University of Belgrade, Technical Faculty in Bor

29th International Conference Ecological Truth & Environmental Research

EcoTER'22

Proceedings

Editor
Prof. Dr Snežana Šerbula

21-24 June 2022, Hotel Sunce, Sokobanja, Serbia

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PROCEEDINGS

29th INTERNATIONAL CONFERENCE

ECOLOGICAL TRUTH AND ENVIRONMENTAL RESEARCH – EcoTER'22

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Publisher: University of Belgrade, Technical Faculty in Bor

For the Publisher: Prof. Dr Nada Štrbac, Dean

Printed: GRAFIK CENTAR DOO Beograd, 120 copies

Year of publication: 2022

ISBN 978-86-6305-123-2

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

502/504(082)(0.034.2)
574(082)(0.034.2)

INTERNATIONAL Conference Ecological Truth & Environmental Research (29 ; 2022 ; Sokobanja)

Proceedings [Elektronski izvor] / 29th International Conference Ecological Truth and Environmental Research - EcoTER'22, 21-24 June 2022, Sokobanja, Serbia ; [organized by University of Belgrade, Technical faculty in Bor (Serbia)] ; [co-organizers University of Banja Luka, Faculty of Technology – Banja Luka (B&H) ... [et al.]] ; editor Snežana Šerbula. - Bor : University of Belgrade, Technical faculty, 2022 (Beograd : Grafik centar). - 1 USB fleš memorija ; 5 x 5 x 1 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tiraž 120. - Bibliografija uz svaki rad. - Registar.

ISBN 978-86-6305-123-2

а) Животна средина -- Зборници б) Екологија -- Зборници

COBISS.SR-ID 69053705

29th International Conference
Ecological Truth and Environmental Research 2022

is organized by:

UNIVERSITY OF BELGRADE, TECHNICAL FACULTY IN BOR (SERBIA)

Co-organizers of the Conference:

University of Banja Luka, Faculty of Technology – Banja Luka (B&H)

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PREFACE

In today's world, the environment has been endangered by the use of outdated technology, fossil fuels and environmental law violations. Therefore, environmental and many other scientists all over the world have been concerned about finding sustainable technology in resolving these issues. That is why environmental research and ecological truth are at the focus of the 29th International Conference Ecological Truth & Environmental Research 2022 (EcoTER'22), which will be held in Sokobanja, Serbia, 21–24 June 2022. On behalf of the Organizing Committee, it is a great honor and pleasure to wish all the participants a warm welcome to the Conference.

We hope to convey the message of the conference, which is that a transformation of attitudes and behavior would bring the necessary changes. This is also an opportunity for the participants who are experts in this field to exchange their experiences, expertise and ideas, and also to consider the possibilities for their collaborative research.

The 29th International Conference Ecological Truth & Environmental Research 2022 is organized by the University of Belgrade, Technical Faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology, the University of Montenegro, Faculty of Metallurgy and Technology – Podgorica, the University of Zagreb, Faculty of Metallurgy – Sisak, the University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Association of Young Researchers, Bor.

These proceedings include 85 papers from the authors coming from the universities, research institutes and industries in 6 countries: Bulgaria, Italia, Albania, Bosnia and Herzegovina, Montenegro and Serbia.

As a part of this year's conference, the 4th Student section – EcoTERS'22 is being held. We appreciate the contribution of the students and their mentors who have also participated in the Conference.

Financial assistance provided by the Ministry of Education, Science and Technological Development of the Republic of Serbia is gratefully acknowledged by the Organizing Committee of the EcoTER'22 conference.

The support of the Platinum donor and their willingness and ability to cooperate have been of great importance for the success of EcoTER'22. The Organizing Committee would like to extend their appreciation and gratitude to the Platinum donor of the Conference for their donation and support.

We appreciate the effort of all the authors who have contributed to these Proceedings. We would also like to express our gratitude to the members of the scientific and organizing committees, reviewers, speakers, chairpersons and all the Conference participants for their support to EcoTER'22. Sincere thanks go to all the people who have contributed to the successful organization of EcoTER'22.

Prof. Snežana Šerbula,

President of the Organizing Committee

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ENVIRONMENTALLY SAFE CORROSION INHIBITORS: AMINO ACIDS

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Abstract

Copper, brass, aluminum and steel are considerably used in many industries due to their good electrical and mechanical properties. Most industrial environments are highly aggressive and corrosive for metals and alloys which leads to their decay during use. This further leads to operating problems which can cause a partial or total shutdown of the process. Stoppage of the process for even a short time causes economic and financial losses. Due to high economic losses, protection from corrosion is the focus of many industries as well as scientific research. The use of different compounds which possess characteristics of the inhibitor is extensively examined over the years. Most compounds that show good inhibition efficiency are toxic and considered environmental pollutants. In recent years demands for environmental protection are high which lead to needing for finding new environmentally safe inhibitors of corrosion of metals and alloys. Amino acids are cheap for production, highly soluble in water, and can be produced in high purity. Amino acids also contain heteroatoms in their structure which makes them almost ideal candidates for green corrosion inhibitors in different aggressive solutions. Different amino acids were tested as corrosion inhibitors in many aggressive mediums and showed good results in inhibition efficiency. The action mechanism of amino acids is based on the adsorption of molecules of amino acids on the metal surface and the formation of the protective film which prevents further dissolution of metals. Often, amino acids react with metal ions through coordinative bonds and form complexes that protect the surface of the metal. Also, amino acids in combination with other compounds manifest a synergistic effect. The synergistic effect is detected in the combination of two amino acids and in the combination of amino acids and surfactants. Surfactants provide better adsorption of the molecules of the amino acids on the metal surface and lead to higher inhibition efficiency.

Keywords: amino acid, corrosion, inhibition, copper, steel

INTRODUCTION

Corrosion of metals and alloys are one of the biggest sources of accidents in a number of industries which lead to huge material and economic losses [1]. According to the available literature data, annual losses caused by corrosion of metals and alloys in the USA achieved 4.2 % of GDP [2,3]. Implementation of available methods for the protection of metals from corrosion leads to the reduction of annual costs originated by corrosion up to 35 %. This is one of the main reasons for constant effort for finding new and more efficient methods for inhibiting corrosion [4]. The cause of corrosion of metals and alloys are chemical and/or electrochemical interaction between the metal surface and corrosive medium which as results have the formation of stable products or fatigue of metals. The electrochemical corrosion encompasses processes with release of electrons (anodic dissolution of metals) and processes

that accept electrons (cathodic processes). Oxygen, oxidizing agents and hydrogen are usually used as substances which accept electrons in cathodic processes [5]. The inhibition of the corrosion of metals and alloys may be achieved in many ways. One of the most represented method for inhibition of corrosion is use of protective coatings. Moreover, the usage of inorganic and organic compounds as corrosion inhibitors in different solutions is a very promising method for metals protection. The data collected from research done up to now, reveals that the inhibition action of organic compounds is based on adsorption of organic molecules or/and formation of protective film onto metal surface. The inhibitors effect on corrosion rate by decreasing the anodic or/and cathodic reactions, by decreasing diffusion of reactants to the metal's surface and by decreasing electrical resistance of the surface of the metal. The organic compounds which are used as corrosion inhibitors block active sites on a metal's surface. Blocking of the active sites is the result of adsorption of inhibitor molecules on the metal's surface. Four types of adsorption of inhibitors are [6]:

- Electrostatic interaction between inhibitors molecules and metal
- Interaction between lone electron pair in inhibitors structure and metal
- Interaction between metal and π-electron in inhibitor structure
- Simultaneous electrostatic interaction and interaction between metal and π-electron in inhibitor structure

Existence of the heteroatoms (oxygen, nitrogen, sulfur, phosphorus) or double bond in the inhibitor structure are necessary for interaction between inhibitors and metals.

Inhibition efficiency of a tested compound depends on the presence of heteroatoms in the molecular structure. The dependence of the inhibitor efficacy on the heteroatoms present increases in the following order: O < N < S < P [7]. Numerous compounds that show high value of inhibition efficiency are toxic and have a negative impact on the environment which limits their usage. The effect of this is that research groups all around the world have focused on finding corrosion inhibitors that are environmentally safe and nontoxic. Years of research confirms that a large number of organic compounds which belong to „green" inhibitors have acceptable inhibition efficiency. Amino acids, pharmaceutical products and plant extracts are one of the most prominent compounds which belong to „green" inhibitors with confirmed high protection ability for corrosion of copper, brass, steel, aluminum and other metals and alloys in different solutions [8–16].The cost of inhibitors is an important factor during the selection of adequate inhibitor in a tested system. Besides that, inhibitor must be readily available when considering its applicability. Accordingly, amino acids are one of the most interesting groups of compounds which achieve these demands. Also, amino acids are an integral part of proteins and thus a part of the human body, which makes them suitable choice for the inhibitors of corrosion in body solutions. Further, amino acids are well soluble in water solutions, relatively inexpensive and can be easily obtained with a high degree of purity [17].

INHIBITION MECHANISM OF AMINO ACIDS

According to the available literature data, amino acids were intensively investigated as environmentally friendly corrosion inhibitors for different metals and alloys [17–20]. Many studies have been performed on mild steel and copper in HCl and H_2SO_4 solutions [21–24]. Cysteine and methionine are the most tested amino acids in these solutions as corrosion inhibitors [25–27]. Other amino acids were sporadically tested. Amino acids are compounds that were investigated as potential inhibitors for preventing corrosion of biomaterials. It is well known that amino acids are bio compounds present in the human body. The understanding of the influence of amino acids on the corrosion of biomaterials is of huge significance for further implementation. Due to that, corrosion properties of biomaterials such as stainless steel were examined in different artificial physiological solutions [28,29]. Lysine and threonine are amino acids that were tested as stainless steel corrosion inhibitors in BM - 3 solution [30]. Threonine differs from other amino acids because it is a polar amino acid with heteroatoms and aliphatic hydroxyl groups in structure and electron pairs available for bonding with metals. Lysine is more interesting as a potential corrosion inhibitor. First, lysine is a basic amino acid with two N atoms in structure which provide more active centers for bonding with metals. Also, lysine is an amino acid with a chain longer than a chain in most amino acids, which can provide better surface coverage and better inhibition efficiency [30].

Six amino acids were tested as potential corrosion inhibitors for copper and carbon steel in H_2SO_4 solution by Mendonca *et al.* [18]. Inhibition efficiency of tested amino acids ranks in order: Arg > Gln > Asn > Met > Cys > Ser for copper and Met > Cys > Ser > Arg > Gln > Asn for steel. Asparagine (Asn), Glutamine (Gln), and Arginine (Arg) are long-chain amino acids with a different number of amino groups (more than one) in their structure which make them suitable for corrosion inhibitors in aggressive solutions. Cysteine (Cys), Methionine (Met), and Serine (Ser) are interesting because of differences in structure and the influence of various groups on the forming bond between the metal surface and inhibitor molecules. Electrochemical tests reveal that all tested amino acids act like mixed-type corrosion inhibitors in aerated H_2SO_4. In an acidic medium in the presence of amino acids, cathodic reactions stay unchanged and can be shown as follows [31,32]:

$$H^+_{(aq)} + e^- = \frac{1}{2} H_{2(g)}$$

$$O_{2(g)} + 4H^+_{(aq)} + 4e^- = 2H_2O_{(l)}$$

Cathodic current density decreases due to the adsorption of an amino acid's molecule on the metal surface blocking cathodic active sites. Anodic dissolution of steel in acidic solutions starts with the exchange of the water molecules adsorbed on the metal surface with the amino acid's molecule [18]:

$$Inh_{(solution)} + xH_2O_{(adsorbed)} = Inh_{(adsorbed)} + xH_2O_{(solution)}$$

During the reactive dissolution of steel, Fe^{2+} ions are generated according to the equation [18]:

$$Fe_{(s)} = Fe^{2+}_{(aq)} + 2e^-$$

Generated Fe^{2+} ions react with adsorbed inhibitor molecules and form the Fe(II)-Inh complex with protective ability on the metal surface [18]:

$$Fe^{2+}_{(aq)} + (Inh)_{(adsorbed)} = Fe(Inh)^{2+}_{(adsorbed)}$$

On the other hand, during the corrosion of copper in the H_2SO_4 solution, the cathodic process was under the control of the diffusion of the dissolved oxygen. In this system, oxygen reduction is a dominant cathodic reaction that can be inhibited by the adsorption of amino acids molecules on the cathodic active sites. Anodic dissolution of copper in acidic solutions includes two steps. In the first step, the Cu^{+} ions adsorb on the metal surface [18]:

$$Cu = Cu^{+}_{(adsorbed)} + e^{-}$$

The second step is actually oxidation of the Cu^{+} to the Cu^{2+} [18]:

$$Cu^{+}_{(adsorbed)} = Cu^{2+}_{(adsorbed)} + e^{-}$$

In the presence of amino acids such as cysteine and methionine, Cu(I)-Cys and Cu(I)-Met complex were formed which have protective characteristics and prevent metal from further dissolution.

The methionine was examined as a potential corrosion inhibitor of stainless steel in 1 M H_2SO_4 and shows that it successfully inhibits anodic and cathodic corrosion processes. In the concentration higher than 50 ppm methionine reduces anodic dissolution of iron and postpone the hydrogen evolution reaction [26]. Tafel slopes indicate the influence of tested inhibitors on the corrosion mechanism. If the addition of inhibitor has no influence on the shift of Tafel slopes, it means that corrosion reactions are under the control of the activation process. Also, this indicates that with the addition of an inhibitor, the corrosion mechanism stays unchanged. The shift of the corrosion potential (E_{corr}) in the presence of an inhibitor points to the class of the inhibitor type. If the shift of the E_{corr} is lower than 85 mV in the presence of an inhibitor that indicates that the tested inhibitor is the mixed-type inhibitor. The shift of the E_{corr} higher than 85 mV in the presence of an inhibitor indicates examined inhibitor is an anodic or cathodic type of the inhibitor [33–36]. Methionine and valine show inhibition activity on corrosion of carbon steel in phase change materials solution. The best results were achieved in solution with the molar ratio of amino acids 1/1. The inhibition mechanism is associated with the adsorption of methionine and valine molecules on the steel surface through heteroatoms (N and S) and –COOH group as main active sites [27].

Loto [17] examined influence of L-Leucine on the steel corrosion in HCl solution. L-leucine is a weak acid and during the electrochemical reaction the carboxylic acid functional group deprotonates and becomes negative $–CO_2^-$ group, while the amino functional group protonates and becomes a positive ammonium group. At low concentration, the ammonium group is dominant while at high concentration, the carboxylate group becomes dominant. The nitrogen atom from the ammonium group and the oxygen atom from carboxylate consist lone pair of electrons that are involved in the reaction between the amino acid molecule and metal which as a result has adsorption of leucine on the metal surface. The inhibition activity of leucine strongly depends on concentration. At the lower concentration of the leucine adsorption occurs dominantly on cathodic active sites and determines that leucine inhibits cathodic corrosion process. With the increase of the leucine concentration, molecules

of the inhibitor start to adsorb on the entire surface of metal, increasing the impedance of the metal. Adsorption on the entire surface of the metal means that the inhibitor adsorbs equally on cathodic and anodic active sites, inhibiting cathodic and anodic corrosion processes. This suggests that at the higher concentration, leucine acts like a mixed-type inhibitor in hydrochloric solution [17].

Also, the visible-light illumination can affects the adsorption of cysteine on low-alloy steel surfaces in sodium chloride solution. The illumination of a steel surface according to the existing photovoltaic effect comes to the adsorption of the photons in the visible-light range and to the formation of an electron-hole pair. This leads to the intensive relocation of chloride ions that cause more intensive corrosion as a result. However, in the presence of cysteine, formation of holes in the process of photon adsorption is difficult, which leads to a decrease in the relocation of chloride ions. The result is a decrease in corrosion of the steel surface [37]. The inhibition efficiency of tested amino acids in different aggressive solutions was present in Table 1.

Table 1 *Inhibition efficiency of amino acids as corrosion inhibitor*

Amino acid	Material	Concentration	Solution	IE [%]	References
Arginine	Copper	$1 \cdot 10^{-2}$ M	0.5 M H_2SO_4	93.7^{EIS}	[18]
Glutamine				88.5^{EIS}	
Asparagine				74.91^{EIS}	
Methionine				60.03^{EIS}	
Cysteine				58.98^{EIS}	
Serine				42.82^{EIS}	
Cysteine	Copper	$1 \cdot 10^{-2}$ M	0.5 M Na_2SO_4	82.73^{PP}	[20]
Cysteine	Carbon steel	50 mg/dm^3	3.5 % NaCl	74.7^{EIS}	[25]
Methionine	Stainless steel	700 ppm	1 M H_2SO_4	97^{EIS}	[26]
Methionine	Carbon steel	0.05 M	Phase change materials	79.43^{EIS}	[27]
Valine		0.05 M		59.51^{EIS}	
Methionine + Valine		0.05 M		95.09^{EIS}	
Lysine	Stainless steel	0.1 M	BM - 3	71.1^{PP}	[30]
Threonine				88.4^{PP}	
Lysine + SDS		0.1 M + $1 \cdot 10^{-2}$ M		93.8^{PP}	
Cysteine	Copper	$1 \cdot 10^{-2}$ M	0.5 M Na_2SO_4	75.68^{PP}	[33]
			0.5 M Na_2SO_4 + NaOH	88.16^{PP}	
Cysteine	Brass	$1 \cdot 10^{-3}$ M	0.5 M Na_2SO_4	85.1^{PP}	[34]
Cysteine	Steel	5 mM	1 M HCl	54^{PP}	[38]
Arginine	Steel	900 mg/dm^3	1 M HCl	70.53^{EIS}	[39]
Arginine			3.5 % NaCl	88.20^{EIS}	[40]
Cysteine	Brass	$1 \cdot 10^{-2}$ M	0.05 M HCl	88.9^{PP}	[41]
Methionine	Copper	10 mM	1 M NaOH	90.8^{PP}	[42]
Cysteine	Copper	200 ppm	1 M H_2SO_4	84.60^{EIS}	[43]
Alanine		200 ppm		82.40^{EIS}	
Cysteine + Alanine		150 ppm + 50 ppm		95.59^{EIS}	
Methionine	Copper-Nickel alloy	40 ppm	3.5 % NaCl	68^{PP}	[44]
Methionine + sodium silicate		20 ppm + 20 ppm		92^{PP}	
Cysteine	Copper	$1 \cdot 10^{-2}$ M	3.5 % NaCl	97.08^{PP}	[45]

Table 1 *continued*

Proline	Copper	$1 \cdot 10^{-3}$ M	8 M H_3PO_4	39.6^{PP}	[46]
Cysteine				52.17^{PP}	
Alanine				36^{PP}	
Histidine				54.34^{PP}	
Glycine				32.9^{PP}	
Glycine	Copper	15 mM	0.5 M HCl	60^{EIS}	[47]
Cysteine		15 mM		92.9^{EIS}	

ADSORPTION ISOTHERM (THERMODYNAMICS OF THE INHIBITION MECHANISM OF AMINO ACIDS)

The inhibition efficiency of amino acids is connected with the strength of adsorption of amino acid's molecules on the metal surface. The adsorption of the inhibitor on the metal surface is one of the most important steps in the inhibition mechanism [34]. Adsorption of amino acids on the metal surface depends on many parameters but the most important are: orientation of the inhibitor molecule, ionization and polarization of the amino acid molecules [48]. Besides, the adsorption of inhibitors depends on several more factors, such as the nature of the metal surface, the distribution of charge in the inhibitor molecule, the chemical structure of the inhibitor, and the type of interaction between the inhibitor and metal surface [49]. An illustration of amino acids adsorption on the metal surfaces is shown in Figure 1. Inhibitory effect can be associated with physical adsorption or with chemisorption of the inhibitor [8,50]. Metal surface must be electrically charged in physical adsorption process and charged species should be present in the bulk of the solution. Nonetheless, chemical adsorption requires existence of vacantlow-energy electron orbital in metal structure and inhibitors with relatively loosely bonded electrons in molecules or heteroatom with lone pair electrons [51].

Langmuir, Freundlich, Tempkin and Frumkin adsorption isotherms are the most frequently used for fitting results of the amino acids adsorption on metal surface in different solutions [20,30]. According to the Langmuir adsorption isotherm on the metal surface exists a certain number of sites are available for the adsorption of inhibitor molecules. This leads to the definitive number of inhibitor molecules which can be adsorbed on the metal surface without lateral interaction between adsorbed molecules.

Literature data reveals that the Langmuir adsorption isotherm is the most often used isotherm in thermodynamically investigation of the adsorption of amino acids on the metal surface [38,52,53]. The Frumkin adsorption isotherm was used in systems where metal surface was heterogeneous. This adsorption isotherm describes the interaction between adsorbed inhibitor molecules. The Freundlich isotherm describes the relationship between adsorbed molecules, their interaction and influence on the adsorption process [17]. The Gibbs free energy, an important thermodynamic parameter, is calculated from a Langmuir adsorption isotherm according to the equation [17,53]:

$$-\Delta G = \left(lnK - ln\left(\frac{1}{55.5}\right)\right) \cdot R \cdot T$$

Where R stands for universal gas constant, T is the thermodynamic temperature and 55.5 represents the molar concentration of water in solution. The value of Gibbs free energy lower

than 20 kJ/mol indicates the physisorption of inhibitor molecules on the metal surface. Chemisorption of inhibitor molecules is determined by the value of Gibbs free energy higher than 40 kJ/mol. At these values charge sharing or a transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond occurs. Values between 20 and 40 kJ/mol indicate mixed adsorption of inhibitor molecules.

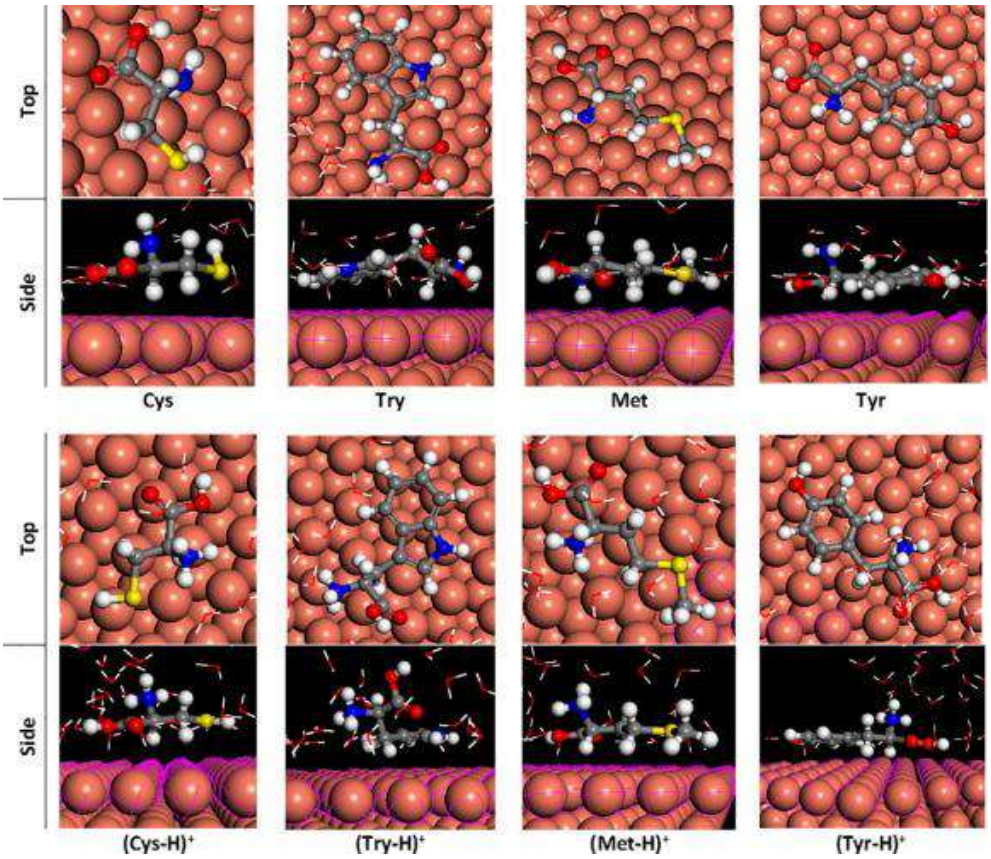

Figure 1 *Optimized systems of some amino acids in neutral and protonated forms on Cu (111) in aqueous phase. Reprinted from B. El Ibrahimi et al. (2020) published in accordance with the principles of open access under CC BY-NC-ND 4.0 (B. El Ibrahimi et al. Journal of King Saud University – Science 32 (1) (2020) 163)*

QUANTUM CHEMICAL CALCULATIONS

In order to study the influence of electronic properties and molecular structure on the corrosion inhibition efficiency of amino acids and to prove that the inhibitor molecules can adsorb on the metal surface, quantum chemical calculation was used [27,35,54]. The quantum chemical calculation enable the determination of parameters such as: energy of the highest occupied molecular orbital (E_{HOMO}), energy of th elowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE), dipole moment (μ), ionization potential (I), electron affinity (A), electronegativity (χ), global hardness (η) and number of transferred electrons (ΔN). Equations used for calculations are [30]:

$I = -E_{HOMO}$

$A = -E_{LUMO}$

$\chi = 0.5 \cdot (I + A)$

$\eta = 0.5 \cdot (I - A)$

$\Delta N = (\chi_{Fe} - \chi_{inh})/[2 \cdot (\eta_{Fe} + \eta_{inh})]$

Donor-acceptor interaction explains the adsorption mechanism of inhibitor molecules on the metal surface. E_{LUMO} represents the ability of a molecule to accept charge from the donor pair of electrons. E_{HOMO} is the capacity of the molecules to donate electrons to the metal with vacant d-orbitals. In the structure of amino acids, HOMO is usually located in the vicinity of the heteroatoms, making it a reaction center for interaction with metal. The values of E_{HOMO} and E_{LUMO} indicate inhibition efficiency of tested compounds. Published data reveal that a higher value of E_{HOMO} and a lower value of E_{LUMO} point to stronger inhibition efficiency of tested amino acids as corrosion inhibitors in different solutions [30]. The energy gap is a useful parameter that indicates the inhibition efficiency of the tested compounds. The minor difference in E_{HOMO} and E_{LUMO} values suggests the higher inhibition efficiency due to the lower energy necessary to remove electrons from the last occupied orbital [55]. Also, the lower value of electronegativity points to better inhibition efficiency due to easier electron transfer between reaction center in inhibitor structure and vacant d-orbitals in metal structure [56]. Global hardness is also parameter which can point out to the efficiency of tested amino acids as corrosion inhibitor in tested solution. A lower value of η implies higher polarizability and indicates better inhibition efficiency [30]. The dipole moment is used for determining the polarity of a molecule and it is a parameter that was used for the prediction of inhibition efficiency of the examined compounds [57]. The number of transferred electrons describes the intensity and direction of the electron transfer. The value of ΔN below 3.6 indicates the tendency of a molecule to donate electrons to the metal. In that case, stronger inhibition efficiency was determined by the higher value of ΔN [30].

SYNERGISTIC EFFECT

The inhibition efficiency of amino acids used as corrosion inhibitors in aggressive solutions was enlarged through a synergistic effect with other compounds [30,41,44,58]. For the estimation of the synergistic inhibition effect of two used inhibitors, the synergistic parameter was utilized [27,59]. The synergistic parameter was calculated according to the equation [60]:

$$S = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}}$$

$$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \cdot \theta_2)$$

θ_1 – surface coverage by the first inhibitor

θ_2 – surface coverage by the second inhibitor

θ'_{1+2} – surface coverage by binary inhibitor composition

The synergistic parameter's value higher than 1 reveals a synergistic effect due to cooperative adsorption. In the case when S is lower than 1, an antagonistic effect is observed as a result of competitive adsorption. Finally, if the synergistic parameter's value is 1, it indicates no interaction between inhibitors.

The synergistic effect of cysteine and alanine was investigated in a 1 M H_2SO_4 solution and it was observed due to the co-adsorption mechanism. The combination of cysteine and alanine in an acidic environment suppresses anodic and cathodic corrosion processes [43]. The concentration of tested inhibitors has a great influence on the synergistic effect. In the phase change materials solution, methionine and valine show synergistic adsorption at concentrations higher than 0.04 M. However, at concentrations lower than 0.03 M competitive adsorption was achieved leading to the antagonistic effect [27].

Surfactants are used often as corrosion inhibitors in combination with other tested compounds [25,38]. Radovanović *et al.* [30,41] examined influence of sodium dodecyl sulfate (SDS) on the protection ability of cysteine and lysine in HCl and BM – 3 solutions. SDS molecules adsorb on the electrode surface through electrostatic forces and hydrogen bonding, leading to the enhanced adsorption of amino acid molecules. Improved adsorption of amino acids leads to the decrease of the anodic and cathodic current density [30]. SEM-EDS and AFM investigations confirmed the formation of protective film in aggressive solution in the presence of amino acids and sodium dodecyl sulfate (Figure 2 and 3).

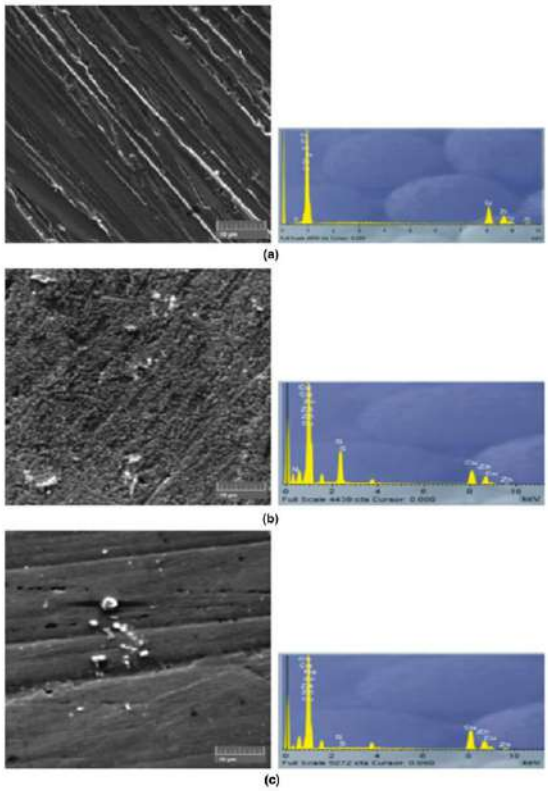

Figure 2 *SEM and EDS analysis of a) the polished brass surface without any treatment; b) brass surface after immersion of the electrode for 1140 min in $1 \cdot 10^{-2}$ M cysteine solution and c) brass surface after immersion of the electrode for 4080 min in $1 \cdot 10^{-3}$ M SDS solution. Reprinted from M. B. Radovanović et al. (2018) published under Creative Commons Attribution License CC BY 4.0 (M. B. Radovanovic et al. Advances in Materials Science and Engineering (2018) 9152183)*

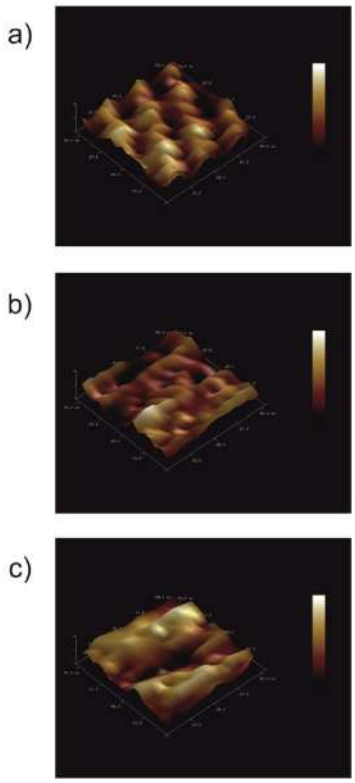

Figure 3 *3D AFM images of stainless steel surface after immersion in a) BM – 3 solution (5 days); b) 0.1 M L-Lysine (5 days) and c) 0.01 M SDS (24h) + 0.1 M L-Lysine (5 days). Reprinted from M. B. Radovanović et al. (2021) with permission of Elsevier (M. B. Radovanovic et al. Journal of Molecular Liquids 342 (2021) 116939)*

CONCLUSION

Corrosion of metals leads to great loss. One of the main achievements is to find an adequate method to prevent and inhibit the corrosion of metals and alloys. Some of that methods are the use of inorganic and organic compounds which act as corrosion inhibitors in different media. Today, scientists around the globe always have in mind that compounds which can be used as corrosion inhibitors must be environmentally friendly. Different groups of compounds meet that condition such as amino acids, plant extracts, purines etc.

Amino acids are one of the most prominent classes of compounds that are tested as corrosion inhibitors in different solutions. The low cost, easy production, and existence of different heteroatoms in their structure provide wide application in the protection of metals and alloys. Some amino acids have numerous active centers in their structure or some others have a longer chain or electron pairs that are available for bonding with metals. All of these provide better inhibition efficiency in aggressive solutions. Tested amino acids act, in numerous solutions, like mixed-type inhibitors. The inhibition action of amino acids is linked with the adsorption of amino acids molecules on the cathodic and anodic active sites.

The formation of a protective complex is also observed in the presence of amino acids. Langmuir, Freundlich, Tempkin, and Frumkin adsorption isotherms are used for fitting results of the amino acids adsorption on metal surfaces in different solutions and Langmuir adsorption isotherm is the most often used isotherm in thermodynamically investigation of the

adsorption of amino acids on the metal surface. The synergistic effect of amino acids with other compounds was confirmed.

The synergistic effect was observed between two different amino acids and between amino acids and surfactants. Surfactants enhance the adsorption of amino acids on the metal surface and improve inhibition efficiency in tested solutions.

The quantum chemical calculation in recent years was extensively used for the examination of the influence of electronic properties and molecular structure on the corrosion inhibition efficiency of amino acids. This calculation provides an abundance of information on compounds that may be used for further experimental investigation.

In further years, the main focus of the researchers can be an increase in the inhibition efficiency mentioned compounds as well as the synthesis of new compounds which are derivatives of purines, amino acids, and others, which can achieve better inhibition efficiency in aggressive solutions.

ACKNOWLEDGEMENT

The authors would like to acknowledge financial support from the Ministry of Education, Science and Technological Development of the Republic of Serbia (Agreement No 451-03-68/2022-14/200131).

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ISBN 978-86-6305-123-2