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Review

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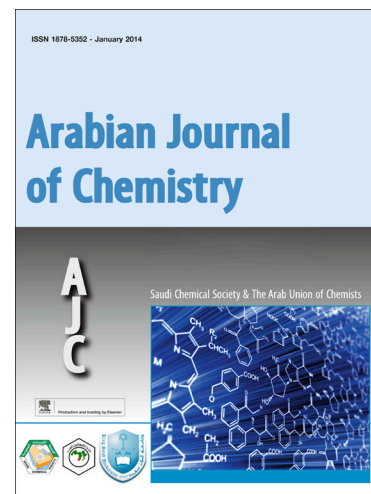
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Review article

Amino Acids and their Derivatives as Corrosion Inhibitors for Metals and Alloys

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Abstract

In the last two decades, research in the field of corrosion inhibitors had been directed toward the goal of using cheap effective molecules of low or non-negative environmental impact to replace the environmentally hazardous compounds. One of the encourager compounds which can be used as safe corrosion inhibitors are amino acids. They are environmentally friendly, non-toxic, biodegradable and relatively cheap. On other hand, the development of computational modeling helps to understand the inhibition mechanism of those compounds and to develop the newly designed inhibitors. In this review, most of contribution made in literature on the use of amino acids and their derivatives as corrosion inhibitors for metallic alloys materials were presented and discussed.

Keywords

Corrosion inhibitor; amino acid; amino acid derivative; metal; alloy; green inhibitor

1. Introduction

Corrosion is more than just an inevitable natural phenomenon; its impact is felt in three areas of concern, namely economics, safety, and environmental damage. Metallic corrosion, seemingly innocuous, affects many sectors (Sastri 2011). **Fig. 1** shown the elements of the costs of corrosion included capital, design, and control, as well as associated costs. The high costs of corrosion have a significant effect on the national economy, in general, corrosion costs amount to about 2–4% of gross national product. Therefore, it is necessary that corrosion personnel adopt corrosion control measures in order to avoid corrosion losses, which are about 25% of the costs are avoidable when these measures are adopted. Furthermore, corrosion prevention arrests the degradation of metals, and hence contributes in a significant way to the preservation of resources with minimum damage to the environment. In another hand, one of the most important impacts of corrosion is safety. While safety should be uppermost in the mind of industrial personnel, accidents do occur, in spite of great precautions. So, corrosion is not only expensive but also poses risks to human life and safety. For these reasons research on this phenomenon and its prevention have been highly interesting from the number of published scientific papers in the literature from 1907 to 2003

that increase from 35 to 10655 papers, respectively (Sastri et al. 2007). According to the corrosion aspect, its mechanism or the conditions where it is developed, Fontana defined eight forms of corrosion, as general corrosion, pitting corrosion, intergranular corrosion, parting, galvanic corrosion, crevice corrosion, stress-corrosion cracking, and erosion corrosion (Fontana 1975).

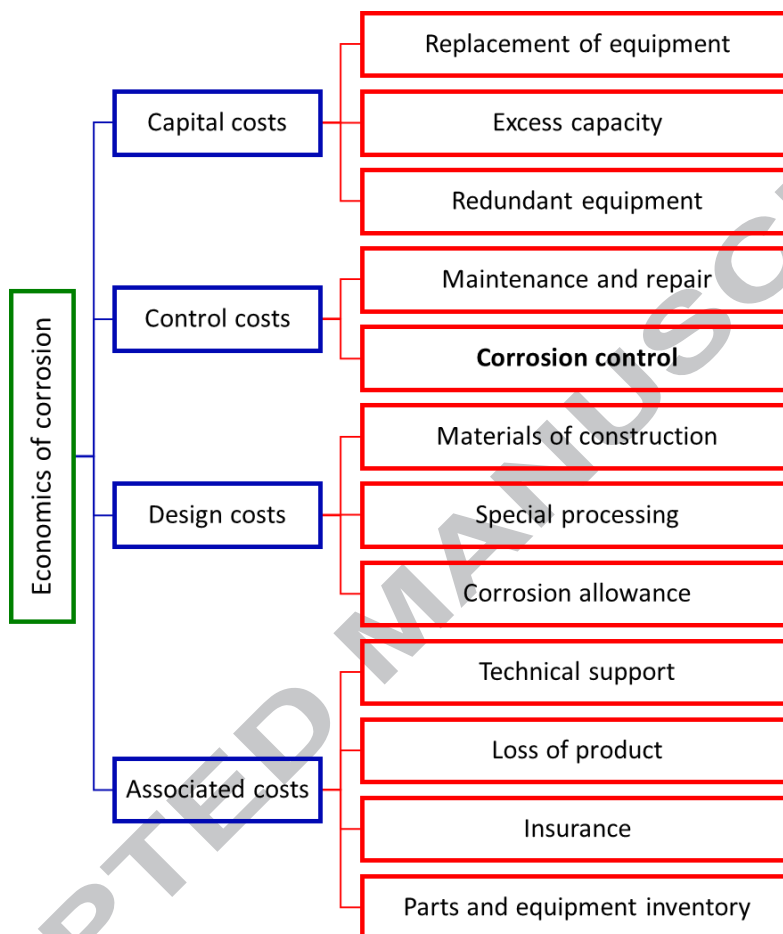


Fig. 1. The economic costs of corrosion

In 1957, Vernon presented an outline scheme of “Methods of Preventing Corrosion” which are defined in four categories: modification of procedure, modification of environment, modification of metal, and protective coatings (Sheir et al. 1994). In our case, we will focus on the second method of combating corrosion, in particular by using the corrosion inhibitor. The last is a chemical substance that, upon addition to a corrosive environment, results in reduction of corrosion rate to an acceptable level. It can function in two ways: first, situations where the added inhibitors can alter the corrosive environment into a noncorrosive or less corrosive environment through its interaction with the corrosive species. Secondly, the corrosion inhibitor interacts with the metal leading to the formation of protective film on surface.

2. Eco-friendly corrosion inhibitor

The field of corrosion inhibitors is undergoing dramatic changes from the viewpoint of environmental compatibility, due to the environmental agencies in different countries which have imposed the strict rules and regulations for the use and

discharge of corrosion inhibitors, like toxicity, biodegradability and bioaccumulation criterions (Sastri 2011). Thus, the development of novel corrosion inhibitors with a minimal or zero negative effects has been considered to be more important and desirable, so called eco-friendly or green corrosion inhibitors (Raja and Sethuraman 2008).

As in the case of “conventional corrosion inhibitors”, eco-friendly inhibitors can be classified into two categories, namely organic and inorganic eco-friendly inhibitors (**Fig. 2**). As Amitha Rani et al. cited in their review (Rani and Basu 2012), some researcher groups have reported the successful use of naturally occurring substances (e.g. plant extracts) as green corrosion inhibitors for metallic materials in various corrosives media. The same conclusion has been pointed out by Gece (Gece 2011) in using the drugs. Moreover, in several published papers (Jmiai et al. 2017; Malik et al. 2011; Oukhrib et al. 2017; Umoren 2009; Umoren and Eduok 2015; Verma et al. 2017), the authors have noted the significance of some biopolymers (like chitosan and cellulose or theirs derivatives), surfactants, and ionic liquids against corrosion of metals. By means of heteroatom(s) localized on functional group(s) or aromatic ring(s) in their molecular structures, those compounds can be interacted chemically or/and electrostatically with metal surface to form adsorbed molecular layer, which prevents or limits the contact of the surface with the aggressive agents in solution. It is knowing that at industrial-scale, generally, the organic inhibitors are used in acidic conditions, whereas inorganic inhibitors in near-neutral medium. In search of alternatives for chromate salts, nitrite and nitrates inhibitors, during the last decade a few research works were reported on the use of some rare earth compounds (e.g. CeCl_3 and LaCl_3) which can be considered as inorganic green corrosion inhibitors (Arenas et al. 2001; Arenas et al. 2002a; Arenas et al. 2002b; Behrsing et al. 2014; Bethencourt et al. 1998; de Damborenea et al. 2014). Especially, the lanthanide salts are found to exhibit the excellent inhibition properties (Arenas et al. 2001). This effect is attributed to the precipitation of rare earth particles on the metal surface, leading to formation of protective coherent film.

Despite all that, the application of such compounds as green corrosion inhibitors is judged by using cheap and environmental friendly compounds and process to produce it. Whereas, extraction and purification of naturally occurring substances, like plant extracts, is expensive and laborious as well as time-consuming process. Additionally, employing of organic solvents for extraction at high level may damage the environment. In the same way, use of complex organic synthesized molecules, such as drugs or ionic liquids, as corrosion inhibitors is also limited due to their multi-steps synthesis and extremely expensive (Grassino et al. 2016). Concerning the application of rare earth elements as corrosion inhibitors, it is limited by some disadvantages. Firstly, it is very complicated to separate rare earth element one from another in the rock. This reveals the efficiently limitation of employed technology. Secondly, the extraction process involves the production of a lot of waste such as acids, ammonia, and some radioactive elements, which can potentially affect the environment if not properly treat. Finally, the instability of the rare earth elements market, which can be a considerable problem in using those elements as corrosion inhibitors (Engineers 2009). All these reasons can be showed the limitation to apply those compounds as future green corrosion inhibitors.

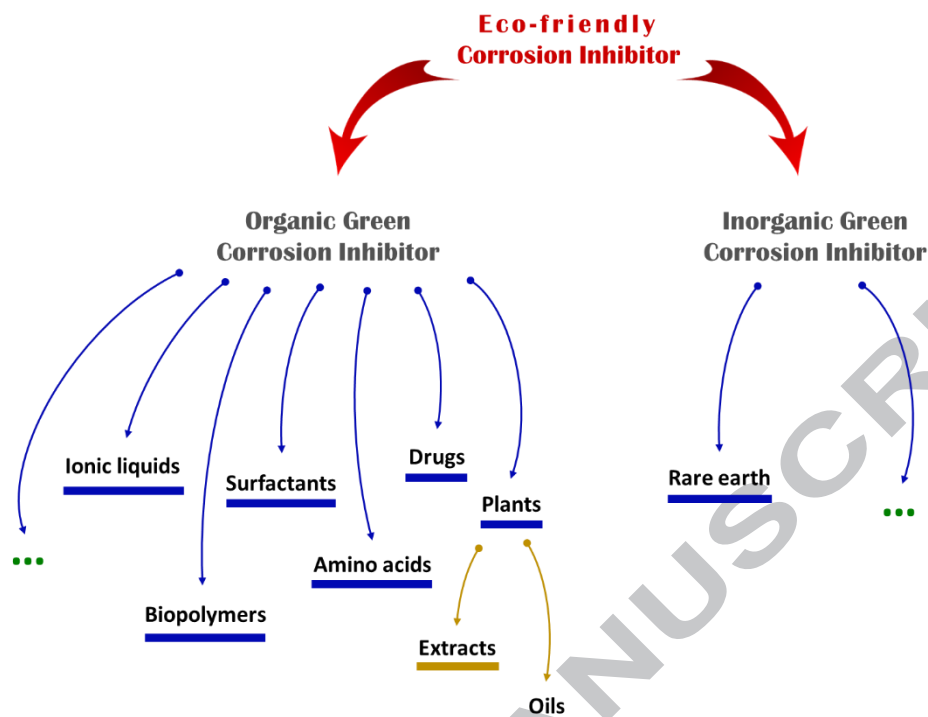


Fig. 2. Illustration of reported eco-friendly corrosion inhibitors

In this context, the corrosion inhibition property of some amino acids was evaluated by several researchers worldwide (Aouniti et al. 2013a; Ismail 2007; Oguzie et al. 2007a; Zhang et al. 2008a; Zhang et al. 2009a; Zhang et al. 2008b). These compounds have a particular importance to cite it as green corrosion inhibitors, due to their nontoxicity and biodegradability. Moreover, they are soluble in aqueous media, relatively cheap and easy to produce at high purity (Kilberg and Häussinger 1992; Zhang et al. 2011b). Amino acids (**Fig. 3**) are molecules that must possess at least one carboxyl ($-\text{COOH}$) group and one amino ($-\text{NH}_2$) group usually bonded to the same carbon atom (α - or 2-carbon). The other ligands of the α -carbon are $-\text{H}$ and R-group of different size, shape, and chemical properties (side chain). In physiological media, there are twenty different amino acids (**Fig. 3**) which are used to build up proteins in all species from bacteria to humans (Kilberg and Häussinger 1992). As shown in **Fig. 3**, the amino acids can be classified into subgroups according to their similarity in carbon skeleton and substituent groups (indicated by blue color in **Fig. 3**). In addition to environmental aspect, the presence of heteroatoms (e.g. S, N and O) and eventual conjugated π -electrons system on their molecular structures has attracted the attention of scientists to explore more their potential ability to act as eco-friendly corrosion inhibitors.

Besides, amino acids find various applications in food and animal feed technology as well as intermediates for the chemical industry (e.g. for pharmaceuticals and cosmetics applications). Essential amino acids are used in human parenteral nutrition, and glutamic acid and glutamates are used as flavor-enhancing compounds in the food industry (Lee and Wendisch 2017). The biotechnological production of amino acids occurs at the million-ton scale, which their demand has been steadily increased with annual growth rates of 5–7%. Amino acid producing strains of *Corynebacterium glutamicum*, which has been used safely for more than 50 years in food biotechnology, and of *Escherichia coli* are continuously improved using metabolic engineering approaches. Annually, about 6 million tons of L-glutamate and L-lysine were produced by fermentation

worldwide. The growth of the amino acid market is due to a growing world population and a higher demand for animal products (Al-Dahir et al. 2017; Deferrari et al. 2010; Lee and Wendisch 2017; Wendisch 2014).

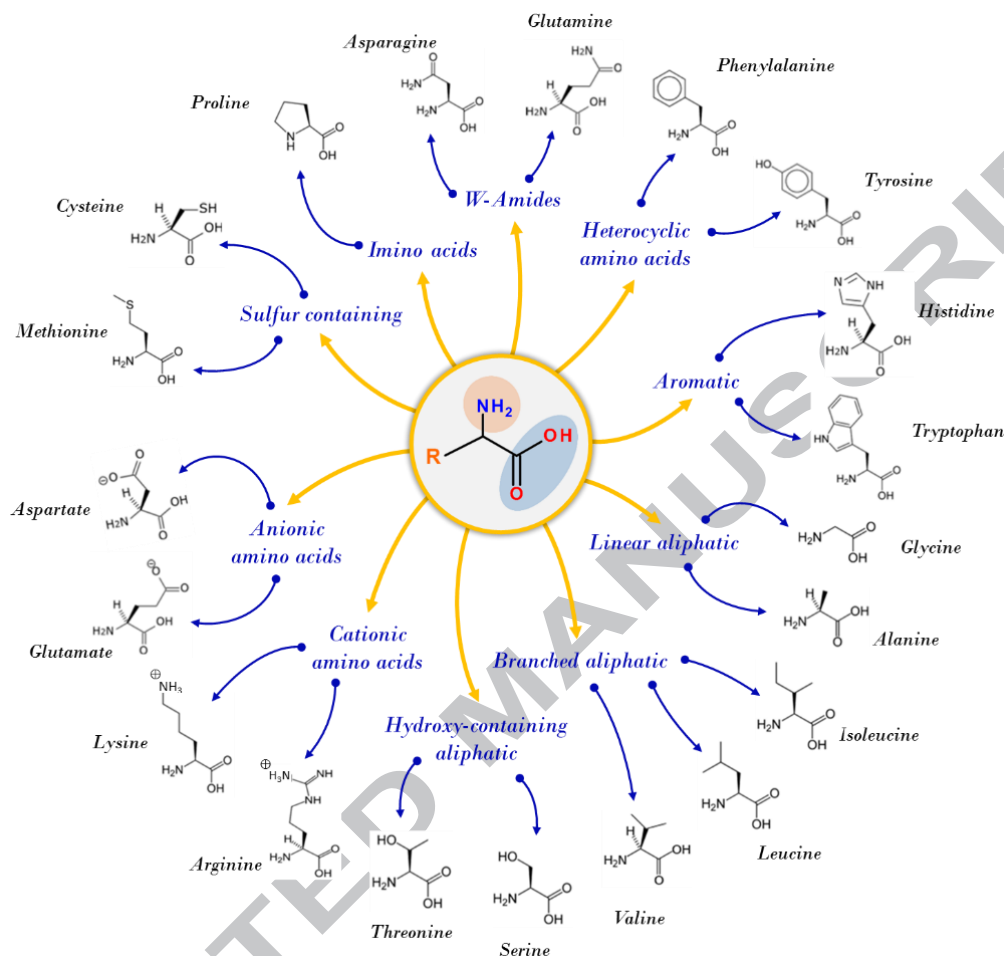


Fig. 3. Structures of the twenty physiological amino acids and their chemical classification

As our literature research showed, more than four decades preceded the first tentative use of amino acids compounds as corrosion inhibitors for metals (Mihara et al. 1969). Lately, because of the new environmental restrictions as mentioned above, the investigators had to evaluate the potential inhibitive effect not only of common amino acids but also of their derivatives for many metals in a variety of aggressive media (El-Hafez and Badawy 2013; Hammouti et al. 1995; Qian et al. 2013; Zhang et al. 2011c). As shown in **Fig. 4**, the authors have so far investigated the application of amino acids, as well as their derivatives against corrosion of iron and its alloys, which present more than the half of published work. Such interesting of authors can be related to tremendous industrial applications of these metallic materials.

To the best of our knowledge, there is no similar report on the use of those compounds or their derivatives as corrosion inhibitors for metals and alloys. In this view, we wrote this review paper to present and discuss the sum of published results on this topic. In the other hand, we hope to make it a landmark for the future research in this item. Hereinafter, the appeared works in the literature over the last four decades will be presented in the first part of this review via four sections (based on

the metal nature). The first section pointed on copper and its alloys, the second was about iron and its alloys, the third section concerned aluminium and its alloys, and other metallic materials are illustrated in the last section. Regarding the limitations of space, we summarized some other works on copper, iron and their alloys in tables A.1 and A.2 (in the appendices). The tables summarize studied metallic material, corrosive medium, tested compound(s) with or without additive, using experimental and/or computational methods, and the relevant findings including the inhibition effectiveness. In the second part of this two-part review, we will discuss the effect of some factors on the inhibition ability of amino acids compounds (section 4.1), using computational and modeling methods to explain this ability (section 4.2). Further, the limitations and disadvantages of applied theoretical methods will be presented. Afterward, the action mechanism (section 4.3) of amino acids compounds by different modes will be given. Finally, in the last section (4.4), we will define and present the new trends in using amino acids compounds to control corrosion phenomena through self-assembly monolayer and smart coating treatments.

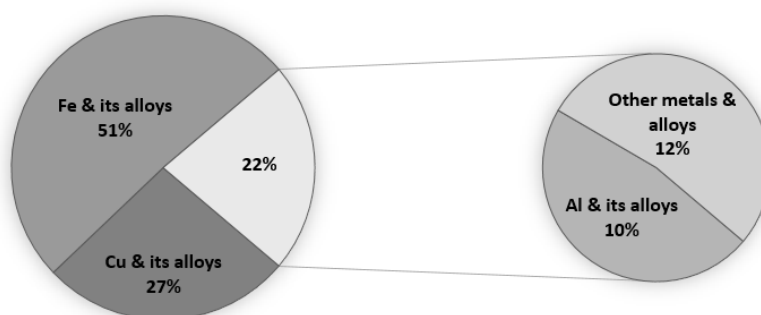


Fig. 4. The distribution of published papers (from 1970 to 2017) in the use of amino acids and their related compounds as corrosion inhibitors for various metal materials (These values occur as a result of our literature research based on Scopus, Thomson Reuters and Google Scholar data basis)

3. Amino acid compound as corrosion inhibitor

3.1. Copper and its alloys

Copper is a metal that has a wide range of application fields due to its good properties, especially, electric and thermal properties. It is used in electronics, for the production of wires, tubes, sheets, and forming their associated alloys. Copper is resistant toward the influence of atmosphere and many chemical species. However, it is known that in some aggressive medium, it is susceptible to corrosion (Antonijevic and Petrovic 2008). The use of corrosion inhibitors in such conditions is mandatory. The possibility to protect the copper and their alloys against corrosion has attracted many researchers, so until now numerous amino acids compounds have been investigated (Gomma and Wahdanb 1994; Zhang et al. 2014b). In following, we will cite almost published works on this topic.

By using electrochemical methods, Gomma et al. (Gomma and Wahdanb 1994) have investigated the anticorrosion activity of alanine (Ala), aspartic acid (Asp-A), glutamine (Glu) and lysine (Lys) in the corrosion of copper in 1M HCl solution. The results showed that at 10^{-3} M the inhibition efficiency follows the sequence: Ala > Glu > Asp-A > Lys.

However, at 10^{-5} M the sequence had changed to Lys > Ala > Asp-A > Glu, which indicated the importance of inhibitor concentration on the inhibition efficiency and consequently its effect on the adsorption processes. In their work, Moretti et al. (Moretti and Guidi 2002) reported the good inhibiting action of tryptophan in the short-time exposure and at the highest concentration for the corrosion of pure copper in aerated sulfuric acid, and by using spectrophotometric technique this amino acid even underwent over time (6 months) a photodegradation, but surprisingly enough this it did not affect its inhibition efficiency. In another study, the effect of pH of a 0.5M Na₂SO₄ solution on the inhibition performance of cysteine for copper has reported by Petrović et al. (Petrović et al. 2012) and Simonović et al. (Simonović et al. 2014). According to their results, cysteine was strongly physically adsorbed with slight chemisorption character on the copper surface in neutral and alkaline (pH 9) solutions, although, in acidic solution (pH 2) was mainly chemisorbed. Besides, its inhibitory activity was great in alkaline and acidic than in neutral solution. In addition to cysteine and histidine amino acids, Levin et al. (Levin et al. 2012) have discussed the action of two other bioorganic molecules, namely: adenine (**Fig. 5 (a)**) and purine (**Fig. 5 (b)**) on the corrosion of copper in a hydrocarbon medium. By using in-situ ellipsometry, atomic absorption spectroscopy, and a standard corrosion test, they found that adenine and purine have formed a thin film (in order of “nm” thickness) on the copper substrate, which explains its protective qualities regarding tested amino acids.

In aerated 0.5 M HCl solution, Zhang et al. (Zhang et al. 2005) conducted by using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy a comparative study between benzotriazole (BTA, **Fig. 5 (c)**)¹, alanine and cysteine. They noted that the sequence of inhibition efficiency was cysteine > alanine > BTA, and they acted all as anodic inhibitors for copper metal. In other study, Matos et al. (Matos et al. 2004) have related the cysteine inhibitory performance at higher concentrations (10^{-3} and 10^{-2} M) in de-aerated sulfuric media to film formation on the copper surface and it was a Cu(I)–cysteine complex.

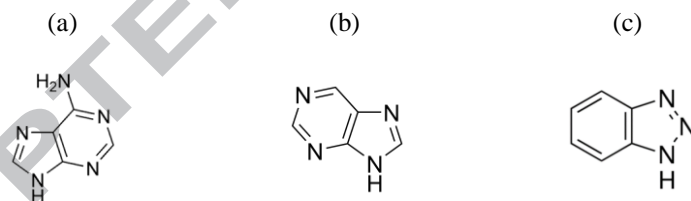


Fig. 5. Molecular structure of (a) adenine, (b) purine, and (c) benzotriazole

The anti-corrosion effect of two kinds of amino acids for copper in molar nitric acid solution (Barouni et al. 2010a; Barouni et al. 2008; Barouni et al. 2014; Barouni et al. 2013; Barouni et al. 2010b) has been reported by our laboratory. According to the findings of gravimetric and electrochemical measurements, cysteine and methionine revealed the best inhibition efficiency for the linear chain and tryptophan for the nonlinear chain amino acids category. Moreover, by using two semi-empirical quantum methods (i.e. AM1 and MNDO), we have established a good linear correlation between inhibition efficiency and the calculated quantum parameters of tested amino acids in vacuum phase. It is well known that container sulfur-molecule gives great inhibition efficiency (Bouzidi et al. 2012; Fekry and Tammam 2012; Helal and Badawy 2011;

¹ For decades, the most used corrosion inhibitor for copper is BTA, owing to its high inhibitive ability and low cost. Recently, the use of BTA and its derivatives has been restricted worldwide due to their high toxicity (Hammouti et al. 2012; Milošev et al. 2015).

Morad 2005; Oguzie et al. 2007b; ÖZCAN et al. 2008). In this context, the influence of methionine (MIT) and its derivatives, namely methionine sulfoxide (MITO, **Fig. 6 (a)**) and methionine sulfone (MITO2, **Fig. 6 (b)**) on copper in molar nitric acid medium, were investigated by combined experimental and theoretical study (Khaled 2010). The findings reveal that the inhibition efficiency of studied compounds increases as follows: MITO2 (90.7%) > MITO > MIT (81.6%) at 5×10^{-3} M, this behavior had correlated to their molecular structures by using quantum chemical at density functional theory (DFT) level and molecular mechanics calculations on Cu (111) surface.

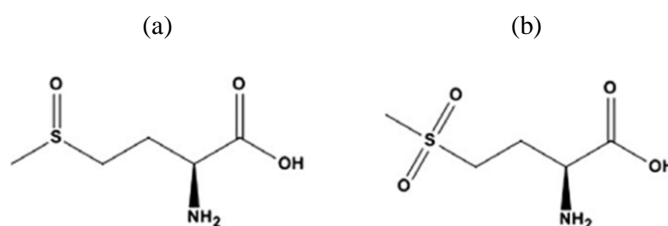


Fig. 6. Molecular structures of the methionine derivatives. (a) L-methionine sulfoxide (MITO) and (b) L-methionine sulfone (MITO2)

In the last years, the interaction between inhibitor and metal surface has attracted more attention by using the molecular dynamic simulations, as a suitable tool to model such interaction (Cang et al. 2012a; Cang et al. 2012b; Fu et al. 2010b; Fu et al. 2011; Khaled et al. 2012). Dai et al. (Dai and Zhang 2012) reported that glutamic acid (Glu-A) and aspartic acid (Asp-A) can adsorb on Cu (001) surface through their polar sites, which is important in the case of Glu-A amino acid. This can explain the high inhibition efficiency of Glu-A regarding Asp-A. For the same metal, but in 3% of amino-sulfonic acid solution, Wang et al. (Wang et al. 2013) have conducted a comparative study between a polymer of aspartic acid (polyaspartic acid / PASP) and a kind of environmental friendly corrosion inhibitor, namely imidazole (IM, **Fig. 7**). The electrochemical measurements indicated that polymer acts as a mixed-type inhibitor and it showed a better inhibition efficiency than IM compound. Further, as a notable result, the authors were found that there are a synergistic effect between those compounds, which the inhibition efficiency reached 89.8% at 1 g L^{-1} of PASP and 95.4% for 1 g L^{-1} of PASP + 0.5 g L^{-1} of IM formulation.

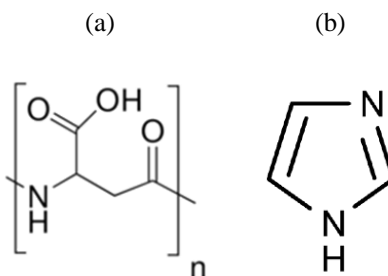


Fig. 7. Molecular structure of (a) polyaspartic acid and (b) imidazole

Milošev et al. (Milošev et al. 2013) conducted an experimental and a theoretical study through DFT/B3LYP method (with 6-311G** as basis set) coupled to molecular dynamic simulations to investigate the effect of some amino acids on the corrosion process of copper in 0.5 M HCl solution. In one hand, alanine and leucine were modestly accelerated the corrosion process

and for the rest tested amino acids, the inhibition efficiency was increased as follow: cysteine (50%) > histidine \approx arginine (25%) > threonine \approx tyrosine \approx tryptophan (12%) > methionine (10%) > glycine (3%) at 10mM. In another hand, the theoretical study has not supported the participation of nitrogen atom of amine group in the adsorption process of protonated amino acids forms, which the $-\text{NH}_3^+$ group was oriented away from the copper surface into the solution.

By combining copper with other metals (Ni, Zn, Sn, Al etc.), alloys can be made to fit almost any application where can be in contact with different environments. In this context, several researchers have pointed out the benefic effect of some amino acids to act as corrosion inhibitors, especially for copper-nickel and brass alloys. Badawy et al. (Badawy et al. 2006) have studied the effect of glycine, alanine, leucine, cysteine, lysine, histidine and glutamic acid against the corrosion of Cu-Ni alloys (with 5% and 65% of Ni) in neutral 0.06 M NaCl solution. The experimental findings have shown that the inhibition efficiency of tested substances depends on the content percent of nickel in the alloys. Further, a simple amino acid like glycine can be used as an efficient corrosion inhibitor for the Cu-Ni alloys in studied conditions. In other work, by using potentiodynamic polarization, electrochemical frequency modulation (EFM), scanning electronic microscopy coupled to EDX analysis and quantum chemical calculations via MNDO method, Nazeer et al. (Nazeer et al. 2012) have found that cysteine can be used to inhibit the corrosion of Cu10Ni alloy in sulfide-polluted salt water, moreover, a synergistic effect was observed when is mixed with KI. Moreover, the calculated quantum parameters validated the authors' experimental findings. The same trend has been noted by Saifi et al. (Saifi et al. 2010) for Cu30Ni alloy.

In three studies, Varvara et al. (Varvara et al. 2009; Varvara et al. 2010; Varvara et al. 2011) reported that cysteine gives adequate protection to bronze in $0.2 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4$ and $0.2 \text{ g L}^{-1} \text{ NaHCO}_3$ mixture solution regarding phenylalanine at pH 3, and alanine at pH 5. In addition, they noted that the inhibition efficiency depends on time immersion and concentration of tested amino acids. Radovanović et al. (Radovanović et al. 2013) have evaluated the capacity of cysteine to act as brass (Cu37Zn) corrosion inhibitor in 0.5 M Na_2SO_4 (at pH 7 and 9) solutions. Their results showed the considerable inhibition efficiency of this substance in weakly alkaline solution, which is attributed to the formation of a stable Cu(I)-cysteine complex on the copper surface, as reported previously by Matos et al. (Matos et al. 2004) for pure copper in sulfuric acid solution. Other works about using several amino acids or their derivatives as corrosion inhibitors for copper and its alloy are summarized in **Table A.1**.

3.2. Iron and its alloys

As can be seen in **Fig. 4**, the half of published works on the use of amino acids as corrosion inhibitor topic are devoted to evaluating this property for iron and their alloys. This can be related to the tremendous applications of those metallic materials in different industries fields, which implied more the interest of researchers. In this regard, Abd-El-Nabey et al. (Abd-El-Nabey et al. 1985) have determined the inhibitive action of cysteine, cystine (**Fig. 8**), methionine and alanine on mild steel metal in 1 N H_2SO_4 solution. The employed experimental approaches were gravimetric and potentiodynamic polarization methods. Among tested compounds, the best inhibitive effect was obtained for methionine, and the adsorption of the amino acids on the steel occurs in two steps: a monolayer of the adsorbate is formed on the metal surface, and this is followed by the deposition of a second adsorption layer. Proved by electrochemical measurements, Özcan (Özcan 2008) has reported that oxidize form of cysteine (i.e. cystine, **Fig. 8**) provides a good protection effect (86% at 5 mM) against mild steel

corrosion in sulfuric acid, and this effect was related to physical and chemical adsorption combination mode, as the ΔG_{ads} value indicated. As novel idea in valorization of excess sewage sludge (EES) generated by wastewater treatment plants, Su et al. (Su et al. 2014) have reported and confirmed the feasibility to use hydrolysate EES product as a cheap raw material for extracting value-added product as an ecofriendly corrosion inhibitor for steel in hydrochloric acid media. This effect was attributed to the presence of amino acids compounds (15 kinds) in the hydrolysate EES product, which can form a barrier at the metal/solution interfaces via adsorption process.

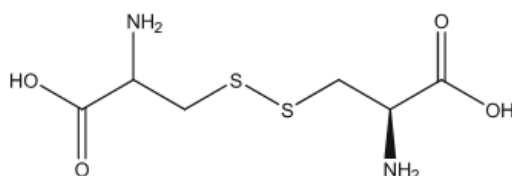


Fig. 8 Molecular structure of cystine

In other hands, the inhibition effect of twenty-two amino acids and four related compounds was studied by Hluchan et al. (Hluchan et al. 1988) against the corrosion of iron in de-aerated 1 M HCl solution. The obtained results indicated that hydroxyproline, creatine (**Fig. 9 (a)**), cystine and cysteine acted as corrosion accelerators. However, the best common amino acid was tryptophan, and for related compounds was 3,5-diiodotyrosine (**Fig. 9 (b)**) with an inhibition efficiency of 80% and 87% at 10 mM, respectively. This result can be attributed to the presence of favorable sites of adsorption on molecule, like the aromatic ring and iodine atoms. For the same metal and through weight loss method, DC and AC measurements, Zerfaoui et al. (Zerfaoui et al. 2004b) have tested the effect of the addition of five amino acids (glycine, leucine, aspartic, arginine and methionine) in citric acid media. They reported that the methionine is the best inhibitor and its inhibitive power was affected by the pH values of the solution, which increases with pH to reach 90% at pH 5. Moreover, the polarization measurements showed that the tested compounds are cathodic type inhibitors. The influence of hydrodynamic conditions on the inhibition efficiency of methionine versus the corrosion of mild steel in molar sulfuric acid solution was investigated by Ashassi-Sorkhabi et al. (Ashassi-Sorkhabi and Asghari 2008). As notable results, it was found that the surface becomes nobler with increasing rotation speed in blank solution. The inhibition efficiency for still electrode and low-speed rotations did not have a noticeable effect, in contrast at higher rotation speeds an increase in the efficiency was observed.

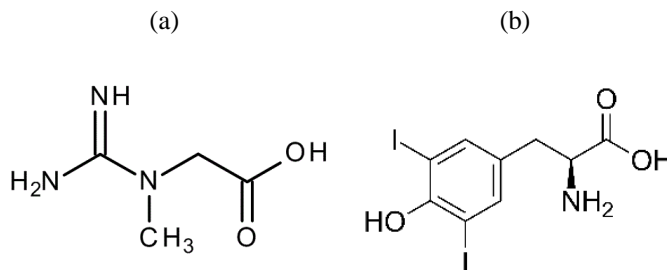


Fig. 9. Molecular structures of (a) creatine and (b) 3,5-diiodotyrosine.

Ashassi-Sorkhabi et al. (Ashassi-Sorkhabi et al. 2004) have studied the inhibition ability of some amino acids (alanine, glycine, and leucine) versus steel corrosion in different hydrochloric acid concentration solutions. The results indicated that

the inhibition efficiency ranged from 28% to 91% and these substances are physically adsorbed on the metal surface. In other work, Amin et al. (Amin et al. 2009) reported that glycine (Gly) acts as a mixt-type inhibitor, and the inhibition process was attributed to the formation of adsorbed film which is conformed by scanning electron microscopy coupled to energy dispersive X-rays. Further, the electrochemical and chemical results are in a good agreement and indicated that Gly is a good corrosion inhibitor for low alloy steel (ASTM A213) in 0.5 M hydrochloride solution. A team of researchers (Khaled and Abdel-Shafi 2013; Khaled and Al-Mhyawi 2013) have reported the effect of medium nature on the inhibition property of arginine for steel. The values of 60% and 79% as inhibition efficiency at 0.9 g L⁻¹ of studied substance was found in molar HCl and 3.5% NaCl solutions, respectively. By analysis of electrochemical curves, it is found that arginine acts as a mixed-type inhibitor. Furthermore, the shape of adsorption on Fe (111) was elicited by employing molecular dynamics simulations. A mixture solution of the acetic acid (0.50 M) and acetate (0.25 M) was used as aggressive media for carbon steel to explore the property of histidine and tryptophan amino acids to act as green corrosion inhibitors (Bobina et al. 2013a; Bobina et al. 2013b). As findings, the two compounds showed a near inhibition efficiency which was up to 80% at 10⁻² M, and adsorbed on metal surface through physical interactions.

Silva et al. (Selvakumar et al. 2013; Silva et al. 2006) have investigated the effect of cysteine (Cys) on the corrosion of 304L stainless steel in de-aerated molar sulfuric acid solution. Through electrochemical measurements and surface analysis technique, the authors showed that the presence of Cys at high concentration turns the metallic surface electrochemically active. However, Oguzie et al. (Oguzie et al. 2007b), in the case of low carbon steel, have found that the addition of Cys at low concentrations promoted the corrosion process, whereas an inhibiting effect was observed at higher concentrations, which was enhanced on de-aeration solution. The same authors (Oguzie et al. 2007b) were weight up the inhibition ability of another sulfur-containing amino acid, namely methionine (Met), against the corrosion of mild steel in sulfuric medium, also the synergistic effect of iodide ions was evaluated. Potentiodynamic polarization technique and atomic force microscopy were used in this study. The results reveal that Met inhibited the corrosion reaction by adsorption mechanism and the inhibition efficiency was significantly increased by addition of small amounts of KI. In this context, Abiola et al. (Abiola et al. 2004) reported the effect of acid solution nature (HCl or H₂SO₄) on its inhibition efficiency.

In his work, Morad (Morad 2005) has studies the effect of addition of some ions; namely, F⁻, Cl⁻ and Fe³⁺ on the inhibition efficiency of some amino acids containing sulfur atom on the corrosion of mild steel in phosphoric acid (40%) solution. According to the results of electrochemical investigation, the synergism or antagonism properties of added ions were found to depend on their nature and their blinding, for instance, the binary mixtures of Cl⁻ or F⁻ with cysteine or methionine are showed a good anti-corrosion ability, in contrast to those containing Fe³⁺ ions or ternary mixture ions and an amino acid. In addition, the benefic effect of copper ions (Cu²⁺) on the corrosion inhibition by cysteine in de-aerated sulfuric acid has been reported by El-Deab (El-Deab 2011). The inhibition efficiency was reached to 95% using 5 mM of cysteine + 25 μM of Cu²⁺ ions formulation, this good ability was attributed to the formation of Cu(I)-cysteine complex and/or cysteine self-assembly monolayer at Cu above the iron surface as affirmed by XPS measurement. In their published paper, Gowri et al. (Gowri et al. 2013) have inspected the action of glutamic acid (Glu-A) with and without addition of zinc ions (Zn²⁺) against the corrosion of carbon steel in natural sea water of India. In this case, a highest synergistic effect between tested amino acid and Zn²⁺ ions was found, which the inhibition efficiency increases from 35% at 200 ppm of Glu-A to 87% with

addition of small amount of zinc ions (at 25 ppm). In addition, the synergistic effect of some organic compounds has been reported elsewhere (Mobin et al. 2017; Mobin et al. 2016; Zhang et al. 2016). It was found (Mobin et al. 2016) that the inhibition effectiveness of cysteine (Cys) at 500ppm increases by addition (around 1 and 5 ppm) of three surfactants, namely: triton X-100 (TX), sodium dodecyl sulfate (SDS), and cetyl pyridinium chloride (CPC). The authors showed that the inhibition efficiency increased in the order: Cys + TX (97.76%) > Cys + CPC (91.99%) > Cys + SDS (95.09%) > Cys (85.62%) for mild steel in molar hydrochloride acid solution. The FTIR spectroscopy was employed to confirm the adsorption of inhibitors molecule on the metal surface.

In another side, the inhibition performance of novel amino acids derivatives for iron and its alloys have been reported by several authors (Amin and Ibrahim 2011; Amin et al. 2010a; Deng et al. 2012a; Deng et al. 2012c; Deng et al. 2012d; El-Sawy 1992; Morad 2008; Pech-Canul and Chi-Canul 1999; Shaban et al. 1993). The obtained results indicate the high ability of such compounds to act as efficient corrosion inhibitors. For instance, the alkyl N-(aminoethylene)-beta-aspartamates derived from aspartic acid has shown a good inhibition efficiency for steel in acidic solution (El-Sawy 1992). Another glycine derivative called: N-phosphonomethylglycine (NPMG, **Fig. 10 (a)**) was tested for the corrosion inhibition of carbon steel in two solutions: NaClO_4 and $\text{NaHCO}_3 + \text{MgSO}_4 + \text{CaCl}_2 + \text{CaSO}_4$ mixture solution. They also sought to explore the synergistic effect of calcium and zinc ions addition on the performance of NPMG. The chemical measurements revealed that NPMG molecule form more complex corrosion-inhibiting films under calcium containing water than in NaClO_4 solutions, and the addition of supplementary ions forms a passivating complex with NPMG, which produced a better inhibition efficiency especially in the presence of Zn^{2+} ions (Pech-Canul and Chi-Canul 1999; Shaban et al. 1993). In 5% of sulfamic acid solution and at 40 °C, Morad (Morad 2008) has evaluated the inhibition effect of methionine (Met), cystine (CysI) and cysteine (Cys) compounds on the corrosion of mild steel, also two new derivatives of cysteine, namely acetylcysteine (ACC) and S-benzylcysteine (BzC) was tested (**Fig. 10 (b)** and **(c)**). At 1000 μM , the experiment's data revealed that the inhibition efficiency of studied compounds follows this order: ACC (97.3%) > Cys (94.3%) > CysI (92.7%) > BzC (91.7%) > Met (86.5%), and the thermodynamic calculations indicated that those compounds are chemically adsorbed on the metal surface.

Amin et al. (Amin et al. 2010a) have synthesized a derivative of glycine (i.e. 2-(bis(2-aminoethyl)amino)acetic acid, **Fig. 10 (d)**) noted GlyD1 and evaluated its inhibition action on the corrosion of cold-rolled steel in molar hydrochloride acid solution. By electrochemical and chemical techniques, they have found that the inhibition efficiency of GlyD1 (96%) was better than of glycine alone (74% at 5 mM), and through computational study, the authors conclude that the high inhibiting effect of glycine derivative was attributed to the presence of an extra NH link in its structure. The same authors (Amin and Ibrahim 2011) have developed the second new derivative of glycine (i.e. 2-(4(dimethylamino)benzylamino)acetic acid hydrochloride, **Fig. 10 (e)**) noted GlyD2 and compared its inhibition performance to glycine and GlyD1 compounds for the corrosion of mild steel in 4 M H_2SO_4 medium. Their findings showed that the inhibition efficiency increased in the order: GlyD1 (98%) > GlyD2 (76%) > Gly (64%) at 5 mM, and the protective activity of GlyD2 was associated to their physisorption onto the metallic surface.

In other paper, Gupta et al. (Gupta et al. 2016) synthesized three lysine derivatives (noted SB-X, **Fig. 10 (f)**, **(g)** and **(h)**), and then tested them as potential eco-friendly corrosion inhibitors for mild steel in 1 M HCl solution. According to weight loss and electrochemical measurements, the authors reported that the inhibition effectiveness increased in the order: SB-3 (91%) >

SB-2 (92%) > SB-1 (94%). The highest inhibition ability of SB-3 among three studied lysine derivatives was due to the presence of strong electron releasing $-N(CH_3)_2$ group. Regarding ΔG_{ads}^0 values, both chemical and physical adsorption modes were proposed as the mechanism for all these compounds. In the same context, S. Vikneshvaran and S. Velmathu (Vikneshvaran and Velmathi 2017) synthesized two L-tryptophan derivatives, namely: methyl 2-((2-hydroxybenzylidene)amino-3-(1H-indol-3-yl) propanoate (S1, **Fig. 10 (i)**) and 2-(((1-hydroxy-3-(1H-indol-3-yl)-1,1-diphenylpropan-2-yl)imino)methyl) phenol (S2, **Fig. 10 (j)**) and tested it as inhibitors in the corrosion of mild steel in 1 M HCl solution, using electrochemical and surface analysis techniques coupled to DFT computational method. The derivatives showed good inhibition property, which increased by increasing compounds concentration. At almost tested concentrations, the S2 derivative exhibited better inhibitive performance regarding S1. The authors attributed that to the strong electron-donating ability and the presence of additional phenyl rings in S2 molecule. All those studies and other (Al-Sabagh et al. 2016; Deng et al. 2012b; Deng et al. 2012e; Fu et al. 2011; Kowsari et al. 2016; Migahed et al. 2016; Yadav et al. 2014), reported the higher ability of amino acids derivatives to act as corrosion inhibitors for iron alloys material in different medium. Nevertheless, those works presented a laboratory-scale investigation, which the synthesis economic feasibility remained unstudied.

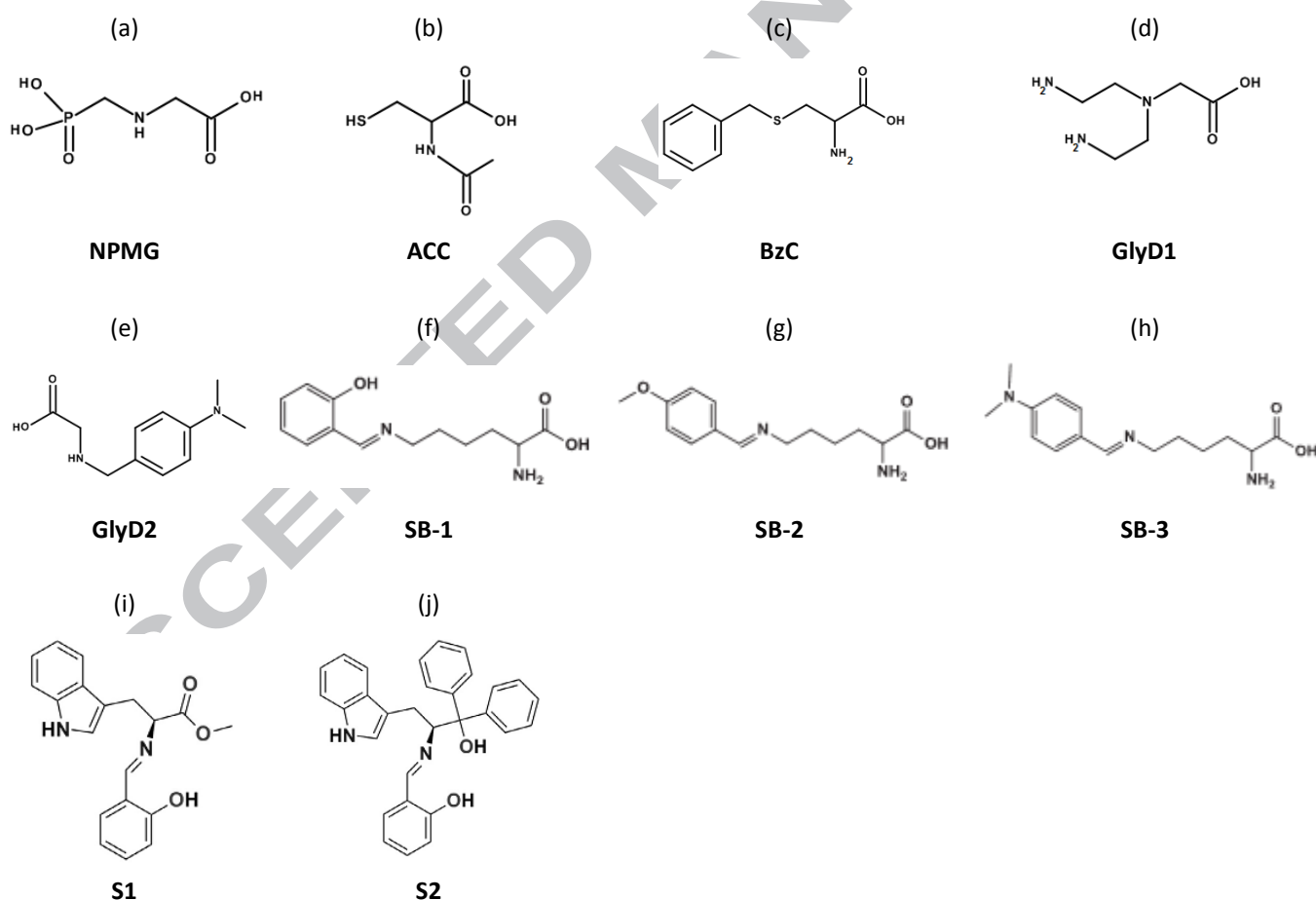


Fig. 10. Tested amino acids derivatives for iron alloys

The using of quantum chemical and molecular dynamic methods in the corrosion inhibition research are becoming popular in currently reported studies (Eddy 2011; Fouda et al. 2011; Fu et al. 2011; Khaled et al. 2012; Rahman et al. 2012; Singh and Ebenso 2013). The growing interest to these methods can be attributed, firstly to the development of calculation algorithms, and secondly to the improvement of hardware and software capabilities (El Ibrahimi et al. 2016). In their paper, further to the electrochemical methods and FT-IR spectroscopy, Zor et al. (Zor et al. 2009) were used the quantum chemical calculation via HF method employing the 6-311G(d,p) as basis set to study the inhibition property of methionine (Met) and tyrosine (Tyr) on the corrosion of iron in acidic solution. As results, the Met was found to inhibit the corrosion more than Tyr, and these substances were adsorbed on the metallic surface through an electrostatic interaction. Furthermore, the experimental inhibition has supported by the theoretical calculations results. In another study, using quantum chemical and molecular dynamic approaches, Amin et al. (Amin et al. 2010b) were attempted to explain the inhibition effect of alanine (Ala), cysteine (Cys) and S-methyl cysteine (S-MCys) against iron corrosion in 1 M HCl solution. They are found that the inhibition efficiency increases with the increasing in E_{HOMO} energy and decreasing of E_{LUMO} energy, energy gap and dipole moment of tested compounds. Moreover, the low inhibition efficiency recorded for S-MCys compared with of Cys was attributed to steric effects. In another published paper, the inhibitive effect of cysteine, histidine, tryptophan and serine on the corrosion of mild steel in de-aerated molar hydrochloric solution was determined using usual electrochemical techniques and then supported by the theoretical results. The molecular dynamics simulation data showed that those molecules can adsorb on the iron surface through the heteroatoms and heterocyclic ring, and the high values of binding energy of tryptophan molecule can explain its highest inhibition efficiency (Fu et al. 2010a).

To complete the sight and explain the inhibition efficiency of histidine and some derivatives of imidazole on A36 steel, Mondal et al. (Mondal and Taylor 2014) have conducted a computation study by using quantum chemical calculations. As interesting finding, the combination of calculated bonding energy and hydrophobicity provide an elicitation of the inhibitive activity of studied compounds. By using Monte Carlos simulation, Khaled (Khaled 2009) has simulated the adsorption of some methionine derivatives (**Fig. 6**) on Fe (110) surface. He has noted a close contact between methionine derivatives and surface, which form stable layers and protect iron from corrosion. Further, the quantum chemical parameters obtained by using semi-empirical SCF-MO method (PM3) were in a good agreement with the experimental findings. As well, the augury studies have been reported by Kabanda et al. (Kabanda et al. 2013b) for some amino acid derivatives (**Fig. 11**) as possible corrosion inhibitors for Fe, FeCO_3 , FeS_2 and Fe_2O_3 surfaces in various mediums. In the same way, the effect of microstructure of iron (nanocrystalline and polycrystalline) on the corrosion inhibitory of methionine (Met) and phenylalanine (PhA) in 0.5 M H_2SO_4 has been reported (Oguzie et al. 2011). Electrochemical measurements and computational studies level were employed in this work. It was found that the inhibition efficiency of Met was better than PhA for both iron structures, and it was decreased for PhA passing from poly to nanostructure, however, it was increased for Met compound. The reasons of these findings have debated by authors in their published paper.

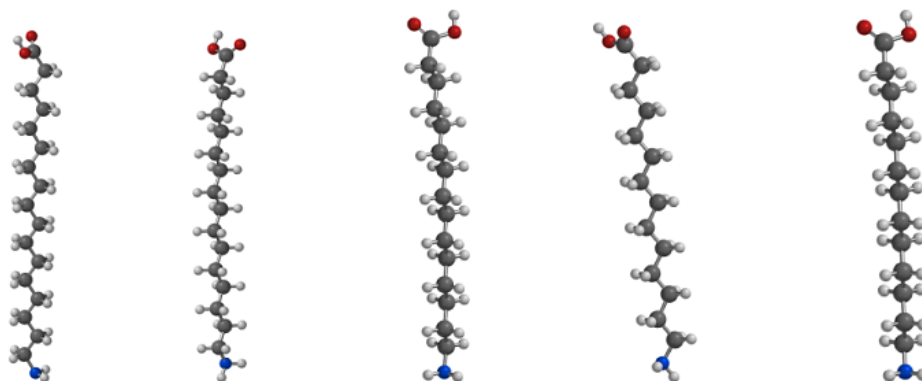


Fig. 11. Structures of the studied amino acid derivatives by Kabanda et al. (Kabanda et al. 2013b)

By combining direct chemical technique and three kinds of quantum chemical calculation (namely: semi-empirical, ab-initio (MP2), and DFT methods), Eddy et al. (Eddy et al. 2011a) have developed a quantitative structure activity relationship (noted, QSAR) model to correlate the inhibition efficiency of tested amino acids and their corresponding relevant quantum chemical parameters (i.e. descriptors) for mild steel in 0.1 M HCl solution. The same author and in another published paper (Eddy 2010) has concluded that the substituent constants, global and local reactivity indices can be used to assess the direction of the inhibition and the favorable sites of adsorption for amino acids compounds.

In two distinct works, Khaled et al. (Khaled and El-Sherik 2013a; Khaled and Sherik 2013b) have exploited two intelligence algorithms, namely: genetic function approximation (GFA) and artificial neural networks (ANN), to run a regression analysis and establish a nonlinear correlation between different types of quantum descriptors and the obtained corrosion inhibition efficiency of 28 amino acids compounds in molar hydrochloride solution for iron. Through these studies, it was approved the complicity of the inhibition phenomenon and the contribution of different molecular structural parameter on the inhibition efficiency of amino acids compounds. In an interesting study, based on DFT/B3LYP 6-311+G(d,p) calculations and molecular dynamics simulations on Fe (110), Zhao et al. (Zhao et al. 2014a) have built a QSAR model by using an artificial intelligence algorithm, namely the support vector machine (SVM), on 19 amino acids used as corrosion inhibitors for iron in 1 M HCl solution. Further, the authors have designed novel efficient amino acids by incorporation of halogen atoms (I, Br and Cl) on the tyrosine molecule structure, the **Fig. 12** presents some ones and their corresponding predicted inhibition efficiencies. Other reports are available on the use of amino acids and their related compounds as corrosion inhibitors for iron and its alloys in various mediums as shown in **Table A.2**.

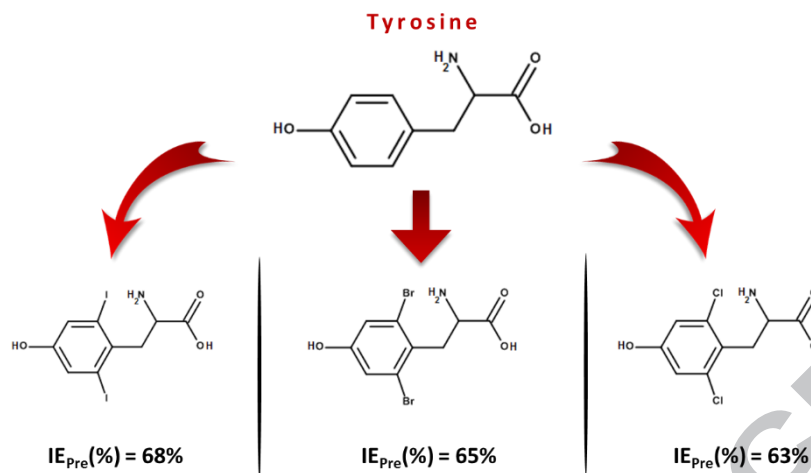


Fig. 12. Molecular structures and predicted inhibition efficiencies of the three designed amino acids for iron by SVM model (Zhao et al. 2014a)

3.3. Aluminium and its alloys

Like copper and iron materials, the aluminum is an important substrate because of its high technological value and a wide range of derivative materials, especially used in aerospace and household industries (Lumley 2011; Mathers 2002). The aluminium is a very reactive metal, involves the formation of a thin solid protecting film of oxide (i.e. Al_2O_3) that prevents the further corrosion of this metal. However, in contact with solutions containing complexing agents (i.e. halides), aluminium undergoes localized corrosion (DABOSI et al. 1994; Sheir et al. 1994; Vargel 2004).

As our literature research showed, the first works concerning the evaluation of amino acids compound to act as corrosion inhibitors for aluminum were taking in 70's (Issa et al. 1970; Mihara et al. 1969; Ramakrisi-Inaiah and Sltbramanyan 1970). These studies revealed that the additives were effective only in acid media. However, in alkaline media, the additives were either without effect or promoted dissolution process of aluminium. In contrast, Saleh et al. (Saleh and Din 1972) have noted that some amino acids act as corrosion inhibitor both in 2 M HCl and in 1.5 M NaOH mediums. In his work, Al Mayouf (Mayouf 1996) has investigated the inhibition performance of aspartic acid (Asp-A) on the corrosion of aluminium in acidic chloride solution. The results revealed that Asp-A can act as a mixed-type inhibitor and strongly interact with the metal surface which explains its great inhibition property. As reported in the previous sections, methionine compound has shown a good ability to use it as an efficient corrosion inhibitor for copper, copper alloys, iron and their alloys. The same trend has reported by Salghi et al. (Salghi et al. 1997) for an aluminium alloy (i.e. AA6063) in de-aerated carbonate solution compared to alanine, glycine, and serine.

A series of six amino acids were analyzed for their inhibitive action on the corrosion of pure aluminium in 0.1 M NaCl solution by El-Shafei et al. (El-Shafei et al. 1997). The results confirm that the inhibition efficiency of tested amino acids depends on the number of adsorption active centers, molecule size and mode of adsorption, which is in agreement with the conclusions of a recent study (Ashassi-Sorkhabi et al. 2005). In the same corrosive medium, Bereket et al. (Bereket et al. 1996) have examined the inhibition effect of few amino acids and hydroxyl carboxylic acids on the dissolution of pure

aluminium and some of their alloys. They have found that the inhibitory effect of studied compounds was depended to the kind of metal and their molecular structures. It is well known that chromate (K_2CrO_4) acts as efficient pitting corrosion inhibitor (Sastri et al. 2007). In this context, some authors (Bereket and Yurt 2001; Yurt et al. 2005) have reported the comparable effect of some amino acids, like alanine, glycine, valine and phenylalanine for AA7075 alloy in 0.05 M NaCl solution with and without nitrate addition. Further, they found that aqueous phase PM3 calculation method is satisfactorily sufficient to explain the inhibition mechanism of evaluated amino acids.

The inhibition effect of tryptophan (Try) on the corrosion process of AA2024 alloy was examined in three mediums: 1 M HCl, 20 wt.% of $CaCl_2$, and 3.5 wt.% of NaCl (Li et al. 2011). The researchers found that tested compound inhibits the corrosion and the best inhibition efficiency was 87% in 1 M HCl at 8 mM. Moreover, the effect of solution nature on the electrochemical property of tryptophan was noted, which it was a cathodic inhibitor in HCl whereas anodic inhibitor in the other solutions.

Amin (Amin 2010) has synthesized a new glycine derivative (2-(4(dimethylamino)benzylamino) acetic acid hydrochloride, **Fig. 10 (e)**) and studied its effect on aluminium by electrochemical and physical techniques. The author reported that the derivative acted as a mixed-type inhibitor and was much better than glycine in controlling uniform and pitting corrosion of aluminium induced by SCN^- anions at pH 6.8. However, its environmental implication are not fully understood. In another study (Ashassi-Sorkhabi and Asghari 2010), erosion-corrosion of AA7075 alloy investigation was conducted through rotating disc electrode in 3.5% NaCl solution, also, the inhibition action of glutamine was studied. The results showed that an increase in rotation speed increases the corrosion process, and the efficiency was lower in stagnant solution but enhanced significantly under middle hydrodynamic conditions. Latest behavior was explained by the increasing mass transport of inhibitor molecules toward the electrode surface. Recently, an investigation on the use of glutamic acid as a corrosion inhibitor against aluminium corrosion in 0.1 M HCl solution has been reported by Zapata-Loria et al. (Zapata-Loria and Pech-Canul 2014). Polarization curves indicated that glutamic acid acted as a mixed-type inhibitor, and the corrosion inhibition was attributed to a chemisorption process of inhibitor molecules onto the metal surface by forming a stable chelate system, as affirmed by XPS surface analysis. In a paper published by Brito et al. (Bruto and Sequeira 2014), the influence of glycine, alanine and other non-related compounds on the electrochemical behavior of aluminium-air batteries in a strong alkaline medium was investigated. The electrochemical measurements exhibited that tested amino acids have a modest inhibition efficiency at a concentration of 10 g L^{-1} .

3.4. Other metals and alloys

In 1992, more than 10 amino acids were tested by Aksüt et al. (Aksüt and Bilgiç 1992) as inhibitors for the corrosion of nickel in 1 N H_2SO_4 solution. The electrochemical measurements revealed that some amino acids are inhibitors; however, there is others accelerating the corrosion process. In this work, the lysine has shown the highest efficiency of all compounds studied. In order to explain these findings, Gece et al. (Gece and Bilgiç 2010a) have been used the quantum chemical calculations through DFT/B3LYP method with LANL2DZ as a base set. The authors discovered that calculations results agree well with experimental values, which is confirmed by linear regression analysis parameters. In addition to usual electrochemical techniques, Hamed et al. (Hamed et al. 2012) had used the electrochemical frequency modulation technique

to evaluate the inhibition performance of alanine (Ala) and the potential synergistic effect of iodide anions for nickel metal in stagnant 1 M H_2SO_4 solution. The results indicated that the inhibition efficiency (IE) increases by immersion time increasing, and I^- ion was greatly enhanced this ability (IE = 50.5% at 0.03 M of Ala, and 90% with addition of 0.03 M of KI).

As well, the lead and its alloys (Ghasemi and Tizpar 2006; Helal et al. 2008; Kiani et al. 2008; Salghi et al. 2003; Salghi et al. 2000) were the subjects of the use of some amino acids as corrosion inhibitors. Helal et al. (Helal et al. 2008) have investigated the effect of pH values (2, 7 and 12) of an aqueous solution on the inhibitive effect of glutamic acid (Glu-A), alanine, valine, glycine, histidine and cysteine (Cys) at 25 mM on the corrosion of lead. They reported that Cys activates the corrosion process in acidic and neutral medium, but acts as an inhibitor in alkaline media. Likewise, the high inhibition was recorded with Glu-A in neutral solutions which reached to 87%. Ghasemi et al. (Ghasemi and Tizpar 2006) have evaluated the protective effect of some amino acids. The results showed that studied compounds can act as good inhibitors for Pb-Sb-Se-As alloy corrosion in sulfuric acid solution, and the inhibition efficiency increases as follow sequence: tryptophan > methionine > proline at concentration of 0.1 M. In the same corrosive medium, Kiani et al. (Kiani et al. 2008) reported that inhibition performance of cysteine was better than methionine and alanine, as well, it acts as mixed-type inhibitors for Pb-Ca-Sn alloy.

Tinned iron or tin-plat (i.e. steel coated by a small coat of tin) is one of the most commonly used materials for the canning industries to conserve food. However, the contact of tin with acidic food (e.g. fruit juices) leads to dissolution process of tin, which latter becomes anodic to steel in acidic medium. This process causes a contamination of food by metallic elements inducing enormous wastage of food (Han 2014). In aims to avoid such wastage, several researchers have evaluated the potential inhibitive action of amino acids compounds on the corrosion of tin in the various organic acidic medium. In an aqueous solution containing 2% of citric acid, Quraish et al. (Quraish et al. 2004) have evaluated the ability of several amino acids to act as corrosion inhibitors for tin. The results of this study revealed that N-containing molecules gave inhibition efficiency up to 70% at 5 ppm and further increases in concentration causes a decrease in the latter; this may be due to the formation of the soluble complexes. In de-aerated citric-chloride solution, Zerfaoui et al. (Zerfaoui et al. 2004a) have reported that among a series of tested amino acids molecules, the arginine was showed the best inhibition efficiency, which reached to 81% at 10 mM and acted as a cathodic inhibitor.

El-Sherif et al. (El-Sherif and Badawy 2011) have investigated the effect of the addition of alanine, glycine, glutamic acid and histidine at 0.02 M on the dissolution process of tin in tartaric acid (pH 1.8). In this work, the authors found that glycine gives the highest corrosion inhibition, which adsorbs on the tin surface through physical interactions. In another study more matched to realistic conditions, the corrosion inhibition of tin-plate in three fruit juices (Orange, Mango and Pineapple juices) by glycine has reported by Quraishi et al. (Quraishi and Rawat 2000). This study indicated that the inhibition efficiency of tested compound was more than 90% in the three juices, which point the possible to use it as a corrosion inhibitor for industries tin cans.

As El-Rabieeb et al. (El-Rabieeb et al. 2008) found that the pH value (2, 7 and 12) has shown an important effect on the inhibition efficiency of glycine, alanine, valine, histidine, glutamic and cysteine (at 25 mM), which the presence of the latter compounds increases the corrosion resistance of the vanadium metal in neutral and basic solutions. However, in acidic

medium, tested molecules showed opposite effect in the presence of halide ions (Cl^- ions), which acted as the accelerators of corrosion phenomena. This finding, provide the sensibility of amino acids to the pH environmental conditions.

In another study (Helal and Badawy 2011), four categories of amino acids were tested, namely: aliphatic, aromatic, acidic and sulfur containing amino acids, as corrosion inhibitors for Mg-Al-Zn alloy in chloride free neutral solution. The electrochemical measurements showed that the phenylalanine has the highest corrosion inhibition efficiency (93% at 2 mM) than other tested compounds, which attributed to the presence of phenyl ring in its structure. Fekry et al. (Fekry and Tammam 2012) have investigated the corrosion inhibition of two magnesium alloys (i.e. AZ91E and AZ31E) by tyrosine and a non-amino acid compound (2-thiouracil, **Fig. 13**) in phosphate buffer saline solution (pH 7.4). The electrochemical measurements revealed that the corrosion resistance of AZ91E alloy is better than AZ31E alloy, and at 1 mM, the inhibition efficiency of tyrosine is higher than of 2-thiouracil for AZ91E alloy. This study points out the potential of non-containing sulfur atoms amino acids to protect metal regarding other compounds with this atom, like 2-thiouracil.

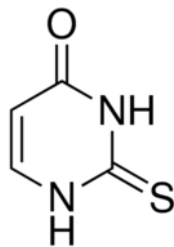


Fig. 13. Chemical structure of 2-thiouracil

Zinc is one of the most widely used metallic materials in many applications, like coating for steel or as an alloying element in brass (Cu-Zn alloy) and other alloys. It ranks fourth among the metals in worldwide production and consumption (Buschow et al. 2001). As found in the literature, little work appears to have been carried out on the inhibition of zinc corrosion by using amino acids or their derivatives. Rajappa et al. (Rajappa and Venkatesha 2003) have conducted a research on the inhibitive property of glycine (Gly), methionine (Met) and a non-related amino acid compound, namely: glutaraldehyde (GTD, **Fig. 14 (a)**), also two of their mixture solutions were studied (CP1 = GTD + Gly and CP2 = GTD + Met). As the results indicated, the inhibition efficiency of the tested inhibitors follows the order CP2 (92.6% at 10^{-2} M in 0.05 M HCl) > CP1 > Met > Gly > GTD, and electrochemically acted as cathodic inhibitors. In other side, a new derivative of glycine called Tricine (N-(Tri(hydroxymethyl)methyl)glycine) (**Fig.14 (b)**) has been tested in neutral 0.5 M chloride solution (Nady 2016). The results indicated that is an effective green corrosion inhibitor for zinc at low concentration (IE = 86.7% at 3 mM). This efficiency was attributed to the presence of oxygen and nitrogen atoms in its molecular structure, which favors the electrostatic interactions with surface atoms, leading to form a blocking barrier against aggressive agents.

(a)

(b)



Fig. 14. (a) Glutaraldehyde and (b) Tricine (N-(Tri(hydroxymethyl)methyl)glycine)

4. Discussion

4.1. Factors affecting the inhibition ability of amino acids compounds

The inhibition of corrosion is a complex phenomenon and the efficiency of inhibitors depends on a variety of factors and on the interplay between various competitive effects (Sheir et al. 1994). According to literature analysis, we presented the most evaluated factors on the inhibition efficiency of amino acids compounds in **Fig. 15**. Amongst them, we limit here to cite the effect of two factors, namely immersion time and hydrodynamic conditions.

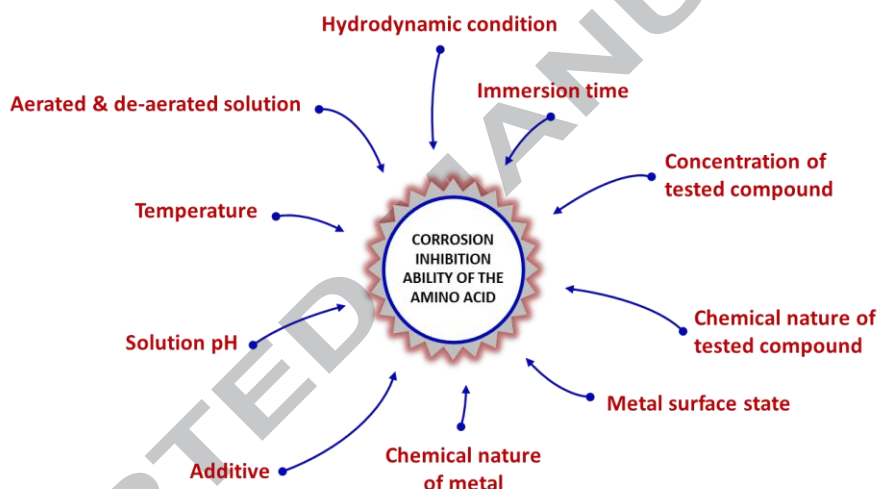


Fig. 15. Factors affecting the inhibition performance of amino acids compounds

Immersion time can play a decisive role in the prevention of corrosion ability. In one hand, V. Shkirskiy et al. (Shkirskiy 2015; Shkirskiy et al. 2015) have noted that cysteine showed a double effect on the corrosion of galvanized steel, which acted both as corrosion inhibitor at short exposure time and as corrosion accelerator at long immersion time. In other hands, some amino acids have shown an increasing in its inhibition performance by rising exposure time as reported in the case of alanine for nickel (Hamed et al. 2012) and glutamine for mild steel (Singh and Ebenso 2013). Such phenomena can be attributed to the instability/stability of adsorbed amino acid film on the metal surface and its affinity to react with metallic ions in solution.

Hydrodynamic conditions (i.e. stagnant or dynamic solution) can also affect the inhibition performance. Generally, in the presence of inhibitor, two opposite effects for hydrodynamic conditions can be pointed out, which influence its inhibition efficiency. Firstly, the flow can increase mass transport of inhibitor molecules toward the metal surface and rise the inhibition ability, as noted in the case of glutamine (Ashassi-Sorkhabi and Asghari 2010) and methionine (Ashassi-Sorkhabi and

Asghari 2008) for aluminium alloy (Al7075) and mild steel, respectively. Secondly, the highest shear stress resulting from flow speed can lead to desorption of adsorbed inhibitor molecules from the metal surface, which act a negative role on the inhibition efficiency. The same behavior was reported by Abdel-Fatah et al. for low alloy steel by using a series of amino acids (Abdel-Fatah et al. 2014).

It is very important to know that little work appears to have been done on the effect of these two factors on the inhibition performance of amino acid compounds. Therefore, we encouraged searchers to paid more attention in their studies to these factors.

4.2. Computational methods and amino acids compounds

In aim to explore and understand how the molecular structure of amino acids affects the inhibition efficiency, computational chemistry methods were applied. For this purpose, as reported in several studies, researchers have limited to investigate the amino acid molecule (acted as corrosion inhibitor) alone in vacuum or in aqueous phase (considered implicitly) in its neutral, protonated or un-protonated forms (depends to pH solution) by using quantum chemical calculations. Commonly, the density functional theory derived methods as DFT/B3LYP method with different Gaussian basis set (e.g. 6-311++G**) is employed. Afterwards, through some global and local reactivity indicators, they attempted to link an indicator or more to obtain the inhibition efficiency by mean of a mathematical model. Using quantum chemical computations in the field of corrosion inhibition has been reviewed elsewhere (Gece 2008; Obot et al. 2015). However, the inhibition of corrosion is a complex phenomenon, which implies many competitive effects, such as, the inhibitor-metal surface bonding (adsorption energy), the solubility of inhibitor, and the complexation of inhibitor with metallic ion in solution and so on. All these factors and other should to be taken into account, if we want to understand and complete the vision about such phenomenon as required by several authors (Guo et al. 2014; Gustincic and Kokalj 2015; Kokalj 2010; Kovačević and Kokalj 2011; Kovačević and Kokalj 2013a; Kovačević and Kokalj 2013b; Kovačević et al. 2015; Taylor et al. 2015).

Recently, the use of Molecular Dynamic (MD) simulation with periodic boundary condition (employing the Metropolis Monte Carlo statistical method) to calculate the adsorption energy and to identify the adsorption configuration (with lower energy) of several amino acid compounds on metal surface has reported (Kabanda et al. 2013a; Kaya et al. 2016; Khaled and El-Sherik 2013b; Khaled and Sherik 2013a). The trend to employ MD simulations is attributed to its lower time consuming regarding quantum chemical methods on those -biggest- systems. Mostly, during MD simulations the COMPASS (Condensed phase Optimized Molecular Potentials for Atomistic Simulation Studies) ab-initio force field is used to calculate the energy of all components of the system. For instance, the MD simulation results showed that $-\text{NH}_3^+$ group of protonated amino acid was oriented away from the metal surface into the solution, which can explain its lower adsorption energy regarding neutral form.

Despite that, there are some works on no related amino acid compounds which the interaction energy between molecule and metal surface was calculated by mean of DFT method, like azole derivatives on copper surface (Guo et al. 2014; Gustincic and Kokalj 2015; Kovačević and Kokalj 2011; Kovačević and Kokalj 2013b). As our literature research showed, there are alone work (Wang et al. 2016) on using merely the quantum chemical approach to evaluate this energy for amino acid

compound, it is for cysteine on aluminium surface. This showed that the researchers are invited to devoted more attention to using this reliable approach in the case of amino acids and theirs related compounds.

In other hand, by combining of some reactivity indictors obtained from those computational methods and statistical tools, several researchers (Al-Fakih et al. 2016; Aouniti et al. 2013b; Eddy et al. 2011b; Eddy et al. 2011c; Gece and Bilgiç 2010b; Gece et al. 2010; Khaled and El-Sherik 2013b; Khaled and Sherik 2013a; Zhao et al. 2014b) have found a relationship between the inhibition efficiency of amino acids compounds and theirs reactivity indictors, such approach is called quantitative-structure activity relationship (QSAR) (Carlsen 2009; Liu and Long 2009; Myint and Xie 2010; SELASSIE 2003). The main steps of QSAR modeling process are reactivity indictors' selection, data splitting, training and testing of model (**Fig. 16**). Commonly, the simple and multi-linear regression are used to construct QSAR model (Amin et al. 2012; Aouniti et al. 2013b; Eddy et al. 2011b; Eddy et al. 2011c; Gece and Bilgiç 2010b; Gece et al. 2010; Kandemirli et al. 2014). However, there is a trend in recent works on amino acids to use some derived mathematical methods from artificial intelligence, called “machine learning methods”, like: support vector machine (Zhao et al. 2014b), genetic function approximation (Aouniti et al. 2013a; Khaled and El-Sherik 2013b) and artificial neural network (Khaled and Sherik 2013a). Almost of those studies were limited in the building of the QSAR model to predict the inhibition efficiency of tested amino acids. Although, it is important to predict the activity (i.e. inhibition efficiency) of new designed amino acids derivatives as reported by H. Zhao et al. (Zhao et al. 2014b). Lately, the investigation of inhibitor efficiencies through QSAR using electronic properties of molecule has been criticized by Taylor et al. Since in this approach, the extrinsic factors (e.g. concentration of inhibitor, temperature, solution flow, and so on) have not taken into consideration. Afterword, the latter factors become obscured within the process of parameter fitting during training step. Therefore, to build a predictive model for corrosion science and engineering, it is essential to consider the extrinsic factors, such approach called “multiphysics modeling” (Taylor et al. 2015).

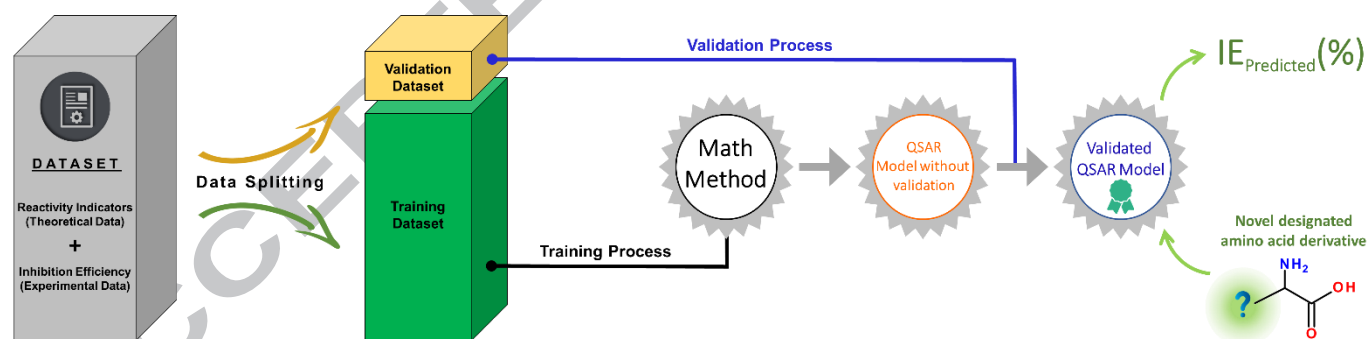


Fig. 16. Illustration of QSAR modeling steps

As seen in previous sections of this paper, few authors noted a duplicate action of some amino acids compounds on metal. Depending on operating conditions, such as pH solution or additive concentration, the molecule can decrease metal dissolution process (corrosion inhibitor) or increase it (corrosion accelerator). Therefore, using these compounds as metallic corrosion inhibitor should be accompanied by some precautions to avoid its corrosion catalytic effect. Regardless extensive employing of theoretical approach to understand the action of amino acids compounds, no attention is paid to explain this particular “duality inhibitor-accelerator” effect. In this view, we suggested that in the gas phase, such behaviors can be

explained by comparing the interaction energy of molecule with the surface ($E_{\text{Adsorption}}$, **Eq. 1**) and its corresponding ($E_{\text{int-cation}}$, **Eq. 2**) with the metallic cation in solution (complex system). The higher absolute energy is associated to more stable and favorite system for studied amino acid. Actually, the effect of solvation must be taken into consideration for more readable and accurate results (**Eq. 3 and 4**).

$$E_{\text{Adsorption}} = E_{(\text{Metal surface-Inhibitor}) \text{ system}} - (E_{\text{Inhibitor}} + E_{\text{Metal surface}}) \text{ (Eq. 1)}$$

$$E_{\text{int-cation}} = E_{(\text{Complex}) \text{ system}} - (E_{\text{Inhibitor}} + E_{\text{Metal cation}}) \text{ (Eq. 2)}$$

$$E_{\text{Adsorption}} = E_{(\text{Metal surface-Inhibitor} + \text{Solution}) \text{ system}} - (E_{\text{Inhibitor} + \text{Solution}} + E_{\text{Metal surface} + \text{Solution}}) + E_{\text{Solution}} \text{ (Eq. 3)}$$

$$E_{\text{int-cation}} = E_{(\text{Complex} + \text{Solution}) \text{ system}} - (E_{\text{Inhibitor} + \text{Solution}} + E_{\text{Metal cation} + \text{Solution}}) + E_{\text{Solution}} \text{ (Eq. 4)}$$

where, $E_{(\text{X}) \text{ system}}$ was the total energy of the system X; $E_{\text{Metal Y}}$ and $E_{\text{Inhibitor}}$ were the energies of the system without the inhibitor and the system without the metal crystal (i.e. Y), respectively; E_{Solution} was the energy of the solution.

4.3. Mechanism of action

Based on previously displayed facts in this review, the amino acids and their related compounds have shown a good ability to control corrosion of different metallic materials in various environment. Similar to most of the organic corrosion inhibitors, the inhibitive effect of those compounds was attributed to the accumulation of the inhibitor molecules by “direct” or/and “indirect” adsorption onto the metal surface, which reduces the contact of the metal with the corrosive agents in solution (**Fig. 17**). The charge (nature and magnitude) and chemical nature of surface and the inhibitor nature and protonation statue are the main factors, which influence on the mode of adsorption. Generally, two modes of adsorption could be considered. In one mode, the neutral inhibitor may be adsorbed on the surface through a chemisorption mechanism, and in another mode, the charged inhibitor can be interacted electrostatically with charged metal surface.

Firstly, the direct electrostatic interaction of the charged amino acid with charged metal surface with opposite charge. For instance, if the metal surface is negatively charged with respect to potential of zero charge (PZC), the protonated amino acids would be directly adsorbed on the metal surface (**Fig. 17 (a)**). By electrostatic interaction, the adsorption can occur “indirectly” via the already-adsorbed anions (e.g. halide ions) at the positively charged metal surface, with respect to PZC, as shown in **Fig. 17 (b)**. The adsorbed anions on metal surface make it negatively charged which increases the adsorption ability of protonated amino acid. Such behavior has been noted, especially, in acidic medium. However, if metal surface charge becomes zero, none of cations or anions will be adsorbed on the surface. It is probable; in this case, that amino acid molecule is chemically adsorbed.

Since amino acids are the electron donor’s species and the metallic atoms on the surface are electron acceptors. Another mode can be exhibit, it is “donor-acceptor” interactions, which unshared electron pairs of heteroatoms (i.e. O, N and S) and/or the π electrons of the aromatic ring of amino acid transfer to vacant “d” orbital of surface metal atoms (**Fig. 17 (c)**). In other side, the inhibiting effect of some amino acids on metal corrosion was attributed to the formation of insoluble complex between the metallic ions present on surface and the amino acid via functional groups (**Fig. 17 (d)**). For instance, this mode

has been reported for cysteine on copper (Ismail 2007; J. Matos 2004; M.B. Petrovic 2012), which the inhibitor molecules form the complex with Cu(I) species via mercapto group ($-SH$).

Recently, by using XPS studies, some authors reported the possibility of inhibitor adsorption onto metal surface through hydrogen bond formation. This type of bond can occur in the presence of the oxide film and corrosion intermediates species on metal surface (Amin et al. 2009; Olivares et al. 2006a).

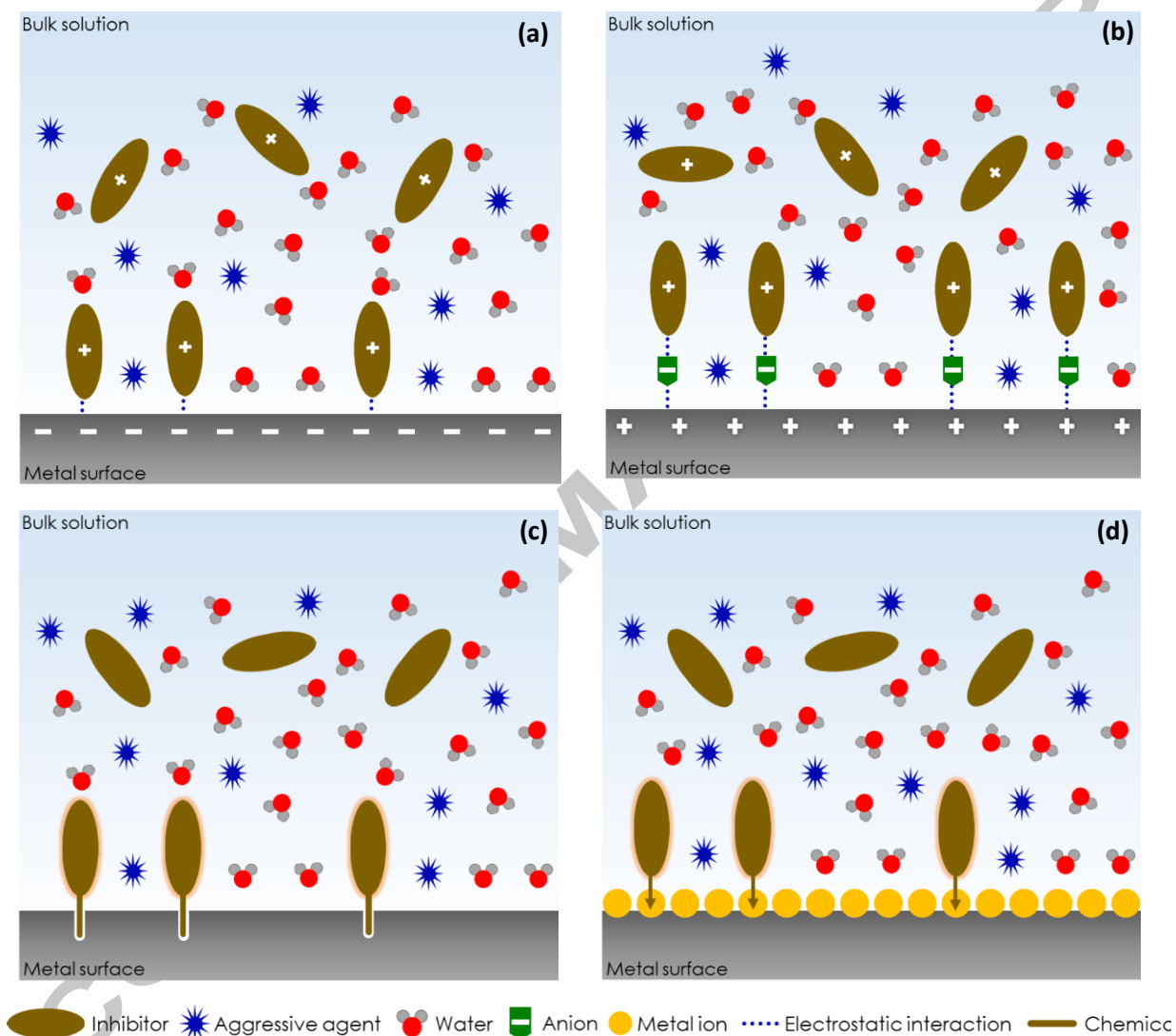


Fig. 17. Simplified schema of some interaction modes of amino acid with metallic surface in inhibition process

4.4. The new trends in using of amino acid for protection against corrosion

As mentioned and discussed above, the use of amino acids and their derivatives to protect against metallic corrosion can be performed by direct addition of those compounds to the desired environment. However, there are another techniques and manners to accomplish this function, namely by self-assembly monolayer (Migahed et al. 2009; Zhang et al. 2009b; Zhang et al. 2010; Zhang et al. 2011a; Zhang et al. 2014a) and smart coating technique (Feng et al. 2007; Maile et al. 2000). Recently,

the studies on these topics have been attracted the attention of many researchers and the number of published works go to increase.

4.4.1. Self-assembly monolayer

The Self-Assembled Monolayer (SAM) is prepared by utilizing the strong interaction between the heads of the amphiphiles molecules and the surface of the solid support on one hand, and intermolecular forces (involving van der Waals and hydrophobic forces) between backbone hydrocarbon chains in amphiphiles molecules on the other (**Fig. 18**). The preparation method is quite simple, which consists to submerge the support into a solution containing the corresponding amphiphiles induces (spontaneous) self-assembly of the amphiphiles components as a monolayer on the support surface. Washing the support removes excess adsorbent, resulting in a strongly immobilized monolayer. Among SAMs, the most popular are those of thiols, dithiols, silanes, phosphonates and fatty acids (Ariga and Kunitake 2006; Vericat et al. 2010). These SAMs have great potential for a wide range of application. Among them is the prevention of material against corrosion, where they are used as ultrathin layers for protection.

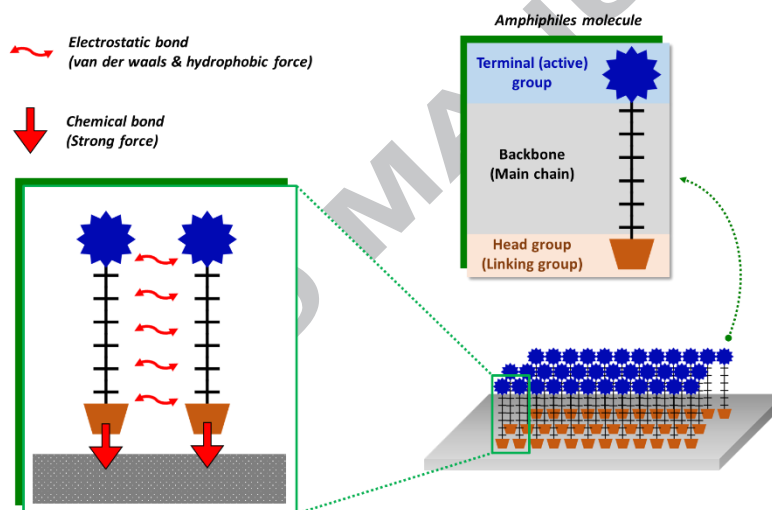


Fig. 18. Schema of Self-Assembly Layer (SAM) system

In this context, the SAM of some amino acids and their related compounds were prepared on some metal surfaces, and tested its capability to control the corrosion rate of some metallic materials (Migahed et al. 2009; Zhang et al. 2009b; Zhang et al. 2010; Zhang et al. 2011a; Zhang et al. 2014a). **Table 1** summarized some found studies in this topic for copper. It has been noted that the protection efficiency (PE %) of formed SAM strongly depends on some factors, such as the pH of used amino acid assembling solution and its concentration, and the contact time between metal and solution. Moreover, as in conventional corrosion inhibitor system, some studies (Zhang et al. 2009b; Zhang et al. 2010; Zhang et al. 2014a) have shown the synergistic effect of some anions (e.g. I^- , MnO_4^- , etc.) which enhance the protection efficiency of amino acid SAM (**Table 1**). This leads to research the optimal conditions to form the efficient monolayer that exhibits the great performance. Among tested amino acids, the cysteine has exhibited the highest protection efficiency due to the high affinity of thiol group ($-SH$) to link with metal surface, hence to form a stable SAM on surface. In other hand, the mechanism and stabilization of formed amino acid layer were attributed to the combining of electrostatic and chemical interactions forms, as showed

previously in **Fig. 18**. These studies revealed the high ability of amino acid compounds to control the corrosion processes via this kind of treatment with low compound consumption.

Table. 1. Summarized conditions to form SAM by some amino acids on copper, and their corresponding protection efficiency (PE %).

N°	Assembling solution	Concentration	Immersion time	Medium	PE	Ref
1	Arginine	1 mM	6 h	0.5 M HCl	63 %	(Zhang et al. 2009b)
	Iodide ion	10 mM	2 h		30 %	
	Arginine + iodide ion	5/5 mM			87 %	
2	Histidine	10 mM (pH=10)	2 h	0.5 M HCl	74 %	(Zhang et al. 2010)
	Iodide ion	15 mM (pH=10)			47 %	
	Histidine + iodide ion	10/5 mM (pH=10)			89 %	
3	Cysteine + bubbling N ₂ in solution	0.1 mM	1 h	3% NaCl	76 %	(Zhang et al. 2014a)
	Cysteine + bubbling air in solution	0.1 mM			83 %	
	Cysteine + ascorbic acid	0.1 mM /10 ⁻² mM			86 %	
	Cysteine + KMnO ₄	0.1 mM /10 ⁻² mM			91 %	

4.4.2. Smart coating

Recently, one of the “hot topics” on the corrosion protection field is the smart coating (Feng et al. 2007; Kendig et al. 2003; Li and Calle 2007). This special attention is due to the high capability of these coatings to provide long-term active protection against corrosion of metal surface after the coating failure. In addition to corrosion protection and repair, the smart coatings' functionalities include also sensing and warning function. For protection purpose, the idea of such coating consists to embark corrosion inhibitors into microcapsules prior to its incorporation into a protective film, which permits to control the inhibitor release in case of coating damaged. The microcapsules-based smart anti corrosion coating mechanism is shown in **Fig. 19** (Kendig et al. 2003). In this regard, V. Shkirskiy et al. (Shkirskiy 2015; Shkirskiy et al. 2015) have investigated the possibility to apply this system on galvanized steel by using cysteine for corrosion protection in saline medium. As findings, they noted that the action of cysteine on this material showed a double effect, namely: as corrosion accelerator at high concentrations and long exposure times, and as corrosion inhibitor at low concentration and short exposure times, which render dubious its practical use in smart coatings system for galvanized steel. Despite that, for the best of our knowledge, there is no other mention in the literature about using amino acid compounds in this system for corrosion protection.

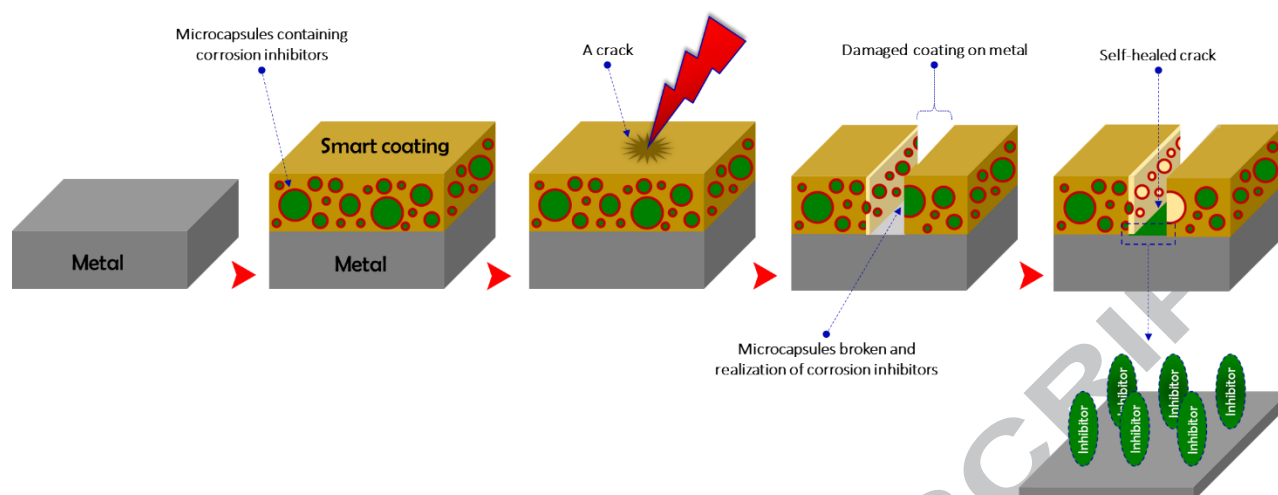


Figure 19. Microcapsules-based smart anti-corrosion coating mechanism

5. Conclusion

A thorough examination of the available literature revealed that almost tested amino acids compounds have been exhibited a good ability to use it as the eco-friendly inhibitors against metal corrosion in different mediums. However, there is no a universal amino acid compound that is applicable to most of the metal/solution systems. Hence, the inhibition capability of those compounds was depended to their molecular structure, their concentration, corrosive medium, metallic surface nature and to other factors. Whereas, some amino acids can act as effectiveness corrosion inhibitors, but it can also show an opposite effect, which accelerates the corrosion process; all depend on the operating conditions.

Actually, the recent research axes in the using of amino acids as corrosion inhibitors, it is to synthesize the new derivatives with high corrosion inhibition efficiency than its corresponding simple compounds (i.e. amino acid), and explain their inhibition mechanism using quantum chemical calculation and/or simulation by molecular mechanic approach. In this context, the density functional theory (DFT) has been widely used to study these compounds alone (i.e. without interaction with a metal surface) regarding molecular mechanic simulation (based on classical mechanic) due to its readable and accurate results. Except that, the disadvantage of DFT methods is the time consumption and the limitation of studied system size. Especially, when the “inhibitor molecule-metal surface” system was considered. In other hands, there are a few works on the use of QSAR modeling with computational chemistry methods to design new amino acids derivatives to act as efficient corrosion inhibitors. For this propose, we invite the researchers to devote more attention to this subject.

As reported in this review, the ability of some amino acids to protect metal against corrosion have tested through new systems like self-assembly monolayer (SAM) and smart coating system. Despite that, this ability has been poorly studied, especially in the case of the smart coating. In this context, we encourage researchers to explore more this property in those new systems, which we believed that will be promising.

Appendices

Table A.1 Amino acids and their derivatives used as corrosion inhibitors for Copper and its alloys.

N ^o	Metal	Medium	Inhibitors. (± Additives)	Study Methods a, b	Findings	Ref
1	Cu	0.6 M NaCl and 1.0 M HCl	Cysteine. (± Cu ²⁺)	PP. EIS.	Cathodic inhibitor. Physisorption. In presence of Cu ²⁺ ions the IE increases.	(Ismail 2007)
2	Cu	0.5 M HCl	Serine, threonine, and glutamic acid.	PP. EIS. FT-IR. PM3.	Cathodic inhibitors. IE: Glutamic acid (90.4%) > Threonine > Serine (54.7%) at 1mM. Chemisorption.	(Zhang et al. 2008a)
3	Cu	0.5 M HCl	Aspartic acid (Asp), glutamic acid (Glu), asparagine (Asn), and glutamine (Gln). (± I ⁻)	PP. EIS.	Mixed-type inhibitors. IE: Gln (73%) > Asn > Glu > Asp at 0.1M. Physisorption. Synergistic effect between Gln and I ⁻ ions.	(Zhang et al. 2008b)
4	Cu	0.5 M HCl	Methionine. (± Zn ²⁺)	CV. PP. EIS.	Methionine has shown limited inhibiting properties. Physisorption. Synergic effect between methionine and Zn ²⁺ ions.	(Zhang et al. 2009a)
5	Cu	0.5 M H ₂ SO ₄ in O ₂ -saturated solution	Glycine, alanine, valine, and tyrosine.	PP. LP. EIS. EFM. ICP-AES.	Mixed-type inhibitors. IE depends to amino acids chemical structure. IE: Valine = alanine << glycine < tyrosine.	(Amin and Khaled 2010)
6	Cu	0.5 M HCl	Glycine, threonine, phenylalanine, and glutamic acid.	PP.	Cathodic inhibitors (except phenylalanine). The strongest protective effect (IE = 53.6%) is exhibited by glutamic acid.	(Makare nko et al. 2011)
7	Cu	0.5 M HCl	Methionine. (± Cetrim-onium bromide (CTAB) and Cetylpyridi-nium bromide (CPB)).	PP. EIS. CV. PM3.	Methionine was a cathodic inhibitor. The mixed CTAB/methionine has a better synergistic effect compared with the mixed CPB/methionine. Stronger electrostatic interaction.	(Zhang et al. 2011c)
8	Cu	0.5 M HCl	Glutamic acid (Glu-A), cysteine (Cys), glycine (Gly), and its derivative (glutathione).	EIS. CV. PM3.	Physisorption. IE increases in the following order: Glutathione > Cys > Cys + Glu-A + Gly > Glu-A > Gly.	(Zhang et al. 2011b)
9	Cu	2M HNO ₃	Cysteine methyl ester hydrochloride.	WL.	The adsorption process is a spontaneous. Increase of temperature leads in a decrease of IE.	(Zarrouk et al. 2011)
10	Cu	0.5, 1.0, and 1.5M of H ₂ SO ₄	Cysteine.	WL. PP. EIS.	Mixed-type inhibitor. The adsorption involved is mixed adsorption.	(Kuruvill a et al. 2012)
11	Cu	8M H ₃ PO ₄	Proline, cysteine, phenylalanine, alanine, histidine, and glycine.	PP. PM6.	Physisorption. histidine, cysteine and phenylalanine give the maximum efficiency. A good correlation was found between the theoretical calculations and experimental observations.	(Rahman et al. 2012)
12	Cu	0.5M HCl	Phenylalanine (Phe). (± Ce ⁴⁺)	WL. PP. EIS. FT-IR. SEM-EDX.	Phenylalanine with Ce ⁴⁺ ions produced a strong synergistic effect by forming Phe/Ce ⁴⁺ complex film on the copper surface. IE = 72% for 5mM Phe + 2mM Ce ⁴⁺ .	(Zhang et al. 2012)
13	Cu	3.5% NaCl (pH 8.5)	Cysteine (Cys).	PP. EIS. SEM.	Anodic inhibitor. Cys it was a good corrosion inhibitor for Cu in studies conditions at 10mM. Physisorption.	(Kılınççe ker and Demir 2013a)
14	Cu	3.5% NaCl (pH 8.5)	Methionine (Met).	PP. EIS. SEM.	Mixed-type inhibitor. IE increases with decreasing MET concentration. Physisorption.	(Kılınççe ker and Demir 2013b)
15	Cu	1M HCl	Alanine, aspartic acid, glutamine, and lysine.	PP. PR.	The amino acids act as a corrosion inhibitor in HCl solution through adsorption on the Cu	(Gomma and

					surface. The order of IE of the tested compounds depend to its concentration.	Wahdanb 1994)
16	Cu	0.1 M H ₂ SO ₄	Methionine, cysteine, serine, arginine, glutamine and asparagine.	PP. EIS. DFT/BLYP-3.5 DNP. <i>Molecular dynamic Fe(100)</i> .	IE(%): Arg > Gln > Asn > Met > Cys > Ser at 10 ⁻² M. Arg was a cathodic inhibitor. However, et, Cys, Ser, Gln and Asn were classified as mixed corrosion inhibitors.	(Mendonça et al. 2017)
17	Cu10Ni	3.5% NaCl + 16ppm Na ₂ S	Valine, alanine, and glycine. (± I ⁻)	PP. EIS. EFM. SEM-EDX. <i>MNDO</i> .	Mixed-type inhibitors. IE: valine > alanine > glycine. Physisorption. A synergistic effect was observed between these inhibitors and I ⁻ ions.	(Fouda et al. 2011)
18	Cu10Ni	3.5% NaCl + 20ppm Na ₂ S	Glycine (Gly). (± I ⁻)	EFM. PP. SCC. SEM	Mixed-type inhibitor. IE = 87.4% at 500ppm Gly + 100ppm KI. S ²⁻ ions increase the SCC of alloy. Gly act as good inhibitor for Cu10Ni alloy.	(Nazeer et al. 2011)
19	Cu10Al 5Ni	Neutral 3.5% NaCl	Cysteine, N-acetylcysteine, and methionine.	OCP. PP. EIS. SEM.	IE: cysteine (96%) > N-acetylcys (88%) > methionine (77%) at 6.0mM. Langmuir adsorption isotherm. A strong physical adsorption.	(El-Hafez and Badawy 2013)

Table A.2 Amino acids and/or their derivatives used as corrosion inhibitors for Iron and its alloys.

N ^o	Metal	Medium	Inhibitors. (± Additives)	Study Methods ^{a, b}	Findings	Ref
1	Iron	9 g L ⁻¹ NaCl	Methionine and some amino esters: methionine methyl ester (MME), and methionine ethyl ester (MEE).	PP. with a RCE.	IE: MEE (80%) > MME (40%) > methionine (28%) at 10 ⁻² M. The sulfur atom enhances the adsorption, whose electro negativity is enhanced by the ethyl group, an electron donor in structure of MEE. The adsorption of MEE follow Frumkin isotherm.	(Bouzidi et al. 2012)
2	Iron	1 M HCl	Methionine, cysteine, cystine, glycine, leucine, arginine, serine, glutamic acid, ornithine, lysine, aspartic acid, alanine, valine, asparagine, glutamine, and threonine.	WL. PP. EIS. <i>DFT/B3LYP DNP. QSAR (with Genetic Function Algorithm)</i> .	Cathodic type inhibitors. Methionine, cysteine and cystine are the best inhibitors due sulfur atom. E _{HOMO} , total dipole moment, total energy and binding energy are important predictive descriptors.	(Aouniti et al. 2013a)
3	Iron	Citric-chloride solution (pH 5)	Methionine ethyl ester.	PP. EIS.	Very good inhibitor. Mixed-type inhibitor. Temkin adsorption isotherm. IE slightly modified with increasing temperature.	(Zerfaoui et al. 2002)
4	Iron	1M HCl	Methionine methyl ester, glycine methyl ester, leucine methyl ester, phenylalanine methyl ester, and cysteine methyl ester.	WL. PP.	Methionine methyl ester was the best inhibitor, which its IE reached 95% at 10mM. Cathodic inhibitor. Frumkin isotherm adsorption. IE increase with temperature increasing (20-50°C).	(Hammouti et al. 1995)
5	Mild steel	1N H ₂ SO ₄	Leucine.	OCP. PP. SEM. IR.	IE = 78% at 0.1M. Mixed-type inhibitor. Passivating type of inhibitor. Freundlich adsorption isotherm. Physisorption. -NH ₃ and C=O involve in the adsorption process.	(Singh et al. 2008)

6	Mild steel	0.5M H ₂ SO ₄	Cysteine.	PP. EIS. <i>DFT/B3LYP 6-311++G(d,p)</i>	IE = 96% at 10mM. Langmuir isotherm model. Chemisorption mechanism. The sulfur atom is the electrophilic site.	(ÖZCAN et al. 2008)
7	Mild steel	0.1M H ₂ SO ₄	Cysteine (Cys), serine (Ser), amino butyric acid (Abu), threonine (Thr), alanine (Ala), valine (Val), phenylalanine (Phe), tryptophan (Trp), and tyrosine (Tyr).	WL. <i>PM6, PM3, AM1, RM1 and MNDO. + MP2 and DFT/B3LYP 6-31G**, with Statistical analyses.</i>	IE = Cys > Ser > Abu, Thr > Ala > Val and Trp > Tyr > Phe. The high IE of Trp, Tyr, and Phe due to the presence of aromatic ring. For other amino acids –SH and –OH functional groups are favorable adsorption site.	(Eddy 2011)
8	Mild steel	1M HCl	Cysteine (Cys) and its derivatives: N-acetyl-L-cysteine (NACYS), N-acetyl-S-benzyl-L-cysteine (NASBCYS), and N-acetyl-S-hexyl-L-cysteine (NASHCYS).	WL. PP. <i>DFT/B3LYP 6-31G(d,p). Molecular dynamic Fe(110).</i>	IE: NASBCYS (96%) > NASHCYS > NACYS > Cys (90%) at 10 ⁻² M. Mixed-type inhibitors. E _{HOMO} , ΔE, and molecular volume are good correlate with experimental results.	(Fu et al. 2011)
9	Mild steel	1M HCl	Alanine.	PP. EIS. <i>Molecular dynamic Fe(111).</i>	IE = 80% at 50mM. Mixed-type inhibitor. Alanine could adsorb on Fe surface through the N/O atoms.	(Khaled et al. 2012)
10	Mild steel	1M HCl	Poly (vinyl alcohol-histidine).	WL. PP. LPR. EIS. SEM.	IE = 95% at 0.6% wt. Mixed-type inhibitor. Temkin adsorption isotherm. Physisorption.	(Rahiman and Subhashini 2013)
11	Mild steel	1M HCl	Poly (vinyl alcohol-leucine). (± Br ⁻ and I ⁻)	WL. PP. EIS. UV-Visible.	IE = 95% at 0.6% wt. IE depend to concentration, temperature, and immersion time. Mixed-type inhibitor. Synergism effect of inhibitor with Br ⁻ and I ⁻ ions.	(Rahiman et al. 2013)
12	Mild steel	1M HCl and 0.5M H ₂ SO ₄	Cysteine.	PP. EIS. <i>PM3. Molecular dynamic Fe(001).</i>	The higher inhibition efficiency is obtained in 1M HCl (90.4% at 0.1M) due to adsorption of Cl ⁻ . Cysteine molecules adsorb on the iron surface in the vertical manner.	(Cang et al. 2012a; Cang et al. 2012b)
13	Mild steel	1 M HCl	Triazolyl bis-amino acid of threonine and of phenylalanine.	WL. PP. SIE. SEM. <i>DFT/B3LYP 6-31*G.</i>	The 1,4-disubstituted triazolyl bis-amino acid derivatives is better than the two natural amino acid alone. The triazole ring involved in inhibition effect.	(Deng et al. 2012d)
14	Mild steel	0.5 M H ₂ SO ₄	Polyaspartic acid. (± I ⁻)	WL. PP. EIS. SEM. XPS. FT-IR.	IE = 88% at 2g L ⁻¹ and 95.4% in presence of 1mM of I ⁻ . Cathodic inhibitor. The iodide ions promotes the film formation of PASP greatly. XPS analysis revealed a co-adsorption of I ⁻ and Polyaspartic acid molecules on metal surface.	(Qian et al. 2013)
15	Mild steel	0.1 M H ₂ SO ₄	Methionine. (± Sodium dedecyl sulfate: SDS and cetyl trimethyl ammonium bromide: CTAB)	WL. PP. SEM. AFM.	Methionine acts as a mixed type inhibitor. Physisorption. The mixed methionine and CTAB is more effective as an inhibitor than mixture of methionine and SDS (Synergism effect).	(Mobin et al. 2013)
16	Mild steel	1 M HCl	Glutamine.	WL. <i>DFT/B3LYP 6-31G* (d,p).</i>	IE = 96% at 100ppm. IE increase with time immersion. Chemisorption. Langmuir isotherm adsorption.	(Singh and Ebenso 2013)
17	Mild steel	1 M HCl	Poly(vinyl alcohol cysteine).	UV. FT-IR. SEM-EDX. WL. PP. EIS.	IE = 96% at 0.6wt% of inhibitor. Mixed-type inhibitor. IE depend to rate of doping of PVA by Cys. Above 50°C the adsorbed	(Rahiman and Subhashini)

					film behave instable. Physisorption. SEM reveals film formation of Poly(vinyl alcohol cysteine).	2014)
18	Mild steel	1 M HCl	Decylamides of tyrosine (Try), glycine (Gly), alanine (Ala) and valine (Val).	WL. PP. XPS. IR.	IE = Tyr > Gly > Ala > Val. Protection efficiency of 90% were obtained with 100 ppm of Tyr and Gly, while Ala and Val reached only 80%. Flory–Huggins adsorption isotherms. The XPS analyses confirmed the presence of a chemisorbed film of Decylamides derivatives on the metal.	(Olivares et al. 2006b)
19	Mild steel	Synthetic salt solution 35 ppt (pH 8).	Thermal polyaspartate.	OCP. LP. EIS. SEM-EDX.	PASP is a mild inhibitor of corrosion. Mixed-type inhibitor. Polysapartate binds to surfaces of mild steel.	(Little and Sikes 1991)
20	Mild steel	2 M HCl	Glutaraldehyde + glycine = (CP1), and glutaraldehyde + methionine = (CP2).	WL. PP. IR.	IE varies with immersion time, inhibitor concentration and temperature. The condensation product CP2 shows better inhibition than CP1 for 1 and 2 h of immersion time and the opposite for 3, 4 and 6 h.	(Rajappa and Venkatesh a 2002)
21	Mild steel	1 M HCl	1,4-disubstituted 1,2,3-triazolyl bis-amino acid derivatives constituted by serine, threonine, phenylalanine, and tyrosine.	WL. PP. EIS. SEM. AMI.	IE of these compounds are better than that of their natural amino acid counterparts in these conditions.	(Deng et al. 2012b)
22	Mild steel	15% HCl	Two derivatives: 2-(2-oxo-2-phenothiazin-10-yl)ethylamino)-3-mercaptopropanoic acid (OPEM) and 2-(2-oxo-2-phenothiazin-10-yl)ethylamino) acetic acid (OPEA).	WL. PP. EIS. SEM. AMI.	IE = OPEM (97.5%) > OPEA (95.8%) at 200ppm. Mixed-type inhibitors. Langmuir adsorption isotherm. Theoretical calculations were consistent with the experimental results.	(Yadav et al. 2014)
23	Carbon steel	0.5 M H ₂ SO ₄	Polyaspartic acid (PASP).	WL. PP. EIS. SEM. FT-IR.	PASP is a good anode-type inhibitor. IE = 80% at 10°C. Formation of protective films. Freundlich adsorption isotherm.	(Cui et al. 2011)
24	Carbon steel	200 ppm NaCl (in different pH values)	N,N-Bis(phosphonomethyl) glycine. (\pm Zn ²⁺)	WL. PP. EIS. XPS. FT-IR. SEM.	The inhibitor formulation is effective in the pH range 5 to 8. A strong synergistic effect glycine derivative and Zn ²⁺ was showed. Mixed-type inhibitor. The film containing the oxides/ hydroxides of iron (III), Zn(OH) ₂ and [Zn (II)-inhibitor] complex.	(Appa et al. 2011)
25	Carbon steel	200ppm NaCl (pH 5 to 9)	N,N-Bis(phosphonomethyl) glycine + Zn ²⁺ ions. (\pm Tungstate)	WL. PP. EIS. XPS. FT-IR. SEM.	Tungstate has a synergistic action. Ternary inhibitor formulation is effective in neutral and slightly acidic as well as slightly alkaline media. Mixed-type inhibitor. The protective film is composed of iron oxides/hydroxides, zinc hydroxide, heteropolynuclear complex and WO ₃ .	(Appa et al. 2010)
26	Carbon steel	Low chloride environment	N,N-Bis(phosphonomethyl) glycine + Zn ²⁺ ions.	WL. PP. EIS. XPS. FT-IR. SEM.	The binary system consisting of 20ppm of BPMG and 30ppm of Zn ²⁺ accelerated corrosion of carbon steel. However, by	(Appa et al. 2008)

			(± Ascorbate ions)		addition of 25ppm of ascorbate to the above system afforded an IE of 94%. This inhibitor system functions as a mixed inhibitor and it is effective between pH 5 and 11.	
27	Carbon steel	Well water (pH 8)	Phenylalanine (PA) + Zn ²⁺ ions.	WL. PP. EIS. SEM-EDX.	A synergistic effect exists between PA and Zn ²⁺ system. IE = 33% at 150ppm of PA, and 90% in presence of 5ppm of Zn ²⁺ and PA at 150ppm. Anodic type inhibitor.	(Raja et al. 2013)
28	Carbon steel	1 M HCl	Fours alkylamides derived from tyrosine and glycine.	PP. WL.	80% < IE < 90% at ≥ 50ppm. Mixed-type inhibitors. Dodecyl amine of tyrosine showed the high IE due to its large steric body of the last against glycine. The IE correlate with the length of alkyl chain. Temkin isotherm.	(Olivares-Xometl et al. 2008)
29	Carbon steel	2 M H ₃ PO ₄	Cysteine derivative: methyl ester hydrochloride (MEH).	WL. PP. EIS.	The dissolution of metal occurs as a result of charge-transfer mechanism. IE = 93% at 10 ⁻² M. Mixed-type inhibitor. Physisorption.	(Zarrok et al. 2013)
30	Carbon steel	Saturated CaOH solution + NaOH 0.01 M (pH 12.6) + NaCl (0.1, 0.3 and 1 M).	Serine, cysteine, phenylalanine, aspartate, asparagine, and other more 70 organic compounds.	CP.	Tested amino acids showed some inhibition effect, but not sufficient for an industrial applications.	(Ormellese et al. 2009)
31	NST-44 Mild Steel	Cassava and Lime fluids	Leucine (Leu), alanine (Ala), methionine (Met), and glutamic acid (Glu-A).	WL. OM.	For the Cassava fluid, the IE increase as follow Ala (50%) > Leu (46%) > Met (45%) > Glu-A (30%). In the case of Lime fluid, IE: Ala > Met > Leu > Glu-A and increases with concentration, but there are peaks beyond which drops.	(Alagbe et al. 2006; Alagbe et al. 2009)
32	Low carbon steel(SN CLCS) and Bulk steel (BLCS).	0.5 M H ₂ SO ₄	Methionine (Met). (± I ⁻)	OCP. PP. EIS. AFM. DRX.	Synergism effect of I ⁻ ions, which facilitate the adsorption of Met. For BLCS, IE= 53% at 5mM of Met and 97.7% in presence of 5mM of KI, and for SNCLCS, the IE=53% at 5mM of Met and 71% in presence of 5mM of KI. Mixed-type inhibitor for both metals.	(Oguzie et al. 2007c)
33	Low carbon steel	1 M HCl	Tryptophan.	WL. PP. <i>Molecular dynamic Fe(110). DFT/B3LYP 6-311*G (d,p).</i>	IE = 91% at 10 ⁻² M. Cathodic inhibitor. Langmuir adsorption isotherm. Physic and chemisorption mechanism. Tryptophan molecules assumed a nearly flat orientation with Fe (110) surface.	(Fu et al. 2010b)
34	Low alloy steel	0.2 M Ammoniated citric acid	Tryptophan (Try), tyrosine (Tyr), and serine (Ser).	PP. EIS. EFM. OM.	IE = Try (86%) > Tyr (83%) > Ser (82%) at 0.06M. Physisorption. IE decreases with increasing solution stirring speed as a result of removal of layers of inhibitor from the metal surface.	(Abdel-Fatah et al. 2014)
35	Low alloy ASTM A213	0.5 M HCl	Serine.	PP. EFM. XPS.	Cathodic inhibitor. XPS confirmed the film formation of inhibitor. Physical adsorption. Temkin isotherm adsorption.	(Amin et al. 2011)

36	Low alloy steel	0.6 M HSO_3NH_2 and 0.6 M HCl	Tryptophan (Try).	WL. EIS. EFM. OM.	Mixed type inhibitor. Physisorption. Try behaved better in 0.6M HCl (IE=94.5%) than in 0.6M HSO_3NH_2 (IE=91.6%). The adsorption can occur via adsorbed SO_3NH_2^- and Cl^- anions at metal surface.	(Abdel-Fatah et al. 2013; Abdel-Fatah et al. 2012)
37	Low alloy steels (39 and 44).	1 M H_2SO_4 + 1 mM NaCl	Methionine (Met).	PP.	Increasing in Met concentration decrease the pitting current density. IE = 74% for Steel 39 and 81% for steel 44 at 1g L^{-1} of Met. Mixed-type inhibitor.	(Jano et al. 2014)
38	Steel	$\text{CaSO}_4+\text{MgCl}_2+\text{NaHCO}_3+\text{Na SO}_4$ solutions and deionized water (pH 3.5 to 12).	Polyaspartic acid (PASP).	WL. EIS. With RDE.	At low to neutral pH values, PASP increased the corrosion rate and at high pH, PASP act as corrosion inhibitor for steel. At lower pH values, Fe-PASP complexes were stable, at higher pH values, no such complexes were predicted.	(Silverman et al. 1995)
39	Steel (UNS G10180)	Solutions with different pH values (8 to 12)	Aspartic acid (Asp-A).	WL. EIS. With RDE.	At a pH less than 9.5, Asp-A appeared to accelerate corrosion, above that pH, it acted as a corrosion inhibitor. The inhibition was caused by the most stable form of Fe changing from a dissolved iron-aspartate complex at lower pH to an oxide of Fe at higher pH.	(Kalota and Silverman 1994)
40	Cold-rolled steel.	1 M HCl	Serine (Ser), threonine (Thr) and glutamine (Glu).	WL. PP. EFM. AFM. SEM. <i>DFT/B3LYP [6-311G(d,p) and 6-311++G(2d,2p)], MP2/6-311G(d,p), and CBS-APNO methods. QSAR (Genetic Function Approximation).</i>	IE of Glu was better than Ser and Thr. Mixed-type inhibitors. Temkin adsorption isotherm. The results show that inhibition increases with increasing total negative charge values of the molecules. It was also observed a good relationship with molecular volume and IE. $R^2 = 0.96$ with B3LYP/6-311G(d,p) was found as the best model among the other models generated by genetic function approximation.	(Amin et al. 2012; Kandemirli et al. 2014)
41	16/14 austenitic stainless steel	HCl	Methionine, alanine and glycine. citrulline, and hydroxyproline.	PP. PR.	There is more passivation at wide potential rang in the presence of amino acids. IE depend to kind of alloy and the nature of tested inhibitor.	(Madkour and Ghoneim 1997)
42	Stainless steel (S41000)	Synthetic seawater	Tyrosine (Tyr), polyacrylic acid (Paa), and yeast.	PP. EIS.	The results show that yeast acts as a very good corrosion inhibitor. The beneficial effect of yeast compare with Paa and Tyr is due to its composition.	(Emran et al. 2013)
43	Low chromium alloy steel	0.5 M HCl	Tyrosine.	EFM. PP. EIS. WL. SEM-EDX.	Mixed-type inhibitor. Formation of adsorbed film of tyrosine on the metal surface. Temkin-type isotherm.	(M.A. Amin 2009)
44	Steel 08-kp	0.5 M H_2SO_4	Cysteine (Cys).	WL. PP. SEM.	IE = 66% at 5g L^{-1} . Mixed-type inhibitor. Cys form a protective phase layer (3D structure).	(Tkalenko et al. 2010)
45	Mild steel	0.1 M H_2SO_4	Methionine (Met). (\pm sodium dodecyl sulfate (SDS) and cetyltrimethyl ammonium bromide (CTAB))	ML. PP. SEM. AFM.	At 200 ppm of Met, IE(%): Met + CTAB (1 ppm) > Met + SDS (5 ppm) > Met. Mixed type inhibitor. Physical adsorption. Langmuir adsorption isotherm.	(Mobin et al. 2017)

46	Carbon steel	CO ₂ -saturated brine solution	Cysteine. (\pm imidazoline derivative)	OCP. PP. EIS. WL. XPS. Contact angle	At 50 ppm of Cys, IE(%) = Cys (91.8%) < Cys + IM (96.7%). Mixed-type inhibitor. Formation a compact inhibitor film on surface.	(Zhang et al. 2016)
47	Carbon steel	1 M HCl	Leucine, phenylalanine and methionine derivatives.	PP. EIS. <i>MINDO</i> .	Phenylalanine based derivative has high efficiency (94.14% at 10 ⁻³ M). Mixed-type inhibitor. Physical adsorption. Langmuir adsorption isotherm.	(Al-Sabagh et al. 2016)
48	Carbon steel	0.1 M H ₂ SO ₄	Methionine, cysteine, serine, arginine, glutamine and asparagine.	PP. EIS. <i>DFT/BLYP 3.5 DNP. Molecular dynamic on Fe(100).</i>	IE(%) = Met > Cys > Ser > Arg > Gln > Asn at 10 ⁻² M. Mixed-type inhibitors.	(Mendonça et al. 2017)
49	Carbon steel	Sea water	Polyaspartic acid-glycine.	PP. EIS. SEM-EDS.	IE = 83.8% at 250 ppm.	(Migahed et al. 2016)
50	Mild steel	1 M HCl	Tetra-n-butyl ammonium methioninate.	OCP. PP. SEM-EDX. <i>DFT/B3LYP 6-311++G**.</i>	IE = 95.1% at 1.59×10 ⁻³ M. Mixed-type with dominant anodic inhibitor. Frundlich isotherm. Physisorption process.	(Kowsari et al. 2016)

^a Abbreviations: **IE**: Inhibition Efficiency./ **WL**: Weight Loss method./ **ICP-AES**: Inductively Coupled Plasma - Atomic Emission Spectroscopy./ **RDE**: Rotating Disc Electrode./ **OCP**: Open Circuit Potential./ **PP**: Potentiodynamic Polarization./ **LP**: Linear Polarization./ **PR**: Polarisation Resistance./ **CV**: Cyclic Voltammetry./ **CP**: Cyclic Potentiodynamic./ **CA**: Chrono-amperometry./ **EIS**: Electrochemical Impedance Spectroscopy./ **EFM**: Electrochemical Frequency Modulation./ **OM**: Optical Microscopy./ **SEM**: Scanning Electronic Microscopy./ **AFM**: Atomic Force Microscopy./ **EDX**: Energy Dispersive X-rays./ **XPS**: X-ray Photoelectron Spectroscopy./ **AES**: Auger Electron Spectroscopy./ **DRX**: Diffraction Ray-X./ **IR**: Infrared Spectroscopy./ **FT-IR**: Fourier Transform Infrared Spectroscopy./ **SCC**: Stress Corrosion Cracking./ **DFT**: Density Functional Theory./ **PM3**: Parameterized Model number 3./ **MINDO**: Modified Neglect of Diatomic Overlap./ **QSAR**: Quantitative Structure Activity Relationship.

^b The used computational method is under italic form.

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Review article

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