



Corrosion inhibitors for acid cleaning of desalination heat exchangers: Progress, challenges and future perspectives

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ABSTRACT

Heat exchangers represent vital equipment for the production and heat recovery in thermal desalination processes. However, with operation under scale control practices, scale growth reduces the performance and efficiency. To restore this performance, acid cleaning is the most adopted and efficient descaling method. Usually, strong mineral acids are used for acid cleaning and corrosion inhibitor addition represents a necessity to protect the underlying metal. Development of cost-effective and low toxic corrosion inhibitors for acid cleaning purpose has, therefore, becomes an essential area of research. In the present work, acid cleaning corrosion inhibitors research and development efforts reported in scientific publications and patent inventions over the last thirty years is reviewed. The review strictly considers works directly related to acid cleaning (descaling) publications rather than the usual acid corrosion inhibition of metals. Critical knowledge gaps are identified and future research perspectives are highlighted.

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1. Introduction

During operation, inorganic deposits mixed with corrosion products are usually formed on the surfaces of industrial heat exchanger tubes. These deposits reduce the efficiency of heat transfer and fluid–flow mass [1]. Also, these deposits induce under deposit corrosion attack

and eventually endanger the lifespan of the equipment [2,3]. Consequently, operation costs in these industries are increased and plant shutdown becomes necessary to frequently conduct descaling operation by acid cleaning.

The industrial practice of acid cleaning originally emanated from the desire to develop a technology for improving fluid recovery from oil wells [2]. Acid cleaning involves the use of highly reactive acids such as hydrochloric acid (HCl), sulfuric acid (H₂SO₄), citric acid (C₆H₈O₇), sulfamic acid (NH₂SO₃), or even complexing agents like Ethylene-

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Diamine-Tetra-Acetic (EDTA) acid to dissolve surface deposits and scales [4]. It is reported that acid cleaning with HCl solution had been practiced prior to 1930 and, by 1941, HCl constituted the major component of acid cleaning solutions deployed for utility boilers [2,5]. However, industrial acid cleaning processes simultaneously inflict serious corrosion attack on the underlying metal substrate in the absence of a suitable corrosion inhibitor in the cleaning solution.

Unsaturated organic compounds containing electronegative elements such as oxygen, nitrogen, and sulfur are the primary active components of acid cleaning corrosion inhibitors. The free, unbound electrons in the unsaturated bonds and lone pair electrons on the electronegative atoms serve as interaction sites between inhibitor molecules and the surface metal atoms. The interaction facilitates the formation of a hydrophobic film, which isolates the metal surface from attack by the acid solution [6–12].

The first corrosion inhibitor formulation developed for industrial acid cleaning was patented by Grebe in 1935 and involved the use of environmentally benign chemistries based on gelatin, saponin, gum Arabic and licorice [13]. Over the years, many more chemistries have been investigated, and the advancement in the technology of acid cleaning corrosion inhibitors is evident in the several books written [14,15], and review works [2,16,17] published on the topic.

Frenier [2] presented a review of the advancements in acid cleaning technology between 1978 and 1998. A critical part of the review involved understanding the chemical basis of acid cleaning process and the chemistry of corrosion inhibitors reported for acid cleaning during the review period. More so, the authors identified acid cleaning inhibitor chemistries/formulations which transformed from scientific publications and patent discoveries to becoming commercialized products for industrial applications. Nevertheless, the review focused strictly on the cleaning technology for iron and steel-based industrial equipment. Since the review by Frenier [2], no review on acid cleaning corrosion inhibitors is visible in the literature. The recent reviews by Goyala et al. [16] and Singh and Quraishi [17] are related, respectively, to acidizing condition (which is a more aggressive condition than acid cleaning) and general acid corrosion (because it is strongly devoid of citations specifically related to acid cleaning publications).

In the present review, we surveyed thirty years of the development of acid cleaning corrosion inhibitors between 1989 and 2019. Rather than the usual inhibition studies of acid corrosion of metals, this review is based strictly on scientific publications and patent inventions of corrosion inhibitors for acid cleaning. A summary of toxicity properties and inhibition performance of reported inhibitor chemistries is presented from the perspective of heat exchangers acid cleaning. A special focus is made on the acid cleaning in Multi-stage flash (MSF) desalination plants. Furthermore, existing knowledge gaps are identified, and future research perspectives are highlighted.

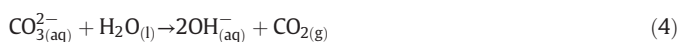
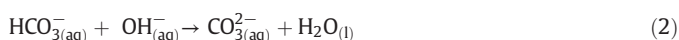
2. Multistage flash (MSF) desalination process and acid cleaning

About 97% of the earth's water is saline water contained in the vast oceans and seas distributed all over the world. The remaining 3% is freshwater, out of which only 0.0067% can be used directly [18]. With desalination technology, the abundant ocean/seawater can be converted into freshwater for both domestic and industrial applications. The first industrial-scale desalination plants operated based on the thermal distillation technique. The technology involves the application of thermal energy to vaporize the pure water part of a seawater feed [19]. Its merits include operation simplicity, greater reliability, and the ability to generate high water production capacity [20,21]. The multi-stage flash (MSF) thermal desalination, Fig. 1, accounts for 34% of the world seawater desalination capacity [22,23]. Its operation has been described elsewhere [24–27].

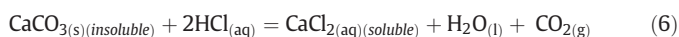
Materials for the construction of the MSF desalination plant are selected according to the characteristics of the unit. For instance, efficient heat transfer and excellent corrosion resistance are properties of

commercial titanium (ASTM B338–2) and cupronickel alloys, such as (90Cu–10Ni), (70Cu–30Ni) and (66Cu–30Ni),¹ which make them useful for heat rejection and condenser units, respectively, [26,28,29]. More so, the cupronickel alloys with higher content of nickel can be used for MSF units which operate at higher temperatures, typically between 70 °C and 112 °C. On the other hand, steel-based materials find importance in units like the evaporator bottom and shell where strength is a priority.

Continuous operation of the MSF desalination plant leads to the deposition of two very important alkaline scales; namely, calcium carbonate (CaCO₃) and magnesium hydroxide (Mg(OH)₂), on the heat exchanger tubes [30]. The chemistry involves the thermal decomposition of soluble calcium bicarbonate in the seawater to precipitate CaCO₃, which could further react with water to release CO₂ and hydroxyl (OH[−]) ions. The released hydroxyl ions react with Mg²⁺ ions in solution to eventually precipitate Mg(OH)₂ scale [31,32]. The MSF operating conditions, like temperature and pH, influence the rate of scaling and the crystallographic properties of the CaCO₃ and Mg(OH)₂ scales formed [33–37]. Eqs (1)–(5) describe the scale formation process.



Fundamentally, acid cleaning involves the use of inorganic or organic acids to convert the insoluble scales into soluble products which can be easily flushed during the cleaning process. For this purpose, it is important to select acid solutions which can furnish anions that react with the cations in the scale to form soluble products. Eqs (6) and (7) show the use of HCl for the acid cleaning of CaCO₃ and Mg(OH)₂ scales. Table 1 presents a list of common industrial deposits and scales and some corresponding acids currently used for their cleaning.



Hydrochloric acid (HCl) is, by far, the most utilized acid for acid cleaning because of its high descaling performance [38]. HCl can be employed at concentrations between 2% and 5% and it is very suitable for the cleaning of deposits containing carbonates, phosphates, sulfates, and iron oxides [39]. Malik et al. [40] showed that, depending on the chemistry of the scale, HCl was the most efficient for the removal of CaCO₃ scale while H₂SO₄ was the most efficient for Mg(OH)₂ scale. Phosphoric acid has also been suggested as an effective solvent for the cleaning of seawater cooling heat exchangers used in the shipping industry [41,42]. On the other hand, Garcia [43] reported a formulation containing HCl, HF, citric acid, oxalic acid and an amine (such as hexamethylenetetramine) suitable for chemical cleaning with minimal corrosion attack on the substrate.

3. New generation inhibitors for acid cleaning

Usually, corrosion inhibitor formulation includes the active ingredient, the inhibitor aids (salts), the surfactant (which promotes dispersion in the media), and solvent. With environmental restrictions and cost competitiveness criteria, corrosion inhibitor formulators are faced with severe

¹ Called modified 70Cu30Ni.

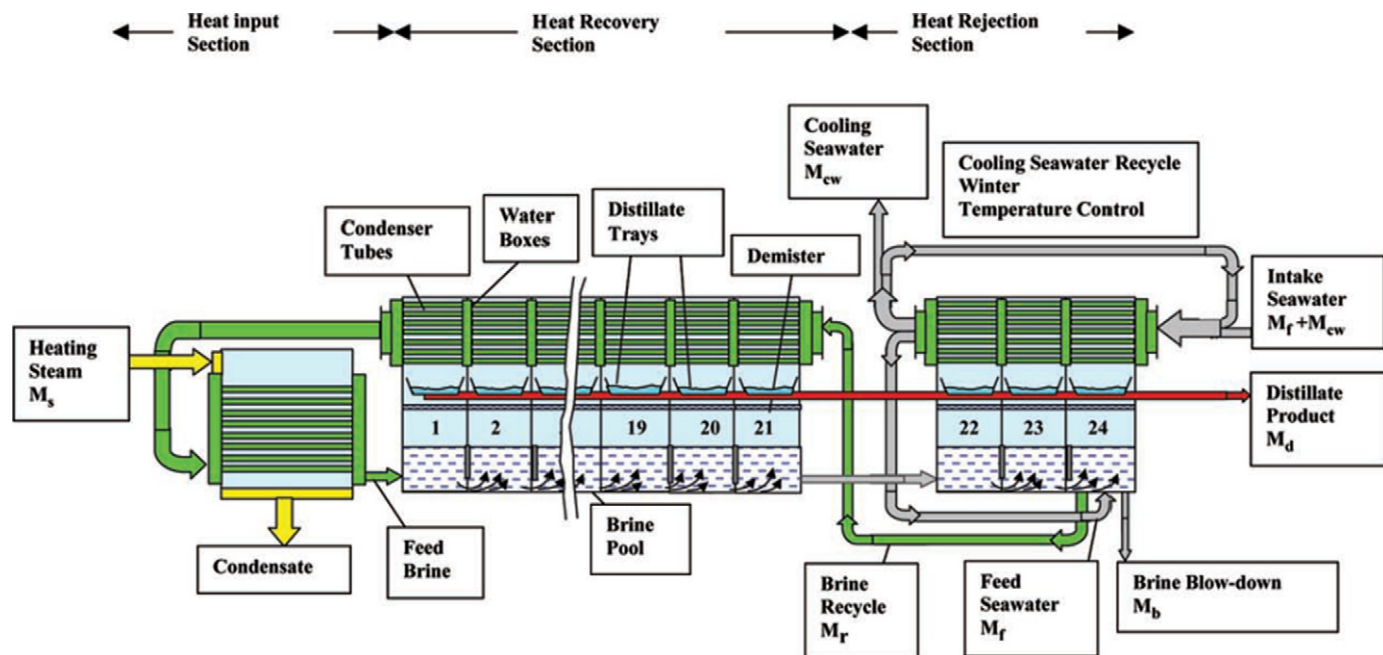


Fig. 1. Schematic representation of a multi stage flash (MSF) distillation plant [24].

challenges. Important environmental considerations include the partition coefficient and biodegradability of the active ingredient in the formulation. The minimum requirement for each of these physicochemical criteria has been stipulated by the Paris commission (PARCOM) regulation [44] and the Globally Harmonized System (GHS) of chemical classification [45,46]. According to the requirements, a corrosion inhibitor can be regarded as environmentally safe if it exhibits a biodegradability greater than 70% in 28 days, has lethal dosage (LD_{50}) value greater than 10 mg/L, and has bioaccumulation ($\log P_{o/w}$) value less than 3. In the following sections, we will critically assess scientific and patent literatures and progress made towards the development of effective and less hazardous corrosion inhibitors for acid cleaning application for alloys commonly employed in the heat exchangers of water desalination plants.

3.1. Scientific literature

Fig. 2a shows the number of scientific publications related to acid cleaning corrosion inhibitors between 1989 and April 2019. The details

were derived from the *google.com* and *onpetro.org* search engines using the search key–phrase “Corrosion Inhibitors for Acid Cleaning”. Analysis of the figure indicates a scarcity of scientific publications in this regard. This may imply that the majority of corrosion inhibitors developed for acid cleaning purpose are rather patented than presented as scientific publications. From the pie chart in Fig. 2b, the spread of chemistries that have been applied as acid cleaning corrosion inhibitors reveals the dominance of nitrogen–based organic compounds. This may not be unconnected to their high propensity to become protonated in the acid solutions used for cleaning. Such protonation enhances their adsorption and protective coverage of the metallic material. Nevertheless, a reasonable percentage of chemistries identified as “others” are formulations which have no specific information about their chemistry as reported by the authors. This unknown information, again, supports the notion towards greater preference for patent inventions than scientific publications regarding acid cleaning corrosion inhibitors. Corrosion inhibitors for acid cleaning, reported in scientific publications and patent inventions, will be discussed in the following sections based on the alloy types. These include typical alloys used for condenser and MSF evaporator parts.

3.1.1. Iron and its alloys

Frenier [47] developed a low toxicity corrosion inhibitor formulation containing cinnamaldehyde, quaternary nitrogen salts and a nonionic surfactant (Fig. 3) useful for acid cleaning of steel in 5% and 7.5% HCl solution under static and dynamic conditions. The formulation was aimed at replacing the commonly used carcinogenic formaldehyde–based formulations. The use of cinnamaldehyde was encouraged because of its tendency to adsorb on a steel surface to form a low molecular weight polymer with assured protection from the acid corrosion [48,49]. The acute toxicity tests conducted for the formulation on *Pimephales promelas* and *Ceriodaphnia dubia* revealed lethal dosage (LD_{50}) value greater than 500 mg/kg which confirmed the low toxicity of the proposed formulation. Under static and dynamic conditions at 65 °C, the formulation could provide corrosion resistance with up to 90% inhibition efficiency. The new formulation was highly comparable in performance with a toxic commercial inhibitor formulation based on formaldehyde. Nevertheless, it was suggested to restrict the formulation to a temperature not exceeding 49 °C when applied in hydrochloric acid with concentration up to 7.5% HCl solution.

Table 1

Current cleaning formulations for some known scales and deposits [2].

Deposit/Scale	Acid	Temperature (°F) and conditions for application
Iron oxide	5–15% HCl	150–180
	Ammonium citrate	180–275 (Under circulation)
	Sodium citrate	180–200 (Under circulation)
	Sodium HEDTA (pH 1.4)	100–150 (Under circulation)
CaCO ₃ , MgCO ₃	5–15% HCl	<150
	7–10% Sulfamic acid	<140
CaSO ₄	Tetrasodium EDTA	180–300 (Under circulation)
	1% NaOH followed by 5% HCl	100–150 (Under circulation)
	EDTA-organic acid mixture	120–150 (Under circulation)
	Tetrasodium EDTA	180–300 (Under circulation)
CaPO ₄	5–10% HCl	100–150
	7–10% Sulfamic acid	<140
	Tetrasodium EDTA	180–300 (Under circulation)
Silicates	HCl + HF	150–170
	5–10% HCl	Slow heating with mechanical scrubbing
Sulfides	5–10% HCl with aldehydes	100–160
	5–10% H ₂ SO ₄ with aldehydes	100–160

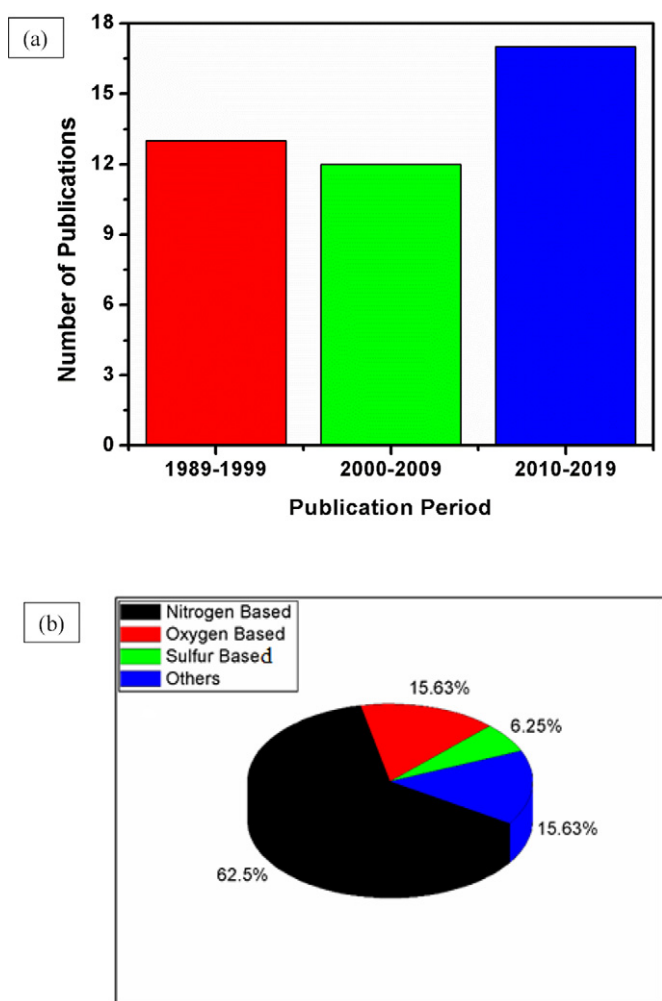


Fig. 2. Distribution of scientific publications for corrosion inhibitors for acid cleaning between 1989 and 2019 based on (a) number of publications and (b) corrosion inhibitor chemistry.

Lindert and Johnson [50] synthesized some Mannich oligomers from an optimized reaction between amines, aldehydes and ketones, and tested the products as inhibitors for acid cleaning of steel in 5% HCl. The knowledge that the polymeric inhibitors could form protective chelating structures on the steel surface was the motivation for such investigation. By adopting an optimized synthesis technique, the authors ensured that the release of residual formaldehyde from incomplete Mannich reaction was avoided to achieve environmental friendly products. Toxicity tests on water flea revealed that the inhibitor formulation exhibited moderate toxicity with the value of half-maximal effective concentration (EC_{50}) approximately 9.48 mg/L for 48 h testing. After 6 h exposure of C1008 cold rolled steel to 5% HCl solution with different inhibitor concentration at 93 °C, the authors observed that increasing the inhibitor concentration from 0.5 ml/L to 1 ml/L sharply lowered corrosion rate by 50%. The corrosion rate continuously decreased until a concentration of 2 ml/L provided corrosion inhibition efficiency above 90%. The authors also reported that the performance of the Mannich oligomers, as acid cleaning inhibitor, was more outstanding at lower temperature between 67 °C and 82 °C.

Singh and Gaur [51] reported that 0.1 wt% concentration of dibenzyl sulfoxide (DMSO) exhibited very low efficiency as an inhibitor against corrosion (corrosion rate 0.3×10^4 mdd) during the acid cleaning of low carbon, hot-rolled steel by sulfuric acid (H_2SO_4). However, the addition of copper ions (Cu^{2+}) in the form of $CuSO_4 \cdot 5H_2O$, chloride ions (Cl^-) in the form of NaCl, and thiourea, significantly increased the

efficiency of the sulfoxide. An optimum combination was achieved with 0.01% sulfoxide + 0.02% $CuSO_4$ + 0.2% NaCl. The formulation exhibited an inhibition efficiency of 81% after 1 min of addition, with an optimum of 99% observed after 10 min of addition after. The instantaneous increase in inhibition efficiency indicates that the DMSO-based formulation could be useful where higher speed acid cleaning is required. The formulation also exhibited higher efficiency as the temperature increased up to 60 °C, beyond which the inhibition efficiency began to decline. In addition, the accumulation of $FeSO_4 \cdot 7H_2O$ in the acid cleaning bath at 60 °C, as a result of the scale dissolution, initially caused a sharp decrease in efficiency after which the inhibition efficiency improved when $FeSO_4 \cdot 7H_2O$ concentration reached 10%. The inhibition efficiency of the DMSO formulation was largely attributed to the addition of $CuSO_4$ which furnished Cu^{2+} ions to reduce the sulfoxide into a protective sulfide that forestalled the dissolution of iron (Fe) atoms from the steel surface. The toxicity report of dibenzyl sulfoxide is not available in the literature and toxicity testing needs to be conducted on the molecule to ascertain its safety for humans and the environment.

The structural features of 5-[2-(4-methoxyphenyl)-vinyl]-3-phenyl isoxazole (MVI) and 5-[2-(4-methoxyphenyl)-vinyl]-1,3,8-triazacyclopenta[a]indene (MCI), Fig. 4, were utilized to comparatively study their effective corrosion inhibition for acid cleaning of mild steel in 1 M HCl and 0.5 M H_2SO_4 solutions at 30 °C and 70 °C [52]. At 30 °C, the inhibition efficiency reached a maximum of 97.57% during 6 h in HCl and 78.23% in H_2SO_4 during 3 h which reduced to 71.74% and 57.98% during 24 h in HCl and H_2SO_4 respectively for MVI. On the other hand, the efficiency for MCI attained a maximum of 98.72% during 6 h in HCl and 88.64% in H_2SO_4 during 3 h which then decreased to 71.91% and 73.05% during 24 h in HCl and H_2SO_4 respectively. Both compounds acted as mixed-type inhibitors which retarded both anodic and cathodic reactions on the steel surface. However, higher temperature lowered the performance of the azoles by favoring metal dissolution over inhibitor adsorption. Based on computational calculations,

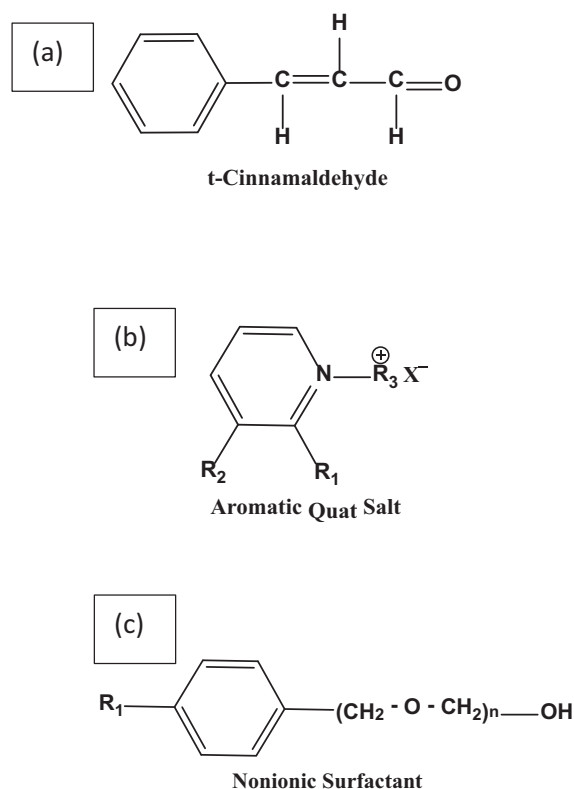


Fig. 3. Chemical components of inhibitor formulation for the cleaning of carbon steel in 5% HCl [47].

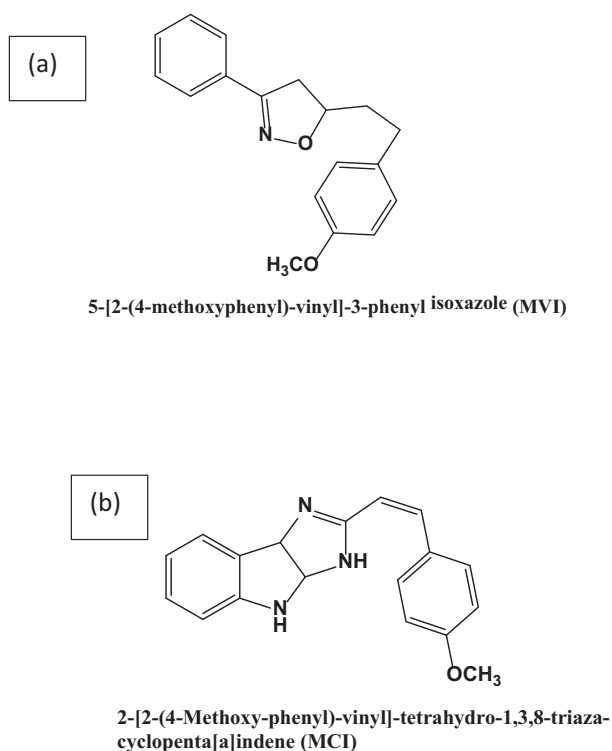


Fig. 4. (a) Isoxazole and (b) indine derivatives tested for the cleaning of carbon steel in 1 M HCl and 0.5 M H₂SO₄ [52].

some conjugation effects were observed to restrict the free rotation of C–N bonds in the imidazoline rings of both compounds. However, while this phenomenon results in a rigid planar structure in the MCI, there is loss of planarity in MVI due to the presence of a styryl substituent orienting itself perpendicularly to the isoxazole ring. Furthermore, the orbitals responsible for electron donation to the Fe atoms in the steel were saturated all over the MCI molecule unlike in the MVI where they concentrate around the heterocyclic ring. This enhances bonding between MCI and the steel surface and explains its greater inhibition efficiency than MVI for the acid cleaning of the steel surface. From a toxicity perspective, the isoxazole exhibits a lipophilicity (Log $P_{o/w}$) value of 0.08 but is, nevertheless, a highly flammable liquid. In the same vein, the triazacyclopenta[a]indene derivatives are very important constituents of drugs and can rationally be regarded as non-toxic [53].

Al Sarawy et al. [54] were among the few authors that studied the inhibition efficiency and mechanism of four thiazole derivatives (–1,3-thiazolidin-5-one based) on carbon steel in 2 M HCl acid in the presence of cations representative of MSF acid cleaning environment including Cu²⁺, Ni²⁺, Co²⁺ and Ca²⁺. The authors considered inhibitor chemistry, concentration, temperature and synergy with medium cations. The presence and position of a methoxy group attached to the aromatic ring was significant in determining the inhibition efficiency of the thiazole derivatives. The thiazole derivative with a *para*-methoxy group provided the highest inhibition efficiency and the absence of a methoxy group conferred the least performance on the thiazole. Relative to other substituents, the position of the methoxy group at the *para*-position provided higher resonance effect and the least free energy for adsorption of the inhibitor on the steel surface. Divalent cations of Cu, Ni and Co significantly enhanced the inhibition efficiency of the thiazoles, through the formation of stable complexes between the thiazole derivatives and the chloride salts of the metals. The adsorption of these complexes on the steel surface significantly lower the charge transfer processes due to the acid attack. Unfortunately, duration of the

corrosion tests was limited to 4 h and under static conditions which is not representative of MSF acid cleaning conditions.

A commercial formulation containing some keto–amines, isopropyl alcohol and propargyl alcohol was tested for carbon steel A516 Grade 2 and stainless steel 304 L in 5% HCl acid at temperatures between 25 °C and 93 °C [55]. At room temperature, an optimum concentration of 2 vol% of the formulation achieved a corrosion inhibition efficiency of 90% and 87.5% on carbon steel and stainless steel respectively. Although the corrosion rate of the inhibited alloys increased with temperature, the formulation completely failed to protect carbon steel at temperature up to 93 °C. However, the formulation minimized the susceptibility of the stainless steel to the localized pitting and crevice corrosion which occurred at the points of welds within the matrix of the alloy. Unfortunately, this formulation contains propargyl alcohol which currently faces stringent environmental regulations and is definitely not a green inhibitor for acid cleaning purpose. We recall that a chemical can be considered as “green” if it meets three conditions including non-toxicity, non-bioaccumulation and biodegradation [44–46,56].

Markhali et al. [57] used electrochemical techniques including EIS, ECN and polarization curves to characterize the corrosion inhibition of benzotriazole and benzothiazole on austenitic 316L stainless steel in aerated 1 mol/L HCl solution at 25 °C. The three electrochemical techniques agree that both inhibitors showed anodic inhibition behavior with high efficiency. However, the inhibitor performance was assessed for a duration limited to 4 h which is very low in the context of MSF acid cleaning. Although the 1977 report of the United State Environmental Protection Agency (EPA) categorizes benzotriazoles as low-toxicity chemicals with low health hazards to human [58], they have the tendency to induce morphological changes in a variety of plants [59] and toxic effect on the aquatic environment [60]. On the other hand, the metabolism of benzothiazole involves a ring–opening mechanism which leads to the formation of hydroxylamines as metabolites with mutagenic and carcinogenic potentials [61].

Recently, Deyab [62] investigated the corrosion inhibition performance of cationic surfactant benzethonium chloride on 316L stainless steel in 1 M H₂SO₄ solution. Based on weight loss and electrochemical tests, the author concluded that the optimum performance was achieved around the critical micelle concentration (CMC) which was approximately 2.9×10^{-4} M in the 1 M H₂SO₄ solution. The author concluded that the lower inhibition efficiency displayed by the inhibitor at concentration below the CMC was due to an incomplete coverage of the stainless steel surface while at concentration greater than the CMC, the stainless steel became effectively covered by one monolayer of the inhibitor which did not, however, significantly increase the performance of the inhibitor observed at the CMC. The benzethonium chloride could become protonated in the acid solution such that the electron density for interaction with the stainless steel surface was concentrated around the quaternary nitrogen group. Consequently, the benzethonium chloride acted as an anodic inhibitor and increased the tendency of stainless steel towards passivation. However, the sulfuric acid was not added to seawater representative medium which play an important role on both corrosion risk and CMC of the inhibitor. In addition, it is well established that stainless steel corrosion inhibition should be investigated in terms of localized corrosion (pitting) inhibition. This aspect was totally ignored by the author. From a toxicity perspective, benzethonium chloride is well-known for its broad spectrum antimicrobial property. It has a solubility value of 44.8 g/L and log $P_{o/w}$ value of 1.08 at 20 °C [63]. However, its toxicity has not been reported.

Jaralla and Al-Darbi [64] reported a highly effective industrial cleaning solution capable of cleaning effectively with minimal corrosion attack on the substrate. The formulation was composed of one or more chelating agents, a surfactant, a complexing agent, and a nontoxic acridine orange inhibitor. The acridine orange inhibitor (Fig. 5) functioned to block the anodic and cathodic sites on the steel surfaces of the process equipment and can be regarded as the active chemistry in the formulation. The merits of the acridine include a high tendency for protonation

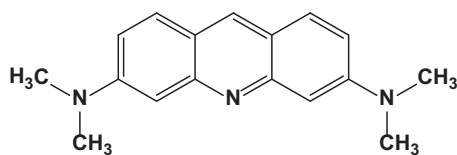
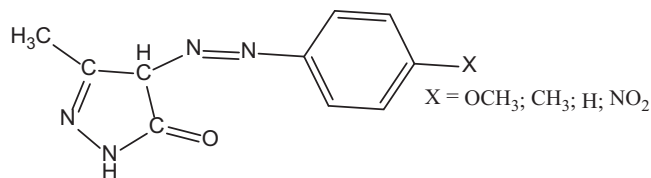


Fig. 5. Molecular structure of acridine orange used for acid cleaning of steel in 5% HCl [64].

and strong binding to metal surfaces. The acridine interaction, with a metal surface, is enhanced by a mixture of 2% citric acid and EDTA, each, which functions as a complexing agent during the cleaning. The formulation containing 80 ppm of acridine orange was able to bring about corrosion inhibition efficiency of 92% under 1000 rpm rotation speed in 5% HCl solution at 50 °C. Table 2 provides a summary of reported acid cleaning corrosion inhibitors for Fe-based alloys.

Some derivatives of the pyrazolone (Fig. 6) were tested as corrosion inhibitors for carbon steel in 2 M HCl acid cleaning solution using weight loss and polarization methods [65]. The inhibitor interaction with the steel surface using their nitrogen and oxygen atoms enabled effective adsorption that retarded the acid corrosion. Inhibition efficiencies ranging from 60 to 78% were obtained after the corrosion measurements. Inhibition efficiency increased with the presence of electron donating groups attached to the para-position of an aromatic ring in the inhibitor moiety. Due to positive inductive effect and enhancement in the



4-phenylazo-3-methyl-2-pyrazolon-5-one derivatives

Fig. 6. Pyrazolone derivatives as corrosion inhibitors for carbon steel in 2 M HCl solution [65].

delocalization of pi-electrons on the molecule, the attachment of a methoxy group provided the highest efficiency while a NO₂ attachment provided the least efficiency. The least inhibition efficiency in the presence of the NO₂ group was attributed to the higher hydrophilic property and tendency to be reduced in the acid solution. Furthermore, the pyrazolones interacted via physical adsorption since their efficiency diminished with increase in temperature. The inhibition efficiency was enhanced by the addition of some potassium salts like KI, KBr and KSCN as synergists. The anions from these salts enhanced inhibitor adsorption by chemically adsorbing on the steel surface to provide more stabilized inhibitor adsorption with greater surface coverage. As synergists, the potassium salts performed according to the increasing order of magnitude: KBr < KSCN < KI. As significant components of analgesic and

Table 2

Summary of reported acid cleaning corrosion inhibitors for Fe-based alloys.

Corrosion Inhibitor	Alloy	Experimental conditions	Maximum Protection	Ref.
Cinnamaldehyde + quat. Nitrogen salt	Steel	–Test Solution: HCl, 65 °C –Inhibitor concentration: 5%, 7.5%. –Technique: Static & Dynamic	% IE = 90%	[47]
2-mercaptobenzazole derivatives	Iron	–Test Solution: Tannic Acid, 25 °C –Inhibitor concentration: 1 mM –Technique: Static	% IE = 93%	[48]
Benzamide	Steel	–Test Solution: H ₂ SO ₄ , 25 °C –Inhibitor concentration: 1000 ppm –Technique: Static	% IE = 90%	[49]
Mannich Base	Steel	–Test Solution: HCl, 65–93 °C –Inhibitor concentration: 4 ml/L –Technique: Static	% IE = 90%	[50]
Dibenzyl sulfoxide + 0.02% Cu ²⁺ + 0.2% Cl [–]	Steel	–Test Solution: H ₂ SO ₄ , 60 °C –Inhibitor concentration: 0.01% –Technique: Static	% IE = 92%	[51]
(1) Isoxazole (2) Indene	Steel	–Test Solution: HCl, H ₂ SO ₄ , 30 °C –Inhibitor concentration: 250 ppm. –Technique: Static	(1) % IE = 97.57% (2) % IE = 98.72%	[52]
Thiazole	Steel	–Test Solution: HCl, 30 °C –Inhibitor concentration: 21 μM ppm. –Technique: Static	% IE = 64%	[54]
Keto-amines + Isopropyl alcohol + Propargyl alcohol	Steel Stainless- Steel	–Test Solution: HCl, 25 °C –Inhibitor concentration: 2 %vol –Technique: Static.	Steel: % IE = 87.5% Stainless steel: % IE = 90%	[55]
(1) Benzotriazole (2) Benzothiazole	Steel	–Test Solution: HCl, 25 °C –Inhibitor concentration: (1) 300 ppm; (2) 400 ppm –Technique: Static.	(1) % IE = 90% (2) % IE = 94%	[57]
Benzethonium chloride	Steel	–Test Solution: HCl, 25 °C –Inhibitor concentration: 0.35 mM –Technique: Static.	% IE = 92.3%	[62]
Acridine orange	Steel	–Test Solution: HCl, 25 °C –Inhibitor concentration: 80 ppm –Technique: Dynamic.	% IE = 92%	[64]
Pyrazolone	Steel	–Test Solution: HCl, 25 °C –Inhibitor concentration: 11 μM –Technique: Static.	% IE = 78%	[65]
Polysaccharide derivatives		–Test Solution: HCl, 60 °C –Inhibitor concentration: 1000 ppm –Technique: Static.	% IE = 84%	[68]
Crown ethers	Steel Stainless- Steel	–Test Solution: HCl, 60 °C –Inhibitor concentration: 0.11 μM –Technique: Static.	% IE = 82%	[71]

%IE = inhibition efficiency.

anti-inflammatory drugs, pyrazolones have diverse pharmacological and biological properties. Some pyrazolones have LD₅₀ values as high as 1915 mg/kg and log P_{o/w} value greater than 2 [66], making them safe chemicals for use as corrosion inhibitors. However, pyrazolone intoxication was reported to account for 52% of mild analgesic poisoning which led to impaired consciousness that culminated into coma and convulsions [67].

Acid cleaning corrosion inhibitors have also been derived from natural plants. Some quaternary ammonium salts derived from corn stalk polysaccharides were tested for as inhibitors for the acid corrosion of carbon steel in 1 M HCl solution [68]. The synthesis involves the use of readily available and cost effective starting materials such as imidazole and pyridine. The inhibitors adsorb chemically using the nitrogen and oxygen heteroatoms in the molecule and their inhibition efficiency increased with temperature such that 1000 ppm inhibitor concentration could provide efficiency up to 84% at 60 °C. Imidazole-containing derivatives provided the most efficient corrosion inhibition. Obviously, these acid corrosion inhibitors can be adjudged as safe, given the natural source of the polysaccharides and the low toxicity properties of the modifying agents (imidazole and pyridine) [69,70].

Some crown ethers have also been applied as corrosion inhibitors for Fe alloys like 430 stainless steel in 2 M HCl solution [71]. The large cyclic ring structure of these oxygen-based molecules enables them to adsorb strongly and efficiently on the alloy surface, wherein they block both cathodic and anodic reactions and behave like mixed-type corrosion inhibitors. Although the stainless steel could form some protective chromium oxide on its surface, the alloy was still susceptible to localized corrosion in the blank acid solution but could be covered effectively with an inhibitor film which provided significant protection. Larger molecular size with more benzene rings in the crown ether enhance the surface coverage on the substrates and provide higher corrosion inhibition efficiency because of increase in the number of oxygen heteroatoms. Thus, a dibenzo-24-crown-8 delivered corrosion inhibition efficiency approximately 82% while a dibenzo-18-crown-6 provided

inhibition efficiency of 63% in the presence of 11×10^{-7} M inhibitor concentration. Not much is known about the biological activity of crown ethers. However, one report on acute oral toxicity studies showed that 18-crown-6 caused central nervous system effects [72]. In other reports, however, LD₅₀ values for 12-crown-4, 15-crown-5 and even 18-crown-6 were greater than 500 mg/kg, although increasing ring size decreased the solubility of the crown ethers [73].

3.1.2. Copper

The efficiency of some imidazole derivatives as corrosion inhibitors for the acid cleaning of copper in 1 M HCl and 1 M H₂SO₄ acids was reported by Stupnisek-Lisac et al. [74]. The chemistry of the imidazoles can be seen in Fig. 7. At 0.01 M inhibitor concentration, the 4-methyl imidazole provided the best protection for the copper with an inhibition efficiency of 89.6% whereas the least protection was provided by 4-methyl-5-imidazolecarbaldehyde. In fact, the corrosion current density measured from polarization determination concluded that the 4-methyl-5-imidazolecarbaldehyde accelerated the corrosion of the copper, causing the metal to corrode even more than in the absence of a cleaning inhibitor. The remarkable performance of the 4-methyl imidazole, relative to other derivatives with larger substituents, was attributed to a negative effect of steric hindrance on the larger molecules. The imidazole actives performed better in HCl than in H₂SO₄ solution. The formidable protection provided for the copper by the imidazoles was linked with the tendency for the copper-imidazole interaction to form the relatively insoluble di-imidazolato copper complex. Synergistic interaction between the protonated imidazole and chloride ions was responsible for the higher efficiency displayed in HCl than in H₂SO₄ solution. In addition to an oral toxicity (LD₅₀) value of 970 mg/kg (for rat), a GHS classification of 4 and a Log P_{o/w} value of -0.02 [75], the imidazole derivatives also exhibited low toxicity based on the analysis of chemical oxygen demand and bacterial growth of the effluent water collected after the cleaning process.

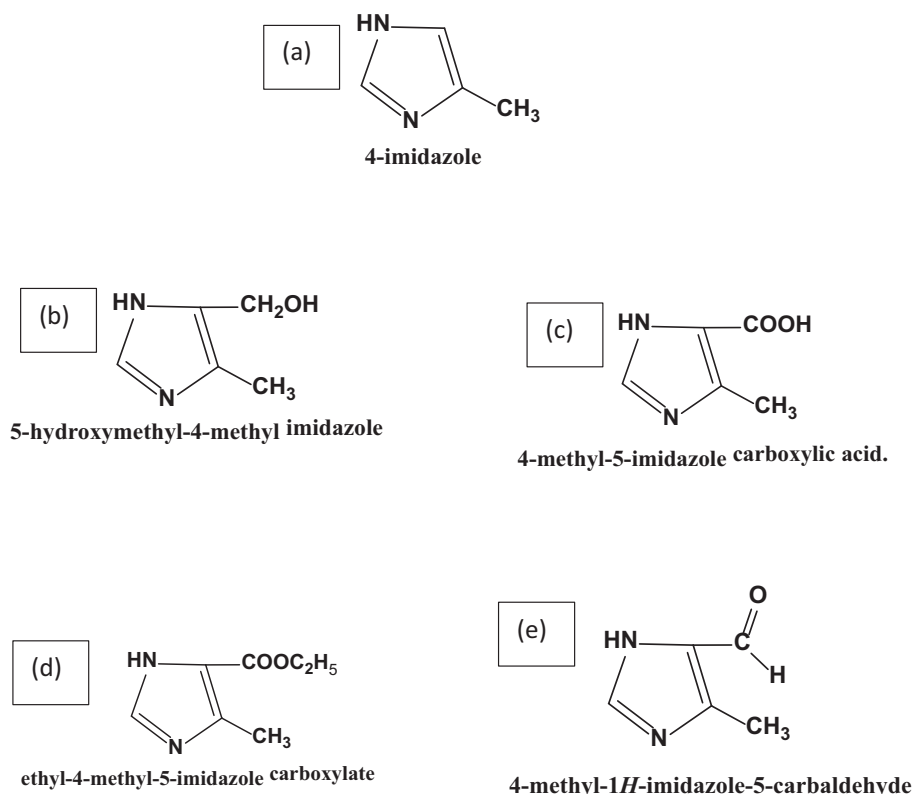


Fig. 7. Imidazole derivatives for cleaning of copper in 1 M HCl and 1 M H₂SO₄ solutions [74].

Some fuchsin base (Fig. 8a) and fuchsin acid (Fig. 8b) were tested as new inhibitors for the acid cleaning of copper in HCl solution [76]. The fuchsin molecules were targeted as candidate replacements for the benzotriazole, which is a heavily used inhibitor for the acid cleaning of copper in the industry but has been marked for its toxicity. By testing twelve different fuchsin bases and fuchsin acids at temperatures between 298 K and 328 K, in comparison with benzotriazole, the fuchsin acids were observed to perform approximately as the commercial benzotriazole which, in turn, performed better than the fuchsin bases for the range of concentration investigated. The authors deduced that at low inhibitor concentrations, an increase in the inhibitor concentration did not produce any significant increase in surface coverage of the copper metal. At intermediate inhibitor concentrations, a small increase in the inhibitor concentration caused a high surface coverage, while at high inhibitor concentrations, the surface coverage was independent of the inhibitor concentration. The inhibition mechanism involved the formation of $\text{Cu}(\text{inhibitor})_{\text{ads}}$ species adsorbed on the Cu surface. The inhibitors cover a larger copper surface when adsorbed via a horizontal orientation than a perpendicular adsorption orientation. Such adsorption orientation enables the incoming inhibitor to effectively displace primarily adsorbed water molecule from the metal surface. Although no toxicity test was performed for the fuchsin molecules, they belong to the category 4 of the GHS standard [77] and, thus, can be accepted as green actives.

Bastidas et al. [78] employed different isotherms to study the adsorption of benzotriazole (BTA) as an active inhibitor chemistry for the copper surface in a citric acid cleaning solution. The use of organic acids, such as citric acid, for the descaling of metals usually provides the merits of less corrosive attack on the underlying metal due to the formation of protective metal complexes. The study was conducted between temperatures 298 K and 328 K. Increasing the BTA concentration favored a decrease in copper corrosion rate. Higher temperature

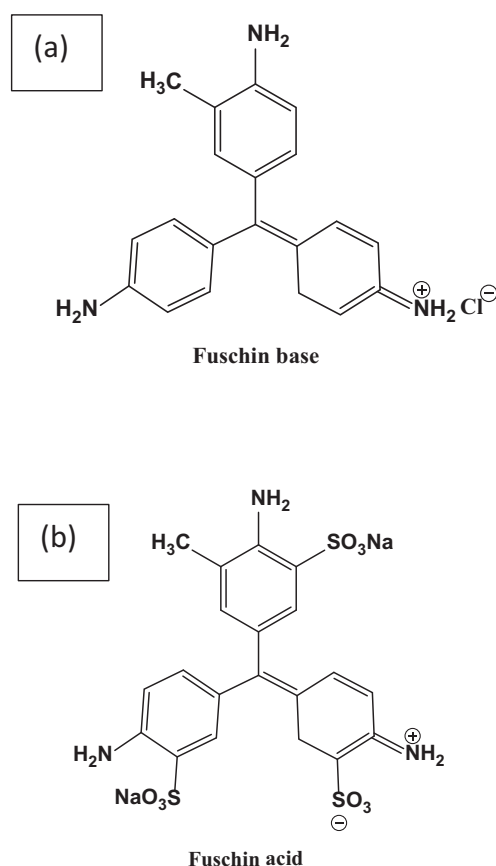


Fig. 8. Fuchsin derivatives for cleaning of copper in 1 M HCl and 1 M H_2SO_4 solutions [76].

depreciated the efficiency of the benzotriazoles, and this was more significant at lower inhibitor concentrations. With inhibition efficiency greater than 95%, the BTA protected the copper surface through a chemical adsorption mechanism, according to the Frumkin isotherm whereby BTA molecules displaced water molecule in a 1:1 ratio. However, benzotriazole has a structure which resembles that of auxin. This structure makes it toxic to plants when released into the environment [79]. It also exhibits long-term stability in water in the soil where it has been found to be a potent inhibitor of plant growth with the capability to kill several soil species at a concentration about 0.1 mg/ml [80].

Glutathione (Fig. 9), a non-toxic active inhibitor containing a carbonyl, a thiol, a hydroxyl and an amine functional group was tested as an efficient candidate for the cleaning of copper with HCl solution [81]. Based on cyclic voltammetry studies of the copper-acid interaction, the glutathione could suppress the anodic dissolution of the copper by shifting the potential for Cu^+ transition to Cu^{2+} towards more positive values. The inhibitor adsorbed onto the copper surface using electrons from its $-\text{NH}_2$ and $-\text{SH}$ groups. The inhibitor (up to 5 mM concentration) altered the preferred corrosion mechanism of copper from being controlled by mass transport of either chloride ion to the copper surface or the copper-chloride complexes from the metal surface to the solution phase. Although an optimum concentration of 10 mM provided an efficiency of approximately 93%, the efficiency of the glutathione decreased as temperature increased up to 45 °C. Nevertheless, the authors did not provide detailed information concerning the toxicity of the inhibitor.

Curkovic et al. [82] showed that the application of imidazole derivatives (4-methyl-1-phenyl imidazole (PMI) and 4-methyl-1-(*p*-tolyl) imidazole (TMI)), Fig. 10, as corrosion inhibitors for the acid cleaning of copper was strongly influenced by the chemical state of the compounds. In a protonated form, it was difficult for the imidazole cation to interact with and adsorb onto the copper surface. Thus, the protonated imidazole could only lower the cathodic half-reactions during the copper corrosion in an acid solution, whereas it could reduce both anodic and cathodic reactions in a neutral solution. It was noted that the imidazole derivatives adsorbed more readily on a copper surface with pre-adsorbed Cu^+ ions (at higher pH) than on bare copper surface in an acidic medium with low pH. Consequently, the imidazole derivatives provided relatively poor inhibition efficiency (not greater than 20%) when tested as inhibitors for the cleaning of copper with 0.5 M HCl solution. Nevertheless, it was deduced that, although the imidazole derivatives could interact with the copper surface using the N-3 atoms of the imidazole ring, the presence of a phenyl ring (in PMI) provided stronger interaction and protection than a methyl substituent (in TMI). As a polar and ionizable aromatic compound, the imidazole ring is a major component of several natural products and pharmaceutical products. With a relatively high solubility of 633 g/L at 20 °C, a $\log P_{\text{ow}}$ value of -0.02 at 25 °C, imidazole possesses an LD_{50} (oral rat) value of 970 mg/kg [83]. All these properties indicate that imidazole can be regarded as a safe and green corrosion inhibitor active.

Some triazole thiols, Fig. 11, were concluded to protect the copper surface during acid corrosion in HCl solution via a cathodic inhibition mechanism [84]. The inhibitors could shift the corrosion potential towards more negative values and display more significant reduction in cathodic current density than anodic current. The inhibitor-substrate interaction was facilitated by the nitrogen atoms on the triazole and

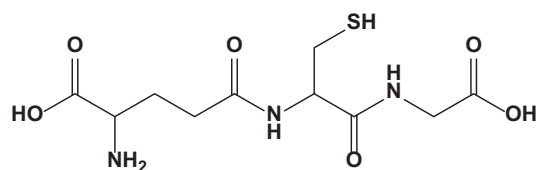


Fig. 9. Structural formula of glutathione corrosion inhibitor for the cleaning of copper with HCl [81].

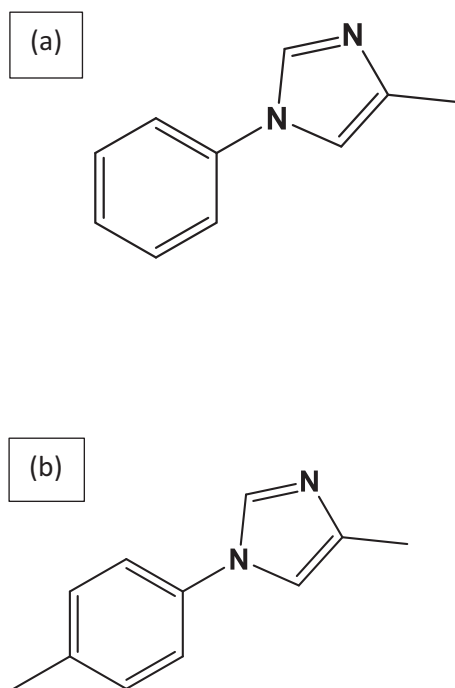


Fig. 10. Structural formula for (a) 4-methyl-1-phenyl imidazole (PMI) and (b) 4-methyl-1-(p-tolyl) imidazole (TMI) [82].

the sulfur atom on the thiol. The attachment of an alkyl group to the triazole thiol increased the energy of the highest occupied molecular orbital (E_{HOMO}), decreased the energy of the lowest unoccupied molecular orbital (E_{LUMO}) and lowered the energy gap needed for electron transition between inhibitor and copper atoms. This conferred significant inhibition efficiency on the triazole thiols so that they

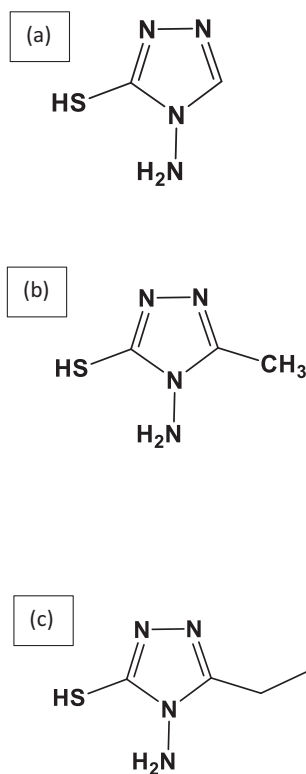


Fig. 11. Structural formula for (a) 4-amino-4H-1,2,4-triazole-3-thiol (ATT) (b) 4-amino-5-methyl-4H-1,2,4-triazole-3-thiol (AMTT) and (c) 4-amino-5-ethyl-4H-1,2,4-triazole-3-thiol (AETT) [84].

performed in the following order of magnitude: AETT² > AMTT³ > ATT.⁴ Increasing temperature from 30 to 65 °C clearly lowered the efficiency of the inhibitors, which was attributed to increasing desorption of the adsorbed inhibitor molecules from the copper surface. Triazoles constitute the most promising heterocyclic compounds used in medicine and agriculture. The antimicrobial activities of sulfur-substituted triazoles have been attributed to the N–C–S linkage in the molecule [85]. Particularly, triazole thiol is categorized as a class 4 chemical according to the Globally Harmonized System of Classification and Labeling of Chemicals [46] which infers that it is a safe and green active chemical.

Tansug et al. [86] synthesized methyl 3-((2-mercaptophenyl)imino)butanoate (MMPB), Fig. 12, as a potential corrosion inhibitor for copper protection in acid chloride media. The molecule was designed with azole, thiol functional groups and carboxylate tail group. The inhibition property of the compound was courtesy of the complexation with Cu⁺ ions on the copper surface, such that the thiol group provided improved adsorptive interaction with the copper surface while the carboxylate group provided additional intermolecular attraction. The enrichment of the copper surface with the copper–inhibitor complex caused a shift in corrosion potential towards more positive values. The inhibitor adsorbed competitively with chloride ions, so that high inhibitor concentration is required to effectively displace the chloride ions from the copper–acid solution interface and hinder the formation of the less protective CuCl on the surface. This was confirmed by EDX elemental analysis which showed that the intensity of a prominent chloride peak (detected on the copper surface after corroding in the blank acid solution) was significantly diminished in the presence of the optimum inhibitor concentration. Consequently, the adsorption of the inhibitor using the sulfur atom was confirmed based on the intensity of the sulfur peak detected after the corrosion. Although 10 mM of the synthesized compound could provide inhibition efficiency of 99.3%, the efficiency slightly decreased with an increase in temperature and time up to 7 days. Table 3 provides a summary of reported acid cleaning corrosion inhibitors for copper.

3.1.3. Titanium

The three aromatic nitro compounds in Fig. 13 were investigated as inhibitors for the corrosion of titanium tubes deployed as heat exchanger tubing materials in MSF desalination plants [87]. They are based on phenylenediamines and an aminophenol. While the aminophenols exhibit oral toxicity (LD₅₀) value of 951 mg/kg and classified as category 4 chemicals based on GHS standard, the phenylenediamines are in the category 3 of GHS classification which indicates toxicity of the chemistry [88,89]. In 1 M H₂SO₄ solution at 298 K, an optimum of 600 ppm of each inhibitor could deliver inhibition efficiency 73.0% (NI), 82.6% (NII) and 94.6% (NIII), respectively. The most efficient inhibitor (NIII) exhibited a corrosion rate of 0.014 mg cm⁻² h⁻¹, relative to 0.260 mg cm⁻² h⁻¹ in the blank acid solution. The efficiency of the nitro compounds improved with the addition of nitrogen, oxygen and π -electron functionalities. An increase in temperature from 298 K to 338 K depreciated the performance of the inhibitors due to desorption from the titanium surface and increase in titanium dissolution. Table 4 provides a summary of reported acid corrosion inhibitors for titanium.

Andijani et al. [90] also investigated a commercial acid cleaning corrosion inhibitor, CP 20, for the corrosion of titanium grade 2 and carbon in 0.5% H₂SO₄ in the deaerated system at 50 °C. The active chemistry of the commercial inhibitor is a β -ethylphenylketo-cyclohexylamino hydrochloride (Fig. 14). Based on weight loss and electrochemical determinations, the corrosion rate of the titanium was clearly below 0.1 mpy (equivalent with inhibition efficiency approximately 99%) under

² 4-amino-5-ethyl-4H-1,2,4-triazole-3thiol.

³ 4-amino-5-methyl-4H-1,2,4-triazole-3thiol.

⁴ 4-amino-4H-1,2,4-triazole-3thiol.

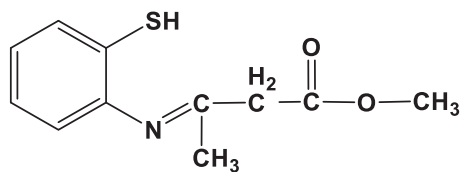


Fig. 12. Structure of synthesized 3-((2-mercaptophenyl)imino)butanoate (MMPB) [86].

erated and deaerated conditions without and with the inhibitor, which signifies that titanium is outstandingly resistant to the acid corrosion attack. Under the similar condition, carbon steel inhibited by the CP20 yielded corrosion rate 62 mpy and 22 mpy (equivalent with 89% inhibition efficiency) in aerated and deaerated systems, respectively. According to the authors, the value of 62 mpy is slightly higher than the industrial permissible limit, while the corrosion rate of carbon steel in the deaerated system is well under the permissible limit. The β -ethylphenylketo-cyclohexylamino hydrochloride is available commercially as a formulation of β -(ethylphenylketo-cyclohexyl) amino hydrochloride, formaldehyde, cinnamaldehyde and methanol [91]. Fig. 15 shows that a major component of the acid cleaning inhibitor is benzophenone which is completely insoluble in water and belongs to category 1 in the chronic aquatic toxicity classification, confirming its significant capability to endanger aquatic life [92].

4. Patent literature

A composition for the inhibition of the corrosion of steel and stainless steel surfaces during acid cleaning was invented by Carandang [93]. The invented inhibitor formulation was composed of a protein-derived polymer, a sugar-derived polymer, sorbitol, tannin or vinyl-based polymer. Iodide can also be employed for the purpose of synergism. The protein-based polymer may include gelatin hydrolysates or casein. The sugar polymer may include molasses, algin, sorbitol etc. The addition of inhibitor concentration between 0.001 and 0.005 wt%, to 5% HCl or H₂SO₄ as cleaning solvent, exhibited very good corrosion rate in the range of 0.01–0.2 mpy for in HCl but performed poorly in H₂SO₄ during the cleaning of cold-rolled steel C1010 and stainless steel 316 SS at 32 °C.

Carrie et al. [94] developed a maleic acid-based acid cleaning corrosion inhibitor with pH in the range of 0.1–4.5 for the cleaning of stainless steel with a calcium carbonate scale. The authors remarked that

the inhibitor would function more efficiently when utilized in an acid with pKa <4. Such acids include HCl (pKa <0), HNO₃ (pKa <0), H₃PO₄ (pKa = 2.1) or even formic acid (pKa = 3.75). It was also emphasized that the inhibitor formulation must be devoid of citric acid because of its poor performance as a calcium carbonate remover at pH < 2. Suitable ionic, non-ionic and amphoteric surfactants could be added to improve inhibitor performance. Unfortunately, the assessment of the inhibitor was only conducted by surface safety tests whereby the inhibitor is simply introduced to the top of the substrate and the visual analysis after some allowed period of time. Nevertheless, the claimed formulation performed excellently well as an acid cleaning corrosion inhibitor in the selected acid solutions.

A cleaning formulation based on aryl quaternary ammonium ions, fluoride ions and di-anionic functional substituted compounds containing two aryl groups per molecule was developed for the protection of titanium and its alloys [95]. The inventors noted that, although aqueous solutions containing acidic fluorides had been applied for cleaning and deoxidizing titanium and its alloys, the combination of these fluorides with quaternary ammonium salts and di-anionic aryl-based moieties exhibited strong synergistic properties. The addition of 10 g/L of inhibitor formulation to a solution containing 7.35% H₂SO₄, 1.89% HF and an amount of aluminum sulfate equivalent to 0.395% of Al³⁺ provided the least corrosion rate for titanium (as determined by weight loss calculations) compared with several commercially available inhibitors.

A formulation for the inhibition of steel during scale removal with some reducing agents was disclosed by Gill et al. [96]. The formulation was composed of reducing agent, chelating agent, surfactant and a dispersant. As a dramatic improvement, compared with previous inventions, the inventors discovered that the reducing agent was capable of converting iron oxide to more soluble form and transforming the metal substrate surface into less reactive state by forming a magnetite layer on the surface. Typical reducing agents include thiosulfates, persulfates, peridates, or sodium/ammonium/potassium sulfites. Treatment time, which is dependent on the dosage concentration and degree of scaling, could be as short as 6 h and as long as 10 days. The chelating agents could include EDTA, oxalic acid, citric acid or maleic acid. The formulation was tested at 60 °C during 22 h with carbon steel samples which were corroded for 5 days in tap water at pH 7, using the weight loss method. At a dosage of 0.1 wt%, the formulation containing sodium sulfite as reducing agent and sodium EDTA as complexing agent provided the best efficiency by causing the most minimal dissolution of the steel sample.

Table 3
Summary of reported acid cleaning corrosion inhibitors for copper.

Corrosion Inhibitor	Alloy	Experimental conditions	Maximum Protection	Ref.
Imidazoline	Copper	•Test Solution: HCl, H ₂ SO ₄ , 25 °C •Inhibitor concentration: 0.01 M •Technique: Static.	IE = 89.6%	[74]
Fuchsin Acid/Base	Copper	•Test Solution: HCl, 25 °C •Inhibitor concentration: 0.1 M •Technique: Static.	%IE = 99%	[76]
Benzotriazole	Copper	•Test Solution: Citric acid, 25 °C •Inhibitor concentration: 0.1 M •Technique: Static.	%IE > 95%	[78]
Glutathione	Copper	•Test Solution: HCl, 30 °C •Inhibitor concentration: 10 mM. •Technique: Static	IE = 93%	[81]
Imidazole	Copper	•Test Solution: HCl, 25 °C •Inhibitor concentration: 5 mM •Technique: Static.	% IE = 20%	[82]
Traizole thiol	Copper	•Test Solution: HCl, 30 °C •Inhibitor concentration: 2.58 mM •Technique: Static.	% IE = 96%	[84]
Imino butanoate	Copper	•Test Solution: •Inhibitor concentration: 10 mM •Technique: Static.	% IE = 99.3%	[86]

%IE = inhibition efficiency.

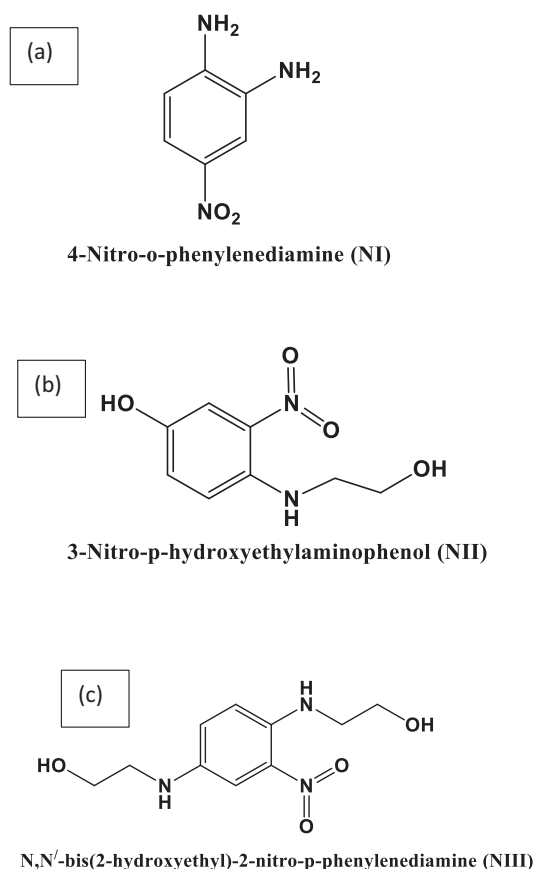


Fig. 13. Aromatic nitro compounds as acid cleaning corrosion inhibitors for titanium in 1 M H₂SO₄ [87].

Similarly, Treybig [97] also developed an inhibitor formulation based on quaternary ammonium compounds (*N*-alkyl,*N*-cycloalkyl and *N*-alkylaryl pyridinium halides), a sulfur-containing compound and a nonionic surfactant employed for the acid cleaning of carbon steel and stainless steel. The alkyl group of the quaternary ammonium salt could either be a C₁₂–C₂₀ long chain alkyl group, a cycloalkyl group or even an aryl group and heterocyclic groups. Other suitable quaternary ammonium compounds include monochloromethylated and bischloromethylated ethylated pyridinium halides, ethoxylated and propoxylated quaternary ammonium compounds, sulfated ethoxylates of alkylphenols and primary and secondary fatty alcohols. A mixture of 90.64 g of alkoxyated tridecyl alcohol, 300 g of alkylpyridine benzylchloride quaternary and 60.11 g of 2-mercaptoethanol in 150 g of isopropanol served as formulation from which 1526 ppm (equivalent to 0.153%) was extracted for the cleaning of carbon steel and stainless steel to give a zero pitting index and corrosion rate of 34.4 mpy when cleaning in 100 g/L H₂SO₄ during 24 h immersion at 60 °C.

An acid cleaning corrosion inhibitor formulation composed of a polyamino-aldehyde resin (such as quaternized polyethylenepolyamine-glyoxal resin) and acetylenic alcohol,

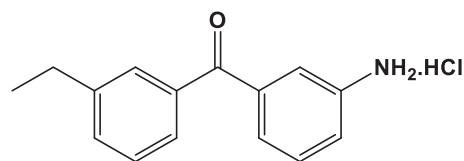


Fig. 14. β -ethylphenylketo-cyclohexylamino hydrochloride corrosion inhibitor for titanium in 0.5% H₂SO₄ [90].

ethoxylated fatty amines, ethoxylated fatty amine salts and aldehyde-releasing compounds like hexamethylenetetramine [98]. The polyamino-aldehyde resins may be in cationic, salt and/or quaternized form in order to exhibit significant water solubility required for the inhibition effect. The resin can be synthesized from polyamine compounds which should have a plurality of nitrogen atoms, preferably up to five nitrogen atoms. Such polyamines include polyvinylamines, polyallyl amines or even polyvinylguanidines. The aldehyde-releasing compounds, such as Schiff bases, trioxanes, or polyoxymethylenes, are capable of releasing an aldehyde (specifically formaldehyde) once introduced into the acid cleaning solution typically with pH between 3 and 4. The performance of 0.5%wt of the formulated inhibitor was tested for cold-rolled steel in 10% HCl cleaning solution showing efficiency approximately 90%. Addition of 0.69 g of hexamethylenetetramine further enhanced the performance of the inhibitor so that the corrosion inhibition efficiency increased further to 95%.

Acid cleaning and corrosion inhibiting blend composed of gluconic acid were invented by Miralles [99]. The formulation was claimed to be biodegradable and effectively applicable for the acid cleaning of nickel and stainless steel with a sulfuric or phosphoric acid solution. The formulation is a combination of gluconic acid and urea sulfate. A remarkable feature of the inhibitor formulation is the ability of gluconic acid (a traditionally alkaline corrosion inhibitor) to work effectively in an acid cleaning solution. The formulation was tested in cleaning solution containing 16.6% H₂SO₄, 11.5% urea prill and 0.3% gluconic acid where low corrosion rates of 0.0230 mpy and –0.0001 were calculated for the Ni and 304 stainless steel, respectively, based on weight loss measurement after 6 h.

An acridine orange-based formulation was invented by Jaralla for the descaling, cleaning and corrosion inhibition of steel [100]. The acridine orange, *N*·*N*·*N*'·*N*'-tetramethyl-3,6-acridinediamine monohydrochloride, is a non-toxic active chemistry which exhibits fast and direct flow-dependent protonation when added into an acidic cleaning solution. To bind strongly to the metal substrate, it uses its aromatic rings and assumes parallel orientation during binding so that the position of the positively charged hydrogen ring in the acridine orange is close to the predominant negatively-charged electric double layer on the metal surface. The inhibitor formulation could be effectively added to the HCl solution for the cleaning of steel surfaces with iron oxide and silicate scales. The inventors encouraged the addition of 2% citric acid and EDTA to the formulation to enhance the chelating effect of the acridine orange. Using potentiostatic polarization method, a working formulation containing 80 ppm acridine orange with 2% citric acid and 2% EDTA was tested as an inhibitor for the cleaning of cold-rolled C1020 carbon steel in 8% HCl +1.5% HF at 50 °C and

Table 4

Summary of reported acid cleaning corrosion inhibitors for titanium.

Corrosion Inhibitor	Alloy	Experimental conditions	Maximum Protection	Ref.
Diamine, Aminophenol	Titanium	–Test Solution: H ₂ SO ₄ , 25–65 °C –Inhibitor concentration: 600 ppm –Technique: Static.	% IE = 94.6%	[87]
β -ethylphenylketo-cyclohexylamino hydrochloride	Titanium	–Test Solution: H ₂ SO ₄ , 50 °C –Inhibitor concentration: 600 ppm –Technique: Static.	%IE \approx 99%	[90]

%IE = inhibition efficiency.

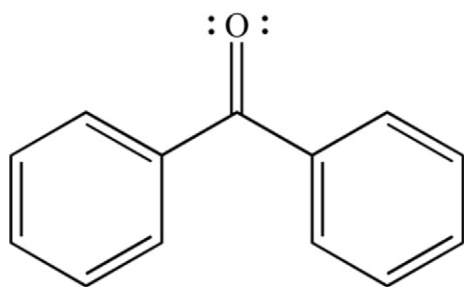


Fig. 15. Benzophenone, a major component of commercial inhibitor CP20 [90].

hydrodynamic condition up to 1400 rpm rotation speed. The acridine orange formulation could effectively lower both cathodic and anodic current densities and provide an inhibition efficiency up to 91% in the acid cleaning mixture.

The use of ethoxylated amines and/or ethoxylated alcohols as a corrosion inhibitor in the vapor phase for cleaning stainless steel with a blend of H_2SO_4/HF acid solution was invented by Schact and Schmidt [101]. The invention was motivated by the postulation that ethoxylated alcohols as well as other such ethoxylated surfactants, being less water soluble at higher temperatures, oil out of solution and form an oily layer on top of the solution that it minimizes the release of acidic vapors that corrode and stain the stainless steel. Furthermore, it is postulated that the ethoxylated amines volatilize at high temperatures and protect the stainless steel surface by forming a barrier via adsorption of the amine group to the metal surface. The addition of up to 5 %wt of the ethoxylated amine to, at least, 1% of the acid cleaning blend strongly lowered the tendency for acid vapor staining of the stainless steel surface at a temperature between 4 and 93 °C by 94%.

Bennett and Mancuso [102] developed an effective cleaning formulation based on sulfonic acid (selected from the family of aryl sulfonic acid such as dodecylbenzenesulfonic acid). The formulation could contain an imidazolines or imidazolium salt having the general structural formula as detailed in Fig. 16. Where R could either be an alkyl, aryl or arylalkyl group with 1–18 carbon atoms. The inventors further claimed that 3,3'-dithiodipropionic acid, thiourea, thiosulfate or even 2-mercaptoethanol could serve as a synergist for the formulation. The effective formulation dosage can range between 5 and 25 %wt.

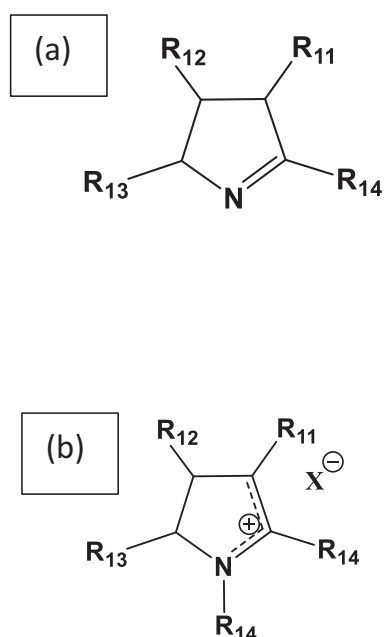


Fig. 16. Imidazoline and imidazolium salt based corrosion inhibitors [102].

5. Gap areas

Based on the scientific and patent literature reviewed in this paper, the following can be identified as important knowledge gaps:

- (1) Development of corrosion inhibitors suitable for multiple alloys is scarce in the literature. Most of the acid cleaning corrosion inhibitors reported is for one or (at most) two types of alloys.
- (2) Effect of hydrodynamic on corrosion inhibitor performance is scanty in the literature. Most of the reported acids cleaning corrosion inhibitors are tested under static conditions without consideration for real industrial application which involves flow and hydrodynamic conditions.
- (3) Development of localized corrosion inhibitor is scarce. Acid cleaning with, especially, HCl usually causes localized pitting corrosion. Most reported corrosion inhibitors focus on the effect of the inhibitor on general corrosion without considering the development of inhibitors which can simultaneously inhibit localized corrosion.
- (4) Mechanism of inhibition of acid cleaning corrosion inhibitors at the molecular level is not well understood. Most of the reports have merely considered the inhibitive properties of acid cleaning corrosion inhibitors without molecular level interpretations of the phenomenon. Such molecular level interpretations will provide a detailed understanding of the inhibitor–metal adsorption interaction.
- (5) A thorough assessment of toxicity properties of most acid cleaning corrosion inhibitors is scarce in the literature.
- (6) The chemistry of reported acid cleaning corrosion inhibitors is limited to nitrogen–based compounds. Comparatively, reports concerning inhibitor chemistries based on oxygen and sulfur are scarce.
- (7) Developing an effective inhibitor formulation for acid cleaning usually involves the mixing of different chemistries such as actives, surfactants and synergists. The compatibility and stability of these components in the mixture must be assessed over a period of time, known as the shelf life. The consistency of their inhibition efficiencies over the same period of time must also be ascertained. Such reports are lacking in both the scientific and patent literature.

6. Future research directions

For future research on the development of corrosion inhibitors for acid cleaning, the following may be considered:

- (1) Assessing developed acid cleaning corrosion inhibitors underflow and hydrodynamic conditions. Although a given inhibitor formulation may perform efficiently under static conditions, flow conditions can seriously modify the inhibition mechanism and depreciate the inhibitor performance. Flow and hydrodynamic conditions can induce wall shear stress which causes delamination of the adsorbed inhibitor from the metal surface.
- (2) It will be necessary to subject the developed acid cleaning corrosion inhibitors to toxicity tests. Although several softwares are readily available for the prediction of toxicity parameters of chemicals, a more practical approach should involve exposure of the formulations to specific aquatic toxicity testings using animal models according to known standards.
- (3) Detailed understanding of the inhibitor–metal interaction is an important research area; this can be achieved through in-depth surface characterizations using advanced techniques such as x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Such characterizations provide relevant

mechanism of interaction such as physical adsorption of inhibitor molecules or chemical complexation with metal atoms. Density functional theory (DFT) and molecular dynamics simulation can also be used for atomic and molecular level interpretations of the inhibition mechanism.

- (4) Based on the conventional desire to develop greener corrosion inhibitors, attention can be focused on naturally occurring chemicals as promising substitutes for synthetic chemical substances. The naturally occurring chemicals are readily available, less toxic and cost-effective.

7. Summary and conclusion

In summary, it is important to state that the scientific literature and patent inventions are scarce in publications related to the development of corrosion inhibitors for acid cleaning of industrial heat exchangers. Most reported corrosion inhibitors for acid cleaning were investigated for iron-based alloys, especially, steel. Studies on copper and titanium alloys, which also find a great deal of application for heat exchangers, have also been reported, howbeit with fewer publications, compared with the ferrous alloys.

While other chemistries have been studied, it is clear that nitrogen-based compounds are the most investigated chemistries for the development of acid cleaning corrosion inhibitors. Of these chemistries, amines and azoles find immense application. Other chemistries based on oxygen and sulfur is scarce in the literature. Although most of the reported chemistries from the scientific literature are non-toxic, the same cannot be concluded for the patent inventions. All the reported chemistries have also provided corrosion inhibition efficiency greater than 80% with corrosion rates largely within permissible ranges.

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