*Review:*

# A Review on Expired Drug-Based Corrosion Inhibitors: Chemical Composition, Structural Effects, Inhibition Mechanism, Current Challenges, and Future Prospects

**Muhamad Jalil Baari[1*] and Carla Wulandari Sabandar[2]**

[1]*Department of Chemistry, Faculty of Science and Technology, Universitas Sembilanbelas November Kolaka, Jl. Pemuda, Kolaka 93517, Indonesia*

[2]*Department of Pharmacy, Faculty of Science and Technology, Universitas Sembilanbelas November Kolaka, Jl. Pemuda, Kolaka 93517, Indonesia*

* ***Corresponding author:***

*email: jalilbaari@gmail.com*

*Received: February 13, 2021*
*Accepted: June 14, 2021*

**DOI:** 10.22146/ijc.64048

***Abstract:*** *This comprehensive review highlighted how the expired drugs manage corrosion reactions on metal/alloy surfaces, especially types of carbon/mild steel, Sabic iron, copper, and aluminium in NaCl or acid solution. Several types of expired drugs and the optimum conditions presented in this review were summarized from relevant studies. The performance of expired drugs which covers inhibition efficiency, inhibition mechanisms, and metal surface analysis was informed. The contribution of the chemical composition, molecular structure, compatible treatment conditions, and some corrosion analysis methods were mentioned. Current challenges and future prospects were also discussed for further investigations and developments to obtain superior inhibitors and save the environment.*

***Keywords:*** *corrosion; corrosion inhibitor; expired drugs; carbon steel; copper; aluminium*

## ■ INTRODUCTION

Corrosion can occur through contact between a material with the surrounding environment. It is an unavoidable process and significantly afflicted on the metals or alloys which are in an aqueous solution. Water or seawater, dissolved carbon dioxide, oxygen, acids such as $H_2CO_3$, HCl, and $H_2SO_4$ are corrosive substances in the fluids [1-3]. Corrosion becomes a principal problem for some industries in the world, mainly in oil and gas industries. Transportation of fluids containing crude oil, natural gas, and corrosive substances creates rust in the inner part of the pipeline by electrochemical reactions [4]. Repairing and replacement of the rusted pipeline required a very expensive cost and spent a lot of time. As a result, operational steps like transportation, processing, storage, and producing oil and gas will be disrupted and become less efficient. Besides that, corrosion effects could harm the safety of the workers and inflict the environmental pollution [5]. Several countries have been spending a lot of cost on corrosion treatments [6].

Not only that, the fluid that contains oil, gas, seawater, $CO_2$, $SO_2$, and alkaline earth ions have the potential to form $CaCO_3$, $CaSO_4$, $SrCO_3$, and $BaSO_4$ scales [7-8]. Scaling will clog the flowing fluid throughout the pipeline from the oil wells to the processing steps. It can also degrade the metal and lead to pitting corrosion [9]. Various acids like sulfuric acid, hydrochloric acid, sulphamic acid, phosphoric acid, and the combination of two or more acids are used for descaling, cleaning, dissolving, or degreasing those deposits [10]. However, this acidification presents another problem due to the accelerating corrosion process.

The compatible method is important to retard corrosion reactions in metals. Several known methods include the utilization of corrosion-resistant material alloy [11], development of protective coating substances [12-13], corrosion-resistant plastics [14], and corrosion inhibitors [15-17]. In our previous work, we synthesized an oligomer and the modified polymer compounds showed a potent corrosion inhibitor for carbon steel

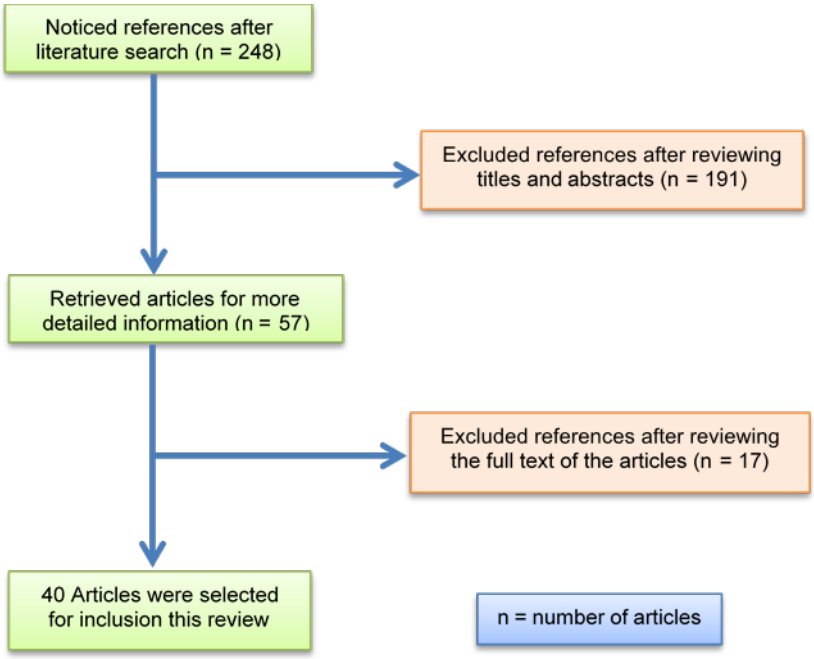


**Fig 1.** Scheme of the review process

protection [16-17]. The application of a corrosion inhibitors is an effective, economical, and practical method for the corrosion process in the inner part of the pipeline. Corrosion inhibitors are the chemical substances used to decrease the corrosion rate of the metals which are added in immensely low concentrations to the fluids [18].

A bad impact on environmental safety from the application of inorganic inhibitors made researchers turn their attention to organic compounds or natural products. The inhibition capability of these compounds corresponds to the availability of π electrons and functional groups such as $-CO_2H$, $-CO_2R$, $-NR_2$, $-NH_2$, –OH, –OR, and –SR [19-20]. Nevertheless, most commercial organic inhibitors are ineffective at high temperatures and the price is relatively expensive [21]. Besides, inhibitors from organic compounds must be synthesized and purified from natural sources. Consequently, more chemicals and energy are also required. This condition leads an increase in chemicals waste production.

In recent years, corrosion inhibitors from drugs have been applied. Drugs are eco-friendly substances since most of the drugs have been synthesized from organic compounds. Hence, they can be used as an alternative corrosion inhibitor apart from conventional organic inhibitors [22]. Several drugs like Irbesartan [23], Cephapirin [24], Chloramphenicol [25], Tramadol [26], Ampicillin [27], and Diclofenac sodium salt [28] have been used as corrosion inhibitors for carbon or mild steel in acidic solutions. However, the conventional drugs are still required as medicines for hospitals and patients. The price also leads to the lack of utilization of conventional drugs [29]. Therefore, the use of expired drugs is suggested to take the advantage of drug waste. Both economical and environmental problems will be solved in this way [22,29-30].

There is no information about the direct use of expired drugs as corrosion inhibitors in petroleum industries so far. The studies of corrosion inhibitors from expired drugs are still being conducted to obtain superior inhibitors (the inhibition efficiency of more than 99%) that can be compared with the conventional inhibitors. The expired drugs are unsuitable for consumption as the result of the degradation of active substances as well as the excipients after physical, chemical, or microbiological effects such as humidity, pressure, temperature, bacteria, and light [31]. The conventional and expired drugs have similar structure with general organic inhibitors which are equipped with functional groups and π electrons to support their performance as corrosion inhibitors.

Based on our extensive search, reviews on drugs as corrosion inhibitors have been reported previously. Some types of drugs as corrosion inhibitors in metal and alloy with various methods and mediums have been reviewed [32–34]. A review also elaborated on the use of herbal drugs for inhibiting corrosion on alloy steel in corrosive media [18]. Another review reported the electrochemical processes of expired drugs as inhibitors [35]. However, there is no detailed explanation about chemical composition and structure effects on the performance of expired drugs. In other that, isotherm adsorption, current challenge, and future prospect of expired drugs as corrosion inhibitors have not been informed. The present review describes the current state of several types and performance, experimental methods, chemical composition, structural effects, optimum condition, and inhibition mechanism of expired drugs as corrosion inhibitors from 40 articles. The current challenges and future prospects of this corrosion inhibitor kind are also elaborated.

## ■ METHODOLOGY

The study of this review was conducted through extensive literature searches using online databases and libraries, such as Google Scholar, ScienceDirect, Scopus, SpringerLink, PubMed, ACS Publications, and DrugBank. The scheme of this review process is displayed in Fig. 1. The searching used several keywords like corrosion, expired drugs, corrosion inhibitors, inhibition mechanism, surface analysis, and adsorption isotherm. The obtained literatures were screened based on the usage period of expired drugs (have expired or not) and the specific utilization of expired drugs as corrosion inhibitors with proper and clear methods in corrosion inhibition analysis. In addition, the similarity of expired drug structures was noticed because several drugs with similar structures usually have a different trade name.

## ■ TYPES OF EXPIRED DRUGS FOR CORROSION INHIBITOR

Studies have shown the benefits of expired drugs for corrosion inhibitor applications. Several drugs with different clinical uses have been explored, including antibiotic, antihypertension, gastroesophageal problems, antipyretic, anticonvulsant, chronic bronchospasm, mucolytic, antihistamine, anti-anxiety, anti-inflammatory, antiviral, hypogonadism, antidepressant, antidiabetic, and analgesic drugs. There are drugs that have more than one clinical use. Several types of drugs, clinical uses, and their functional groups are listed in Table 1.

**Table 1**. Types of drugs, clinical uses, and the functional groups in the molecular structures

| Drug name | Clinical uses | Functional groups for corrosion inhibitor performance |
|---|---|---|
| Ranitidine (**1**) | Gastroesophageal problems | Heteroatoms, amine, heterocycle, nitro, sulfide |
| Carbamazepine (**2**) | Anticonvulsant/antiepileptic | Heteroatoms, aromatic ring, amine, amide, heterocycle |
| Paracetamol (**3**) | Analgesic, antipyretic | Heteroatoms, aromatic ring, amide, hydroxyl |
| 1-Phenytoin sodium (**4**) | Anticonvulsant/antiepileptic | Heteroatoms, aromatic ring, amide, heterocycle |
| Declophen (**5**) | Analgesic | Heteroatoms, aromatic ring, amine, carboxylic acid |
| Lupicof: dextromethorphan (**6**), chlorphenamine (**7**) | Antihistamine | Heteroatoms, aromatic ring, amine, heterocycle, methoxy |
| Voltaren (**8**) | Analgesic | Heteroatoms, aromatic ring, amine, carboxylic acid |

**Table 1**. Types of drugs, clinical uses, and the functional groups in the molecular structures (*Continued*)

| Drug name | Clinical uses | Functional groups for corrosion inhibitor performance |
|---|---|---|
| Farcolin: salbutamol (**9**) and ammonium chloride | Chronic bronchospasm, asthma | Heteroatoms, aromatic ring, amine, hydroxyl |
| Ambroxol (**10**) | Mucolytic | Heteroatoms, aromatic ring, amine, hydroxyl |
| Asthalin: salbutamol (**9**) | Chronic bronchospasm, asthma | Heteroatoms, aromatic ring, amine, hydroxyl |
| Amlodipine besylate (**11**) | Antihypertension | Heteroatoms, aromatic ring, amine, heterocycle, ester |
| Atorvastatin (**12**) | Antihyperlipidemic | Heteroatoms, aromatic ring, amine, amide, heterocycle, hydroxyl, carboxylic acid |
| Atenolol (**13**) | Antihypertension | Heteroatoms, aromatic ring, amine, amide, heterocycle, ether, hydroxyl |
| Gentamicin (**14**) | Antibiotic | Heteroatoms, amine, heterocycle, hydroxyl |
| Nifedipine (**15**) | Antihypertension | Heteroatoms, aromatic ring, amine, heterocycle, ether, ester |
| Carvedilol (**16**) | Antihypertension | Heteroatoms, aromatic ring, amine, ether, heterocycle, hydroxyl |
| Tramadol (**17**) | Analgesic | Heteroatoms, aromatic ring, amine, ether, hydroxyl |
| Pantoprazole sodium (**18**) | Gastroesophageal problems | Heteroatoms, aromatic ring, amine, heterocycle, ether, sulfoxide |
| Concor: bisoprolol (**19**) | Antihypertension | Heteroatoms, aromatic ring, amine, ether, hydroxyl |
| Doxercalciferol (**20**) | Secondary hyperparathyroidism | Heteroatom, hydroxyl |
| Lorazepam (**21**) | Sedative agent, anticonvulsant, antianxiety, and hypnotic agent | Heteroatoms, aromatic ring, amide, heterocycle, hydroxyl |
| Bactrim: sulfamethoxazole (**22**), trimethoprim (**23**) | Antibiotic | Heteroatoms, aromatic ring, amine, heterocycle, ether, sulfonamide |
| Moxifloxacin (**24**) | Antibiotic | Heteroatoms, aromatic ring, hydroxyl, ketone |
| Betnesol (**25**) | Antiinflammatory | Heteroatoms, aromatic ring, amine, heterocycle, ketone, carboxylic acid, methoxy |
| Podocip: cefpodoxime proxetil (**26**) | Antibiotic | Heteroatoms, aromatic ring, amine, amide, heterocycle, ether, hydroxyl, ester, sulfide |
| Fluoxymesterone (**27**) | Hypogonadism, breast cancer | Heteroatoms, hydroxyl, ketone |
| Amoxicillin (**28**) | Antibiotic | Heteroatoms, aromatic ring, amine, amide, heterocycle, hydroxyl, carboxylic acid , sulfide |
| Cefdinir (**29**) | Antibiotic | Heteroatoms, amine, amides, heterocycle, carboxyl, oxime, sulfide |

**Table 1**. Types of drugs, clinical uses, and the functional groups in the molecular structures (*Continued*)

| Drug name | Clinical uses | Functional groups for corrosion inhibitor performance |
|---|---|---|
| Acetazolamide/Cidamex (**30**) | Diuretic and carbonic anhydrase inhibitor, Analgesic | Heteroatoms, amide, amine, heterocycle, sulfamoyl, thiadiazol |
| Etoricoxib (**31**) | antiinflammatory | Heteroatoms, aromatic ring, heterocycle, sulfone |
| Acyclovir (**32**) | Antiviral, antibiotic | Heteroatoms, amine, amide, ether, heterocycle, hydroxyl |
| Omeprazole (**33**) | Gastroesophageal problems, antibiotic | Heteroatoms, aromatic ring, amine, amide, heterocycle, ether, sulfoxide |
| Cefuroxime (**34**) | Antibiotic | Heteroatoms, amide, heterocycle, ether, sulfide, carboxylic acid, carbamate |
| Ethambutol (**35**) | Antibiotic | Heteroatoms, hydroxyl, amine, |
| Metoclopramide (**36**) | Antiemetic | Heteroatoms, ether, amine, amide, aromatic ring |
| Amitriptyline (**37**) | Antidepressant | Heteroatoms, amine, aromatic ring |
| Oxazepam (**38**) | Anti-anxiety | Heteroatoms, amide, heterocycle, hydroxyl, aromatic ring |
| Perindopril (**39**) | Antihypertension | Heteroatoms, amide, carboxyl, amine, ester |
| Alprazolam (**40**) | Anti-anxiety | Heteroatoms, heterocycle, aromatic ring |
| Naftifine (**41**) | Antifungal | Heteroatom, aromatic ring |
| Ixabepilone (**42**) | Antineoplastic agent and a microtubule-destabilizing agent | Heteroatoms, carbonyl, amide, heterocycle, hydroxyl, epoxy, sulfide |
| Indomethacin (**43**) | nonsteroidal anti-inflammatory | Heteroatoms, amide, heterocycle, carboxyl, aromatic ring |
| Tobramycin (**44**) | Antibiotic | Heteroatoms, ether, amine, heterocycle, hydroxyl |
| Metformin (**45**) | Antidiabetic | Heteroatoms, amine, imine |
| Desloratadine (**46**) | Antihistamine | Heteroatoms, amine, heterocycle, aromatic ring |

## ■ EXPERIMENTAL METHODS FOR ANALYSIS OF CORROSION INHIBITION PERFORMANCE

Several studies have been reporting about the application of expired drugs for corrosion inhibitors in various environments (Table 2). Performance or inhibition corrosion analysis toward each expired drug can be conducted by several methods such as weight loss, potentiodynamic polarization/galvanostatic polarization (GAP), potentiostatic polarization, electrochemical impedance spectroscopy (EIS), electrochemical frequency modulation (EFM), atomic absorption spectroscopy (AAS), thermometry, colorimetry, gasometric, and zero-charge potential method (PZC). In addition, there are metal surface analyses of corroded metal and adsorbed inhibitor on the metal surface by scanning electron microscopy (SEM), atomic force microscopy (AFM), energy-dispersive X-ray spectroscopy (EDX), and Fourier transform infrared spectroscopy (FTIR). The combination of two or more measurement methods can generate good or accurate results in the experiment.

A weight-loss test is carried out to calculate the weight of the remaining metal, corrosion rate, and inhibition efficiency after dipped in a corrosive solution.

**Table 2.** Corrosion inhibitor studies on expired drugs

| Drug name | Expired time | Corrosion inhibitor parameters | | | | | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| | | Metal/alloy | Testing method | Media | Concentration | Temperature (°C) | Immersion period (h) | Max IE | |
| Ranitidine (**1**) | - | Mild steel | Weight loss, open circuit potential, EIS, Potentiodynamic polarization | 1.0 M HCl | 50, 100, 150, 250, 400 ppm | 30, 40, 50, 60 | 168 (weight loss), 6 (EIS, potentiodyn. polarization) | 92.0% (400 ppm, 30 °C, EIS, 6 h) | [57] |
| Carbamazepine (**2**) | 12 months | Carbon steel | Potentiodynamic polarization | 0.1 M $H_2SO_4$ | 0.005 M | 25 | - | 90.0% (0.005 M, 25°C, potentiodyn. polarization) | [29] |
| Paracetamol (**3**) | 12 months | Carbon steel | Potentiodynamic polarization | 0.25 M acetic acid, 0.25 M sodium acetate | 0.01 M | 25 | - | 85.0% (0.01 M, 25°C, potentiodyn. polarization) | [29] |
| 1-Phenytoin sodium (**4**) | - | Carbon steel | Weight loss, open circuit potential, EIS, potentiodynamic polarization, SEM | 1.0 M HCl | 100, 200, 300, 400, 500 ppm | 25, 35, 45, 55 | 72 | 81.78% (500 ppm, 25 °C, potentiodyn. polarization) | [56] |
| Declophen (**5**) | - | Mild steel | Weight loss, open circuit potential, potentiodynamic polarization | 1.0 M HCl | 0.5, 1.0, 1.5, 2.0% (v/v) | 30, 40, 50, 60 | 168 | 87.50% (2.5%, potentiodyn. polarization, 30 °C) | [66] |
| Lupicof: dextromethorphan (**6**), chlorphenamine (**7**) | - | Mild steel | Weight loss, potentiodynamic polarization, EIS | 1.0 M HCl | 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0% (v/v) | 30, 40, 50, 60, 70 | 0.5, 2, 4, 6, 8, 24 | 92.28% (0.9%, 60 °C weight loss, 4 h) | [59] |
| Voltaren (**8**) | - | Aluminium | Weight loss, open circuit potential, potentiodynamic polarization | 1.0 M HCl | 25, 50, 75, 100, 125 ppm | 30 | 8 | 91.70% (125 ppm, 30 °C, potentiodyn. polarization) | [50] |
| Farcolin: salbutamol (**9**) and ammonium chloride | - | Carbon steel | Weight loss, open circuit potential, potentiodynamic polarization, potentiostatic polarization | 1.0 M HCl | 1.0, 2.0, 10.0, 20.0% (v/v) | 20, 30 | 0.25, 0.5, 0.75, 1, 1.5, 2 | 98% (20%, 20 °C, weight loss, 2 h) | [31] |
| Ambroxol (**10**) | - | Mild steel | Weight loss, EIS, potentiodynamic polarization, SEM, AFM | 1.0 M HCl, 1.0 M $H_2SO_4$ | 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0% (v/v) | 30, 40, 50, 60, 70 | 0.5, 2, 4, 6, 8, 24 | 94.03% in 1.0 M HCl and 95.54% in 1.0 M $H_2SO_4$ solutions (9.0%, 60 °C, weight loss, | [22] |

**Table 2.** Corrosion inhibitor studies on expired drugs (*Continued*)

| Drug name | Expired time | Corrosion inhibitor parameters | | | | | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| | | Metal/alloy | Testing method | Media | Concentration | Temperature (°C) | Immersion period (h) | Max IE | |
| | | | | | | | | 4 h in HCl and 6 h in $H_2SO_4$) | |
| Asthalin: salbutamol (**9**) | - | Mild steel | Weight loss, EIS, potentiodynamic polarization, SEM | 1.0 M HCl, 1.0 M $H_2SO_4$ | 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0% (v/v) | 30, 40, 50, 60, 70 | 0.5, 2, 4, 6, 8, 24 | 94.76% in HCl and 95.48% in $H_2SO_4$ solutions (9.0%, 60 °C, weight loss, 4 h for HCl and 6 h for $H_2SO_4$) | [52] |
| Amlodipine besylate (**11**) | - | Low carbon steel | Weight loss, EIS, potentiodynamic polarization, SEM, AFM | 1.0 M HCl | 50, 100, 150, 200, 250 ppm | 30, 45 | 0.5, 1.0, 1.5, 2.0, 2.5, 3 | 94.3% (250 ppm, 30 °C, EIS) | [30] |
| Atorvastatin (**12**) | - | Mild steel | Weight loss, EIS, potentiodynamic polarization, SEM | 1.0 M HCl | 50, 100, 150 ppm | - | 3 | 99.08% (150 ppm, potentiodyn. polarization) | [45] |
| Atenolol (**13**) | - | Mild steel | EIS, potentiodynamic polarization, SEM | 1.0 M HCl | 200 ppm | - | - | 93.29% (200 ppm, 30 °C, EIS) | [61] |
| Gentamicin (**14**) | - | Mild steel | Weight loss, EIS, potentiodynamic polarization, SEM | 1.0 M HCl | 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 % (v/v) | - | 0.5, 2, 4, 6, 8 24 | 92.36% (0.9%, weight loss, 6 h) | [36] |
| Nifedipine (**15**) | - | Mild steel | EIS, potentiodynamic polarization, SEM | 1.0 M HCl | 200 ppm | - | - | 95.61% (200 ppm, EIS) | [61] |
| Carvedilol (**16**) | - | Carbon steel | Weight loss, EIS, potentiodynamic polarization, EFM, AFM | 1.0 M HCl | $1 \times 10^{-5}$, $4 \times 10^{-5}$, $8 \times 10^{-5}$, $1.2 \times 10^{-4}$, $1.6 \times 10^{-4}$ M | 25, 35, 45, 55 | 0.5, 1, 1.5, 2, 3 | 98.94% ($1.6 \times 10^{-4}$ M, 25 °C, weight loss, 0.5 h) | [67] |
| Tramadol (**17**) | - | Mild steel | Weight loss, EIS, potentiodynamic polarization, AFM, SEM | 1.0 M HCl | 25, 50, 75, 100 ppm | 35, 45, 55, 65 | 3 | 97.20% (100 ppm, 35 °C, EIS) | [44] |
| Pantoprazole sodium (**18**) | - | High carbon steel | Mass loss, EIS, potentiodynamic polarization, EFM, FTIR, AFM, SEM, EDX | 1.0 M HCl | 100, 150, 200, 250, 300 ppm | 25, 30, 45, 40, 45, 50 | 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 | 95.10% (300 ppm, 25°C, potentiodyn. polarization) | [43] |
| Concor (**19**) | - | 304 stainless steel | Weight loss, EIS, Potentiodynamic polarization, EFM | 2.0 M HCl | 50, 100, 150, 200, 250, 300 ppm | 35, 40, 45 | 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 | 85.80% (300 ppm, 30 °C, EIS) | [37] |
| Doxercalciferol (**20**) | - | Mild steel | EIS, potentiodynamic | 3.0 M HCl | 0.1, 0.2, 0.3, 0.4 mg | 60 | - | 95.40% (0.4 mg, 30 °C, AAS) | [68] |

**Table 2.** Corrosion inhibitor studies on expired drugs (*Continued*)

| Drug name | Expired time | Corrosion inhibitor parameters | | | | | | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | Metal/alloy | Testing method | Media | Concentration | Temperature (°C) | Immersion period (h) | Max IE | |
| | | | polarization, AAS, SEM | | | | | | |
| Lorazepam (**21**) | - | Mild steel | Weight loss, EIS, Potentiodynamic polarization, AAS, SEM | 3.0 M HCl | 0.1, 0.2, 0.3, 0.4 $g.L^{-1}$ | 60 | 3, 6, 9, 12, 15 | 96.49% (0.4 $g.L^{-1}$, 30 °C, AAS, 3 h) | [51] |
| Bactrim: sulfamethoxazole (**22**), trimethoprim (**23**) | 6 months | Mild steel | Weight loss, EIS, potentiodynamic polarization, SEM, EDX, FTIR | 2.0 M HCl | 100, 200, 300, 400, 500 ppm | 30, 40, 50, 60 | 2, 4, 6, 10, 16, 24 | 94.38% (400 ppm, 30 °C, 4 h, potentiodyn. polarization) | [42] |
| Moxifloxacin (**24**) | 12 months | Aluminum | Weight loss, EIS, Potentiodynamic polarization, SEM | 1.0 M $H_2SO_4$ | 100, 200, 300, 400 ppm | 30, 40, 50, 60 | 24 | 86.17% (400 ppm, weight loss, 30 °C) | [60] |
| Betnesol (**25**) | 12 months | Aluminium | Weight loss, EIS, potentiodynamic polarization, SEM | 1.0 M $H_2SO_4$ | 100, 200, 300, 400 ppm | 30, 40, 50, 60 | 24 | 95.4% (400 ppm, 30 °C potentiodyn. polarization) | [60] |
| Podocip: cefpodoxime proxetil (**26**) | - | Carbon steel | Weight loss, EIS, potentiodynamic polarization, SEM | 1.0 M HCl | 25, 50, 75, 100 ppm | 35, 45, 55, 65 | 3 | 97.93% (100 ppm, 35 °C, EIS) | [58] |
| Fluoxymesterone (**27**) | - | Mild steel | AAS, potentiodynamic polarization, AC impedance spectroscopy, SEM | 3.0 M HCl | 0.05, 0.10, 0.15, 0.20 mg | 60 | - | 94.20% (0.2 mg, 60 °C, AAS) | [69] |
| Amoxicilin (**28**) | - | Mild steel | Weight loss, EIS, potentiodynamic polarization, Zero charge potential, SEM, AFM | 1.0 M HCl | 1200, 1400, 1600, 1800, 2000 ppm | 25 | 0.5, 2, 4, 6, 8 | 94.4% (1800 ppm, 25 °C, weight loss, 8 h) | [70] |
| Cefdinir (**29**) | - | Mild steel | Weight loss, EIS, Potentiodynamic polarization, AFM | 1.0 M HCl | $0.63 \times 10^{-4}$, $1.26 \times 10^{-4}$, $2.52 \times 10^{-4}$, $3.79 \times 10^{-4}$, $5.05 \times 10^{-4}$, $6.32 \times 10^{-4}$ M | 35 | 3 | 97.9% ($6.32 \times 10^{-4}$ M, 35 °C, weight loss, 3 h) | [71] |
| Acetazolamide/ Cidamex (**30**) | 6 months | Mild steel | Weight loss, EIS, Potentiodynamic polarization, SEM, EDX, FTIR | 2.0 M HCl | 100, 200, 300, 400, 500 ppm | 30, 40, 50, 60 | 1, 3, 6, 9, 15, 24 | 96.39% (500 ppm, 35 °C, EIS) | [39] |
| Etoricoxib (**31**) | - | Low carbon steel | Potentiodynamic polarization, SEM, EDX, FTIR | 0.5 M $H_3PO_4$ | 75, 125, 175, 225, and 275 ppm | 30, 60 | - | 80.63% (225 ppm, 30 °C, potentiodyn. | [72] |

**Table 2.** Corrosion inhibitor studies on expired drugs (*Continued*)

| Drug name | Expired time | Corrosion inhibitor parameters | | | | | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| | | Metal/alloy | Testing method | Media | Concentration | Temperature (°C) | Immersion period (h) | Max IE | |
| | | | | | | | | polarization) | |
| Acyclovir (**32**) | - | Sabic iron | Weight loss, GAP, potentiostatic anodic polarization, EIS | 1.0 M HCl | 100, 200, 300, 400, 500 ppm | 25, 35, 45, 55 | 1, 2, 3, 4, 5, 6, 7, 8 | 94.47% (500 ppm, 25 °C, GAP) | [40] |
| Omeprazole (**33**) | - | Sabic iron | Weight loss, GAP, potentiostatic anodic polarization, EIS | 1.0 M HCl | 100, 200, 300, 400, 500 ppm | 25, 35, 45, 55 | 1, 2, 3, 4, 5, 6, 7, 8 | 95.50% ((500 ppm, 25 °C, EIS) | [40] |
| Cefuroxime (**34**) | - | Sabic iron | Weight loss, GAP, potentiostatic anodic polarization, EIS | 1.0 M HCl | 100, 200, 300, 400, 500 ppm | 25, 35, 45, 55 | 1, 2, 3, 4, 5, 6, 7, 8 | 96.58% (500 ppm, 25 °C, GAP) | [73] |
| Ethambutol (**35**) | - | Mild Steel | Weight loss, EIS potentiodynamic polarization, SEM, molecular dynamics | 0.5 M HCl | 200, 400, 800, 1000 ppm | 30, 40, 50, 60 | 4 | 98.29% (1000 ppm, 60 °C, potentiodyn. Polarization, 4 h) | [46] |
| Metoclopramide (**36**) | - | Carbon steel | Potentiodynamic polarization, SEM, EDX, FTIR | 5.0 M $H_3PO_4$ | 75, 125, 175, 225, 275 ppm | 30, 60 | - | 82.24% (175 ppm, 30 °C, potentiodyn. polarization) | [74] |
| Amitriptyline (**37**) | - | Mild steel | EIS, potentiodynamic polarization, AAS, SEM | 3.0 M HCl | 0.5, 1.5, 2.0 ppm | Room temperature | 1 | 94.00% (2.0 ppm, AAS, room temperature) | [41] |
| Oxazepam (**38**) | - | Carbon steel | Weight loss, EIS gasometric, calorimetry, SEM, AAS | 5.0% NaCl | 0.1, 0.2, 0.3, 0.4 ppm | 60 | 2, 4, 6, 8, 10 | 94.06% (0.4 ppm, 60, calorimetry, 2 h) | [47] |
| Perindopril (**39**) | - | Carbon steel | Weight loss. AAS | 3.0% NaCl | 0.1, 0.2, 0.3, 0.4 g/L | 30, 40, 50, 60 | 24 | 90.00% (0.4, 30 °C, weight loss, 24 h) | [75] |
| Alprazolam (**40**) | - | Carbon steel | Weight loss. AAS | 3.0% NaCl | 0.1, 0.2, 0.3, 0.4 g/L | 30, 40, 50, 60 | 24 | 85.78% (0.4, 30 °C, weight loss, 24 h) | [75] |
| Naftifine (**41**) | - | Copper | Weight loss, EIS, potentiodynamic polarization, SEM | 5.0 M HCl | 1, 2, 3, 4 ppm | 60 | 2, 4, 6, 8, 10 | 97.19% (4 ppm, 60 °C, potentiodyn. polarization) | [48] |
| Ixabepilone (**42**) | - | Copper | Weight loss, EIS, potentiodynamic polarization, SEM | 5.0 M HCl | 0.1, 0.2, 0.3, 0.4 ppm | - | 2, 4, 6, 8, 10 | 97.60% (0.4 ppm, potentiodyn. polarization) | [49] |
| Indomethacin (**43**) | - | Carbon steel | Weight loss, open circuit | 1.0 M HCl | 100, 200, 300, 400, 500 ppm | 25, 35, 45, 55 | 12, 24, 36, 48, 60, 72 | 83.81% (500 ppm, 25 °C, | [55] |

**Table 2.** Corrosion inhibitor studies on expired drugs (*Continued*)

| Drug name | Expired time | Corrosion inhibitor parameters | | | | | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| | | Metal/alloy | Testing method | Media | Concentration | Temperature (°C) | Immersion period (h) | Max IE | |
| | | | potential, EIS, potentiodynamic polarization, SEM | | | | | 83.81% (500 ppm, 25 °C, | |
| Tobramycin (**44**) | - | Carbon steel | Thermometry, EIS, potentiodynamic polarization, SEM | 2.0 M HCl | 50, 100, 200, 300, 500 ppm | 30, 50 | 0.5 | 92.60% (500 ppm, 50 °C, potentiodyn. polarization) | [38] |
| Metformin (**45**) | - | C1018 carbon steel | EIS, potentiodynamic polarization, SEM | $CO_2$-saturated 3.5% NaCl + 340 ppm acetic acid | 50, 100, 150, 200 ppm | - | 24 | 89.47% (200 ppm, EIS, 24 h) | [54] |
| Desloratadine (**46**) | - | Carbon steel (X52) | Weight loss, potentiodynamic polarization, SEM, AFM | 2.0 M HCl | $3.2 \times 10^{-5}$, $6.4 \times 10^{-5}$, $12.8 \times 10^{-5}$, $19.3 \times 10^{-5}$ M | 30 | 24 | 92.70% ($19.3 \times 10^{-5}$ M, 30 °C, weight loss, 24 h) | [53] |

-: Not mentioned

Dissolution of metal can be observed through discoloration in solution after a certain range of testing time. This method usually needs a longer time from 0.5 up to 168 h to get satisfying data [36-57]. Different from the weight loss method, the AAS method measures the metal ions concentration in the testing solution with and without the inhibitors to determine inhibition efficiency [47]. The potentiodynamic polarization or the Tafel technique allows us to find corrosion rate, inhibition efficiency, and type of inhibitor from corrosion current density and shifting in corrosion potential [16,58-59]. Both anodic and cathodic reactions as well as inhibition mechanisms were known based on cathodic and anodic polarization curves [43,45,60]. EIS is a convenient and rapid technique to evaluate the efficiency of corrosion inhibition, inhibition mechanisms, and protective properties of the corrosion inhibitors [61-62]. EIS also provides kinetics and electrochemical information on metal/solution interface [42]. The principal benefits of the EIS technique correspond to a non-destructive technique and providing information about the electrochemical/ corrosion mechanism (concentration, activation, or diffusion) [44]. Data interpretation is described by Nyquist plots that resemble an equivalent circuit. This plot relates real ($Z_r$) and imaginary ($Z_{im}$) impedances. EFM also is a non-destructive technique for corrosion measurement [63]. The values of corrosion current can be determined without Tafel slopes data and worked at a small polarization signal. These advantages are suitable for electrochemically corrosion monitoring [63]. Moreover, potentiostatic anodic polarization method is conducted to analyze the performance of inhibitors in overcoming the pitting or localized corrosion problem based on anodic polarization peaks and the shift of pitting potential [40]. Then, the colorimetry method is based on the presence/amount of metal ion in the solution [47], while the thermometric method is conducted in a calorimeter and water bath. This method correlates the rise of temperature with reaction time [38].

The SEM and EDX methods are exclusively used to analyze the appearance and find element composition in

protected and unprotected metallic surfaces respectively after contacts with a corrosive solution. Similar to EDX, AFM also identified atoms at the surface and evaluating the interactions between a specific atom and its neighboring atoms. AFM test displays photos with the atomic or near-atomic resolution to observe surface topography and surface roughness of coins [64]. In the meanwhile, FTIR was conducted to observe the protective film from inhibitor molecules on the metal surface via the vibrations of functional groups in expired drug molecules [42-43].

## ■ CORROSION INHIBITOR PERFORMANCE ON METALS (CHEMICAL COMPOSITION AND STRUCTURAL EFFECTS)

All expired drugs in this review can reduce the corrosion rate on metal surfaces. Their abilities are quite varied from fairly to very effective. Besides, none of the expired drugs contains phosphate group or phosphor element as the main cause of the eutrophication process which is harmful to water organisms [65]. Meanwhile, information about the expired time/date is necessary. This corresponds to the presence and properties of active substances that may change/decompose/degrade after reaching the expired date [44]. The solubility property of most expired drugs requires them to be tested in the acidic media. Hydrochloric acid and sulfuric acid solution are examples of the most used corrosive media in every analysis of expired drugs-based corrosion inhibitors. These acid solution become the first choice for the descaling and cleaning agents for the pipeline in many petroleum industries. Apart from those, there are phosphoric acid and acetic acid as the alternatives. The NaCl solution is only used in the study of expired Oxazepam (**38**), Perindopril (**39**), and Alprazolam (**40**) as corrosion inhibitors. Different from other expired drugs, those expired drugs have good solubility in neutral pH solution. Hydrogen bonds between electronegative atoms from these expired drugs and hydrogen atoms from water molecules may be stronger in this case. Comparison experiments showed that HCl is more aggressive than $H_2SO_4$ based on experiments metal protection using expired Ambroxol (**16**) and Asthalin (**9**) [22,52]. It is displayed by lower values of charge transfer resistance ($R_{ct}$) and corrosion inhibition efficiency (IE) from EIS analysis and corrosion rate (CR) in the weight loss method.

The chemical structures of several expired drugs are displayed in Fig. 2. Corrosion inhibition activity of expired drugs on the metal surface is via adsorption. The adsorption of inhibitor molecules is primarily affected by the electronic structure, aromaticity, steric factor, electron density of functional groups, and molecular weight [47]. The structural functionalities of the expired drugs like heteroatoms and functional groups such as aromatic ring, amine, amide, heterocyclic ring, ether, hydroxyl, ester, carboxylic acid, sulfoxide, etc play a pivotal role in corrosion inhibitor consideration. These constituents are supporting agents for interactions between metal and/or metal ions and inhibitor molecules so that inhibitor compounds will be adsorbed and protect the outer part of the metal from direct contact with the corrosive solution.

The expired drugs **1**–**2**, **6**–**7**, **9**, **11**–**18**, **20**–**23**, **26**–**30**, **32**–**35**, **37**, **44**, and **46** (Fig. 2) have shown high corrosion inhibition efficiency (IE ≥ 90%) to protect carbon steel/mild steel/Sabic iron/copper in HCl solution. Most of these expired drugs contain amine and some of them also contain sulfide/sulfoxide/sulfonamide functional groups in their molecular structures. The expired drugs with nitrogen and sulfur atoms in the molecules ensure high protection for the metals in acid media [76]. Amines and alkanolamines commonly generate both anodic and cathodic inhibitors that exchange the chloride ions, thus establish a physical barrier and/or durable thin passivating film [77]. The reinforcement adsorption of the expired drugs with amine and/or amide group is also affected by methyl and methylene groups near the nitrogen atoms [78]. These groups can increase the electron density of nitrogen through inductive effects [76]. Besides, longer hydrocarbon chains form a hydrophobic layer in the outer part of the inhibitor film for repelling water molecules [79]. The hydrophobic film was also produced from the adsorption of the carboxyl group as lewis base on the metal surface as Lewis acid [80]. Then, the

availability of heterocyclic groups effectively covers active sites on the metal surface via Van der Waals interactions and/or chemical bonds between free electron pairs from their heteroatoms (N, O, S) and 3*d* orbitals of Fe atom on the surface [81]. Furthermore, expired Ambroxol (**10**) and Asthalin (**9**) effectively protect mild steel in HCl and $H_2SO_4$ solutions (IE ≥ 90%), whereas, the expired Betnesol (**21**), Voltaren (**8**), Naftifine (**41**), Ixabepilone (**42**), are very effective to preserve aluminium/copper (IE ≥ 90%) in the same acid solutions. Meanwhile, Oxazepam (**38**) and Perindopril (**39**) are very effective (IE ≥ 90%) for carbon steel protection in NaCl solution.

Expired atorvastatin **(12)** gave the highest inhibition efficiency (> 99%) than the other expired drugs. The presence of three aromatic rings, three hydroxyl groups, amide groups, *N*-heterocyclic group, carboxyl group, and fluor element is a better combination to produce the most effective protective layer for the metal

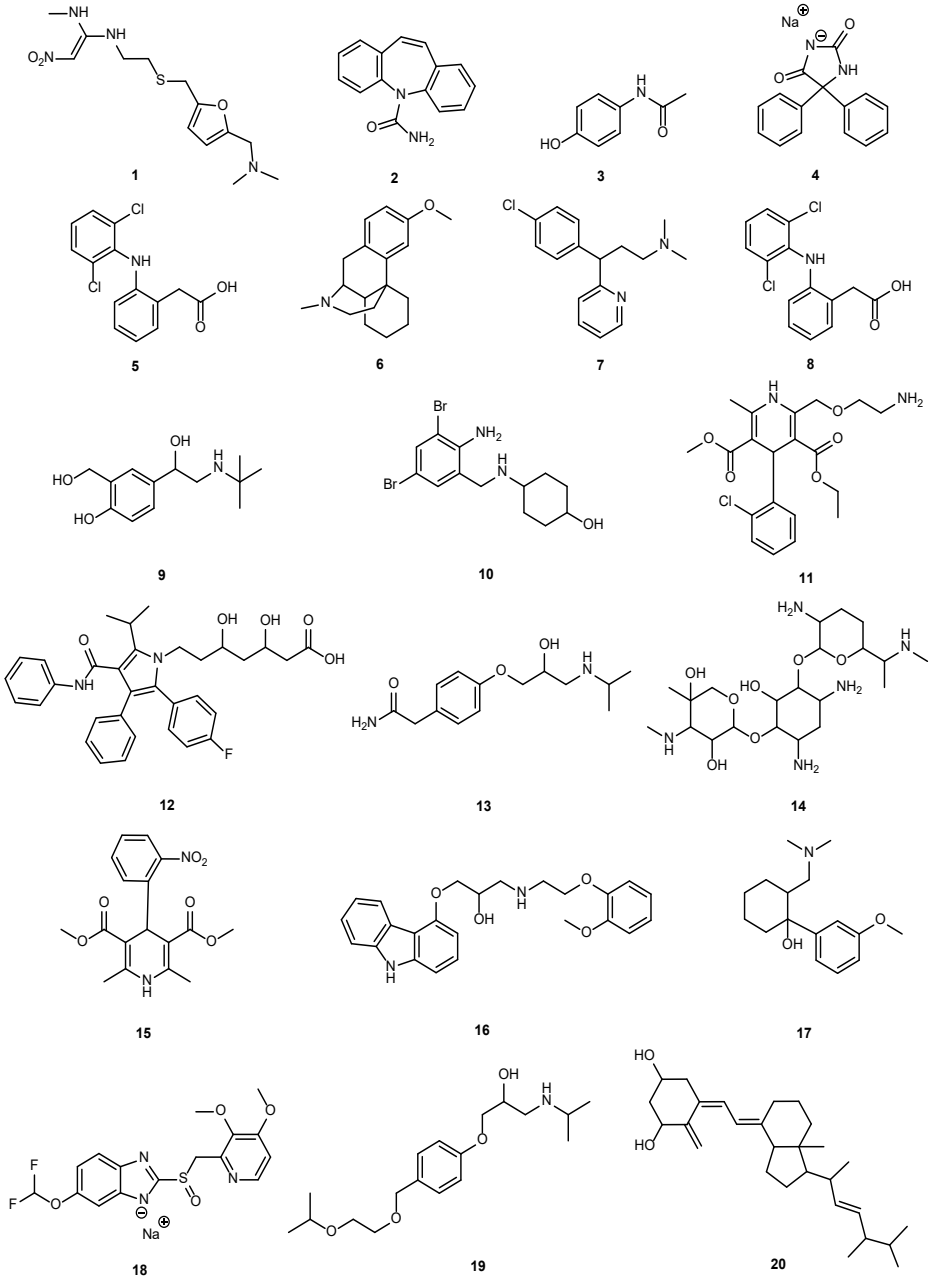


**Fig 2.** Chemical structures of active compounds in the expired drugs as corrosion inhibitors

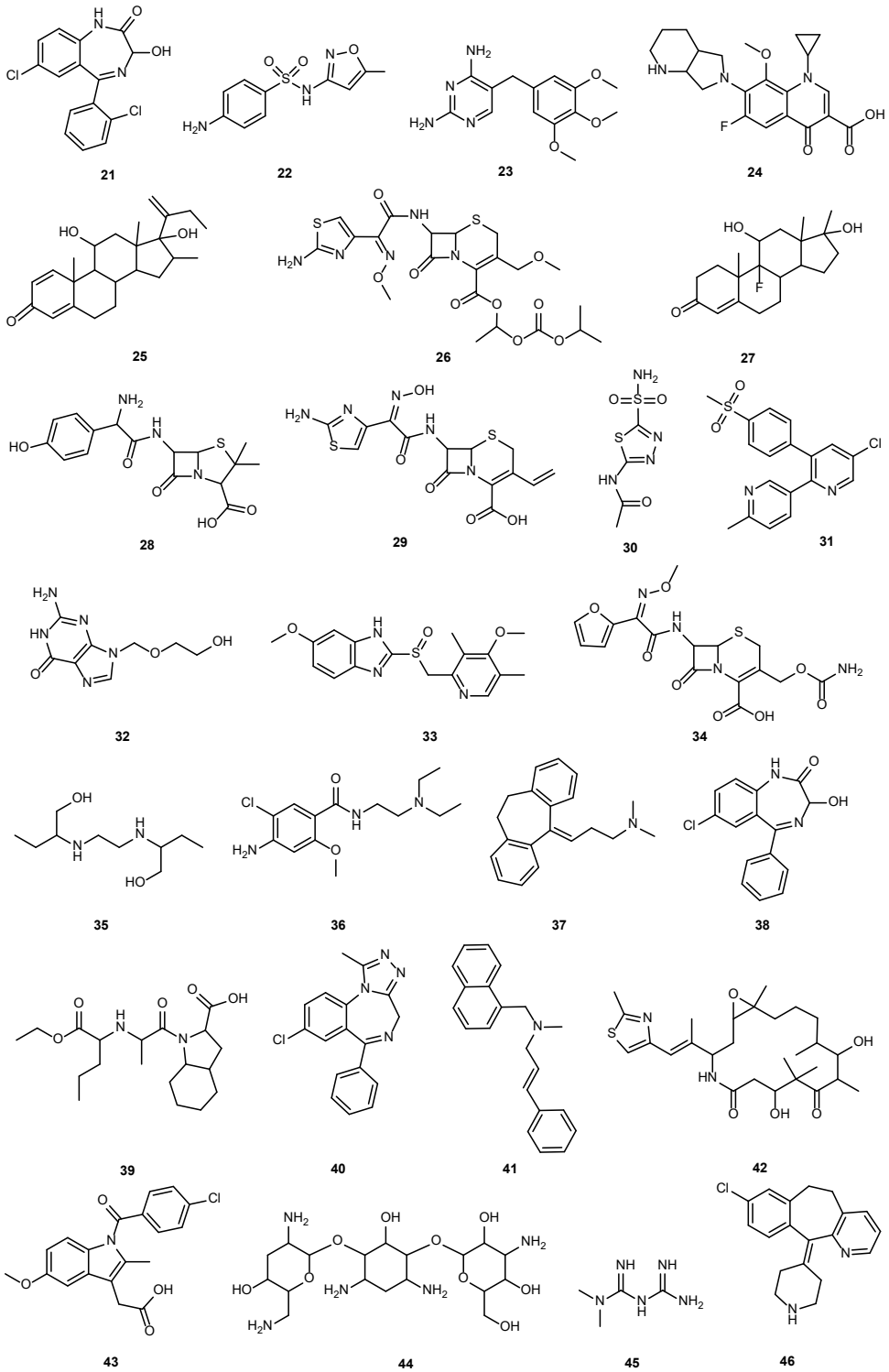

**Fig 2.** Chemical structures of active compounds in the expired drugs as corrosion inhibitors (*Continued*)

surface at a concentration of 150 ppm. the presence of the carboxylic acid group plays a role to prevent rust formation for carbon steel, has good anti-oxidation stability, and chemical stability if combined with the aromatic rings [82]. It is also supported by conjugated double bonds which contain π-electrons as another

center of adsorption for metal surface protection [83]. Meanwhile, the inhibition efficiencies of expired Lorazepam (**21**), Doxercalciferol (**20**), and Fluoxymesterone (**23**) reach more than 90% without the amine group. However, these results are obtained from the AAS method that was not a conventional method for corrosion inhibition analysis. Measurements by electrochemical methods inform corrosion inhibition efficiency of those expired drugs < 90%. Cefuroxime (**34**) also has IE ≥ 90% without amine group. However, the performance may be still affected by other functional groups such as carbamate, furan, amide, and sulfide. Then, the expired Declophen (**5**), Concor (**19**), Metoclopramide (**36**), Alprazolam (**40**), and Metformin (**45**), contain the amine group, but the inhibition efficiency is < 90%. This indicates that since there are specific functional groups or elements with the unshared electrons in an expired drug compound, then it still has the potency to protect the metal from corrosion deterioration.

Corrosion inhibition tests are commonly conducted at various inhibitor concentrations and temperatures. The inhibition efficiency increases by raising the concentration of inhibitor but mostly decreases when the temperature is raised. The number of expired drug molecules will be desorbed again from the metal surface at higher temperatures. This relates to the character of physical adsorption [84]. In this condition, the more surface area of carbon steel can contact directly to the corrosive environment followed by decreasing the inhibition efficiency [44,58]. Besides, all electrochemical reactions and diffusion activities of corrosion substances will be increased [85].

In the case of the expired Asthalin (**9**), Lupicof (**6**, **7**), Ambroxol (**10**), Ethambutol (**35**), and Tobramycin (**44**) drugs, the highest inhibition efficiency does not occur at relatively low or room temperature, but at 60 °C. Asthalin (**9**), Ambroxol (**10**), Ethambutol (**35**), and Tobramycin (**44**) almost have similar functional groups which contain amine and hydroxyl groups. The difference lies in the type of heteroatoms and the number of functional groups. While Lupicof (**6**, **7**) does not contain hydroxyl, primary and secondary amine in its molecular structure. In this case, the Increasing temperature can rise the adsorption propensity of drug molecules to the metal surface until trigging chemical bonding between iron atoms or iron ions and specific constituents in the expired drugs. Therefore, those expired drugs are chemically adsorbed on the metal surface. Meanwhile, the expired Farcolin and Asthalin contain salbutamol (**9**) as an active compound. The expired Farcolin is effective at 20 °C, while the expired Asthalin is more effective at 60 °C. This may relate to the activity of other ingredients in those expired drugs and/or different expired dates when the experiment was conducted.

## ■ INHIBITION MECHANISM AND SURFACE ANALYSIS

The corrosion phenomenon leads the metal surface to be covered with negative charges from the reactions between metal and anions for instance chloride, hydrogen sulfate, or sulfate ions [57]. The inhibition mechanism of expired drugs was similar to conventional organic inhibitors. Expired drugs and organic inhibitors are mostly mixed-type (anodic and cathodic) inhibitors [86]. They protect corrosion reactions via the adsorption process on the metal surface. This adsorption depends on the charge and the nature of the tested metal, chemical composition, molecular structure of the expired drug, and the aggressiveness of the electrolyte solution [87]. The protonated atoms from expired drug compounds generate electrostatic interaction to chemical bonds with metal-anion [88]. Electrostatic, dipole-dipole, dipole-ion interactions induce the formation of the physical barrier (physisorption) [89-90]. Whereas chemical bonds establish strongly thin film on the metal surface (chemisorption). These chemical bonds also occur through the acceptance of lone pair electrons that are available in functional groups with vacant orbitals in Fe atoms [81]. Adsorption and desorption of inhibitor molecular on the metal surface are continuous processes until reach equilibrium. The time required to reach this equilibrium is affected by temperature and the nature of the inhibitor [76]. For temperature effect, the increase of IE after increasing temperatures refers to chemical adsorption, on the

contrary, the increase of the corrosion rate by increasing temperature indicates that the inhibitor is physically adsorbed on the metal surface [85].

Adsorption of Acyclovir (**32**), Omeprazole (**33**), and Cefuroxime (**34**) is considered by replacement of adsorbed water molecules on the testing metal surface [40,73]. The number of water molecules that are repelled by an expired drug molecule from the adsorption sites is different for a specified expired drug. The adsorption mechanism of their molecules is investigated by fitting all of the inhibition efficiency values on corrosion tests with types of adsorption isotherm such as Langmuir, Freundlich, Temkin, Frumkin, El-Awardy, Flory–Huggins, Volmer, Dubinin-Radushkevic, Jovanovic, Elovich, etc. The percentages of inhibition efficiency indicate surface coverage of inhibitor (θ) on the metal surface. Mostly expired drugs **4**, **8**, **9**, **12**, **14**, **16**–**19**, **26**, **29**–**36**, **43**–**46** were found to follow the Langmuir isotherm in their adsorption process. These are shown by straight line resulted from plots of C/θ vs C, with regression coefficient values close to 1. Their active substances will be adsorbed and form a single layer on the metal-solution interface. In this condition, all active sites have uniform adsorption energy [91]. Then, there is no transmigration, attraction, and repulsion between neighboring adsorbed molecules in the surface plane. Further adsorption cannot occur and the attractive force rapidly decreases with the additional distance [92]. The equation of Langmuir isotherm is displayed as in Eq. (1).

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

where $K_{ads}$ is the equilibrium constant of adsorption-desorption (L $mol^{-1}$) and C is the inhibitor concentration (mol $L^{-1}$). Meanwhile, the expired Bactrim obeyed El-Awardy adsorption isotherm (Eq. (2)) which is modified from Langmuir isotherm [42].

$$\log\left(\frac{\theta}{1-\theta}\right) = \log K_{ads} + y \log C \quad (2)$$

where y is the number of inhibitor molecules that occupy one active site. The value of 1/y obtained from calculated results is more than 1. It indicates that molecules of expired drugs fill in two or more active sites on the metal-solution interface [42].

The adsorption of expired drugs on the metal surface and the condition of protected and unprotected metal surfaces are shown by SEM micrographs and EDX spectra. Metals that are immersed in acid solution without expired drugs as corrosion inhibitor appear rougher due to faster electrochemical reactions. However, the surface appearance of metal is maintained relatively smoother by the presence of expired drugs in the solution [45,61,69]. According to the EDX spectra, the formation of the protective layer from adsorbed inhibitor in the metallic surface can be confirmed via heteroatom peaks like nitrogen, sulphur, and fluorine from inhibitor molecules. Whereas the peaks of corrosives elements like chloride and oxygen from the solution will decrease [42]. The presence of dissolved oxygen in the corrosive solutions and the oxygen element in inhibitor molecules even will increase oxygen content on the metal surface [30]. Meanwhile, the presence of chloride in the expired Voltaren (**8**), Amlodipine besylate (**11**), Declophen (**5**), Metoclopramide (**36**), Oxazepam (**38**), Indomethacin (**43**), and Lupicof (**6**, **7**) may generate a confusing conclusion due to overlapping chloride peak in the EDX spectra.

## ■ CURRENT CHALLENGE AND FUTURE PROSPECTS

The use of corrosion inhibitors has become a necessity to maintain the continuity of the transportation, processing, and production process in the petroleum industry. The expired drugs are another choice as corrosion inhibitors besides existing commercial and other natural substances. However, there are limitations by using the expired drugs as corrosion inhibitors including:

1. Most expired drugs are only soluble in the acidic solution, therefore brine solution like sodium chloride is still rarely used as a corrosive medium/ electrolyte for corrosion inhibition experiments.
2. This water/brine insolubility also shows that most expired drugs do not have double functions (both of the corrosion and scale inhibitors). The expired drugs only act as scale inhibitors if they can dissolve in water or neutral solutions.

3. It is difficult to make sure the most contributing substance for corrosion inhibition when a drug contains two or more active substances.
4. It is important to analyze the ability and durability of expired drugs after 1 month, 6 months, 1 year, or 2 years of storage time due to the number of substances used for inhibitor solution is extremely small. This also explains that the use of expired drugs as corrosion inhibitors does not fully solve the environmental problems from medical wastes.

However, there are still opportunities from the experimental gap to develop experiments utilizing expired drugs that have been discussed. Most of the experiments do not inform the stirring process as well as stirring speed in weight loss and electrochemical measurements. Even though the information about the stirring process and speed will show the durability of an expired drug toward mechanical shocks. Besides, some types of expired drugs like medicals and herbals have not been tested. Then, further treatments may be conducted to separate water-soluble parts of the expired drugs, thus produced specific active substances which are effective not only in acid solutions but also in a brine solution. Meanwhile, there is not much information about the study of expired drugs as corrosion inhibitors in $CO_2$-saturated solution. Hence, research opportunities on this topic are prominently promising.

## ■ CONCLUSION

All types of expired drugs applied as corrosion inhibitors in this review were able to slow down corrosion reactions in metals. The utilization of expired drugs for corrosion inhibitors was effective, economic, and environmental considerations to solve drug waste problems. The chemical composition and molecular structure of the inhibitor mainly affect inhibition activity. Active substances in expired drugs that contain heteroatoms, lone pair electrons, double bonds, and aromatic rings act to protect metal surfaces from corrosives agents. The low solubility in neutral solution/brine solution made most expired drugs can only be used in acidic solution. The validity and reliability of inhibition evaluation are obtained by using several methods and comparing the experiment results of those methods. The inhibition efficiency of several expired drugs reaches > 90%. Most of these drugs obey Langmuir adsorption isotherm when adsorbed on the metal surface. So far, the expired atorvastatin generated the highest inhibition efficiency (> 99%), thus becomes the most potential corrosion inhibitor compared to other expired drugs. Further studies are required to ensure the eligibility of expired drugs for industrial application.

## ■ REFERENCES

[1] Ye, Y., Yang, D., Chen, H., Guo, S., Yang, Q., Chen, L., Zhao, H., and Wang, L., 2020, A high-efficiency corrosion inhibitor of N-doped citric acid-based carbon dots for mild steel in hydrochloric acid environment, *J. Hazard. Mater.*, 381, 121019.

[2] Burstein, G.T., Liu, C., Souto, R.M., and Vines, S.P., 2004, Origins of pitting corrosion, *Corros. Eng. Sci. Technol.*, 39 (1), 25–30.

[3] Song, F.M., Kirk, D.W., Graydon, J.W., and Cormack, D.E., 2004, Predicting carbon dioxide corrosion of bare steel under an aqueous boundary layer, *Corrosion*, 60 (8), 736–748.

[4] Hagarová, M., Cervová, J., and Jaš, F., 2015, Selected types of corrosion degradation of pipelines, *Koroze Ochr. Mater.*, 59 (1), 30–36.

[5] AER, 2013, *Report 2013-B: Pipeline Performance in Alberta, 1990–2012*, Alberta Energy Regulator, Calgary, Alberta, Canada.

[6] Koch, G., Varney, J., Thopson, N., Moghissi, O., Gould, M., and Payer, J., 2016, *International Measures of Prevention, Application, and Economics of Corrosion Technologies Study*, Eds. Jacobson, G., NACE International, Houston, Texas, USA.

[7] Jafar Mazumder, M.A., 2020, A review of green scale inhibitors: Process, types, mechanism and properties, *Coatings*, 10 (10), 928.

[8] Dickinson, W., Sanders, L., and Lowen, C., 2011, Development and Performance of Biodegradable Antiscalants for Oilfield Applications, *Offshore Technology Conference 2011 (OTC 2011)*, Houston, Texas, USA, 2–5 May 2011.

[9] Popoola, L.T., Grema, A.S., Latinwo, G.K., Gutti, B.,

and Balogun, A.S., 2013, Corrosion problems during oil and gas production and its mitigation, *Int. J. Ind. Chem.*, 4 (1), 35.

[10] Dahiya, S., Lata, S., Kumar, R., and Yadav, O.S., 2016, Comparative performance of Uroniums for controlling corrosion of steel with methodical mechanism of inhibition in acidic medium: Part1, *J. Mol. Liq.*, 221, 124–132.

[11] Kumar, C.M., Chandrashekarappa, M.P., Kulkarni, R.M., Pimenov, D.Y., and Giasin, K., 2021, The effect of Zn and Zn–$WO_3$ composites nano-coatings deposition on hardness and corrosion resistance in steel substrate, *Materials*, 14 (9), 2253.

[12] Duong, N.T., Hang, T.T.X., Nicolay, A., Paint, Y., and Olivier, M.G., 2016, Corrosion protection of carbon steel by solvent free epoxy coating containing hydrotalcites intercalated with different organic corrosion inhibitors, *Prog. Org. Coat.*, 101, 331–341.

[13] Cotting, F., and Aoki, I.V., 2016, Smart protection provided by epoxy clear coating doped with polystyrene microcapsules containing silanol and Ce (III) ions as corrosion inhibitors, *Surf. Coat. Technol.*, 303 (Part B), 310–318.

[14] Eugenio, F.D.T., and Pajarito, B.B., 2019, Potential anti-corrosion additives derived from waste plastic sachets, *IOP Conf. Ser.: Mater. Sci. Eng.*, 634 (1), 012039.

[15] Singh, A., Ansari, K., Quraishi, M., and Banerjee, P., 2021, Corrosion inhibition and adsorption of imidazolium based ionic liquid over P110 steel surface in 15% HCl under static and dynamic conditions: Experimental, surface and theoretical analysis, *J. Mol. Liq.*, 323, 114608.

[16] Baari, M.J., Bundjali, B., and Wahyuningrum, D., 2020, Synthesis of oligosuccinimide and evaluation of its corrosion inhibition performance on carbon steel in $CO_2$-saturated 1% NaCl solution, *J. Math. Fundam. Sci.*, 52 (2), 202–221.

[17] Baari, M.J., Bundjali, B., and Wahyuningrum, D., 2021, Performance of *N,O*-carboxymethyl chitosan as corrosion and scale inhibitors in $CO_2$ saturated brine solution, *Indones. J. Chem.*, Article in Press.

[18] Pahuja, P., Dahiya, S., and Lata, S., 2018, Review on herbal drugs as corrosion inhibitor for low alloy steel, *BMIET J. Sci. Technol. Manage.*, 2 (1), 7–19.

[19] Agrawal, Y.K., Talati, J.D., Shah, M.D., Desai, M.N., and Shah, N.K., 2004, Schiff bases of ethylenediamine as corrosion inhibitors of zinc in sulphuric acid, *Corros. Sci.*, 46 (3), 633–651.

[20] Ashassi-Sorkhabi, H., Shaabani, B., and Seifzadeh, D., 2005, Effect of some pyrimidinic Shciff bases on the corrosion of mild steel in hydrochloric acid solution, *Electrochim. Acta*, 50 (16-17), 3446–3452.

[21] Tamalmani, K., and Husin, H., 2020, Review on corrosion inhibitors for oil and gas corrosion issues, *Appl. Sci.*, 10 (10), 3389.

[22] Geethamani, P., and Kasthuri, P.K., 2015, Adsorption and corrosion inhibition of mild steel in acidic media by expired pharmaceutical drug, *Cogent Chem.*, 1 (1), 1091558.

[23] Srivastava, M., Tiwari, P., Srivastava, S.K., Prakash, R., and Ji, G., 2017, Electrochemical investigation of Irbesartan drug molecules as an inhibitor of mild steel corrosion in 1 M HCl and 0.5 M $H_2SO_4$ solutions, *J. Mol. Liq.*, 236, 184–197.

[24] El-Haddad, M.N., Fouda, A.S., and Hassan, A.F., 2019, Data from chemical, electrochemical and quantum chemical studies for interaction between Cephapirin drug as an eco-friendly corrosion inhibitor and carbon steel surface in acidic medium, *Chem. Data Collect.*, 22, 100251.

[25] Ayoola, A.A., Fayomi, O.S.I., and Ogunkanmbi, S.O., 2018, Data on inhibitive performance of Chloraphenicol drug on A315 mild steel in acidic medium, *Data Brief*, 19, 804–809.

[26] Abdallah, M., Gad, E.A.M., Sobhi, M., Al-Fahemi, J.H., and Alfakeer, M.M., 2019, Performance of tramadol drug as a safe inhibitor for aluminum corrosion in 1.0 M HCl solution and understanding mechanism of inhibition using DFT, *Egypt. J. Pet.*, 28 (2), 173–181.

[27] Adejoro, I.A., Ojo, F.K., and Obafemi, S.K., 2015, Corrosion inhibition potentials of ampicillin for mild steel in hydrochloric acid solution, *J. Taibah Univ. Sci.*, 9 (2), 196–202.

[28] Ansari, K., Quraishi, M., Prashant, and Ebenso, E.,

2013, Electrochemical and thermodynamic investigation of diclofenac sodium drug as a potential corrosion inhibitor for mild steel in hydrochloric acid, *Int. J. Electrochem. Sci.*, 8 (12), 12860–12873.

[29] Vaszilcsin, N., Ordodi, V., and Borza, A., 2012, Corrosion inhibitors from expired drugs, *Int. J. Pharm.*, 431 (1-2), 241–244.

[30] Fouda, A.S., Mahmoud, W.M., and Abdul Mageed, H.A., 2016, Evaluation of an expired nontoxic amlodipine besylate drug as a corrosion inhibitor for low-carbon steel in hydrochloric acid solutions, *J. Bio- Tribo-Corros.*, 2 (2), 7.

[31] Attia, E.M., 2015, Expired farcolin drug as corrosion inhibitor for carbon steel in 1 M HCl solution, *J. Basic Appl. Chem.*, 5 (1), 1–15.

[32] Pathak, R.K., and Mishra, P., 2016, Drugs as corrosion inhibitors: A review, *Int. J. Sci. Res.,* 5 (4), 671–677.

[33] Shamnamol, G.K., Sreelakshmi, K.P., Ajith, G., and Jacob, J.M., 2020, Effective utilization of drugs as green corrosion inhibitor-A review, *AIP Conf. Proc.*, 2225, 70006.

[34] Gece, G., 2011, Drugs: A review of promising novel corrosion inhibitors, *Corros. Sci.*, 53 (12), 3873–3898.

[35] Vaszilcsin, N., Duca, D.A., Flueraş, A., and Dan, M.L., 2019, Expired drugs as inhibitors in electrochemical processes – A mini-review, *Stud. Univ. Babes-Bolyai Chem.,* 64 (3), 17–32.

[36] Srinivasulu, A., and Kasthuri, P.K., 2017, Study of inhibition and adsorption properties of mild steel corrosion by expired pharmaceutical Gentamicin drug in hydrochloric acid media, *Orient. J. Chem.*, 33 (5), 2616–2624.

[37] Fouda, A.E.A., and El-Azaly, A.M., 2018, Expired concor drug as potential nontoxic corrosion inhibitor for 304 stainless steel in hydrochloric acid solution, *Zast. Mater.*, 59 (2), 226–236.

[38] Abeng, F.E., Anadebe, V.C., Idim, V.D., and Edim, M.M., 2020, Anti-corrosion behaviour of expired Tobramycin drug on carbon steel in acidic medium, *S. Afr. J. Chem.*, 73, 125–130.

[39] Chaudhari, L.P., and Patel, S.N., 2019, Corrosion inhibition study of expired acetazolamide on mild steel in dilute hydrochloric acid solution, *J. Bio-Tribo-Corros.*, 5 (1), 20.

[40] Abdallah, M., Fawzy, A., and Al Bahir, A., 2020, The effect of expired acyclovir and omeprazole drugs on the inhibition of sabic iron corrosion in HCl solution, *Int. J. Electrochem. Sci.*, 15, 4739–4753.

[41] Raghavendra, N., 2019, Expired amitriptyline drug as a new nontoxic inhibitor protecting mild steel corrosion in HCl solution, *Sci. Lett.*, 7 (1), 26–31.

[42] Chaudhari, L.P., and Patel, S.N., 2018, Green approach to corrosion inhibition on mild steel in acidic media by the expired sulpha drug, *Int. J. Manage. Technol. Eng.*, 8 (11), 665–678.

[43] Fouda, A.S., Ibrahim, H., Rashwaan, S., El-Hossiany, A., and Ahmed, R.M., 2018, Expired drug (pantoprazole sodium) as a corrosion inhibitor for high carbon steel in hydrochloric acid solution, *Int. J. Electrochem. Sci.*, 13, 6327–6346.

[44] Dohare, P., Chauhan, D.S., Sorour, A.A., and Quraishi, M.A., 2017, DFT and experimental studies on the inhibition potentials of expired Tramadol drug on mild steel corrosion in hydrochloric acid, *Mater. Discovery*, 9, 30–41.

[45] Singh, P., Chauhan, D.S., Srivastava, K., Srivastava, V., and Quraishi, M.A., 2017, Expired atorvastatin drug as corrosion inhibitor for mild steel in hydrochloric acid solution, *Int. J. Ind. Chem.*, 8 (4), 363–372.

[46] Dahiya, S., Saini, N., Dahiya, N., Lgaz, H., Salghi, R., Jodeh, S., and Lata, S., 2018, Corrosion inhibition activity of an expired antibacterial drug in acidic media amid elucidate DFT and MD simulations, *Port. Electrochim. Acta*, 36 (3), 213–230.

[47] Raghavendra, N., 2019, Effect of expired Oxazepam medicine on the corrosion of carbon steel in 5% NaCl solution: An experimental approach towards mitigation of dissolution process, *Front. Chem. Res.*, 1 (1), 1–4.

[48] Raghavendra, N., 2019, Use of expired Naftifine drug as corrosion inhibitor for copper in hydrochloric acid, *J. Adv. Electrochem.*, 5 (1), 177–179.

[49] Raghavendra, N., Hublikar, L.V., and Ganiger, P.J., 2019, Expired Ixabepilone as a corrosion inhibitor

on copper metal protection in 5 M HCl medium, *Int. J. Res. Chem. Sci.*, 6 (4), 1–3.

[50] Abdel Hameed, R.S., Ismail, E.A., Abu-Nawwas, A.H., and Al-Shafey, H.I., 2015, Expired voltaren drugs as corrosion inhibitor for aluminium in hydrochloric acid, *Int. J. Electrochem. Sci.*, 10, 2098–2109.

[51] Raghavendra, N., 2019, Expired lorazepam drug: A medicinal compound as green corrosion inhibitor for mild steel in hydrochloric acid system, *Chem. Afr.*, 2 (3), 463–470.

[52] Geethamani, P., and Kasthuri, P.K., 2016, The inhibitory action of expired asthalin drug on the corrosion of mild steel in acidic media: A comparative study, *J. Taiwan Inst. Chem. Eng.*, 63, 490–499.

[53] Eid, S., 2021, Expired Desloratidine drug as inhibitor for corrosion of carbon steel pipeline in hydrochloric acid solution, *Int. J. Electrochem. Sci.*, 16, 150852.

[54] Onyeachu, I.B., Abdel-Azeim, S., Chauhan, D.S., and Quraishi, M.A., 2021, Electrochemical and computational insights on the application of expired Metformin drug as a novel inhibitor for the sweet corrosion of C1018 steel, *ACS Omega*, 6 (1), 65–76.

[55] Abdel Hameed, R.S., Ismail, E.A., Al-Shafey, H.I., and Abbas, M.A., 2020, Expired Indomethacin therapeutics as corrosion inhibitors for carbon steel in 1.0 M hydrochloric acid media, *J. Bio- Tribo-Corros.*, 6 (4), 114.

[56] Al-Shafey, H.I., Abdel Hameed, R.S., Ali, F.A., Aboul-Magd, A.E.A.S., and Salah, M., 2014, Effect of expired drugs as corrosion inhibitors for carbon steel in 1 M HCL solution, *Int. J. Pharm. Sci. Rev. Res.*, 27 (1), 146–152.

[57] Abdel Hameed, R.S., 2011, Ranitidine drugs as non-toxic corrosion inhibitors for mild steel in hydrochloric acid medium, *Port. Electrochim. Acta*, 29 (4), 273–285.

[58] Dohare, P., Chauhan, D.S., and Quraishi, M.A., 2018, Expired podocip drug as potential corrosion inhibitor for carbon steel in acid chloride solution, *Int. J. Corros. Scale Inhib.*, 7 (1), 25–37.

[59] Geethamani, P., Kasthuri, P., and and Aejitha, A., 2014, A new pharmaceutically expired drug acts as corrosion inhibitor for mild steel in acid medium, *Elixir Corros. Dye*, 76, 28406–28410.

[60] Nathiya, R.S., Perumal, S., Murugesan, V., and Raj, V., 2018, Expired drugs: Environmentally safe inhibitors for aluminium corrosion in 1 M $H_2SO_4$, *J. Bio- Tribo-Corros.*, 4 (1), 4.

[61] Gupta, N.K., Gopal, C.S.A., Srivastava, V., and Quraishi, M.A., 2017, Application of expired drugs in corrosion inhibition of mild steel, *Int. J. Pharm. Chem. Anal.*, 4 (1), 8–12.

[62] Rout, T.K., 2007, Electrochemical impedance spectroscopy study on multi-layered coated steel sheets, *Corros. Sci.*, 49 (2), 794–817.

[63] Berdimurodov, E., Akbarov, K., and Kholikov, A., 2019, Electrochemical frequency modulation and reactivation investigation of thioglycolurils in strong acid medium, *Adv. Mater. Res.*, 1154, 122–128.

[64] Nagalakshmi, R., Nagarajan, L., Rathish, R., Prabha, S., Vijaya, N., Jeyasundari, J., and Rajendran, S., 2014, Corrosion resistance of SS316l in artificial urine in presence ff D-glucose, *Int. J. Nano Corros. Sci. Eng.*, 1, 39–49.

[65] Huang, H., Yao, Q., Jiao, Q., Liu, B., and Chen, H., 2019, Polyepoxysuccinic acid with hyper-branched structure as an environmentally friendly scale inhibitor and its scale inhibition mechanism, *J. Saudi Chem. Soc.*, 23 (1), 61–74.

[66] Abdel Hameed, R.S., AlShafey, H.I., and Abu-Nawwas, A.H., 2014, 2-(2, 6-Dichloranilino) phenyl acetic acid drugs as eco-friendly corrosion inhibitors for mild steel in 1 M HCl, *Int. J. Electrochem. Sci.,* 9, 6006–6019.

[67] Fouda, A.S., El Morsi, M.A., and El Mogy, T., 2017, Studies on the inhibition of carbon steel corrosion in hydrochloric acid solution by expired Carvedilol drug, *Green Chem. Lett. Rev.*, 10 (4), 336–345.

[68] Raghavendra, N., 2018, The corrosion inhibition study of expired Doxercalciferol drug as nontoxic inhibitor for mild steel (MS) in 3 M HCl medium, *J. Chem. Pharm. Res.*, 10 (12), 1–6.

[69] Raghavendra, N., 2018, Expired Fluoxymesterone

drug as sustainable corrosion inhibitor for mild steel (MS) in 3 M HCl solution: Experimental investigations towards mitigation of metal dissolution, *Int. J. Chem. Mater. Res.*, 6 (1), 1–7.

[70] Fadila, B., Sihem, A., Sameh, A., and Kardas, G., 2019, A study on the inhibition effect of expired amoxicillin on mild steel corrosion in 1 N HCl, *Mater. Res. Express*, 6 (4), 46419.

[71] Singh, A.K., Chugh, B., Saha, S.K., Banerjee, P., Ebenso, E.E., Thakur, S., and Pani, B., 2019, Evaluation of anti-corrosion performance of an expired semi synthetic antibiotic cefdinir for mild steel in 1 M HCl medium: An experimental and theoretical study, *Results Phys.*, 14, 102383.

[72] Anaee, R.A., Tomi, I.H.R., Abdulmajeed, M.H., Naser, S.A., and Kathem, M.M., 2019, Expired Etoricoxib as a corrosion inhibitor for steel in acidic solution, *J. Mol. Liq.*, 279, 594–602.

[73] Abdallah, M., Fawzy, A., and Al Bahir, A., 2020, Expired amoxicillin and cefuroxime drugs as efficient anticorrosives for Sabic iron in 1.0 M hydrochloric acid solution, *Chem. Eng. Commun.*, 0 (0), 1–28.

[74] Anaee, R.A., Abd Al-Majeed, M.H., Naser, S.A., Kathem, M.M., and Ahmed, O.A., 2019, Antibacterial inhibitor as an expired metoclopramide in 0.5 M phosphoric acid, *Al-Khwarizmi Eng. J.*, 15 (1), 71–81.

[75] Raghavendra, N., Hublikar, L.V., Patil, S.M., Ganiger, P.J., Bhinge, A.S., and Chitnis, S., 2019, Corrosion protection of expired Perindopril and expired Alprazolam drug in carbon steel in the 3% NaCl solution, *Int. J. Pharm. Biol. Sci.*, 9 (3), 838–842.

[76] Quraishi, M.A., and Rawat, J., 2000, Corrosion inhibition of mild steel in acid solutions by tetramethyl-dithia-octaazacyclotetradeca hexaene (MTAT), *Anti-Corros. Methods Mater.*, 47 (5), 288–293.

[77] Jamil, H.E., Shriri, A., Boulif, R., Montemor, M., and Ferreira, M., 2005, Corrosion behaviour of reinforcing steel exposed to an amino alcohol based corrosion inhibitor, *Cem. Concr. Compos.*, 27 (6), 671–678.

[78] Yoo, S.H., Kim, Y.W., Chung, K., Baik, S.Y., and Kim, J.S., 2012, Synthesis and corrosion inhibition behavior of imidazoline derivatives based on vegetable oil, *Corros. Sci.*, 59, 42–54.

[79] Kasshanna, S., and Rostron, P., 2017, Novel synthesis and characterization of vegetable oil derived corrosion inhibitors, *J. Mater. Environ. Sci.*, 8 (12), 4292–4300.

[80] Weng, C.J., Peng, C.W., Chang, C.H., Chang, Y.H., and Yeh, J.M., 2012, Corrosion resistance conferred by superhydrophobic fluorinated polyacrylate–silica composite coatings on cold-rolled steel, *J. Appl. Polym. Sci.*, 126 (S2), E48–E55.

[81] Liu, F.G., Du, M., Zhang, J., and Qiu, M., 2009, Electrochemical behavior of Q235 steel in saltwater saturated with carbon dioxide based on new imidazoline derivative inhibitor, *Corros. Sci.*, 51 (1), 102–109.

[82] Tang, Z., 2019, A review of corrosion inhibitors for rust preventative fluids, *Curr. Opin. Solid State Mater. Sci.*, 23 (4), 100759.

[83] Gupta, R.K., Malviya, M., Ansari, K.R., Lgaz, H., Chauhan, D.S., and Quraishi, M.A., 2019, Functionalized graphene oxide as a new generation corrosion inhibitor for industrial pickling process: DFT and experimental approach, *Mater. Chem. Phys.*, 236, 121727.

[84] Barmatov, E., Hughes, T., and Nagl, M., 2015, Efficiency of film-forming corrosion inhibitors in strong hydrochloric acid under laminar and turbulent flow conditions, *Corros. Sci.*, 92, 85–94.

[85] Kahyarian, A., and Nesic, S., 2019, A new narrative for $CO_2$ corrosion of mild steel, *J. Electrochem. Soc.*, 166 (11), C3048–C3063.

[86] Lee, H.S., Saraswathy, V., Kwon, S.J., and Karthick, S., 2018, "Corrosion Inhibitors for Reinforced Concrete: A Review" in *Corrosion Inhibitors, Principles and Recent Applications*, Eds. Aliofkhazraei, M., IntechOpen, London, UK.

[87] Shukla, S.K., and Quraishi, M.A., 2009, Cefotaxime sodium: A new and efficient corrosion inhibitor for mild steel in hydrochloric acid solution, *Corros. Sci.*, 51 (5), 1007–1011.

[88] Singh, A.K., and Quraishi, M.A., 2010, Effect of Cefazolin on the corrosion of mild steel in HCl solution, *Corros. Sci.*, 52 (1), 152–160.

[89] Subekti, N., Soedarsono, J.W., Riastuti, R., and Sianipar, F.D., 2020, Development of environmental friendly corrosion inhibitor from the extract of areca flower for mild steel in acidic media, *East.-Eur. J. Enterp. Technol.*, 2 (6 (104)), 34–45.

[90] Loto, R.T., Loto, C.A., Joseph, O., and Olanrewaju, G., 2016, Adsorption and corrosion inhibition properties of thiocarbanilide on the electrochemical behavior of high carbon steel in dilute acid solutions, *Results Phys.*, 6, 305–314.

[91] Saadi, R., Saadi, Z., Fazaeli, R., and Fard, N.E., 2015, Monolayer and multilayer adsorption isotherm models for sorption from aqueous media, *Korean J. Chem. Eng.*, 32 (5), 787–799.

[92] Langmuir, I., 1916, The Constitution and fundamental properties of solids and liquids. Part I. Solids, *J. Am. Chem. Soc.*, 38 (11), 2221–2295.