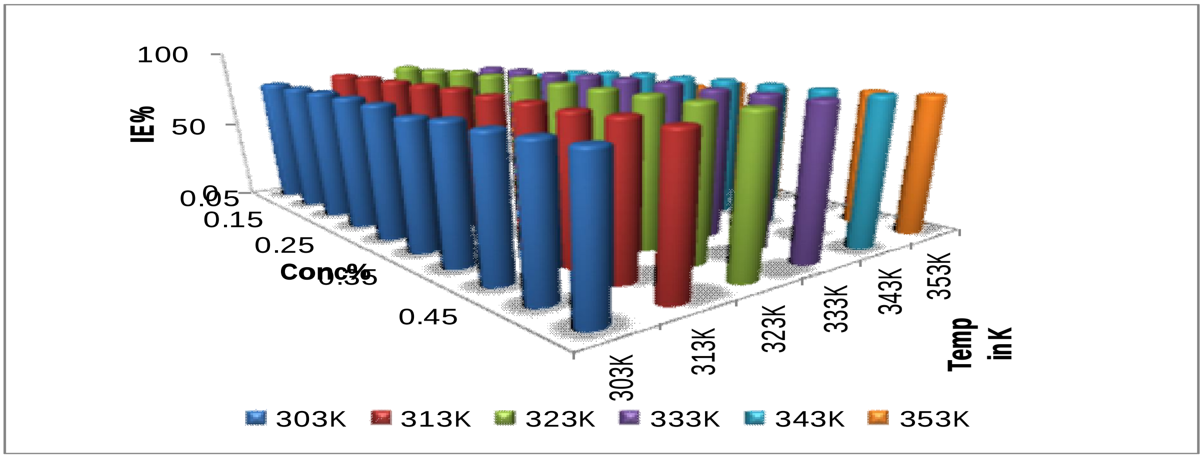

Figure 1: Effect of temperature on the corrosion of mild steel in the presence of BH extract in 1M H_2SO_4

From the figure, it was inferred that in 1M H_2SO_4 the inhibition efficiency increases with increase in concentration of the seed extract at all investigated temperature in acid medium. The inhibition efficiency also increased with increase in temperature of the test solution up to 333K. A slight decrease in inhibition efficiency was observed at 343 and 353K. In the present investigation, it is apparent that the BH extract functions as a promising inhibitor at higher concentration and at higher temperature. According to Putilova [14] the decrease in the inhibition efficiency of the inhibitor with increase in temperature might be due to the shift in the adsorption and desorption equilibrium leading to a higher desorption rate than adsorption until equilibrium is again established at a different value of equilibrium constant.

Adsorption Isotherm: Adsorption isotherms are very important in determining the mechanism of electrochemical reactions. The surface coverage (θ) values for different concentration of the inhibitors in acid medium have been evaluated from the weight loss data. The data were tested graphically to find a suitable adsorption isotherm. A plot of log (θ/1- θ) against log C (fig 2) shows a straight line indicating that adsorption follows the Langmuir adsorption isotherm. It is clear from the linear plot that the inhibitors follow Langmuir adsorption isotherm with R^2 values of 0.99-0.78 (table 2).

It is observed that although these plots are linear, the gradients are never unity, contrary to what is explained ideal Langmuir adsorption equation. Organic molecules having polar atoms (or) groups which are adsorbed on the metal surface may interact by mutual repulsion (or) attraction and this may be advocated as the reason for the departure of the slope values from unity. A straight line was obtained when the surface coverage was plotted against log C for the inhibitor. This shows that the adsorption obeys a Temkin adsorption isotherm which is graphically represented in figure 3.

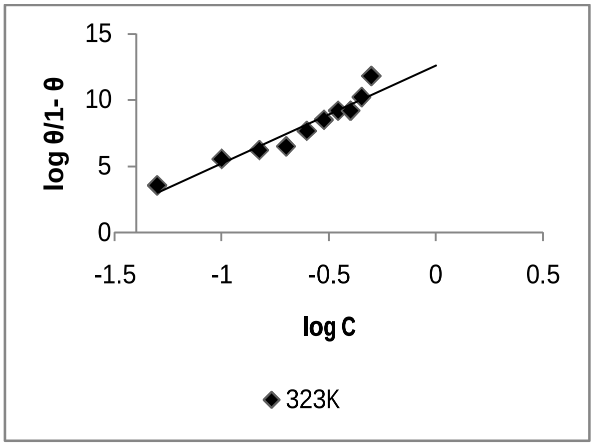

Figure 2: Langmuir adsorption isotherm

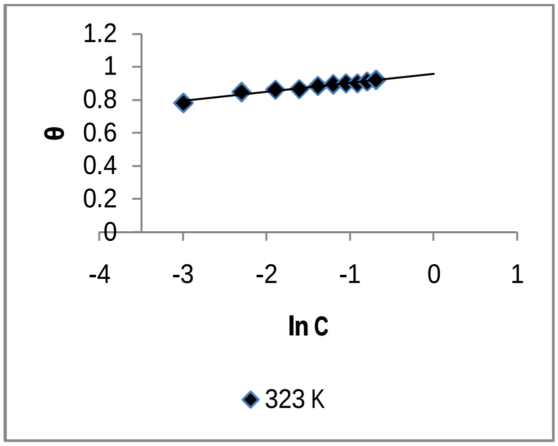

Figure 3: Temkin adsorption isotherm

Table 2 Adsorption Parameters calculated from Langmuir and Temkin Adsorption Isotherm

S.No	Temp in K	Langmuir Adsorption Isotherm				Temkin Adsorption Isotherm			
		log K	Slope	ΔG*ads (KJmol^{-1})	R^2	LogK	A	ΔG*ads (KJmol^{-1})	R^2
1	303	1.07	0.97	-10.29	0.99	0.86	0.020885	-12.28	0.74
2	313	1.04	0.97	-10.56	0.99	0.91	0.027438	-12.82	0.97
3	323	1.03	0.965	-10.85	0.99	0.94	0.030797	-13.32	0.97
4	333	1.02	0.94	-11.16	0.99	0.96	0.054711	-13.77	0.98
5	343	0.98	0.85	-11.41	0.99	1.00	0.114236	-14.32	0.96
6	353	0.92	0.60	-11.53	0.98	1.04	0.229427	-14.85	0.99

Kinetic and thermodynamic parameter: According to Arrhenius equation,

$$\text{Log CR} = \frac{-E_a}{2.303\,RT} + \text{Constant}$$

where CR = Corrosion Rate, E_a = Activation energy, T = Temperature

Corrosion rates of mild steel calculated in the presence and in the absence of the inhibitor by weight loss method are plotted against the temperature (log CR Vs 1/T) (figure 4).

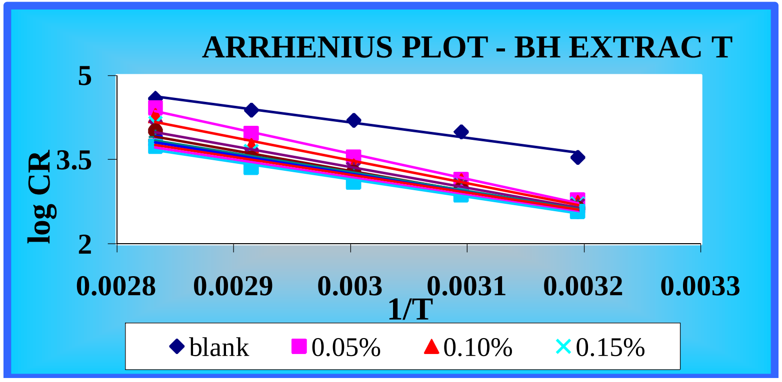

Fig 4 Arrhenius plot

Activation energies were calculated from the slopes. The estimated values of E_a for mild steel in BH extract in 1M HCl are listed in table 3. Linear plots were obtained, and from the slope (-Ea/2.303R) activation energy (Ea) values are deduced.

Table 3: Thermodynamic parameters for the dissolution of mild steel in the presence of BH in 1M H_2SO_4

Conc. (%)	Ea KJ mol^{-1}	ΔG, KJ mol^{-1}					ΔH KJ mol^{-1}	ΔS KJ mol^{-1}
		313K	323K	333K	343K	353K		
Blank	52.75	-	-	-	-	-	-	-
0.05	86.41	-22.33	-23.58	-22.93	-21.36	-18.42	-15.15	-0.100
0.1	78.00	-20.83	-21.88	-22.23	-21.39	-18.70	-35.76	-0.044
0.15	72.97	-19.92	-21.38	-21.43	-21.09	-19.02	-22.03	-0.004
0.2	70.72	-19.46	-20.74	-20.75	-20.75	-18.94	-23.55	-0.004
0.25	69.70	-19.16	-20.65	-20.59	-20.63	-18.92	-21.65	-0.005
0.3	64.38	-18.61	-20.02	-20.37	-20.29	-19.22	-14.74	-0.014
0.35	63.94	-18.29	-19.75	-20.15	-20.21	-18.83	-14.31	-0.015
0.4	61.06	-17.90	-19.51	-19.80	-19.99	-18.95	-10.63	-0.025
0.45	60.62	-18.02	-19.32	-19.76	-19.92	-19.14	-9.77	-0.028
0.5	59.48	-14.16	-15.64	-16.03	-15.88	-15.06	-8.56	-0.020

The temperature dependence of the inhibiting effect and the comparison of the values of the apparent activation energy of the corrosion process in the absence and presence of inhibitor can provide further evidence concerning the mechanism of the inhibiting action. The decrease of the inhibitor efficiency with temperature raise, which refers to a higher value of Ea, when compared to that in an acid with no inhibitor, is interpreted as an indication for an electrostatic character of the inhibitor's adsorption. Unchanged or lower values of Ea in inhibited systems compared to the blank have been reported to be indicative of chemisorption mechanism, whereas higher values of Ea suggest a physical adsorption mechanism. The higher Ea values in the presence of inhibitor compared to the blank solution, in the present case, indicates that the inhibitor will be effective at low temperatures, than at higher temperatures [15].

The values of ΔG obtained are lower than that of blank. Generally, values of ΔG around -20 kJmol-1 or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption); those around -40 $kJmol^{-1}$ or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [15]. The values of ΔG suggest physical mode of adsorption. The negative sign of enthalpies (ΔH) reflect the endothermic nature of dissolution process. The positive value of entropies (ΔS) reflect that the activated complex in the rate determining step is dissociation rather than association, meaning that disordering increases on going from reactants to the activated complex.

Electrochemical measurements

Potentiodynamic polarization results: The electrochemical parameters calculated from Tafel plots (fig 4) are given in table 4. Inspection of the data reveals the lower corrosion current density (I_{corr}) values in the presence of the inhibitor. This behaviour reflects the ability of the extract to inhibit the corrosion of mild steel in acidic media. Both the anodic and cathodic current densities were reduced which is indicative of the mixed nature of the inhibitor (i.e. inhibit both anodic and cathodic reaction) In all concentrations b_a is greater than b_c suggesting that though the inhibition is under mixed control, the effect of the inhibitor on the anodic polarization is more pronounced than on the cathodic polarization.

Table 4: Tafel polarization and impedance measurements of mild steel in the presence of seed extract of BH in 1M H_2SO_4.

Conc. (%)	I_{corr} ×10^{-3} (amp/ cm^2)	E_{corr} (V/dec)	b_a (mV/ dec)	b_c (mV/ dec)	IE (%)	R_{ct} (Ohm cm^2)	IE (%)	R_p (Ohm cm^2)	IE (%)
Blank	4.21	- 481	233	170	-	4.8	-	6.1	-
0.05	1.92	- 461	175	102	54.34	16.9	71.32	13.5	54.43
0.1	1.92	- 458	154	105	54.17	21.9	77.86	13.5	54.17
0.15	1.83	- 458	151	101	56.46	24.1	79.84	14.2	56.46
0.2	1.30	- 460	152	88	69.11	30.4	84.02	20.0	69.11
0.25	1.24	- 460	158	92	70.37	40.1	87.88	20.9	70.37
0.3	1.25	- 459	156	91	70.17	49.0	90.08	20.7	70.17
0.35	1.31	- 459	163	94	68.87	59.8	91.86	19.9	68.87
0.4	1.29	- 459	146	82	69.18	59.7	91.85	20.1	69.18
0.45	1.25	- 457	150	85	70.25	67.2	92.75	20.8	70.25
0.5	1.23	- 458	137	82	70.65	73.4	93.37	21.1	70.65

Electrochemical impedance spectroscopy results: Impedance diagram (Nyquist plot) obtained for mild steel in 1M H_2SO_4 in the presence of various concentrations of the inhibitor is depicted in fig (7). They are single depressed semicircles and the diameter of the semi circle increased with increasing concentration of the inhibitor. This was attributed to charge transfer reaction occurring at the electrode / solution interface, and this contributes to the control of mild steel corrosion. The depressed condition of the semi circles into the real axis, are often attributed to inhomogeneities on the surface of the electrode [16]. Impedance parameters derived from Nyquist plots are tabulated in table (4). From the table, it is clear that Rct increases in concentration of inhibitor and CdI decreases. The increase in R_{ct} values may suggest the formation of a protective layer on the surface of the electrode, which acts as a barrier to mass and charge transfer [17]. Maximum inhibition efficiency using R_{ct} values was found to be 96% at 0.5% concentration .The decrease in CdI could be attributed to adsorption of the inhibitor forming a protective adsorption layer [18].

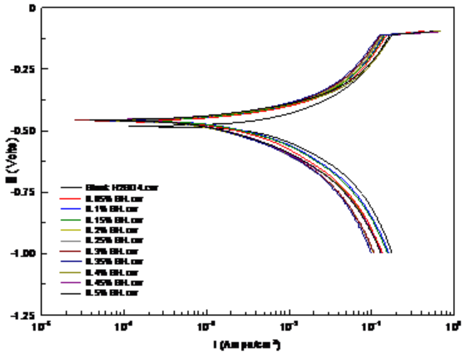

Figure 6: Tafel plot

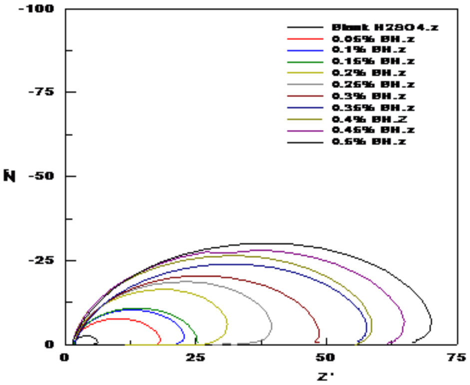

Figure 7: Nyquist plot

Surface Analysis Technique: The polished specimen and the test specimens which are immersed in the blank (1M H_2SO_4) and in the inhibitors BH was observed under a metallurgical microscope and photo micrographs are shown in the figure 8,9 and 10.

Fig 8. Photo micro graph of MS

Fig 9. Photo micro graph of MS in the presence of H_2SO_4

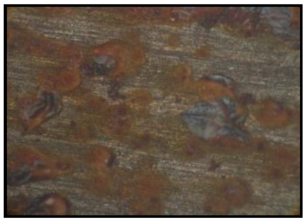

Fig 10. Photo micro graph of MS in the presence of BH

Figure 8 shows the polished MS steel surface before exposure to the corrosion solution, which is associated with polishing scratches. It is clear from figure 9, the surface of the MS was heavily corroded in 1M H_2SO_4 whereas, in the presence of the inhibitor in 1M H_2SO_4, the surface condition was comparatively better (Fig 10), suggesting that the presence of the protective adsorbed layer of the inhibitor on MS surface impedes corrosion rate of metal appreciably.

Mechanism of inhibition: Most organic inhibitors contain at least one polar group with an atom of nitrogen or sulphur or in some cases selenium and phosphorus. The inhibiting properties of many compounds are determined by the electron density at the reaction center [19]. With increase in electron density in the centre, the adsorption between the inhibitor and the metal are strengthened [20]. Literature survey reveal that the seeds of BH contain the phytochemical constituents such as amino acids, fixed oil, mucins, 24 –z ethylidene cholesterol- 7 enol (Avanasterol) and 24 β – ethyl cholesterol – 7,25 dienol [21]. The above said phytochemical constituents present in BH, having many active centers such as nitrogen and oxygen, are adsorbed on the metal surface and the effectiveness of these inhibitors on the corrosion of mild steel may be due to the electron densities on the active centers. The adsorption takes place through the active centers. In the current investigation the seed extract of BH was found to perform as a good inhibitor for mild steel corrosion.

APPLICATIONS

Acid inhibitors application in pickling baths happens to be a prerequisite in prevention of metals against corrosion. They are considered as indispensable component for any pickling baths as they protect metal components from corrosive action while maintaining the pickling performance of the system.

CONCLUSIONS

The seed extract of *Benincasa hispida* shows significant inhibitive action of H_2SO_4 induced corrosion of mild steel and the inhibitive action may be due to strong adsorption of the chemical constituents of the extract on the surface of mild steel. Weight loss method furnishes 94% IE at 0.5% concentration and electrochemical measurements could give 70% using I_{corr} values and 70% using R_p values and 93% using R_{ct} values at 0.5% concentration of extract. Experimental data are well fitted to Langmuir and Temkin adsorption isotherms. Electrochemical methods also confirm the mixed mode of inhibition. Surface analytical techniques confirmed the adsorption of seed extract on mild steel surface.

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