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Expired drugs as potentially sustainable corrosion inhibitors for metals: Critical narrative review

ABSTRACT

Corrosion processes adversely affect many industries, including oil and gas, petroleum refining, construction, power generation, manufacturing, production, and others. Aggressive media in direct contact with different materials, including metals, cause material decay and usually result in a loss of structural integrity, increasing the risk of pollution from corrosion by-products and other environmental issues. Applying corrosion inhibitors is one of the most effective ways to address metal corrosion. Various chemicals have been recognized as corrosion inhibitors, including inorganic and organic substances and, more recently, waste-derived inhibitors, among which expired pharmaceuticals have attracted significant interest. Many studies show that expired drugs can act as effective metal corrosion inhibitors, with efficiencies often exceeding 90% under specific experimental conditions. Their performance depends not only on the inhibitor's molecular structure and active sites that promote adsorption and protective film formation on metal surfaces, but also on the inhibitor's physicochemical state and the characteristics of the metal–medium interface. Similar to conventional organic inhibitors, pharmaceuticals suppress anodic, cathodic, or both electrochemical corrosion reactions. This review provides an updated comparative and critical analysis of expired pharmaceuticals, with particular emphasis on relationships among their molecular structure, metal substrate, corrosive medium, inhibitor concentration, temperature, adsorption behavior, and inhibition mechanism. Additionally, this review criticizes the environmental sustainability and practical applicability of pharmaceuticals, including differences in formulations, their stability and degradation, testing conditions, and limited validation of these inhibitors under industrially relevant conditions. This integrated approach also identifies the knowledge gaps that currently limit the translation of expired pharmaceuticals from promising laboratory inhibitors to practically applicable corrosion-controlling agents.

***Keywords**: Corrosion, corrosion inhibitors, expired drugs, pharmaceutical waste valorization, circular economy*

1. INTRODUCTION

Corrosion is a physicochemical phenomenon that attacks various materials and degrades their properties. In metals (or alloys), corrosion is a chemical or electrochemical reaction between the substrate and its surrounding medium that typically results in gradual material degradation. Corrosion usually reduces mechanical strength, lowers material performance, shortens equipment shelf life, and ultimately causes fatal failures in technical systems [1, 2]. Hence, current studies focus not only on analyzing corrosion processes but also on examining existing material-protection methods [2, 3] and developing innovative corrosion-prevention techniques [4, 5].

This reflects the growing importance of the fact that the success of many industries, such as manufacturing, petrochemical processing, construction, energy production, and other sectors, depends on materials' resistance to corrosion [6,7].

Corrosion affects several areas, including the global economy, direct and indirect costs, impacts on human life and safety, material and energy losses, and environmental impacts. Economic concerns about metal corrosion are high and increase with industrialization. Thus, the World Corrosion Organization [8] estimated the global annual cost of corrosion at about $2.5 trillion, accounting for approximately 3% to 4% of the GDP of developed countries. The real costs of metal corrosion are difficult to calculate because they include not only direct costs but also substantial indirect costs. Direct costs include expenses associated with recovering and replacing corroded infrastructure, corrosion-protection activities, maintaining protection systems, using corrosion-resistant alloys, and other activities related to

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repairing corrosion damage. Indirect costs usually include expenses associated with reduced production efficiency and resource leakage (oil, gas, water, etc.) from corroded pipes. More importantly, corrosion damage to installations and equipment compromises human health and safety and contributes to environmental pollution [9]. As the literature shows, implementing effective, high-quality corrosion protection methods can prevent a quarter of corrosion-related failures [10].

Because corrosion is a continuous problem, industries use different methods to prevent it rather than eliminate it. Implemented techniques include material modification and alloy design, adaptation to the corrosive environment, surface coatings, cathodic and anodic protection, and inhibitors. The method, which involves material modifications and the selection of corrosion-resistant alloys, aims to increase the system's thermodynamic stability [5]. Yet this method is expensive and, in some industries, used as a last resort. With alterations in the corrosive medium, the removal of species that promote corrosion, such as moisture and oxygen, or changes in pH, the corrosion rate is reduced [12]. One common method is barrier protection, or applying a coating to a metal surface, using techniques such as galvanization [13, 14], electroplating [14], organic paints and emulsions [15], and sol-gel coatings [16]. Advanced techniques include self-healing epoxy coatings [17] and metal-organic frameworks [18]. Cathodic and anodic protection are two electrochemical methods used to inhibit corrosion. Cathodic protection prevents metal surfaces from losing electrons by converting them into cathodes, thereby increasing corrosion resistance. Anodic protection works by applying a controlled electric current to polarize a metal into its "passive region", accompanied by the formation of thin metal oxide films on the surface that act as a protective barrier against further corrosion [1-3].

Inhibitors are another effective way to inhibit corrosion. Corrosion inhibitors are chemical substances used in aggressive media at low concentrations (10 to 10000 ppm) to reduce corrosion rates to technologically acceptable values. These substances restrict the electrochemical reactions at metal surfaces, namely, oxidation and reduction, and prevent metal degradation. The type of inhibitor selected depends not only on the nature of the metal substrate but also on the conditions under which the material is used, e.g., high temperature or severe hydrodynamic regimes [2, 3].

Inhibitors act in accordance with one or a combination of the following mechanisms [2, 3]:

- By forming a barrier film between the metal surface and the corrosive environment, it restricts the transport of reactive species to or from the metal surface, as well as the transport of corrosion products from the metal surface to the medium.
- Creation of a film with a high electrical resistance, enough to restrict the flow of electrons between the places acting as anode and cathode.
- By surface refinement, which makes the metal surface less accessible to corrosion.

The most efficient inhibitors apply more than one of the above-mentioned mechanisms. Corrosion-protection efficiency depends on the metal being protected, the nature and chemical structure of the inhibitors, their concentrations, their adsorption on the metal surface, and the extent of interaction between inhibitor molecules and the metal surface. Corrosion inhibitor application is strictly controlled. Certain corrosive systems require careful inhibitor selection to ensure effective material protection, as an inhibitor effective in one system may be ineffective or even dangerous in another [2, 3].

Many traditional corrosion inhibitors, such as chromates [19], phosphates [20], nitrates [21], and other inorganic [22, 23] and organic compounds [24, 25], demonstrate excellent inhibition performance. Yet, surprisingly, only a small number are used commercially, mostly because of complex production protocols and, consequently, higher costs, as well as their toxicity to humans and harm to the environment, which limits their industrial applications and raises doubts about their sustainability. These and similar uncertainties have prompted intensive research to develop environmentally benign, i.e., “green” alternatives to synthetic inhibitors. Most eco-friendly inhibitors are of natural origin, derived from plants [26-29], natural polymers, and biomass [30-32], or from the reuse of pharmaceuticals and expired drugs [33].

A very interesting subset of potentially more sustainable corrosion-control alternatives involves pharmaceutical products with expired shelf life. A large quantity of expired drugs is generated every year that cannot be used for therapeutic purposes and, as waste, creates serious disposal and environmental issues. Improper disposal of expired drugs can contaminate water and pose ecological and public health challenges [34]. Reusing waste drugs as corrosion inhibitors and giving them another value is a strategy within the sustainability and circular economy frameworks [35, 36].

As indicated in recent studies, drugs from different therapeutic classes, such as antibiotics [37], anti-inflammatory agents [38],

antihypertensive drugs [39], and others, exhibit potent anti-corrosion activity against various metals, including steel alloys, aluminum, and its alloys, across a range of media, including acidic, alkaline, saline, and other adverse industrial settings. Molecular structures and functional groups facilitate adsorption onto metal surfaces and contribute to the effectiveness of pharmaceuticals as corrosion inhibitors [37-40].

Several reviews have previously examined pharmaceuticals, including expired ones, as corrosion inhibitors. Earlier studies have examined the effects of drug chemical composition and molecular structure, adsorption and inhibition mechanisms, inhibitor efficiency, environmental considerations, and challenges associated with practical application [33, 35, 36, 40]. These studies have established an important foundation for understanding the anticorrosive behavior of pharmaceutical compounds. However, ongoing research in this field, including studies published in recent years, offers an opportunity to move beyond compiling individual inhibition efficiencies and to identify broader relationships among pharmaceutical class, molecular characteristics, corrosion system, and inhibitor performance [41, 42].

Accordingly, this review provides an updated comparative and critical analysis of expired pharmaceuticals, using therapeutic class as the principal organizational framework while comparing their behavior across different metal-corrosive medium systems. It pays particular attention to relationships among inhibitor molecular structure, active adsorption sites, inhibitor concentration, temperature, metal substrate, corrosive medium, adsorption behavior, and electrochemical inhibition mechanisms. This approach enables the identification of recurring structure–performance relationships and system-dependent variations across different pharmaceutical classes. In addition, reported inhibition efficiency is considered together with factors relevant to practical sustainability, including pharmaceutical formulation, active-component stability and degradation, environmental implications, methodological comparability, and the predominance of short-term laboratory investigations over studies conducted under industrially relevant conditions. Thus, this work aims not only to summarize the corrosion-inhibition performance of expired pharmaceuticals but also to critically assess the conditions under which their reported performance may translate into environmentally and technically viable corrosion-control applications.

This study presents a critical narrative review based on a structured literature search from two sources, Web of Science and Google Scholar, covering literature mainly published between January 2013 and May 2026, including experimental and theoretical publications on expired pharmaceuticals as metal corrosion inhibitors that provide sufficient evidence to compare different pharmaceutical classes, metal substrates, and corrosive environments. We also included earlier publications that address this topic or provide mechanistic or historical context. Relevant contributions were retrieved using keywords including “expired drug”, “expired pharmaceutical”, “waste pharmaceutical”, “corrosion inhibitor”, “corrosion inhibition”, “anti-corrosion”, and “corrosion protection”, combined with terms describing metallic substrates, such as “metal”, “mild steel”, “carbon steel”, “low-carbon steel”, “stainless steel”, “aluminum/aluminium”, “copper”, “zinc”, and “nickel”. Search terms were used individually and/or in Boolean combinations (“expired drug*” OR “expired pharmaceutical*” OR “unused drug*” OR “waste pharmaceutical*”) AND (“corrosion inhibit*” OR “corrosion protection” OR “anti-corrosion”) AND (metal* OR steel OR “mild steel” OR “carbon steel” OR aluminium OR aluminum OR copper OR zinc OR nickel).

The article selection process involved two stages. After reviewing the titles and abstracts of retrieved articles, we conducted a full-text assessment to select publications following criteria such as peer-reviewed articles published in English that address corrosion inhibition of metallic materials using expired drugs as inhibitors and provide sufficient information to characterize the metal–medium–inhibitor system, excluding those that analyze only pharmaceuticals from therapeutic and environmental perspectives. We selectively considered studies involving non-expired pharmaceuticals when they provided directly relevant mechanistic or comparative information on compounds also investigated in the context of pharmaceutical-based corrosion inhibition.

2. FUNDAMENTALS OF CORROSION INHIBITION

The process of controlling, i.e., regulating, reducing, or preventing the destructive interaction between a metal and its surroundings by adding chemical substances at low concentrations, which, upon adsorption, form a thin protective layer on metal surfaces, serving as a physical barrier against corrosive media.

According to the mechanisms of protection, inhibitors can operate to provide anodic, cathodic, or mixed inhibition. Namely, anodic or passivation inhibition stops the anodic corrosion reaction by creating insoluble deposits, usually oxides or salts, on anodic sites, shifting the corrosion potential to more positive values. On the other hand, insufficient concentrations of anodic inhibitors may

result in incomplete surface coverage and local pitting corrosion of metals. Cathodic inhibitors shift cathodic reactions to more negative potentials, reducing their rates, such as hydrogen production in acidic solutions or oxygen reduction in alkaline solutions. Inhibitor adsorption on the metal substrate, precipitation of insoluble barrier films in cathodic regions, or preventing reactive species from reaching the electrode interface by reducing their diffusion rate are among the characteristics of cathodic inhibition. Inhibitors that act via both mechanisms simultaneously are highly flexible and, by forming a protective layer on metal surfaces, prevent aggressive species from accessing both anodic and cathodic sites. Almost 80% of organic inhibitors, including pharmaceutical compounds, are mixed-type inhibitors [43-45].

An important class of inhibitors comprises organic substances whose protective activity is achieved through adsorption on metal surfaces, blocking the diffusion of species involved in the corrosion reaction [43-47]. Organic molecules adsorb on metal surfaces via physical, chemical, and mixed-type mechanisms [48]. Physical adsorption, i.e., physisorption, occurs when electrostatic interactions exist between the inhibitor and the metal surface. And, the formation of covalent bonds or donor-acceptor interactions is typical for chemical adsorption. The molecular structure and the presence of potential adsorption sites, e.g., heteroatoms, polar functional groups, aromatic rings, and π-electron systems, facilitate interactions between organic molecules and metal surfaces [48,49]. Structural characteristics alone cannot reliably predict inhibition efficiency. So, researchers also consider the combined characteristics of the inhibitor, the metal surface, and the corrosive environment [50]. Factors such as protonation state and molecular geometry of the inhibitor, its solubility in the corrosive medium, the charge and chemical state of the metal surface, adsorption energy, inhibitor concentration and temperature, and competitive adsorption involving water molecules, aggressive ions, or other species present at the metal–solution interface influence the adsorption and inhibition behavior of drugs [41, 51-54].

Inhibitor adsorption and surface coverage are also affected by the inhibitor concentration and temperature in the corrosion system. Inhibitor efficiency usually increases with increasing its concentration until adsorption approaches saturation [43-47]. Temperature effects on inhibition are system-dependent. Inhibition systems can show both improved and decreased inhibition as the temperature increases [50]. Higher temperatures often reduce inhibition by promoting desorption [52, 55], although efficiency can increase in systems that favor stronger chemisorptive interactions [56, 57].

The literature reports various empirical techniques to assess inhibition efficiency. For example, gravimetric methods determine average corrosion rates and the inhibition efficiency over time [58]. Electrochemical methods [58, 59], such as potentiodynamic polarization and electrochemical impedance spectroscopy, have been used to determine metal corrosion behavior, characterized by corrosion current, corresponding potential, and the charge-transfer resistance of the active species. Researchers have usually assessed the morphology of protective layers using sensitive microscopic techniques, namely scanning electron microscopy and atomic force microscopy [58]. In addition, evidence for functional groups and chemical bonds involved in inhibitor–metal interactions can be obtained using a range of spectroscopic methods, such as Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy [60]. Inhibition efficiencies obtained with different techniques should not be treated as numerically equivalent because they use different measurement bases and time scales. Recently, researchers have used computational methods, such as density functional theory [61, 62] and Monte Carlo simulation [62], as complementary techniques to traditional methods to provide theoretical insight into inhibitor molecular reactivity, preferred adsorption sites, and possible inhibitor–metal interactions. Understanding the basics of inhibition principles is important not only for evaluating the suitability of organic compounds, including pharmaceuticals, as corrosion inhibitors for metals. In this regard, because of their complex molecular structures, diverse functional groups, and active adsorption sites, pharmaceuticals are promising high-potential corrosion inhibitors.

3. EXPIRED DRUGS AS CORROSION INHIBITORS

Typical organic corrosion inhibitors used in industry include acetylenic alcohols, amides, imidazolines, dimer and trimer acids, quaternary amines, surfactants, and other substances. Due to their adverse effects, including high cost, complex synthesis, toxicity, and other issues, in addition to the strict environmental rules, the usage of many effective inhibitors has been limited or banned. Increased environmental concerns have led to strict regulations on the use of chemicals with adverse environmental effects, resulting in a reduction or complete cessation of use for numerous favorably effective corrosion inhibitors [15, 48]. Thus, due to their toxicity, chromates have been removed from the list of technically applicable inhibitors [63]. Similarly, the use of polyphosphates

has been reduced because their discharge into natural waters can lead to excessive algal growth (eutrophication) [64]. Also, because of their toxicity, the use of amines as corrosion inhibitors in steam boilers has been limited [65]. Compounds used as corrosion inhibitors in oil wells, such as arsenic oxides [66] and propargylic alcohol [67], had to be replaced with less toxic alternatives.

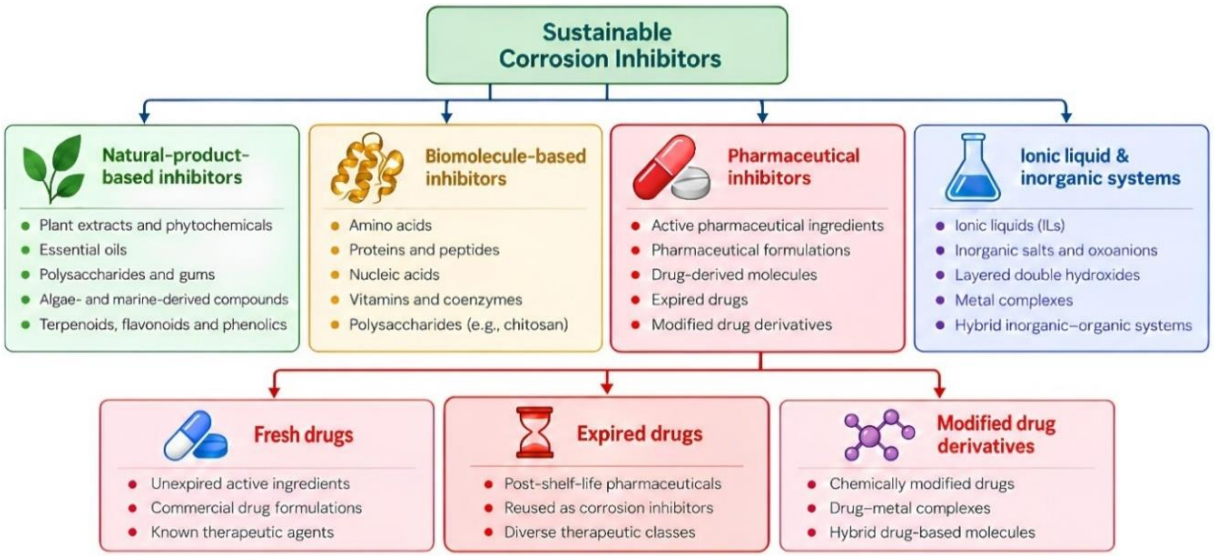


Figure 1. Alternative corrosion inhibitors commonly discussed within the framework of sustainable corrosion-control strategies [4, 30, 32, 33, 36, 41]

Researchers have recently focused on potentially more sustainable corrosion-control alternatives [33]. As shown in Fig. 1, alternative corrosion inhibitors commonly discussed within green corrosion-control strategies include natural product-based, biomolecule-based inhibitors, ionic liquid and inorganic systems and pharmaceuticals [4, 30, 32, 33, 36, 41]. The major advantage of pharmaceuticals is that they are commercially available, have defined active ingredients, and have comparatively standardized formulations, which are important for therapeutic application and may additionally facilitate reproducibility in corrosion-inhibition studies [35, 36]. Yet approved therapeutic use does not guarantee the environmental safety of pharmaceuticals that are reused as corrosion inhibitors. A comprehensive analysis is required to ensure the environmental compatibility of reused drugs, evaluating each drug ingredient and formulation for toxicity, persistence, environmental fate, degradation products, and potential environmental effects.

Repurposing expired pharmaceuticals may offer a potential economic advantage by valorizing materials that would otherwise require disposal [68, 69]. However, the current literature does not provide sufficient quantitative techno-economic data to indicate that expired pharmaceuticals can fully substitute commercial corrosion inhibitors [12, 41, 50]. Comparing the two classes of inhibitors would need to consider not only acquisition cost but also the effective inhibitor dosage, collection and sorting, formulation characterization, preparation and dosing, storage, replenishment requirements, and waste-management and environmental-compliance costs [41, 42].

An interesting subgroup of pharmaceutical-based inhibitors is expired ones, Fig. 2. Many expired drugs are treated as regular waste and usually buried in landfills or spread into soil and aquatic systems, causing pollution and disrupting ecological balance. One sound approach to reducing the environmental problems associated with expired drugs is repurposing them for other applications, specifically using them beyond their medical expiration date as corrosion inhibitors. This strategy aligns with the sustainability goals and the principles of green chemistry and circular economy [41, 70].

On the other hand, a drug's therapeutic activity does not determine its success as a corrosion inhibitor. Rather, its inhibition performance depends on the chemical species present in the expired formulation and their ability to adsorb onto and interact with the metal surface [41,69]. Following the historical FDA studies showing that about 90% of drugs remained stable years past their expiration dates, researchers often generalize that expired drugs retain their molecular integrity and they are therefore suitable as corrosion inhibitors [69]. Yet this oversimplification does not automatically mean that pharmaceuticals retain their original molecular structure or composition [70].

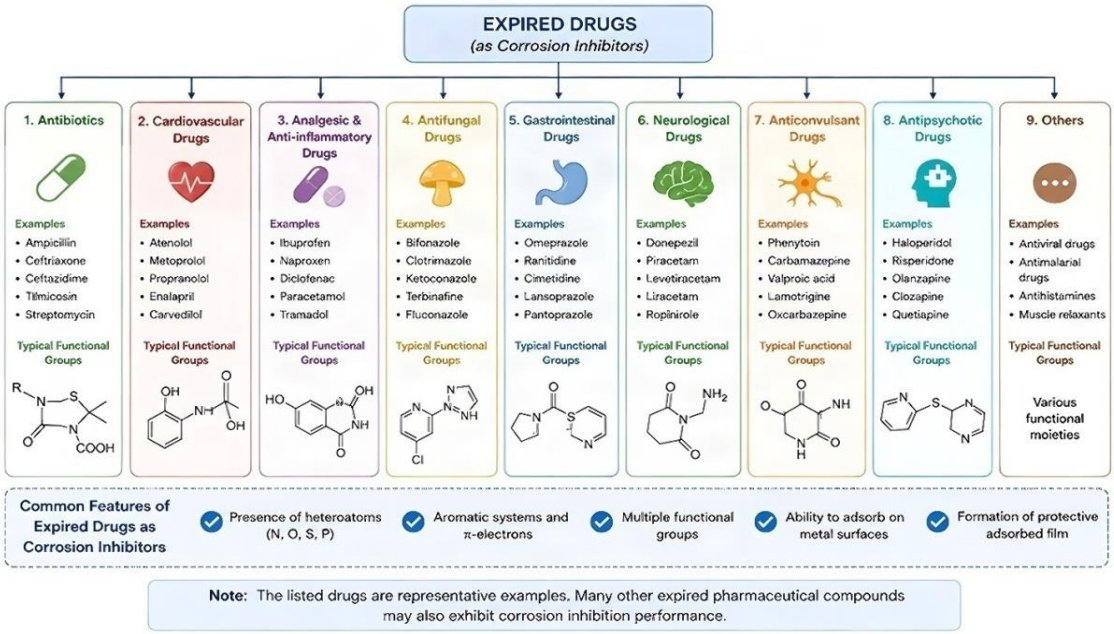


Figure 2.Classification of expired drugs by therapeutic class used as corrosion inhibitors

Thus, it should be considered that a pharmaceutical's stability is influenced by many factors, including the chemical stability of the active pharmaceutical ingredient, excipients, dosage formulations, storage conditions (temperature and humidity, exposure to light and oxygen), and the time elapsed since its labeled expiration [41, 50]. Based on these factors, degradation may reduce the anti-corrosive efficiency of the original active component and/or form degradation products with physicochemical and adsorption properties different from those of the parent compound [50, 71, 72]. Consequently, the conclusions about the effectiveness of an expired pharmaceutical as a corrosion inhibitor should not be inferred solely from the molecular structure of its nominal active ingredient but should, where possible, be evaluated in relation to the actual composition and condition of the expired formulation [12, 41, 73]. Another gap in the available literature is that the time elapsed between the labeled expiration date and corrosion-inhibition testing is not consistently reported. A pharmaceutical tested shortly after expiration cannot necessarily be considered chemically equivalent to the same formulation stored for several years beyond its shelf life [41, 50, 71]. Additionally, expired drug samples used in academic studies are usually purchased from local household stocks or medical practitioners, where the storage history is unknown. Differences in storage history may produce different degradation profiles even for products containing the same active pharmaceutical ingredient [51,55]. Hence, one can say that the phrase "expired drug" includes chemically non-equivalent materials unless the expiration period, storage conditions, formulation, and, ideally, compositional stability are adequately characterized [41, 74]. Therefore, future corrosion-inhibition studies should report these parameters and include appropriate analytical characterization of expired formulations before using them as inhibitors.

Standardized chemical composition and their commercial availability are additional advantages of expired medications. Namely, the composition of most "green" inhibitors extracted from plants varies depending on factors such as the geographical region of origin, extraction procedures, seasonality, and storage conditions. On the other hand, drug formulations with well-defined composition follow standard production conditions, enabling their compositional reproducibility [41, 42, 68-70, 73, 75, 76].

Questions about the long-term stability, degradation profiles of certain active components, and the environmental impact of degradation by-products raise additional concerns about the industrial applications of expired drugs as corrosion inhibitors [41,77]. These and similar questions introduce the need for further extensive studies in this area.

Repurposing expired pharmaceuticals as corrosion inhibitors can extend the useful life of products that would otherwise require disposal and may therefore contribute to waste-reduction and circular-economy objectives. However, this benefit alone does not qualify a pharmaceutical compound as environmentally benign or "green". Such a classification requires specific evidence concerning

ecotoxicity, biodegradability and persistence, environmental fate, degradation products, and potential effects on aquatic and terrestrial organisms [41, 77]. Corrosion inhibition studies are generally focused on inhibition efficiency, adsorption behavior, and electrochemical performance, and they usually do not provide the quantitative ecotoxicological data needed to establish environmental safety. Furthermore, the OECD (Organization for Economic Co-operation and Development) studies on pharmaceutical residues in freshwater note a lack of complete environmental toxicity information for many pharmaceuticals. Consequently, although frequently used in the corrosion literature, terms such as “green”, “eco-friendly”, and “environmentally friendly” should be interpreted cautiously when applied to expired pharmaceuticals. In this review, waste valorization is therefore considered a potential sustainability advantage, whereas environmental safety requires independent experimental verification. This difference is especially important for pharmaceuticals, e.g., antibiotics, where ecotoxicological effects and potential contributions to antimicrobial resistance raise environmental concerns [41].

3.1. Antibiotics as Corrosion Inhibitors for Metals

Antibiotics are among the most frequently studied pharmaceuticals as corrosion inhibitors [56, 57, 78-93]. For several metal-medium systems, researchers have reported inhibition efficiencies above 95% under specific experimental protocols, indicating their potential as corrosion inhibitors [41,50, 56, 78]. Their inhibitory activity is commonly attributed to their molecular structure and the presence of active atom centers (mainly nitrogen, oxygen, and sulfur) and functional groups (carbonyl, amide, amino, hydroxyl, and heterocyclic groups), which promote adsorption onto the metal surface and restrict the access of corrosive species to the metal-solution interface, while the magnitude of the reported efficiency remains dependent on the metal-medium system and experimental conditions [70, 76].

The effectiveness of expired antibiotics as corrosion inhibitors has been confirmed for several metals in aggressive environments. Table 1 lists the antibiotics by chemical class and the metal-medium systems in which they were tested.

Table 1. Expired pharmaceutical corrosion inhibitors under the reported experimental conditions

Therapeutic class	Metal / substrate	Corrosive medium	Inhibitor concentration	Temp. (°C)	Reported maximal inhibition efficiency (%)	Experimental method*	Ref.
Antibiotic drugs							
Cephalosporin							
Cephalexin	Aluminum (5083AA)	Saline-acidic (mixture of 0.6 M NaCl and 1 M H_2SO_4)	200 ppm	25	75	PDP	[78]
Cephalexin	Mild steel	3.65% NaCl	100 ppm	25	65.84	PDP	[79]
Cephalexin Monohydrate (not declared as expired drug in the source)	Low carbon steel	1 M HCl	600 ppm	25	67	EIS	[80]
Cefazolin	Carbon steel	0.1M H_2SO_4	5×10^{-4} M	30	99.6	PDP	[80]
Cefdinir	Mild steel	1 M HCl	6.32×10^{-4} M	35	97.9	WL	[81]
Ceftriaxone	Carbon steel	0.5 M HCl	50 ppm	50	93.37	PDP	[81, 82]
Ceftriaxone	Pure (SABIC) iron	1 M HCl	500 ppm	25	98.02	GAP	[94]
Ceftriaxone sodium	Carbon Steel	0.1 M H_2SO_4	10^{-3} M	25	85.0	PDP	[50]
Ceftriaxone	Nickel	0.5 M H_2SO_4	10^{-4} M	25	70.1	PDP	[83]
Ceftriaxone	Nickel	1 M HCl	10^{-5} M	25	73.9	EIS	[83]
Ceftazidime	Zinc	1 M HCl	300 ppm	25	70.3	EIS	[84]
Ceftazidime	Copper	1M HCl	300 ppm	25	94.2	EIS	[85]
Penicillin							
Ampicillin	Mild Steel	5% HCl	10×10^{-3} M	55	96.9	WL	[56]

Therapeutic class	Metal / substrate	Corrosive medium	Inhibitor concentration	Temp. (°C)	Reported maximal inhibition efficiency (%)	Experimental method*	Ref.
Ampicillin	Mild Steel	1 M H_2SO_4	400 ppm	20	93.95	PDP	[86]
Ampicillin	Pure (SABIC) iron	1 M HCl	500 ppm	25	95.83	PDP	[41, 94]
Ampicillin	Cast Carbon Steel	0.5 M H_2SO_4	10^{-2} M	25	89.22	PDP	[87]
Amoxicillin	Low-Carbon Steel	3.5% NaCl	750 mg/L	25	67.18	WL	[88]
Amoxicillin	Carbon Steel	0.6 M NaCl	6×10^{-3} M	40	82.15	PDP	[50]
Amoxicillin	Carbon Steel	1 M HCl	10×10^{-3} M	25	93.7	EIS	[50]
Amoxicillin	Mild Steel	1 M HCl	1800 ppm	25	94.47	WL	[89]
Amoxicillin	Mild Steel	0.1 M HCL	3×10^{-4} M	30	94.29	WL	[50]
Amoxicillin	Mild Steel	0.1 M H_2SO_4	0.001 M	30	80.06	WL	[50]
Amoxicillin	Pure (SABIC) iron	1 M HCl	500 ppm	25	94.47	PDP	[90]
Cloxacillin	Mild Steel	1 M H_2SO_4	15×10^{-4} M	Room temp.	91.47	PDP	[91]
Cloxacillin (not declared as expired drug in the source)	Mild Steel	1 M HCl	15×10^{-4} M	Room temp.	81.19	WL	[92]
Cloxacillin (collected for two years in the source)	Low-Carbon Steel	3.5% NaCl	750 mg/L	45	90.4	EIS	[88]
Macrolide antibiotics							
Azithromycin	Aluminum (5083AA)	Saline-acidic (mixture of 0.6 M NaCl and 1 M H_2SO_4)	200 ppm	25	71.9	PDP	[78]
Azithromycin	Mild Steel	2 M HCl	800 ppm	30	88.77	WL	[50]
Azithromycin	Mild Steel	1 M H_2SO_4	400 ppm	25	88.32	PDP	[93]
Roxithromycin	Mild Steel	1 M H_2SO_4	400 ppm	25	86.75	EIS	[93]
Aminoglycoside							
Streptomycin	Carbon Steel	0.5 M CH_3COOH / 0.25 M CH_3COONa	10^{-3} M	45	90.2	PDP	[57]
Antihypertensive / Cardiovascular Drugs							
Beta-Blockers							
Metoprolol, (not declared as expired in the source)	Mild Steel	1M HCl	300 ppm	25	94	PDP	[95]
Metoprolol (not declared as expired in the source)	Mild Steel	0.5 M H_2SO_4	300 ppm	25	83	PDP	[95]
Metoprolol	Carbon Steel (OLC45)	3.5% NaCl	10^{-3} M	Room temp.	69.1	PDP	[74]
Atenolol	Mild Steel	1M HCl	200 ppm	Room temp.	93.29	EIS	[41]
Atenolol	Aluminum	3M HCl	400 mg/L	Room temp.	98.7	PDP	[41]
Carvedilol	Carbon Steel	1M HCl	1.6 10-4 M	25	98.9	WL	[41]

Therapeutic class	Metal / substrate	Corrosive medium	Inhibitor concentration	Temp. (°C)	Reported maximal inhibition efficiency (%)	Experimental method*	Ref.
Diuretics							
Furosemide (not declared as expired in the source)	Carbon Steel	1.0 M HCl	300 ppm	45	90.5	WL	[96]
Hydrochlorothiazide	Carbon Steel	2 M HCl	15 10-5 M	30	83.1	EIS	[42, 97]
Spironolactone (not declared as expired in the source)	C38 carbon steel	10% HCl	7.2 10-3 M	30	98.1	WL	[98]
Angiotensin-converting enzyme (ACE)							
Enalapril Maleate (not declared as expired in the source)	Carbon Steel	3.5% NaCl	1200 ppm	25	89.74%	PDP	[99]
Perindopril	Mild Steel	3 M HCl	4 mg/100 mL	60	93.75	PDP	[100]
Angiotensin II Receptor Blockers (ARBs)							
Candesartan	Aluminum	1 M HCl	40 ppm	30	92.9	PDP / EIS	[42, 101]
Irbesartan	Mild steel	1 M HCl	300 mg/L	Room temp	94.0	EIS	[42]
Irbesartan	Mild steel	0.5 M H_2SO_4	300 mg/L	Room temp.	83.0	EIS	[42]
Cardiovascular and Related Medications							
Atorvastatin	Mild steel	1 M HCl	150 ppm	NR	99.1	PDP	[51]
Amiodarone	Mild steel	1 M HCl	0.001 M	30	88.8	WL	[52]
Hydralazine (Vasodilator)	Mild steel	1 M HCl	120 ppm	50	91.4%	EIS	[42]
Detralex (Diosmin + Hesperidin) (expired 3 months)	Zn	3.5% NaCl	7.82 mM	25	96%	PDP	[73]
Anti-inflammatory and analgesic drugs							
Non-steroidal anti-inflammatory drug (NSAID)							
Aspirin (Acetylsalicylic Acid) (not declared as expired in the source)	Carbon steel XC48	1 M HCl	5×10^{-3} M	35	96.3	EIS	[53]
Aspirin (Acetylsalicylic Acid) (not declared as expired in the source)	Mild steel	1 M HCl	50 ppm	30	78.94	WL	[102]
Naproxen (not declared as expired in the source)	Carbon Steel	1 M HCl	8×10^{-3} M	25	94.96	WL	[54]
Naproxen	Al	3 M HCl	1 g/L	Room temp.	99.0	PDP	[103]
Ibuprofen	Copper	Synthetic Acid Rain	$1\cdot10^{-2}$ M	Room temp.	97.3	PDP	[104]
Ibuprofen	Copper	0.5 M H_2SO_4	5 mM	Room temp.	95.25	EIS	[105]

Therapeutic class	Metal / substrate	Corrosive medium	Inhibitor concentration	Temp. (°C)	Reported maximal inhibition efficiency (%)	Experimental method*	Ref.
Analgesic							
Paracetamol (expired 1 month)	Low-carbon steel	1.0 M H_2SO_4	275 mg/L	27	94.2	GAP	[106]
Paracetamol	Mild Steel	0.5M HCl	8.0 mM	Room temp.	73.24	WL	[107]
Tramadol	Carbon Steel	0.1M H_2SO_4 (pH = 3)	500 ppm	30	93.2	WL	[108]
Analgin (Metamizole or Dipyrone) (not declared as expired in the source)	Mild Steel	1 M HCl	4000 ppm	25 °C	96.1	WL	[109]
Anti-inflammatory							
Ardosons	API 5L X65 Steel	1 M HCl	100 ppm	25 °C	77.1	EIS	[110]
Antifungal, neurological, and miscellaneous pharmaceutical drugs							
Antifungal drugs							
Bifonazole	X65CSCarbon Steel	1 M HCl	375 mg/L	26 °C	92.08	GAP	[111]
Terconazole	X65CS Carbon Steel	1 M HCl	375 mg/L	26 °C	94.19	GAP	[111]
Neurological and Psychotherapeutic Drugs							
Donepezil (not declared as expired in the source)	EN24 Steel	NH_2SO_3H Sulfamic Acid	$1{\cdot}10^{-3}$ M	30	77.66	PDP	[112]
Lircetam	Low-carbon steel	1 M HCl	60 ppm	30	98.16	WL	[55]
Ropinirole	Mild steel	1 M HCl	0.001 M	Room temp.	92.85	WL	[113]
Thiamine (Vitamin B1)	SABIC Iron	0.5 M H_2SO_4	250 ppm	30	91.14	GAP	[114]
Riboflavin (Vitamin B2)	SABIC Iron	0.5 M H_2SO_4	250 ppm	30	92.40	GAP	[114]
Plant extracts (fresh)							
Quercus palustris leaves extract	Low-carbon steel	0.5 M H_2SO_4	1 g/L	~ 25	91.8	WL	[26]
Solanum chryso-trichum fruit extract	Mild steel	1 M HCl	1.20 g/L	25	93.38	WL	[27]
Piper chaba extract	Mild steel	2 M H_2SO_4	1 g/L	25	86.53	WL	[28]
Calyptocarpus vialis extract	Mild steel	2 M H_2SO_4	1 g/L	25	82.69	WL	[29]

*Experimental method for which the maximal inhibition efficiency is obtained: GAP - Galvanostatic polarization, GS - Gasometric studies EIS - Electrochemical Impedance Spectroscopy, OCP - Open-circuit potential measurements, PAP - Potentiodynamic anodic polarization, PDP - Potentiodynamic polarization, WL – weight loss (gravimetric) technique. NR – Not reported in the cited literature

The Langmuir adsorption model is often used to fit the adsorption of pharmaceutical corrosion inhibitors on metal surfaces [57, 71, 88, 94], although it does not universally capture the drugs' adsorption behavior [50]. This isotherm assumes monolayer adsorption on sites with similar adsorption energy, with little or no lateral interaction between adsorbed molecules. Yet, several studies show better or complementary agreement with other isotherms. Thus, Fayomi et

al. [79], in their study on the inhibition properties of expired Cephalexin on mild steel in saline media, indicated that drug adsorption follows both the Langmuir and the Freundlich isotherms. Adsorption following the Freundlich model occurs on uneven, heterogeneous surfaces with molecules piling up. Al-Nami [80] suggested the Temkin isotherm as the best model to describe the adsorption behavior of expired Cephalexin monohydrate on low-carbon steel in an HCl-corrosive environment, assuming that, due to adsorbent-adsorbate interactions, the heat of adsorption decreases as surface coverage increases [84].

Namely, protonated molecules of Cephalexin monohydrate experience electrostatic interaction with the negatively charged metal surface originating from the attached chloride anions. Partial electron transfer from the drug's heteroatoms to the metal surface may lead to the formation of a coordinate covalent bond. Complex formation between the drug and the metal is also possible due to the free electrons on heteroatoms in the drug molecule, which connect with freshly formed ferrous cations on the metal surface [80]. Similarly, the Temkin model best described the adsorption of Ceftazimide on copper in HCl, with the adsorption identified as physical and the drug desorbing as the temperature increased [85]. Conversely, using weight loss analysis, Alarmy et al. [56] showed that the inhibition efficiency of expired Ampicillin on mild steel in the presence of HCl as a corrosive medium increases with temperature and, at the same concentration of 10 mM, after 6 h of exposure, achieves approximately 77% at room temperature, and it reaches its maximum of 97% at 55 °C. The authors attributed this behavior to a shift from physical adsorption to chemisorption, which is enhanced by the desorption of water molecules from the metal surface [56]. In this case, the authors [56] confirmed mixed inhibition (i.e., both cathodic and anodic) following the Langmuir adsorption isotherm. These findings indicate that the adsorption behavior of pharmaceutical inhibitors is system-dependent and may vary with the inhibitor, metal surface, corrosive medium, and experimental conditions.

The inhibitor concentration in the corrosive medium also affects the efficiency of the expired antibiotic, as shown by Kamel et al. [84], who analyzed the effect of expired Ceftazidime on zinc dissolution in 1 M HCl, varying the temperature and the drug concentration. The maximum inhibition efficiency of approximately 70% was observed at 300 ppm and decreased with increasing concentration, most likely due to adsorption of drug molecules on the metal substrate, thereby preventing further adsorption [84]. The absence of vacant d-orbitals in zinc metal might indicate that expired drug adsorption occurs via physisorption only, resulting in lower inhibition efficiency. Yet, other types of interactions, such as charge transfer or s-p orbital hybridization, may result in strong adherence of the inhibitor to the metal surface [84].

Although most studies have been performed in acidic media, some have been conducted in brine solutions or mixed saline-acidic solutions. Some studies [50, 88], using various experimental protocols, reported lower or more variable inhibition efficiencies of expired drugs in saline media than in acidic media, which is considered a qualitative trend. This occurrence is attributed to limited solubility in saline solutions, reduced protonation and electrostatic attraction, the formation of soluble complexes, and molecular size and coverage. For example, for expired Ampicillin, the higher inhibition efficiency in HCl solutions was attributed to a synergistic “bridging” effect between protonated drug molecules, chloride ions, and the positively charged metal surface. Conversely, in neutral brine media, antibiotics do not undergo a high degree of protonation, but they likely exist in a zwitterionic or neutral form, which results in weaker electrostatic attraction to the metal surface [50]. In addition, rather than forming insoluble protective layers, some drug inhibitors form soluble complexes with metal ions, thereby carrying them away from the surface. If these complexes remain in solution, metal dissolution is facilitated [75]. Similarly, Jawad et al. [88], within the same experimental study, examined expired Cloxacillin, Amoxicillin, and Cephalexin as inhibitors of low-carbon steel in a 3.5% NaCl solution, where, using the weight loss method, for the same drug concentration of 750 mg/L, the highest inhibition efficiency of 82.81% was observed for Cloxacillin. As the authors stated, the lower efficiency of Amoxicillin and Cephalexin may be related to their lower numbers of functional groups, smaller molecular weight, and molecular surface area, implying that even when they adsorb, they cover less of the metal surface than Cloxacillin, leaving more sites vulnerable to attack by corrosive species [88]. On the other hand, Ahmed et al. [78] studied the inhibition potential of Cephalexin and Azithromycin for aluminum in a saline-acidic medium (mixture of 0.6 M NaCl and 1 M H_2SO_4), and noticed moderate efficiencies of 75% and 72%, respectively, under a given set of conditions (200 ppm, 25 °C, potentiodynamic polarization), suggesting physical adsorption and a mixed-type inhibition mechanism.

Traditional techniques provide valuable information about the mechanism of metal-expired drug inhibition, but methods such as quantum simulations (e.g., Density Functional Tight-Binding and Monte Carlo) offer a deeper understanding of the inhibitor-metal interactions. For example, for the antibiotic Ceftazidime [84], quantum

simulations suggested that interactions between the drug molecule and the metal arise from the π-electrons in the aromatic ring and the lone electron pairs of oxygen-containing groups. Similarly, theoretical analysis identified electron-donating regions that could participate in adsorption on the low-carbon-steel surface for Cephalexin monohydrate [79]. Mainly, computational methods offer mechanistic support for experimentally observed inhibition behavior as proposed molecular-level interactions, but they don't provide direct experimental evidence.

From the above discussion, and as indicated in other studies, a simple conclusion about the conditions under which a given antibiotic would be most successful is not possible. It is a complex subject that includes analysis of a wide range of factors influencing corrosion and its prevention. The potential environmental effects of antibiotics and other drugs in general increase the complexity of antibiotic reuse. One reason for repurposing antibiotics is to reduce pharmaceutical waste. However, their potential ecotoxicity and concerns about antimicrobial resistance mean that, from an environmental perspective, antibiotics are not always an ideal selection as corrosion inhibitors. Therefore, their application in open systems should be undertaken with great care to prevent inhibitor residues from entering aquatic environments. Yet, to avoid this and similar problems, further studies should focus not only on inhibition efficiency but also on the analysis of degradation products, toxicity assessments, and comparisons with commercial inhibitors. In that regard, simulation techniques and the application of Artificial Intelligence would be highly beneficial in addressing these issues.

3.2. Antihypertensive and Cardiovascular Drugs as Corrosion Inhibitors for Metals

Antihypertensive and cardiovascular drugs showed considerable corrosion-inhibition activity under the experimental conditions investigated. Their molecular structures contain heteroatoms and polar functional groups, such as amino, hydroxyl, amide, and aromatic rings, which may boost strong drug-metal interactions and facilitate the formation of protective layers [41, 69].

Table 1 presents the corrosion-inhibition performance of expired antihypertensive and cardiovascular drugs reported across available studies under certain test conditions. Researchers examined these drug classes primarily as steel corrosion inhibitors, and they reported high inhibitory effectiveness in acidic media. Lower or more variable inhibition efficiencies were recorded in neutral saline environments, which was attributed to decreased solubility, reduced protonation, and weaker electrostatic attraction of the organic molecules to the metal surface [42]. However, differences in experimental design prevent attributing this trend solely to the corrosive medium.

One of the most analyzed drugs in this group is Metoprolol, which belongs to the β-blocker class of medications. In a study of Metoprolol on mild steel, revealing inhibition efficiencies of 94% and 83% for 1 M HCl and 0.5 M H_2SO_4, respectively, the influence of the corrosive medium is more clearly demonstrated when comparable conditions are maintained (drug concentration of 300 ppm, at 25 °C, and a 30-min stabilization period, using the potentiodynamic polarization method) [95]. In a separate study of expired Metoprolol on OLC45 carbon steel in 3.5% NaCl, an efficiency of 69.1% was obtained at 10^{-3} M after 1 h [74]. Because the latter study differs in substrate, inhibitor concentration, exposure time, and formulation status, its numerical value should not be directly compared with those obtained in more acidic systems, but it can be just a qualitative signal of drug inhibition behavior in acidic media due to the molecule's protonation and better adsorption onto negatively charged metal surfaces. As the literature indicates, under the given experimental setup, this class of corrosion retardants, similar to antibiotics, generally showed better inhibition performance at higher drug concentrations because of stronger adsorption and improved surface coverage of metals, e.g., in studies including angiotensin-converting enzyme inhibitors, Spironolactone, Enalapril Maleate, and Perindopril [98-100]. However, the analysis of Metoprolol as an inhibitor of mild steel in HCl and H_2SO_4, at room temperature, indicated reaching the optimal concentration, after which the inhibition efficiency decreases [95], which could be explained by competitive pushing between an excess of inhibitor molecules or their improper sticking to the metal surface. Oxygen-containing functional groups and aromatic rings are the main reactive species involved in the adsorption of organic molecules on the metal surfaces. Electrochemical analysis confirmed the formation of a protective layer and generally revealed predominantly mixed-type inhibition of antihypertensive medications, implying restrictions in both anodic metal oxidation and cathodic reduction [95].

Adsorption behavior of antihypertensives [42, 96, 98-100, 115, 116] and cardiovascular drugs [42, 50-52], among other factors, depends on their molecular architecture. Most of these drugs contain aromatic rings bonded to amino and other functional groups, creating an electron-density distribution that fosters their adsorption on metal surfaces. As electron donors, oxygen and nitrogen

atoms from the inhibitor molecule form coordinate interactions with empty d-orbitals of the metal, while the donor-acceptor interactions with the metal surface through π-d orbital overlap are promoted by the π-electrons in the aromatic rings. As mentioned earlier, these structural characteristics indicate potential adsorption affinity, not independent predictors of inhibition efficiency [51, 52, 96, 98, 99, 100, 116].

Many studies have suggested the Langmuir model as the best fit for the adsorption of antihypertensives and cardiovascular drugs. However, the Temkin isotherm has also been used to describe adsorption in this pharmaceutical class [74, 96, 98, 99, 116]. Antihypertensives and other cardiovascular drugs [39, 42], like all medications, after fulfilling their therapeutic functions in humans, are disposed of in regular household waste and end up in landfills, potentially polluting the environment. Expired drugs repurposing, in general, contributes to pharmaceutical waste valorization and supports the principles of the circular economy.

Given that most studies have been conducted under laboratory conditions with limited knowledge of their industrial implementation, the lack of information on the drug's long-term stability and on degradation products from drug decomposition implies the need for further investigations in this area [39, 42].

3.3. Anti-Inflammatory and Analgesic Drugs as Corrosion Inhibitors for Metals

Another group of pharmaceuticals that attracts significant attention for their use as environmentally friendly corrosion inhibitors is the anti-inflammatory and analgesic drugs. Their molecular structures contain oxygen- and nitrogen-containing functional groups, aromatic π-electron systems, and polar groups such as –COOH, –OH, –NH, –C=O, and –SO_2NH_2, as adsorption sites and facilitators of protective-film formation on metallic surfaces [35], which is needed but not a determining factor for efficient corrosion inhibition.

Researchers have reported the Langmuir adsorption model for several anti-inflammatory drugs investigated as corrosion inhibitors [53, 54, 102-105], although adsorption behavior should be considered specific to the inhibitor–metal–medium system. Table 1 collects some of the most common anti-inflammatory and analgesic drugs tested as corrosion inhibitors for metals.

Merimi et al. [53] and Prasanna et al. [102] examined expired Aspirin as a corrosion inhibitor for carbon steel and mild steel in 1.0 M HCl solutions in a given test set and, using gravimetric analysis and electrochemical impedance spectroscopy, reported maximum inhibition efficiencies of 96% and 79%, respectively. As previously noted, these results are system-specific and reflect differences in experimental conditions, so they cannot be used for cross-study comparison. Electrochemical impedance spectroscopy, indicated by increased polarization resistance and decreased double-layer capacitance as drug concentration increases, confirmed the formation of a passive layer of Aspirin on mild steel in HCl that further restricts metal oxidation [102]. In the same study, increasing temperature decreased Aspirin efficiency, which is attributed to possible drug desorption from mild steel surfaces due to the physical attachment of inhibitors to the substrate [102]. Similar findings apply to the reported results for Naproxen and ibuprofen, which were obtained under different concentrations, exposure conditions, and measurement techniques. It is proposed that ibuprofen in acidic media (e.g., synthetic acid rain, pH = 2.42, room temperature) is protonated, and that adsorption on the positively charged metal (copper) is mediated by negatively charged ions present in the acidic media that are pre-attached to the metal surface in corrosive solutions. Energy-Dispersive X-ray Spectroscopy and Cyclic Voltammetry suggest the formation of a complex between ibuprofen and copper ions that adsorbs onto the metal surface, thereby suppressing corrosion [104].

Monte Carlo simulations of the inhibition process of Naproxen on carbon steel in 1.0 M HCl indicated a strong association of organic molecules with the metal surface, while quantum chemical calculations assumed possible electron transfer from the inhibitor's carbonyl group to the vacant d-orbitals of the metal. These theoretical results support a proposed mixed adsorption mechanism previously proposed by experimental methods [54].

Expired analgesic drugs, including Paracetamol, Tramadol, and Analgin, tested as corrosion inhibitors of different steels and under different experimental conditions, were described in several studies by Langmuir adsorption isotherm and the mixed-type inhibition mechanism [106-109]. Expired paracetamol was shown to be a suitable inhibitor of pitting corrosion of low-carbon steel in 1.0 M H_2SO_4, and galvanostatic polarization at 27 °C showed 94.2% inhibition efficiency. A protective film of Paracetamol molecules on the low-carbon steel surface in acid media (1 M H_2SO_4) acts as a barrier, forming complexes via lone electrons of nitrogen and oxygen of the carbonyl group with metal ions, namely ferrous cations [106]. As a mixed-type inhibitor, paracetamol showed acceptable inhibitory efficiency in protecting mild steel in 0.5 M HCl when exposed to the drug inhibitor for 48 h at room temperature [107]. The suitability of Tramadol [97]

as an inhibitor for carbon steel from the corrosion attack of sulfuric acid (0.1 M, pH = 3, 25 °C) was explained to be the result of the presence of electron donors - nucleophiles in the molecule, like hydroxy, methoxy, methylamino groups, and aromatic rings.

Ardosons [110], an anti-inflammatory and antirheumatic drug that acts as a mixed-type inhibitor, as determined by electrochemical impedance spectroscopy (EIS), achieved up to 77.1% efficiency at room temperature at 100 ppm, protecting API 5L X65 steel in 1 M HCl. Several complementary experimental techniques confirmed the physical adsorption of the drug molecules on the steel surface. As indicated by EIS, increasing the temperature to 40 °C reduces inhibition efficiency to 51.6%, because thermal agitation accelerates the desorption of physically adsorbed drug molecules from the metal interface. Spontaneous adsorption of drug molecules was confirmed by the negative values of Gibbs free energy (-19.06 kJ/mol at 25 °C and -8.50 kJ/mol at 40 °C). Surface characterization by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) confirmed the formation of a protective organic film that physically isolates the alloy from the aggressive acid and revealed a smoother surface with a decrease in adsorbed corrosive chloride ions (0.56 wt%) compared to the severely pitted sample free of inhibitor (18.43 wt%) [110].

As with other medications, although analgesic and anti-inflammatory drugs have potential as corrosion inhibitors with excellent protective efficiency, their use after their shelf life has expired raises concerns about the toxicity of degradation products and long-term stability, which require further investigation to mitigate these and similar concerns.

3.4. Antifungal, Neurological, and Miscellaneous Pharmaceutical Drugs as Corrosion Inhibitors

Some studies [55, 111-114] also identify other classes of pharmaceuticals, such as antifungal, neurological, and psychotherapeutic agents, as well as miscellaneous therapeutics, as “green” inhibitors of corrosion in various metal/aggressive-media systems. Table 1 summarizes some of them.

Due to their molecular complexity, multiple nitrogen atoms, and aromatic rings that act as active adsorption sites, antifungal agents such as Bifonazole and Terconazole, as well as other azole-based medications, have been promoted as efficient corrosion inhibitors. Abdullah et al. [111] tested these expired antifungal drugs in the carbon steel / 1.0 M HCl system at room temperature (26 °C). Using galvanostatic polarization, at 375 mg/L for both drugs, the observed inhibition efficiencies exceeded 90%. The adsorption mechanism of these antifungal agents involves both physical and chemical adsorption, with a dominant physisorption following the Langmuir isotherm, and Tafel plots proposed a mixed-type inhibition mechanism that restricts both anodic and cathodic corrosion reactions. Standard Gibbs adsorption energy values between –38 and –33 kJ/mol indicate mixed adsorption, as verified by several complementary parameters. Namely, thermal desorption of the physically adsorbed molecules was observed as the temperature increased to 56 °C, and the apparent activation energy increased from 19.14 kJ/mol for uninhibited acid to 36.37 kJ/mol and 38.28 kJ/mol in the presence of 375 mg/L Bifonazole and Terconazole, respectively. EIS analysis, showing decreased double-layer capacitance and increased charge-transfer resistance, and SEM micrographs confirmed the formation of a protective barrier and a smoother surface. Furthermore, using quantum mechanical modeling, it was suggested that the anticorrosion efficiency of Terconazole was slightly higher than that of Bifonazole, which was attributed to its larger molecular size, providing better coverage of the metal surface, a smaller frontier orbital energy gap (4.21 eV vs. 5.15 eV), greater global softness, ability to form a stable six-membered ring complex with Fe^{2+} ions, and higher binding energy on the Fe(110) crystal plane (-154.22 kcal/mol vs. -94.43 kcal/mol) [111].

The neurological pharmaceutical Donepezil, used to treat dementia linked to Alzheimer's disease, is another drug shown to be suitable as an anti-corrosion agent for EN24 steel in sulfamic acid [112]. Potentiodynamic polarization studies indicated a mixed-type inhibition mechanism, with cathodic inhibition prevailing. Poojary et al. [112] suggested a mixed adsorption mechanism, with physisorption dominance. While the standard free energy of adsorption fit the range typical for mixed adsorption, the EIS analysis indicated physisorption dominance, as shown by reduced inhibition efficiency at elevated temperatures, increased charge-transfer resistance, and reduced double-layer capacitance. Reduced surface roughness due to drug adsorption was confirmed by Atomic Force Microscopy (AFM). In contrast, as revealed by computational Density Functional Theory (DFT) studies, the nitrogen atom of the piperidine ring was proposed to be the primary HOMO center responsible for electron donation to vacant metal d-orbitals, while the dimethoxyindanone species, which accommodates the LUMO density, acts as an electron-acceptor segment [112].

Licetam, a pyrrolidone derivative and an

antiepileptic drug, was recently shown to be an effective inhibitor of low-carbon steel in an acidic environment [55], following the Langmuir model and a mixed-type adsorption mechanism, as shown by complementary parameters, including temperature-dependent efficiency trends, negative adsorption free-energy values, and reduced double-layer capacitance. The higher activation energy values at higher drug concentrations reflect the formation of a protective energy barrier against metal dissolution. FTIR spectroscopy suggests that oxygen- and nitrogen-containing functional groups are involved in inhibitor–metal interactions. Quantum-chemical calculations and molecular simulations further suggested that oxygen and nitrogen atoms from the amide and carbonyl groups are likely adsorption centers contributing to drug–metal interaction [55].

Similarly, expired Ropinirol, originally used to treat Parkinson's disease and restless legs syndrome, showed inhibition efficiency above 90% for mild steel in 1 M HCl for 2 h at room temperature, as confirmed by gravimetric analysis [113]. Scanning electron microscopy and energy-dispersive X-ray spectroscopy revealed the formation of a protective layer of drug molecules on the mild steel surface. Ropinirol's inhibition efficiency increased with increasing concentration in the corrosive medium. Conversely, as the experimental temperature increases, the effectiveness of this pharmaceutical decreases, which is explained by its desorption with temperature, indicating a physical adsorption mechanism. Electrochemical methods proposed a cathodic corrosion-inhibition mechanism [113].

Many medications that don't fit into any previously defined pharmaceutical classes, such as vitamins, also showed promising anti-corrosive features for both general and pitting corrosion. Thus, Abdallah et al. [114] tested Thiamine (Vitamin B1) and Riboflavin (Vitamin B2) as corrosion retardation agents for the system SABIC iron/0.5 M H_2SO_4 at 30 °C. Both B1 and B2 vitamins exhibited inhibition efficiencies above 90%. The authors tested the inhibition efficiency at different temperatures. Inhibition efficiency decreased, and adsorption activation energy increased with increasing temperature and drug concentration in the corrosive medium, respectively, which is characteristic of physical adsorption on metal substrates. The negative standard Gibbs free energy indicates that drug adsorption onto the metal surface is spontaneous. Experimental adsorption data fit the Langmuir isotherm. The inhibition efficiency of these agents depends on molecular structure, the presence of active sites, and complex formation with ferrous cations. The decrease in inhibition efficiency with increasing temperature, together with the activation parameters and computational analysis, provides additional evidence for interpreting the nature of the inhibitor–metal interactions. For Thiamine, coordination of iron with the nitrogen atoms of the amino and imine groups forms a four-membered ring, or, with sulfur-containing or hydroxyl groups, a six-membered chelate ring. On the other hand, for Riboflavin, coordination between iron and carbonyl and imine groups leads to the formation of a five-membered ring, and coordination with two hydroxyl groups creates a six-membered chelate ring. Computational quantum-mechanical modeling, which shows higher HOMO and lower LUMO energies for Riboflavin, suggests better inhibition performance than Thiamine [114].

4. COMPARATIVE DISCUSSION OF CORROSION INHIBITION PERFORMANCE

The preceding analysis demonstrates that expired pharmaceuticals from different therapeutic classes can provide substantial corrosion inhibition; however, comparison based only on maximum inhibition efficiency may obscure important differences among the investigated systems. The present comparative analysis therefore considers inhibitor performance as the combined outcome of molecular characteristics, pharmaceutical class, metal substrate, corrosive medium, inhibitor concentration, temperature, and adsorption behavior. Although the therapeutic function of a pharmaceutical is not directly responsible for its anticorrosive activity, classification by therapeutic class provides a useful framework for identifying recurring molecular features and adsorption characteristics among structurally related compounds [41,69, 117]. Such comparison can help explain why pharmaceuticals belonging to different therapeutic classes may exhibit similar inhibition efficiencies while responding differently to changes in the metal–medium environment.

Many researchers investigate repurposing drugs for uses beyond their initial goal, rather than disposing of them in landfills after expiry. Repurposing additionally provides an opportunity for pharmaceutical-waste valorization and supports the circular economy agenda. Studies show that the inhibition efficiency of expired pharmaceuticals varies widely, with some exceeding 90% across several therapeutic classes [41, 42, 50, 51, 55, 56, 94, 81, 98, 103, 104, 109]. However, one should not use maximum efficiency values obtained under different experimental conditions to rank inhibitor performance [41, 77]. Differences in metal composition, corrosive medium, inhibitor concentration, temperature, exposure time, and measurement technique can greatly affect calculated inhibition efficiency [41, 55, 56, 90, 99].

Thus, the values in Table 1 reflect inhibition performance only under specific experimental conditions, suggesting that the reported performance of an expired pharmaceutical cannot be separated from the metal–medium system and experimental conditions under which it was evaluated, and should not be attributed exclusively to molecular structure or therapeutic classification. In some cases, higher temperatures decrease inhibition efficiency because inhibitors desorb from the metal surfaces [85], but the opposite is true in other systems, improving inhibition through stronger chemisorptive interactions, as is the case for expired Ampicillin at a concentration of 20 mM, studied as an inhibitor of mild steel in 5% HCl, with a 6 h exposure time, where the inhibition efficiency, determined by the weight-loss analysis, changed from 75.7% at 25 °C to 96.7% at 55 °C. Higher inhibitor concentrations generally improve drug adsorption on the metal until surface saturation is reached [56].

Cross-study comparisons are further complicated by different methods used to determine efficiency [41]. While gravimetric weight-loss measurements integrate corrosion behavior over a defined exposure period, electrochemical techniques such as potentiodynamic polarization and electrochemical impedance spectroscopy characterize the corrosion behavior under different measurement conditions and various time scales [41, 50, 55]. Therefore, inhibition efficiencies obtained by different techniques should not be assumed numerically equivalent, even when the same inhibitor–metal–medium system is investigated. Immersion or exposure time also matters because adsorption-layer formation, surface coverage, inhibitor desorption, degradation, and changes in the corrosive medium may evolve over time [55, 70, 76,100]. Hence, quantitative cross-study interpretations of the therapeutic inhibitor efficiencies are appropriate only when comparable experimental conditions are used [12, 41, 50,55]. For example, at the same concentration (7.2×10^{-3} M) of Sironolactone in 10% HCl, and temperature (30 °C), the original study reported efficiencies obtained by three different methods, WL, EIS, and PDP, as 98.1%, 95.0%, and 95.8%, respectively, on C38 carbon steel [42]. Under uncertain conditions, broader qualitative comparisons are more appropriate than numerical rankings.

When one compares the metals as subjects of the research in the current literature, it can be seen that mild steel and carbon steel dominate, followed by low-carbon steel, stainless steel, aluminum and its alloys, zinc, copper, and specialized industrial steel. Given that steel-based materials are the primary materials used in industrial settings, including pipelines, storage tanks, and reactors, as well as in construction applications, their dominance in scientific research on corrosion protection is not surprising [118]. The other reason could be the fact that steel is particularly susceptible to acid-induced corrosion, making it an attractive model substrate for inhibitor evaluation [119].

Acid solutions, mainly hydrochloric acid, are used in many industrial processes, such as pickling, cleaning, descaling, and acidization, which makes them attractive for experimental studies of corrosion and techniques for its mitigation [120]. Additionally, protonation of organic molecules is facilitated by hydrochloric acid, which enables stronger interactions between drugs and metal surfaces, thereby further enhancing interest in analyzing drug adsorption behavior in the presence of HCl [121]. On the other hand, the lack of research on other corrosive media, such as synthetic acid rain, seawater, and alkaline media, highlights the need for broader, more extensive research in this area.

Molecular characteristics, i.e., the presence of heteroatoms containing nitrogen, oxygen, and sulfur, polar functional groups, aromatic rings, and extended π-electron systems, can promote inhibitor–metal interactions by providing sites for electrostatic attraction, electron donation, back-donation, or coordination with the metal surface [41, 69, 117]. Stable, compact layers and coverage of larger metal surfaces may form when higher-molecular-weight drugs are used [41, 69]. Yet, molecular architecture alone does not define inhibition efficiency [41, 50]. It rather depends on combined characteristics such as the inhibitor's physicochemical properties [52, 90, 96], the metal surface [94, 112], and the nature of the corrosive medium [73]. The protonation state and distribution of the different chemical forms that an inhibitor molecule takes when dissolved in a specific corrosion medium influence its charge and adsorption behaviour [41]. Inhibitor solubility in the corrosive medium affects the amount of inhibitor available at the metal–solution interface, whereas the metal surface charge influences electrostatic attraction or repulsion [35, 41, 53, 96]. Experimental evidence supports adsorption energy values that indicate adsorption favorability and the strength of inhibitor–surface interactions [55, 106, 111]. In addition, strict numerical thresholds of adsorption free energy should not be used alone to assign drug adsorption mechanisms, but require confirmation from temperature and activation behavior, electrochemical measurements, spectroscopic or surface characterization, and computational evidence [41,73,87,94,112]. Additional complications arise from species usually present in

corrosive media, which may compete with pharmaceutical molecules for available surface sites or alter their adsorption behavior, such as water molecules [53, 94, 88, 90, 93], aggressive ions [73,71,122], drug formulation components [12, 69,105], degradation products [69,123], and others [124]. Therefore, heteroatoms and π-electron systems should be considered potential adsorption features rather than sufficient predictors of inhibitor performance.

Many researchers have reported the Langmuir adsorption isotherm [54, 79, 104, 108-112] as the best model for pharmaceutical adsorption behavior, assuming adsorption on a relatively homogeneous metal surface with binding sites of similar energy, monolayer formation, and limited or no lateral interactions between adsorbed molecules. Although the idealized Langmuir model is employed well in some corrosion systems, it does not always accurately represent inhibitor adsorption. In contrast, several studies show that for some corrosion systems, the Temkin or Freundlich models fit the adsorption better, indicating that the idealized assumptions of Langmuir adsorption models do not apply in all cases [74, 79, 80, 85, 96].

The Freundlich adsorption model assumes adsorption on heterogeneous surfaces, the formation of multiple adsorbate layers, and a logarithmic decrease in adsorption energy as the surface fills up. The Temkin model suggests adsorbate-adsorbate interactions and a linear decrease in adsorption energy as surface coverage increases [74, 80, 85, 96]. Accordingly, the best-fit adsorption models, which deviate from the ideal case, suggest that the adsorption process should be treated as system-specific evidence rather than proof that pharmaceutical inhibitors generally follow an ideal Langmuir adsorption mechanism [50].

A decrease in inhibition efficiency with increasing temperature suggests predominantly physical interactions between the molecules and the metal surface [75, 79, 95]. In most cases, adsorption occurs via a mixed mechanism that includes both physical and chemical adsorption [51, 54, 56, 74, 86-90, 96, 98-100, 103-109, 116].

The interpretation of these structure–performance relationships is further complicated by limited characterization of pharmaceutical stability after expiration. Many studies suggest that the inhibition efficiency and adsorption behavior of expired drugs are attributed to the molecular structure of the active pharmaceutical ingredient [41, 50, 107], indirectly implying that, at the time of testing, the active component remains chemically intact in the expired formulation. Since many factors such as formulation, excipients [12, 69, 70], packaging, storage conditions, environmental exposure [86, 92], degradation pathways [41, 124], and drug expiration time [71] can influence the composition of expired drugs, this assumption should be treated with caution. For example, degradation processes may decrease the concentration of the original active ingredient and generate products with adsorption and electronic properties different from those of the parent compound [41, 124]. Namely, chemical degradation pathways, such as hydrolysis initiated by trace water present in commercial drug formulations, photolysis, or oxidation, which occur as a result of drug exposure to air and sunlight, can significantly alter the active pharmaceutical ingredient (API), leading to decarboxylation or heterocycle-closing reactions [41].

For example, structural modifications in expired Metoclopramide and Amoxicillin compared with non-expired drugs were indicated by changes in characteristic functional-group bands in FTIR spectra, including loss of the NH_2-related band and additional spectral changes [41]. These findings show that, without analytical verification, one should avoid assuming that the nominal pharmaceutical structure is retained after expiration. As indicated in the literature, the influence of temperature and medium composition further complicates the explanations about structure-performance relations. Harsh conditions, typical of industrial applications, such as high temperatures and complex corrosive media, most likely due to changes in adsorption, desorption, chemical stability, or competitive interactions between drug active ingredients and other species in the medium, may alter the drug's inhibition efficiency [12]. Furthermore, except for the active therapeutic ingredient, commercial pharmaceuticals contain complex excipients such as binders, fillers, disintegrants, lubricants, preservatives, antioxidants, colorants and flavorings, and coatings. The type and proportion of these components may differ among manufacturers and dosage formulations containing the same active ingredient [6]. In a corrosive environment, excipients may raise additional concerns related to drug availability, modify solubility and dispersion, compete with the active ingredient for adsorption sites, and thus participate in, or disrupt, the surface films [12, 50]. Differences in drug-formulation composition, even when the active ingredient is the same, may contribute to variations in the measured inhibition performance, and may create uncertainty about which drug components, including the parent pharmaceutical, its degradation products, excipients, or their combined effects, are responsible for the anti-corrosion properties of expired drugs [41, 42, 50, 124]. Therefore, before drawing conclusions about mechanistic relationships between molecular structure and inhibition performance, more rigorous studies are

needed to report commercial formulations and, where possible, to characterize relevant excipients, which the observed literature has neglected.

Collectively, these observations show that high maximum inhibition efficiency alone is not sufficient evidence that expired drugs are suitable in practice as a corrosion inhibitor. Reported efficiency is strongly conditional on the experimental system. The predominance of mild and carbon steels and highly acidic media, particularly HCl, means that the current evidence base is concentrated around conditions that favor the protonation and adsorption of many pharmaceutical molecules. In contrast, considerably less information is available for neutral, saline, alkaline, seawater-like, and other industrially relevant environments [12, 41, 50]. Consequently, an inhibitor that performs well in a strongly acidic laboratory system cannot automatically be expected to provide comparable protection under other service conditions [12, 73].

Studies on repurposing expired pharmaceuticals as corrosion inhibitors and showing high inhibition efficiencies are mainly performed under laboratory conditions, using streamlined settings restricted to simplified static or low-agitation acidic or saline media. In contrast, real operating conditions in industrial systems, e.g., pipelines, reactors, circulating-water systems, and process equipment, may involve continuous or discontinuous fluid flow [6]. High flow velocities and turbulent shear stress can alter mass transfer at the metal–solution interface and affect the formation, stability, or removal of adsorbed inhibitor films. Thus, inhibition performance observed under laboratory conditions may differ from that obtained under industrial settings [12, 108]. This indicates that before practical implementation, i.e., translating bench-to-industry transition, the inhibition process must be evaluated under representative flow and real-world operational constraints, including the hydrodynamic shear threshold of expired drug films.

High temperatures may introduce similar issues, such as changes in inhibitor solubility, adsorption/desorption equilibria, pharmaceutical stability, degradation pathways, and the stability of the protective surface film. Although some drug molecules exhibit specific high-temperature stability or transition to chemisorption, others, e.g., Donepezil Hydrochloride and Tilmicosin, lose activity and structural integrity when exposed to temperatures above room temperature (82 °C for Donepezil and 45 °C for Tilmicosin) [12].

The protection efficiency of many expired drugs decreases significantly after prolonged immersion because desorption and/or progressive breakdown of the adsorbed film occur under prolonged attack by aggressive ions [100]. Moreover, depending on the industrial application, as drug molecules may be consumed to form the protective film, or diluted, degraded, desorbed, or removed with the process stream, their concentration in the corrosive medium decreases, which may involve periodic or continuous replenishment to maintain an optimal inhibitor concentration and keep the corrosion rate minimal. However, when the drug amount exceeds the threshold, unadsorbed molecules may aggregate due to their proximity, or compete with adsorbed species for priority at the adsorption sites on the metal surface. The frequency and feasibility of such replenishment have rarely been considered in expired-pharmaceutical corrosion studies and would directly influence operational practicality and cost [100].

Additional complexities in transitioning drug inhibitors to large-scale applications arise from complex corrosive media and incompatibility with industrial additives found in industrial fluids. Industrial corrosive environments are not simple corrosive media consisting of a single acid solution, as used in simple laboratory settings. Petroleum and sour crude contain hydrocarbons, hydrogen sulfide, and heavy brine, which may promote competitive adsorption between organic crude constituents (such as sulfur-containing species) and drug molecules, preventing the drug from forming a cohesive barrier [12]. In addition to the active ingredient, commercial inhibitor formulations often contain other components, such as surfactants, dispersants, anti-foaming agents, demulsifiers, and biocides. Conversely, drug solutions used in laboratory analysis are usually simple test solutions free of additives, and when they contact non-acidic or oily environments, the drug inhibitors often exhibit poor solubility, form emulsions, and undergo phase separation [108].

Validating drug formulations and integrating them under industrial conditions as a viable alternative to conventional industrial corrosion inhibitors requires extensive long-term testing that simulates real operational conditions, including dynamic flow, temperature stability, inhibitor-retention or replenishment requirements, and process-compatibility assessment.

Another concern is classifying expired pharmaceuticals as “green” and environmentally friendly compounds, as many researchers have done [38, 54, 70, 76, 100,115]. Repurposing pharmaceutical waste only alters its usage pathway without eliminating its environmental impact. In fact, it offers a potential circular-economy benefit that shouldn’t be analyzed in isolation, but must be considered alongside the chemical and environmental characteristics of the specific drug

formulation [50,73-75]. For many inhibitory systems, the stability of the active component after the expiration date, excipients in commercial formulations, degradation products, toxicity, solubility, long-term inhibition performance, and potential environmental release remain insufficiently evaluated [41, 50, 69, 75, 124].

The post-use fate of pharmaceutical waste inhibitors, i.e., their environmental risk, must also be considered after the pharmaceutical has been used as a corrosion inhibitor, especially knowing that process fluids may contain different species, such as residual active pharmaceutical ingredients, unadsorbed or desorbed drug molecules, and degradation or transformation products, that may enter subsequent wastewater streams [74, 75]. These species may retain the biological activity of the parent pharmaceuticals, while their durability and toxicity may differ from those of their source [41, 50, 74, 75], creating a need for future investigations that follow the environmental flow of re-used pharmaceutical waste, including biodegradability, persistence, ecotoxicity, wastewater-treatment compatibility, and safe disposal of inhibitor-containing streams.

Moreover, most investigations are short-term laboratory studies, and direct benchmarking against established commercial corrosion inhibitors remains limited [12, 40, 41, 68]. Quantitative comparisons of inhibitor performance for expired pharmaceuticals and commercial corrosion inhibitors are difficult because they are evaluated under different experimental and operational conditions, including different inhibitors, metals, corrosive media, concentrations, temperatures, exposure times, and measurement methods. Comparing inhibition efficiencies while ignoring these other conditions may lead to misleading conclusions [12, 41, 50]. Thus, future comparisons should consider not only inhibition efficiency but also factors such as the concentration needed to achieve the required corrosion protection, inhibition durability, inhibitor chemical and thermal stability, toxicity and ecotoxicity, formulation consistency, inhibitor availability, inhibitor replenishment requirements, and total application cost [41, 68, 74, 124]. The literature lacks sufficiently standardized quantitative data across the above-mentioned criteria to demonstrate the equivalence or superiority of expired pharmaceutical inhibitors compared with commercial inhibitors. This lack of direct head-to-head benchmarking is an important research gap that future studies should address [12, 40, 50]. Therefore, the principal research gap is no longer simply whether expired pharmaceuticals can inhibit metal corrosion, since this has been demonstrated for numerous compounds, but whether their inhibition performance is sufficiently reproducible, environmentally acceptable, stable, and scalable under realistic operating conditions to justify practical implementation. This distinction between demonstrated laboratory efficiency and practical corrosion-control readiness represents an important basis for directing future research.

5. CONCLUSIONS

An effective strategy to control metal corrosion, a problem in many industries causing material wear and degradation, leading to industrial failures, substantial economic losses, environmental risks, and safety concerns, is the use of corrosion inhibitors. Recent studies show that expired pharmaceuticals from different therapeutic classes can exhibit notable corrosion-inhibition activity for metals, particularly steel, under specific experimental conditions. Their corrosion-protection performance is linked to adsorption at the metal–solution interface and the resulting suppression of anodic and/or cathodic corrosion reactions. One required feature for promoting adsorption of expired drugs on metal surfaces is molecular structure, including heteroatoms, polar functional groups, aromatic systems, and π-electrons. However, these structural features alone are not sufficient to reliably predict inhibition efficiency. Combined effects, including inhibitor speciation and protonation, its molecular geometry, solubility, metal-surface characteristics, corrosive medium, inhibitor concentration, temperature, exposure time, and competitive adsorption among species present in the medium influence the drug inhibition performance.

Although the Langmuir isotherm often fits pharmaceutical adsorption well, it is not generalized to all pharmaceutical inhibitors. Yet, some studies have also used the Temkin and Freundlich models, reflecting differences in surface heterogeneity and interactions among adsorbed species, to describe pharmaceutical adsorption behavior. Interpreting the adsorption mechanism requires complementary experimental evidence from temperature and activation behavior, electrochemical studies, and spectroscopic and surface characterization, as well as computational approaches such as Density Functional Theory, Monte Carlo, and molecular simulations that provide valuable molecular-level interpretations of possible adsorption sites and inhibitor–metal interactions.

A key limitation of the current evidence is that many researchers consider expired pharmaceuticals chemically equivalent to their nominal active pharmaceutical ingredient without characterizing the actual formulation. Different excipients present in the formulations of different producers, including binders, fillers, lubricants,

disintegrants, and coatings, as well as storage conditions, time after expiration, and degradation of the active component, may alter solubility, adsorption, film formation, and ultimately corrosion-inhibition performance. Therefore, future studies should more consistently report formulation composition, analytical characterization, expiration history, and storage conditions of the inhibitor material used.

Most investigations of expired drugs as corrosion inhibitors rely on short-term laboratory studies that do not reflect real industrial conditions and use simple corrosive media, mainly acidic or saline solutions. More comprehensive analyses and validation under representative operating conditions, such as complex process fluids, dynamic flow, elevated temperatures, and longer exposure times of pharmaceuticals to severe conditions, are required for the efficient bench-to-industry transition. While accounting for potential interactions between active drug components and other species or degradation products, further analyses would establish long-term stability of the protective films, inhibitor depletion and replenishment frequency, formulation compatibility, and reproducibility. Additionally, because current studies lack standardized head-to-head comparisons with commercial inhibitors, and despite the high inhibition efficiencies observed in individual studies, the statement that expired pharmaceuticals are appropriate substitutes for traditional ones can't be taken for granted. Furthermore, such a benchmarking should also consider required dosage, durability, chemical and thermal stability, toxicity, availability, formulation consistency, replenishment requirements, and total application cost.

Repurposing expired pharmaceuticals doesn't imply inherent environmental benignity, but it supports pharmaceutical-waste valorization and circular-economy objectives. Namely, before and after use, the active pharmaceutical component, residual formulation ingredients, and degradation or transformation products might exhibit toxicity, persistence, biological activity, or other environmental effects. This indicates that future studies should include environmental assessment and evaluation of drug ecotoxicity, biodegradability, persistence, environmental fate, potential release to wastewater or receiving streams, and appropriate management of media containing spent inhibitors.

Expired pharmaceuticals should not be presented as replacements for commercial inhibitors, but as promising candidates for corrosion inhibition. Thus, future laboratory studies should focus not only on the inhibition performance of expired pharmaceuticals, but also on reducing the gap between laboratory studies and realistic industrial conditions by confirming that inhibition performance is reproducible, environmentally and economically acceptable, and stable and scalable under real conditions. Establishing standardized comparative testing, drug-formulation characterization, long-term industrially relevant experiments, environmental risk assessment, and techno-economic evaluation is essential for determining the practical role of expired drugs in future corrosion-control strategies.

6. REFERENCES

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IZVOD

LEKOVI KOJIMA JE ISTEKAO ROK TRAJANJA KAO POTENCIJALNO ODRŽIVI INHIBITORI KOROZIJE METALA: KRITIČKI PREGLED

Procesi korozije negativno utiču na mnoge industrijske grane, uključujući naftnu i gasnu industriju, preradu nafte, građevinarstvo, proizvodnju električne energije, proizvodni sektor i druge. Agresivne sredine u direktnom kontaktu sa različitim materijalima, uključujući metale, dovode do njihovog propadanja, što obično rezultira gubitkom strukturnog integriteta i povećava rizik od zagađenja nusproizvodima korozije, kao i od drugih ekoloških problema. Primena inhibitora korozije predstavlja jedan od najefikasnijih načina za suzbijanje korozije metala. Različite hemijske supstance – kako neorganske, tako i organske – prepoznate su kao inhibitori korozije, a u novije vreme pažnju privlače i inhibitori dobijeni iz otpada, među kojima posebno mesto zauzimaju lekovi kojima je istekao rok trajanja. Brojna istraživanja pokazuju da takvi lekovi mogu delovati kao efikasni inhibitori korozije metala, pri čemu efikasnost u određenim eksperimentalnim uslovima često prelazi 90%. Njihov učinak ne zavisi samo od molekulske strukture inhibitora i aktivnih mesta koja podstiču adsorpciju i formiranje zaštitnog filma na površini metala, već i od fizičko-hemijskog stanja samog inhibitora, kao i od karakteristika granične površine između metala i sredine. Slično konvencionalnim organskim inhibitorima, farmaceutski preparati potiskuju anodne, katodne ili obe elektrohemijske reakcije korozije. Ovaj pregled pruža ažuriranu, uporednu i kritičku analizu upotrebe lekova kojima je istekao rok trajanja, sa posebnim naglaskom na odnose između njihove molekulske strukture, metalne podloge, korozivne sredine, koncentracije inhibitora, temperature, procesa adsorpcije i mehanizma inhibicije. Pored toga, rad kritički razmatra ekološku održivost i praktičnu primenljivost ovih supstanci, uzimajući u obzir razlike u formulacijama, njihovu stabilnost i razgradnju, uslove testiranja, kao i činjenicu da je validacija ovih inhibitora u uslovima relevantnim za industrijsku primenu još uvek ograničena. Ovaj sveobuhvatni pristup takođe ukazuje na praznine u znanju koje trenutno ograničavaju prelazak sa laboratorijskih ispitivanja – gde ovi lekovi deluju kao obećavajući inhibitori – na njihovu praktičnu primenu kao sredstava za kontrolu korozije.

Ključne reči: *Korozija, inhibitori korozije, lekovi sa isteklim rokom trajanja, valorizacija farmaceutskog otpada, cirkularna ekonomija*

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