Indian Journal of Chemical Technology
Vol. 30, March 2023, pp. 180-186
DOI: 10.56042/ijct.v30i2.66263

A case study on expired drugs: The potential corrosion inhibitory activity of expired labetalol drug in 1M HCl for plain carbon steel

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Received 7 September 2022; accepted 3 February 2023

In this work expired drug namely, labetalol has been used as a corrosion inhibitor in a stirred acidic medium (1M HCl) with mass loss measurement and electro analytical techniques. . The efficiency of the inhibitor increases as the temperature increases from 30-60°C. The results reveal that maximum inhibition efficiency is observed as 91.66% for 500 ppm. Potentiodynamic polarization measurement implies that it perform as a mixed type inhibitor. FT-IR analysis prove that corrosion product is formed on the mild steel surface. When compared with metal in IM HCl, it includes a shielding layer on the surface of mild steel by controlling further attack of acid. SEM and SFM surface morphology study have also been performed to confirm the effect of labetalol on metal. In addition to that, DFT is also carried out to analyse HOMO, LUMO, ΔE and Mulliken charges.

Keywords: Acidic medium, Corrosion inhibitor, Expired drugs, Labetalol, Mild steel

In the recent scenario, electrochemical rust is a long term ferocious effect on the surface of the metal, which is associated with the physical and mechanical properties of the metals. The corrosion study of iron and non-iron metals are used in the diverse medium of acid and seawater in many industries. Also, the lifetime circumstance of metallic materials plays a vital role in the safety of products from metals[1-3]. Among them, the mild steels are used for most of aggressive environments due to their mechanical and good resistance properties in electrochemical corrosions. This property of mild steel susceptibility is due to the homogeneity of the steel and its alloy compositions[4-8].

Effectively reduction of corrosion on metals in a variety of environments remains an ongoing challenge in the current century. Because of the sustained economic progress and the cost of living efforts to reduce corrosion[9], various methods were used to keep metals from a corrosive atmosphere, together with electrochemical defense and the addition of a small quantity of substances (inhibitor) that reduces the corrosion process in acidic environments. Inhibitors are added to the metal to protect the metal surface forming stable compounds. It also forms a layer that separates the metal from the aggressive environment[10,11]. In addition to that various organic, Inorganic, herbal extracts, Pharmaceutical drugs, Ionic liquids, and synthetic compounds were constantly used as inhibitors. Pharmaceutical drugs have been expansively used as corrosion inhibitors in mild steel, aluminium, copper, and their alloys because of their outstanding properties like non-volatile nature. Labetalol drug is used as an effective gastrointestinal agent to treat hypertension and prevent chest pain due to angina pectoris. It can be administrated orally owing to its low toxicity, less expensive, and environment friendly nature. In this work labetalol expired drug is used as a potential corrosion inhibitor for plain carbon steel in acidic environments. In recent years, experiments like mass loss, polarization, AC impedance techniques, and theoretical approaches were used to study the inhibitory mechanisms of corrosion inhibitors at the molecular level. This is essential for understanding the inhibitory potential of corrosion inhibitors by analyzing the quantum chemical parameters. So the theoretical calculations like DFT, ΔE, HOMO, and LUMO were also calculated. In addition to that, the FT-IR, SEM and SFM were analyzed to examine for the metal surface morphology.

Experimental Section

Mild steel plate

The mild steel plate composition is C-0.10 %, P-0.03 %, S-0.02 %, Mn-0.60 %, (in weight %) was used for the corrosion studies.

Inhibitor

The inhibitor labetalol commercially named labetalol was bought from Sigma Aldrich chemicals in Delhi. It has two nitrogen atoms, three oxygen atoms, and two heterocyclic rings. The above mentioned functional group easily reacts in an acid solution and protects the outside of the metal by formed a surface layer. The 1M HCl solution has prepared by taking AR grade 35 % HCl and diluted with deionized water. Inhibitor range varied from 100 to 700ppm, the stock solution has been prepared by the formula 1000 parts per million = 1000 parts per million made in 1=1 reserved solution made different concentrations of inhibitor (100-700 ppm) it can be prepared by using volumetric law ($V_1N_1=V_2N_2$).

Mass loss measurements

The mild steel plates have been used in rectangular shapes for mass loss observations. The scales of metal plate size were engaged with 3.6 × 1.6 × 0.3 cm, which reduced a minute gap on the top fringe of the mild steel plate. Moreover, it has been refined with specific results of emery sheets (1/10-1/8) cleaned with acetone. The metal plate masses were measured by an electrical balance meter dipped in various molar concentrations of inhibitor range is 100-700 ppm. The metal mass loss methods were carried out by immersing in an acidic medium for two hours. Experimental studies like Tafel and Polarization were examined by varying the temperature from 30– 60°C. All the stock acid solutions have been stored in the open air after immersion for two hours the specimens have been taken and washed with a brush under strolling water to get rid of the rust product dried out with warm air and mass was measured properly to calculate mass reduced values. All the experiments have been performed in triplicate procedure to obtain the reproducibility results within measurements. Among them, the triplicate experiments were significantly good in 500 ppm inhibitory concentration. Also, the hotness observation done between 30– 60°C, the corrosion rate has been observed through the subsequent equation[12,13].

$$CR=W/St \qquad \text{... (1)}$$

Here,

$$IE\ \% = (W_0 - W_I / W_0) \times 100 \qquad \text{... (2)}$$

$$\theta = (W_0 - W_I / W_0) \qquad \text{... (3)}$$

Where,

CR = Corrosion rate

W = standard weight loss of all mild steels

S = entire area of mild steel

t = is concentration time (2 hour),

W_0 and W_i the lack of corrosion rates in the existence of labetalol.

IE = Inhibition Efficiency

θ = Surface coverage

Electrochemical measurements

Tafel polarization and EIS techniques were analyzed using the model 600 D/E series to compute the electrochemical values. All the experiments were performed in platinum foil, and saturated calomel electrode as a reference, and 1cm^2 mild steel plate acts as the working electrodes respectively. In addition, the open circuit potential of the working electrode was polished with an emery sheet for 46 min to reach a steady state.

The impedance spectrum of open circuit potential and EIS measurements have been studied using AC signal at 0.01Volt and the range of amplitude from 100 Hz to 0.01Hz. The inhibition performance has been observed from the electrochemical impedance spectrum through the subsequent equations.

$$IE\ (\%) = (R^i_{ct} - R^0_{ct} / R^i_{ct}) \times 100 \qquad \text{... (4)}$$

$$\theta = (R^i_{ct} - R^0_{ct} / R^i_{ct}) \qquad \text{... (5)}$$

Presence and absence of labetalol, the charge transfer resistance is R^i_{ct} and R^0_{ct} in that order. The surface coverage value (θ) was obtained from the polarization curves.

$$IE\ (\%) = (I^o_{corr} - I^i_{corr} / I^o_{corr}) \times 100 \qquad \text{... (6)}$$

$$\theta = (I^o_{corr} - I^i_{corr} / I^o_{corr}) \qquad \text{... (7)}$$

Presence and absence of inhibitor, the corrosion current densities is $I^i_{corr\ and}\ I^0_{corr}$ respectively.

Surface morphology

The mild steel plate surface morphology studies were evaluated by surface photographs of the nonappearance and appearance of inhibitors at most selected concentrations separately after three hours of immersion. A.P.E Research srl, Italy scanning electron microscope and the atomic force microscopy model is A-100 be used for taken surface images. The FT-IR spectrum was recorded by the JASCO 460 plus spectrometer (400-4000 cm^{-1}) with a resolution of 4 cm^{-1} through the potassium bromide disk procedure.

Results and Discussion

Mass loss technique

The mass loss has been accomplished on a mild steel plate by mass loss technique, which is straightforward and standard method. By using this easy method the inhibition efficiency had been obtained from unique and two reference samples. This reference sample result has a very unique error within (2%). The inhibition effect of labetalol is shown in Table 1. It was analyzed that the absorption of the labetalol increases with decreases in corrosion rate[14].

Effect of inhibitor concentration

The rate of corrosion and inhibition efficiency was deliberated from the various concentration values of labetalol in 1M HCl medium in Table 1. The effectiveness of the inhibitor was displayed from 55.88 to 91.66%, In addition, the corrosion rate values were decreased from 3.94 to 0.02 mm^{-y} with the extension of 100-700 ppm concentration of labetalol.

Furthermore, the inhibition effect of mild steel plate enhances regularly, when the concentration of inhibitor increases in 1M HCl at 60°C owing to the surface coverage area and adsorption of inhibitor takes place on the mild steel plate. The efficiency of the inhibitor gradually increases from 100 to 500 ppm. Also, the drug was examined for the efficiency of inhibitor concentration of 500-700 ppm. Interestingly, it has been found out the efficiency of inhibition decreases more than 500 ppm due to all the active sites may be fully covered by the metal surface area.

Table 1 — Weight loss values of various concentration of labetalol in 1 M HCl

Concentration (ppm)	Weight loss (mg cm -^{2})	Corrosion rate (mm y-^{1})	Surface coverage (θ)	IE %
Blank	0.036	3.94	-	-
100	0.016	1.97	0.5588	55.88
200	0.011	1.36	0.6277	62.77
300	0.013	0.33	0.6344	63.44
400	0.004	0.07	0.8856	88.56
500	0.003	0.02	0.9136	91.66
600	0.006	0.12	0.8333	83.33
700	0.011	0.09	0.6944	69.44

Electrochemical study

Tafel polarization

The Tafel polarization results are shown in Fig. 1 and Table 2, which deal with the existence and non-existence of labetalol concentrations in 1M HCl at 30 °C. Also, the results were observed the corrosion potential (E_{corr}), corrosion current (I_{corr}), and anodic and cathodic Tafel slopes of the metal plates. The E_{corr} values were performed in positive shift, when the addition of inhibitor in 1M HCl concentration Table 2. From the literature survey, an uninhibited solution E_{corr} shift values were ±85 mV in this condition which act as a mixed type of inhibitor[15]. In addition, the results obtained the E_{corr} values varied within ± 50 mV for labetalol, it showed that the labetalol act as a mixed type inhibitor.

Moreover, the inhibitor inhibits the metal dissolution at the anode as well as hydrogen release at the cathode. In addition there are no specific variations among the anodic and cathodic slopes. This revealed that the labetalol adsorption takes place on the plain carbon steel surface first and it blocked all the lively sites which are present in the mild steel. Both anodic and cathodic curves prove lower current density in presence of an

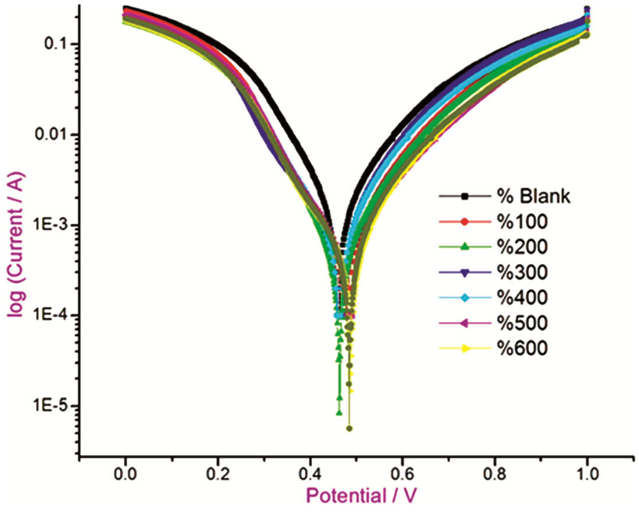

Fig. 1 — Tafel polarization curves of mild steel in 1M HCl

Table 2 — Tafel polarization parameters of mild steel in 1M HCl

Conc. (ppm)	b_am Vdec^{-1}	b_c m V dec^{-1}	E_{corr} (mV/SCE)	I_{corr} (mA/cm^{2})	R (Ohm)	IE %
Blank	655.3	657.3	-455.8	1.1243	28	-
100	703.4	745.6	-460.6	1.5131	63	58.82
200	722.5	764.4	-475.4	1.5214	76	67.43
300	705.4	689.5	-477.5	1.4781	83	71.22
400	688.6	754,1	-471.2	1.2055	118	92.41
500	834.7	878.8	-478.7	1.2079	123	98.23
600	857.8	838.5	-485.4	1.1827	141	88.54
700	780.4	865.2	-497.2	1.1642	205	75.12

inhibitor also Tafel Polarisation values mostly obey the conventional mass loss experiment values[16,17].

From this observation, the concentration of H^+ ions decreases on the plain carbon steel surface in 1M HCl at 60°C, when the labetalol added to the same solution. It may be occurred the hetero atom of the functional groups in the inhibitor absorbed the H^+ ions from the HCl medium. Owing to this working electrode (1cm^2 mild steel plates) was inhibited from the corrosion[18]. As a result, the labetalol perhaps categorized as a mixed type of inhibitor in 1 M acidic medium.

Electrochemical impedance

The Nyquist plots have been disclosed for the decay rate of plain carbon steel plate in the occurrence and nonoccurrence of labetalol in 1 M HCl medium at 60°C shown in Fig. 2. From this plot, the rate of charge transmission process obtained has a lone half circle for the working electrode. As well as, it controls the corrosion of plain carbon steel. These plots were not identical due to the irregularity and homogeneity on the surface of electrode[19-22]. Also, the electrochemical spectra of plain carbon steel for an uninhibited acidic medium have been drastically transformed after including the labetalol in 1M HCl solution[23]. The results revealed in plots showed small and larger frequencies for the presence and absence of labetalol respectively (Table 3). In this regard, the semicircle radius and impedance increase with a higher concentration of labetalol in 1M Hydrochloric acid medium[24-27].

Effect of temperature

The study of this experiment was disclosed on mild a steel plate in the existence and nonexistence of labetalol at 1M HCl concentration with various temperatures (30-60)°C in Fig. 4. Moreover, the inhibition activity of the labetalol at the temperature (30-50°C) and inhibition efficiency increased vice versa. Also, increasing the temperature (50-60°C), inhibition efficiency were decreasing due to the desorption process. In this regard, the temperature plays a vital role in the desorption process in the metal surfaces[28-30]

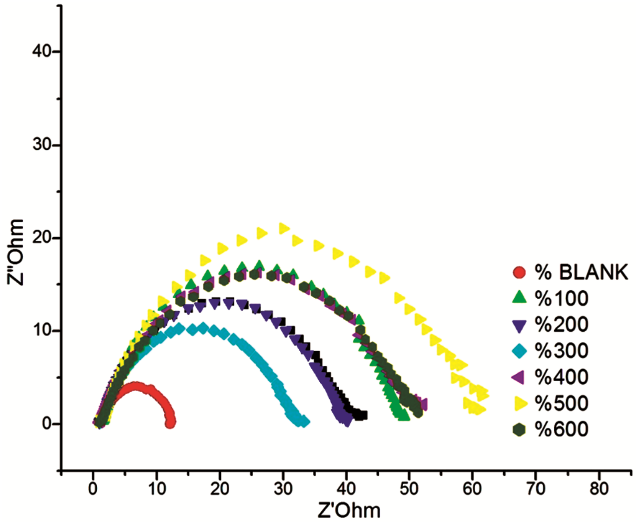

Fig. 2 — Electrochemical impedance curves of mild steel in 1M HCl

Molecular quantum mechanics

The inhibition mechanism of corrosion has been described in this experiment, which discussed the presence of electrons in different geometrics[31-33]. In addition, the structure and rate of inhibitor reactivity were determined by using the HOMO, LUMO, dipole moment and Mullikan charges Also, the quantum mechanics values are shown in Table 4, and the labetalol was adsorbed on the mild steel outside *via* donor acceptor process. The labetalol are having a highly occupied molecular energy level due to the pair of electrons for adsorption. Moreover, the Energy gap of HOMO (E_{HOMO}) was mainly associated with the electron donor potential and electron affinity in the inhibitor molecule. From this observation, the E_{HOMO} and electron donating potential were increased and vice versa due to the energy gap of E_{HOMO} is more than the E_{LUMO} in the inhibitor. Consequently, the rate and energy gap of the inhibitor was closely related to the chemical activity. As a result, the decreasing ΔE value in the electron transfer process is considered and ΔE value for labetalol is 3.4888eV shown in Table 4.

Surface studies

Experimental study of Scanning Electron Microscopy (SEM)

The technique is discussed as a clear observation of the surface morphology of the plain carbon steel in

Table 3 — Electrochemical impedance parameters of mild steel in 1M HCl containing different concentration of labetalol.

Concentration (ppm)	Y_{max} (Ωcm^2)	R_{ct} (Ωcm^2)	C_{dl} (μFcm^2)	IE %
Blank	11.056	22.102	1339.51	-
100	18.043	36.076	254.54	61.44
200	26.651	53.297	135.65	67.65
300	32.764	65.447	77.456	71.32
400	39.532	79.015	75.789	92.13
500	46.876	93.647	58.657	97.54
600	54.887	109.562	49.789	89.15
700	63.775	127.345	12.876	76.43

Table 4 — Quantum chemical parameters of labetalol

E_{HOMO} (eV)	E_{LUMO} (eV)	$\Delta E=(E_{HOMO}-E_{LUMO})$	μ (D)	Total Energy(E)	IE %
-5.6254	-1.4164	4.209	14.2634	-957.6543	98.23

existence and the absence of labetalol molecule. The newly polished mild steel SEM image has in smooth and some scratched nature in Fig. 3 (a). However, the absence of an inhibitor the surface morphology of the plain carbon steel occurred vital corrosion in dipped at 1M HCl Fig. 3 (b). Also, the corroded surface was initiated for the development of porosity on the plain carbon steel in uniform nature[34]. On the other hand, the smooth surface of carbon plain steel was occupied at 1M HCl in presence of an inhibitor without any porosity shown in Fig. 3(c). As a result, the labetalol protected the mild steel surface from the attacking of corrosion particles, which are in the following SEM images[35-37].

Scanning Force Microscopy (SFM) study

The surface morphology of plain carbon steel has been accomplished by the SFM techniques for metallic corrosion. Additionally, the SFM morphology images were shown in Figs. 4 and 5

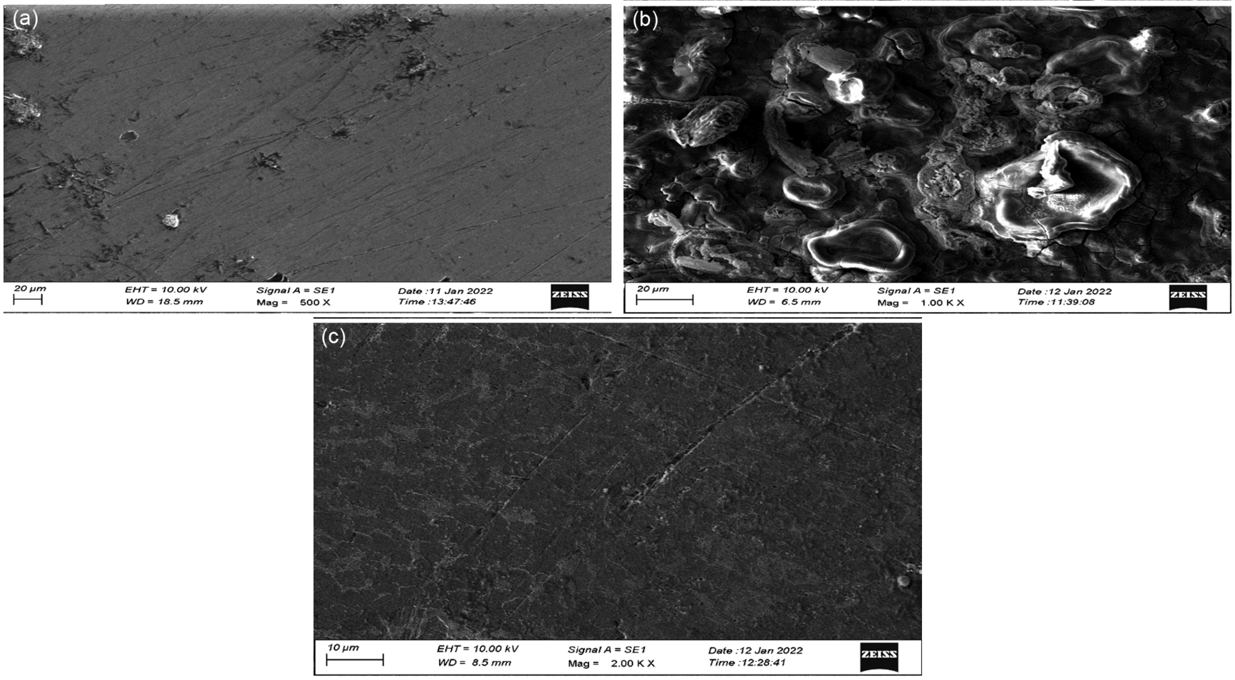

Fig. 3 — SEM images of mild steel (a) polished metal; (b)1M HCl solution without Labetalol and (c) 1M HCl with optimum concentration of Labetalol

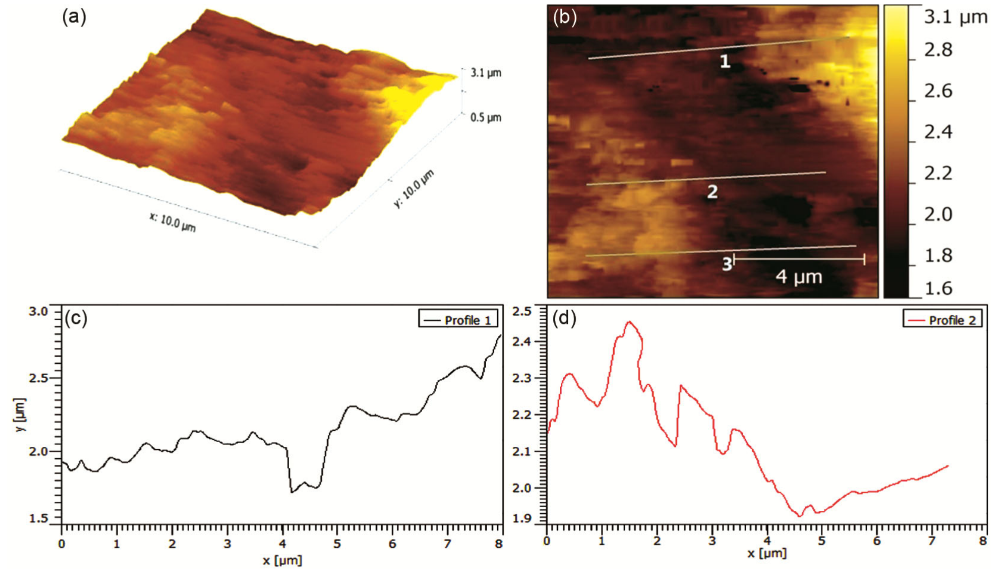

Fig. 4 — SFM images of mild steel in 1M HCl (a) 3D; (b) Histogram analysis; c) 2D and (d) Cross section line profile

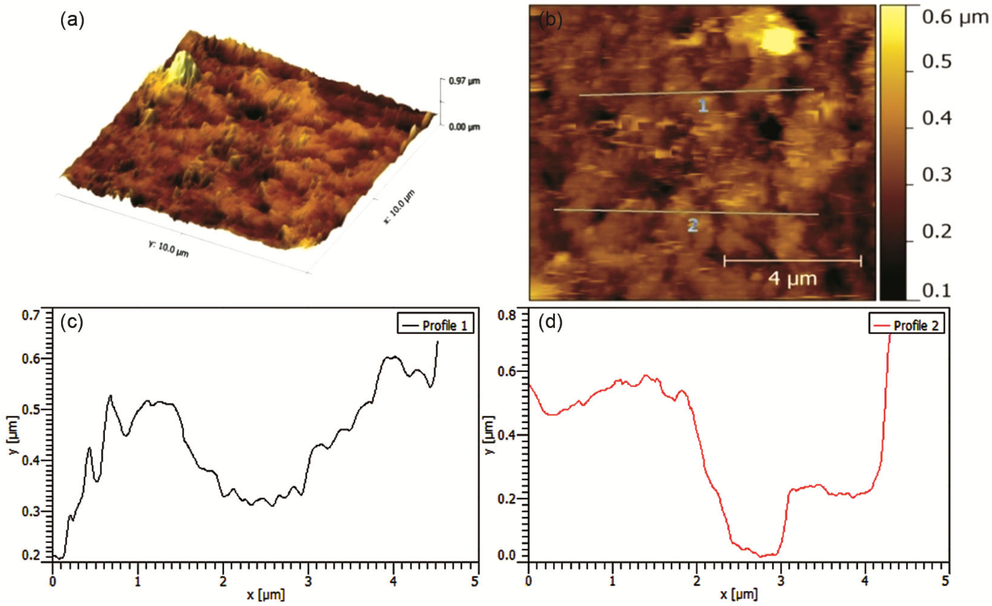

Fig. 5 — SFM images of mild steel in 1M HCl with labetalol (a) 3D; (b) Histogram analyses; (c) 2D and (d) Cross section line profile.

Table 5 — FT-IR values of inhibitors and its corresponding protective film formed on mild steel shown

Group Responsible	IR frequency of pure EPAB (cm^{-1})	Protective film (cm^{-1})
O-H	3341	3377
N-CH$_3$	2916	2939
C=O	3341	1681
C-N	1071	1056

for the mild steel surface under the presence and absence of labetalol in 1 M HCl. This study, the common irregularity rate and root mean square (rms) values was scrutinized for the plain carbon steel surface in the presence and absence of inhibitor molecule[38-42]. Also, the expected irregularity rate and rms (25.0328 nm) values were trim down in the existence of inhibitor molecule attributable to the shield layer formation on the plain carbon steel surface in an acidic medium (1 M HCl). Even though, the rms value (169.835 nm) was increased for the plain carbon steel surface in non-existence of labetalol molecule at 1 M HCl. As a result, fascinatingly a homogeneity layer is produced on the metal surface in the presence of labetalol molecule, which protects the mild steel plate from the corrosive nature[43-47].

FT IR Spectroscopic studies

The FT IR spectrum values are displayed in Table 5 for the labetalol and the protecting layer. The characteristic bands show at 2916 cm^{-1} (N-CH$_3$), 1656 cm^{-1} (C=O), 3341 cm^{-1} (O-H) and 1071 cm^{-1} (amide C-N). Herein, it was observed the IR bands for the protecting layer are 2939 cm^{-1} (N-CH$_3$), 1681 cm^{-1} (C=O), 3377 cm^{-1} (O-H) and 1056 cm^{-1} (amide C-N). From the findings notably, the O-H and N-CH$_3$ bands values were increased simultaneously the other bands C=O and amide C-N were decreased in the IR spectrum [48-52] revealed Table 5.

Conclusion

From those mentioned above, our remarkable findings are presented below,

- The mass loss results suggested the expired drug molecule labetalol act as an excellent corrosion inhibiting agent.
- From the electrochemical and impedance study, the labetalol molecule acts as a diversifying corrosion inhibitor.
- From the FTIR spectrum shows, the inhibitor is formed a shielding layer on top of the mild steel plate surface.
- The inhibitor molecule has been adsorbed on metal surface; the results are shown in SEM and SFM techniques.
- Molecular quantum mechanics calculations are revealed for the labetalol donated electrons to the metal plate.

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