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Effect of *Allium sativum* Extracts on Mild Steel in 1 M HCl-An Eco-friendly Corrosion Inhibitor

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ABSTRACT

This study investigated the effect of Allium sativum extract on mild steel in order to show corrosion behavior in acidic medium (1 M HCl) by weight loss and Scanning Electron Microscopy (SEM) analysis. This test was performed on various temperatures viz. 298K, 313K and 323K for determination of corrosion rate. There was increasing inhibition performance with increasing concentration of inhibitor. The best inhibition performance (76.47%) was achieved at 298K in the presence of 4 g/l of extract. These finding is also supported by the resistance of mild steel to corrosion in this medium decreased with the increase in austenitic temperature, which is observed from corrosion rate of 31.62 mmpy. Test results obeyed the Langmuir adsorption Isotherm with a correlation coefficient (R^2) of 0.999.

Keywords: Green corrosion inhibitors, Mild steel, Microstructures, *Allium sativum,* Weight loss, Adsorption isotherm

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INTRODUCTION

Corrosion of metals is mainly due to an irreversible oxidation-reduction reaction, where an oxidizing agent in an environment attacks the metal. An electrochemical reaction is a chemical transformation that implies charge transport at the interface from a metallic conductor (electrode) to an ionic conductor (electrolyte). Recently, the use of plant extracts as inhibitors for the corrosion of metals/alloys, has gained very wide interest among researchers [1-12]. In addition, plant extracts have also been used as effective additives in electroplating processes [13,14].

Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Some research groups have reported the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment. In an attempt to find corrosion inhibitors that are environmentally safe and readily available, there has been a growing trend in the use of natural products such as leaves or plant extracts as corrosion inhibitors for metals [15,16]. Several investigations have been reported using such naturally occurring substances as corrosion inhibitor for several metals in different media [17-19]. Our group’s earlier finding [20,21] supports that the green corrosion inhibitor plays vital role in this concern.

In this present work, extract of garlic, *Allium sativum*, was investigated. *A. sativum* is of the Genus Onions; Class: *Equisetopsida* in the family of Amaryllidaceae. *A. sativum* has been cultivated for thousands of years and is used throughout the world for its aromatic, spice and health giving properties. It is known to consist of calcium, vitamin-C, vitamin-B6, Iron and magnesium. It also contains protein, carbohydrates, potassium and sodium. With the major chemical constituents, *A. sativum* contains 0.1-0.36% of a volatile oil.

EXPERIMENTAL SECTION

Preparations of *A. sativum* extract (GE)

An aqueous *A. sativum* extract was prepared by mixing 50g of *A. sativum* powder in 500 ml distilled water and kept it overnight. After that heated up to 50-60°C and then extract was filtered through Whattmann No.1 filter paper. This extract can be used for corrosion inhibitor and were characterized by UV-Visible spectroscopy using a Shimadzu UV-Visible 1800 Spectrophotometer.

Preparation of specimens

Mild steel of dimensions 4.0 cm × 1.0 cm × 0.2 cm were polished by different emery papers and weighed before the experiments.

Solutions preparation

1 M HCl solution was prepared using distilled water and concentration range *A. sativum* extract employed was varied from 1-4 g/l.

Mass-loss method

A very simple weight loss method used for the determination of corrosion rate. The corrosion of mild steel in *A. sativum* extract was investigated at room temperature using weight loss measurements. The weight of the specimens before and after immersion was determined using Shimadzu balance, model AY62. The Corrosion Rate (CR), Surface Coverage (θ) and Inhibition efficiency (%IE) was calculated using the equation given below:

$$\text{Corrosion rate} = \frac{87.6 \times \text{w}}{\text{DAT}} \qquad (1)$$

Where, mmpy=Millimeter per year, W=Weight loss in milligrams, D=Density of mild steel (gm/cm^3), A=Surface area of steel (cm^2), T=Time of exposure in hours.

The inhibition efficiency (%IE) and degree of surface coverage (θ) were calculated using Equations 2 and 3, respectively.

$$\%\text{IE} = \frac{\text{w}_1 - \text{w}_2}{\text{w}_1} \times 100 \qquad (2)$$

$$\theta = \frac{\text{w}_1 - \text{w}_2}{\text{w}_1} \qquad (3)$$

Where, w_1 and w_2 are the corrosion rates in the absence and presence of the inhibitor respectively.

RESULTS AND DISCUSSION

UV-Visible spectroscopy analysis

The UV-VIS spectroscopy of the *A. sativum* extract was studied at a wavelength range of 200 to 800 nm. One major band was recorded between 200-400 nm shows the presence of hetero atoms in extract (Figure 1).

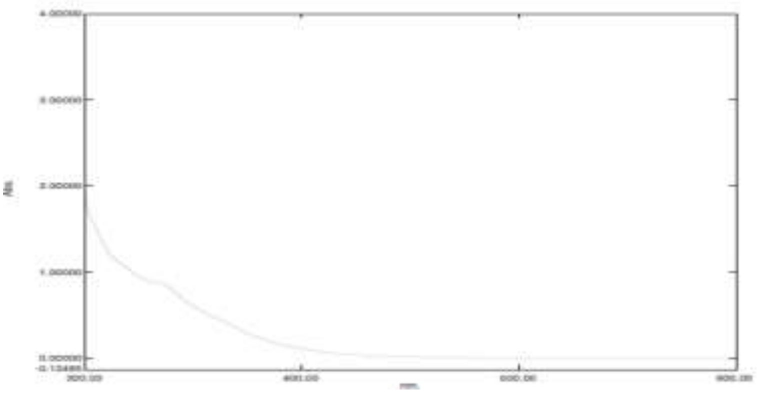

Figure 1: UV-VIS spectrum of *Allium sativum* extract

Results obtained from the tests in 1 M HCl with the addition of different concentrations of *A. sativum* extract is discussed below.

Weight loss method

Weight loss of mild steel in 1 M HCl + different concentrations of *A. sativum* extract (at 298K). The results obtained from the gravimetric experiment performed with the different concentrations of the *A. sativum* extract used as the inhibitor in 1 M HCl are presented in Figures 2 and 3 and results is given in Table 1.

Table 1: Inhibition efficiency at various concentrations (C) of the inhibitor with respect to the corrosion of mild steel in 1 M HCl, as determined by mass loss measurements at 298K

Immersion period	Concentration of inhibitor	Weight loss (mg)	Corrosion rate (mmpy)	Surface coverage (θ)	% IE
6 h	BLANK	170	31.62		
	1	85	15.81	0.5000	50.00
	2	80	14.88	0.5294	52.94
	3	60	11.16	0.6471	64.71
	4	40	7.44	0.7647	76.47

The value for the corrosion rate (without inhibitor addition) is 31.62 mmpy. The mild still test samples immersed in the 1 M HCl test medium with different concentration of green corrosion inhibitor (1-4 g) for 6 h. The percentage inhibition efficiency for various test samples was observed. There were gradual increase is observed from blank sample to sample contains 4 g of extract. 12% growth were observed in every test sample and surface area coverage is also increased. Figure 2 shows clearly the effect of the acid concentration on the corrosion of mild steel in 1 M HCl. The result shows that there was a decrease in the weight loss and the corrosion rate as the concentration of *A. sativum* extract was increased.

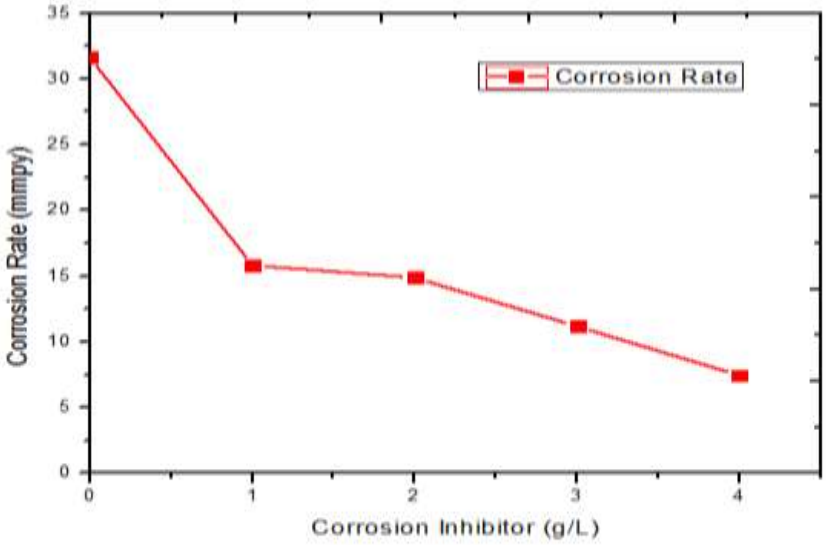

Figure 2: Plot of corrosion rate and concentration of inhibitor at 298K

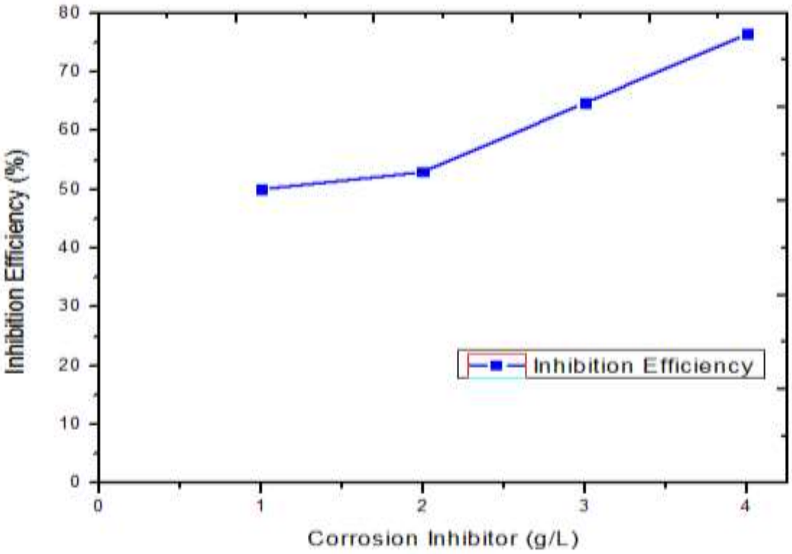

Figure 3: Plot of % inhibition efficiency and concentration of inhibitor at 298K

Weight loss of mild steel in 1 M HCl + different concentrations of *A. sativum* extract (at 313K)

Results of corrosion rate obtained from the calculations of weight loss values for the specimen immersed in 1 M HCl in the presence of different concentrations of *A. sativum* extract are presented in Figures 4 and 5. The date related with this set of test is given in Table 2. The highest corrosion rate of 26.97 mm/y as at the end of the experiment, was recorded with the test.

Table 2: Inhibition efficiency at various concentrations (C) of the inhibitor with respect to the corrosion of mild steel in 1 M HCl as determined by mass loss measurements at 313K

Immersion Period	Concentration of inhibitor	Weight loss (mg)	CR	θ	% IE
6 h	Blank	330	61.38	--	--
	1	170	31.62	0.4849	48.49
	2	161	29.94	0.5122	51.22
	3	153	28.46	0.5364	53.64
	4	145	26.97	0.5606	56.06

Test solution without added inhibitor (The control experiment) of 61.38 mmpy. In this set of experiment the %IE values for the test samples were very close to each other. The extent of surface coverage was also close. So compare to first test sample the results are not satisfactory in terms of %IE and corrosion rate.

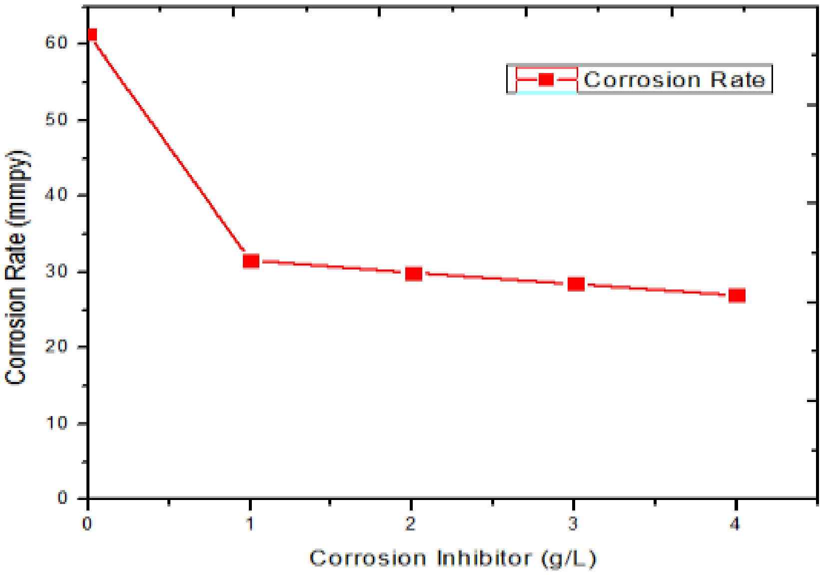

Figure 4: Plot of corrosion rate and concentration of inhibitor at 313K

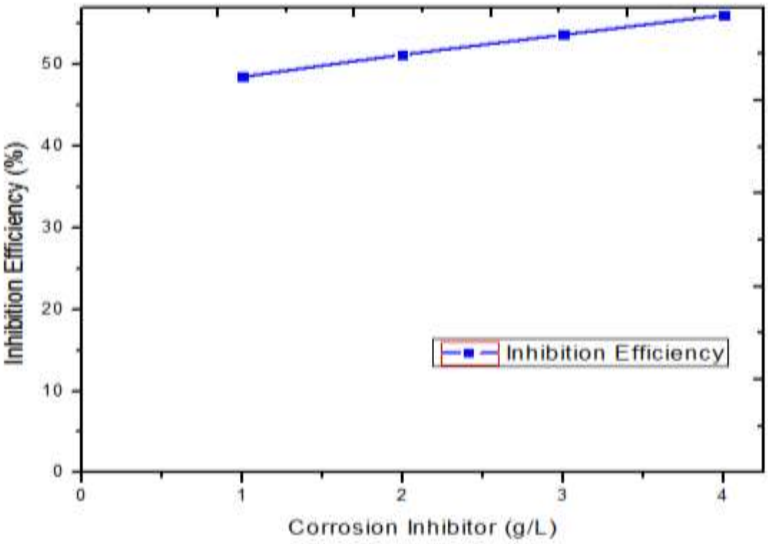

Figure 5: Plot of Inhibition efficiency (%IE) and concentration of inhibitor at 313K

Weight loss of mild steel in 1 M HCl + different concentrations of *A. sativum* extract (323K)

Curve of the surface coverage and inhibition efficiency of *A. sativum* extract concentration for corrosion inhibition of mild steel in acidic media are presented in Figures 6 and 7. The data of Table 3 shows the %IE is increase in much better extent compare to earlier data. This shows as increase the temperature the efficiency of extract will decreases. The highest %IE 72.73 observed for this set of test and so as the surface area coverage is 0.7273. The active adsorbing molecules within the inhibitor concentration would have presumably been insufficient to be more effective. However, the overall trend was that of very fairly surface coverage achievement.

Table 3: Inhibition efficiency at various concentrations (C) of the inhibitor with respect to the corrosion of mild steel in 1 M HCl, as determined by mass loss measurements at 323K

Immersion period	Concentration of inhibitor	Weight loss (mg)	CR	θ	% IE
6 h	Blank	110	20.46	--	--
	1	70	13.02	0.3637	36.37
	2	60	11.16	0.4546	45.46
	3	55	10.23	0.5	50
	4	50	9.3	0.5455	54.55

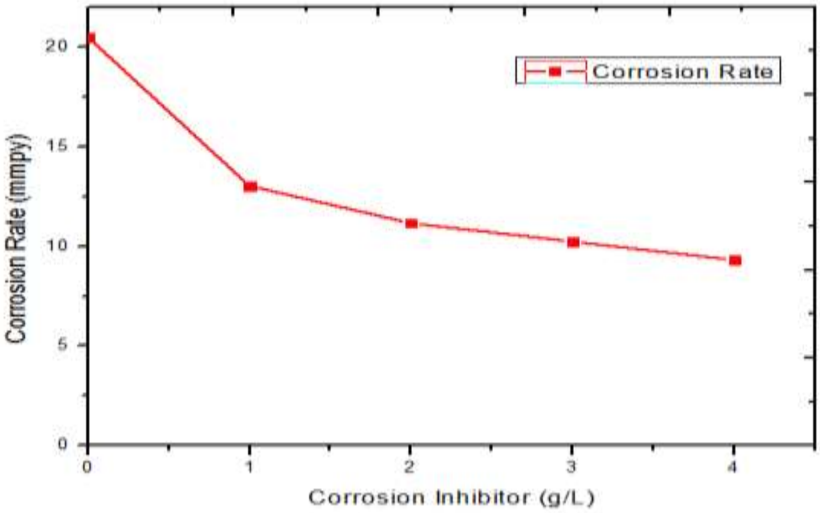

Figure 6: Plot of corrosion rate and concentration of inhibitor at 323K

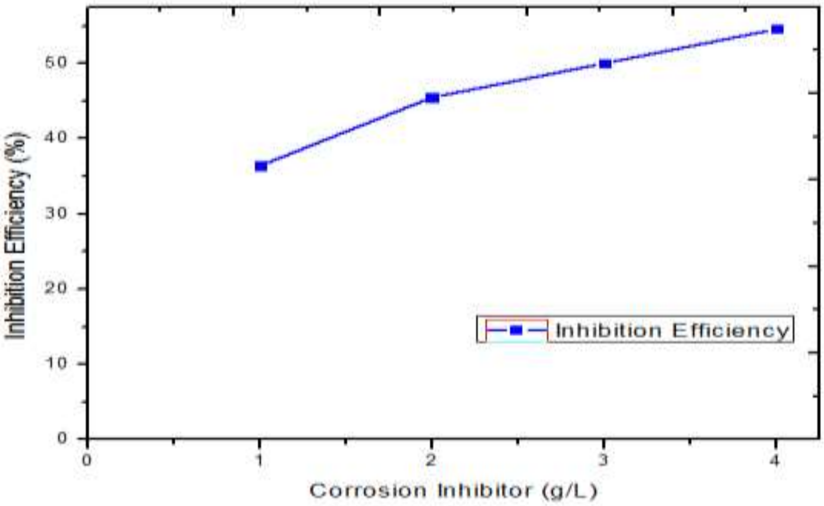

Figure 7: Plot of Inhibition efficiency (%IE) and concentration of inhibitor at 323K

Adsorption isotherm

Generally, mechanism of inhibition of corrosion better understood by adsorption isotherm, which can provide the necessary information regarding the interaction between metal and inhibitor molecules. The %IE of the *A. sativum* extract depended on the coverage of surface area by inhibitor molecules. Two types of adsorption are possible chemical or physical or both which shows the stability of the adsorbed molecules. The Langmuir isotherm explored using the surface coverage values obtained from the weight loss measurements, the best fit was observed. The Langmuir adsorption isotherm can be expressed as follows:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (4)$$

Where, C is the inhibitor concentration, θ is the surface coverage and K_{ads} is the adsorption equilibrium constant.

The plot of C/θ against C yielded straight lines is shown in Figure 8 gives a linear plot. A correlation coefficient obtained tends to unity, thus, confirming the applicability of the Langmuir Isotherm model.

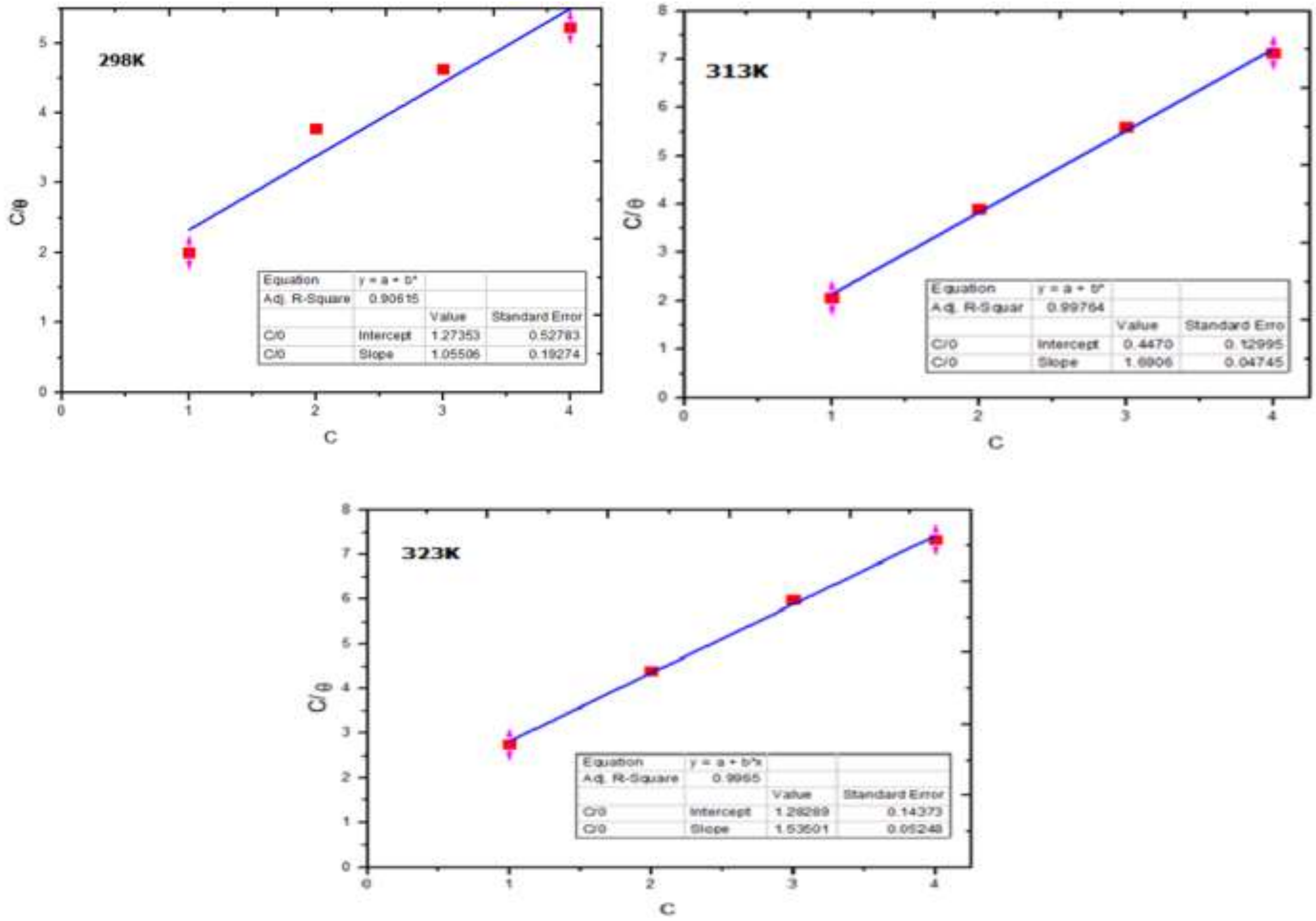

Figure 8: Langmuir adsorption isotherm plots for mild steel in 1 M HCl solutions in the absence and presence of the inhibitor in various concentrations at 298K, 313K and 323 K

Free energy

It has been established that a decrease in inhibition efficiency with respect to an increase in temperature is characteristic of a physical adsorption mechanism. The free energies of adsorption, ΔG_{ads}, were calculated from the equilibrium constant of adsorption using the following Equation:

$$\Delta G = -2.303RTlog[55.5K_{ads}] \qquad (5)$$

Where, 55.5 is the molar concentration of water in the solution, R is the universal gas constant and T is the absolute temperature.

Table 4: Langmuir adsorption constant and change in free energy at different temperatures

Temperature (K)	K_{ads} (l/g)	Slope	$-\Delta G_{ads}$ (kJ/mol)
298	-0.10501	1.0550	9.3535
313	0.349692	1.6906	12.549
323	-0.10819	1.5350	10.118
Average	0.593	1.4268	10.67

Generally, values of Δ_{Gads} around -20 kJ/mol or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (Physisorption), those around -40 kJ/mol or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of bond. The calculated free energy values, ΔG_{ads} show that the adsorption of extract molecules on the surface of the metal is a very feasible and spontaneous process. The average value of free energy is -10.67 kJ/mol indicate (Table 4) the adsorption of extract molecules on the metal surface is physisorption.

SEM analysis

The SEM microstructural analysis of the samples was also examined after immersion in *A. sativum* extract to study the dissolution or resistance of these samples in the corrosive medium. Figures are shows the SEM images of mild steel samples after immersion in *A. sativum* extract. From Figure 9, it can be seen that passive layer films are observed for all SEM images. SEM images of the sample shows the uniform and rough shapes of the metal surface. From Figure 10 it is clear that by using the inhibitor mild sheet protects very much extent. This passive layer films appear whitish in colour and cover the corrosion surfaces of the samples. The passive layer observed on the surface of these samples is due to the oxidative reaction.

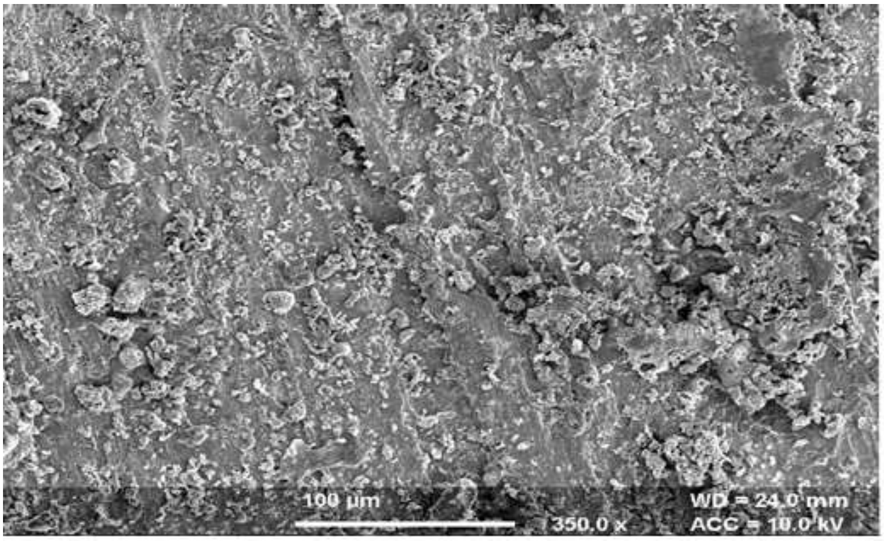

Figure 9: SEM Analysis of mild steel in 1 M HCl with 4 g/l of the inhibitor at 100 μM

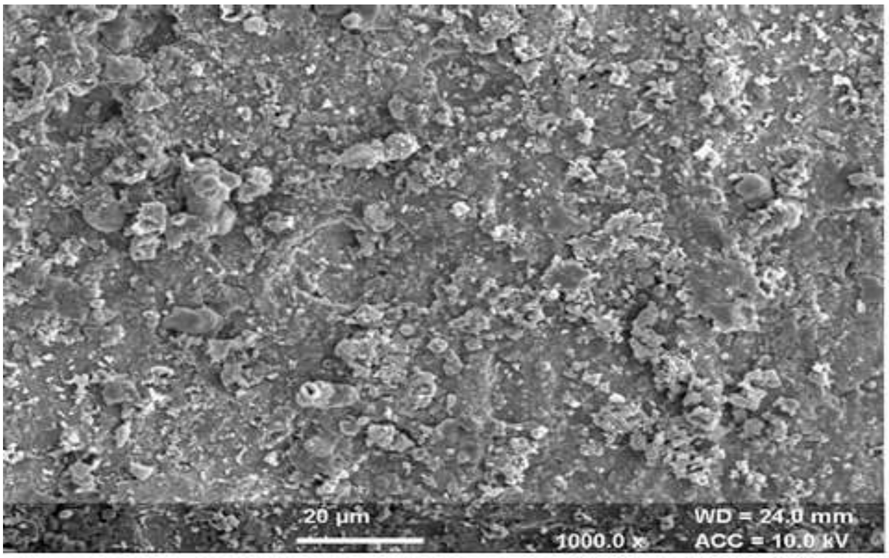

Figure 10: SEM analysis of mild steel in 1 M HCl with 4 g/l of the inhibitor at 20 μM

CONCLUSION

The obtained results in all the tests-gravimetric confirmed the extract of *A. sativum* as an effective inhibitor for mild steel in hydrochloric acid under the experimental conditions in which this investigation was performed. The inhibition performance, in most cases was concentration sensitive as all the result parameters in this work responded positively-either increasing or decreasing with increase in per cent concentration of the extract inhibitor. The %IE and surface coverage of mild steel increased with concentration of inhibitor and inhibition efficiency and surface coverage decreases as temperature increases in acidic environments for weight loss method considered. The results of weight loss were all in very good agreement to support the above experiments. The *A. sativum* extract can be considered as a source of eco-friendly, biodegradable and effective corrosion inhibitors.

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