Journal of Materials and Environmental Science
ISSN : 2028-2508
e-ISSN : 2737-890X
CODEN : JMESCN

J. Mater. Environ. Sci., 2024, Volume 15, Issue 10, Page 1383-1402

http://www.jmaterenvironsci.com

Protection of copper in contact with an aggressive medium using various inhibitors: review

Salim R. [1] *, Oukhrib R. [2], Zaidi K. [3]**

[1] *Euromed University of Fes, UEMF, 30000 Fes, Morocco*
[2]*Team of Physical Chemistry and Environment, University of Ibn Zohr, Agadir, 8016, Morocco*
[3]*Laboratory of Applied Chemistry and Environment (LCAE), Mohammed First University, Oujda, Morocco*

**Corresponding author, Email address: r.salim@ueuromed.org*
***Corresponding author, Email address: rachid.oukhrib@edu.uiz.ac.ma*

Received *28 July 2024,*
Revised *05 Oct 2024,*
Accepted *06 Oct 2024*

Citation*: Salim R., Oukhrib R., Zaidi K. (2024) Protection of copper in contact with an aggressive medium using various inhibitors: review,, J. Mater. Environ. Sci., 15(10), 1383-1402*

Abstract: This review focuses on the corrosion of copper and copper alloys in aggressive environments and the corrosion inhibitors used to remedy this problem. Indeed, the main objective of this study is to explore copper resistance when it is in contact with corrosive environments and the inhibitors used in these environments to protect this metal. The literature is reviewed to assess the corrosion inhibition efficacy of organic inhibitors and their derivatives compared to inorganic inhibitors. In addition, the paper reviewed several results of using a combined organic and inorganic compound as corrosion inhibitors without forgetting the use of natural products. Understanding a particular inhibitor's maximum corrosion inhibition efficiency in a specific environment is crucial to selecting the most appropriate compound.

Keywords: *Copper; Corrosion; Inhibitor; Sustainable development;*

1. Introduction

Having good conductivity of electricity and heat is combined with strength, ductility, and excellent corrosion resistance, copper and its alloys (copper, nickel, bronze, brass, etc.) find a very wide of applications in the production of wire, sheets, and pipelines in electronic industries, marine industries, power stations, heat exchangers and cooling towers (Bouyanzer *et al.*, 2004; Hamidah et al., 2021). Near about 30,000 documents on Scopus (Corrosion & Copper), the most cited paper (>3150 times) treated the chemical states in XPS analysis of metal oxides and hydroxides of Sc, Ti, V, Cu, and Zn (Biesinger *et al.*, 2010). During manufacture, the use of a sulphuric acid solution to remove any undesirable products formed at the surface (oxidation films, incrustations, scale, etc.) to obtain a shiny final copper surface is generally accompanied by Corrosion of copper (Mzioud *et al.*, 2020; Yoo *et al.*, 2020; Dahmani *et al.*, 2017). Therefore, corrosion of copper can be retarded or stopped by the use of inhibitors (Fouda *et al.*, 2022; Oukhrib *et al.*, 2017; EL Mouaden & Bazzi, 2017; Zarrouk *et al.*, 2013; EL Khadom & Yaro, 2011).

Organic and inorganic inhibitors and natural extracts were used to avoid corrosion attacks and save time and money (Hossain *et al.*, 2023; Zarrouk *et al.*, 2012b; Bouklah *et al.*, 2006). Antonijevic & Petrovic (2008) summarized the influence of compound structure, concentration, method of

application, and media that inhibitors use on inhibition efficiency. he field of inhibitor studies has witnessed remarkable development in recent years. This is done by developing the theoretical aspect of the study. Whether to enhance the experimental results or for a predictive study. This is particularly on the engineering of molecules with specific molecular properties that increase their corrosion-inhibiting effectiveness under certain conditions. This is what made many researchers try to find models to predict the possibilities of newly synthesized compounds acting as corrosion inhibitors, combining theory and practical investigations.

2. Inorganic inhibitors

Inorganic inhibitors are substances designed to slow down or prevent unwanted chemical reactions, such as corrosion, particularly in metals. These inhibitors are composed of inorganic compounds, often derived from elements like phosphates, silicates, chromates, molybdates, and nitrates (Dueke-Eze *et al.*, 2022; Mo *et al.*, 2017; Baach *et al.*, 2022; Zehra *et al.*, 2022). They protect materials by forming a thin layer on the surface or reducing the corrosive reaction rate. Depending on their chemical nature, they can either create a barrier that prevents corrosive substances from reaching the material or inhibit specific reactions, such as the oxidation of metals or the reduction of oxygen at the surface (Shweetha *et al.*, 2024; Palanisamy, 2019).

Chromates are highly effective inorganic inhibitors, though they pose significant environmental and health risks due to their toxicity. As a result, safer alternatives, like molybdates, are increasingly used. Phosphates and silicates are also common because they form protective layers without overly harming the environment. These inhibitors have broad applications in water treatment systems, protecting pipes and equipment, and paints and coatings that prevent rust on metal surfaces. In the oil and gas industry, inorganic inhibitors are vital for safeguarding pipelines and storage tanks, and in construction, they are used to protect steel reinforcements in concrete from corrosion.

Despite their effectiveness, the environmental impact of specific inorganic inhibitors, mainly those containing chromates, has led to regulations and a shift towards more environmentally friendly alternatives. These inhibitors are essential for extending the lifespan of materials, but their selection must balance effectiveness with safety and environmental considerations. In literature, numerous inorganic inhibitors are used as corrosion inhibitors for copper in aggressive mediums. For example, Muñoz et al. (Muñoz *et al.*, 2004) investigated three inorganic inhibitors on copper, nickel, and two copper–nickel in 850 g/L LiBr solution. Thus, the most effective protection is achieved by adding chromate to the 850 g/L LiBr solution, as the inhibition efficiencies of molybdate and tetraborate ions are comparatively low. Under the present experimental conditions, aggressive anions such as bromides significantly reduce the effectiveness of the less efficient inhibitors (molybdate and tetraborate) but not that of the more effective chromate. The study indicates that the nickel content influences the inhibiting properties in the alloy. Nickel enhances the overall corrosion resistance by shifting the free corrosion potential to more noble values and reducing corrosion current densities. In chromate and molybdate solutions, nickel broadens the passivation range and lowers the passivation current densities. Also, nickel's presence improves resistance to localized corrosion in bromide environments.

Moreover, Toumiat et al. (Toumiat *et al.*, 2016) investigated the Iodate inhibition mechanism on the copper surface. As a result, the electrochemical measurements using potentiodynamic polarization and

electrochemical impedance spectroscopy (EIS), along with chemical analysis via the weight-loss method, show consistent results. Notably, iodate maintains a stable % inhibition efficiency of 72% even after 16 days of immersion in aerated 0.5 M NaCl solution. In addition, the Molecular modeling and quantum chemical simulations reveal that the highest occupied molecular orbital (HOMO) is located on the oxygen atoms of the iodate molecule, indicating that these sites are preferred for electronic interaction with the metal surface. This observation suggests that the iodate molecule effectively adsorbs onto the Cu (110) surface, confirming its role in corrosion inhibition. In addition, Anadebe et al. (Anadebe *et al.*, 2023) investigate the corrosion inhibition of Ce-MOF on copper in aqueous chloride environment. The findings of this paper revealed that Ce-MOF forms a compact coating on the Cu surface, mitigating metal degradation by enhancing surface coverage and blocking active sites. Electrochemical analysis showed improved impedance with increasing Ce-MOF concentration, confirming its role as an effective cathodic inhibitor. Additionally, XRD, FT-IR, and HR-TEM characterization validated the formation of Ce-MOF through a wet chemical method. Thus, they report that Ce-MOF is recommended as a potential corrosion inhibitor in chloride-rich marine environments.

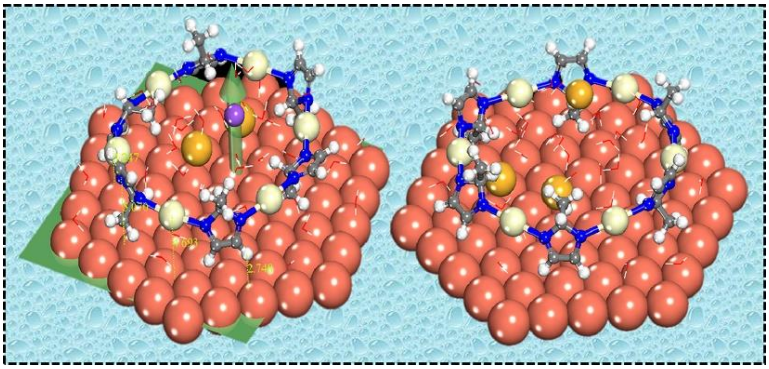


Figure 1: Adsorption strength of Ce-based metal-organic framework (Ce-MOF) on copper (Anadebe *et al.*, 2023)

Furthermore, there are metal-organic frameworks, such as Manganate—MnO_4^-, chromate—CrO_4^{2-}, molybdate—MoO_4^{2-}, tetraborate— $B_4O_7^{2-}$ and phosphate—PO_4^{3-} that are useful as corrosion inhibitors in a different medium. In another paper, saber et al. (Anadebe *et al.*, 2023) evaluate the behavior, inhibition efficiency, and corrosion mechanisms of inorganic corrosion inhibitors on copper-based metals in a 0.5 M H_2SO_4 corrosive medium. As a result, polarization (PDP) and electrochemical impedance spectroscopy (EIS) results indicated that both inhibitors achieved high efficiencies at an optimal concentration of 10^{-3} M, with BiB-Ba0.2 reaching 91.2% efficiency and BiB-Ba0.6 achieving 90.8% efficiency. Thus, the authors suggest that the inorganic compounds exhibit strong adsorption on copper substrates, functioning as mixed-type corrosion inhibitors. Further, XRD, FTIR, SEM/EDS, and AFM analyses confirmed that both inhibitors adsorb onto the copper surface, forming a protective layer that mitigates damage and corrosion of the metal.

Inorganic inhibitors are typically classified as anodic or cathodic (Fateh *et al.*, 2020; El Mouaden *et al.*, 2018; Ashassi-Sorkhabi *et al.*, 2004). Anodic inhibitors decrease the rate of anodic reactions and react with corrosive products to generate insoluble hydroxides and oxides. When their concentration exceeds a specific threshold, the corrosion current density surpasses the critical anodic current density, leading to metal passivation (Garg *et al.*, 2023; Sedik *et al.*, 2020; El Mouaden *et al.*, 2018; Khaled *et al.*, 2009).

Table 1. Previous studies of Inorganic inhibitors on copper alloy

Inhibitor	Metal/Alloy	Medium	Efficiency, E%	Reference
CrO_4^{2-}	copper	850 g/L LiBr	78%	Muñoz *et al.*, 2004
	nickel	850 g/L LiBr	72%	
	copper–nickel	850 g/L LiBr	26%	
MoO_4^{2-}	copper	850 g/L LiBr	1%	
	nickel	850 g/L LiBr	-	
	copper–nickel	850 g/L LiBr	17%	
$B_4O_7^{2-}$	copper	850 g/L LiBr	51%	
	nickel	850 g/L LiBr	-	
	copper–nickel	850 g/L LiBr	59%	
IO_3^-	copper	0.5 M NaCl	72%	Karima *et al.* 2016
Ce-MOF	Copper	3.5 wt.% NaCl	81%	Anadebe *et al.*, 2023
BiB-$Ba_{0.2}$	Copper	0.5 M H_2SO_4	91%	Saber *et al.*, 2024
BiB-$Ba_{0.6}$	Copper	0.5 M H_2SO_4	90%	

3. Organic inhibitors

Thousands of published papers have used organic compounds as inhibitors (OCIs) for copper and its alloys during these last decades. OCIs generally act on both the anodic and cathodic branches, according to Langmuir, Temkin, Frumkin, etc. The nature of corrosion leading to Cu^+ and/or Cu^{2+} facilitated the formation of a copper ion–inhibitor complex at the metal surface (Radi *et al.*, 2022; Youda *et al.*, 1990). However, many organic compounds, such as azoles, amines, Schiff bases, imidazolines, hydropyrimidines, amino acids, etc., are helpful corrosion inhibitors in acidic, neutral, and alkaline media. Depending on the structure, they act as a protective layer formed by physisorption in the metal/electrolyte interphase or as an insoluble chelate barrier developed by chemisorptions, which avoid direct contact with the metal/alloy with the aggressive media. The ability of an organic molecule to inhibit metal corrosion depends on several factors, and some of them are shape, branching or conformation, aromaticity, conjugation, bond strength to the metal substrate, the presence of nitrogen, oxygen, and or sulfur atoms, and several bonding groups or atoms. Temperature, pH, and stability in the aggressive media are also factors related to the efficiency of the inhibitor. As can be seen from **Table 2**, Ech-chibi et al. (Ech-chibi *et al.*, 2023) examine the corrosion resistance copper alloy in 1 M HCl containing a novel imidazothiazole derivative. The inhibitor achieved high inhibition efficiencies of 96.9% (Cu) at 10^{-4} M concentration, forming a protective layer on the metal surfaces. Corrosion resistance improved with longer immersion times. SEM, EDX, and DFT calculations confirmed adsorption via aromatic rings and N, O, and S atoms, while MD simulations revealed stronger adsorption on the copper surface.

Moreover, another molecule of this derivative was investigated by Salim et al. (Salim *et al.*, 2024). They evaluated the corrosion inhibition behavior of the Imidazothiazoles molecule on copper using electrochemical techniques, surface analysis, and theoretical approaches. This inhibitor showed high efficiencies (97% for Cu) at a concentration of 10^{-4} M. They also reported that the adsorption mechanism followed the Langmuir isotherm model and indicated mixed-type inhibition. Theoretical studies, including DFT calculations and molecular dynamics, supported the experimental findings and confirmed the strong adsorption on metal surfaces. Furthermore, Luo et al. (Luo *et al.*, 2022) synthesized

a novel pyridazine derivative (EPD) and evaluated it as a corrosion inhibitor for copper in 0.5 M H_2SO_4. The inhibitor performed well by adsorbing on the copper surface through N-Cu and Cu-S bonds. Inhibition efficiency increased with higher EPD concentrations but slightly decreased at elevated temperatures. EPD followed the Langmuir isotherm model and showed mixed adsorption behavior. Indeed, they report that EPD adsorption follows the Langmuir isotherm model, indicating a mixed adsorption mode based on chemical interactions. Quantum chemical calculations identify the pyridazine ring as the active adsorption center, with N and S atoms in the HOMO orbital donating electrons to form stable covalent bonds with copper.

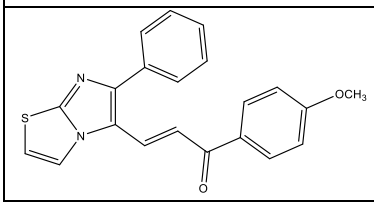
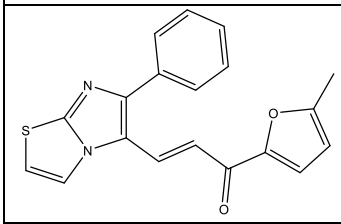
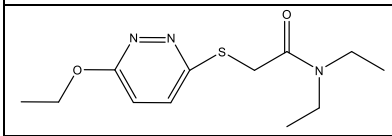
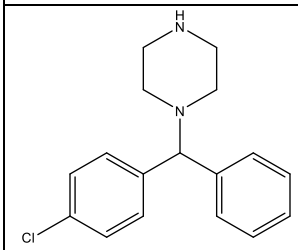
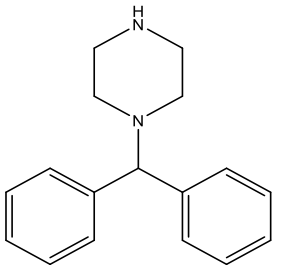
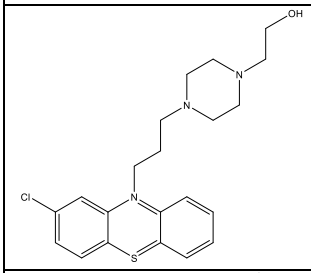
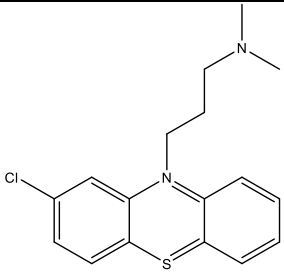
Different bases were applied as corrosion inhibitors for copper in the sulfuric medium. For example, Zeng et al. (Zeng *et al.*, 2022) investigate the corrosion resistance mechanisms of two piperazine derivatives on copper in 0.5 M H_2SO_4 using electrochemical methods, surface analysis, and theoretical calculations. This study found that CBP and BP are cathodic inhibitors with excellent anti-corrosive properties, achieving 97.40% and 95.26% inhibition efficiency, respectively, at 5 mM. XPS analysis revealed that CBP formed additional Cl-Cu bonds, enhancing its performance over BP. Theoretical calculations further confirmed that the Cl atom in CBP binds to copper's vacant orbitals, resulting in stronger adsorption and improved corrosion resistance. In the adsorption mechanism explanation, both inhibitors exhibit mixed adsorption, forming electrostatic interactions (physisorption) and coordination bonds (chemisorption) between N atoms and Cu. CBP has additional Cl atoms compared to BP, forming Cl-Cu bonds and allowing CBP to align more parallel to the copper surface. This results in stronger adsorption and better corrosion resistance for CBP than BP.

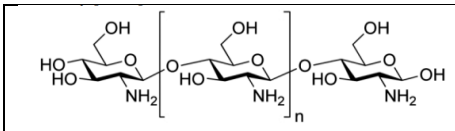
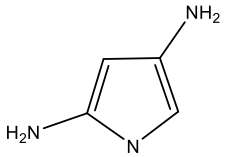
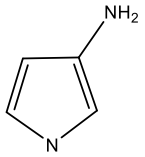
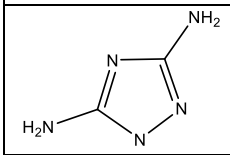
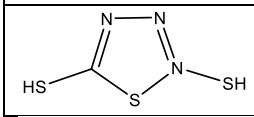
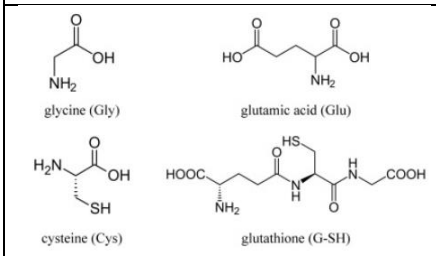
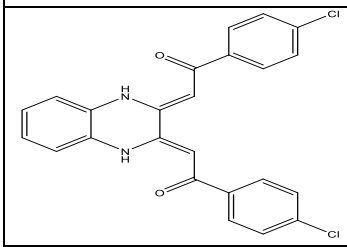
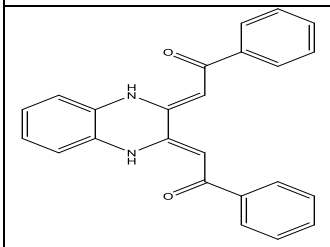
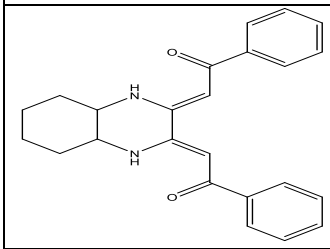
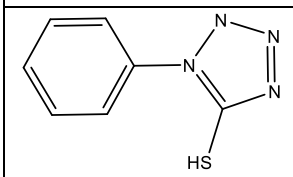
In another study, Zhou et al**. (**Zhou *et al.*, 2021**)** evaluated the corrosion inhibition and adsorption mechanisms of two phenothiazine drugs (CPZ and PPZ) on copper in 0.5 M H_2SO_4. The electrochemical tests demonstrated that both inhibitors effectively reduce metal corrosion, with CPZ showing higher efficiency at an optimal 400 mg/L concentration. In addition, the FTIR and XPS characterizations were performed, and the formation of N-Cu and S-Cu bonds was confirmed. Also, the authors report that both inhibitors follow Langmuir isotherm adsorption with a mixed physical and chemical adsorption mode. However, the theoretical calculations validated the experimental findings, highlighting that electron-rich regions enhance adsorption and corrosion resistance on copper.

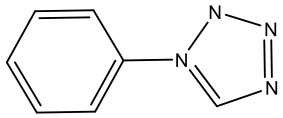
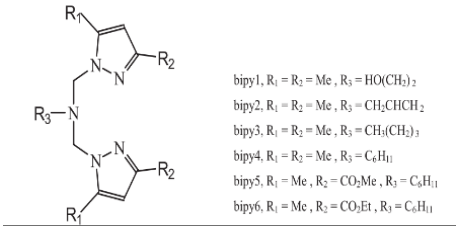
The application and study of corrosion inhibitors have been explored for a long time, highlighting their significance in preventing metal degradation and extending the lifespan of materials. Their development has evolved to include various inhibitors tailored for different metals and environments, demonstrating their critical role in industrial applications. As **Table 2** shows, several molecules were applied as corrosion inhibitors for copper in several media. For example, Oukhrib et al. (Oukhrib *et al.*, 2017) studied chitosan biopolymer in a 3% NaCl medium, whereas Dafali et al. (Dafali et al., 2002) studied the anticorrosive properties of five molecular structures of bipyrazole derivatives. In the HCl medium, El Issami et al. (El Issami *et al.*, 2007) studied two triazoles in an HCl medium, and Ting Qin et al. (Ting Qin *et al.*, 2011) studied thiadiazole. Zhang et al. investigated the Intramolecular synergistic effect of glutamic acid, cysteine, and glycine (Zhang *et al.*, 2011). Several studies on copper using different derivatives were employed in nitric acid. For example, zarrouk et al. (Zarrouk *et al.*, 2012) evaluated a triazole molecule anti-corrosion activity for copper in nitric acid with a 10^{-2} M concentration. Also, other studies were investigated by the same author in 2011 using a Quinoxaline

basis (Zarrouk *et al.*, 2011). These studies report that these derivatives acted as effective corrosion inhibitors for copper in a 2M nitric acid solution.

Table 2. Previous studies of inorganic inhibitors on copper alloy

Inhibitor derivatives	Inhibitor concentration	Medium	Efficiency, E%	Reference
	10^{-4} M	1 M HCl	97%	Ech-chihbi *et al.*, 2023
	10^{-4} M	1 M HCl	97%	Salim *et al.*, 2024
	0.4 mM	0.5 M H_2SO_4	94%	Luo *et al.*, 2021
	0.5 mM	0.5 M H_2SO_4	97%	Zeng *et al.*, 2022.
			95%	
	400 mg/L	H_2SO_4	94%	Zhou *et al.*, 2020
			97%	

	1000 ppm	NaCl	83%	Oukhrib *et al.*, 2017
	10^{-2} M	0.5 M HCl	85%	El Issami *et al.*, 2007
			80%	
	10^{-2} M	2M HNO_3	86%	Zarrouk *et al.*, 2012
	7.5 mM	0.5 M HCl	84%	Ting Qin *et al.*, 2011
	10 mM	0.5 M HCl	94%	Zhang *et al.*, 2011
	10^{-3} M.	2M HNO_3	90%	Zarrouk *et al.*, 2011
			88%	
			77%	
	10^{-3} M	0.1 M HNO_3	97%	Mihit *et al.*, 2010 & 2006

			94%	
	10^{-3} M.	NaCl	bipy1: 98% bipy1: 98% bipy1: 97% bipy1: 92% bipy1: 93%	Dafali *et al.*, 2002

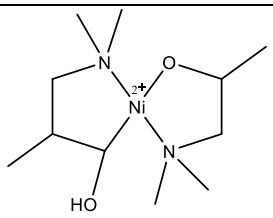
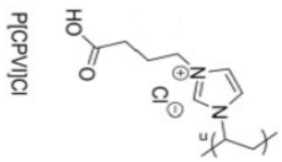
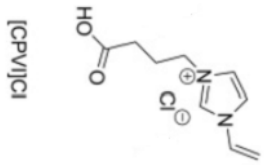
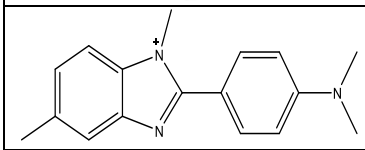
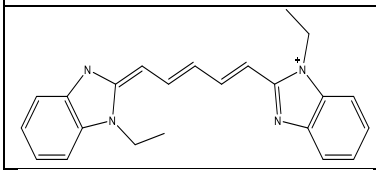
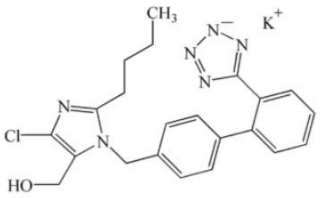
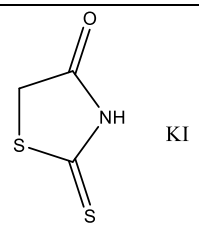
4. Combined Organic-Inorganic inhibitors

It's also important to mention that inhibition protection can be ensured by more than one inhibitor, such as adding halide ions (I^-, Cl^-, Br^-…). Generally, the synergistic effect between organic compound and halide ion interprets the inhibition process. The synergistic effect is significant because it describes how the combined action of two or more agents can produce a more substantial impact than the sum of their individual effects. Ionic liquids have gained significant attention in recent decades due to their diverse physics, chemistry, and engineering applications. Recent research has explored ionic liquid-based nanomaterial composites and highlighted their enhanced stability and utility when combined with nanoconfined materials. As Verma et al. reviewed in their paper, the physical and chemical properties of ionic liquids and their various applications, mainly as lubricants (Verma *et al.*, 2022). The ionic liquid characteristics are precious in fields like chemistry and material science, where they can enhance the effectiveness of corrosion inhibitors. By understanding these interactions, the performance of corrosion molecular structures can be improved in various applications. Many papers examined several ionic liquids as corrosion inhibitors in different metals and other mediums, such as El-Hajjaji *et al.*, 2023a &b, Nahlé *et al.*, 2022. Several corrosion inhibitors were regrouped in **Table 3** for the copper metal**,** indicating their experimental condition and inhibition behavior.

For example, Wang et al. developed a mixed-type corrosion inhibitor by complexing a Ni^{2+}cation with a tertiary amine (1-dimethylamino-2-propanol) and applying it as a corrosion inhibitor of copper in an alkaline solution. The findings indicate that introducing the mixed-type inhibitor (Ni^{2+}-1-dimethylamino-2-propanol) enhances the polarization resistance of the copper surface, achieving an inhibition efficiency of 48%, compared to 25% for the cation-free inhibitor (1-dimethylamino-2-propanol). This increased efficiency is attributed to the mixed inhibitor's stronger adsorption on the copper surface, as validated by X-ray photoelectron spectroscopy analysis and quantum chemical calculations. In another paper, Sun et al. (Sun *et al.*, 2024) incorporated into an ionic liquid monomer a vinyl and carboxyl functional groups to create a polymerized carboxylic acid ionic liquid (P[CPVI]Cl). This structure exhibited an inhibition efficiency of 88.28% in 0.5 mol·L^{-1} H_2SO_4 at 200 mg·L^{-1}, which is significantly higher than [CPVI]Cl's 66.56%. So, they explain this increase by stronger interactions and more excellent surface coverage. Moreover, they report that the P[CPVI]Cl and I^- ion combination synergized, achieving an inhibition efficiency of 98.83%. The I^- ions act as a bridge, forming a protective film that enhances corrosion resistance. This study offers an approach for developing high-performance corrosion inhibitors. Before this in 2019, Feng et al. (Feng *et al.*, 2019) studied the synergistic corrosion inhibition performance of 3,3′-Diethylthiadicarbocyanine iodide (DI)

and Thioflavin T (TT) for copper in 0.1 M HCl solution using electrochemical methods, weight loss tests, and SEM analysis. Also, they employed X-ray photoelectron spectroscopy (XPS) to explore the inhibition mechanism between the anions and cations of the ionic liquid. Indeed, as a result, they report that the inhibitor molecules interacted with copper to form a protective film, inhibiting corrosion through both physical and chemical adsorption and that the organic cations and halogen ions exhibited synergistic corrosion inhibition.

Table 3. Previous studies of synergistic effect used to protect the copper alloy

Inhibitor	Inhibitor concentration	Medium	Efficiency E%	Reference
	0.54 (wt.%)	KOH	48%	Wang *et al.*, 2024
	100 mg/L 5KI=14.4 mg/L	0.5M H_2SO_4	98%	Sun *et al.*, 2024
	100 mg/L KI=14.4 mg/L		93%	
	TT 4mM	0.1 M HCl	92%	Feng *et al.*, 2019
	DI		96%	
	40 mg/l	0.5 M H_2SO_4	92.8	Li *et al.*, 2020
	10 mM 10 mM	0.5 M H_2SO_4	99%	Solmaz *et al.*, 2011

In more detail, in a corrosive environment, halide ions enhance the adsorption ability of organic cations by forming interconnecting bridges between the negatively charged metal surface and the organic inhibitor, thereby significantly boosting the inhibition efficiency of organic compounds. The synergistic effect of halide ions follows the $I^- > Br^- > Cl^-$ order, with iodide providing the most substantial impact due to its larger ionic radius and high polarizability. So, the adsorption of halide ions renders the copper surface positively charged, facilitating the physical adsorption of organic cations through electrostatic interactions. Concurrently, the inhibitor molecules can chemically react with copper to form coordination bonds, resulting in chemical adsorption. This combined physicochemical adsorption process forms a protective film on the copper surface, shielding it from corrosive ions. The synergism between halide ions and the anions of ionic liquids further enhances the protection of copper against corrosion.

In 2020, Li and their collaborators (Li *et al.*, 2020) examined the corrosion inhibition performance of Losartan Potassium (LP)on copper in 0.5 M H_2SO_4 using electrochemical methods, surface morphology, and quantum chemical calculations. As a result, they found that LP functions as a mixed-type inhibitor, effectively suppressing both cathodic and anodic reactions by forming a protective film that follows the Langmuir adsorption model, primarily through chemisorption. From XPS analysis, they confirm the formation of a coordination compound between the nitrogen atoms in LP and copper. Moreover, this observation was confirmed by the Quantum chemical calculations, which identified the active sites on the nitrogen atoms.

Additionally, a paper by Solmaz demonstrated that Rhodamine (Rdn) molecules and iodide ions (KI) exhibit a robust synergistic inhibition effect on copper corrosion in 0.5 M H_2SO_4 solution. Rdn's inhibition efficiency increased with concentration, and adding KI significantly enhanced this effect. Potentiodynamic polarization revealed that Rdn and Rdn + KI inhibit both anodic dissolution and oxygen diffusion, with adsorption following the Langmuir isotherm and an adsorption energy of approximately -40 kJ mol^{-1}, indicating chemical adsorption. SEM and EDX analyses confirmed the formation of CuI(k) particles and a smoother surface in the presence of inhibitors. The study highlights the adequate corrosion protection the Rdn and KI combination provides(Solmaz *et al.*, 2011).

The inhibition of the dissolution of copper in HNO_3 solution has been studied by the thermometric technique in the presence of amino compounds and Cl^-. The results obtained by El-Kot & Al-Suhybani, (1987) show that the dissolution of copper in HNO_3 is retarded. The synergistic of organic compound and halide ion is widely studied by several authors (Bouklah *et al.*, 2006; Sisso *et al.*, 2020)

5. Natural extract inhibitors

Plant extracts are emerging as effective corrosion inhibitors due to their eco-friendly, biodegradable, and non-toxic properties. They offer a cost-effective alternative to synthetic inhibitors, often utilizing agricultural waste or by-products. The diverse chemical composition of plant extracts, containing compounds like alkaloids and flavonoids, enables them to adsorb onto metal surfaces and form protective films that prevent corrosion. These inhibitors were investigated in several metals, such as mild steel (Adil Mahraz *et al.*, 2024; Marsoul *et al.*, 2023; Fernine *et al.*, 2022; Hbika *et al.*, 2023; Lazrak *et al.*, 2020) and aluminum (Chaudhary *et al.*, 2022; Emembolu *et al.*, 2022Nambiar *et al.*, 2021) besides the copper alloy. Moreover, these extracts can be tailored to various environments, such

as acidic or saline conditions, making them versatile for industrial applications. Their non-toxic nature reduces health risks and safety concerns, making them safer. Overall, plant extracts present a sustainable and efficient solution for corrosion protection. Each of the thousands of uses employs a combination of these properties to help ensure that the material is ideally suited for the purpose. Good conductivity of electricity and heat is combined with strength, ductility, and excellent corrosion resistance, just a few of the properties of copper and its alloys (Mao *et al.*, 2024).

Several studies investigated copper using plant extract as a corrosion inhibitor in different media. For example, Wang et al. (Wang *et al.*, 2023) used natural plants as a source for extracting corrosion inhibitors is consistent with the principles of environmentally sustainable development. They studied the corrosion inhibition properties and mechanisms of sycamore leaf extract (SLE) on copper in a 0.5 M sulfuric acid solution. As a result, the electrochemical analysis demonstrated that SLE exhibited anti-corrosion solid performance. Also, the adsorption isotherm analysis indicated that the adsorption between the copper/solution interface at all temperatures involved a combination of physical and chemical interactions. They found that detecting Cu-N bonds on the copper surface after immersion in the SLE solution suggested that SLE formed a protective shield-like layer on the copper. However, molecular dynamics simulations revealed that the multi-anchor solid adsorption of SLE molecules was due to the presence of N and O atoms. In the same acidic solution, Gu et al. (Wang *et al.*, 2023) explored the corrosion protection properties of *Lycium barbarum* leaf extract (LBL) on copper in 0.5 mol/L sulfuric acid using a water-based extraction method, and Xu et al. (Xu *et al.*, 2022) utilized a water-based extract from *Leonurus japonicus* Houtt leaves (LLE). Indeed, they found that these extracts exhibit the copper surface from the corrosion process. Also, they used puissant characterization techniques such as XPS. Before this, in 2021, Feng et al. (Feng *et al.*, 2021) studied the anticorrosive effect of Veratrum root extract (VRE) on copper in H_2SO_4 using electrochemical tests and quantum chemistry calculations. So, the VRE showed excellent inhibition performance at various temperatures, reaching 97% efficiency at 200 ppm. However, Tafel analysis identified VRE as a mixed-type inhibitor, controlling both cathodic and anodic reactions. Moreover, they found that the quantum chemical calculations provided insights into the adsorption mechanism and the relationship between VRE's electronic structure of the studied compounds and its corrosion inhibition efficiency.

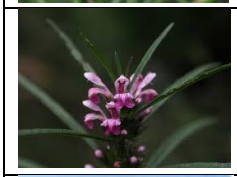
The copper alloy was also applied in a hydrochloric acid solution, as Feng, Ahmed, and Krishnaveni investigated with their collaborators. Indeed, Feng et al. (Neagu *et al.*, 2015) investigate the anti-corrosion potential of *Alchemilla vulgaris* (ALV) extract on pure copper in 1 M HCl. The study employed weight loss experiments, potentiodynamic polarization tests, scanning electron microscopy (SEM), and electrochemical impedance spectroscopy (EIS) to assess the effectiveness of ALV. As results indicated, ALV significantly inhibited corrosion, increasing effectiveness at higher concentrations, and the inhibition occurs via the adsorption of ALV molecules on the copper surface, consistent with the Langmuir adsorption isotherm. This research highlights the potential of ALV extract as a natural corrosion inhibitor in industries utilizing pure copper. Ahmed et al. (Ahmed *et al.*, 2020) identified BPE as an effective green inhibitor for copper corrosion in 1 M HCl. The corrosion inhibition efficiency increased with BPE concentration, achieving 94.5% at the highest studied concentration of 7 g/L, with comparable results of 94.2% from weight loss measurements over 48 hours. The adsorption of BPE on the copper surface fits the Langmuir isotherm model, indicating that it acts as a mixed-type corrosion inhibitor. XPS and FT-IR spectroscopy revealed that BPE's adsorption results from various components in the extract containing aromatic rings. These findings support the

potential use of BPE as a corrosion inhibitor for copper metal. In addition, Krishnaveni (Krishnaveni *et al.*, 2014) identified PJ extract as effective in inhibiting copper corrosion in 1 M HCl solutions. It serves as a strong eco-friendly green inhibitor for copper in this medium. The inhibition efficiency increases with the concentration of the PJ extract, reaching 93% at a concentration of 1 g/L. However, the polarization studies indicated that PJ functions as a cathodic-type inhibitor. Additionally, they report that surface analysis techniques, including SEM, EDS, AFM, and FT-IR, revealed that copper dissolution is significantly reduced due to the adsorption of PJ molecules on the surface, which forms a protective film.

The nitric acid solution was also investigated using several plants. For example, Fouda et al. (Fouda *et al.*, 2018) investigated Moringa Oleifera extract (MOL) as a corrosion inhibitor for copper. It achieved an inhibition efficiency (%IE) of 89% at 0.300 mol L^{-1}. The extract adsorbs physically and spontaneously on the copper surface, following the Langmuir adsorption isotherm. Surface analysis confirmed the formation of a protective film on the copper surface, with strong agreement between weight loss and electrochemical measurement results. In another paper, Fouda et al. (Fouda *et al.*, 2015) investigated *Ceratonia siliqua* extract, which was found to inhibit the corrosion of copper and brass in 1 M nitric acid, confirmed by several techniques, such as weight loss, polarization, EIS, and EFM techniques. SEM and EDX analyses confirmed the surface protection. The extract acted as a cathodic inhibitor, decreasing efficiency as temperature increased.

On the other hand, copper corrosion inhibition was also investigated when it was in contact with a seawater solution. For example, Rai et al. (Rai *et al.*, 2023) focused on the effectiveness of a water extract of mint leaves (AEML) as a green corrosion inhibitor for copper in 0.5 M NaCl. The study found that AEML's effectiveness increases with concentration through electrochemical measurements and surface imaging, achieving a maximum inhibition efficiency of 70% at 300 mg/L. Moreover, they found that the functional analysis using UV-visible and Fourier transform infrared spectroscopy confirmed the extract's properties, and the optical microscopy images demonstrated AEML's ability to protect copper in the saline solution. In addition, (Zdravković *et al.*, 2023) BLE extract contains caffeic acid, quercetin-3-O-glucoside, and kaempferol-3-O-glucoside. The authors report that, at the highest BLE concentration (15 g/L), the corrosion mechanism on the surface is governed by charge transfer rather than diffusion. Indeed, the inhibition efficiency improves with increasing BLE concentration, achieving a maximum of 97.19% in 0.5 M NaCl at 15 g/L BLE. Adsorption of the inhibitor onto the Cu-DHP surface follows the Langmuir adsorption isotherm, and the Gibbs free energy values suggest that the adsorption process is spontaneous and driven by physical adsorption. Moreover, Fekri et al. (Fekri *et al.*, 2022) studied Turnip peel extract (TPE) as a green corrosion inhibitor for copper in 3.5 wt% NaCl solution, achieving a maximum inhibition efficiency of 91.2% at 20% v/v. However, the GC-MS analysis revealed that S, O, and N heteroatoms in the TPE form a protective layer on the copper surface. In another paper, Bazzi et al. (Bazzi *et al.*, 2017) investigated Ziziphus lotus (wild jujube) as a corrosion inhibitor for copper. The effectiveness of the extracts was assessed through polarization methods and weight loss measurements, with surface morphology analyzed via SEM after immersion in both inhibited and uninhibited electrolytes. The results of this study demonstrated that the inhibitor significantly reduced the corrosion kinetics of copper, achieving an efficiency of 93% at 5 g/L, with increased effectiveness at higher concentrations.

Table 4. Previous studies of plant extract used to protect the copper alloy

Natural Plant	Name	Conc.	Medium	Efficiency	Reference
	sycamore leaf	400 mg/L	0.5 M H_2SO_4	91.7%	Wang *et al.*, 2023
	Lycium barbarum leaf	400 mg/L	0.5 M H_2SO_4	92.9%	Gu *et al.*, 2023
	Leonurus japonicus Houtt	400 mg/L	0.5 M H_2SO_4	90.9%	Xu *et al.*, 2022
	*Veratrum root* extract	200 mg/L	0.5 M H_2SO_4	97.5%	Feng *et al.*, 2021
	Alchemilla Vulgaris	7 g/L	1 M HCl	95.5%	Neagu *et al.*, 2015
	Bee pollen extract	7 g/L	1 M HCl	94.5%	Ahmed *et al.*, 2020
	*Zizyphus Lotuse - pulp of Jujube*	1 g/L	1 M HCl	93.1%	Krishnaveni *et al.*, 2014
	Moringa Oleifera	0.300 M	1M HNO_3 + H_3PO_4	89%	Fouda *et al.*, 2018
	Ceratonia siliqua	300 ppm	1M HNO_3	90%	Fouda *et al.*, 2015
	mint leaves	300 mg/L	0.5 M NaCl	91.2%	Rai *et al.*, 2023
	blackberry leaf	15 g/L	0.5 M NaCl	97.1 %	Zdravković *et al.*, 2023

	Turnip peel	20% v/v	3.5 wt% NaCl	91.2%	Fekri *et al.*, 2022
	Ziziphus lotus	5 g/L	Sea Water	93%	Bazzi *et al.*, 2017

Conclusion

Research on copper corrosion protection emphasizes the application of various inhibitors to prevent corrosion, particularly in harsh environments. Evaluating these inhibitors under different conditions enables the selection of efficient and cost-effective solutions for specific scenarios. Acidic and chloride-containing environments are noted to be particularly corrosive for copper. Therefore, current research aims to develop inhibitors that are not only effective and economical but also non-toxic and environmentally friendly. Future studies may prioritize the development of new organic or natural inhibitors and explore the synergistic effects of multi-component systems to improve copper protection.

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