

Expired atorvastatin drug as corrosion inhibitor for mild steel in hydrochloric acid solution

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Abstract The application of expired drugs as corrosion inhibitors provides a cost effective and environmentally benign alternative to otherwise tedious and costly disposal/ degradation process. In this context, we herein investigate the use of expired atorvastatin (EA) for corrosion inhibition of mild steel in 1 M HCl solution using weight loss, electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization (Tafel) methods. Fresh atorvastatin (FA) drug was also used for above studies for comparison purpose to understand whether there is any significant difference between the inhibition efficiency of the two after the expiration date of the drug. EIS analysis shows an increase in polarization resistance due to the adsorbed inhibitor molecules on metal surface. Potentiodynamic polarization indicates that both the EA and FA act as mixed-type inhibitors but predominantly behave as cathodic inhibitors. The adsorption of EA and FA on mild steel surface follows the Langmuir adsorption isotherm. SEM shows a smoother surface of mild steel in the presence of FA and EA drug in acidic solution. Both the fresh drug and its expired counterpart showed almost similar results in all the studies, thereby verifying the validity of the expired atorvastatin drug as a novel and efficient corrosion inhibitor for mild steel.

Keywords Atorvastatin · Mild steel · Weight loss · Electrochemical measurements · Adsorption

Introduction

Since the onset of industrial revolution, mild steel has been used as an alloy for a number of structural and industrial applications [1]. Acid solutions are used in various industries during acid pickling, acid descaling, industrial cleaning and oil-well acidization, etc. [2]. Acidic media results in a uniform corrosion of mild steel with pitting at high concentrations of acid [3–6]. The use of inhibitors is one of the most proficient methods for protection of metals from corrosion in acid medium. Organic compounds containing N, O, S heteroatoms and π electrons in their molecules are considered as effective corrosion inhibitors [2–5]. The inhibitor molecules form a protective film on metal surface that prevents corrosion [7]. Nowadays, researchers are mainly focusing on the use of non-toxic and “green” corrosion inhibitors, e.g., plant extracts and drugs to obviate the harmful effect of chemicals on environment [8–10]. Because of their non-toxic characteristics [18] and negligible negative impacts on the aquatic environment [19], drugs (chemical medicines) seem to be the ideal candidates to replace traditional toxic corrosion inhibitors [9]. A number of studies are available describing the application of drugs as efficient corrosion inhibitors [9–17].

However, most of the pharmaceutically active substances are far more costly than the organic inhibitors presently employed. It is reported that the active constituent of a drug degrades only infinitesimally and more than 90% of the drugs maintain stability long time after the expiration date [20]. Physicians, however, never recommend the practice of administering a medicine past its expiration date. Hence, the only possible fate an outdated drug can have is either a trashcan or worse, a toilet flush after either of which it comes into direct contact with an environment where it can either get exposed to sunlight or

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moisture or both. This situation is most likely to induce an uncontrolled change in the chemical constituents of the drug, e.g., degradation, impurity formation or change in dissolution profile, etc. Worse part is, unlike the known industrial waste effluents, since the origin of the influx of an outdated drug in the environment is unknown, its course also becomes unpredictable. Hence, once a well-known and acknowledged biocompatible substance may directly get converted to a potential biohazard.

In this context, the use of expired drugs as corrosion inhibitors can not only reduce environmental pollution, but can also lead to a reduction in the disposal and degradation costs of expired drugs. Atorvastatin is a member of the drug class known as statins, which are used principally as a lipid-lowering agent and for prevention of issues associated with cardiovascular disease. Atorvastatin, marketed under the trade name Lipitor manufactured by Pfizer, is among the most highly prescribed and one of the top selling drugs in the world [21] and hence is highly likely to enter the environment and cause contamination.

Hence, prompted by the above observations, the objective of the present study is to investigate the use of the expired atorvastatin drug as a novel material for corrosion inhibition of mild steel. To validate the applicability of the expired drug for corrosion inhibition, a detailed comparison with its fresh counterpart is carried out to verify whether there is any significant difference in the corrosion inhibition behavior of fresh atorvastatin (FA) and expired atorvastatin (EA). The corrosion inhibition action of FA and EA was studied on mild steel in 1 M HCl solution using weight loss studies, potentiodynamic polarization and electrochemical impedance spectroscopy techniques.

Experimental

Materials

All the tests were performed on the mild steel (MS) coupons having the following composition (wt%): 0.076% C, 0.192% Mn, 0.012% P, 0.026% Si, 0.050% Cr, 0.023% Al, 0.123% Cu and balance Fe. MS strips were cut into dimensions of 2.5 cm × 2 cm × 0.025 cm for use in weight loss studies. For electrochemical studies, the MS coupons were cut into 8 cm × 1 cm × 0.025 cm sizes with an exposed area of 1 cm² (the rest being covered with epoxy resin) and were used as working electrode.

Corrosion Inhibitors

The fresh and expired atorvastatin (FA and EA) drug marketed under the trade name Lipitor was used for corrosion testing. The molecular formula of the drug is

(C₃₃H₃₅FN₂O₅) and its chemical structure is shown in Fig. 1. Different amounts of FA and EA were dissolved in acid solution to prepare the desired concentrations in ppm (parts per million).

Weight loss studies

The MS coupons having a rectangular size and dimensions as mentioned above were abraded with a series of emery papers (600–1200 grade) and then washed with distilled water. After weighing the MS coupons accurately, the specimens were immersed in a conical flask containing 100 mL of 1 M HCl in the absence and presence of different concentrations of FA and EA. The test solutions were kept in thermostat for 3 h followed by washing, drying and weighing. The corrosion rate (C_R) was computed from the following equation:

$$C_R(\text{mm/year}) = \frac{87.6W}{atD} \quad (1)$$

where W is the average weight loss of MS coupons, a represents the total surface area of one MS coupon, t is the immersion time (3 h) and D is the density of MS in g cm⁻³.

Electrochemical measurements

The electrochemical experiments were performed in a three-electrode cell assembly using a Potentiostat/Galvanostat G300-45050 (Gamry Instruments Inc., USA). Echem Analyst 5.0 software package was used for data fitting. A three-electrode assembly was prepared using MS coupon with an exposed area of 1 cm² as working electrode, platinum electrode as an auxiliary electrode, and a saturated calomel electrode (SCE) as a reference electrode. All potentials were measured versus SCE. Tafel curves were obtained by varying the electrode potential from -0.25 to +0.25 V versus open circuit potential at a scan rate of 1.0 mV s⁻¹. Electrochemical impedance spectroscopy measurements were carried out under potentiostatic condition in a frequency range of 100 kHz to

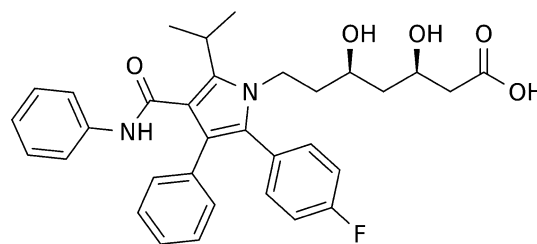
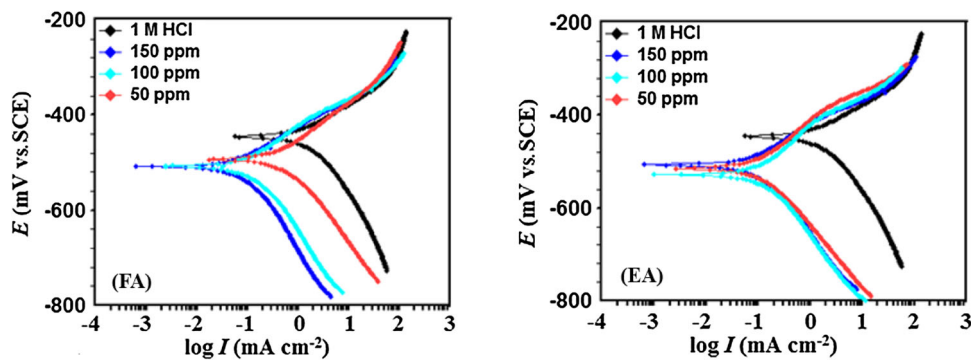


Fig. 1 Molecular structure of (3R,5R)-7-(2-(4-fluorophenyl)-5-isopropyl-3-phenyl-4-(phenylcarbamoyl)-1H-pyrrol-1-yl)-3,5-dihydroxyheptanoic acid (Atorvastatin)

Fig. 2 Polarization curves for MS in the absence and presence of different concentrations of FA and EA



0.01 Hz, with an amplitude of 10 mV AC signal. All experiments were performed after immersing the MS coupons in 1 M HCl in the absence and presence of different concentrations of inhibitor for 30 min.

Surface analysis

The surface morphology of MS coupons was investigated using SEM model FEI Quanta 200F scanning electron microscope at 1000 \times magnification. The MS coupons having 2.5 cm \times 2.0 cm \times 0.025 cm dimensions were abraded with emery paper (600–1200 grades) and then immersed in the absence and presence of inhibitors (FA, EA) at 150 ppm. Thereafter, MS coupons were taken out, washed with water and mechanically cut into 1 cm² for surface analysis.

Results and discussion

Electrochemical measurements

Potentiodynamic polarization measurements

The potentiodynamic polarization curves recorded over the MS coupons in the absence and presence of different concentrations of FA and EA in 1 M HCl are shown in Fig. 2. To get a detailed insight into the corrosion inhibition process, electrochemical parameters, i.e., corrosion potential (E_{corr}), corrosion current density (i_{corr}) and inhibition efficiency ($\eta\%$) values were determined from the corresponding Tafel plots and the obtained data are shown in Table 1. The inhibition efficiencies can be calculated from i_{corr} values using the following equation:

$$\eta\% = \frac{i_{\text{corr}} - i_{\text{corr(inh)}}}{i_{\text{corr}}} \times 100 \quad (2)$$

where i_{corr} and $i_{\text{corr(inh)}}$ are the corrosion current densities of MS in 1 M HCl in the absence and presence of inhibitor.

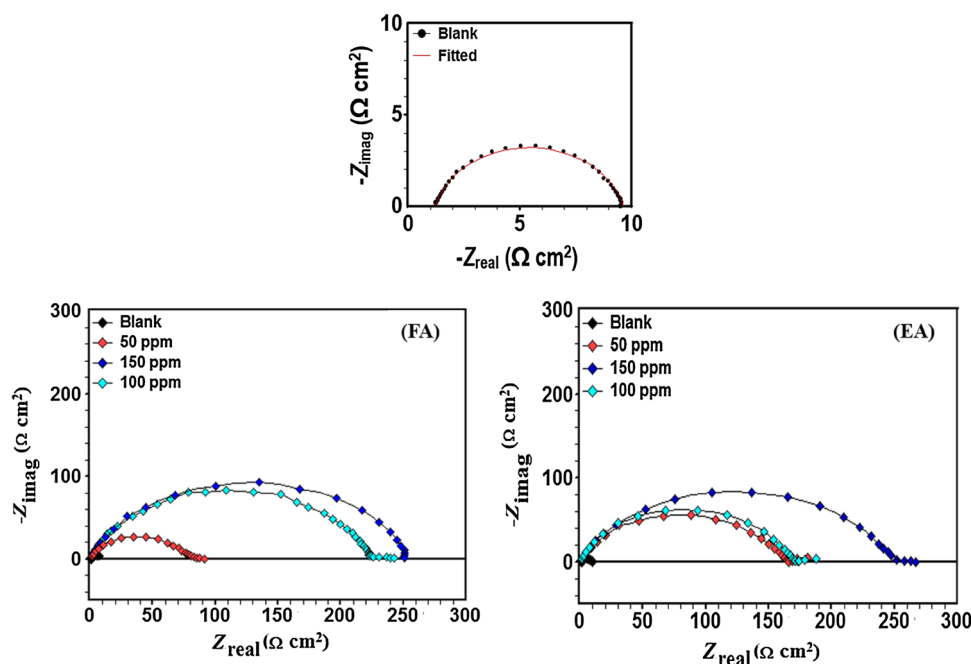
It can be observed from Fig. 2 that in the presence of the inhibitors, both the anodic and cathodic curves shift

Table 1 Polarization data for MS in the absence and presence of different concentrations of FA and EA

Inhibitor	Conc. (ppm)	i_{corr} ($\mu\text{A cm}^{-2}$)	E_{corr} (mV/SCE)	$\eta\%$
Blank		1390	−445	–
FA	50	471	−493	66.11
	100	58.7	−508	95.77
	150	22	−508	98.41
EA	50	164	−514	88.20
	100	121	−528	91.29
	150	12.7	−506	99.08

towards lower current density, indicating the suppression of both the cathodic and anodic reactions. This trend is also corroborated by the data of inhibition efficiencies in Table 1 and suggests the adsorption of inhibitor molecules on the surface of mild steel and the formation of a protective film. However, the shift in the cathodic branch is considerably more pronounced which confirms a greater effect of inhibitors on the suppression of hydrogen evolution [18]. On the other hand, the anodic part of the polarization curves exhibits a different trend altogether. It can be clearly seen from Fig. 2 that the inhibitors do not affect the corrosion rate at potentials more positive than -320 mV [22, 23]. This potential can be termed as desorption potential [23] and the results suggest that the corrosion inhibition process, under the present condition, is dependent on the electrode potential [22, 23]. The electrochemical behavior of the inhibitors above -320 mV may arise from a considerable dissolution of iron leading to desorption of the inhibitor film from the MS surface. Moreover, in the presence of the inhibitors, a pronounced shift in the E_{corr} values can be observed towards the cathodic direction which is indicative of the cathodic predominance of the inhibition process. However, the decrease in both the anodic and cathodic currents in the presence of inhibitors suggests that the FA and EA can be categorized as mixed-type inhibitors [23, 24]. The maximum inhibition efficiencies obtained for EA and FA are 99.08 and 98.41%, respectively, at 150 ppm.

Fig. 3 Nyquist plot for MS in the absence and presence of different concentrations of FA and EA



Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy (EIS) curves for MS in the absence and presence of FA and EA at different concentrations are shown in Fig. 3. The Nyquist plots show depressed semi-circles, having one capacitive loop. The analysis of Nyquist plots reveals that the corrosion process is mainly charge transfer controlled [19]. The diameter of the capacitive loops increases with increasing concentrations of inhibitors suggesting that both FA and EA act as efficient corrosion inhibitors for MS.

The Equivalent circuit model shown in Fig. 4 was used to analyze the Nyquist curves and it consists of R_s and CPE (constant-phase element) parallel to the R_p [25–28]. Here, the R_p represents the polarization resistance which consists of the charge transfer resistance (R_{ct}), double layer resistance (R_d), film resistance (R_f) and the resistance due to the accumulation of adsorbed molecules (R_a). The contributions of the adsorbed species can be visualized in the form of elongations in the low frequency region of the Nyquist loops [28–30]. The inhibition efficiency is calculated from polarization resistance (R_p) as follows:

$$\eta\% = \frac{R_{p(\text{inh})} - R_p}{R_{p(\text{inh})}} \times 100 \quad (3)$$

where $R_{p(\text{inh})}$ and R_p are the values of polarization resistance in the absence and the presence of inhibitor in 1 M HCl, respectively. An analysis of the impedance data shows that the R_p increases with increase in the concentration of inhibitors. A large value of R_p can be attributed to a slow corroding system, arising due to a decreased active

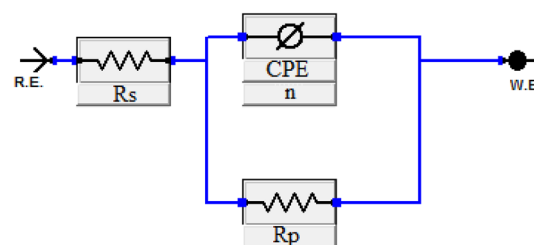


Fig. 4 Equivalent circuit used for simulation of data

surface area necessary for the corrosion reaction [23]. The inhibition efficiency obtained for EA and FA is 96.38 and 96.36% respectively.

To define the capacitance of the depressed Nyquist semi-circles, in the place of a pure capacitor, a non-ideal capacitor is introduced in the circuit (defined as constant-phase element: CPE) whose impedance is given by [31–33]:

$$Z_{\text{CPE}} = Y_o^{-1} (j\omega)^{-n} \quad (4)$$

where Z_{CPE} is the impedance of CPE, Y_o is the CPE coefficient (reciprocal of impedance and also known as admittance) and ω is the angular frequency given by $\omega = 2\pi f$ (having units in rad s^{-1}). The double layer capacitance (C_{dl}) can be evaluated as follows:

$$C_{dl} = \frac{Y_o \omega^{n-1}}{\sin(n(\pi/2))} \quad (5)$$

where ω is given by $\omega_{\text{max}} = 2\pi f_{\text{max}}$ at which the imaginary part of the impedance ($-Z_{\text{imag}}$) is maximum and other symbols are as defined above. The impedance parameters such as R_s (solution resistance), R_p and C_{dl} (double layer

Table 2 Electrochemical impedance parameters and corresponding efficiencies of MS in the absence and presence of different concentrations of FA and EA

	Conc. (ppm)	R_s (Ω)	R_p (Ωcm^2)	C_{dl} (μFcm^{-2})	$\eta\%$
Blank		1.02	9.0	106	–
FA	50	0.85	79.3	95	88.65
	100	0.55	223.2	72	95.96
	150	0.66	247.3	69	96.36
EA	50	0.79	161.3	64	94.42
	100	0.68	168.4	62	94.65
	150	0.99	249.2	51	96.38

capacitance) calculated from these plots are given in Table 2.

It can be observed that an increase in the concentration of inhibitors causes an increase in R_p values and a corresponding decrease in C_{dl} . This situation was a result of increasing surface coverage by the inhibitor, leading to an increase in $\eta\%$. The thickness of the protective layer of inhibitor δ_{org} can be related to the C_{dl} as follows:

$$C_{dl} = \frac{\epsilon_0 \epsilon_r}{\delta_{org}} \quad (6)$$

where ϵ_0 is the vacuum dielectric constant and ϵ_r is the relative dielectric constant. The decrease in the values of C_{dl} might result from the lowering of local dielectric constant or from the increase in thickness of the electrical double layer, which suggests that the inhibitor molecules function by adsorbing at the metal/solution interface [28, 33]. Thus, the observed decrease in the C_{dl} values is caused by the gradual replacement of water molecules by the adsorption of inhibitor molecules on the metal surface, which decreases the metal dissolution.

Bode and phase angle plots for FA and EA are shown in Fig. 5. In case of an ideal capacitor, the values of Bode slope and phase angle are -1° and -90° , respectively. The slope and phase angle values for blank solution are -0.53° and -40.40° and in the presence of FA and EA are 0.76° , 0.80° , and 68.28° , 68.95° at 150 ppm, respectively. The deviation in the values of Bode slope and phase angle in the

presence of inhibitor suggests the capacitive performance of the inhibited system [34].

Weight loss studies

Effect of inhibitor concentration

The data obtained from weight loss measurements for MS in 1 M HCl in the absence and presence of different concentrations of FA and EA are summarized in Table 3. It can be observed from the results that the inhibition efficiency increases on increasing the concentration of inhibitor which can be attributed to the adsorption of inhibitor molecules on MS surface [35]. EA shows the maximum inhibition efficiency 97.05% at 150 ppm. The inhibition efficiency ($\eta\%$) is calculated as follows:

$$\eta\% = \frac{C_R - {}^{\text{inh}}C_R}{C_R} \times 100 \quad (7)$$

where C_R and ${}^{\text{inh}}C_R$ are the corrosion rates of MS in the absence and presence of the inhibitors, respectively.

Adsorption isotherm

To understand the adsorption behavior of inhibitors on MS surface, the experimental data were tested on several adsorption isotherms. The best fit was obtained from Langmuir isotherm which assumes that a solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species [36]. A plot of C/θ vs C (concentration of inhibitor) resulted in a straight line with regression coefficient values close to 1 as shown in Fig. 6,

The surface coverage (θ) is calculated according to the following equation:

$$\theta = \frac{C_R - {}^{\text{inh}}C_R}{C_R} \quad (8)$$

where C_R and ${}^{\text{inh}}C_R$ are the corrosion rates of MS in the absence and presence of inhibitor, respectively. The values of equilibrium constant K_{ads} and the standard free energy of adsorption ΔG_{ads}^o are calculated from the equations:

Fig. 5 Bode-impedance and Phase angle plots for MS in the absence and presence of different concentrations of FA and EA

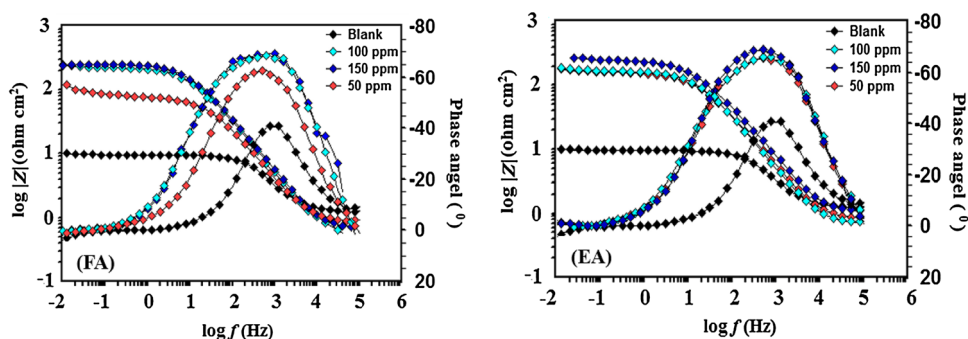
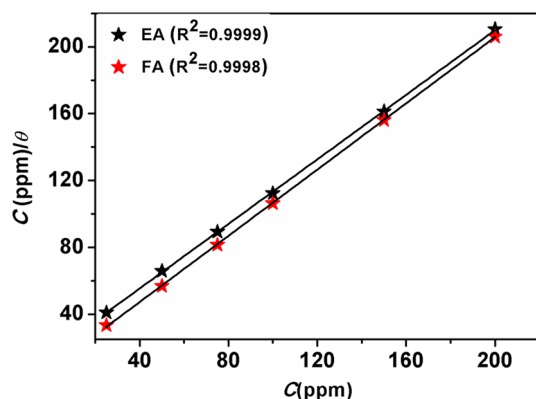


Table 3 Weight loss data for MS in the absence and presence of different concentrations of FA and EA

	Conc. (ppm)	C_R (mm year ⁻¹)	Surface coverage (θ)	$\eta\%$
Blank	–	77.9	–	–
FA	25	24.1	0.61	61.76
	50	14.8	0.76	76.47
	75	10.0	0.84	84.11
	100	6.6	0.89	89.41
	150	4.0	0.93	93.52
	200	2.9	0.95	95.29
EA	25	15.5	0.75	75.29
	50	7.0	0.88	88.82
	75	4.4	0.92	92.94
	100	3.7	0.94	94.11
	150	2.2	0.96	96.47
	200	1.8	0.97	97.05

**Fig. 6** Langmuir adsorption isotherm plots for MS at different concentrations of FA and EA

$$K_{ads} = \frac{\theta}{C(1-\theta)} \quad (9)$$

$$\Delta G_{ads}^{\circ} = -RT \ln(55.5K_{ads}) \quad (10)$$

The value 55.5 in the above equation represents the concentration of water in solution in mol L⁻¹. It is reported that the ΔG_{ads}° values of around -20 kJ mol⁻¹ suggest physical adsorption and around -40 kJ mol⁻¹ suggest chemical adsorption. The values of ΔG_{ads}° for FA and EA at optimum concentration are -38.15 and -39.51 kJ mol⁻¹, respectively, indicating that the adsorption process of the studied compounds on MS surface involves both physical and chemical adsorption [37]. The proposed mechanism of inhibition is discussed in Sect. 3.4.

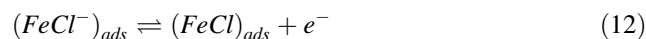
Surface characterization

The scanning electron microscopy (SEM) images of MS coupons in the absence and presence of inhibitors are shown in Fig. 7. The surface of the MS coupon recovered

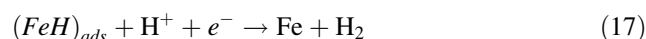
from the HCl solution without inhibitor displays an excessively rough surface showing pronounced striations and isolated furrows due to severe damage from corrosion (Fig. 7a). On the other hand, the surfaces of MS coupons after immersing in acid solution in the presence of optimum concentration of FA and EA show a comparatively smoother morphology (Fig. 7b, c, respectively). In acid solution, the inhibitor molecules are adsorbed on the metal surface and form a protective smooth film on metal surface. The adsorbed layer of inhibitor isolates the metal surface from the surrounding corrosive medium by forming a barrier between metal/solution interfaces [38] and hence mitigates the corrosion.

Mechanism of corrosion and inhibition

In hydrochloric acid solution, the corrosion of iron and steel takes place via the following proposed mechanism [39, 40]. According to this mechanism, the anodic dissolution of iron occurs as follows:



The cathodic evolution of hydrogen is given as:



The inhibitor molecules can get adsorbed on the MS surface through the proposed inhibition mechanism as shown in Fig. 8.

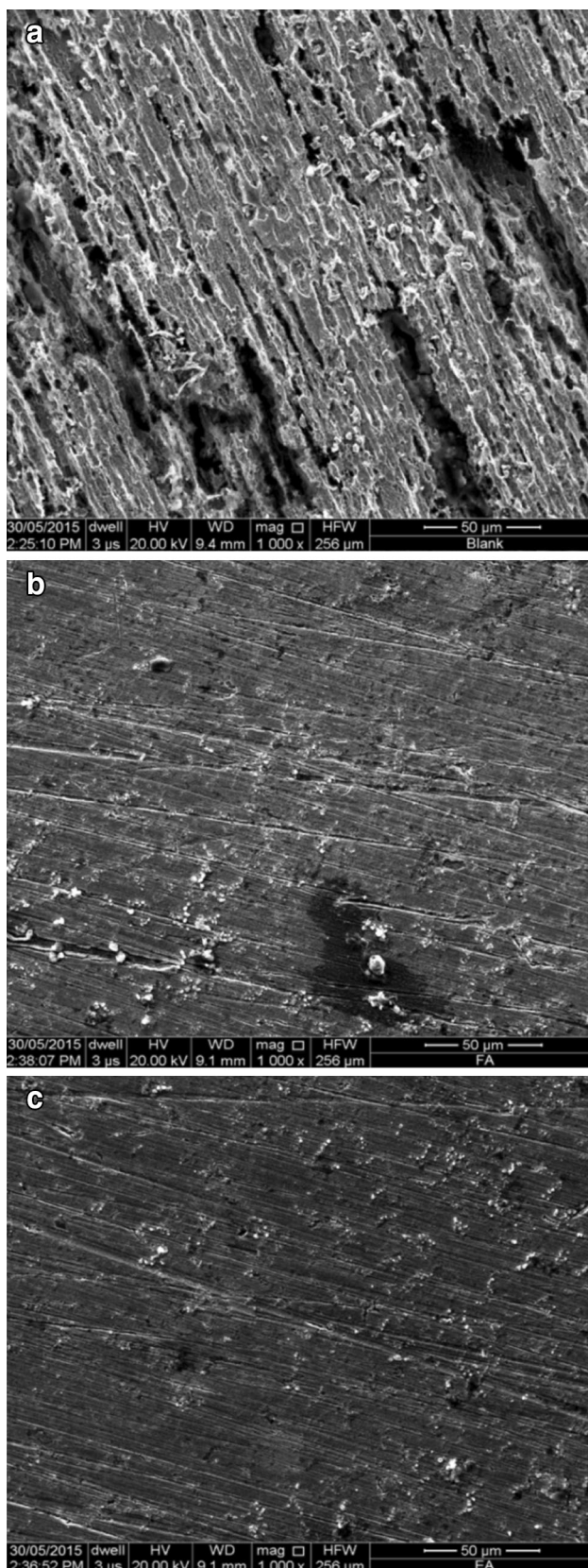


Fig. 7 SEM micrographs in the absence (a) and presence of FA (b) and EA (c) at 150 mg L^{-1}

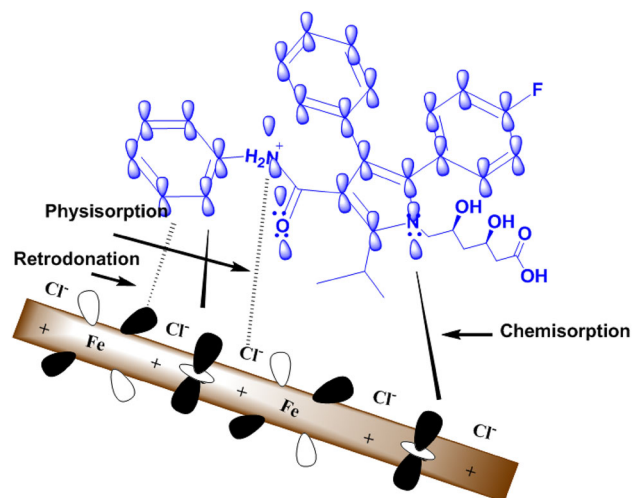
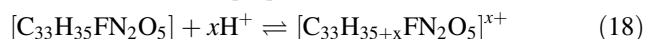


Fig. 8 Pictorial representation of adsorption of atorvastatin drug on MS surface in 1 M HCl

1. In acid solution, inhibitor molecules exist in protonated or neutral form [11]:



Protonated molecules are adsorbed on the MS surface through electrostatic interaction between already adsorbed Cl^- ions on MS surface (physical adsorption). The protonated inhibitor molecules then begin competing with H^+ ions for electrons on MS surface. The cationic form of the inhibitor molecules, after accepting electrons from the metal surface, returns to its neutral form.

2. The presence of heteroatoms having free lone pair electrons promotes chemical adsorption.
3. The accumulation of electrons on the surface of MS makes it more negative. To relieve this excess negative charge from the surface of MS, the electrons from the d-orbital of Fe might get transferred to vacant π (antibonding) orbital of inhibitor molecules (retrodonation), thereby strengthening the adsorption of inhibitor on the metal surface [23, 41, 42].

A comparative data showing corrosion inhibition performance of some of the other expired drugs reported previously is illustrated in Table 4. The present drug shows considerably significant corrosion inhibition efficiency compared to other drugs. Thus, it can be clearly understood that the present drug, i.e., expired atorvastatin can be used for corrosion inhibition application with promising results. The high corrosion inhibition efficiency of the drug can be attributed to the presence of a number of phenyl rings, functional groups as well as nitrogen together in the compound.



Table 4 Comparative chart listing the performances of some expired drugs as corrosion inhibitors

Drug	Medium of testing	Metal surface	$\eta\%$	References
Asthalin	1 M HCl	Mild steel	94.76	[43]
Carbamazepine	0.1 M H ₂ SO ₄	Carbon steel	90	[44]
Paracetamol	0.25 M Acetic acid-0.25 M sodium acetate buffer	Carbon steel	85	[44]
Voltaren	1 M HCl	Aluminum	89.7	[45]
1-Phenytol	1 M HCl	Carbon steel	79.1	[46]
Amlodipine Besylate	1 M HCl	Low Carbon steel	94.3	[47]
2-(2, 6-dichloranilino) phenyl acetic acid	1 M HCl	Mild steel	87.5	[48]
Ranitidine	1 M HCl	Mild steel	90.0	[49]
Lupicof	1 M HCl	Mild steel	70.86	[50]
Amlodipine Besylate	1 M HCl	Low Carbon steel	83.5	[51]
Atorvastatin	1 M HCl	Mild steel	96.38	Present work

Conclusions

Both FA and EA exhibit good inhibition efficiency against the corrosion of mild steel. EIS studies showed that the diameter of capacitive loops and, hence, the polarization resistance (R_p) increased with increase in concentration of FA and EA. Polarization studies indicate that FA and EA act as mixed-type inhibitors. The adsorption process of inhibitor molecules on the MS surface in 1 M HCl solution follows Langmuir isotherm. The spontaneity of the adsorption is supported by the negative values of ΔG_{ads}^o . The noteworthy feature of this investigation is that both EA and FA display similar corrosion inhibition efficiency at as low as 150 ppm. This suggests that the EA, which is the expired version of FA, can be used as a novel material for corrosion inhibition purpose. Thus, this study presents a green and cost-effective alternative in place of fresh atorvastatin drug.

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