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Original Research Article

Enhanced Corrosion Protection of Mild Steel in Synthetic Acid Rain Solution by Expired Ciprofloxacin Drug and Iodide Ions

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Abstract

The search for eco-friendly corrosion inhibitors for mild steel has driven interest in the valorization of expired pharmaceutical products as green alternatives to conventional toxic inhibitors. The present study investigated the synergistic inhibition behaviour of expired ciprofloxacin and iodide ions for mild steel in synthetic acid rain solution using gravimetric, surface morphology analysis and molecular dynamic simulation approaches. The results showed that the corrosion inhibition performance significantly improved in ciprofloxacin-iodide system and the inhibition performance reach approximately 97 % at low concentration. The surface morphology analysis showed that the inhibitor molecules are adsorbed on the mild steel surface, thereby decreasing the corrosion rate. The adsorption process follows the Frumkin adsorption isotherm. The experimental results correlated with the molecular dynamics simulation results. The findings in this research provide a practical strategy for the potential reuse of expired ciprofloxacin waste and the development of novel corrosion inhibitors.

Keywords: Corrosion, mild steel, adsorption, gravimetric, molecular dynamics.

INTRODUCTION

Mild steel remains one of the most extensively used engineering materials because of its excellent mechanical properties, ease of fabrication, and relatively low cost. Its broad application in pipelines, storage tanks, bridges, construction materials, automotive components, and industrial equipment makes protection against corrosion a significant engineering and economic priority. However, mild steel is highly susceptible to corrosion when exposed to acidic environments, mainly those simulating acid rain, where the presences of sulfuric and nitric acids hasten electrochemical degradation (Montaser *et al.,* 2024). The resulting deterioration decreases structural reliability, shortens service life, increases maintenance costs, and poses environmental and safety concerns. Therefore, the development of efficient and environmentally sustainable corrosion mitigation strategies remains a major area of study.

Among the accessible corrosion protection techniques, the utilization of corrosion inhibitors is considered one of the most practical and cost-effective methods because only low concentrations are required to achieve significant decrease in corrosion rate (Nleonu *et al.,* 2022). Organic inhibitors have attracted considerable attention due to their ability to adsorb on metallic surfaces and form protective films that deter corrosion rate. Their inhibition efficiency is largely attributed to the presence of heteroatoms in the organic compounds such as nitrogen, oxygen, sulfur, and phosphorus, together with π-electron systems that facilitate interaction with vacant orbitals of surface metal atoms (Verma *et al.,* 2017; Hsissou *et al.,* 2020). Recent research has increasingly focused on environmentally friendly organic inhibitors that achieve high inhibition efficiencies (Gunasekaran *et al.,* 2025).

In recent years, expired pharmaceutical products have emerged as a promising class of green corrosion inhibitors (Baari & Sabandar, 2021; Vaszilcsin *et al.,* 2023; Shetty *et al.,* 2025). Although drugs may no longer be suitable for therapeutic use after expiration, many retain their molecular structures and functional groups capable of interacting with metallic surfaces. Reuse of expired pharmaceuticals drugs in developing environmentally friendly corrosion inhibitors provides a sustainable approach for reducing pharmaceutical waste (Al Jahdaly *et al.,* 2026; Chauhan *et al.,* 2026). Recent studies have established that numerous expired drugs exhibit excellent inhibition efficiencies for mild steel, carbon steel, copper, aluminium, and other engineering metals in aggressive media, thereby supporting their potential for industrial corrosion control (Alamry *et al.,* 2023; Al-Gorair *et al.,* 2024; Farahati *et al.,* 2020; Sheit *et al.,* 2024; Abdel Hameed *et al.,* 2022).

Ciprofloxacin is the most attractive expired pharmaceutical compounds studied due to its molecular structure. Ciprofloxacin is a fluoroquinolone antibiotic and contains various adsorption-active functional groups, including carboxyl, carbonyl, amino, and piperazine nitrogen groups, together with an aromatic ring system. These functional groups contain lone-pair and π-electrons capable of interacting with iron atoms through electrostatic attraction and donor–acceptor interactions, thereby promoting adsorption on metallic surfaces. Recent experimental and theoretical studies have shown that expired ciprofloxacin behaves as an efficient mixed-type corrosion inhibitor (Montaser *et al.,* 2024; Nunach *et al.,* 2025).

The corrosion inhibition efficiency of organic compounds can be additionally improved through synergistic interactions with halide ions. Among the halides, iodide ions exhibit a strong adsorption on metallic surfaces due to their reasonably large ionic radius and high polarizability. Adsorbed iodide ions create favourable interfacial conditions that facilitate the adsorption of protonated organic inhibitor molecules, thereby increasing surface coverage and improving the stability of the protective film (Ran *et al.,* 2024; Chauhan *et al.,* 2021; Tan *et al.,* 2020). Consequently, inhibitor–iodide mixtures often demonstrate higher corrosion protection compared with individual inhibitor components, making synergistic inhibition an efficient approach for enhancing inhibitor performance at low inhibitor concentration.

Understanding the adsorption behaviour and inhibition mechanism of environmentally sustainable inhibitors requires the incorporation of experimental and theoretical techniques. Gravimetric measurements remain one of the most reliable techniques for estimating corrosion rate and inhibition efficiency of inhibitors on metal because they directly measure metal loss during exposure. Adsorption isotherms and thermodynamic analyses provide valuable information regarding adsorption behaviour, spontaneity, and the nature of inhibitor–metal interactions. Hence, theoretical techniques such as Molecular Dynamics (MD) simulation provide molecular-level understanding of electron distribution, adsorption centres, adsorption configurations, and interaction energies, thereby balancing experimental observations and improving interpretation of inhibition mechanisms (Bahron *et al.,* 2021; Hsissou *et al.,* 2020).

Despite the growing concern in expired pharmaceuticals as sustainable corrosion inhibitors, studies specially studying the synergistic inhibition of mild steel in synthetic acid rain (SAR) using a combination of expired ciprofloxacin and iodide ions remain tremendously inadequate. Recent reported investigations have focused on conventional acidic media or on individual expired drugs without considering synergistic improvement under acid rain conditions (Montaser *et al.,* 2024; Nunach *et al.,* 2025). Furthermore, comprehensive studies incorporating gravimetric measurements, adsorption modeling, thermodynamic analysis, synergism evaluation, and theoretical calculations for this inhibitor system are limited.

Therefore, this study investigates the corrosion inhibition behaviour of mild steel in synthetic acid rain solution using expired ciprofloxacin and iodide ions as a synergistic inhibitor system. The corrosion performance was evaluated using gravimetric techniques, while adsorption isotherms, thermodynamic parameters, and synergism analysis were employed to explain the inhibition mechanism. Theoretical calculations were further used to establish the molecular interactions responsible for adsorption. The results of the present study are anticipated to contribute to the development of sustainable, cost-effective, and environmentally friendly corrosion inhibitors while providing a novel pathway for the valuable reuse of expired pharmaceutical waste.

2. EXPERIMENTAL

2.1 Materials

Mild steel coupons with dimensions of $3 \times 3 \times 0.2$ cm^3 were employed as the test material for the weight-loss experiments. The mild steel coupons were polished several times with fine emery paper of 1200 grade to a metallic brightness. The mild steel coupons were degreased with acetone, rinsed with deionized water, dried with warm air and stored in desiccators before being used for corrosion studies.

2.2 Synthetic Acid Rain (SAR) Solution Preparation

The SAR solution was prepared from the following analytical grade chemicals made by Lobachem. $NaNO_3$ (0.2 g/L), $NaHCO_3$ (0.2 g/L), and Na_2SO_4 (0.2 g/L) using deionized water (Montaser *et al.,* 2023). The solution was adjusted to a pH value of 2.42 by adding 0.1 M H_2SO_4 solution. All of the chemicals used were used exactly as they were given.

2.3 Inhibitor

Stock solution of 2000 ppm of expired ciprofloxacin was prepared using SAR solution. The inhibitor concentration used was in the range of 200-1000ppm of expired ciprofloxacin. For synergistic effect, 400ppm of potassium iodide with ciprofloxacin concentrations of 200, 400, 600, 800 and 1000ppm, respectively, were employed for the study.

2.4 Methods

2.4.1 Weight Loss Measurements

The corrosion rate measurements were conducted in the environment of Synthetic Acid Rain (SAR) by complete immersion of mild steel coupons with a total surface area of 10.2cm^3. The mild steel weight loss was monitored by weighing the polished specimens before and after hanging into 100 mL of SAR solution for 24, 48, 72, 96 and 120 h in the presence and absence of different concentrations (200 – 1000 ppm) of expired ciprofloxacin at 30 ℃.

From the weight loss measurement data, corrosion rate (CR, mmy^{-1}), degree of surface coverage (θ) and inhibition efficiency (IE%), were determined using equations (1) to (3), respectively.

$$CR = \frac{\Delta W}{DAT} \quad (1)$$

$$\theta = \left[1 - \frac{C_{Rinh}}{C_{Rblank}}\right] x\ 100 \quad (2)$$

$$IE(\%) = \theta \times 100 \quad (3)$$

Where CR is the corrosion rate, W is the weight loss, D is the density of the coupon, A is the surface area of the coupon, and T is the immersion time of the coupon in the corrosive environment. CR_{inh} and CR_{blank} are the corrosion rates in the presence and absence of the inhibitor in SAR solution.

2.4.2 Effect of Temperature

The analysis of mild steel coupons corrosion rate on the variation of temperature was investigated at 303, 313, 323 and 333 k respectively by equilibrating the SAR solution in a thermostatic water bath (SHZ-88 model). A clean coupon was weighed and exposed to the corrosive solution. The coupons were retrieved after l h of exposure time in SAR solution in the absence and presence of 100 ppm concentration of ciprofloxacin inhibitors at 100ppm concentration at different investigated temperatures. The retrieved coupons were washed with deionized water, rinsed with acetone, dried with warm air and weighed.

2.4.3 Synergistic Effect

The synergistic effect on the corrosion rate of mild steel coupons was investigated for the inhibited solution. Each mild steel coupon was immersed in 100 mL of SAR solution containing expired ciprofloxacin (200 – 1000 ppm) and 400 ppm of potassium iodide at time interval of 24 h. Also, the temperature variation effect was monitored at different temperatures of 303-333 k containing 400ppm ciprofloxacin and 400ppm potassium iodide for 1 h. The withdrawn coupons were washed with deionized water, rinsed with acetone, dried with warm air and weighed.

2.4.4 Surface Morphology

The surface morphology of the mild steel were studied after an immersion time of 24 h without and with 400 ppm of ciprofloxacin using scanning electron microscopy (SEM) (JSM-IT200).

2.4.5 Theoretical Calculations

The Monte Carlo (MC) simulations were used for the computations of the quantum chemical parameters and assess the process by which organic compounds reduce corrosion. The best placement of the ciprofloxacin on the surface of Fe (110) was evaluated using MC simulations. The total energy, adsorption energy, and the energy of substrate-adsorbate interactions were also evaluated through Monte Carlo simulation.

3.0 RESULTS AND DISCUSSION

3.1 Surface Morphology Studies

Figure 1a depicts micrograph of the mild steel surface after immersion in SAR solution for 24 h without expired ciprofloxacin. In SAR solution without ciprofloxacin, the surface of the mild steel reveals significant surface degradation consistent with active corrosion processes. The heterogeneous and non-adherent corroded surface suggested limited barrier properties upon prolonged exposure. **Figure 1b** depicts the SEM micrograph of mild steel after 24 h immersion in synthetic acid rain solution containing expired ciprofloxacin and iodide ions exhibits a noticeably smoother surface compared to the uninhibited metal surface. The morphology showed a uniform appearance with residual polishing marks and minor surface irregularities. Scattered bright deposits or aggregates are observed across the surface, possibly corresponding to adsorbed inhibitor complexes or sparingly soluble corrosion products. Also, porous corrosion layers feature of aggressive acidic attack were low, suggesting effective surface coverage and suppression of corrosion. These changes observed indicate that the combination of expired ciprofloxacin and iodide acts as an effective corrosion inhibitor, forming a protective adsorbed layer that reduces dissolution of metal and limits the formation of voluminous corrosion products.

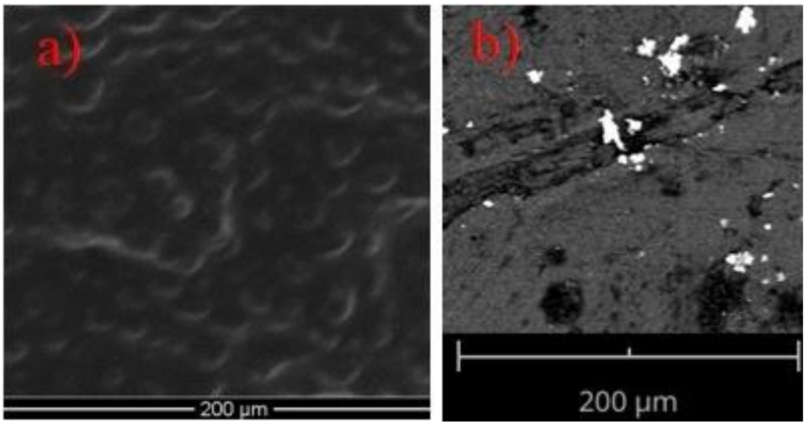

Figure 1: SEM micrograph for (a) mild steel in SAR solution in the absence of inhibitor, (b) mild steel in the presence of 400 ppm expired ciprofloxacin with 400 ppm of iodide

3.2 Corrosion Study

A non-electrochemical method like weight loss measurement was used in this study due to its availability, simplicity, and reliability of measurement. Gravimetric measurement techniques provide a suitable method for monitoring metal corrosion and inhibition immersion tests within a long-term because it gives a direct result on the visual and physical effect of corrosion with regards to a metal loss at the corrodent metal interphase in the presence or absence of inhibitor. The corrosion rate of mild steel coupons in inhibited and blank SAR solutions was determined through weight loss techniques at various concentrations of expired ciprofloxacin after immersion periods (24, 48, 72, 96, 120 h) at 303 k.

3.2.1 Effect of Inhibition Concentration

Figure 2 displays inhibition efficiency of mild steel in SAR solution in the presence of various concentrations of Expired ciprofloxacin and combination of ciprofloxacin and iodide at 24 h exposure time. It is noticed that percentage inhibition efficiency of expired ciprofloxacin drug increased significantly with inhibitor concentration, increasing from 36.49 % at 200 ppm to 92.61 % at 1000 ppm, revealing that higher concentration improved adsorption of the inhibitor and promoted the formation of a stable protective film on the mild steel surface. Furthermore, the ciprofloxacin-iodide mixture exhibited excellent high inhibition performance throughout the studied concentration range, increasing slightly from 97.56 % at 200 ppm to 98.75 % at 1000 ppm. This demonstrates that the introduction of iodide ions greatly enhanced the adsorption of ciprofloxacin, enabling closely completed surface coverage even at low inhibitor concentrations. The superior inhibitor performance of the inhibitor mixture can be attributed to the strong adsorption and high polarizability of iodide ions, which facilitated formation of stable protective film by acting as a bridge between the metal surface and protonated ciprofloxacin molecules (Okeke *et al.,* 2025; Abdullahi *et al.,* 2022). As a result, the ciprofloxacin-iodide system provided a better corrosion protection than ciprofloxacin alone, confirming a strong positive synergistic effect.

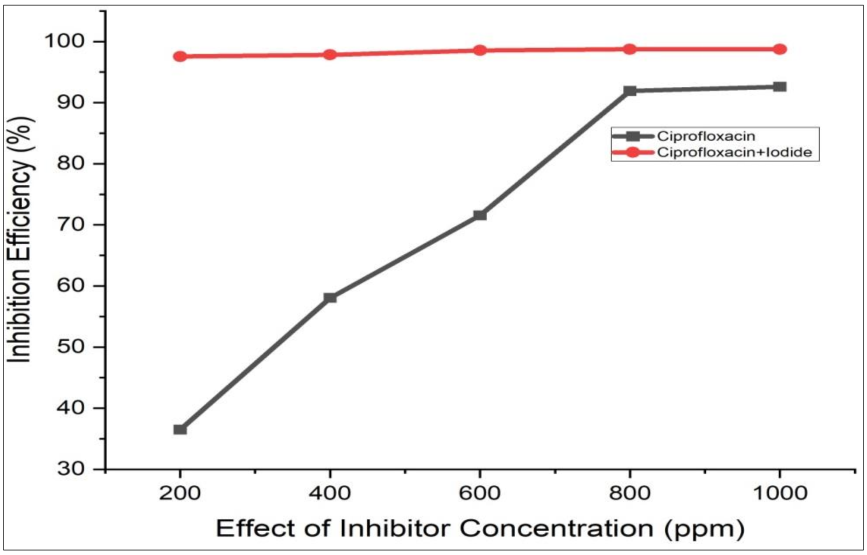

Figure 2: Inhibitor Concentration effect on inhibition efficiency of mild steel corrosion in SAR solution

Effect of Exposure Time

Figure 3 depicts the variation of inhibition efficiency with exposure time. The results of the corrosion inhibition efficiency of 600 ppm expired ciprofloxacin drug notably decrease with increasing immersion time of 24 to 120 h, as noticed by the decrease in inhibition efficiency from 71.56 to 53.30 %. This pattern reveals that expired ciprofloxacin drug initially formed an effective protective barrier on the mild steel surface, while extended immersion in the corrosive media gradually weakened the stability of the adsorbed inhibitor film. The drop in inhibition efficiency indicates that desorption of inhibitor molecule causes continuous dissolution of the metal. Also, the decline in the inhibition efficiency can be attributed to the increasing competition between aggressive sulfate ions in the SAR solution and adsorbed inhibitor molecules on the metal surface affected the persistence of surface coverage over time. The experimental results observed for expired ciprofloxacin drug agrees with the behaviour reported for many organic corrosion inhibitors, whose protective efficiency frequently decreases with increase in immersion time due to partial desorption or weakening of the adsorbed layer on the metal surface (Fouda *et al.,* 2016; Verma *et al.,* 2021). However, the combination of 400 ppm iodide and 600 ppm expired ciprofloxacin drug produced a more stable corrosion inhibition efficiency throughout the immersion period. The improved inhibition efficiency of the inhibitor mixture reveals a synergistic interaction between ciprofloxacin molecules and the iodide ions. The enhanced development suggested that iodide ions are strongly adsorbed on positively charged regions of the mild steel surface, thereby creating a favourable adsorption site for the adsorption of expired ciprofloxacin drug molecules. This cooperative adsorption effect of expired ciprofloxacin drug-iodide mixture increases surface coverage, strengthens the solidity of the protective film, and hinders the accessibility of corrosive species to the metal surface. This shows that the protective film formed by the expired ciprofloxacin drug-iodide system exhibits grater resistance to partial desorption or deterioration during prolonged immersion time than expired ciprofloxacin drug alone. The enhanced inhibition efficiency of expired ciprofloxacin drug-iodide mixture noticed in the present study is consistent with earlier studies demonstrating that halide ions, significantly improve the adsorption efficiency of organic inhibitors (Umoren & Solomon, 2017; Verma *et al.,* 2017)

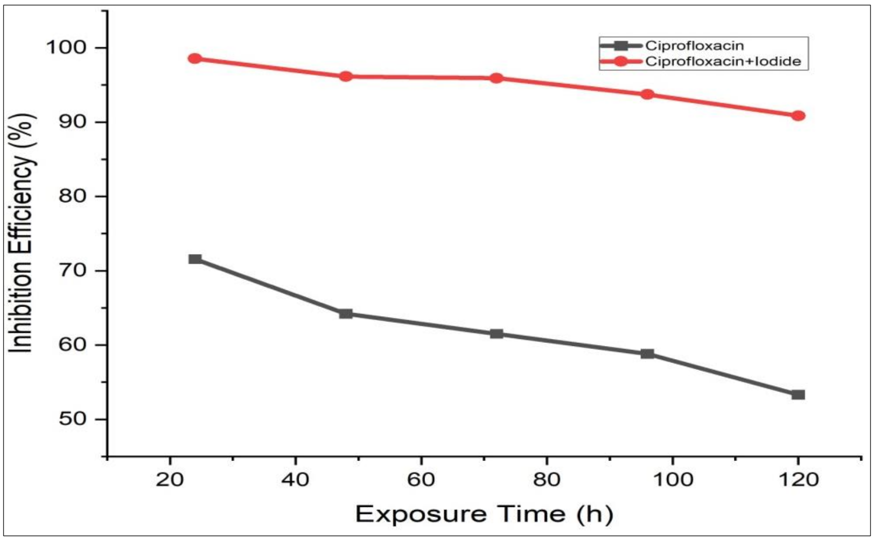

Figure 3: Exposure time effect on inhibition efficiency of mild steel corrosion in SAR solution

Effect of Temperature

Temperature was used to monitor the interaction between the mild steel surface and the corrosive environment in the absence and presence of a tested inhibitor. Figure 4 depicts the inhibition efficiency values obtained from weight loss measurements for mild steel coupons in SAR in the presence of 600 ppm expired ciprofloxacin at temperatures ranging from 303 to 333k. The inhibition efficiency result shows that the percentage inhibition performance decreased with rise in the temperature of the system in the presence of the inhibitor for 1hr immersion time. The inhibition efficiency decreased from 96.94 % at 303 to 66.98% at 333K for ciprofloxacin-iodide ions mixture while ciprofloxacin system only recorded 80 % at 313 K and decreases thereafter, demonstrating that higher temperatures weakened the protective adsorbed film on the metal surface. This adsorption behaviour suggests that corrosion inhibition was mostly controlled by physisorption, where increasing thermal energy promoted desorption of inhibitor molecules from the mild steel surface, thereby, exposing more active sites to corrosion (Nleonu *et al.,* 2022). The high inhibition performance at low temperature demonstrates the strong adsorption potential of expired ciprofloxacin through its nitrogen and oxygen containing fuctional groups, which form a protective film against corrosive species (Gunasekaran *et al.,* 2025; Hsissou *et al.,* 2020)

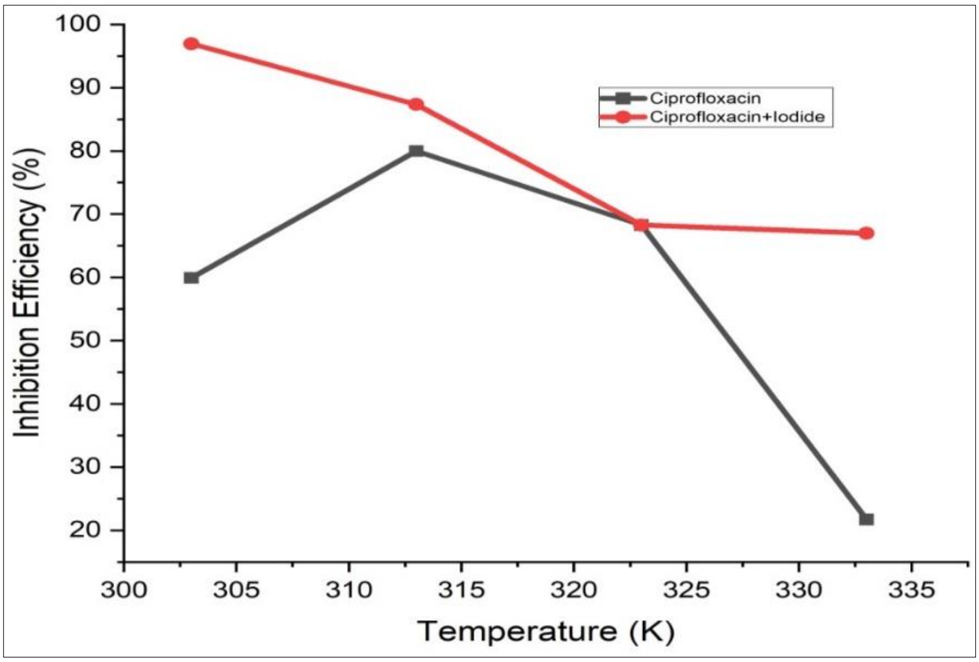

Figure 4: Exposure time effect on inhibition efficiency of mild steel corrosion in SAR solution

Synergistic Effect to Inhibitor Efficiency

To further understand the adsorption behavior of inhibitor molecules on the mild steel surface, a synergistic corrosion inhibition effect between iodide ion and expired ciprofloxacin was studied with expired ciprofloxacin concentrations of 600 ppm with 400 ppm of iodide at 303 k for 24 h. A descriptor synergism parameter (*S*) was introduced and calculated (Eqn 4), which was defined as (Tan *et al.,* 2020):

$$S = \frac{1-\theta_{cipro}}{1-\theta_{cipro+I}} \quad (4)$$

where θ_{cipro} and $\theta_{cipro+I}$ are the surface coverage values by ciprofloxacin and ciprofloxacin-iodide mixture, respectively. Generally, where the inhibitor in combination with the halides have no effect on each other and adsorb on the metal surface, $S = 1$. In the other hand, synergistic effect occurs when $S < 1$, and antagonistic effect occurs when $S > 1$. The synergism value of 2.47 obtain in the present study confirms a strong synergistic interaction between the expired ciprofloxacin and iodide ions at the mild steel-solution interface. The synergism result reveals that ciprofloxacin-iodide system exhibited strong corrosion protection compared with the ciprofloxacin drug alone. The preferential adsorption of iodide ions promotes the adsorption of protonated ciprofloxacin molecules, leading to increase in surface coverage and formation of stable protective film on the metal surface. This synergistic adsorption efficiently inhibits both anodic metal dissolution and cathodic hydrogen evolution, thereby decreasing the corrosion rate (Tan *et al.,* 2020). The findings confirmed that iodide acts as an effective synergistic additive, by enhancing the adsorption stability and corrosion inhibition efficiency of expired ciprofloxacin drug in SAR solution (Umoren and Solomon, 2015).

Adsorption Isotherm

Ciprofloxacin and a combination of iodide ion were utilized for the purpose of reducing the corrosion rate in the corrosive solution due to the adsorption of the inhibitor molecules on the surface of the test metal. The chemical structure of the inhibitor, the stable conformation in the solution, the surface of the tested metal and the solution temperature were all factors that determined the adsorption rates. To further cognize the adsorption behavior of inhibitor molecules on aluminum surface, different and sorption isotherm namely, Flory-Huggins, Temkin, Frumkin, Freundlich and El-Awady, were applied to the tested inhibitor on the surface of the mild steel coupon in the SAR solution. The correlation coefficient (R^2) was used to evaluate the better fit that describes the adsorption mechanisms (Arrousee *et al.,* 2020).

$$\mathrm{L_nC_{inh}}\left(\frac{\theta}{1-\theta}\right) = \mathrm{L_nK_{ads}} + 2\mathrm{d}\theta \text{ (Frumkin)} \quad (5)$$

$$\log\frac{\theta}{c} = L_{og}K_{ads} + x\log(1-\theta)\text{(Flory-Huggins)} \quad (6)$$

$$\log\left(\frac{\theta}{-\theta}\right) = y\log K_{ads} + y\log C_{inh} \text{ (El-Awady)} \quad (7)$$

$$-2a\,\theta = lnK_{ads} + lnC \text{ (Temkin)} \quad (8)$$

Where C is the concentration of inhibitor, K_{ads} represents the adsorption equilibrium constant and θ denotes the surface coverage obtained from the gravimetric measurement. The relationship between the degree of surface coverage and inhibitor concentration in adsorption isotherms was plotted and the values for the adsorption isotherm parameters obtained are presented in **Table 1**. It was observed that adsorption of expired ciprofloxacin molecules only on the mild steel surface in SAR solution as shown in **Table 1** followed the Frumkin adsorption isotherm because its coefficient of linear correlation (R^2) (0.9932) is near unity than other studied isotherms. Furthermore, the adsorption equilibrium constant (K_{ads}) shows the strength of adsorption of the inhibitor molecules on the surface of the mild steel coupon. It was found that the values of K_{ads} of Frumkin inhibitor from the Frumkin isotherm are in better agreement with the experimental findings compared to K_{ads} values from other isotherms. The adsorption isotherm of synergistic effect of ciprofloxacin and iodide ion are shown in **Table 2**, it can be deduced that adsorption of ciprofloxacin in combination with iodide ion on a mild steel surface followed the Freundlich adsorption isotherm as obtained coefficient of linear correlation (R^2) was 0.9839, which was closer to unity than other isotherms. The interaction between the mild steel surface and adsorbed inhibitor species and changes in the heat of adsorption with an increase in the degree of surface coverage accounted for the behavior of the Freundlich isotherm and its corresponding R^2 value. The deviation of k_{ads} in the synergistic effect of iodide and ciprofloxacin inhibitor on the adsorption isotherm implies that the Freundlich isotherm could not be applied in the adsorption mechanism because it suggested some form of divergence from the monolayer adsorption mechanism (Arrousse *et al.,* 2023).

Table 1: Adsorption isotherm parameters for mild steel in the presence of ciprofloxacin

Adsorption Isotherm	R^2	K_{ads}	Parameters
El-Awady	0.9263	3.3×10^{-3}	y=2.00
Flory-Huggins	0.8320	1.85×10^{-3}	x = 0.24
Freundlich	0.9856	1.53×10^{-2}	n =0.60
Frumkin	0.9932	5.16	d = 2.05
Temkin	0.9758	81.19	a = 0.67

Table 2: Adsorption isotherm parameters for mild steel in the presence of ciprofloxacin and iodide ion

Adsorption Isotherm	R^2	K_{ads}	Parameters
El-Awady	0.8872	0.0168	y = 1.375
Flory-Huggins	0.8705	0.0118	x = 0.622
Freundlich	0.9839	2.5×10^{-9}	n = 0.0817
Frumkin	0.9546	0.561	d = 7.75
Temkin	0.9516	0.0040	a=3.144

Thermodynamic Studies

The relationship between adsorption equilibrium constant and free energy of adsorption (ΔG_{ads}) during corrosion of metal at temperature dependent studies is stated in Eqn (9) (Ezeibe *et al.,* 2019a).

$$(\Delta G_{ads}) = -RTln(55.5K_{ads}) \qquad (9)$$

Where, 55.5 represents the water concentration, (mol/L) and other parameters retain their standard meaning.

Generally, the value of ΔG_{ads} up to -20 kJ/mol are considered as physisorption, whereas those around -40 kJ/mol or higher are related to chemisorptions, which involves electronic sharing and /or transfer between organic inhibitors and metal surface to form coordinate type bonds (Tan etal., 2020). The thermodynamic adsorption parameters of the studied inhibitors on the mild steel surface at different temperatures in SAR solution are shown in **Table 3**. It is obvious that the values of expired ciprofloxacin computed for ΔG_{ads} ranged from -14.26 kJ/mol to 15.67 kJ/mol while for expired ciprofloxacin and iodide ion ranged from -39.78 kJ/mol to -43.72 kJ/mol, respectively. The obtained ΔG_{ads} value in this work inferred that the adsorption of the expired ciprofloxacin molecules onto the mild steel substrate is physisorption and the adsorption mechanism of expired ciprofloxacin molecules and iodide ion onto the mild steel in SAR solution is chemisorptions and it occurs spontaneously. The values of ΔG_{ads} for expired ciprofloxacin confirmed that the interaction between expired ciprofloxacin molecules and the charge on the mild steel surface was by electrostatic interaction while the interaction between expired ciprofloxacin molecules, iodide ion and the charge on the mild steel surface was by complex formation (Nleonu *et al.,* 2022). Furthermore, The Gibbs-Helmholtz equation as represented by Eqn (10) was employed for the computation of the standard enthalpy (ΔH^o) of adsorption and standard entropy (ΔS^o) of adsorption.

$$\Delta G_{ads} = \Delta H^o - T\Delta S^o \qquad (10)$$

The variation of ΔG_{ads} against absolute temperature for mild steel corrosion in SAR solution at different studied inhibitor was employed to determine the values of enthalpy (ΔH_{ads}) and entropy (ΔS_{ads}) of the adsorption process respectively, and presented in Table 3. The obtained ΔH_{ads} for expired ciprofloxacin was -0.019 kJ/mol whereas the value increased to 0.005 kJ/mol after addition of iodide ion. Similarly, the ΔS_{ads} increased from 0.047 J/mol/K for expired ciprofloxacin alone to 0.131 J/mol/K for the expired ciprofloxacin-iodide mixture. The slightly negative ΔH_{ads} value obtained for expired ciprofloxacin drug reveals that the adsorption processes were dominated by weak intermolecular interaction and Van der Waals forces, where inhibitor molecules form a protective film that can be partially reversible under prolonged immersion time (Ezeibe *et al.,* 2022). This result supports the observed decline in protective performance with prolonged exposure, which indicated gradual weakening of the adsorbed protective film. However, the slightly positive ΔH_{ads} value observed with ciprofloxacin-iodide system indicates that introduction of iodide ions enhanced the interaction between ciprofloxacin molecules and the metal surface, leading to a more compact and stable protective layer. The low value of ΔH_{ads} for both systems demonstrates that the adsorption processes are controlled by physisorption (Ezeibe *et al.,* 2019b). The positive ΔS_{ads} values recorded for both inhibitor systems shows randomness at the metal-solution interface during adsorption. The higher ΔS_{ads} obtained for the ciprofloxacin-iodide system suggests that the combined inhibitor produced a more favourable interfacial environment for adsorption. The results of this study are in agreement with previous corrosion studies involving pharmaceutical inhibitors and halide ions mixtures (Sundaram *et al.,* 2021; Verma *et al.,* 2017).

Table 3: Thermodynamic parameters for mild steel in the presence of expired ciprofloxacin and synergistic effect in SAR solution

Temperature (K)	$-\Delta G_{ads}$ (kJ/mol)		ΔH_{ads} (kJ/mol)		ΔS_{ads} (J/mol/K)	
	Expired Cipro	Expired Cipro + I^-	Expired Cipro	Expired Cipro + I^-	Expired Cipro	Expired Cipro + I^-
303	14.26	39.78	-0.019	0.005	0.047	0.131
313	14.73	41.09				
323	15.20	42.40				
333	15.67	43.72				

Morte Carlo (MD) Simulation Study

Morte carlo simulation was performed to assess the interfacial interaction of the studied ciprofloxacin drug on to Fe (110) surface using the forcite quench dynamics module of the Material Studio. **Figure 5 and 6** showed the MD equilibrated models of studied ciprofloxacin drug onto FE (110) surface. Quantum chemical parameters calculated for the ciprofloxacin/Fe(110) system (**Table 4**) reveal highly favorable adsorption behavior, corroborating the experimental gravimetric and adsorption studies (Montaser *et al.,* 2024). The adsorption energy (E_{ads}) values are significantly negative: approximately –192.37 (vacuum) and –1.66 (solvated with 100 H_2O molecules), indicating spontaneous and exothermic adsorption of ciprofloxacin molecules onto the iron surface. The rigid adsorption energy (–175.81 in vacuum) and deformation energy (–16.56) further illustrate the stability of the adsorbed configuration, with molecular deformation contributing to stronger surface binding. In the solvated system, the contribution from water molecules (–12.59) suggests a cooperative effect, where solvation enhances inhibitor–surface interactions without compromising adsorption strength. The parameter dE_ad/dNi for ciprofloxacin (–220.40 in the solvated model) underscores the high affinity per molecule, supporting multilayer or dense film formation at higher concentrations. These DFT results align with established principles of corrosion inhibition by organic compounds. Ciprofloxacin, possessing nitrogen, oxygen, and fluorine heteroatoms along with aromatic rings and carbonyl groups, acts as an electron donor (via HOMO) to the vacant d-orbitals of iron, while accepting electrons back into its LUMO. This donor–acceptor interaction facilitates both physisorption and chemisorption, creating a protective barrier that impedes the ingress of corrosive species such as H^+, SO_4^{2-}, NO_3^-, and Cl^- prevalent in synthetic acid rain (Nunach *et al.,* 2025). The enhanced performance in the presence of iodide ions, as noted in the experimental section, likely arises from synergistic co-adsorption, where I^- ions bridge or stabilize the organic layer (Montaser *et al.,* 2024).

Table 4: Determined quantum chemical parameters of ciprofloxacin from DFT studies.

Parameters	Ciprofloxacin/Fe (110)	Ciprofloxacin+100H$_2$O/Fe (110)
Total energy	-218,24215013	-1,575519
Adsorption energy	-192,37119523	-1,661390
Rigid adsorption enegy	-175,81098048	-1,588090
Deformation energy	-16,56021475	-73,30055358
Ciprofloxacin: dEad/:dNi	-192,37119523	-220,39562112
Water: Dead/dNi		-12,58992140

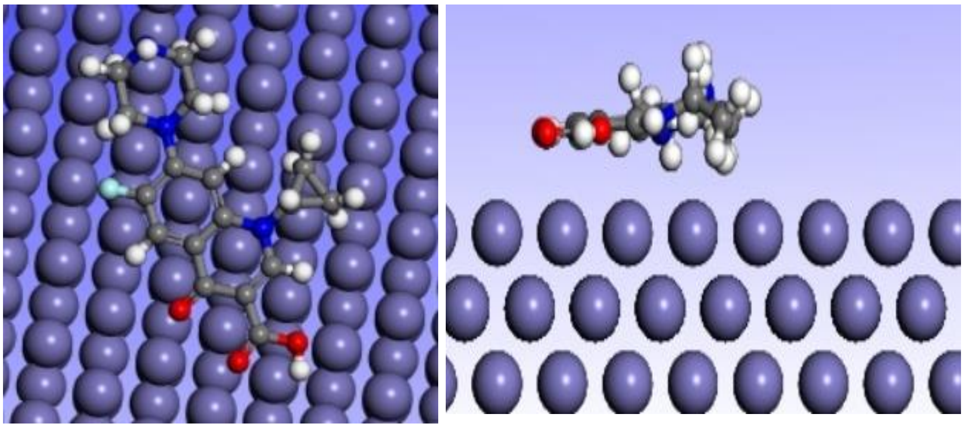

Figure 5: The highest stable configuration for the adsorption of ciprofloxacin molecule on the Fe (110) surface

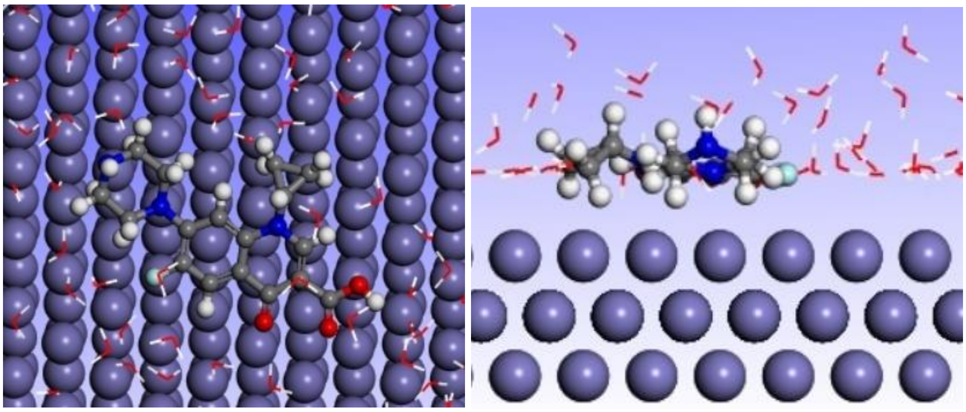

Figure 6: The highest stable configuration for the adsorption of ciprofloxacin+100H_2O/Fe(110) surface

Corrosion Inhibition Mechanism

Figure 7 depicts the synergistic corrosion inhibition mechanism of expired ciprofloxacin-iodide mixture on mild steel in synthetic acid rain solution. The corrosion inhibition mechanism of a ciprofloxacin-iodide mixture followed synergistic adsorption on the mild steel in SAR media form a protective film that decreases corrosion rate in the corrosive environment (Rbaa, *et al.,* 2020). The adsorption is promoted by various electron-rich functional groups present in ciprofloxacin drug, like oxygen and nitrogen atoms which act as the adsorption sites for the process and interact with the mild steel surface. The ciprofloxacin-iodide system enhances the inhibition efficiency through a synergistic effect. The iodide ions in the mixture first adsorb onto the metal surface, creating favourable sites for the adsorption of protonated ciprofloxacin molecules. This cooperative adsorption of expired ciprofloxacin-iodide mixture increases surface coverage and improves stability of the protective film, and retards both anodic metal dissolution and cathodic hydrogen evolution (Montaser *et al.,* 2024). Hence, the inhibitor mixture provides an effective corrosion protection than expired ciprofloxacin drug alone.

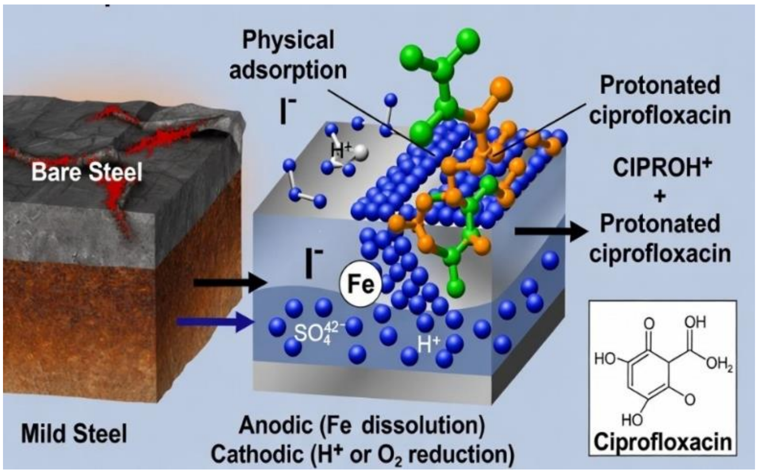

Figure 7: The synergistic corrosion inhibition mechanism of expired ciprofloxacin + iodide on mild steel in SAR

CONCLUSION

The inhibition behaviour of expired ciprofloxacin drug and its synergistic effect with iodide ions on mild steel in synthetic acid rain solution were studied. Gravimetric measurements showed that the addition of iodide to the SAR solution improved the inhibition performance of the expired ciprofloxacin drug considerably. SEM morphology analysis revealed that the inhibitor formed a stable protective film on the mild steel surface. The adsorption behaviour of expired ciprofloxacin-iodide mixture followed Freundlich adsorption isotherm whereas expired ciprofloxacin alone obeyed Frumkin adsorption isotherm. Physisorption of the inhibitor molecules on the mild steel surface was proposed for both inhibitors based on the thermodynamic parameters. Theoretical calculation using MD simulation provided strong support to the experimental findings. The findings of this study demonstrated that the expired ciprofloxacin-iodide system is an effective environmental sustainable corrosion inhibitor for mild steel in synthetic acid rain environment.

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