Inhibition Corrosion by Liquorices

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ABSTRACT

The use of inhibitors for the control of corrosion of metals and alloys which are in contact with aggressive environment is an accepted practice. Large numbers of organic compounds were studied and are being studied to investigate their corrosion inhibition potential. All these studies reveal that organic compounds especially those with N, S and O showed significant inhibition efficiency. But, unfortunately most of these compounds are not only expensive but also toxic to living beings. It is needless to point out the importance of cheap, safe inhibitors of corrosion. Plant extracts have become important as an environmentally acceptable, readily available and renewable source for wide range of inhibitors. They are the rich sources of ingredients which have very high inhibition efficiency The title compound Liquorices (Glycyrrhiza glabra) was synthesized and its inhibiting action on the corrosion of mild steel in 4% hydrochloric acid solutions was investigated by means of weight loss and electrochemical experiment. Results obtained revealed that Liquorices treated excellently as a corrosion inhibitor for mild steel in 4% hydrochloric acid media and its efficiency attains more than 62.4% at 0.5% of inhibitor in weight loss experiment.

Key words: Corrosion, Liquorices, Electrochemical, Inhibitor

1. Introduction

A corrosion inhibitor is a chemical compound that, when added to a fluid or gas, decreases the corrosion rate of a metal or an alloy. The effectiveness, or corrosion inhibition efficiency, of a corrosion inhibitor is a function of many factors like: fluid composition, quantity of water, flow regime, etc. Some of the mechanisms of its effect are formation of a passivation layer (a thin film on the surface of the material that stops access of the corrosive substance to the metal), inhibiting either the oxidation or reduction part of the redox corrosion system (anodic and cathodic inhibitors), or scavenging the dissolved oxygen.

Excessive corrosion attack is known to occur on mild steel in acidic aqueous media. Acid solutions are widely used in different industrial processes, for example, in acid pickling of iron and steel, scale removal in metallurgy, acid cleaning of boilers and oil-well acidizing, therefore the study of corrosion of steel in acid solutions and its inhibition have practical importance. Different corrosion inhibitors are used to control and reduce corrosion of metals in corrosive media. Due to toxicity of most inorganic corrosion inhibitors such as chromates and nitrites and also because of restrictive environmental regulations, these inhibitors are being replaced by new environment-friendly organic compounds. Steel corrosion in different Solutions have also been effectively controlled using organic inhibitors containing nitrogen, oxygen or Sulphur [1-9]. The problems that exist with current inhibitors are that they are toxic and expensive; therefore a new less toxic and inexpensive material or method to reduce corrosion is needed, necessary and proposed. The goal of this work is investigate effective and environmentally safe inhibitors such as liquorices. Acid solutions are commonly used for removal of undesirable scale and rust in the metal working, cleaning of boilers and heat exchangers [10, 11]. In these situations hydrochloric acid is one of the most widely used agents. To prevent unexpected metal dissolution and excess acid consumption in pickling processes of mild steel, inhibitors are added to the acid [12, 13]. The effective inhibitors are organic compounds that have π bonds, heteroatom's (P, S, N and O)[14, 15]. Now the development of novel corrosion inhibitors of natural source and non-toxic type has been considered more important and desirable [16]. In present study, Liquorices (Glycyrrhiza glabra) was investigated as an inhibitor for the corrosion of mild steel in 4% hydrochloric acid (HCl) using weight loss, electrochemical experiments, The liquorices plant is a legume (related to beans and peas) and native to southern Europe and parts of Asia. It is an herbaceous perennial, growing to 1 m in height, with pinnate leaves about 7–15 centimeters (3–6 inches) long, with 9–17 leaflets. Liquorices' inhibition is from the inhibition of the enzyme ([11β-hydroxysteroid dehydrogenize). In this research we use the extraction of roots of liquorices**.** In figures 1, 2 the pictures of liquorices plant and its root's extraction are shown.

Fig1. Liquorices plant liquorices

Fig 2. Extraction of roots of liquorices

2. Experimental

Liquorices was dissolved in 4% HCl solution at various percents (from 0.5 to 10 %) in 100 mL solution. And the solution in the absence of Liquorices was taken as blank for comparison.

The composition (wt. %) of used mild steel given in Table 1.

Table 1 Chemical composition of the used mild steel

Composition	wt%
Fe	0.9910
C	0.0017
Mn	0,0046
Si	0.0026
S	0.00017
Cu	0.00019

Specimens were mechanically cut into 2cm×2.94cm×5.92cm (used in the weight loss and electrochemical experiment) dimensions, polished with SiC abrasive papers up to 1200 grade, washed in distilled water, degreased ultrasonically in ethanol and acetone, dried in room temperature.

2.1. Weight loss experiment

Mild steel specimens in triplicate for each inhibitor concentration were immersed in the test acid solutions for 6 h at 298 K. After that, the specimens were removed, scraped, rinsed in water and acetone, and finally dried in desiccators. Then the loss in weight was determined by analytic balance. (Fig3)

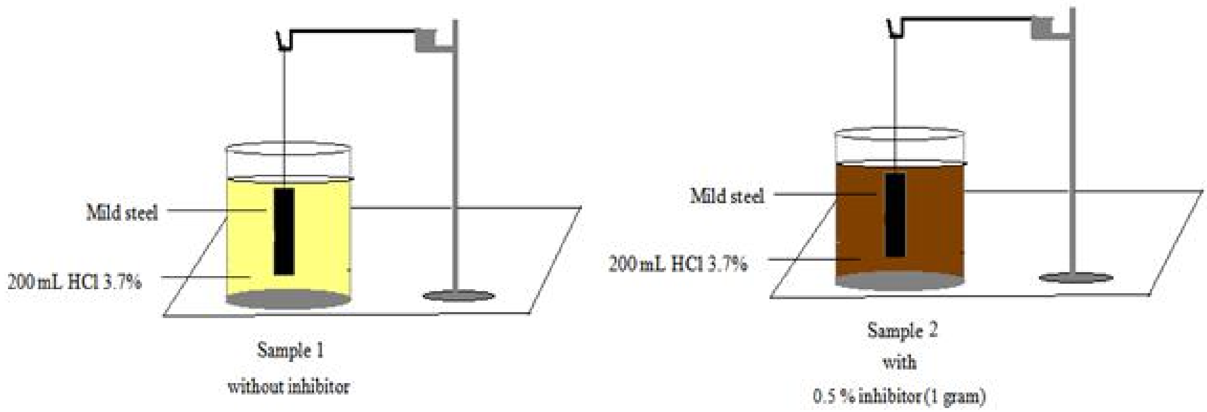

Figure 3 . Experiment 1 - weight loss Experiment

In second part of first experiment we have three samples with below description, after six hours we again measure the mass removal of three steel pieces, noting that we put liquorices in the three samples with theses portion, 1%, 2 %. 5% of the volume of the solution means that 2 gr, 4 gr, and 10 gr liquorices in each solution of 4 % HCl (Fig 4).

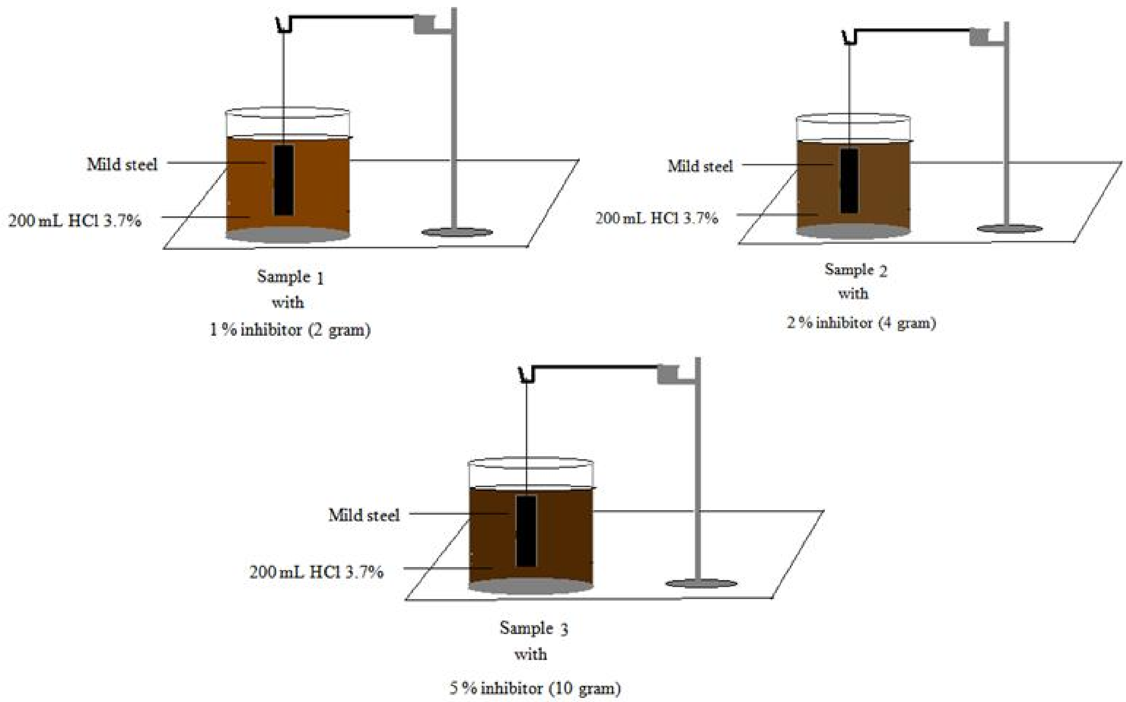

Figure 4 . Experiment 1-2 - weight loss Experiment

These experiments show that our inhibitor (liquorices) only on a definite range of concentration has the positive action on the corrosion, and on out of this rang has the inverse action. For example in the solution of (4gr and 10 gr) has the inverse action.

2.2 Electrochemical experiment

Electrochemical experiments were performed in a conventional two electrodes cell, mild steels sealed by epoxy resin with exposure surface (2.94cm×5.92cm) as working electrodes and a saturated calomel electrode (SCE) provided with a Luggin capillary as reference electrode. Without any inhibitor measured the voltage and current, and then begin our experiment by adding the inhibitor in mL in the solution and measured the current and voltage in this case. (Figure 5)

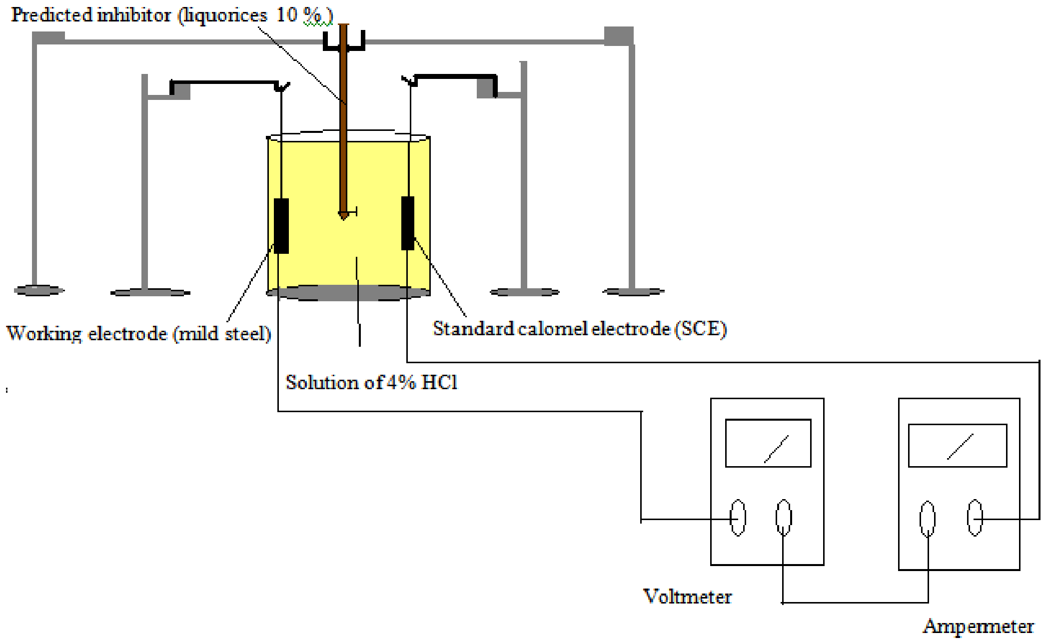

Figure 5. Experiment 3 - Measuring current and voltage with Calomel Ref. electrode by adding inhibitor in mL.

3. Results and discussion

3.1. Weight loss measurements

Values of inhibition efficiency IE $_{(w)}$ and corrosion rate (gr cm^{-2} h^{-1}) obtained from weight loss method for various concentrations of Liquorices at 298 K. The inhibition efficiency IE $_{(W)}$ was obtained by:

$$\text{Inhibitor efficiency} = IE_{(w)} = \frac{R_0 - R_i}{R_0} \quad (1)$$

Where R_0 and R_i are the corrosion rates of mild steel in the absence and presence of the Inhibitor, respectively:

$$R = \frac{\Delta m}{AT} \quad (2)$$

R: rate of corrosion (gr $hr^{-1}cm^{-2}$)

T: time (hour)

It can be found that the increscent in the inhibitor concentration lead to an increase in the inhibition efficiency. At the highest concentration of 1% M, the compound Liquorices has a highest inhibition efficiency of about 62.4% in weight loss measurement. For weight loss, plot the change in weight of each cleaned coupon (metal sample) both before and after exposure using multiple samples. Each one of these can be removed at predetermined times, see the representative curve Figure 6. The slope of the curve at any point is the corrosion rate at that time. The bottom curve shows the corrosion rate for the uninhibited system. The weight loss of the inhibited coupon divided by the loss of the uninhibited coupon provides a measure of inhibition efficiency.

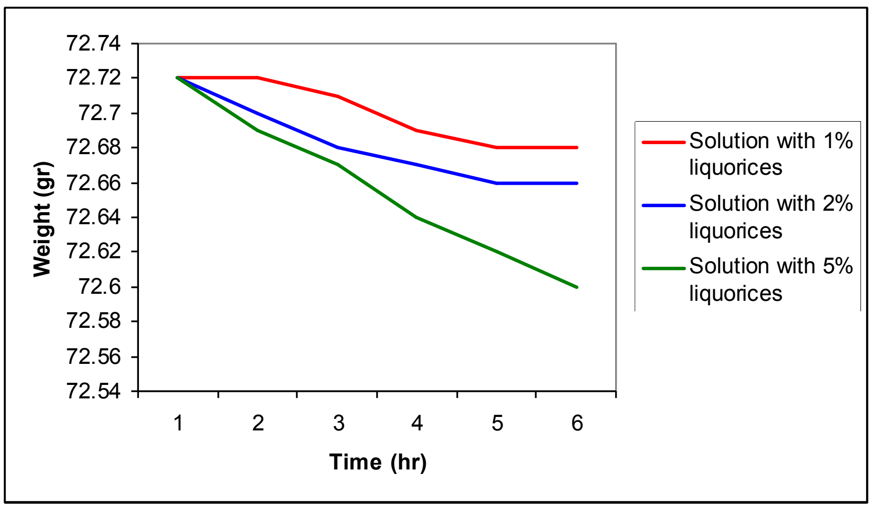

Figure 6-Weight loss of mild steel by weight loss

Figure 6 present the results of weight loss measurements for the corrosion of mild steel, in 1 , 2 , 5% HCl solutions devoid of and containing different concentrations of the liquorices extract. Inspection of the data in the figures reveals that the addition of liquorices extract decreases markedly the corrosion rate of mild steel. This result indicates the inhibitive effect of the added extract on mild steel corrosion in the acidic solution. The inhibition efficiency increases as the concentration of added extract is increased till 0.5 % of inhibitor after that by increasing inhibitor content efficiency will decrease.

It is common practice to assume that the inhibitive effect of the added compound is a result of adsorption of its molecules on the metal surface. Therefore, there is a direct relationship between the inhibition efficiency and the fraction of surface covered by the adsorbed molecules (θ).

3.2. Electrochemical experiments

Measurements are based on calculation of mass of dissolution W (gr hr^{-1} cm^{-}) by the relations given in Table 2 .

Table 2 relations of evaluating electrochemical experiment

(3)$r = \frac{534W}{DAT}$	(4)$W = \frac{iTM}{F}$
r: rate of weight loss (mm/year)	F: faraday number (=96485)
W: weight lost (milligrams)	i: current density (Acm-2)
D; density (gr/cm^3)	W: mass of dissolution (grhr-1cm-2)
A: surface area (cm^2)	T: time (hr)
T: time (hr)	M: (atomic mass/valance number)

Figures 7, 8 represent the curves of current and voltage of the cell versus added volume of predicted inhibitor in mild steel 4% HCl solutions devoid of and containing different concentrations of liquorices extract. Inspection of the figures reveals that the presence of liquorices extract shifts the current and voltage magnitude toward the low amount and the cathodic curves toward active direction. This behavior suggests the inhibitive effect of the additive.

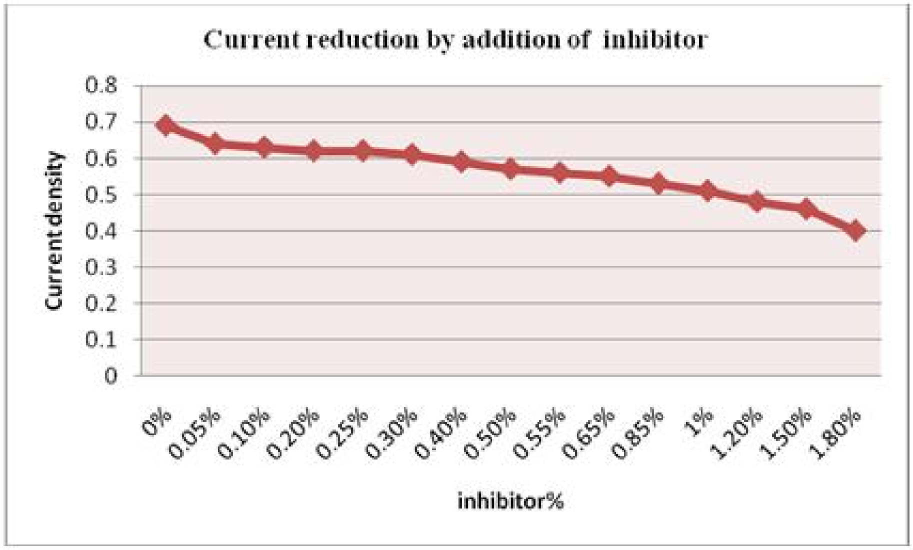

Figure 7- mL of Liquorices vs Current of cell

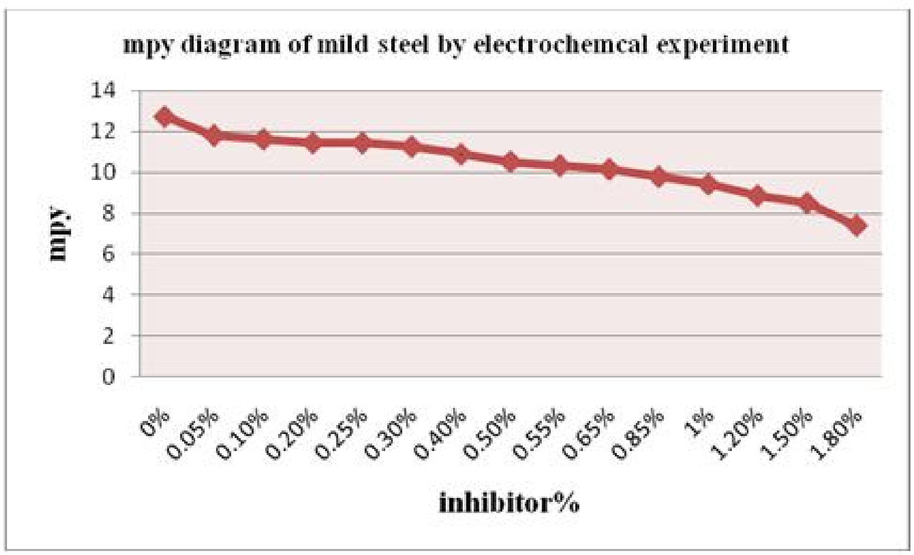

Figure 8 mpy diagram of mild steel vs inhibitor percent

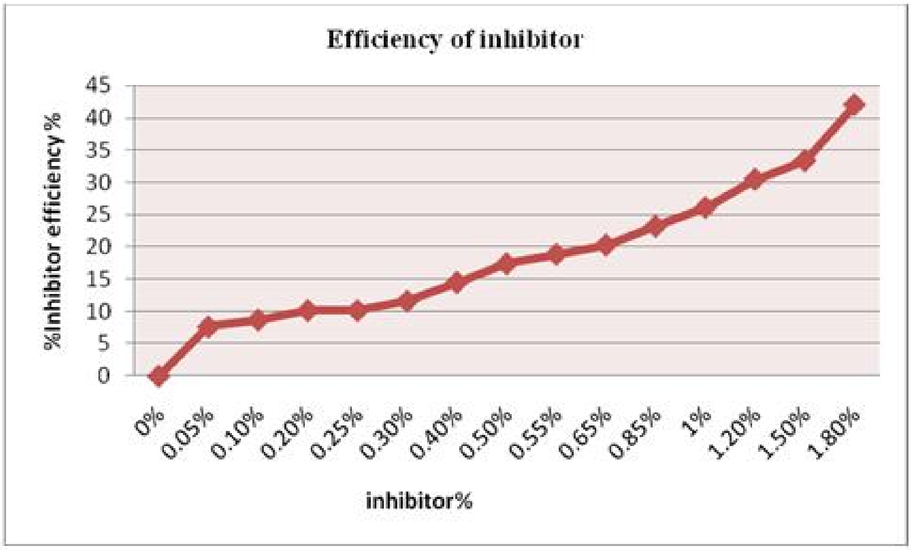

Figure 9 - mL of Liquorices vs efficiency of inhibitor

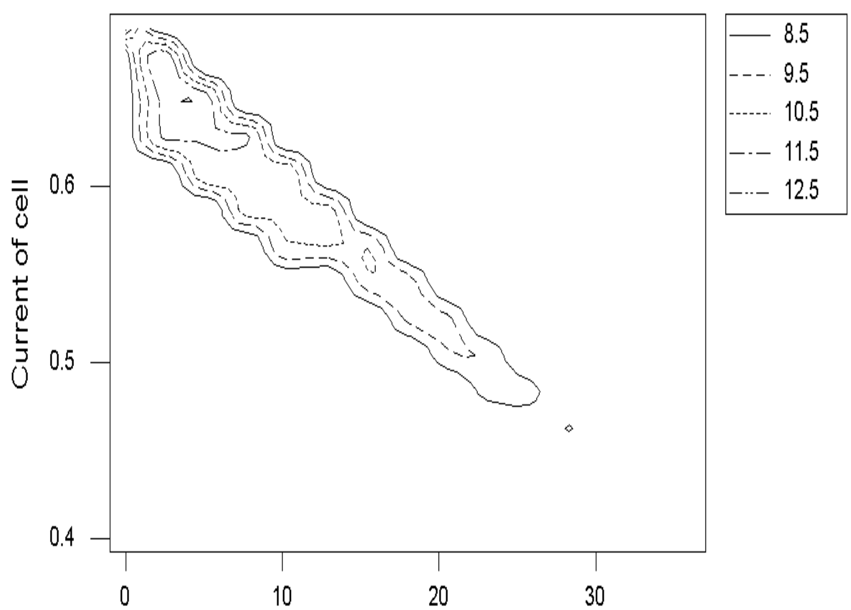

Figure 10 -A - Counter plot of mpy

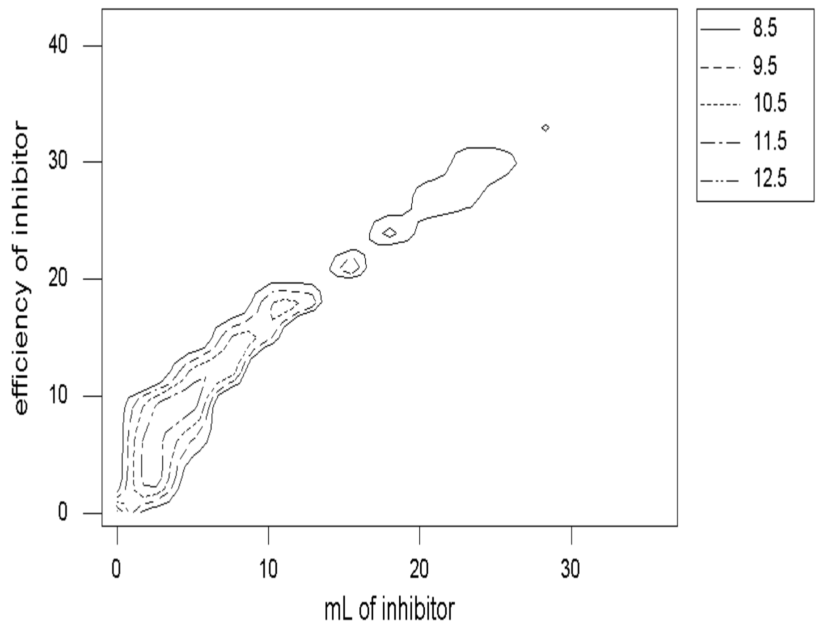

Figure 10 -B - Counter plot of mpy

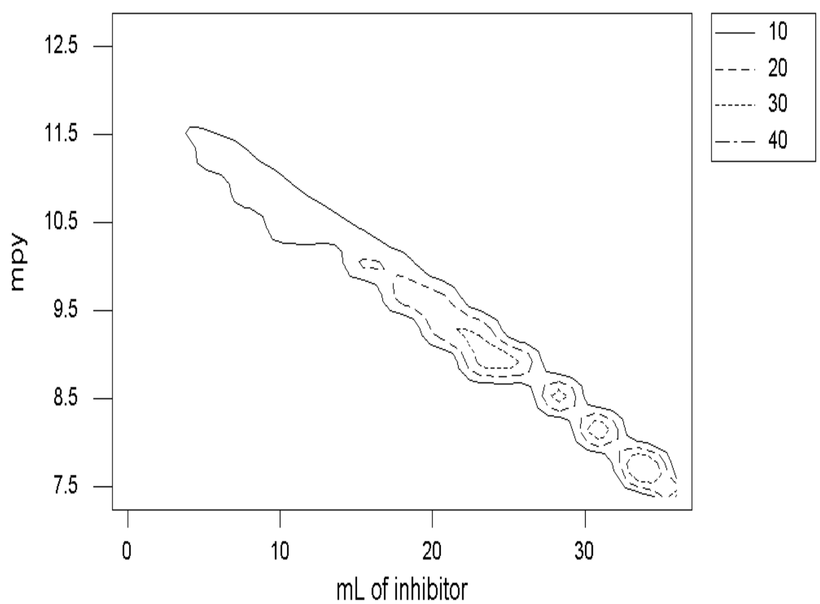

Figure 11 -A - Counter plot of Efficiency

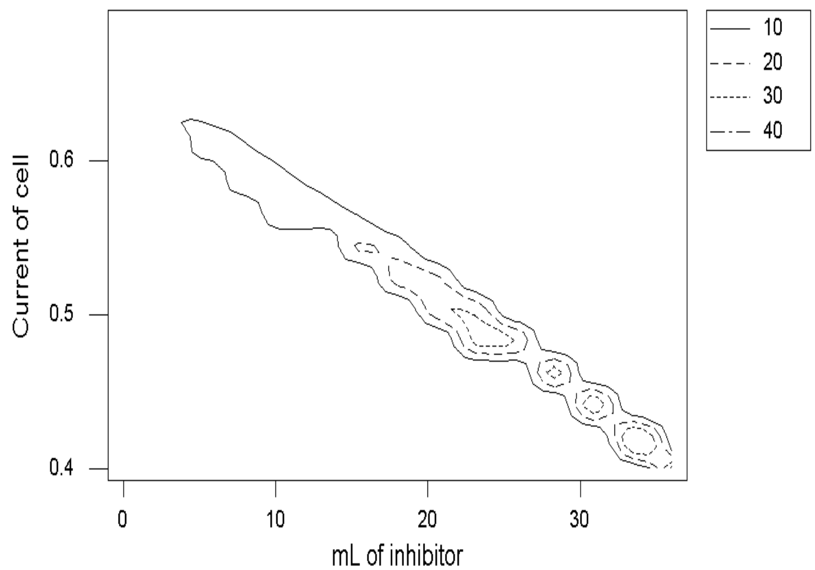

Figure 11 -B - Counter plot of Efficiency

The result indicated that the increase of inhibitor efficiency with concentration may be attributed to the formation of a barrier film, which prevent acid medium to attack the metal surface, because of the adsorption of Liquorices on the mild metal surface

4. Conclusion

The chemicals which can act as corrosion inhibitors may be inorganic or organic. The inorganic compounds such as chromates inhibit the corrosion process via formation of passive oxide film on the metal surface and thus prevent the corrosive medium to attack the bar metal. On the other hand, the organic compounds adsorb on the metal surface forming a barrier between the metal and the corrosive environment. Some structural features of the organic compounds help them to do so. These include the presence of oxygen, nitrogen or sulfur atoms as well as presence of double bonds. The lone pair electrons of the mentioned atoms facilitate the adsorption process. Some criteria should be considered when making a choice of chemical compounds for inhibition of corrosion. Inhibition of metallic corrosion is mainly an economical process. Therefore, the first criterion must be fulfilled by the used inhibitors is their prices. The other very important criterion should be considered when dealing with corrosion inhibitor is its effect on the human and environment. Unfortunately, most of the effective corrosion inhibitors are synthetic chemicals with high cost. At the same time, the use of such synthetic compounds can cause harm to human and environment. Upon looking around we'll find very rich resources for substances with wide varieties of chemical structures. So, why we rush to synthesize harmful chemical while the nature around us full of the safest ones? The plant is the great chemical factory which can supply us with the chemicals required to inhibit the corrosion process. Most of the naturally occurrence substances are safe and can be extracted by simple and cheap procedures. Recent literature full of researches which test different extracts for corrosion inhibition applications.

This plant (Liquorices) showed an excellent inhibition performance. The results obtained from weight loss test and electrochemical measurements were in good agreement.

Weight loss and electrochemical method are used to study corrosion of mild steel in 4% HCl solution and the inhibiting effect of liquorices derivatives. The weight loss measured within 6 hr shows that all studied compounds act as inhibitors in this acid medium. The highest inhibition efficiency is obtained by 0.5% solution of inhibitor in weight loss experiment. Analysis of the electrochemical data show that the inhibiting properties increase with inhibitor concentration.

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