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Investigation of some expired antibiotic drugs: Effect on the corrosion inhibition of mild steel in 0.1 M HCl medium *via* experimental and molecular dynamics simulation

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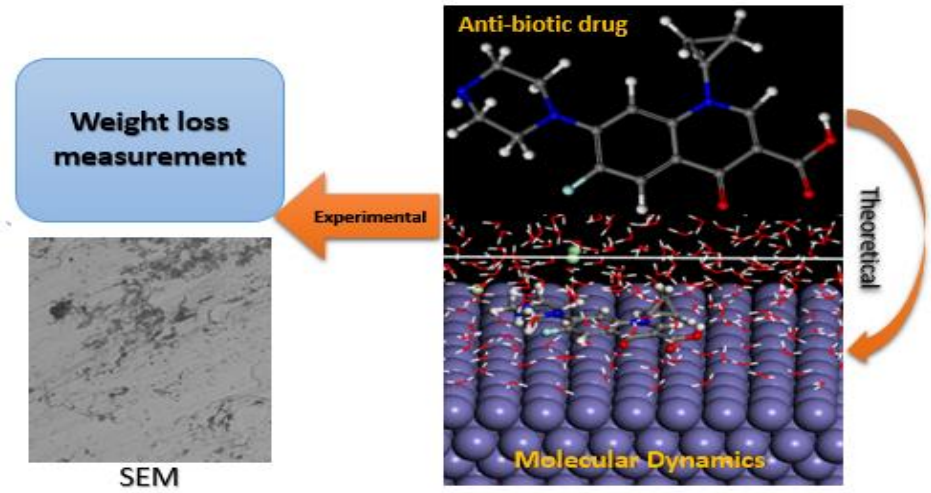
ABSTRACT

Three expired antibiotic drugs namely, ampiclox, ciprofloxacin, and ampicillin were studied at low concentrations on the corrosion inhibition of mild steel (MS) in 0.1 M HCl medium using weight loss and scanning electron microscopy (SEM) techniques. Subsequently, the molecular structures of the antibiotic inhibitors were subjected to molecular dynamic (MD) simulation using Material Studio 8.0 software to have insight into their dynamic binding energy onto the Fe (110) surface in an acidic medium. The results showed that the weight loss and corrosion rate decrease with an increase in the inhibitor concentration, while the inhibition efficiency (%) and surface coverage increase with the increase in the inhibitor concentration respectively. The maximum inhibition efficiency of 97.72 % was attained at 0.009M concentration for ciprofloxacin followed by ampiclox and ampicillin. The SEM analysis of the MS with the expired ciprofloxacin (0.009 M) revealed a soother surface through the formation of a protective film that prevented the corrosion attack which confirms the highest inhibition efficiency. The MD simulation showed that the ciprofloxacin has the highest binding energy of −474.582 kcal/mol, followed by −248.448 kcal/mol for ampicillin and −234.955 kcal/mol for ampiclox respectively. Hence, the ciprofloxacin with the more negative magnitude of the binding energy was predicted to exhibit stronger chemisorption interaction onto the Fe (110) metal surface when compared with ampicillin and ampiclox. The findings in this research reveal good agreement between the experimental and theoretical results in studying the corrosion inhibition of the studied antibiotic drugs.

Keywords:
Corrosion,
Mild steel,
Molecular dynamics,
Binding energy,
Antibiotic drugs



1. Introduction

Corrosion remain one of the utmost challenging factors that affect optimal performance and usage of metals and their alloys since the inception of the industrial revolution which is responsible for the numerous financial damages [1]. Mild steel (MS) is used in numerous industries due of its good thermomechanical properties. Some of the industrial application of MS includes cleaning, stripping, descaling, and many more [2]. Nowadays, corrosion attacks can be controlled through the use of an inhibitor in an aqueous aggressive medium [3]. Several reported

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studies have shown that drugs possess corrosion inhibitory properties against metals because of the presence of the heterocyclic moieties and electron densities [4,5], and the synthesis is time-consuming and expensive [6]. Furthermore, antibiotics were reported to have corrosion inhibition properties in acidic media, where cloxacillin, ampicillin, flucloxacillin, and amoxicillin were investigated for corrosion inhibition of aluminium in 2M HCl, and the results revealed best efficacy of 88.78% for amoxicillin [7]. However, drugs are vulnerable to expiration, and can be either harmful, ineffective, or eventually decompose when expired [8]. Thus, expired drugs must be appropriately disposed or else, it could lead to environmental pollution via medicinal waste or wastewater effluents which can infect the water cycle [9]. The disposal of these expired drugs needs to be eco-friendlier, safe, and economical as in corrosion protection applications [2,10]. Drugs that have passed their usage expiry date could serve as corrosion inhibitors in the industry which is supported by the outcome of many studies [10]. This is because the anti-corrosion activity depends on the chemical structure of the drug, and it is amazing to understand that some certain anti-biotic drugs retain their molecular integrity and activities for over 10 years after usage expiry date [11-17].

In recent times, the molecular dynamics (MD) simulation as a molecular modelling strategy is utilized to correlate the theoretical results with experimental corrosion inhibition effects [18]. The simulation strategy provides the actual interfacial interactions between the studied metallic surface and the inhibitor molecules [18]. Most of the corrosion inhibition studies on the expired ampiclox, ciprofloxacin, and ampicillin drugs were at a higher aggressive medium and inhibitor concentrations with limited theoretical studies via MD simulation. As such, this study focused on investigating the effect of some expired drugs namely; ampiclox, ciprofloxacin, and ampicillin at low inhibitor concentrations on the corrosion inhibition of MS in 0.1 M HCl medium through experimental (weight loss and SEM), and MD simulation.

2. Experimental

2.1. Preparation of the MS

The chemical composition of the MS used in this study are: 98% iron (Fe), 0.97% carbon, 0.3% manganese (Mn), 0.13% phosphorus (P), 0.19% Chromium (Cr), 0.09% sulfur (S), 0.125% molybdenum (Mo), 0.022% silicon (Si) and 0.175 % nickel (Ni) using X-ray fluorescence (XRF) analyzer. The MS coupons in rectangular form with (3 × 2 × 0.3) cm dimension were mechanically cut from the metal sheet, and a 5 mm diameter small hole near the upper edge of the coupons was made to help in the suspending specimen into the corrosive medium. The coupons were degreased in acetone, washed in distilled water, and stored in a moisture-free desiccator before use.

2.2. Preparation of the antibiotic drugs

The three expired antibiotic drugs ciprofloxacin, cloxacillin (ampiclox), and ampicillin were sourced. 500 mg of each drug sample without any further purification was used to prepare lower concentrations of the drugs ranging from 0.003 M to 0.009 M, while the corrosive medium used was 0.1M HCl solution. The 2D and 3D molecular structures of the drugs were presented in Fig. 1, 2, and 3 respectively.

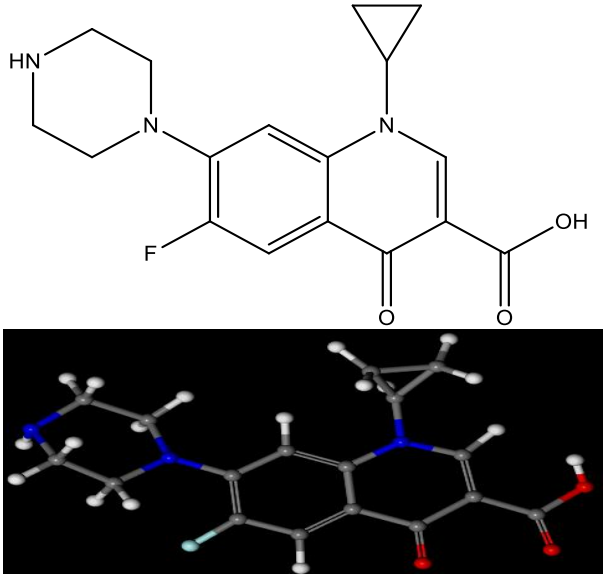

Fig 1. 2D and 3D structure of Ciprofloxacin (1-cyclopropyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-1,4-dihydroquinoline-3-carboxylic acid)

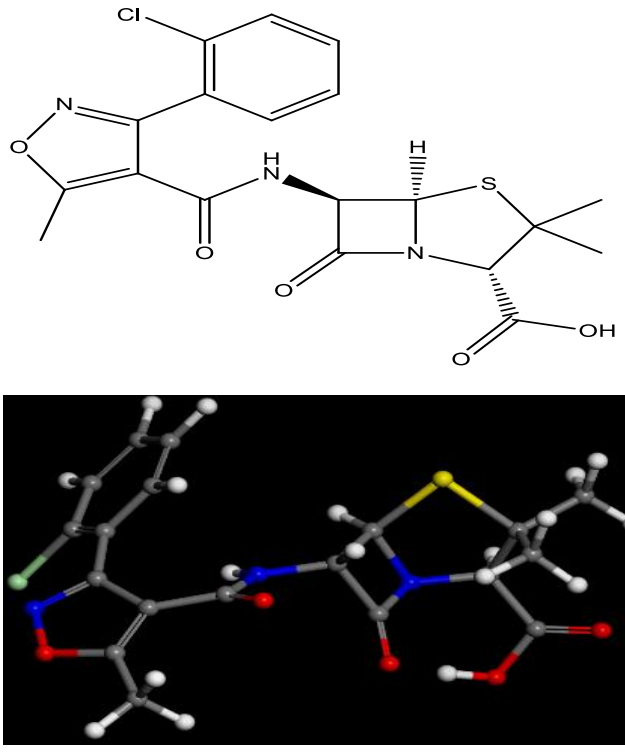

Fig 2. 2D and 3D structure of Ampiclox ((2S,5R,6R)-6-(3-(2-chlorophenyl)-5-methylisoxazole-4-carboxamido)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid)

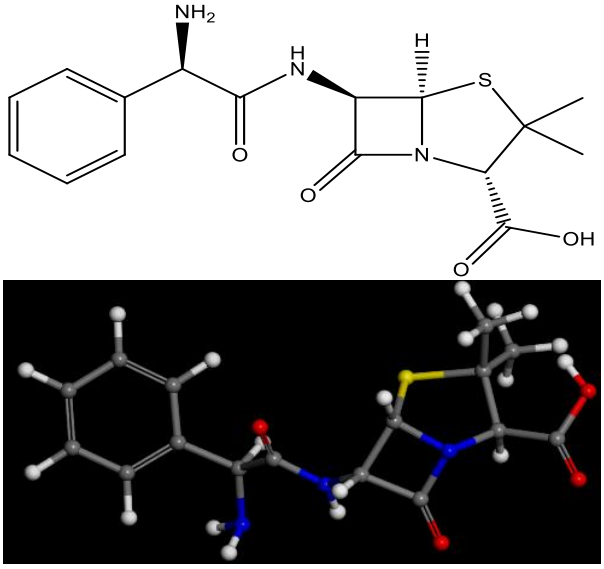

Fig 3. Structure of Ampicillin ((2S,5R,6R)-6-((R)-2-amino-2-phenylacetamido)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid)

2.3. Weight loss measurement

For weight loss measurement, the MS specimens were used in a 250 ml beaker for each experiment at a room temperature of 30ºC. The polished MS coupons were weighed and suspended in the presence and absence of each inhibitor concentration for 48 hours. The specimens were taken out, dried, and reweighed with the help of analytical balance. The tests were run in duplicates and the data showed good reproducibility. The average values of the test results were used in subsequent calculations in each case. The MS coupons 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 0.1 M HCl in the presence of different inhibitor concentrations. The corrosion rate (CR), surface coverage, and the inhibition efficiency from the weight loss were computed from the following equations (1-3) below [15,17];

$$CR(gcm^{-2}hr^{-1}) = \frac{\Delta W}{A \times t} \quad (1)$$

$$\theta = \frac{W_0 - W_I}{W_0} \quad (2)$$

$$IE(\%) = \frac{W_0 - W_I}{W_0} \times 100 \quad (3)$$

Where:

CR = Corrosion rate

Θ= Surface coverage

ΔW= Weight loss (g)

A= Surface area of the specimen (cm^2)

t = Immersion time (hr)

IE = Inhibition efficiency (%)

W_0 = Weight loss in the absence of the inhibitor

W_I = Weight loss in the presence of the inhibitor.

2.4 Scanning Electron Microscopy (SEM)

The scanning electron microscope, model code SM-5600 LV, was used to capture the micrographs of the MS coupon before and after inhibition. The selected coupon recovered from the test solution was placed on the SEM sample holder sputtered with gold to make it conductive. Consequently, the scanned micrographs were obtained at an accelerating voltage of 2.00 and 15 kV.

2.5 MD Simulation study

The MD simulation was carried out to investigate the corrosion inhibition based on the theoretical viewpoint of the adsorption mechanism between the pure Fe metal surface and each of the studied antibiotic drugs [18]. The 3D structure of the Fe (110) simulation box with lattice parameters (a = 28.49 Å, b = 28.49 Å, c = 48.84 Å, α=89.58°, β=89.85°, and γ= 90.01°) as the corrosion medium was geometrically optimized using the COMPASS II force field of Biovia Materials studio version 8.0 as shown in Fig. 4. For a more realistic simulation, the acidic medium of the corrosion system was taken into consideration in which the solution layer containing the inhibitor and solvent molecules (H_2O, HCl) were built on the Fe (110) slab accordingly. The energy values were all computed after the system attains equilibrated energy and temperature [18]. Hence, the dynamic binding energy ($E_{binding}$) as the measure of simulation interaction between the metal surface and the inhibitor was computed using the equation below;

$$E_{binding} = (E_{(Fe\ surface+Inhibitor+H_2O+HCl)} - (E_{Inhibitor} + E_{(Fe\ surface+H_2O+HCl)}) \quad (4)$$

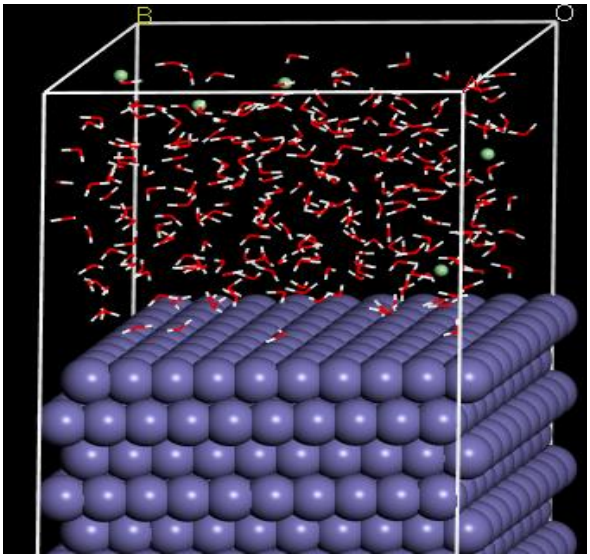

Fig 4. Geometrically Optimized Structures of Fe (110) metal surface soaked with acidic solution layer in the simulation box.

3. Results and Discussion

3.1 Weight loss

The corrosion inhibition efficiency (%) of the expired antibiotic drugs was tested in 0.1 M HCl solution against MS at room temperature using weight loss measurements. The variation of the inhibition efficiency, corrosion rate, and surface coverage with inhibitors concentration are presented in Figs. 5-7. The result for the corrosion rate revealed a significant decrease upon the introduction of the drugs into the medium.

This implies that as the inhibitor concentration increases, the corrosion rate decreases. The trend of the corrosion rate for the various drugs is ampiclox > ciprofloxacin > ampicillin. The surface coverage increased with an increase in the concentration of the drugs which implies that the inhibitors are adsorbed on the steel surface. However, the increase in inhibition efficiency seems to be proportional to the concentration of the inhibitor. Similar trends were previously observed in some related studies [14,19].

The maximum inhibition efficiency was obtained at 0.009M with the highest value of 97.72 % followed by 0.007M with a value of 64.39 %, and the least concentration of 0.003 M with a value of 25 % for the ciprofloxacin drug. The maximum inhibition efficiency of ampiclox was obtained at 0.009M inhibitor concentration with the highest value of 83.73 % followed by 0.007M at 78.31 % and 0.003 M with a value of 58.09 % respectively. This could be attributed to the adsorption or blocking of active sites of the metal surface by the inhibitor molecules.

Similarly, the maximum inhibition efficiency of ampicillin drug was obtained at an inhibitor concentration of 0.009 M with the highest value of 64.48 % followed by 0.007 M with the 55.82 %, while the 0.003M was the least concentration was obtained at 20.85 % efficiency respectively. Although, the trend slightly differs at the highest inhibitor concentration of 0.009M with the maximum inhibition efficiency of 97.72 % for ciprofloxacin. In general, the order of inhibition efficiency is ciprofloxacin > ampiclox > ampicillin at a higher inhibitor concentration of 0.009M. But, the order was not maintained for the other lower inhibitor concentrations. This could be attributed to the slight decrease in the activity of the expired drugs [10,11]. However, the inhibition efficiency (%) of the expired drugs was within the range of 64.5-97.72 % at a higher inhibitor concentration of 0.009 M. It is evident that the weight loss and corrosion rate decrease with an increase in the inhibitor concentration, while the inhibition efficiency (%) and surface coverage increase with the increase in the inhibitor concentration respectively as shown in Table 1.

3.2 Scanning Electron Microscopy (SEM)

SEM micrographs for the uninhibited MS specimen before and after immersion in 0.1 M HCl (blank), and the inhibited MS with the best corrosion performance of the expired ciprofloxacin at 0.009 M were shown in Fig 8. It was observed from the images that the surface of MS immersed in 0.1 M HCl reveals a rough and more clearly corroded surface due to the acidic attack. However, the micrograph of MS with the expired ciprofloxacin at 0.009 M showed a smoother surface through the formation of a protective film that prevented the corrosion attack which confirms the highest inhibition efficiency. Similar observation was previously reported in the literature [19].

3.3 MD simulation study

To have more insight into the adsorption mechanism between the studied inhibitor and the Fe (110) surface, MD simulation was performed to assess the interfacial interaction of the three studied antibiotic drugs onto Fe (110) surface using the forcite quench dynamics module of the Material Studio. The dynamic agitation was done when the system is at a micro-canonical ensemble (NVE) state, such that the trajectory may be seen as an exchange of kinetic and potential energy and the total energy being conserved for 5ps simulation every 500 quenched at an initial temperature of 298K. Figs. (9, 10, and 11) showed the MD equilibrated models of studied antibiotic drugs onto Fe (110) surface.

Table 1. Inhibition efficiencies, corrosion rate, and surface coverage of the various concentration of the expired inhibitors for the corrosion of MS in 0.1 M HCl using gravimetric analysis at room temperature

Name of Inhibitor	Inhibitor concentration (M)	Weight Loss (g)	Inhibition efficiency (%)	Corrosion rate ($gcm^{-2}hr^{-1}$)	Surface coverage (θ)
	Blank	0.0163			
	0.003	0.0129	20.85	0.0129	0.21
Ampicillin	0.005	0.0084	48.46	0.0084	0.48
	0.007	0.0072	55.82	0.0072	0.56
	0.009	0.0053	64.48	0.0053	0.67
	Blank	0.190			

	0.003	0.143	25.00	0.143	0.25
Ciprofloxacin	0.005	0.067	64.39	0.067	0.64
	0.007	0.010	54.54	0.010	0.55
	0.009	0.004	97.72	0.004	0.98
	Blank	0.0166			
	0.003	0.0105	58.09	0.0105	0.58
Ampiclox	0.005	0.0049	70.48	0.0049	0.7
	0.007	0.0036	78.31	0.0036	0.78
	0.009	0.0027	83.73	0.0027	0.84

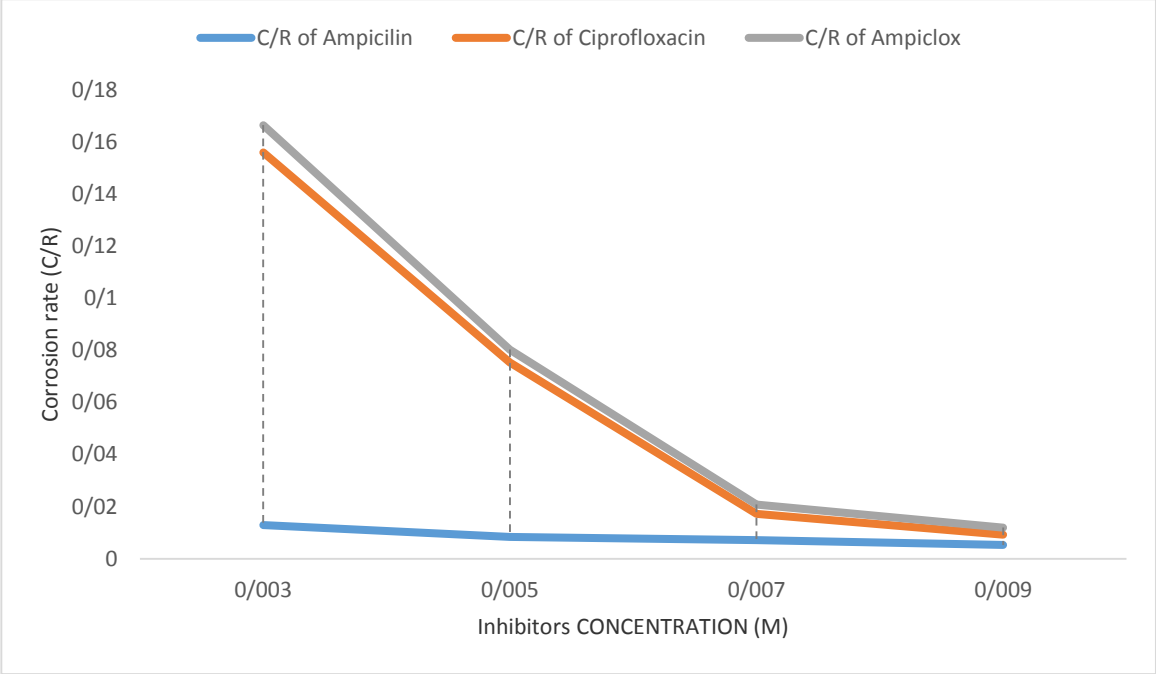

Fig 5. Variation of corrosion rate (C/R) against inhibitors concentration (M) for the corrosion of MS coupons in 0.1 M HCl solution at room temperature

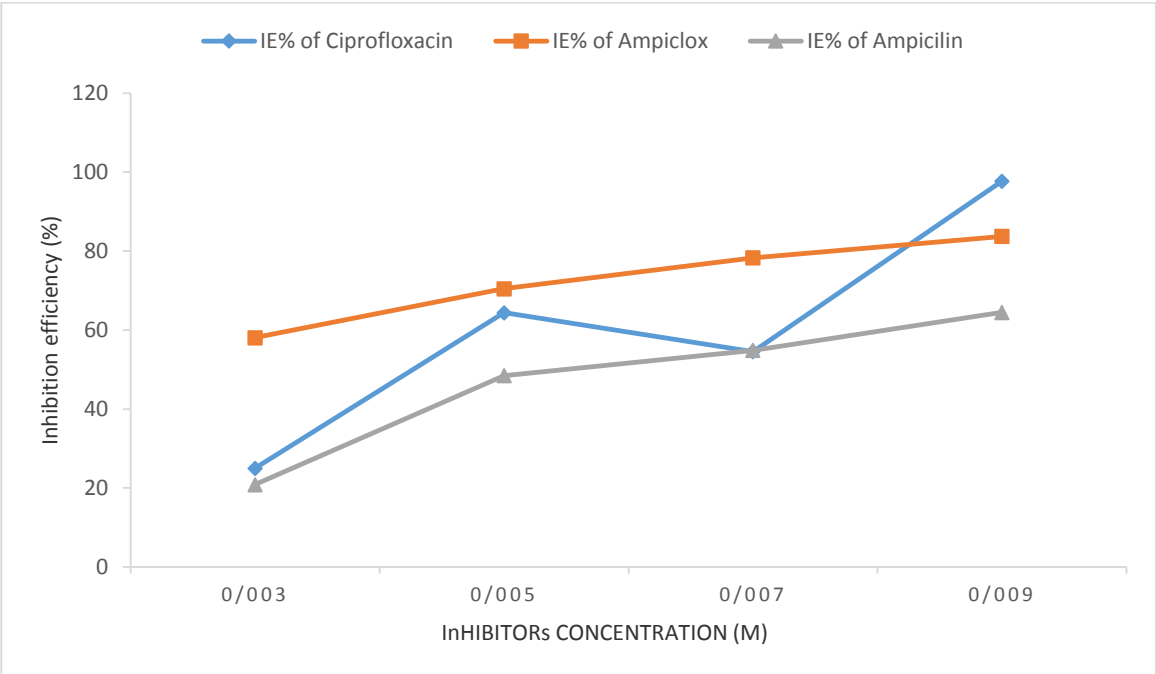

Fig 6. Variation of inhibition efficiency with inhibitors concentration (M) for the corrosion of MS coupons in 0.1 M HCl solution at room temperature

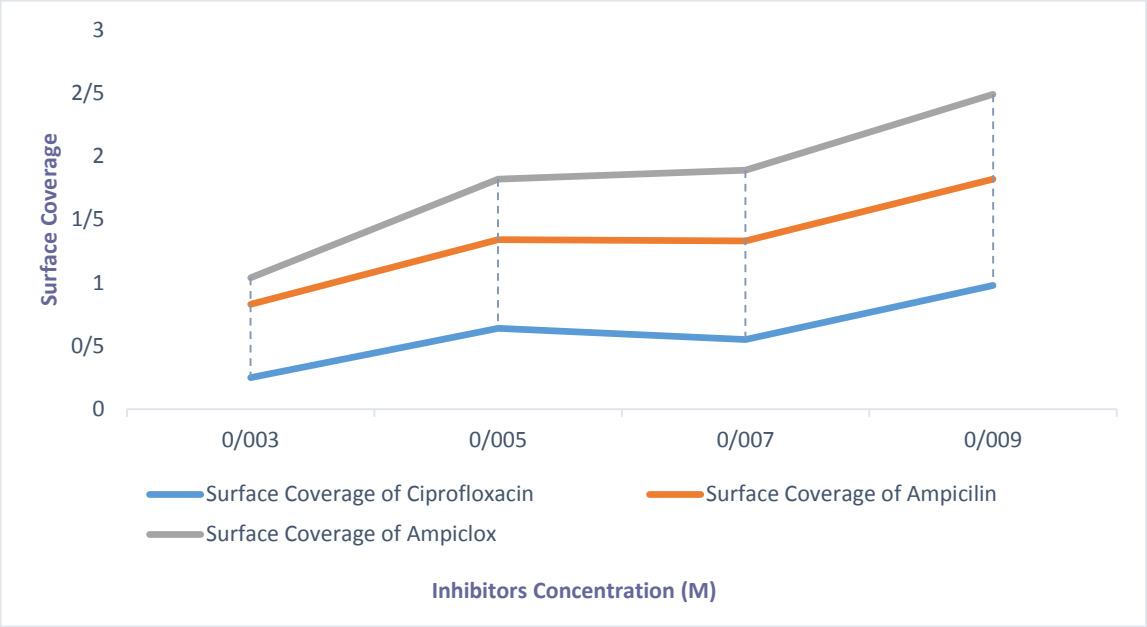

Fig 7. Variation of surface coverage against inhibitors concentration (M) for the corrosion of MS coupons in 0.1 M HCl solution at room temperature

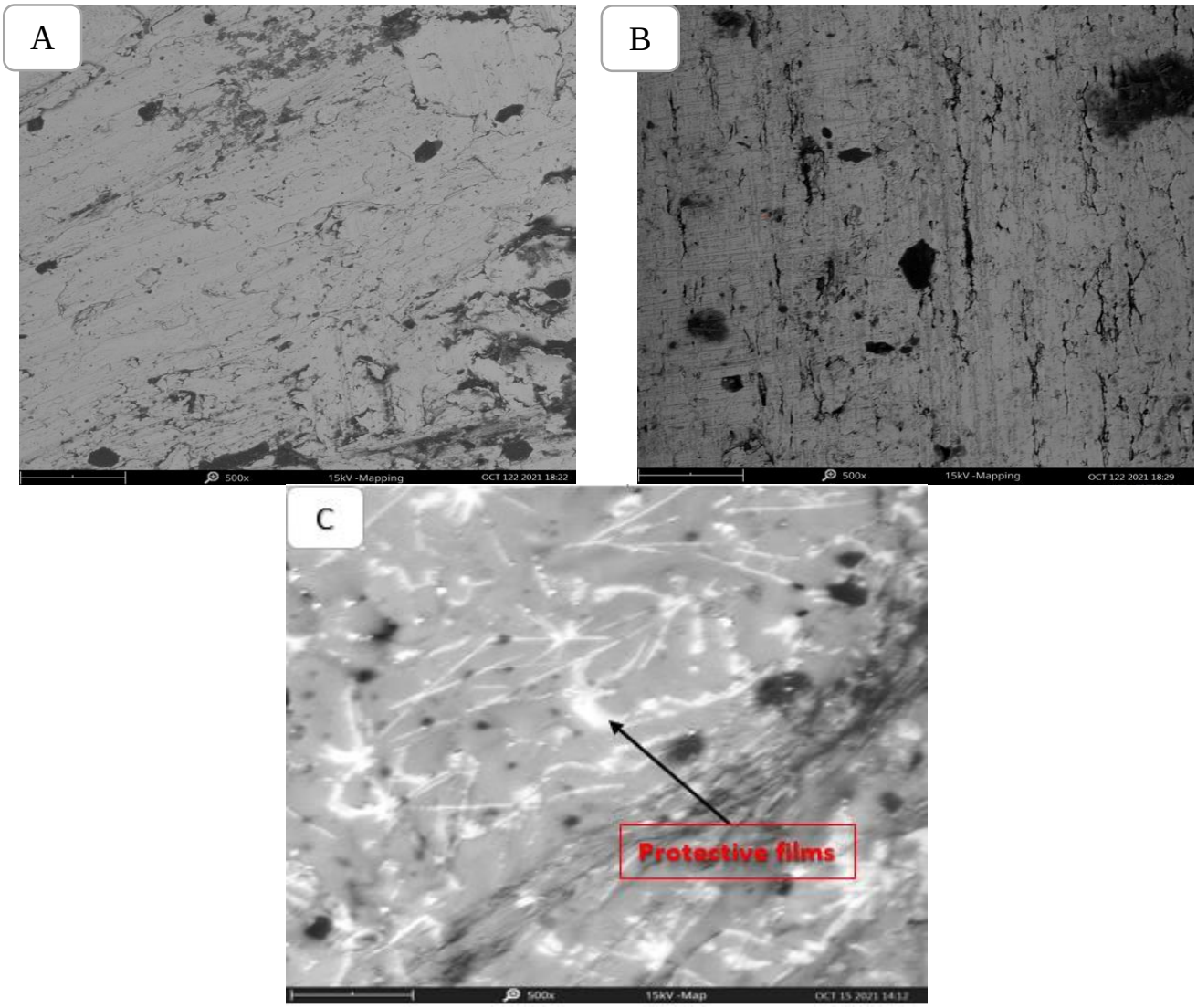

Fig 8. SEM micrographs of (A) uninhibited MS before immersion in 0.1 M HCl [blank] (B) uninhibited MS in the absence of inhibitor after immersion in 0.1 M HCl (C) inhibited MS with 0.009M expired ciprofloxacin at x500 magnification and accelerating voltage of 15kV.

The drug molecules retained a parallel orientation which resulted in a disposition of a large surface area on the Fe (110) surface corresponding to the higher inhibition efficiency as observed experimentally. Their dynamic binding energy ($E_{binding}$) was computed as –234.955kcal/mol for ampiclox, –248.448 kcal/mol for ampicillin, and –474.582 kcal/mol for ciprofloxacin respectively. Hence, the more negative magnitude of the dynamic binding energies can be related to the strong adsorption of the inhibitor onto the Fe (110) metal surface [2,20]. However, the magnitude of the computed dynamic energy is greater than 100 kcal/mol depicting the existence of chemisorption interaction between the inhibitor and the Fe metal surface as suggested in the literature [18,20,21]. The mechanism of adsorption for ciprofloxacin can occur by the electrostatic interaction of the adsorbed oxygen atom and protonated nitrogen atoms in combination with the other donor-acceptor interactions between the unshared electron pairs of fluorine, oxygen, and nitrogen. Similarly, the adsorption mechanism for ampicillin and ampiclox could be due to the sharing of electrons between the heteroatoms (O, N, and S), π-electron, and vacant d-orbital of iron atoms [19, 20].

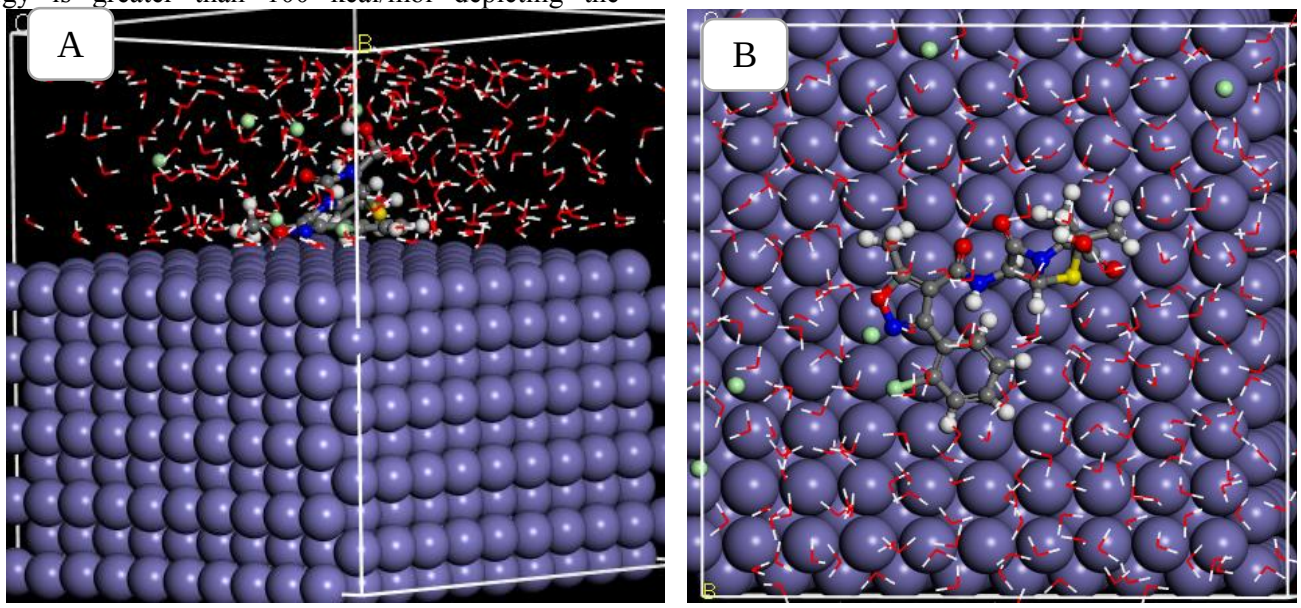

Fig 9. MD equilibrated models of ampiclox onto Fe (110) surface showing (A) side view, and (B) top view models (– 234.955 kcal/mol)

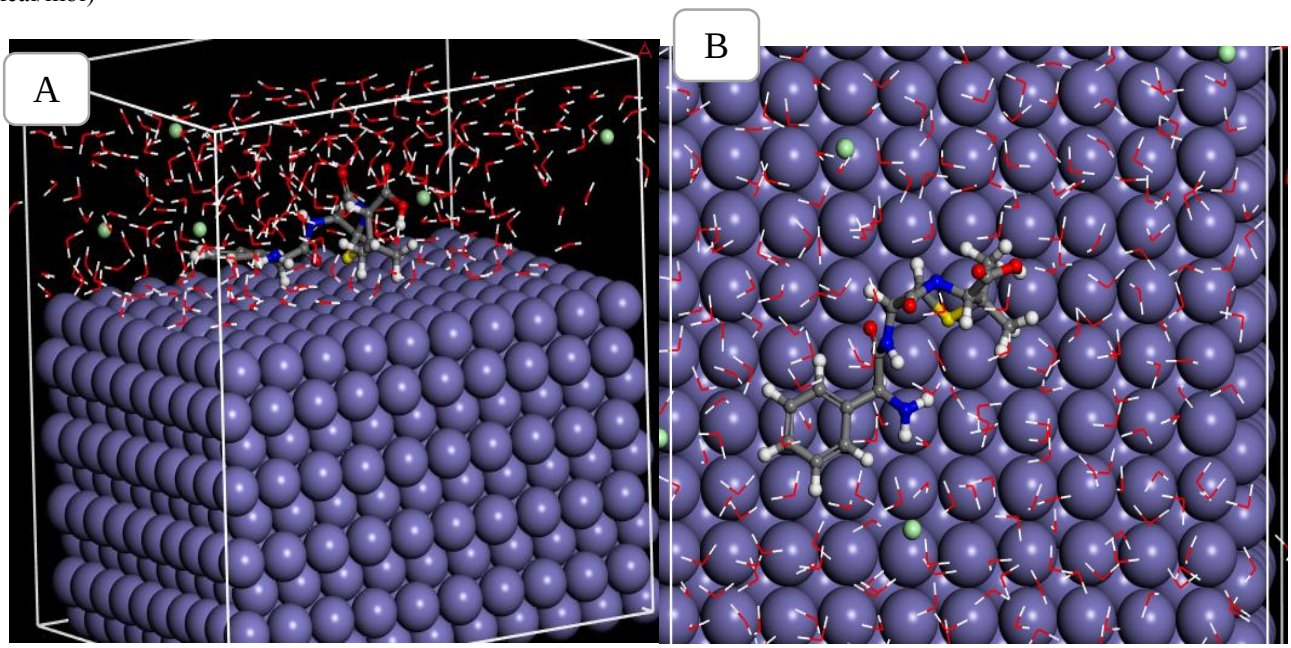

Fig 10. MD equilibrated models of ampicillin onto Fe (110) surface showing (A) side view, and (B) top view models (–248.448 kcal/mol)

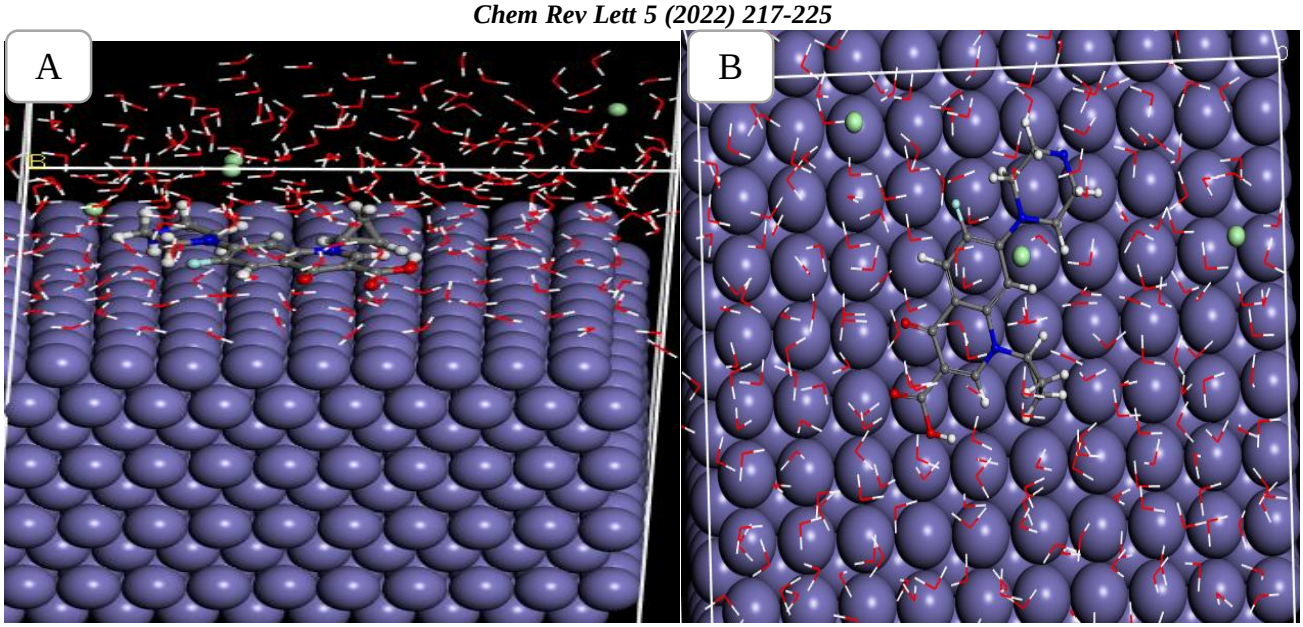

Fig 11. MD equilibrated models of ciprofloxacin onto Fe (110) surface showing (A) side view, and (B) top view models (–474.582 kcal/mol)

4. Conclusion

In conclusion, the results obtained in this work revealed that the studied antibiotic drugs are good inhibitors of MS at 0.1M HCl medium. Furthermore, the expired ciprofloxacin drug scored the highest efficiency of 97.72 % at 0.009M in comparison to the other studied drugs. The corrosion rate decreased with increase in the concentration of the inhibitors ranging from 0.003M to 0.009M, while the inhibition efficiency (%) and surface coverage increase with the increase in the concentrations of the inhibitors. The SEM analysis of MS with the expired ciprofloxacin at 0.009 M revealed a soother surface through the formation of a protective film that prevented the corrosion attack which confirms the highest inhibition efficiency. The MD simulation revealed the computed binding energy of the studied drugs on the Fe (110) metal surface as –474.582 kcal/mol for ciprofloxacin, –234.955 kcal/mol for ampiclox, and –248.448 kcal/mol for ampicillin respectively. This clearly shows the agreement in the results obtained from both experimental and theoretical studies. The outcome of this research cemented the idea of using expired drugs as potential corrosion inhibition even at lower inhibitor concentrations.

Acknowledgments

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References

[1] S. Palit, Recent advances in corrosion science: A critical overview and a deep comprehension. *Direct Synthesis of Metal Complexes*, (2018)379-411. doi:10.1016/B978-0-12-811061-4.00011-6

[2] A.K. Singh, A.K. Pandey, P. Banerjee, et al., Eco-friendly disposal of expired anti-tuberculosis drug isoniazid and its role in the protection of metal. *J. Envir. Chem. Eng*., 7(2) (2019) 02971. doi:10.1016/j.jece.2019.10297

[3] S. Pal, H. Lgaz, P. Tiwari, I.M. Chung, G. Ji, R. Prakash, Experimental and theoretical investigation of aqueous and methanolic extracts of Prunus dulcis peels as green corrosion inhibitors of MS in aggressive chloride media. *J. Mol. Liq*., 276 (2019) 347-361. doi:10.1016/j.molliq.2018.11.099

[4] C. Verma, E.E. Ebenso, M.A. Quraishi, Alkaloids as green and environmental benign corrosion inhibitors: An overview. *Int. J. Corr. & Scale Inh.*, 8(3) (2019) 512-528. doi:10.17675/2305-6894-2019-8-3-3

[5] O. Dagdag, Z. Safi, H. Erramli, et al. Anticorrosive property of heterocyclic based epoxy resins on carbon steel corrosion in acidic medium: Electrochemical, surface morphology, DFT and Monte Carlo simulation studies. *J. Mol. Liq*., 287 (2019) 110977. doi:10.1016/j.molliq.2019.110977

[6] M. Abdullahi, S.E. Adeniji, D.E. Arthur, A. Haruna, Homology modeling and molecular docking simulation of some novel imidazo[1,2-a]pyridine-3-carboxamide (IPA) series as inhibitors of Mycobacterium tuberculosis. *J. Gene. Eng. & Biotech.*, 19(1) (2021) 1-13. doi:10.1186/s43141-020-00102-1

[7] M. Abdallah, Antibacterial drugs as corrosion inhibitors for corrosion of aluminium in hydrochloric solution. *Corr. Sci*., 46(8) (2004) 1981-1996. doi:10.1016/j.corsci.2003.09.031

[8] Y.C. Barenholz, Doxil®—the first FDA-approved nano-drug: lessons learned. Journal of controlled release. 160(2) (2012) 117-134.

[9] N. Chuks, F. Anayo, O.C. Ugbogu, Health Care Waste Management – Public Health Benefits, and the Need for Effective Environmental Regulatory Surveillance in Federal Republic of Nigeria. *Current Topic in Public Health*, 2(2013) 149-178. doi:10.5772/53196

[10] J. Panchal, D. Shah, R. Patel, S. Shah, M. Prajapati, M. Shah, Comprehensive Review and Critical Data Analysis on Corrosion and Emphasizing on Green Eco-friendly Corrosion Inhibitors for Oil and Gas Industries. J. Bio- and Tribo-Corrosion, 7(3) (2021) 1-29. doi:10.1007/s40735-021-00540-5

[11] P. Dohare, D.S. Chauhan, A.A. Sorour, M.A. Quraishi, DFT and experimental studies on the inhibition potentials of expired Tramadol drug on MS corrosion in hydrochloric acid. *Mat. Discov.*, 9(2017) 30-41. doi:10.1016/j.md.2017.11.001

[12] H.M. Elabbasy, H.S. Gadow, Study the effect of expired tenoxicam on the inhibition of carbon steel corrosion in a solution of hydrochloric acid. *J. Mol. Liq.*, 321(2021) 114918. doi:10.1016/j.molliq.2020.114918

[13] M.A. Quraishi, M.Z.A. Rafiquee, S. Khan, N. Saxena. Corrosion inhibition of aluminium in acid solutions by some imidazoline derivatives. *J. Appl. Electrochem.*, 37(10) (2007) 1153-1162. doi:10.1007/s10800-007-9379-0

[14] M. Alfakeer, M. Abdallah, A. Fawzy, Corrosion inhibition effect of expired ampicillin and flucloxacillin drugs for MS in aqueous acidic medium. *Int. J. Electrochem. Sci*., 15(4) (2020) 3283-3297. doi:10.20964/2020.04.09

[15] B. Fadila, A. Sihem, A. Sameh, K. Gülfeza. A study on the inhibition effect of expired amoxicillin on MS corrosion in 1N HCl. *Mat. Research Express*, 6(4) (2019) 46419. doi:10.1088/2053-1591/aafcd7

[16] A. Srinivasulu, P.K. Kasthuri, Study of inhibition and adsorption properties of MS corrosion by expired pharmaceutical Gentamicin drug in hydrochloric acid media. *Orient. J. Chem*., 33(5) (2017) 2616-2624. doi:10.13005/ojc/330559

[17] U. Nazir, Z. Akhter, N.Z. Ali, F.U. Shah, Experimental and theoretical insights into the corrosion inhibition activity of novel Schiff bases for aluminum alloy in acidic medium. *RSC Advances*, 9(62) (2019) 36455-36470. doi:10.1039/c9ra07105a

[18] B.A. Umar, A. Uzairu, G.A. Shallangwa, Understanding inhibition of steel corrosion by some potent triazole derivatives of pyrimidine through density functional theory and molecular dynamics simulation studies. *J. Turk. Chem. Soc.*, Section A: Chemistry. 6(3) (2019) 451-462. doi:10.18596/jotcsa.446084

[19] Akpan, I. A., & Offiong, N. A. O. Inhibition of mild steel corrosion in hydrochloric acid solution by Ciprofloxacin drug. *Int. J. corr.*, (2013).

[20] A.M. Ayuba, M. Abubakar. A Theoretical Study on Isolated Compounds from the Leaves Extract of Guiera Senegalensis as Aluminium Corrosion Inhibitor. *J. Sci. & Tech.*, 13(1) (2021) 47-56.

[21] U. Umaru, A.M. Ayuba, Quantum chemical calculations and molecular dynamic simulation studies on the corrosion inhibition of aluminium metal by myricetin derivatives. *J. New Tech. & Mat.*,10(2020) 18-28.