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Review

The use of amino acids as corrosion inhibitors for metals: A review

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ABSTRACT

The aim of this review is to present and discuss the research work reported in the literature on the use of glutamic acid and its derivatives as corrosion inhibitors for metals in different aggressive solutions. Mass loss and electrochemical techniques were among the most often used techniques to evaluate the corrosion inhibition efficiency of the used inhibitor. Glutamic acid can act as an efficient corrosion inhibitor, but it can in other cases show an opposite effect, which accelerates the corrosion process; all depend on the experimental conditions. Highest values of inhibition efficiency were obtained in the presence of ions as Zn^{2+} and ions halides. Glutamic acid derivatives have shown a good ability to use it as an effective corrosion inhibitor for metal in an acidic solution. The development of computational modeling helps to design new glutamic acid derivatives and to understand the inhibition mechanism of those compounds.

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1. Introduction

The use of inhibitors has been found to be one of the best practical methods available for the protection of metals against corrosion in different corrosive environments [1–3].

An inhibitor is a substance which added in small concentration to a corrosive solution in order to lower the corrosion rate [4,5]. This effect is attributed to the adsorption of inhibitor particles on to the metal surface, leading to formation of protective coherent layer [6].

The effect of many organic and inorganic compounds on the protection of metal in different corrosive media has been investigated [7,8].

The most efficient corrosion inhibitors are attributed to organic compounds that containing heteroatoms (such as N, S, P, O) and multiple bonds, in addition to some functional groups. It's reported also that organic compounds having –OH, –COOH, NH_2 , etc, are excellent corrosion inhibitors, especially in acidic media.

One of the encourager compounds which can be used as safe corrosion inhibitors is amino acids. They are biomolecules that have vital significance to all organism and they are the building blocks of proteins and many essential substances like neurotransmitters, hormones and nucleic acids [9].

Amino acids are environmentally friendly compounds, completely soluble in aqueous media and produced with high purity

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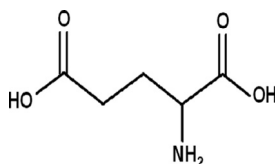


Fig. 1. Chemical structure of glutamic acid [18].

at low cost and nontoxic. These properties would justify their use as corrosion inhibitors.

Some studies implying amino acids on the corrosion of iron [10], bronze [11], carbon steel [12], zinc [13], copper [14], aluminum alloy [15] and tin [16] were reported.

Glutamic acid is an amino acid. Just like protein. It can coordinate with metals, so it has been widely used as corrosion inhibitor because it had the ability to control the corrosion of steel and metal. Some related studies for the adsorption of glutamic acid on to metal surface were reported [17–20]. Glutamic acid is attractive due to the two carboxyl groups in their molecule. Chemical structure of glutamic acid is given in Fig. 1.

Various techniques such as weight loss, electrochemical measurements (such as open-circuit potential, polarization curve method and electrochemical impedance spectroscopy), hydrogen evolution measurements, thermometric method, microscopy techniques, etc, have been used to evaluate the corrosion inhibition efficiency of glutamic acid and to characterize the protective film formed on the metal surface.

Depending on the nature of corrosive environment and nature of metal, glutamic acid follows different types of isotherms and behaves as a different type of inhibitor, namely cathodic, anodic or mixed type.

Recently, computational chemistry methods (semi-empirical and DFT) were applied [19,21–23] to explore and comprehend how the molecular structure of amino acids affects the inhibition efficiency. 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 of several amino acids on metal surface has also reported [24–26].

The aim of the present review is to present most of the contributions made in the literature on the use of glutamic acid and its derivatives as corrosion inhibitors for metals and to explore the effect of some factors on the inhibition ability. To do this, we have collected and discussed the majority of articles published in the literature that focuses on the use of glutamic acid either alone or with other amino acids as a corrosion inhibitor for some metals.

2. Glutamic acid as a corrosion inhibitor

Glutamic acid has shown promising findings as a metal corrosion inhibitor in different corrosive environments. Table 1 features reviewed examples of glutamic acid and some amino acids reported in the literature. The table summarizes studied metal, corrosive solution, tested compound (glutamic acid and some studied amino acids) with or without additive, using experimental techniques and/or computational methods, and the relevant results including the inhibition efficiency.

2.1. For steel and its alloys

It is known that steel is a material widely used in very varied fields. This is due to its different properties. One of the major defects of steels is their modest resistance to corrosion. The protection against this alteration can be realized by the application of the

coatings or by the paints. The use of inhibitors for the protection of steel is also used and investigated by many authors [2,23,44].

The inhibition effect of amino acids; leucine, alanine, methionine and glutamic acid towards the corrosion of NST-44 carbon steel have been tested using weight loss immersion method and optical microscopic techniques. Results reveal that alanine showed the highest inhibition efficiency on the NST-44 carbon steel in the cassava fluid with an average efficiency of about 50% while glutamic acid showed the least inhibition efficiency with less than 23% [28]. The inhibiting ability of the same amino acids on NST-44 mild steel in lime fluid (*Citrus aurantifolia*) was also investigated by Alagbe et al. using weight loss method and optical microscopic techniques. Results showed that alanine is the best corrosion inhibitor while glutamic acid ranked the least. From these two studies, Alagbe indicated that glutamic acid could not effectively inhibit the corrosion of steel in lime fluid and in cassava solution. In this case, glutamic acid can accelerate the corrosion of steel due to two-carboxyl groups and only one amino group, such that their aqueous solutions are relatively more acidic [45]. It is probable that the acid nature of the inhibitor is limiting its inhibitive ability. The acid can dissolve films formed on the surface of steel and can; therefore attack it [1].

The corrosion behavior of steel with four amino acids namely glycine, threonine, phenylalanine and glutamic acid in 0.5 M HCl have been reported using electrochemical methods. In this work, glutamic acid cannot form on the surface of steel a blocking barrier against aggressive agents. In amino acids solutions, a certain speed of the anodic reaction was observed together with an impediment to the cathodic reaction which leads to an acceleration of the corrosion of metal [27].

Many synergistic effects of some organic compounds have been reported [46–48]. In this context, Growi et al. have used mass loss method to inspect the action of glutamic acid with and without the addition of zinc ions (Zn^{2+}) against the corrosion of carbon steel in natural sea water of India. In this case, a highest synergistic effect between tested amino acid and Zn^{2+} ions was found, which the inhibition efficiency increases from 35% at 200 ppm of glutamic acid to 87% (Table 2) with addition of 25 ppm of zinc ions [29].

In the other published paper, the benefit effect of zinc ions (Zn^{2+}) on the corrosion inhibition by L-glutamic acid in well water at different pH has been reported. The inhibition efficiency of L-glutamic acid with Zn^{2+} system in controlling corrosion of carbon steel in well water (pH = 6.7–3.1) has been evaluated by electrochemical and mass loss techniques. At pH = 6.7, the inhibition efficiency was reached to 90% using 250 ppm of L-glutamic acid +5 ppm Zn^{2+} ions formulation. AC impedance spectra reveal that a blocking barrier is formed on the carbon steel surface. Polarization study reveals that L-glutamic acid – Zn^{2+} system function as an anodic inhibitor. At isoelectric point (pH = 3.1), L-glutamic acid exists as a zwitterion, when an electric field is applied there is no movement of ions. The formulation consisting L-glutamic acid – Zn^{2+} is very low, and offers negative inhibition efficiency (–33%). In this case, L-glutamic acid cannot migrate towards the carbon steel surface. So there is an acceleration of corrosion [31]. Similarly, Aksut indicated in his work that the inhibition efficiency of amino acids increases with increasing pH values [20].

By using weight loss measurement and various electrochemical techniques the corrosion inhibition behavior of methionine, cysteine, cystine, glycine, leucine, arginine, serine, glutamic acid, ornithine, lysine, aspartic acid, alanine, valine, asparagines, glutamine and threonine in the iron corrosion was investigated. Quantum descriptors of these amino acids were discussed. Polarization result reveals that glutamic acid and studied amino acids function as a cathodic inhibitor. Highest values of inhibition efficiency were obtained for methionine, cysteine, and cystine which are attributed

Table 1
Glutamic acid and some amino acids used as corrosion inhibitors for some metals and steel.

Metal	Medium	Inhibitor	Experimental techniques	Results	Reference
Steel	0.5 M HCl	Glycine, Threonine, Phenylalanine Glutamic acid	Electrochemical methods	Phenylalanine (74.8%) > glycine (53.9%) > Glutamic acid (8.2%)	[27]
NST-44 carbon steel	Cassava fluid: hydrocyanic acid	Leucine Alanine Methionine Glutamic acid	Weight loss method and optical microscopic technique	Alanine (50%) > leucine (46%) > methionine (45%) > glutamic acid (30%) Alanine, leucine and methionine characterized by equal amino group and carboxylic group while glutamic acid contains one amino group and two carboxylic groups in the molecule in this case acidic solution attack the steel because glutamic acid cannot adsorb on the surface of metal	[28]
NST-44 mild steel	Lime fluid	Leucine Alanine Methionine Glutamic acid	Weight loss method and optical microscopic technique	Methionine (44.70%) > Alanine (43.93%) Leucine (40.97%) > glutamic acid (23.04%)	[1]
Carbon steel	Sea water	Glutamic acid With Zn ²⁺	Weight loss method Scanning electron microscopic studies (SEM) FTIR spectra	200 ppm glutamic acid with 25 ppm Zn ²⁺ (EI = 87%). A strong synergistic effect glutamic acid and Zn ²⁺ was showed. The inhibitor (glutamic acid – Zn ²⁺) functions as an anodic inhibitor	[29]
Carbon steel	Sea water	Glutamic acid With Zn ²⁺	Weight loss method, electrochemical method and AFM analysis	200 ppm glutamic acid with 25 ppm Zn ²⁺ (EI = 87%). The inhibitor (glutamic acid – Zn ²⁺) binds to surface of carbon steel	[30]
Carbon steel	Well water at different pH	L-glutamic acid – Zn ²⁺	Electrochemical and weight loss techniques	E% (L-glutamic acid – Zn ²⁺ at pH 6.7) = 90% E% (L-glutamic acid – Zn ²⁺ at pH 3.1) = 133%. This inhibitor is effective at pH 6.7	[31]
Iron	1 M HCl	Methionine, Cysteine, Cystine Glycine Leucine Arginine Serine, Glutamic acid, Ornithine Lysine Aspartic acid, Alanine Valine Asparagine, Glutamine, Threonine	Weight loss measurement and electrochemical techniques and quantum chemical calculations	All amino acids tested act as cathodic inhibitors. Methionine, cysteine and cystine are the best inhibitors due to the presence of sulfur atom in their molecular structure	[32]
Iron	0.1 M H ₂ SO ₄	Glutamic acid derivatives	Electrochemical methods	N-Phthaloyl-L-glutamic Acid (66.89%) < N-Benzoyl-L-glutamic acid (64.03%) N-(1-oxooctadecyl)-L-glutamic acid (60.04%). Formation of protective films	[33]
Copper	0.5 M HCl	Aspartic acid Glutamic acid Asparagine Glutamine	Potentiodynamic polarization and electrochemical impedance spectroscopy	0.1 M glutamic acid (59.70%). Aspartic acid, glutamic acid, asparagine and glutamine are mixed inhibitors. Langmuir adsorption isotherm. the free energy of adsorption ΔG _{ads} detects strong physical adsorption	[34]
Copper	1 M HNO ₃	Acid aspartic Acid Glutamic Alanine Asparagine Glutamine, Leucine Methionine Threonine	Weight loss method, electrochemical method and quantum chemical calculations	Methionine (80.38%), glutamic (37.55%) Good correlation between inhibition efficiency and quantum chemical parameters	[35]
Copper	0.5 M HCl	Serine Threonine Glutamic acid	Electrochemical method and quantum chemical calculations	1 mM glutamic acid (94.5%)	[36]
Copper	0.5 M HCl	Glycine Threonine Phenylalanine Glutamic acid	Electrochemical methods	In the presence of glycine, threonine, phenylalanine and glutamic acid, the corrosion rate of copper was decreased glutamic acid (53.6%)	[27]
Copper	0.5 M HCl	Glutamic acid Cysteine Glycine and their derivatives	Electrochemical impedance spectroscopy and cyclic voltammetry and quantum chemical calculations	Glutathione > cysteine > cysteine + glutamic acid + glycine > glutamic acid > glycine	[37]
Copper		Glutamic acid, Aspartic acid on Cu (0 0 1)	Molecular dynamics simulation	The inhibition performance of glutamic acid is better than aspartic acid. E _{ads} of glutamic acid is 176.30 KJ/mol and the one of aspartic acid is 142.10 KJ/mol	[38]

(continued on next page)

Table 1 (continued)

Metal	Medium	Inhibitor	Experimental techniques	Results	Reference
Cu–5Ni	0.6 M NaCl	Glycine Alanine Leucine Cysteine Lysine Histidine Glutamic acid	Electrochemical methods	The inhibition effectiveness of tested substances depends on the content percent of nickel in the alloys. At low concentration (0.1 mM), the strongest protective effect (IE = 88%) is exhibited by lysine and IE% (glutamic acid) = 87% At 2 mM, IE% (cysteine) = 96%	[17]
Brass	0.6 NaCl	Glycine L-Aspartic acid L-Glutamic acid and their benzene sulphonyl derivative	Electrochemical methods	The inhibition efficiency increases in the order glycine < L-aspartic acid < L-glutamic acid Benzenesulphonyl derivatives of amino acids are better corrosion inhibitors due to the π electron and presence of more adsorption sites	[39]
Aluminum	0.2–1 M HCl	Glutamic acid	Weight loss, gasometric and thermometric methods	IE: glutamic acid (66.67%). physical adsorption. Langmuir, Frumkin, Flory-Huggins and kinetic and thermodynamic El-Awady adsorption. Isotherms	[40]
Aluminum	0.1 M HCl	Glutamic acid	Electrochemical methods and X-ray photoelectron spectroscopy	IE: glutamic acid (81.5%). A stable chelate was formed on to surface of aluminum. Mixed-type inhibitor. Hill-de Boer isotherm. Chemisorption	[18]
Vanadium		Water	Electrochemical methods	At low concentration (25 mM), some amino acids like glutamic acid and histidine have promising corrosion inhibition efficiency. The inhibition efficiency was found to depend on the structure of the amino acid and the constituents of the corrosive medium	[41]
Mg–Al–Zn alloy	Solution neuter	Glycine Alanine Valine leucine Glutamic acid Threonine Cysteine Tyrosine Phenylalanine	Electrochemical methods. characterization of the surface	The presence of aromatic ring and hetero atoms such as sulfur in the amino acid structure causes a significant increase in the inhibition efficiency. Glutamic acid (52.9%)	[42]
Lead	aqueous solutions at pH (2, 7 and 12)	Glycine Alanine Valine Histidine Glutamic acid Cysteine	Electrochemical methods	At pH = 7, glutamic acid (87.67%) acted as a corrosion inhibitor, at pH= 12, glutamic acid appeared to accelerate corrosion. The inhibition was caused by the adsorption of the amino acid molecule through the (+NH ₃) on lead surface. Physisorption. Langmuir adsorption isotherm	[43]
Nickel	1 N H ₂ SO ₄	Alanine Valine Leucine Isoleucine Glycine Cystine, Phenylalanine, Tyrosine Dihydroxy-3,4phenylala-nine Glutamic acid Lysine Histidine Arginine	Electrochemical methods	Some amino acids (lysine: 94%, glutamic acid: 81%, glycine: 72%) showed good inhibition effect, but others (cystine: –71%) accelerated corrosion of nickel	[20]
Cobalt	0.5 M H ₂ SO ₄	Glycine, Alanine Valine, Leucine Isoleucine, Serine Threonine, Cysteine Methionine Phenylalanine Tyrosine Tryptophan Aspartic acid Asparagine Glutamic acid Lysine Histidine Arginine Proline	Electrochemical methods	Glutamic acid and leucine give the maximum efficiency	[19]

to the presence of sulfur atom in their molecular structures (Fig. 2). Among the descriptors with a major contribution, authors should point quantum chemical parameters such as the energy of highest occupied molecular orbital, total dipole moment, total energy and binding energy are important predictive descriptors [32].

Self Assembled Monolayer (SAM) has great potential for a wide range of application. Among them is the prevention of material against corrosion where it is used as ultra thin layers for protection. In this way, the Self-Assembled Monolayers of glutamic acid derivatives were prepared on the iron surface. Fig. 3 presents the

Table 2

The effect of addition of zinc ions (Zn^{2+}) to different concentrations of glutamic acid as inhibitor for carbon steel in natural sea water of India.

Concentration of glutamic acid (ppm)	Inhibition efficiency (%)		
	Zn^{2+} concentration (ppm)		
	0	15	25
0	–	41	64
50	29	48	69
100	26	53	69
150	64	53	69
200	35	53	87

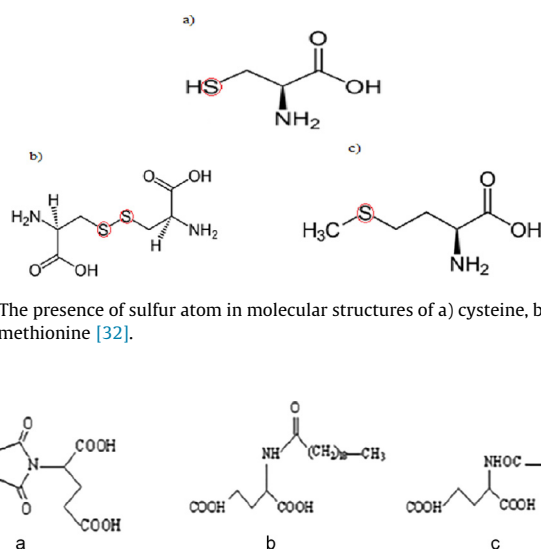


Fig. 2. The presence of sulfur atom in molecular structures of a) cysteine, b) cystine and c) methionine [32].

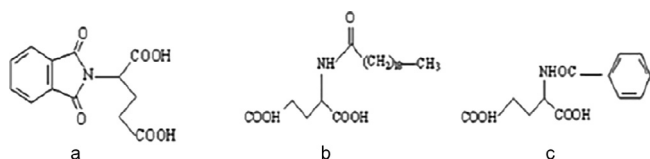


Fig. 3. The structures and names of glutamic acid derivatives, a: N-Phthaloyl-L-glutamic Acid, b: N-(1-oxooctadecyl)-L-glutamic acid, c: N-Benzoyl-L-glutamic Acid [33].

molecular structures of glutamic acid derivatives used in this work. Electrochemical impedance spectroscopy and polarization methods were used to investigate the protection capabilities of these layers against iron corrosion in 0.1 M H_2SO_4 solution. The experimental results have shown that layers of glutamic acid derivatives can protect iron towards corrosion. Polarization measurements revealed that the tested substrates are mixed inhibitors. The inhibition efficiency of glutamic acid derivatives was solely determined by the immersion time of glutamic acid derivatives and follows this order: N-(1-oxooctadecyl)-L-glutamic acid < N-Benzoyl-L-glutamic Acid < N-Phthaloyl-L-glutamic Acid [33].

2.2. For copper and its alloys

As shown in Fig. 4, in contact with the atmosphere, a blue-green layer is formed on the surface of copper (or its various alloys). It's known also that copper is susceptible to corrosion in aggressive solution [49]. So the prevention of copper against corrosion is necessary since it has a wide range of applications due to its good properties. The use of corrosion inhibitors in such conditions is obligatory. Many researchers for the use of different compounds as corrosion inhibitors of copper had been reported [49,50].

In the regards of the use of glutamic acid as corrosion inhibitor of copper, the inhibitive influence of four amino acids namely aspartic acid, glutamic acid, asparagine and glutamine as green corrosion inhibitors for copper in 0.5 M HCl was studied using potentiodynamic polarization and electrochemical impedance spectroscopy. The results showed that at 0.1 M the inhibition efficiency follows the sequence: Gln > Asn > Glu > Asp. Glutamine is the imido derivative of glutamic acid. Chemical structure of glutamine is shown in Fig. 5. The inhibition efficiency was significantly increased by the addition of small amounts of KI. It was found that adsorption of used amino acids on copper surface follows Langmuir isotherm. Amino acids are physically adsorbed on the copper [34].

In another work, Zhang et al. conducted an experimental and a theoretical study through PM3 semi-empirical calculation to investigate the effect of serine, threonine and glutamic acid on the corrosion process of copper in 0.5 M HCl solution. It's found that threonine and glutamic acid have good inhibition efficiency [36].

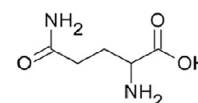


Fig. 5. Chemical structure of glutamine [34].

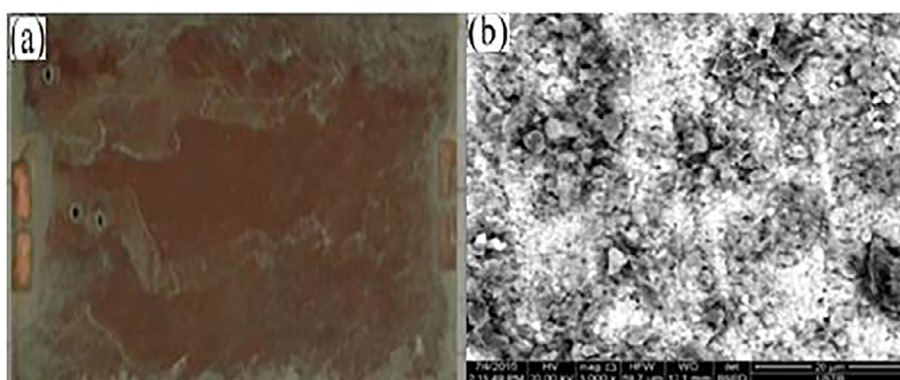


Fig. 4. (a) Macroscopic morphology (b) Scanning electron microscopy (SEM) of an exposed copper substrate in a typical hot and dry atmosphere environment at high temperature after three year [51].

Glutamic acid, cysteine, glycine and their derivatives have been tested for its performance in protecting copper against corrosion in HCl solution by means of electrochemical impedance spectroscopy, cyclic voltammetry, and quantum chemical calculation. The corrosion inhibitor rankings were glutathione > cysteine > cysteine + glutamic acid + glycine > glutamic acid > glycine. The inhibition efficiency of these amino acids is due to their adsorption on the metal surface. This result is also in agreement with quantum chemical calculations [37].

By using electrochemical methods, Makarenko et al. have investigated the anticorrosion activity of glycine, threonine, phenylalanine, and glutamic acid in the corrosion of M3 copper in 0.5 M HCl solution. The result showed that the presence of these amino acids decreases the corrosion rate of copper. Glutamic acid was found to have 53.6% protection ability. The improved inhibition of glutamic acid was due to the stabilization of its adsorption on the copper surface by the oxygen atoms in its structure [27].

Barouni et al. used weight loss and electrochemical polarization measurements to investigate the protective ability of eight amino acids namely acid aspartic, glutamic acid, alanine, asparagine, glutamine, leucine, methionine, and threonine on the corrosion of copper in molar nitric solution. The results obtained from the two different techniques were in good agreement. The strongest protective effect is exhibited by methionine (80.38%). These results showed good correlation between theoretical parameters (AM1 and MNDO methods) [35].

In other hands, glutamic acid and glycine, alanine, methionine, glutamic acid, formic acid, acetic acid, n-butyric acid and glutaric acid were studied against the corrosion of copper in aqueous solutions. Results reveal that the dilute aqueous solutions of amino acids/aliphatic carboxylic acids act better corrosion inhibitors toward copper than the aliphatic carboxylic acids [52].

Dai et al. employed Molecular Dynamics Simulation to investigate the adsorption behavior of aspartic acid and glutamic acid on Cu (0 0 1) surface. It is generally recognized that the adsorption is the primary mechanism of corrosion inhibitor interaction with metal. So the adsorption energy can furnish us with a direct tool to classify inhibitor molecules. Table 3 listed the values of the adsorption energy of the two inhibitors on Cu (0 0 1) surface. Glutamic acid and aspartic acid can be used as an efficient corrosion inhibitor for copper. However, the inhibition performance of glutamic acid is better than aspartic acid because glutamic acid molecules can easily adsorb on the surface of copper. This adsorption depends on the interaction between polar groups (heteroatoms and carboxyl) and metal surface [38].

In another study, Molecular Dynamics Simulation method and Density Functional Theory have been employed to investigate the adsorption behavior of glutamic acid and aspartic acid on Cu (0 0 1) surface in water solution or not. The results revealed that the two corrosion inhibitors could both adsorb on the Cu surface firmly due to the interaction between polar groups and surface. It was shown also that the inhibition efficiency of glutamic acid was better than aspartic acid. These results are in agreement with the experimental results [53].

The electrochemical behavior of Cu-Ni alloys in aqueous chloride solutions containing amino acids was studied using polarization and impedance techniques. The amino acids used in this

Table 3

Adsorption energy of the aspartic acid and glutamic acid on Cu (0 0 1) surface.

Amino acid	$E_{\text{adsorption}}$ (kJ/mol)
Glutamic acid	176.30
Aspartic acid	142.10

Table 4

Inhibition efficiency of Cu-5Ni and Cu-65Ni in 0.6 M neutral NaCl solution with the presence of 0.1 mM of glutamic acid and other amino acids.

Concentration of amino acid (0.1 mM)	Inhibition efficiency (%)	
	Cu-5Ni	Cu-65Ni
Glutamic acid	87	55
Glycine	86	84
Alanine	87	50
Leucine	86	50
Cysteine	75	72
Lysine	88	75
Histidine	84	64

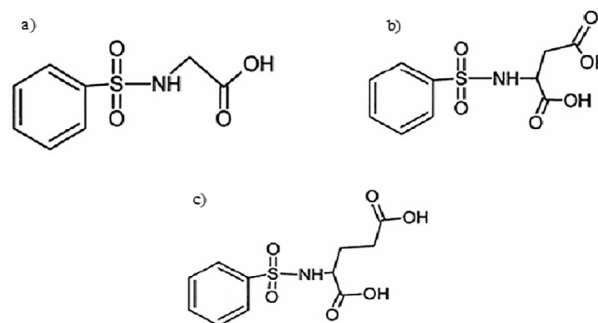


Fig. 6. Chemical structures of: a) N-benzenesulphonyl glycine, b) N-benzenesulphonyl L-aspartic acid and c) N-benzenesulphonyl L-glutamic acid [39].

study are glycine, alanine, leucine, histidine, cysteine, lysine and glutamic acid. It was found from the experimental measurements that some amino acids like lysine have promising corrosion inhibition efficiency at low concentration (0.1 mM). Cysteine shows remarkable high corrosion inhibition efficiency (96%) at 2 mM and glutamic acid gives 87% corrosion inhibition efficiency at 0.1 mM for low Ni content alloy (Cu-Ni). The experimental findings have shown that the inhibition effectiveness of tested substances (Table 4) depends on the content percent of nickel in the alloys. The corrosion inhibition process is based on the adsorption of the amino acid molecules on the metal surface. The adsorption free energy for cysteine on Cu-Ni reveals strong physical adsorption of the amino acids on the alloy surface [17].

Brass is a metallic alloy that is made of copper and zinc. The proportions of zinc and copper can vary to create different types of brass alloys with varying mechanical and electrical properties. Due to its various industrial applications and economic importance, Ranjana et al. have evaluated the capacity of glycine, L-aspartic acid, L-glutamic acid and their benzenesulphonyl derivatives to act as brass corrosion inhibitors in 0.6 M NaCl solution. Molecular structures of benzenesulphonyl derivatives are presented previously in Fig. 6. The obtained results from electrochemical methods indicate that the inhibition efficiency increased in the order: glutamic acid (59.5%) > aspartic acid (47.7%) > glycine (32%) and the same trend is followed for benzenesulphonyl derivatives. N-benzenesulphonyl L-glutamic acid found to be the best inhibitor. The addition of $C_6H_5SO_2$ increases the inhibition efficiency of amino acids due to large molecular size, π electron contribution of the benzene ring and presence of more adsorption sites [39].

2.3. For aluminum and other metals

Aluminum is among the most available metal in nature. It is light, has good thermal and electrical properties and by structural hardening it can acquire good mechanical properties. Aluminum has a natural protection against aggressive agents in the presence

of an oxide layer (Al_2O_3) on its surface, but it is submitted to all forms of corrosion. Fig. 7 shows pitting corrosion of Aluminum. The possibility to protect the aluminum and their alloys against corrosion has attracted many researchers, so until now various amino acids compounds have been

Investigated [54,55]. In this regard, an investigation on the use of glutamic acid as a corrosion inhibitor against aluminum corrosion in HCl solution has been reported by Ayuba Abdullahi.

Muhammad et al. using weight loss, gasometric and thermometric methods. It was found that glutamic acid acts as a good inhibitor for the corrosion of aluminum in HCl solution.

The inhibition efficiency was found to increase with an increase in glutamic acid concentration but decreased with rising in temperature, time immersion, and HCl concentration. The thermodynamic parameters for the adsorption of glutamic acid to the surface of aluminum in HCl solution indicated a spontaneous process and signified a strong physical adsorption of the inhibitor on the metal surface. At varying temperature, Adsorption isotherm model parameters (such as R^2) for the adsorption of glutamic acid on aluminum surface in HCl solution presented as results in this study were found to obey Langmuir, Frumkin, Flory-Huggins and kinetic and thermodynamic El-Awady adsorption isotherms [40].

In another work, the adsorptive and inhibitive action of glutamic acid towards corrosion of aluminum in HCl solution was investigated using linear polarization, potentiodynamic polarization, and electrochemical impedance spectroscopy methods. Polarization curves indicated that glutamic acid acted as a mixed-type inhibitor. The values of polarization resistance obtained by linear polarization (LPR) and electrochemical impedance spectroscopy (EIS) were consistent in showing that inhibition efficiency increased with increasing concentration of glutamic acid (Table 5). The corrosion inhibition was attributed to a chemisorption process of inhibitor molecules onto the metal surface by forming a stable chelate (Fig. 8) system. This result was affirmed by XPS surface analysis [18].

In 1992, Aksüt and Bilgiç studied the inhibition of the corrosion of nickel in sulphuric acid medium with thirteen amino acids. Results reveal that some amino acids are inhibitors to various degrees for nickel but that others accelerate corrosion. Lysine has shown remarkably high corrosion inhibition efficiency up to 94%. Glutamic acid showed considerable benefit, with inhibition efficiency about of 86% [19]. Gece and Bilgiç have expanded the study of Aksüt and Bilgiç by analyzing the inhibitive properties of these

Table 5

Inhibition efficiency for aluminum in 0.1 M HCl solution without and with the presence of Glu from linear polarization (LPR) and electrochemical impedance spectroscopy (EIS) methods.

Concentration of glutamic acid (M)	Inhibition efficiency (%)	
	LPR	EIS
0	–	–
1×10^{-7}	64	44.8
1×10^{-6}	71	56.5
1×10^{-5}	75	67.4
1×10^{-3}	85	81.5

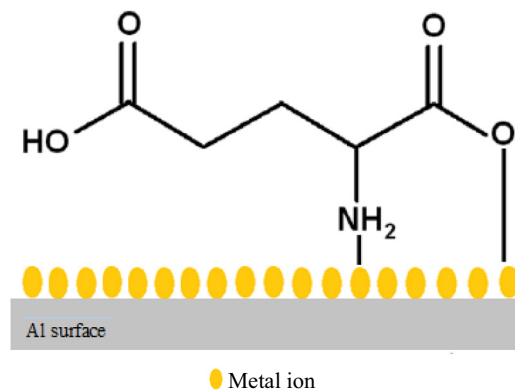


Fig. 8. The adsorption behavior of glutamic acid on aluminum surface (chemisorption mode).

amino acids using DFT calculations. The experimental results are complemented with theoretical calculations in order to provide a commentary of the differences between the probed inhibitors [56].

The inhibitive influence of amino acids as a green corrosion inhibitor for cobalt in H_2SO_4 was studied using electrochemical methods. Good inhibition efficiency of 80% to 90% can be fulfilled with some amino acid derivatives; the highest value of it was obtained with glutamic acid. Authors showed that the improved inhibition efficiency of glutamic acid is affected by the negative charge centers of oxygen atom in its molecule [20]. The inhibitive properties of these amino acids were studied using semiempirical PM3 and DFT methods. Authors found that the theoretical

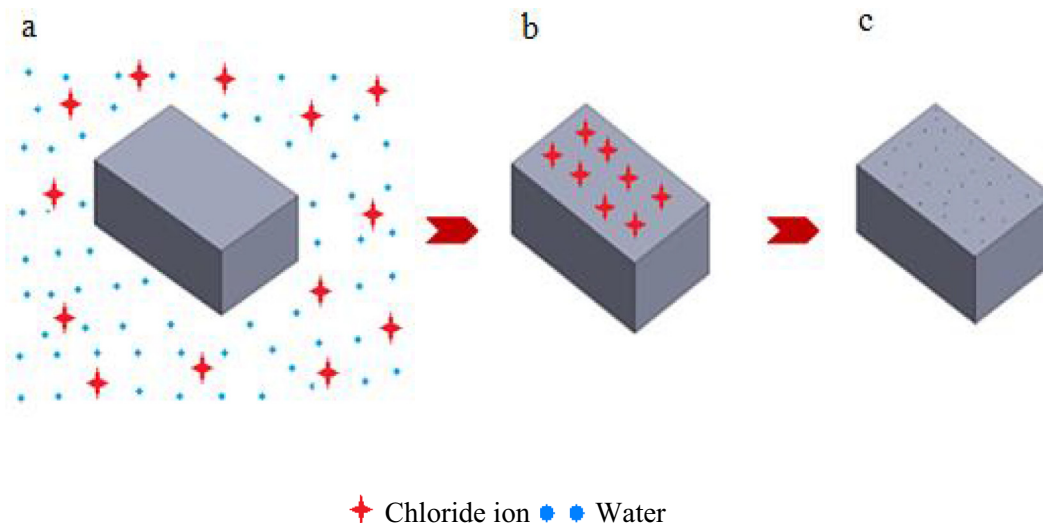


Fig. 7. a) Contact of aluminum with aggressive solution, b) Interaction of Cl^- with passive film (adsorption), c) Formation of pits on to aluminum surface.

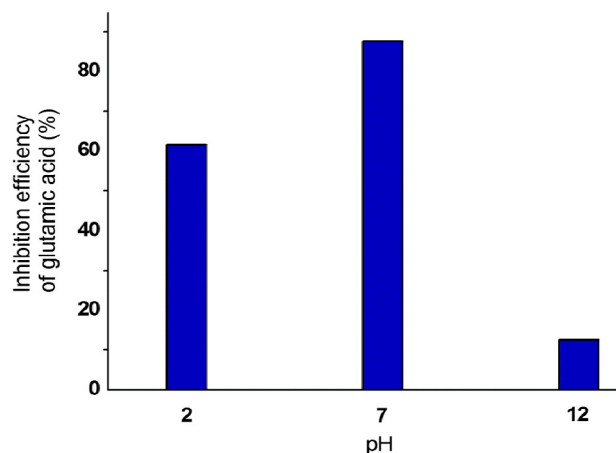


Fig. 9. Inhibition efficiency of lead in aqueous solutions with glutamic acid at different pH.

calculations are in agreement with experimental results in order to provide an elucidation of the differences between the probed inhibitors [3].

In another study, glutamic acid and other amino acids were evaluated as corrosion inhibitors for Mg–Al–Zn alloy in stagnant naturally aerated chloride free neutral solutions by electrochemical methods. The corrosion inhibition process was found to rely on the adsorption of the amino acid molecules on the alloy surface. A significant increase in the inhibition efficiency was caused by the presence of aromatic ring and hetero atoms such as sulfur in the amino acid structure. At a concentration of 2×10^{-3} mol dm⁻³ phenylalanine gives 93% while glutamic acid gives 52.3% corrosion inhibition efficiency [42].

Glutamic acid, alanine, valine, glycine, histidine, and cysteine have been tested for its performance in protecting vanadium against corrosion in water solution at different pH by means of open-circuit potential measurements, polarization techniques, and electrochemical impedance spectroscopy. The experimental results have shown that a simple amino acid like histidine and glutamic acid can be used as an efficient corrosion inhibitor of the vanadium in aqueous solutions. The corrosion inhibition process was found to depend on the adsorption of the amino acid molecules on vanadium surface. The inhibition was found to depend on the structure of the amino acid and the constituents of the corrosive medium. The corrosion inhibition process was found to depend on the adsorption of the amino acid molecules on vanadium surface and the adsorption process follows the Freundlich isotherm [41].

As well, the lead and its alloys were the subject of the use of some amino acids as corrosion inhibitors [57,58]. In this context, glutamic acid and five amino acids were evaluated as corrosion inhibitors for lead in aqueous solutions in different pH (2, 7 and 12) by polarization and impedance techniques. Result reveals that the corrosion inhibitor rankings were: Glutamic acid > alanine > valine > glycine > histidine > cysteine. The highest inhibition efficiency of glutamic acid (87.67%) can be achieved in pH = 7 as compared to that (61.6%) in pH = 2 and (12.6%) in pH = 12. All these values are presented in Fig. 9. In neutral and acidic mediums, the amino acid molecule is adsorbed through the (+NH₃) blocking the active sites for the corrosion process, thus decreasing the exposed free metal area to a corrosive solution. The adsorption free energy of glutamic acid on lead surface reveals that the inhibitor is physically adsorbed on the metal surface. The adsorption process obeys Langmuir adsorption isotherm [43].

3. Conclusion

- Amino acids are effective in inhibiting metal in different aggressive solution. The efficiency of those compounds has been found to be greatly influenced by many factors, such as the metal (surface state, chemical nature), the medium (concentration, pH, and temperature), inhibitor (concentration, structure molecular, solubility, the inhibitor–metal surface bonding), immersion time, etc.
- Glutamic acid can act as an effective corrosion inhibitor for metals due to its large molecular and the stabilization of its adsorption on the metal surface by the oxygen atoms that exist in its structure. In some cases, glutamic acid can also show an opposite effect which accelerates the corrosion process; all depend on the operating conditions
- Highest values of inhibition efficiency were obtained in the presence of (Zn²⁺) ions and halides ions (KI).
- Glutamic acid derivatives have shown a good ability to use it as an effective corrosion inhibitor for metal in an acidic solution; it is for this reason, the recent research axes in the using of amino acids as corrosion inhibitors are to synthesize the new derivatives of these compounds with high corrosion inhibition efficiency
- Some experimental results indicated that the inhibition efficiency of some amino acids increases with increasing in pH values.
- Mechanism of inhibition by glutamic acid is found to be principally due to adsorption of its polar groups onto the metal surface.
- According to literature discussion mentioned in this review, it is very important to do even more experimental studies on the effect of acid glutamic on the corrosion of other metals such as bronze, zinc, stainless steel, giving more attention in these studies to the most factors on the inhibition efficiency of the used inhibitor.
- Computational modeling chemistry methods have also been employed in corrosion inhibition studies using amino acids as inhibitors and have been found to provide helpful insights into the interactions between the metal and the studied amino acids. In addition, these methods help to design new amino acids derivatives and to understand the inhibition mechanism of those compounds.

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