Active Inhibitor as Corrosion Protective of Carbon Steel

مثبط فعّال لحماية الفولاذ الكربوني من التآكل

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Abstract :

The present study is attempted to find new inhibitors that can to easily be prepared and applied, as well as nontoxic, cheap and available. In this study hibiscus leaves extractor was used to protect carbon steel in hydrochloric acid solution (1M, 2M, and 3M).Since the usable inhibitor is considered organic inhibitor, and for evaluating the inhibition performance of this compound, many tests have been conducted which include measuring the corrosion rate through methods known weight loss and microscopic examination test. In losing weight method the inhibitor gives good efficiency in protecting, the carbon steel to be corroded at 1M HCl is 77% while the efficiency is drop to 68% in 3 M HCl at 30 ^oC. Microscopic examination test shows the clearness of the metals surface which is under the corrosion medium and which contains inhibitor, from any kind of corrosion that can be found on those surface, which are under mediums completely empty from inhibitor, and also shows the clearness of that protect layer on the surface. The data of corrosion rate show that the way of doing this organic inhibitor is adsorbing and the inhibitor molecules are adsorbed on the metal surface according to Langmuir adsorption isotherm.

Main Words: Inhibitors, Carbon Steel, hibiscus leaves, corrosion, Langmuir adsorption isotherm.

الخلاصة :

البحث الحالي يمثل محاولة لإيجاد مثبطات جديدة سهلة التحضير والتطبيق، غير سامة، رخيصة الثمن ومتوفرة بكثرة، ففي هذا البحث تم استخدام مستخلص نبات الخباز(hibiscus leaves) في حماية الفولاذ الكربوني في محلول (1M, 2M, 3M) حامض الهيدركلوريك. المثبط المستخدم يعد من المثبطات العضوية (Organic Inhibitors) ولغرض تقييم الأداء التثبيطي لهذه المركبات فقد أجريت عدة اختبارات تضمنت قياس معدل التآكل بطريقة فقدان الوزن واختبار الفحص المجهري . في طريقة فقدان الوزن أعطى المثبط كفاءة جيدة في حماية الفولاذ الكربوني من التآكل إذ بلغت كفاءة المثبط حوالي 77% في محلول حامض الهيدروكلوريك بتركيز 1M في حين انخفضت كفاءة المثبط إلى 68% في محلول حامض الهيدروكلوريك بتركيز 3M بدرجة حرارة $30\ ^oC$. اظهر اختبار الفحص المجهري خلو سطح الفولاذ الكربوني المتعرض لمحلول حامض الهيدروكلوريك الحاوي على المثبط من مظاهر التآكل المتواجدة على سطح النماذج للوسط التاكلي الخالي من المثبط ووضوح طبقة الحماية الممتزه على السطح. بيانات معدلات التآكل بينت إن آلية عمل المثبط العضوي هي الامتزاز(Adsorbing) وان جزيئات المثبط تمتز على سطح المعدن طبقا إلى علاقة لانكمير للأمتزاز (Langmuir Adsorption Isotherm) .

الكلمات الرئيسية : المثبطات ، الفولاذ الكربوني، أوراق نبات الخباز ، التآكل ، علاقة لانكمير للأمتزاز.

1. Introduction :

The acidisation of petroleum oil wells is an important simulation technique for enhancing production. Hydrochloric acid (15- 20%) solution is commonly used for this purpose. Hydrochloric acid is probably the most corrosive solution encountered by oil and gas tubular and down hole tools. Therefore, corrosion inhibitors are added along with the acid to reduce the corrosion attack on the well equipment. (Emranuzzaman et al., 2004). The extracts of some common plants and byproducts (peels, seeds, fruit shells, etc.) contain many organic compounds e.g. organic and amino acids, alkaloids, pigments, protein, and tannins. Most of these constituents are known to have an inhibitive action (Saleh et al., 1984). Therefore, these extracts would exert a retarding action on the dissolution of different metals and would then find application in composite inhibition system for e.g. boilers, heat exchangers, cooling systems, radiators, etc. Naturally occurring substances as inhibition of acid cleaning process, has continued to receive attention as replacement for synthesized organic inhibitors. Investigation into the corrosion inhibition effects of some local plants (Yakoob, 2003) has proposed parts of economic plants as pickling inhibitors. Not much has actually been achieved using these local plants, compared to the extensive research on synthesized organic inhibitors especially N- and S- containing organic compounds (Abiola,, 2004).

Inhibitors are often easy to apply and offer the advantage of in-situ application without causing any significant disruption to the process. However, there are several considerations when choosing an inhibitor (Yee, 2004):

- Cost of the inhibitor can be sometimes very high when the material involved is expensive or when the amount needed is huge.
- Toxicity of the inhibitor can cause jeopardizing effects on human beings, and other living species.
- Availability of the inhibitor will determine the selection of it as if the availability is low, the material is often expensive.
- Environmental friendliness.

In this study assesses the corrosion inhibition effect of the leaves of hibiscus on the corrosion of carbon steel in hydrochloric acid medium. This work aimed to prepare plant extract (hibiscus leaves) which could be used as corrosion inhibitor for carbon steel which have technical important applications like heat exchangers and cooler plants. Further, this work aimed to study the concentration effect of aggressive hydrochloric acid solution on inhibitor efficiency.

2.0 Experimental Work

2.1 Samples Preparation

The material used in this work is carbon steel. Analysis of this material was carried out using (spectrometer DV. 4) in AL- Nasser company. Table 1shows the chemical composition of the carbon steel. The cross sectional surface area of each sample metal depends, of course on the diameter of the stock rod. However, the carbon steel samples were cut into circular shapes of 12 mm as diameter and 3 mm as thickness, and a total surface of 351.85 mm^2. The samples were examined carefully to check for rough edges, which could influence the corrosion monitoring process. Small whole of 2 mm diameter was drilled in each sample for holding. The surfaces of both the cut ends and the body were slightly polished to remove trace of contaminants and to achieve a flat surface at both the cut edges, then the cut samples were degreased in alcohol. This was carried out to improve the adhesion of the epoxy mounting resin to the metal to reduce the tendency of the metal from experiencing crevice corrosion at the edge of the mounting resin. Polishing of the samples was done using SiC papers. The samples were ground on successively smaller grades of SiC paper from 220 grit to 1200 grit using water as lubricant on rotating grinding wheels. After polishing, the samples were washed in deionized water and dried. Then they were kept dry (in a dessicator) until they were needed to be used.

2.2 Inhibitor Preparation

The inhibitor used in this experiment was derived from natural hibiscus leaves. Extract was prepared then added to the test solution for the experiments.

Hibiscus leaves were obtained from a market and, 2 g of this material was immersed in 10 ml alcohol overnight in order to extract the active ingredients. The resultant mixture was filtered and methanol evaporated to dryness at 65 ^oC in a water bath. This left a dark brown sticky residue, which represents hibiscus leaves extract. The concentrations of the hibiscus leaves extract were expressed as vol. / vol. percentage.

2.3 Weight Loss Corrosion Test Method

In the weight loss experiment, five 250 ml beakers containing 1M HCl solutions with 0, 0.5, 1, 1.5, and 2 vol. % hibiscus leaves extractor as additives respectively as a first group. Whereas the second group contains 2M HCl and the third group contains 3M HCl with the same additives indicated in group one. All beakers were placed in thermo stated water bath maintained at 30 ^oC. Small whole of 2 mm diameter was drilled in each sample for holding, and then all samples were suspended in the beakers. The samples were retrieved from their corroding solutions at one-hour material for 7 hours due to the reactivity of carbon steel in HCl solutions. Each set of samples was dipped into saturated ammonium acetate solutions at room temperature, to terminate the corrosion reaction. They were washed by distilled water, dried in acetone, and finally in an oven maintained at 80 ^oC. The weight loss of carbon steel samples was evaluated in grams as the difference in the weight of the samples before and after the test (Venkatesha, 2003):

$W = (W_i - W_f)$ g ……………………………….... 1

Where W= weight loss of sample.

W_i = Initial weight of sample.

W_f = Final weight of sample.

Each reading reported is an average of three experimental reading recorded to the nearest 0.0001 g on a Sartorius electronic balance. The inhibition efficiency of hibiscus extract was calculated using the formula (Klechka, 2001).

$I.E\% = \{1- W_1/ W_2\} *100$ ……………...................... 2

Where W_1 and W_2 are the weight losses (mg) for carbon steel in the presence and absence of inhibitors respectively in HCl solution at the same conditions. The degree of surface coverage, Θ is given by the equation, (Troscelius & Andreasson, 2003).

$\Theta = \{1- W_1/ W_2\}$ ……………………………………..3

The corrosion rate of carbon steel in different HCl concentration solutions was determined for a seven hours immersion period from weight loss using the formula (Haek and Larabi, 2004):

Corrosion Rate (mpy) = 534 w/ DAT …………….. 4

Where: mpy = mils per year

W = weight loss (mg)

D = density of sample g/cm^3

A = area of sample, sq. in.

T = exposure time (hrs.)

3. Results and Discussion

Fig. 1 illustrates the results of FTIR Spectroscopy Measurement of hibiscus leaves extract as inhibitor material used in this research and gives the active groups vs. the wave number. Fig 1 shows that inhibitor material contains many active groups that are rich in alcohols, phenol, alkanes, and aster. All these materials have inhibitor properties. Further, the existence of double bonds in this inhibitor tends to improve inhibitor action. This result is in a good agreement with those given by Saleh et al. (Saleh et al., 1984).

Figures 2-4 show the corrosion of carbon steel in different concentration of (1,2, and 3 M HCl) with and without hibiscus extract concentrations (0.5, 1, 1.5,2) respectively. The results obtained indicate that the weight loss of samples immersed in HCl solutions increased with increasing acid concentrations. This can be attributed to the fact that the rate of chemical reaction increases with increasing acid concentration and/ or probably due to increase in the rate of diffusion and ionization of active species in the corrosion reaction. This conforms to reports by Maayta (Maayta, 2005).Further, Figures 2-4 reveal that hibiscus leaves extract inhibit the corrosion of carbon steel in HCl solutions, since there was a general decrease in weight loss with increasing of hibiscus leaves extract , inhibition though high , was maximum at higher additives concentration of 2% at 30 ^oC. It was expected that most of the sample surface would be coverage by inhibitor molecules. Hence, at the end of the 7 th hours in 1M HCl, with hibiscus leaves extract concentration of 2 % weight loss of 0.11 mg/ cm^2 after 7 hrs. was obtained while for blank samples (without inhibitor), weight loss was 0.51 mg/ cm^2 after 7 hrs was observed at 30 ^oC. Microscopy test was performed to study samples surface topography, which immersed in solutions with and without hibiscus extract. Figures (5a, b, and c) show blank samples after immersed test in 1, 2, and 3M HCl solutions without inhibitor respectively. It seems clearly the dense pitting corrosion with different sizes due to surface corrosion and the effects of chlorine ions. Whereas Figures (6a, b, and c) show the samples surface after immersed in 2 vol. % hibiscus extract with 1,2, and 3 M HCl. It is obvious the large differences in both cases due to the activity of adsorbed inhibitor layer at the sample surface which protected against corrosion. Values of inhibitor concentrations, corrosion rates, inhibition efficiencies, follow similar trend (Table 2). Percentages inhibition efficiency was higher at hibiscus extract concentration of 2% than at 0.5%. This minimum corrosion rate of specific concentration may probably be due to the formation of insoluble complex on metal surface as in the case of polyphosphates or because of protonation of additive molecules and subsequent acceleration of the hydrogen evolution process (Moore, 1994). It was found that maximum inhibition efficiency (77%) was obtained at inhibitor concentration 2% (Figures 7-9). This is due to the adsorption of more inhibitor molecules on the metal surface. However, inhibition efficiency increases with increase in inhibitor concentration. This is in agreement with what is known about the dependence of adsorption on concentration that as concentration rises, the quantity adsorbed increases. It is of generally view that inhibition of metals in acidic solution results from the adsorption of molecules or ions of the inhibitor on the metal surface. The action of organic inhibitors depends on the type of interaction between the substance and the metallic surface. This could cause a change either in the electrochemical process mechanism or on the surface available to the process. The decrease in inhibition efficiency with decreasing inhibitor concentration, suggest weak adsorption interaction between carbon steel and the inhibitor molecules, which is physical in nature (Tuken et al., 2002). The Langmuir adsorption isotherm may be expressed as:

$\Theta = K C / (KC + 1)$ ………………………….5

Where K is the equilibrium constant for the adsorption process, C is the concentration of the inhibitor and **Θ** is the surface coverage, 1 when inhibitor efficiency is 100%. Rearrangement of the Equation 5 yields to:

$C / \Theta = (1 / K) + C$ …………………………….6

It was found that Fig. 10 (plot of C/ Θ) versus C gives straight lines with slop, practically equal to unity, indicating that the adsorption of compound under consideration on carbon steel / acid solution interface obeys Langmuir adsorption isotherm. The deviation of the slope from unity is attributed to the difference in the rate of interaction between the adsorbed species on the metal surface. The interaction between the adsorbed species is not taken into account during deviation of the Langmuir isotherm equation, while the interaction between adsorbed organic molecules, with polar atoms or groups on the anodic and cathodic sites of the metal surface plays a crucial role. This interaction may be either mutual repulsion or attraction (Harek and Larabi, 2004). Finally, from the result of weight loss against time (Figures 2-4), corrosion rate, and percentage inhibitor efficiency (Table 3) for metal dissolution was inhibited to a comparative degree. The inhibition action of leaves, fruits, bark of trees and plant has been attributed to tannins and nitrogenous compounds in the extracts. Both groups have been found effective for corrosion inhibition and inhibitors of high molecular weight (carbon atom 12 and above) are better inhibitors than the methyl derivatives (Loto, 1998).

It may be reasonable to suggest that corrosion inhibition by both additives may be due to bulky nitrogenous organic compound or tannins, which contain polar groups. For hibiscus extract, these may have effected inhibition through nitrogen bond on metal surface with the formation of complex ions on the surface of the metal.

4. Conclusions

From the present work, the following conclusions can be drawn:

- The rate of corrosion of the carbon steel in HCl solutions is a function of the concentration of hibiscus leaves extract.
- The inhibition by this additive increased with increased additive concentration. Inhibition though generally was obvious at an optimum concentration 2%. This may be due to protonation of the

hydrogen evolution process or the formation of an insoluble complex on carbon steel surface by molecules of hibiscus leaves.

• In case of additive concentration of 2% (hibiscus extract) to 1M HCl, the corrosion rate is decreased by 78.43 % in comparison with uninhibited solution for 7 h. at room temperature.

• Hibiscus leaves extract is a corrosion inhibitor for carbon steel in HCl solutions and can be used to replace toxic chemicals.

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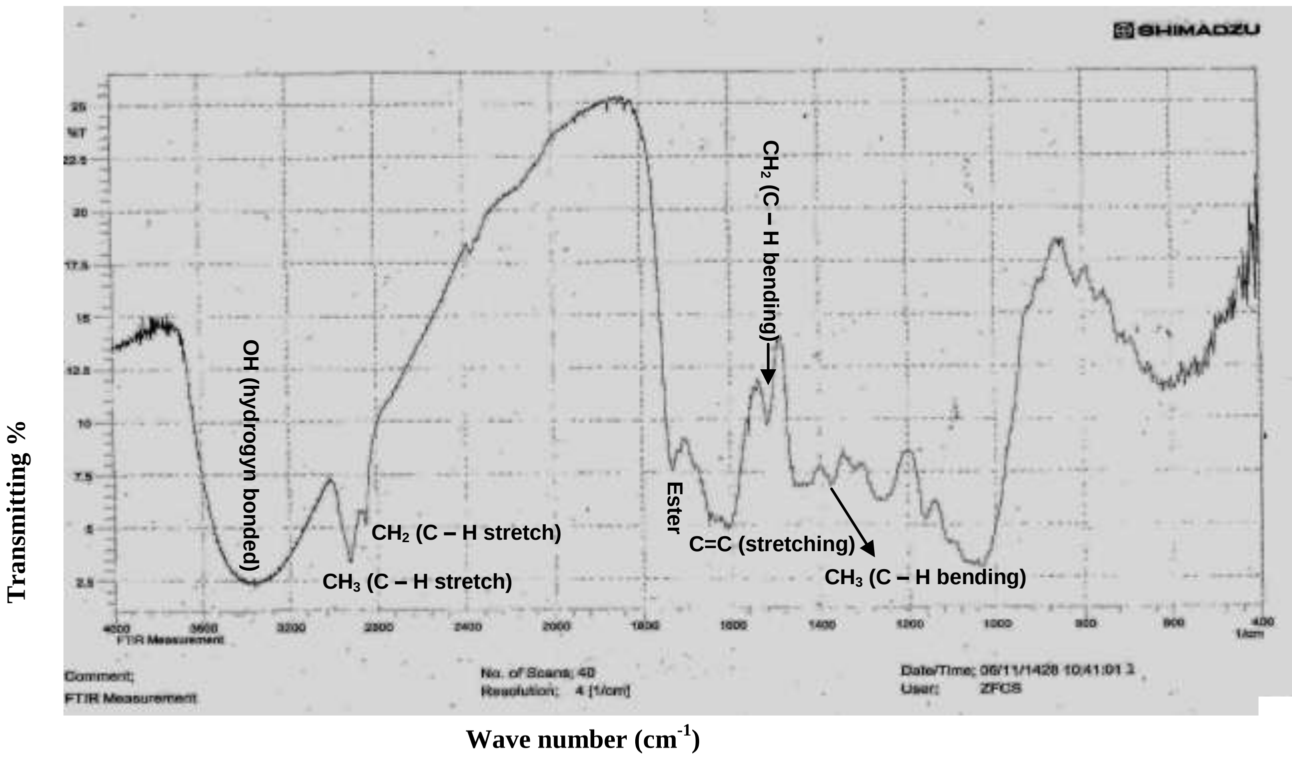

Fig. 1: FTIR pattern for hibiscus leaves.

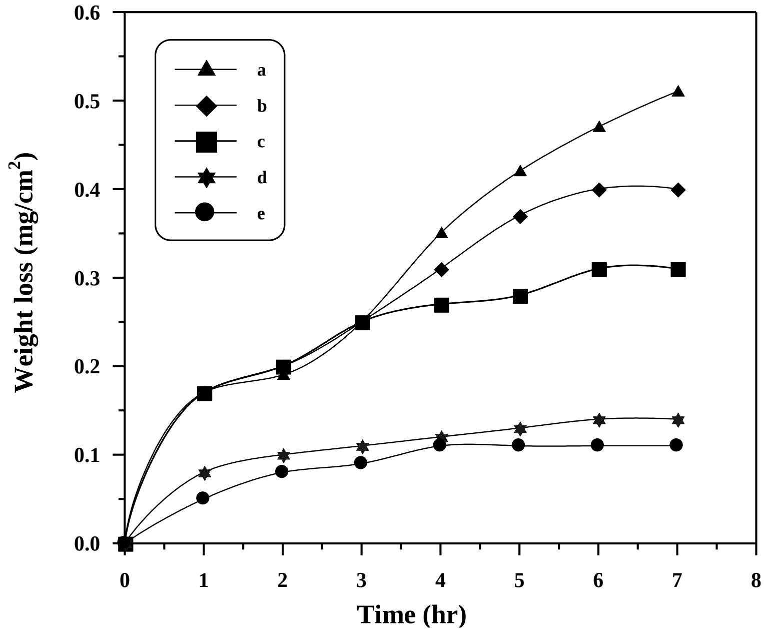

Fig. 2: Variation of weight loss with time in 1M HCl with different concentrations of hibiscus extracts (a-blank, b-0.5%, c-1%, d-1.5%, and e-2%).

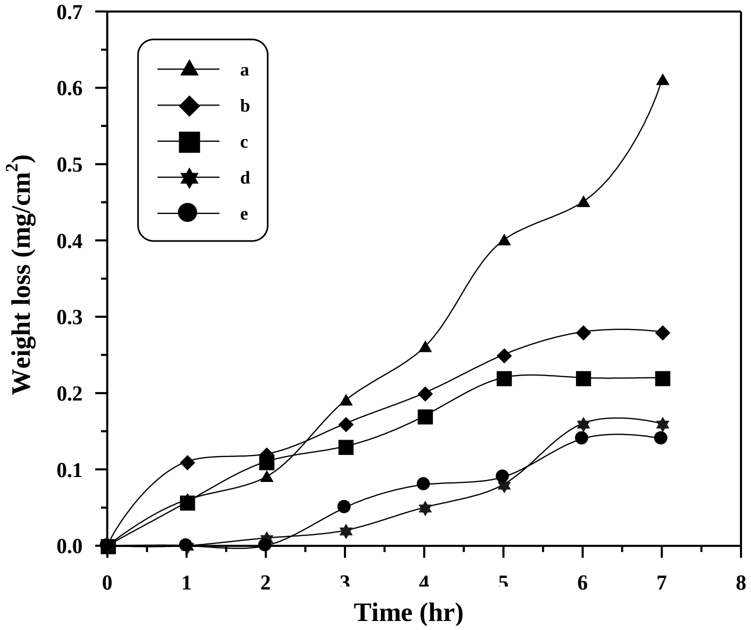

Fig. 3: Variation of weight loss with time in 2M HCl with different concentrations of hibiscus extracts (a-blank, b-0.5%, c-1%, d-1.5%, and e-2%)

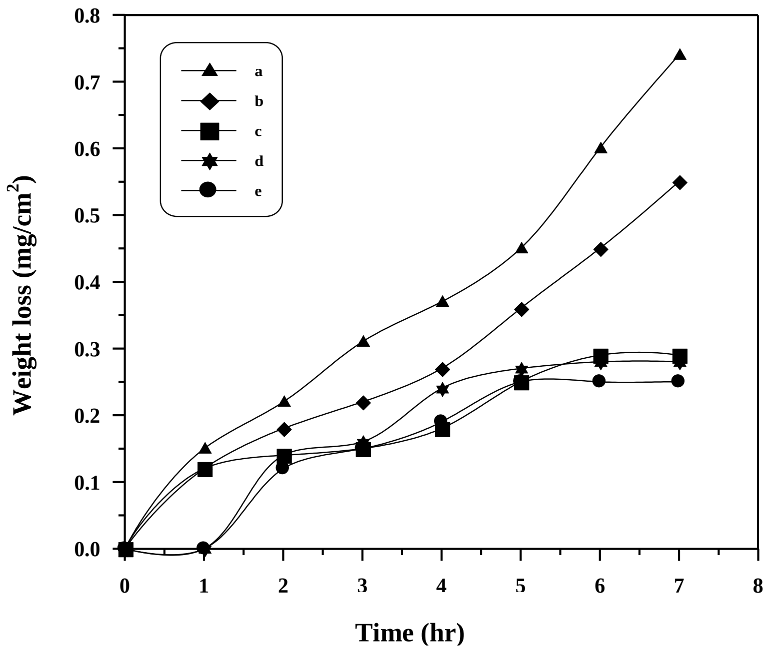

Fig. 4: Variation of weight loss with time in 3M HCl with different concentrations of hibiscus extracts (a-blank, b-0.5%, c-1%, d-1.5%, and e-2%)

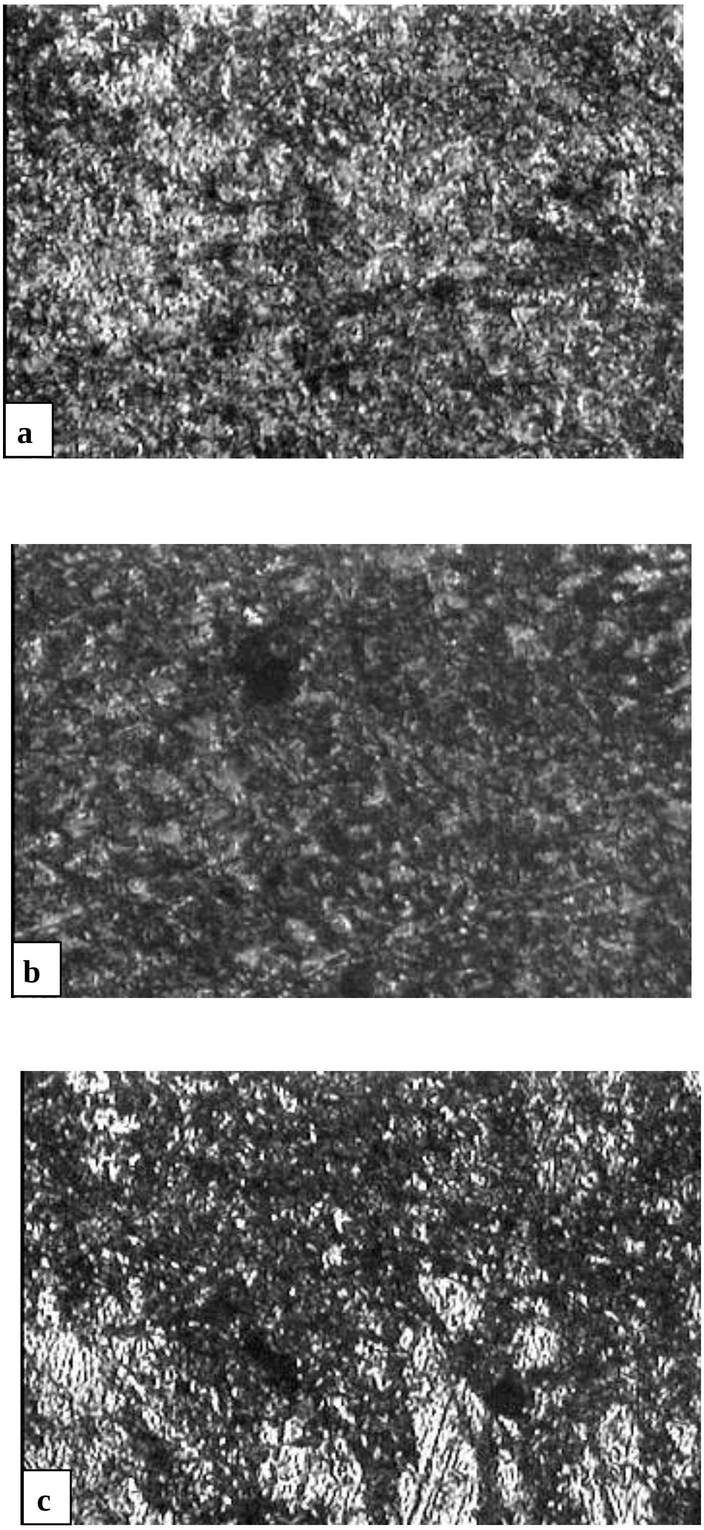

Fig.5: L.O.M. images of carbon steel immersed in HCl solutions (a = 1M HCl, b = 2M HCl, and c = 3M HCl) for seven hrs. (Magnification 400X).

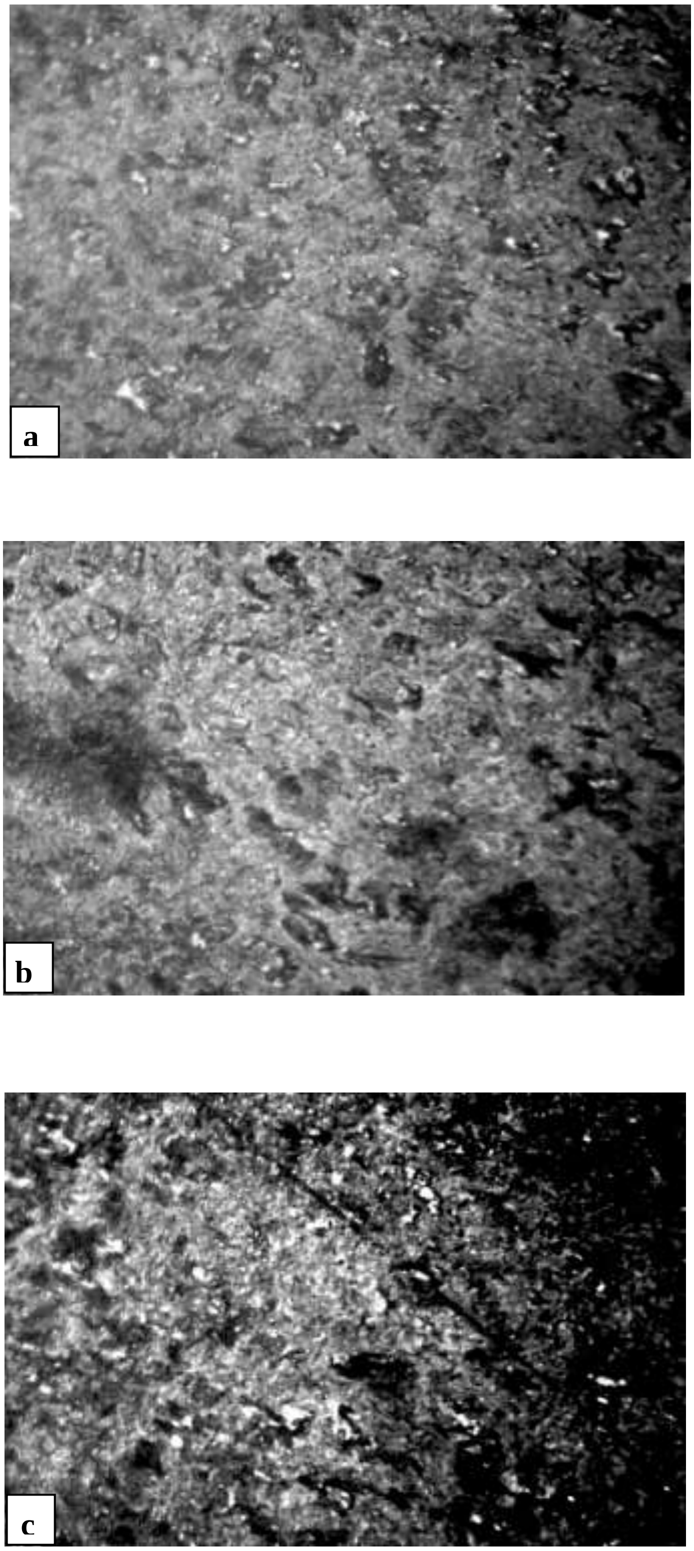

Fig. 6: L.O.M. images of carbon steel immersed in HCl solutions (a = 1M HCl+ 2% Inhibitor), b = 2M HCl+ 2% Inhibitor, and c = 3M HCl+ 2% Inhibitor) for 7 hrs. (Magnification 400X).

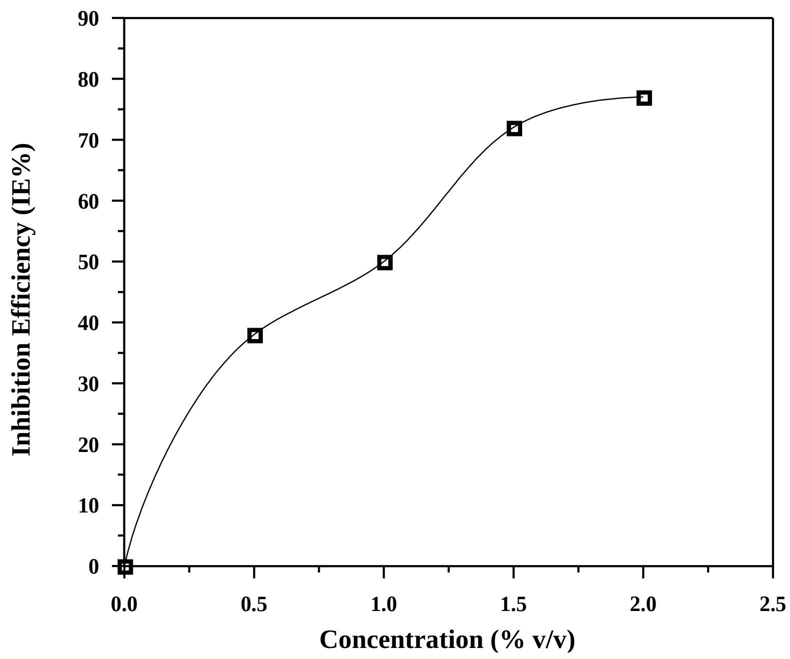

Fig. 7: Variation of inhibition efficiency with concentration in 1M HCl solution

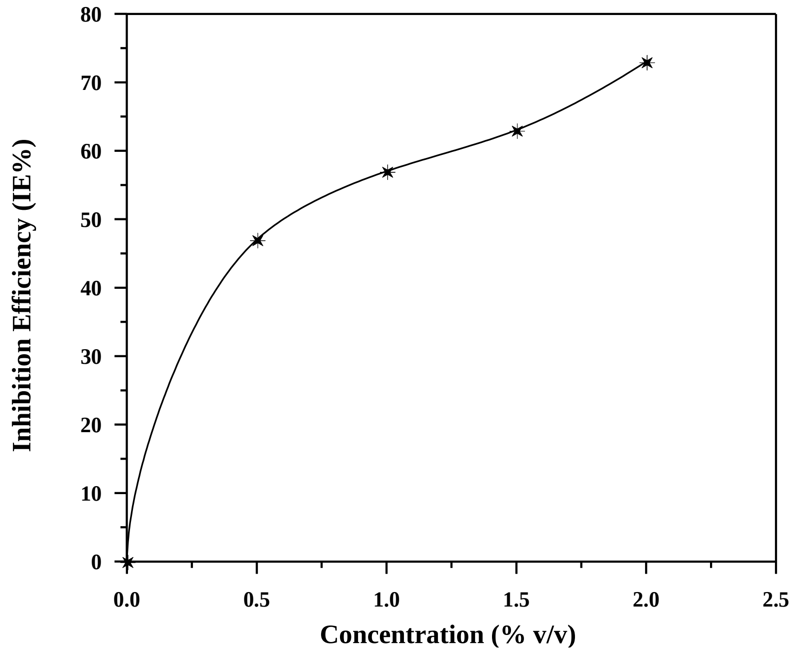

Fig. 8: Variation of inhibition efficiency with concentration in 2M HCl solution

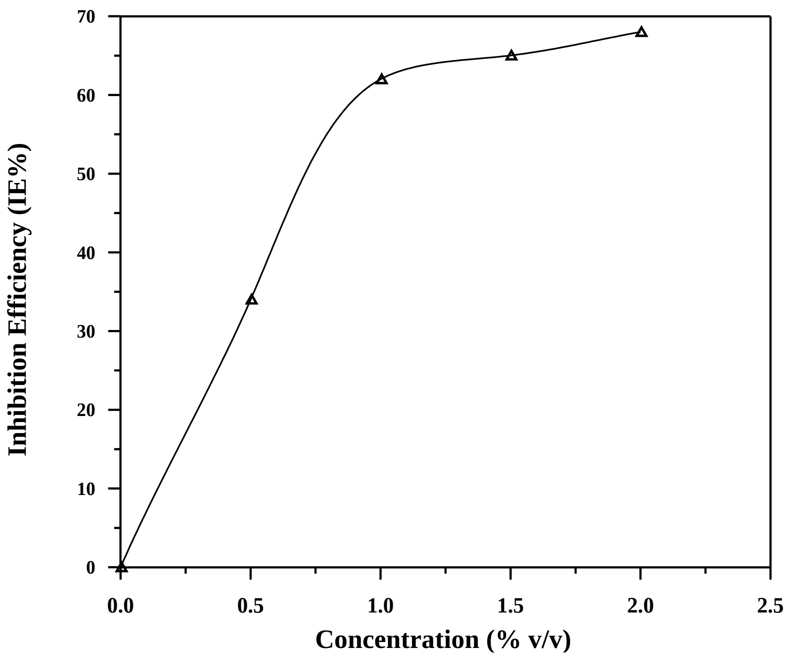

Fig. 9: Variation of inhibition efficiency with concentration in 3M HCl solution

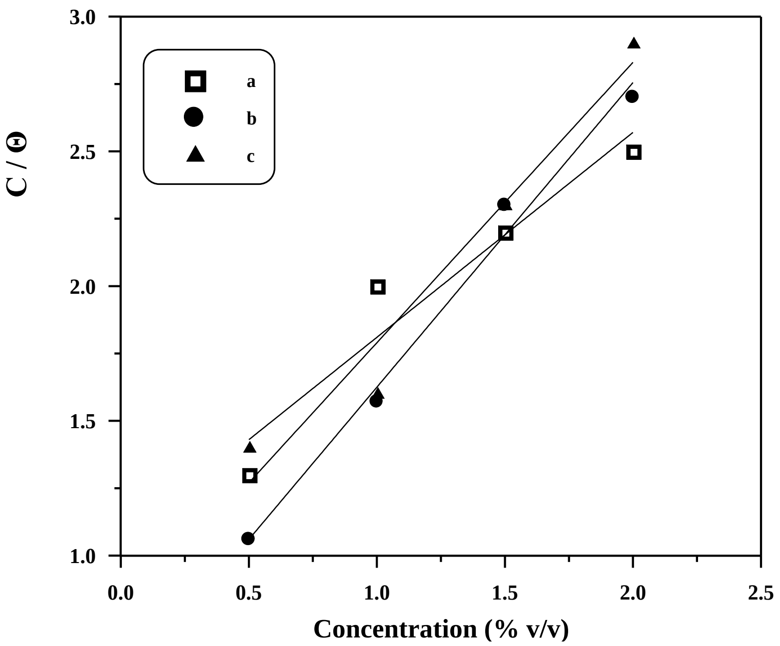

Fig.10: Curves fitting of the corrosion data of carbon steel in the presence of 2% hibiscus extract to Langmuir adsorption isotherm (a = 1M HCl, b = 2M HCl, and c = 3 M HCl solutions)

Table 1: Spectrochemical analysis of carbon steel in wt. %.

Fe	Mn	C	Si	Mo	S	V	P	Cu
Rem.	1.30	0.416	0.223	0.172	0.060	0.006	0.002	0.001

Table 2: Calculated values of % Inhibitor concentration, % Inhibitor efficiency, Corrosion rate (mdd) for corrosion of carbon steel in 1, 2, and 3M HCl at 30 ^{o}C

Corrosion Medium	%Inhibitor Concentration	%Inhibitor Efficiency	Corrosion Rate (mpy)
1M HCl	0	-	31.77
	0.5	38	24.92
	1.0	50	19.31
	1.5	72	8.72
	2.0	77	6.85
2M HCl	0	-	38.07
	0.5	47	17.44
	1.0	57	13.70
	1.5	63	9.96
	2.0	73	8.72
3M HCl	0	-	46.10
	0.5	34	34.26
	1.0	62	18.06
	1.5	65	17.44
	2.0	68	15.57