Wasit Journal for Pure Science

Journal Homepage: https://wjps.uowasit.edu.iq/index.php/wjps/index
e-ISSN: 2790-5241 p-ISSN: 2790-5233

Corrosion Protection of Carbon Steel Using Expired Drug in Acidic Medium

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DOI: https://doi.org/10.31185/wjps.332
Received 01 February 2024; Accepted 16 March 2024; Available online 30 March 2024

ABSTRACT: The inhibiting impact of Orlistat on the corrosion of carbon steel in the hydrochloric acid medium (1.5M) was examined by the weight loss method. Orlistat, proven to be efficient in pipelines in terms of corrosion prevention, was found to be a suitable carbon steel inhibitor. Corrosion was found to be influenced by inhibitors adsorbed onto the surface of carbon steel through a simple blocking mechanism. The outcomes unveiled that IC at high concentrations of inhibitor increased, whereas at elevated temperatures it declined. The highest (89.5%) inhibition efficiency was obtained in the weight of 800 ppm of the inhibitor. The mechanism of action of Orlistat was also studied in terms of its adsorption of the steel surface using the Langmuir isotherm at the saturated condition via physical absorption. Based on (the Langmuir adsorption isotherm), the comparison of the experimental results showed that inhibitor molecules adsorb onto the carbon steel surfaces through physical adsorption, which is indicated by the values, in relation to their signs of the adsorption Gibbs free energy. The surface morphologies of the steel were investigated using FT-IR spectroscopy and SCM electron microscopy. Moreover, computational calculations have been done to assure that their electronic and structural properties are well establish.

Keywords: Expired Orlistat, carbon steel inhibitor, Orlistat’s, Langmuir, Langmuir adsorption isotherm, Gibbs free energy.

1. INTRODUCTION

Corrosion entails the gradual deterioration of properties and materials due to interaction with the surrounding environment. Countries are often faced with the economic impact of material corrosion which enquires huge financial resources to fight against the corrosion.

It is of a great academic and industrial interest, and much efforts are made to get rid of rust and scale in many industrial processes through the application of acidic media (1,2). Eco-friendly chemicals that have minimum adverse environmental effects should be utilized instead for corrosion safeguard system. Lowering the corrosion extent of metals not only decreases the toxic metal dis solution into the environment but also increases the lifespan of the equipment, thus the energy and economic benefits are provided at industrial applications.

Carbon steel is widely employed owing to its properties of inherent corrosion resistance; hence it is applicable across maritime and industrial settings. The use of compound drugs as a corrosion inhibitor is gaining increasing popularity and is considered to be one of the most convenient methods of protecting the metals against corrosion. It is depended on the subsequent:

- They comprise of drug molecules with (sulfurs, nitrogen, and oxygen) containing effective centers
- They are easy to purify and produce.
- Drugs have been found to play important parts in biological systems and are said to be eco-friendly ones [3,4].

They work by sintering to the site of corrosion and replacing water molecules at the active sites. The corrosion subsequently comes to a halt. In the meantime, it is interpreted that these chemicals restrict not only one but both of them (anodic and cathodic reactions) [5].

In the recent days, among one type of pharmaceuticals that has been considered for usage as a corrosion inhibitor. Unlike some other organic and inorganic natural inhibitors, drugs have a more focused approach and provide specific advantages for the same purpose [6]. The nano catalysts are one of the alternative ways of replacing the traditional inhibitors with a good chance of acceptance for their non-toxic nature, cost-efficiency and little environmental foot print [7-11]

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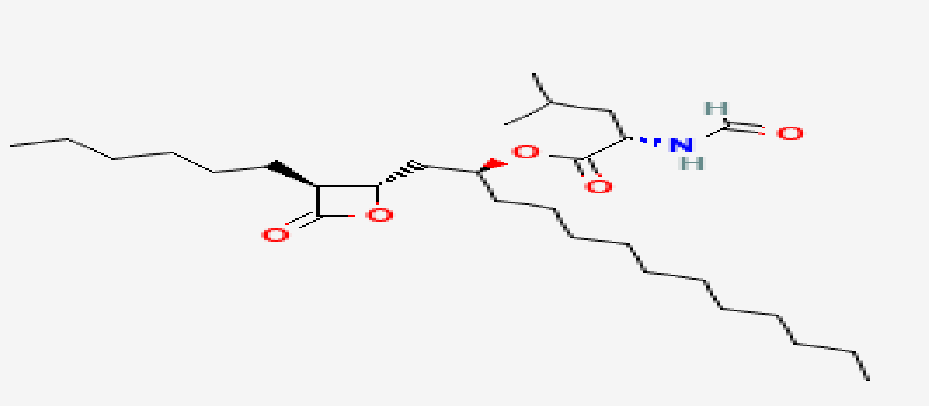


Fig. 1. Chemical structure of orlistat

2. EXPERIMENTAL

2.1 MATERIALS AND METHODS

The carbon steel samples examined in this study are in sheet form and possess the following composition in weight percentage: (0.641% carbon, 0.24% silicon, 0.577% manganese, 0.0243% sulfur, 0.263% copper, and the rest being iron). These steel specimens were bought from a market in Iraq. Prior to immersion, the carbon steel was cut into circular shapes 2 cm in diameter and 2 mm thick. And finally, the samples were grinded in an order using the following emery papers (300, 400, 800, 1200, 1500, and 2000) and then degreased with alcohol, they were then washed with distilled water and they were dried by filter paper.

they were ground using emery papers of different grades (300, 400, 800, 1200, 1500 and 2000), degreased with alcohol, rinsed with distilled water and dried using the filter paper. [12-14]

2.2 WEIGHT LOSS MEASUREMENTS

Impacts of weight loss tests were performed with pre-prType equation here.eared carbon steel samples. The specimens involved were immersed in 1.5 M HCl solutions for a duration of three hours, both with and without varying concentrations of Orlistat, and subsequently re-weighed at temperatures from 293 K to 323 K. Each weight loss measurement was conducted in triplicate, and the results were subsequently compared. The experiments lasted for three hours. During this time different temperatures were explored and fresh acid solutions were used:

Icorr and icorr(inh) = are the measured corrosion current densities in the absence and presence of inhibitors, respectively.

$$\text{EI}\ (\%) = \frac{i_{corr} - i_{corr(inh)}}{i_{corr}} \times 100 \ \ldots\ldots\ldots \qquad (1)$$

Where: CR and CR_i = are corrosion rates in absence and presence of the inhibitor respectively.

$$\boldsymbol{\theta} = \frac{CRo - CRi}{CRo} \ \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

$$CR_{(m\,d\,d)} = \frac{wo - wi}{A \times t} \ \ldots\ldots\ldots\ldots\ldots \quad (3)$$

The carbon steel weight losses in milligrams, with and without inhibitors, are represented by Wo, Wi. K: represents the surface coverage of the inhibitor, while A: represents the surface coverage of the outer layers of the carbon steel specimens. The time spent underwater is determined by the number of days measured [15,16].

3.RESULTS AND DISCUSSION

3.1 INFUENCE OF CONCENTEATION AND TEMPERATURE

Table1 summarizes an obtained conclusion of weight loss tests carried out within varying temperatures (293 K, 303 K, 313 K and 323 K) and inhibitor concentrations in a 1.5 M HCl solution. It was noticed that the %IE increased with the concentration of inhibitors and decreased with temperature elevation. At 293 K, the highest inhibition efficiency was observed which corresponds to the physical adsorption mechanism [17,18].

The latter phenomenon might be caused either by the more efficient adsorption process of the inhibitor on the surface or by the overall coverage of carbon steel surface with the inhibitor. Table (1) below lists the corrosion and inhibitor effectiveness speeds (SP) after 3-hour-immersion in 1.5M hydrochloric acid solution reacted at different temperatures in the later for the tests are carried out with and without expired Orlistat.

Table 1. - The acid reacts at different temperatures in the presence or absence of an inhibitor

Temp.	**C_{inch} *(ppm)***	**CR *(mdd)***	**θ**	**η%**
293 K	blank	818.76	…..	…..
	400 ppm	144.75	0.824	82.4
	500 ppm	138.96	0.831	83.1
	600 ppm	101.91	0.875	87.5
	700 ppm	92.64	0.8869	88.69
	800 ppm	85.697	0.89.54	89.54
303 K	Blank	1224.08	…..	…..
	400 ppm	233.9	0.809	80.9
	500 ppm	216	0.824	82.4
	600 ppm	209.6	0.83	83
	700 ppm	176.02	0.85.7	85.7
	800 ppm	160	0.870	87
313 K	Blank	1742.82	…..	…..
	400 ppm	386.7	0.778	77.8
	500 ppm	347.4	0.80	80
	600 ppm	316.15	0.82	82
	700 ppm	258	0.85	85
	800 ppm	236.24	0.864	86.4
323 k	Blank	2042.82	…..	…..
	400 ppm	530	0.741	74.1
	500 ppm	463	0.774	77.4
	600 ppm	420	0.795	79.5
	700 ppm	391.4	0.809	80.9
	800 ppm	332	0.83	83

In order to follow up the adsorption mechanism of the inhibitor, by using the temperatures ranging from 293 K to the maximum of 323 K and applying carbon steel in the tests with and without the drug Orlistat, we performed a study. Following the data in Table 1, CR level (CR) increase with temperature rise that induced a decrease of corrosion inhibition efficiency. The movment of equilibrium points from absorption/desorption, desorption obviously demonstrates physical adsorption on the surface of carbon steel. The activation energy (*Ea.*) was determined using the Arrhenius equation. [19]:

$$\log CR = \frac{-Ea}{2.303RT + \log A} \quad …………. (4)$$

Thus, Ea. stands for activation energy, R is the gas constant (8.314), and A signifies the Arrhenius constant. Implementing Equation (4) gives us a prediction that by plotting log (CR) vs. 1/T the linear relation would be achieved, as supported with the experimental data. The slope of this line presents us with *-Ea./R* and the extrapolated line intersects at T = 0, providing us with ln A [20]

As illustrated by Fig (2), the Arrhenius plots with and without varying does of expired Orlistat have been presented through the log CR versus 1/T for corrosion of carbon steel in 1.5 M HCl.

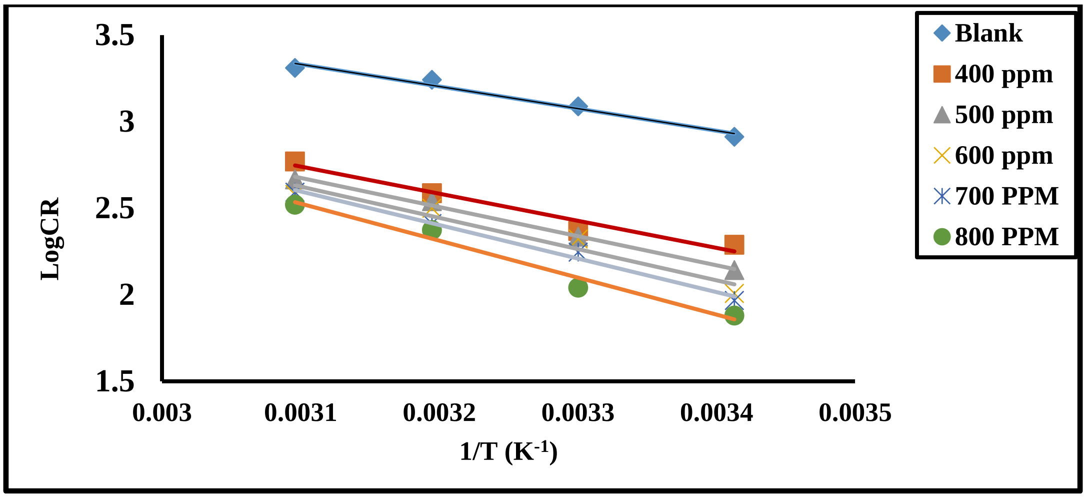


Fig. 2. HCl with and without dissimilar dosage of expired orlistat

By employing an alternative form of the Arrhenius relationship, (ΔH) and (ΔS) can be determined using the equation:

$$\ln (\mathrm{CRL}\ T) = \ln (\mathrm{R\ Nh}) + (\Delta \mathrm{S\ act\ R}) - (\Delta \mathrm{H\ act\ RT}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

In this equation, N = is commonly referred to as the Avogadro number- (6.022 × 10^^{23} mol^$^{-1}$) and (h)= signifies the Planck's Constant - (6.626 × 10^$^{-34}$ J·s). Inequality ln ICP at r can be plotted on a line where the slope represents value of $L\Delta SactR$, and the intercept gives the value of ($ne\ R$Now + Δ Luis). The mentioned effects are listed under. table 2.

Table 2. - Activation energy Ea., activating enthalpies (ΔH), activation entropies (ΔS a) for CS corrosions in 1.5 M presence and absence inhibitor.

Conc. (ppm)	***Ea* (KJ.mol^{-1})**	**-ΔH (KJ. mol^{-1})**	**-ΔS (J. mol^{-1}. K^{-1})**
Blank	24.474	21.918	107.773
400ppm	29.982	27.4253	102.006
500ppm	32.211	29.6549	96.3511
600 ppm	34.559	32.0028	90.0318
700 ppm	37.123	34.5667	82.6191
800ppm	40.906	38.3497	72.2428

Seeing the actual chart is beneficial, (ln $icorr\ T$) vs (1/T) where a slope for a straight line displays its magnitude ($-\Delta Hact\ R$) and the intersection offer its magnitude ($ln\ R\ Nh + \Delta Sact\ R$).

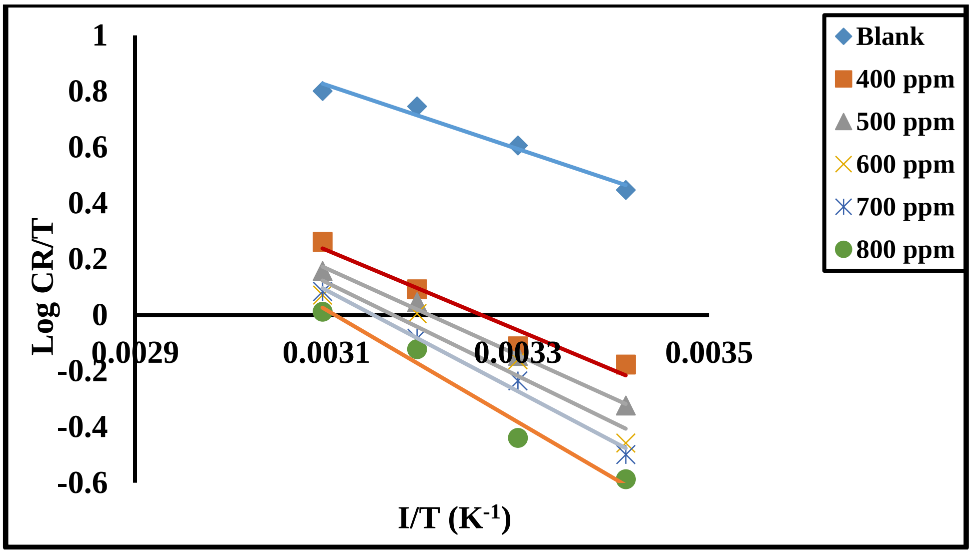


Fig.3. Log (CR/T) to 1 / T corrosion for carbon steel in 1.5M HCl in existence and inexistence of diverse concentrations (C) of orlistat at 4 temperatures ranged from 293 to 323 K.

The above values depend, with the rise in activation energy (E*a) for orlistat corrosion at higher temperatures, the elevation in energy barrier for the corrosion reaction is also supported, which has proved the physical adsorption of orlistat molecules on the surface of CS. While the Arrhenius coefficient(A) and activation energies (Ea.) are not proportional to each other directly, as the corrosion often starting at lower energy sites moving to higher energy sites, the earlier process is much complicated [21].

In simpler words, though is important to note that the corrosion of the Cs in the Chlorine ions containing solutions will still take place, the boosted energy barrier will hinder the process when the inhibitors are present. As well, the intensity of corrosion is enhanced by increment in temperature which affects the effectiveness of inhibitors [22].

An increase in inhibitor concentration results in an increase in saturation of the electron density at the adsorption site of the inhibitor molecule, and hence, the inhibition becomes much more effective.

As for the reported entropy of activation (ΔS*), their magnitudes have been found to be negative. Therefore, let us say that the bond-making step tends to characterize the reversibility of the activated complex. In the essence, the activated molecules are in a more ordered one than in the original state. The negative sign of ΔH* shows that the corrosion is self-accelerating and exothermic in nature [23].

3.2 THE ADSORPATION ISOTHERM

Another usually exploited method is to express adsorption via the models of various kinds of adsorption isotherms. The adsorption of inhibitors onto the metal surface can be categorized into two main types of interaction: physisorption and chemisorption, it is based on the elements of inhibitor measure (molecular structure), electrolyte type (corrosive medium), and corrosive metal (charge and nature). Discussions using adsorption property via adsorption isotherms include the coverage data as one key factor. Its description includes the binding of inhibitory molecules to the metal surface and how they interact with the metal. Adsorption isotherms present a good way of analyzing the effect of expired Orlistat on (θ) surface coverage of (CS) and an inhibitor solution's concentration (Cinh), It describes the optimal Langmuir isotherm. [23,24].

$$Cinh\ \theta = 1\ Kadc + Cinh \quad \ldots\ldots\ldots\ldots\ldots.\ (6)$$

Here, in Kads adsorption and desorption equilibrium constants, where it is obvious that the inhibitor molecules are getting close to the adsorption sites on the surface. for the determination of Gibbs free energies through measurements [25]

$$\Delta G°ads = -RTln\ (55.5Kads)\ \ldots\ldots\ldots\ldots.\ (7)$$

Here, (R)= are gases constants, (T)= is the absolute temperatures, and the (55.5) = is the molar water concentrations in (M.) With the VanHoff formula calculation, the standard enthalpies of adsorption can be obtained.

Plots of Kad's plotted against 1/T are shown as straight lines, and the slope of the straight lines is $-\Delta H_{ads}\ R$. Negative $\Delta H°$ values indicate the phenomenon of adsorption of expired orlistat molecules as exothermic. Negative values of $\Delta G°ads$ with damper are followed by exothermic absorption mechanisms. $\Delta S°ads$ has been taken from the barriers as in. (5): [26]

$$\ln\ (\mathrm{CRL}\ T) = \ln\ (R\ Nh) + (\Delta Sact\ R) - (\Delta Hact\ RT)\ \ldots\ldots\ldots..\ (8)$$

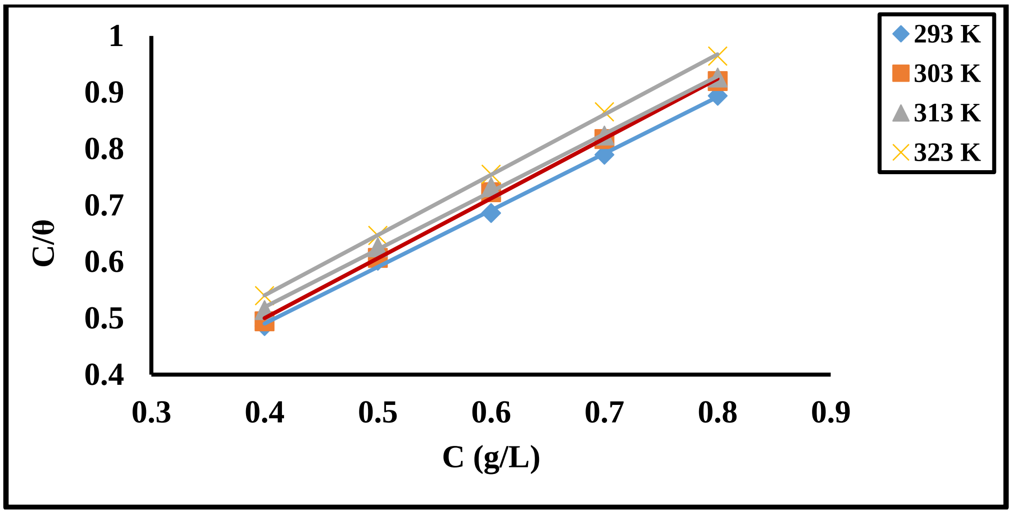


Fig.4. Langmuir Isotherm plots for expired orlistat adsorption of (CR) in 1.5M HCl.

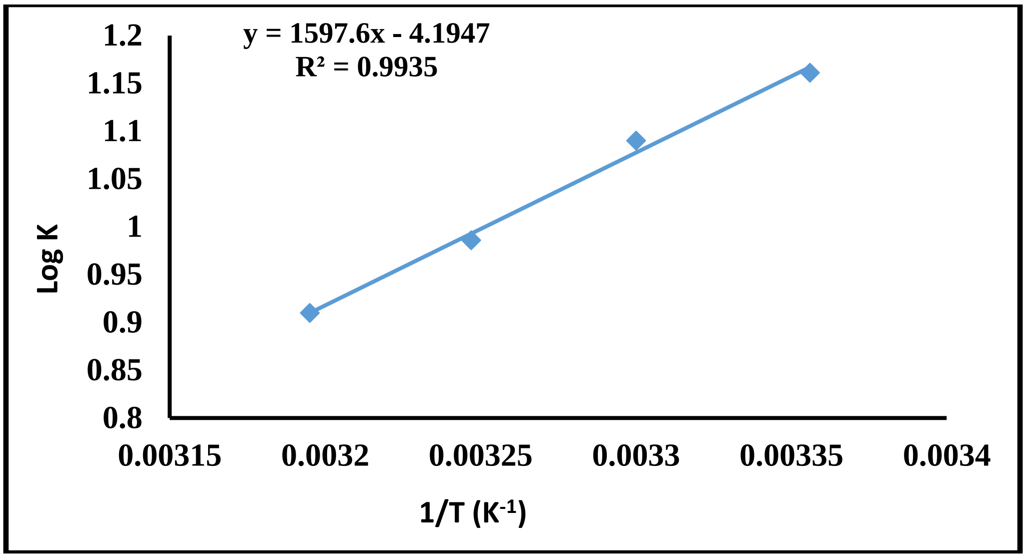


Fig .5. Log $K_{ad\ v}$s. (1/T) curves for the corrosion of carbon steel in (1.5M HCl) solution in nonexistence and existence of Orlistat at diverse temperatures

Table3.- Thermodynamic equations for adsorption of expired orlistat onto CS in 1.5M HCl.

Temp. *(K)*	**K ads**	**-ΔGads** *(KJ. mol^{-1})*	**-ΔH ads** *(KJ. mol^{-1})*	**-ΔSads** *(J.mol^{-1}. K^{-1})*
298	11.24	-15.679	30	111
303	13.16	-16.011		
308	9.03	-16.277		
313	8.8096	-16.629		

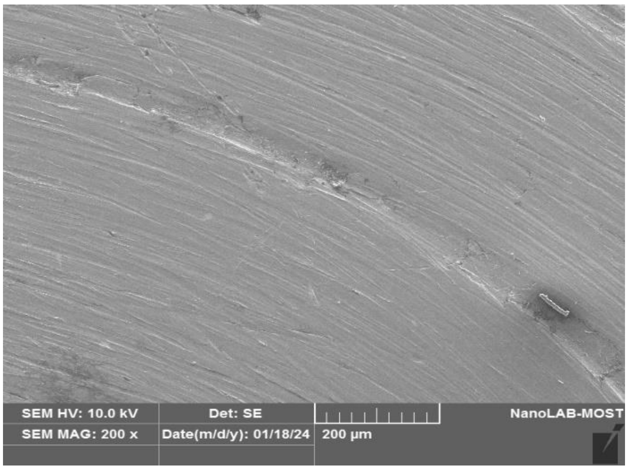
Average values of ΔG_{ads} reach -20 kJ/mol for electrostatic interaction of Charged molecules with external metal layers (physical adsorption). However, ΔGads values are less than −40 kJ/mol, charges transfer from the inhibitor molecules to the surfaces of metal or create coordinate covalent bonds (chemisorption). The values of ΔG_{ads} varied from ($^{-}$15.67 - $^{-}$16.63) kJ. mole-1, which implies that the surfaces of the CS alloys interacting with the inhibitor molecules diffuse through physical adsorption. [27-29].

The negative magnitudes of the adsorption enthalpy ΔH indicate that the adsorption of an expired drug of a carbon steel surface is an exothermic

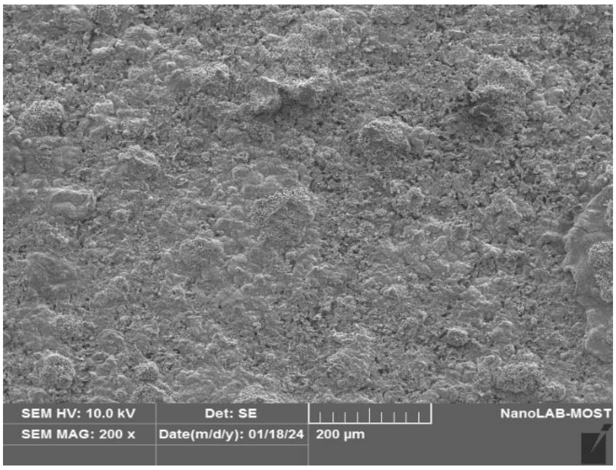
process. It is called physisorption when an expired drug adsorbs onto carbon steel surfaces which gives negative ΔS_{ads} (the exothermic process of adsorption). Thus, the adsorption being an exothermic process, it should have a decrease in change of the entropy, and vice versa. [30]

.3.3 SCANNING ELECTRON MICROSCOPY(SEM)

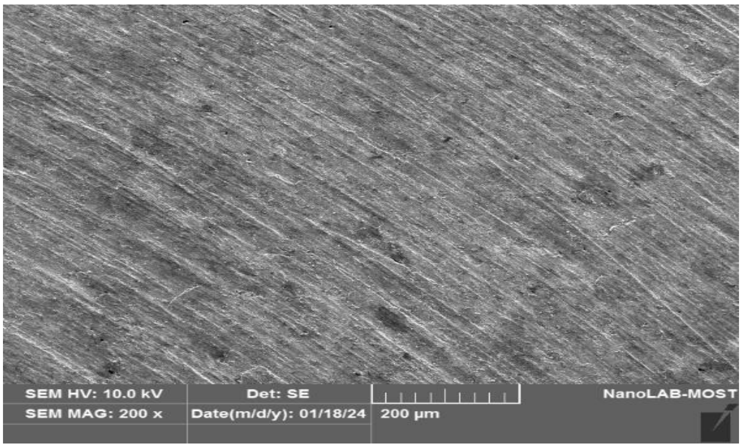
Scanning electron microscope (SEM) to study carbon steel surfaces was performed to determine that the extracted particles were adsorbed on the CS surfaces and not just peeled off. Figure 4 displays SEM micrographs of CS surfaces before and after immersion in HCl (1.5 M) with and without expired orlistat concentrations at the optimum level. The figure shows (a) refined CS alloys, (b) CS alloys with 15 M HCl immersed, and (c) copper alloys immersed of 1. 5 M HCl, with 800 ppm expired orlistat.



(A)



(B)



(C)

CONCLUSION

It has been shown through research that after the expiration of Orlistat, it is used as a good inhibitor of CS 1.5M (HCl) solutions, which leads to weight loss. The inhibitors are spontaneously absorbed by the metal surface and are confirmed by G values that have negative signs. Such a result is further strengthened by the values of Ea and ΔH observed during the corrosion process. However, both the residual and null solutions depict negative trends due to the binding character of the activation complex in the rate-determining phase, in contrast to the dissociation of ΔS^* Ads. Adsorption data of expired orlistat on a metal surface fit the Langmuir adsorption model very well. Furthermore, there is a direct relationship between the specific inhibitor concentration and the protection efficiency, which reaches a maximum of 89.5% when using a dose of 800 ppm of expired Augmentin.

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