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#### Chapter

# Anti-Corrosive Properties of Alkaloids on Metals

Hui-Jing Li, Weiwei Zhang and Yan-Chao Wu

# Abstract

Numerous organic inhibitors have been reported to be used for the corrosion inhibition of various metals, especially, the heterogeneous ring compounds bearing larger electronegativity atoms (i.e., N, O, S, and P), polar functional groups, and conjugated double bonds are the most effective inhibitors. Based on the concept of green chemistry, in recent years, the research of corrosion inhibitor has gradually extracted new environment-friendly corrosion inhibitor from natural animals and plants, because of its advantages in wide source, low cost, low toxicity and subsequent treatment. Alkaloids such as papaverine, strychnine, quinine, nicotine, etc., have been studied as inhibitors for metals corrosion in corrosive media. This chapter aims to review the application of alkaloids for the corrosion inhibition of metals in corrosive media, and the development trend in this field is prospected.

**Keywords:** iron, steel, copper, aluminum, inhibitor, alkaloids corrosion inhibition

#### 1. Introduction

Metals corrosion is a process in which a metal material loses its basic properties due to the action of the surrounding medium. Despite significant advances in the field of corrosion science and technology, corrosion is still a major obstacle to industry in all countries of the world. Steel, copper, zinc, aluminum as well as their alloys, has been extensively applied in construction and other industrial fields owing to its low price and good material properties [1–4]. However, one of the great challenges that metals face in industrial applications is that they are particularly susceptible to corrosion under acidic or alkaline conditions, which could lead to huge economic losses and potential environmental problems. A practical and cost-effective method to address such problems is the usage of corrosion inhibitors due to their easy synthesis, remarkable inhibition effect and economic advantages. The reported corrosion inhibitors against metals corrosion in acidic or alkaline medium are usually polar organic heterocyclic compounds bearing electronegativity atoms (i.e., nitrogen, oxygen, sulfur, and phosphorus), polar functional groups, and conjugated double bonds [5–7]. For example, azoles [8], Schiff bases [9], quinolones [10], thioureas [11] and pyrimidines [12] have been reported as effective corrosion inhibitors for metals in corrosive medium. The polar units of these corrosion inhibitors are regarded as the reaction centers to promote their adsorption on the metals surface, forming a protective layer to prevent the metals from undertaking corrosion attacks. Nevertheless, corrosion scientists are not very satisfied with chemical inhibitors as they are

generally not readily available, expensive, water-insoluble, and pollute the environment in their synthesis and applications processes. With the deterioration of pollution problems, the development and utilization of green, low-toxic organic molecular corrosion inhibitors has received attention. It is highly desirable that the novel metal inhibitors are non-toxic and environmentally friendly.

Recently, the use of natural products as corrosion inhibitors in different media has been widely reported as they are nontoxic, biodegradable and readily available in plenty. Among these natural products, alkaloids (nitrogen as one of their main constituent atoms) such as papaverine, strychnine, quinine, piperine, liriodenine, oxoanalobine and nicotine have been studied as inhibitors for metals corrosion in different media. Moreover, many plants can produce various types of alkaloids which makes this very interesting due to the presence of heteroatoms. These heteroatoms, nitrogen and the oxygen commonly associated with double bonds promote the adsorption between metals and inhibitors [4, 8]. That's why alkaloid plant extracts can reveal the fascinating features about inhibit corrosion, and alkaloids were found to prevent metal corrosion by adsorption of their molecules on metals surface to form a protective layer. Generally, there are two types of interactions of these inhibitors adsorption on metal surface. One is physical adsorption involving the electrostatic force between the ionic charge of the adsorbed species and the charge on the metal surface. The other is chemisorption, which involves charge sharing or transfer from the inhibitor molecules to the metals surface, forming coordination bonds or feedback bonds [9, 13]. Various natural organic inhibitors platforms are needed to develop new cleaning chemicals for green environment, which make the exploitation of late-model alkaloids class of corrosion inhibitors for metal protection a high priority. In this chapter, the corrosion inhibition effects of alkaloids (Table 1) as corrosion inhibitors on steel, copper, aluminum and other metal surfaces in different corrosive media such as hydrochloric acid, sulfuric acid, sodium chloride, etc., is reviewed.

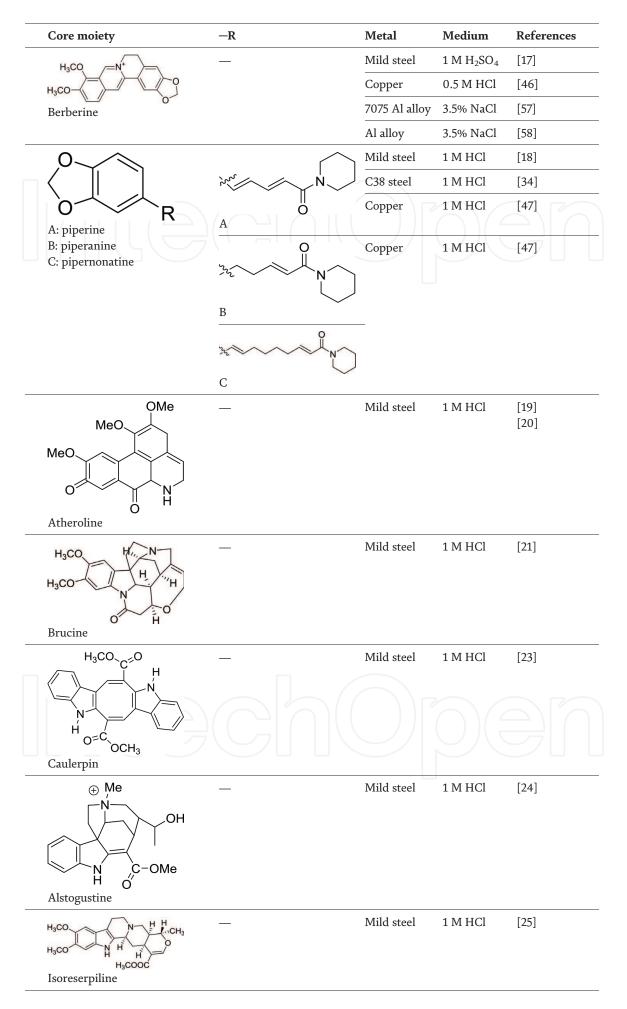
#### 2. Alkaloids as corrosion inhibitors

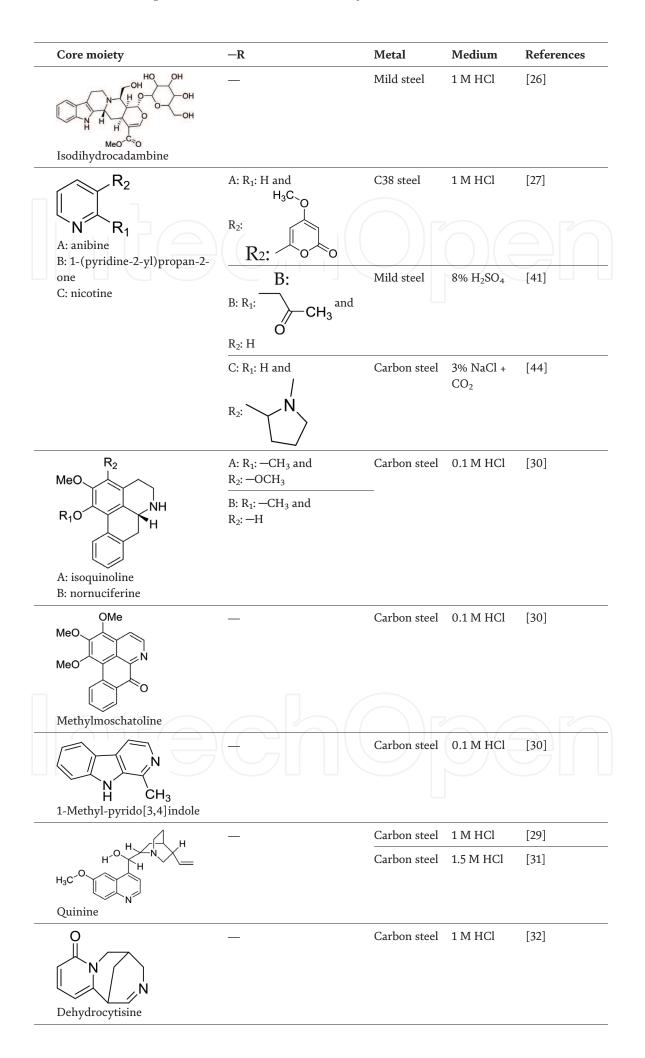
#### 2.1 Iron and steel inhibitor

Iron/steel is a strong metal that is widely used in multitudinous industrial fields, such as machinery manufacturing, petrochemical engineering, constructing and national defensing, etc. The combination of iron and other elements provides many acceptable material properties for application. However, iron materials are highly susceptible to corrosion in acid pickling, acid cleaning, acid descaling and oil well acidification, which will induce potential problems in industrial equipment, consequently leading to huge economic losses and serious environmental pollution. Generally, it is cost-effective to use natural organic inhibitors in acidic media to reduce corrosion of iron and/or steel. It has been reported that the adsorption depends mainly on the electronic and structural properties of the organic inhibitor molecule such as larger electronegativity atoms (i.e., N, O, S, and P), polar functional groups, conjugated double bonds, steric factors, and aromaticity.

Acidic solutions are widely used in various industrial processes, the corrosion and inhibition of iron/steel in this environment constitutes a complex process problem. The use of natural organic inhibitors to reduce the corrosion of iron/steel in acidic media is highly cost-effective, as they are renewable, cheap, easily available and non-toxic. In recent decades, a large number of reports on the inhibition of iron/steel in acid solutions by different types of natural alkaloids inhibitors at

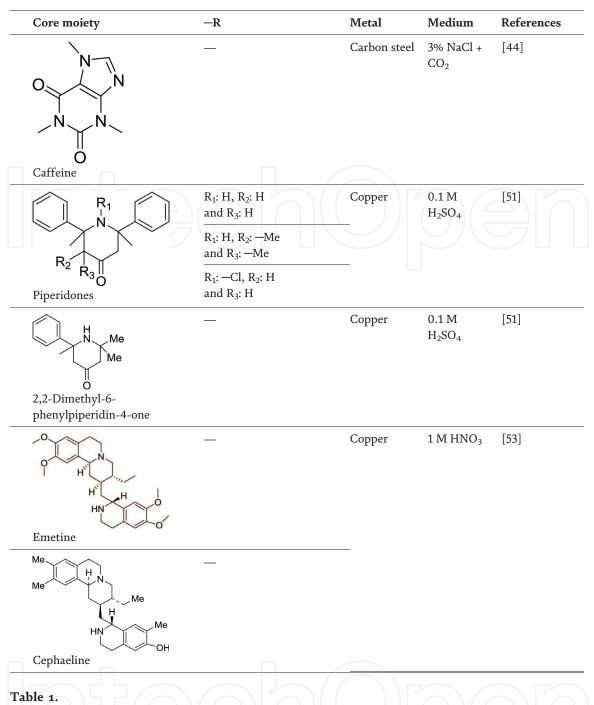
Anti-Corrosive Properties of Alkaloids on Metals DOI: http://dx.doi.org/10.5772/intechopen.81749





Core moiety	—R	Metal	Medium	References
O N N A: cytisine B: methylcytisine C: hydroxylcytisine	А: —H В: —CH <sub>3</sub> C: —OH	Carbon steel 	1 M HCl	[32]
A: liriodenine B: oxoanalobine	A:H B:OH	C38 steel	1 M HCl	[33]
H <sub>3</sub> COOC H <sub>3</sub> COOC Geissospermine	_	C38 steel	1 M HCl	[36]
H N R A: tryptamine B: indole	A:(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>	Iron	0.5 M H <sub>2</sub> SO <sub>4</sub>	[37]
	В: —Н	Mild steel	1 M HCl 1 M H <sub>2</sub> SO	[43]
MeO H H H H H H H H H H H H H H H H H H H	_	Mild steel	1 M H <sub>2</sub> SO <sub>4</sub>	[39]
Brucine	A. 11	Mild at al	05.14	[40]
R N OH A: vasicine B: vasicinone	A: -H B: =0	Mild steel	0.5 M H <sub>2</sub> SO <sub>4</sub>	[40]
	А: —Н	Steel	2 M HCl 01 M H <sub>2</sub> SO <sub>4</sub>	[42]
R A: sparteine		7055-T6 Al alloy	0.5 M NaCl	[59]
B: lupanine	B:=0	Steel	2 M HCl 01 M H <sub>2</sub> SO <sub>4</sub>	[42]
		7055-T6 Al alloy	0.5 M NaCl	[59]
	_	Steel	2 M HCl 01 M H <sub>2</sub> SO <sub>4</sub>	[42]
Multiflorine		7055-T6 Al alloy	0.5 M NaCl	[59]

#### Alkaloids - Their Importance in Nature and Human Life



List of alkaloids for corrosion inhibition properties of various metals.

domestic and foreign scholars. As early as the 1970s, the researchers carried out a large number of preliminary exploratory studies on alkaloids corrosion inhibitors, and made some progress. The research of alkaloid corrosion inhibitors is mainly carried out in hydrochloric acid and sulfuric acid medium. In 1986, Ramakrishniah reported an excellent papaverine pickling inhibitor [14], further introducing the research status of alkaloid corrosion inhibitors. It is pointed out that the organic corrosion inhibitor molecule is usually composed of a polar agent centered on N, O atoms and a nonpolar group composed of C, H atoms, which can be bonded with the metal surface in the form of a bond and produce physical or chemical adsorption. Alkaloids namely pyrrolidine [15] as an inhibitor for iron in 1 M HCl; pomegranate [16], berberine [17], piperine [18], atheroline [19, 20], brucine [21], tropane, pyrrolizidine [22], caulerpin [23], indole [24], isoreserpiline [25], 3β-isodihydrocadambine [26], anibine [27], strychnine and quinine [28] as inhibitors for mild steel in 1 M HCl; quinine [29], *O*-methylisopiline, (–)-nornuciferine, *O*-methylmoschatoline [30], quinine sulfate (6'-methoxycinchonan-9-ol-sulfate

dehydrate) [31] and cytisine [32] as an inhibitor for carbon steel in 1 M HCl; liriodenine, oxoanalobine [33], piperine [34], oxoaporphinoid [35] and geissospermine [36] as inhibitors for C38 steel in 1 M HCl; tryptamine [37] as an inhibitor for iron in 0.5 M H<sub>2</sub>SO<sub>4</sub>; piperine [38], brucine [39], vasicine, vasicinone [40] and isopelletierine [41] as inhibitors for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>; sparteine, lupanine, multiflorine [42] and indole [43] as inhibitors for mild steel in 1 M HCl and  $0.5 \text{ M H}_2\text{SO}_4$  have been investigated against the corrosion of iron/steel by weight loss measurements, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The experimental results revealed that these alkaloids were excellent green inhibitors, and their inhibition efficiency increased with the increase of inhibitor concentration and decreased with increase of temperature. Polarization curve results demonstrate that most of the alkaloids compounds have been classified as mixed inhibitors under the studied acidic conditions. Only the indole alkaloids act as an anodic type inhibitor in HCl and as a mixed type in H<sub>2</sub>SO<sub>4</sub> [43]. The Nyquist plots revealed that the charge transfer resistance increased and the double layer capacitance decreased as the concentration of the inhibitor increased. In addition, the inhibition efficiency obtained by weight loss method and electrochemical tests were consistent in all studies. The adsorption of most alkaloids corrosion inhibitors on the steel surface belongs to Langmuir isothermal type. Howbeit, the adsorption of a small amount of alkaloids inhibitors, namely piperine, caulerpin, brucine and quinine on the metal surface was found to obey Temkin's adsorption isotherm in acid medium. But berberine [17] and tryptamine [37] follow the Flory-Huggins adsorption isotherm and Bockris-Swinkels adsorption isotherm on the metal surface, respectively. These adsorption isotherms were calculated from Eqs (1) to (4):

$$\frac{c}{\theta} = \frac{1}{K_{ads}} + c \qquad \text{Langmuir isothermal} \tag{1}$$

$$\exp(-2a\theta) = K_{ads}c$$
 Temkin's adsorption (2)

$$\log\left(\frac{\theta}{c}\right) = \log x K_{ads} + x \log\left(1 - \theta\right) \qquad \text{Flory} - \text{Huggins adsorption} \tag{3}$$

$$\frac{\theta}{(1-\theta)^{x}} \frac{\left[\theta + x(1-\theta)\right]^{(x-1)}}{x^{x}} = K_{ads}c \quad \text{Bockris} - \text{Swinkels adsorption}$$
(4)

where *c* is inhibitor concentration,  $\theta$  represents surface coverage, *x* means the number of adsorbed water molecules replaced by one inhibitor molecule. The formation and properties of the adsorbed films on the steel surface have been investigated using scanning electron microscope (SEM) [17, 19, 20, 22, 24–26, 36, 38, 39, 43], X-ray photoelectron spectroscopy (XPS) [27, 32], FTIR spectroscopy [19–26, 39, 41, 43] and atomic force microscopy (AFM) [23]. The effect of temperature on inhibitive performances were studied to provide more detailed insights into the kinetics and thermodynamics of metal corrosion in acid solutions. Quantum chemical calculations were employed to provide insightful quantitative information to conclude the correlation between molecular structures and inhibition performance.

Metal corrosion also occurs in industrial processes under neutral conditions. Therefore, inhibiting metal corrosion under neutral conditions is also an important research direction. Numerous studies revealed that caffeine and nicotine can act as effective corrosion inhibitors for iron/steel in neutral environment. Corrosion inhibition of carbon steel by caffeine (1,3,7-trimethyl-purine-2,6-dione) and nicotine (3-(1-methylpyrrolidin-2-yl)pyridine) [44] in 3% NaCl solution with CO<sub>2</sub> was

investigated using various techniques. Potentiodynamic polarization curve results showed that these compounds belonged to mixed-type inhibitors which primarily inhibited the cathodic reaction, and this effect still exists at low inhibitor concentration, indicating that these compounds are good inhibitors in 3% NaCl + CO<sub>2</sub> conditions ( $\eta > 90\%$  for caffeine and > 80% for nicotine). The thermodynamic analysis of Langmuir model shows that the adsorption of these alkaloids is physical adsorption. Surface analysis (SEM-EDS) confirmed that the inhibition effect was due to the adsorption of caffeine or nicotine molecules on the surface of carbon steel solution. The effect of temperature for caffeine and nicotine was also studied by electrochemical impedance spectroscopy (EIS), demonstrating that the best inhibitor was caffeine, as its structure has more active sites in the oxygen and nitrogen heteroatoms, and more easily adsorbed on the steel surface. In addition, caffeine (1,3,7-trimethylamine) and nicotine (1-methyl-2-pyrrolidinyl) pyridine) [45] as corrosion inhibitors for cast iron in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution was evaluated by electrochemical techniques. The results showed that the two compounds added as corrosion inhibitors showed considerable corrosion resistance. The formation of bimolecular layer by additives can effectively inhibit oxidation and improve the protection performance of WD-40 oil.

#### 2.2 Copper inhibitor

Copper and its alloys have a wide range of applications in the industrial field due to their high electrical and thermal conductivity. Nevertheless, copper is extremely sensitive to corrosion in acid and alkaline solutions, and thus result in huge economic losses and potential environmental problems. A practical and effective solution to this problem is to use organic corrosion inhibitors. At present, the copper corrosion inhibitors used in industry mainly include: azole type, amine type and pyridine type corrosion inhibitors mainly containing N compounds. However, such compounds are highly toxic and pose a great hazard to operators and the environment. Therefore, the research and development of high efficiency, low toxicity, environment-friendly corrosion inhibitor is one of the main directions of corrosion inhibitor development. In recent years, researchers have applied natural alkaloids as copper corrosion inhibitors, which are non-toxic, environmentally friendly, simple preparation process and low cost. These organic compounds customarily contain polar functional groups with N, S or O atoms, and have triple or conjugated double bonds in their molecular structure, which are the main adsorption centers.

The research on the inhibition effect of alkaloids on copper is mainly carried out in hydrochloric acid, sulfuric acid and nitric acid. Corrosion inhibition of copper by berberine (5,6-dihydro-9,10-dimethoxybenzo[g]-1,3-benzodioxolo[5,6-a] quinoliziniu-m) [46] in 0.5 M HCl and piperine, piperanine, pipernonatine, N-11-(3,4-methyl-enedioxyphenylhmdecatrienoyl)-piperidine [47] in 1 M HCl; caffeine [48], quinine, strychnine [49, 50], piperidine, piperidones (2,6-diphcnylpiperidin-4-on, 3-methyl-2,6-diphenylpiperidin-4-on, 2,2-dimethyl-6-phenylpiperidin-4one, N-chloro-2-6-diphenylpiperidin-4-on) [51] in 0.1 M H<sub>2</sub>SO<sub>4</sub>; hyoscine, atropine, hyoscyamine [52], emetine, cephaeline [53] in 1 M HNO<sub>3</sub> was investigated by gravimetric, electrochemical, surface, and quantum chemical calculations methods. These compounds were found to exhibit good inhibition performance and the corrosion inhibition efficiency increased with increasing concentration. Polarization curves showed that all of those alkaloids are determined as mixed-type inhibitors in the studied solutions, and the results were consistent with those obtained by weight loss. The adsorption of a majority of alkaloids on copper surface obeys the Langmuir isotherm model, whereas quinine and strychnine were found to follow Bockris-Swinkels adsorption isotherm in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution. The surface morphologies of

copper specimens after immersion in test solution without and with studied alkaloids inhibitors were observed by SEM and AFM. These experimental results were also supported by quantum chemical calculations, which provided insightful quantitative information to conclude the correlation between molecular structures and inhibition performance.

Besides, copper can be severely corroded in sea water and chloride environments due to the presence of large amounts of chloride ions, and the anodic dissolution of copper is affected by the concentration of chloride ions. When the chloride ion concentration is below 1 M, the anode dissolves to form CuCl, followed by the formation of CuCl<sub>2</sub> when excess chloride ions are present [54]. The inhibition effect of some alkaloids on copper has been evaluated by various techniques. For example, see [14] papaverine, brucine, strychnine, ephedrine and cinchonidine was investigated using weight loss in 100 ppm sodium chloride solutions. It's interesting to note that brucine, strychnine and cinchonidine can inhibit the corrosion of copper, while papaverine and ephedrine accelerate the corrosion of copper. The results also showed that cinchonidine had the best inhibition performance with an efficiency of 94%. In addition, the corrosion inhibitive action of copper corrosion in 1.5% sodium chloride solution was studied by various forms of the piperidine moiety [55]. Results indicated that both piperidine and piperidine dithiocarbamate were excellent copper corrosion inhibitors, and the properties of two compounds are classified as mixed-type inhibitors. At the optimum concentration, the maximum inhibition efficiency of the two compounds differs significantly, which is mainly determined by the properties of the substituents in the molecule. These studies have shown that the adsorption of corrosion inhibitor on the copper surface to form a protective film is the main reason for inhibiting copper corrosion. The adsorbed alkaloid forms a complex with Cu<sup>+</sup>, thereby preventing the formation of copper chloride complexes.

#### 2.3 Aluminum and their alloys inhibitor

Aluminum and its alloys are widely used in aviation, construction and automotive industries due to their light, good electrical and thermal conductivity, high reflectivity, high strength-to-density ratio and oxidation resistance. The oxidation layer of aluminum has a natural corrosion protection, but if exposed to an erosive environment, the metal is highly susceptible to corrosion, especially in the presence of chloride ions (Cl<sup>-</sup>), such as in seawater and sodium chloride solution, the oxide is broken down. Therefore, it is still a great challenge to improve the corrosion resistance of aluminum and its alloys. Corrosion inhibitors are widely used in the industry to reduce the corrosion rate of metals and alloys in contact with corrosive environments.

Some literature studies have shown that various alkaloid corrosion inhibitors are widely used to prevent the dissolution of aluminum and its alloys in alkaline and chloride solution. The corrosion inhibition of pyridine for aluminum in 1 M NaOH solution [56], berberine namely 5,6-dihydro-9,10-dimethoxybenzo[g]-1,3-benzodioxolo[5,6-a]quinolizinium for 7075 aluminum alloy in 3.5% NaCl solution [57, 58], sparteine, lupanine and multiflorine for 7075-T6 aluminum alloy in 0.5 M NaCl solution [59] has been evaluated by weight loss, potentiodynamic polarization and EIS techniques. It is found that they are mixed type inhibitors in the studied conditions. In addition to the Temkin's adsorption of 5,6-dihydro-9,10-dimethoxybenzo[g]-1,3-benzodioxolo[5,6-a]quinolizinium, the adsorption of other alkaloids inhibitor on the copper surface follows Langmuir adsorption isothermal type. The thermodynamic parameters were calculated to study the adsorption mechanism. In some alkaloid studies, SEM, SECM, UV were implemented to investigate

the correlation between the surface properties of metals and electrochemical corrosion behavior, and the adsorption behaviors of molecules on the aluminum and its alloys surface was discussed by electrochemical test and surface analysis.

#### 3. Development prospect

With the progress and development of industry and science and technology, the corrosion inhibitor science and technology has been developed and improved, and the researchers have done a lot of work on the research direction of inhibitors. Among them, environment-friendly corrosion inhibitors, especially alkaloids, have aroused wide attention of researchers and become one of the main directions of the development of corrosion inhibitors in the future. Despite the progress and achievements in the study of alkaloids corrosion inhibitors, there are still many problems that need to be solved. There are many varieties of alkaloids corrosion inhibitors developed by researchers, but not many industrialized production, which is mainly due to the large amount of alkaloid inhibitors and high cost compared with the corrosion inhibitors currently used in industry. Therefore, in the future, we should focus on the study of extracting effective constituents from natural plants, marine flora and fauna, and strengthening the study of low toxicity or non-toxic organic molecule corrosion inhibitor synthesized by synthetic multifunctional base, and making the corrosion inhibitor by compounding or modifying to realize the optimum utilization of resources. In addition, the theory is imperfect, the molecular design lacks the theory instruction. Molecular design has been widely used in the development of fine chemicals, but in the development of environmentally friendly corrosion inhibitor new products due to the lack of systematic theoretical guidance, there is still controversy over the mechanism of corrosion inhibition of many corrosion inhibitors. This requires the use of advanced chemical technologies such as quantum chemistry theory and molecular design to synthesize efficient, multifunctional and environmentally friendly organic corrosion inhibitors. At the same time, using modern advanced analytical instruments and computers to study the adsorption behavior and mechanism of inhibitor molecules on metal surface from the molecular and atomic levels to guide the research and development of corrosion inhibitors.

#### 4. Conclusions

The corrosion inhibition effects of alkaloids on different metals in various corrosion media at room and higher temperature was reviewed. Weight loss, electrochemical studies, surface morphology and quantum chemical studies have been reviewed. The inhibition behavior of alkaloid inhibitors on metals was reviewed by weight loss method, electrochemical measurements, surface analysis and quantum chemical calculations. The studies showed that all these alkaloids are good corrosion inhibitors and the majority alkaloids acted as mixed-type inhibitor. Various adsorption isotherms were analyzed, the majority alkaloids were found to follow the Langmuir adsorption isotherm, and a few followed Bockris-Swinkels and Temkin's adsorption. This review will be useful for corrosion inhibitor research and provide new possible considerations in the design of practical alkaloids-type corrosion inhibitors for metals in corrosive solution.

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## **Conflict of interest**

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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