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Application of expired drugs in corrosion inhibition of mild steel

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Abstract

Present work deals with the investigation of corrosion inhibition of mild steel using two expired drugs namely Atenolol and Nifedipine in 1 M HCl solution. Their inhibition properties were evaluated using electrochemical, scanning electron microscopy (SEM) and DFT methods. Atenelol and Nifidipine showed efficiency of 91.30 and 93.91% at low concentration of 200 ppm respectively. Polarization study reveals that the expired drugs inhibit corrosion of mild steel by suppressing both anodic and cathodic reactions occurring on the mild steel surface thus acting as mixed type inhibitors. EIS study shows that the investigated drug increases the polarization resistance by adsorbing on the metal/electrolyte interface. The electrochemical results were well supported by SEM as well as DFT study.

Keywords: Expired Drugs, Mild steel, Acid corrosion, SEM, DFT

Introduction

The global loss due to corrosion is about $2.5 trillion, which is near 3.5% of the world's GDP (NACE March 2016). Thus Corrosion inhibition study is a matter of theoretical as well as practical importance. Mild steel is commonly used for a wide range of applications in many industries due to its very good mechanical property but it has poor corrosion resistance especially in acidic medium.[(1)] Hydrochloric acid is widely used for different applications like pickling, descaling, acid cleaning, and oil well acidizing etc.[(2)] During these applications when mild steel comes in contact with HCl it suffers severe corrosion. To combat his problem, use of organic corrosion inhibitor is regarded as the best technique due to its ease of application as well as cost effectiveness.[(3)] However, most of the compounds that have been tested of being used as inhibitor are either toxic in nature or very expensive. So there existed a need to identify such inhibitors which are non-toxic, cheap and shows good inhibition efficiency at low concentration.

In this view, drugs constitute a potential class of corrosion inhibitors due to the presence of heteroatoms in their structure and their green nature.[(4)] In a recent review, Gece has described 17 classes of drugs that can be used as corrosion inhibitors for various metals and alloys in corrosive environments like HCl, H_2SO_4, H_3PO_4 and NaCl.[(5)] However, most of the pharmaceutical drugs are much more expensive than the organic inhibitors which are currently used in industries. Thus using fresh drug as a corrosion inhibitor is not economically viable.[(6)] Therefore, it is thought worthwhile to investigate the corrosion inhibition properties of expired drugs which are of no use. It is well reported that drugs retain at least 90% of its original potency even after expiry date but their use for the medicinal purpose is restricted due to the professional restrictions and liability concerns.[(6,7)] Use of expired drugs as a corrosion inhibitor can solve two major environmental and economical problems: limitation of environmental pollution with pharmaceutically active compounds and reduction of the disposal costs of expired drugs.

In view of above observation, it is thought worthwhile to investigate the corrosion inhibition properties of two expired drugs namely Atenolol (ATL) and Nifedipine (NDP) (Fig. 1) on mild steel in 1 M HCl solution. Atenolol is a drug used for treating cardiovascular diseases (antagonist) whereas Nifedipine is a medication used for managing angina, high blood pressure, Raynaud's phenomenon, and premature labor. Karthik *et al*. have studied the corrosion inhibition property of fresh Atenolol drug and got 93.8% efficiency at 300 ppm concentration[8] whereas no literature is present on the corrosion inhibition efficiency of Nifedipine drug. The corrosion inhibition behavior of ATL and NDP was studied using electrochemical, SEM and DFT techniques.

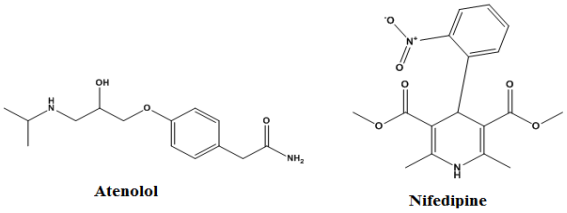

Fig. 1: Chemical Structure of investigated drugs

Experimental section

Corrosion Inhibitor: Two of the expired drugs namely atenolol and nifedipine were taken from the local market and used as inhibitor according to a method described earlier.[(2)] The molecular structures of the drugs are shown in Fig. 1.

Materials and Chemicals: The Mild steel specimens with chemical composition (wt %): C = 0.076, Mn =

0.192, P = 0.012, Si = 0.026, Cr = 0.050, Al = 0.023 and balance Fe. was used for chemical, electrochemical and surface experiments. The specimens' size was 8 × 1 × 0.025 cm for electrochemical experiments having exposed area 1 cm^2. The aggressive test solution of 1M HCl was prepared by dilution of analytical grade HCl (37%) with double distilled water.

Electrochemical Experiment: Electrochemical measurements were performed by the method as described previously.[9] The electrochemical impedance measurements (EIS) were performed on mild steel specimens in the frequency range of 100 kHz to 0.00001 kHz under potentiostatic conditions using an AC at open circuit potential with amplitude of 10 mV peak to peak. The charge transfer resistance was calculated from Nyquist plot from which corrosion inhibition efficiency was calculated using following equation:

$$\eta\% = \frac{R_p^i - R_p^0}{R_p^i} \times 100 \qquad (4)$$

Where R^i_p and R^0_p are the polarization resistance in presence and absence of expired drugs in 1 M HCl solution respectively.

The Potentiodynamic polarization studied were performed on mild steel specimens by automatically changing the electrode potential from −250 to +250 mV/ SCE versus open circuit potential at a scan rate of 1 mVs^{-1}. The corrosion current density (i_{corr}) was calculated by extrapolating the linear segments of the cathodic and anodic Tafel slopes from which corrosion inhibition efficiency was calculated using following equation:

$$\eta\% = \frac{i_{corr}^0 - i_{corr}^i}{i_{corr}^0} \times 100 \qquad (5)$$

where, i^0_{corr} and i^i_{corr} are the corrosion current densities in absence and presence of drugs.

SEM study: The mild steel was immersed in1M HCl solution in absence and presence of the optimum concentration of the drugs for 3h immersion time. Thereafter, the mild steel specimens were taken out, washed with double distilled water, dried and finally analyzed by SEM and EDX method. The SEM study was carried out using a Ziess Evo 50 XVP instrument at an accelerating voltage of 5 kV and 500 × magnification.

Result and Discussion

Electrochemical measurements

Polarization study: The Tafel polarization curves obtained for mild steel in absence and presence of expired drugs at optimum concentration are shown in Fig. 2(a). Table 1 list the important polarization parameters i.e., corrosion potential (E_{corr}), cathodic (β_c) and anodic (β_a) Tafel slopes, corrosion current density (i_{corr}), surface coverage (θ) and the inhibition efficiency (η %) for mild steel corrosion with and without inhibitor. The results showed that in presence of inhibitor corrosion current density is decreased due to formation of protective film.[10] It is also observed that the addition of inhibitor retards both cathodic and anodic reactions. However, the cathodic reactions are comparatively more affected than the anodic reactions suggesting that investigated drugs are mixed type inhibitors and predominantly act as cathodic inhibitors.[11]

Table 1: Tafel Polarization parameters for mild steel in 1 M HCl solution in absence and presence of optimum concentration of expired drugs

inhibitor	E_{corr} (mV/SCE)	i_{corr} (μAcm^{-2})	β_a (mV/dec)	β_c (mV/dec)	θ	η(%)
Blank	-445	1150	70.5	114.6	----	----
ATL	-492	103	97.8	187.4	0.9104	91.04
NDP	-504	79	78.8	118.2	0.9314	93.13

Electrochemical impedance spectroscopic study: Fig. 2(b) represents the Nyquist plots for mild steel in 1M HCl solution in absence and presence of optimum concentration of the drugs. From the Fig. 2(b) it could be observed that Nyquist plots give similar appearance with and without inhibitors suggesting that studied drugs inhibits mild steel corrosion without affecting the mechanism of corrosion process.[10] The Nyquist plot consists of a depressed semicircle at high frequency region which is characteristics response of solid metal electrodes in the corrosion process.[2] Impedance parameters such as R_p, n, C_{dl}, θ and η% were derived from Nyquist plot by implying equivalent circuit shown in Fig. 2(c) and given in Table 2.

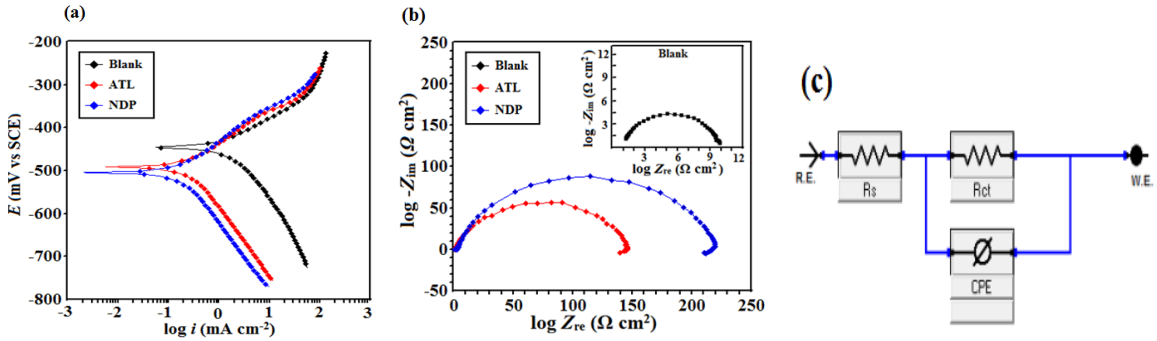

Fig. 2 (a-c): (a) Potentiodynamic polarization plots (b) Nyquist plots for mild steel in 1 M HCl solution in the absence and presence of an optimum concentration of inhibitor (c) Equivalent circuit used to fit the EIS data for mild steel in 1 M HCl solution

The result showed that addition of inhibitor causes significant increase in the R_p value suggesting that inhibitors retard the charge transfer reaction and corrosion occurring on the mild steel surface by forming protective film on the surface.[12] From the results it is also clear that values of C_{dl} is lower in the presence of inhibitors. The decrease in C_{dl} value is due to decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer.

Table 2: Electrochemical impedance parameters obtained from EIS measurements for mild steel in 1 M HCl solution in absence and presence of optimum concentration of expired drugs

Inhibitor	R_s (Ωcm^2)	R_{ct} (Ωcm^2)	C_{dl} ($\mu F cm^{-2}$)	n	θ	η%
Blank	1.12	9.58	106.21	0.827	---	--
ATL	0.98	143.9	61.98	0.849	0.9329	93.29
NDP	1.17	219.6	50.76	0.839	0.9561	95.61

SEM analysis: The SEM micrographs for mild steel in absence and presence of drugs are shown in Fig. 3(a-c). Fig. 3(a), represents the SEM micrograph in absence of the drugs which is severely corroded due to attack of acid on mild steel. However, in presence of drugs (Fig. 3(b-c)) the surface morphology of mild steel is remarkably improved. This observation further supports the protection of mild steel by adsorption of ATL and NDP.

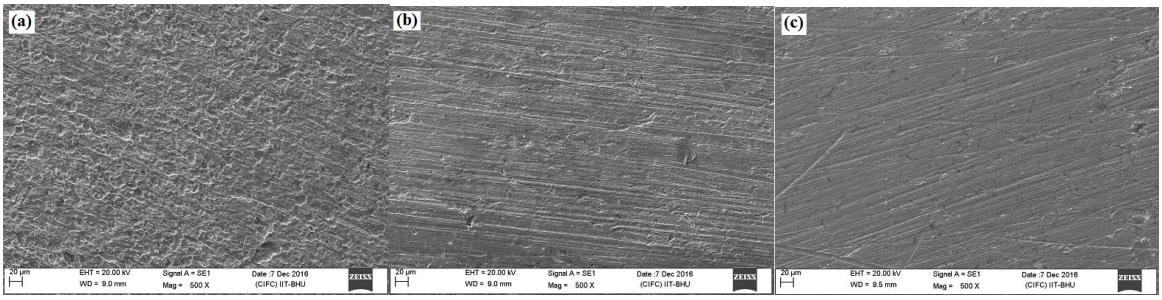

Fig. 3(a-c): SEM image of mild steel surface after 3h immersion (a) without inhibitor (b) with 200 ppm ATL (c) with 200 ppm NDP

Quantum Chemical calculation: The optimized molecular structures and corresponding highest occupied frontier molecular orbital (HOMO) and lowest unoccupied frontier molecular orbital (LUMO) obtained for neutral form of studied expired drugs are given in Fig. 4. The quantum chemical calculations parameters are given in Table 3.

Table 3: Quantum chemical parameters of the investigated expired drugs

Inhibitor	E_{HOMO} (Hartree)	E_{LUMO} (Hartree)	ΔE (Hartree)	σ	η
ATL	-0.17531	-0.00404	0.17127	0.0856	11.682
NDP	-0.20467	-0.03477	0.1699	0.08495	11.771

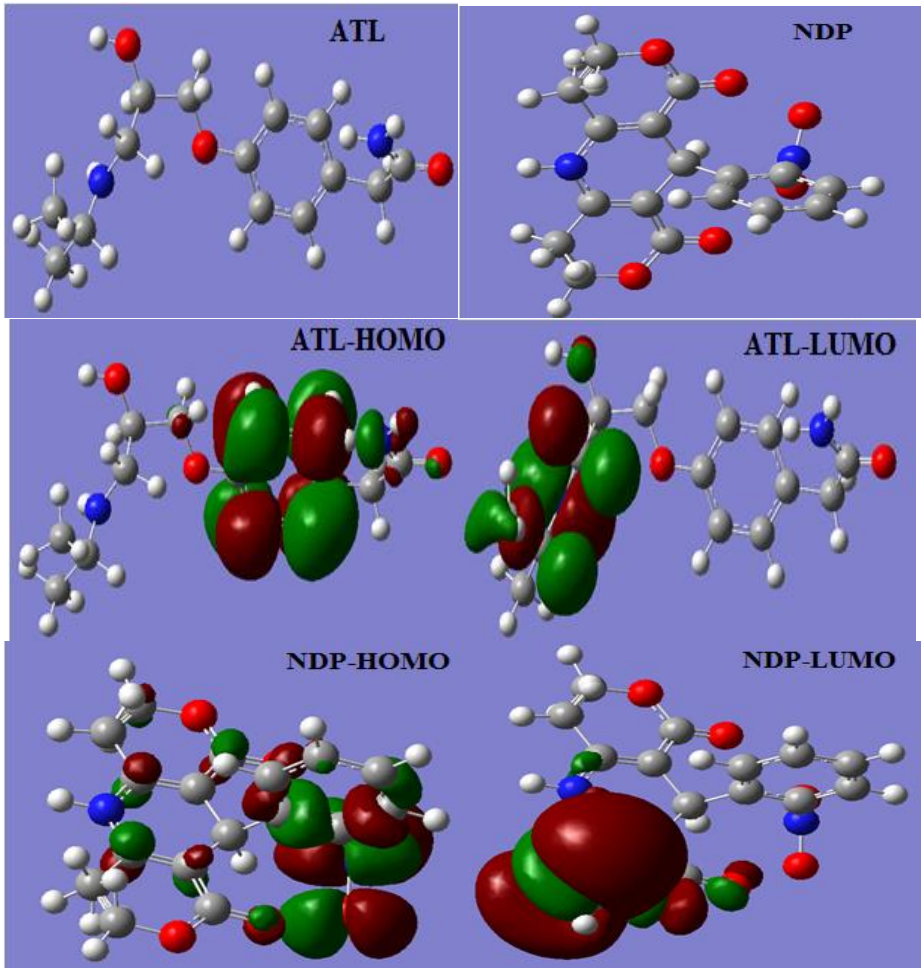

Fig. 4: Optimized molecular structure and the frontier molecular orbitals HOMO and LUMO of ATL and NDP

The HOMO frontier molecular electron distribution gives significant information about the sites or segments of the studied molecules which can act as electron donor during the adsorption process.[13] The energy difference of frontier molecular orbitals (E_{LUMO} - E_{HOMO}) can be used to predict the theoretical reactivity and thereby their relative inhibition property of the studied molecules. Obviously, a molecule with low energy band gap (low ΔE) associated with high chemical reactivity and high inhibition efficiency.[14] In our case, the values of ΔE for NDP is lower than that of ATL therefore associated with better adsorption on metal surface and thus higher inhibition efficiency. Several other parameters such as global hardness (σ) and global softness (η) were calculated and discussed in the present study in order to provide more insight about the interaction between inhibitor molecules and metal surface. Generally, an inhibitor with lower value of global hardness and higher value of softness is associated with high chemical reactivity and thereby exhibits high inhibition efficiency.[15] In our present investigation, NDP has the lower global hardness and higher value of softness than the ATL. This trend of hardness and softness are in accordance to the order of inhibition efficiency obtained experimentally.

Conclusion

The studied expired drugs were found to act as effective and green corrosion inhibitors for mild steel in 1M HCl solution and their inhibition efficiency related with concentration and chemical structure. Among the studied drugs, the NDP shows the best inhibition efficiency of 93.91% at 200 mgL^{-1} concentration. The potentiodynamic study reveals that in presence of drugs the cathodic reaction appears to be much affected than the anodic reaction suggesting that studied drugs act as predominantly cathodic inhibitors. SEM analyses validate the weight loss and electrochemical results. The experimental and theoretical calculations were in good agreement.

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References

1. Odewunmi NA, Umoren SA, Gasem ZM. Utilization of watermelon rind extract as a green corrosion inhibitor for mild steel in acidic media. J Ind Eng Chem 2005;21:239–247.
2. Gupta NK, Quraishi MA, Verma C, Mukherjee A K. Green Schiff's bases as corrosion inhibitors for mild steel in 1 M HCl solution: experimental and theoretical approach. RSC Adv 2016;6:102076–87.
3. Ahamad I, Prasad R, Quraishi MA. Thermodynamic, electrochemical and quantum chemical investigation of some Schiff bases as corrosion inhibitors for mild steel in hydrochloric acid solutions. Corros Sci 2010;52:933–42.
4. Ahamad I, Prasad R, Quraishi MA. Inhibition of mild steel corrosion in acid solution by Pheniramine drug: Experimental and theoretical study. Corros Sci 2010;52:3033–41.
5. Gece G. Drugs: a review of promising novel corrosion inhibitors. Corros Sci 2011;53:3873–98.
6. Vaszilcsin N, Ordodi V, Borza A. Corrosion inhibitors from expired drugs. Int J Pharm 2012;431:241– 4.
7. Gebhart F, Drug Topics, October 10, 2005.
8. Karthik G, Sundaravadivelu M. Studies on the inhibition of mild steel corrosion in hydrochloric acid solution by atenolol drug. Egypt J Petroleum 2016;25:183–91.
9. Gupta NK, Verma C, Quraishi MA, Mukherjee AK. Schiff's bases derived from L-lysine and aromatic aldehydes as green corrosion inhibitors for mild steel: Experimental and theoretical studies. J Mol Liq 2016;215:47–57.
10. Verma C, Quraishi MA, Gupta NK. 2-(4-{[4-Methyl-6-(1-methyl-1H-1,3-benzodiazol-2-yl)-2-propyl-1H-1,3-benzodiazol-1-yl] methyl}phenyl) benzoic acid as green corrosion inhibitor for mild steel in 1 M hydrochloric acid. Ain Shams Eng J 2016; xxx, xxx–xxx.
11. http://dx.doi.org/10.1016/j.asej.2016.07.003.
12. Boumhara K, Tabyaoui M, Jama C, Bentiss F. Artemisia Mesatlantica essential oil as green inhibitor for carbon steel corrosion in 1 M HCl solution: Electrochemical and XPS investigations. J Ind Eng Chem 2015;29:146–55.
13. Haque J, Srivastava V, Verma C, Quraishi MA. Experimental and quantum chemical analysis of 2-amino-3-((4-((S)-2-amino-2-carboxyethyl)-1H-imidazol-2-yl)thio) propionic acid as new and green corrosion inhibitor for mild steel in 1 M hydrochloric acid solution. J Mol Liq 2017;225:848–55.
14. Yıldız R. An electrochemical and theoretical evaluation of 4,6-diamino-2-pyrimidinethiol as a corrosion inhibitor for mild steel in HCl solutions. Corros Sci 2015;90:544–53.
15. Raja PB, Qureshi AK, Rahim AA, Osman H, Awang K. Neolamarckia cadamba alkaloids as eco-friendly corrosion inhibitors for mild steel in 1 M HCl media, Corros Sci 2013;69:292–301.
16. Dasami PM, Parameswari K, Chitra S. Corrosion inhibition of mild steel in 1M H_2SO_4 by thiadiazole Schiff bases. Measurement 2015;69:195–201.