Corrosion Resistance of Copper in Artificial Sweat in the Presence of Sodium Chloride

N. Anitha[1], I. S. Vinnarasi[1], P. S. Kala[1], A. L. Jewelcy[1], T. A. Anucia[1], B. Gomathi[1] and S. Rajendran[1,2*]

[1]Corrosion Research Centre, Department of Chemistry, St Antony's College of Arts and Sciences for Women, Amala Annai Nagar, Thamaraipadi, Dindigul, (Affiliated to Mother Teresa Women's University, Kodaikanal), Tamil Nadu, India
[2]Adjunct Professor, Centre for Nanoscience and Technology, Pondicherry University, Puducherry, India
*Corresponding author: susairajendran@gmail.com

Received 23/11/2023; accepted 27/02/2024
https://doi.org/10.4152/pea.2025430503

Abstract
CR of Cu in AS without and with 100 ppm NaCl was studied by electrochemical methods such as PDP technique, AC impedance spectra and EIS. The study revealed that, in the presence of excess of Cl ions in AS, CR of Cu decreased. This implies that people wearing ornaments or watches made of Cu must be careful about NaCl level in their sweat.

Keywords: AS; CR; Cu; electrochemical studies; NaCl influence.

Introduction•

Human perspiration (sweat) comes in contact with a number of consumer products. Contact can cause a variety of undesirable effects. Dyes can bleed or discolor, components can corrode and/or malfunction, residues can be unsightly. The problem of metal corrosion resulting from palmar sweat is common to many industrial occupations. Constant handling of metal parts by some individuals causes an accumulation of rust. In the manufacture of highly finished metal products, e.g., ball-bearings, and also in subsequent assembling and packing processes, serious consideration must be given to this effect [1-10].

[1] have made a study on microstructure and properties of Pt-Co-Mn alloy in AS. The analyzed alloy exhibited a good CR in AS. Effect of superhydrophobic surface on CR of Mg-Nd alloy in artificial hand sweat has been investigated by [2]. This superhydrophobic surface had an interesting self-cleaning effect, and good CR in hand AS.

Electrochemical studies have been carried out on the CR of: 18K Au and TAA, in AS with and without 100 ppm NaCl, by PDP study and AC impedance spectra [3]; 18/8 SS and 22 K Au alloys in AS with D-Glu [4]; of 21K Au alloy with urea and Glu in AS [5]. In these studies, it was seen that CR increased. Hence, it was concluded that people wearing ornaments made of alloys do need to worry about the excess of NaCl [3], D-Glu [4], or urea and Glu [5] in their sweat. Corrosion assessment of a passivation film

•The abbreviations and symbols lists are on pages 305-306.

generated on the solder surface in an AS solution has been investigated by [6]. This work can provide some suggestions for the personalized design of wearable devices, by considering sweat corrosion effect.
[7] have investigated the antibacterial properties, CR and discoloration resistance of pure Cu containing Zn or Ni. This study provided support for the future application of Cu alloys as antimicrobial surface-contact materials, with safer public and medical environments, in the face of diseases spread by large populations.
[8] have assessed dermal absorption of Be and Cu contained in temple tips of eyeglasses. This study highlighted the importance of avoiding the use of Be alloys in items exposed to long-term skin contact.
Corrosion behavior of Cu-Zn-Ni-Sn replicated-Au/Cu alloy in AS and seawater has been investigated by [9]. They concluded that the main corrosion products at the initial stage of oxidization in AS were mainly loose CuO and unstable SnO. In AS corrosion process, the corrosion product layer formed in the early stage cracked, and the solid phase diffusion at the crack end interface determined the corrosion reaction rate.
Effect of precipitation hardening on CR of Cu-4.5 wt.% Ti has been investigated by [10]. The results showed that the cast sample had the highest CR. Mechanical properties decreased with the homogenization treatment, and increased after the combination of homogenization and aging. A corrosion mechanism correlated to the amount and type of intermetallic material was proposed in the study.
The present study aimed to study CR of Cu, in AS without and with 100 ppm NaCl, by electrochemical studies, such as PDP technique and AC impedance spectra (EIS).
The interaction between Cu jewelry and AS is quite interesting. Cu jewelry is absolutely safe to wear. Naturally antimicrobial, anti-fungal and antibacterial, it can even hinder bacteria, viruses and fungi. Cu is even considered to be an age-old remedy for treating skin conditions and helping wounds heal. Cu bracelets provide a way in which to get the mineral into the body, providing cardiovascular health benefits to the wearer. Wearing Cu rings can improve physiological balance in a person, and also make the body healthier and stronger. Cu helps in purifying the blood, improves hemoglobin formation and increases blood circulation. It protects the body from the negative properties of other toxic metals.
When body sweat comes in contact with Cu jewelry, it will naturally react with O in the air, oils on the skin and salty acidic water that makes up sweat. Over time, this will cause a blue-green discoloration on Cu which, when worn against skin, rubs off and forms a coating on its surface.

Experimental

PDP studies and AC impedance spectra were employed to study the CR of very pure Cu. Cu specimens were immersed in AS (3160-2 ISO standard), of which composition was: 20 g/L NaCl, 17.5 g/L NH_4Cl, 5 g/L acetic acid and 15 g/L d,l lactic acid, with pH adjusted to 4.7 by NaOH. Cu was used as working electrode and AS was used as the electrolyte. The temperature was maintained at 37 ± 0.1 ºC.

Electrochemical studies

CR of Cu in AS without and with 100 ppm NaCl was studied by PDP technique and AC impedance spectra (EIS).

PDP study
A CHI electrochemical work station with impedance, model 660A was used for this purpose. Cu, SCE and Pt were used as working, reference and counter electrodes, respectively. From PDP study, corrosion parameters, such as E_{corr}, I_{corr}, β_a, β_c and LPR, were calculated. SR (V/s) was 0.01. Quit time (s) was 2. Tafel slope potential range was 0.06 V, as a specification for the instrument used in the present study.

AC impedance spectra
AC impedance spectral studies were carried out on a CHI – Electrochemical workstation with impedance, model 660A. Cu, SCE and Pt were used as working, reference and counter electrodes, respectively. The real (Z') and imaginary (-Z'') parts of the cell impedance were measured in ohms, at various frequencies. R_{ct}, C_{dl}, impedance and phase angle values were calculated from Nyquist and Bode plots. The frequency range was selected depending on OCP.

Copper
Cu rings made from 99.99% O-free Cu are becoming increasingly popular, due to their unique properties and health benefits. Thus, pure Cu was used in this study.

Results and discussion
PDP curves of Cu in AS with NaCl are shown in Fig. 1.

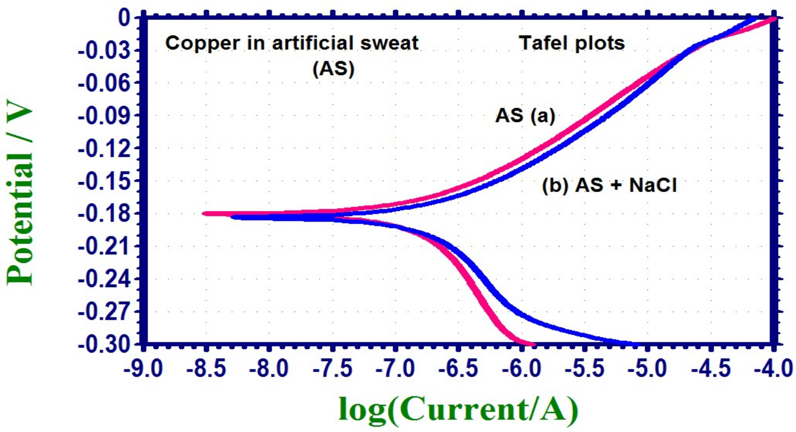

Figure 1: PDP curves of Cu in **(a)** AS and **(b)** AS with NaCl.

Corrosion parameters, namely, E_{corr}, β_c, β_a, LPR and I_{corr} are given in Table 1.

Table 1: Corrosion parameters obtained from PDP study for Cu immersed in AS without and with 50 ppm NaCl.

System	E_{corr} (mV)	β_c (mV/decade)	β_a (mV/decade)	LPR (Ohm/cm^2)	I_{corr} (A/cm^2)
Cu in AS	-180	154	79	97382	2.322 x10^{-7}
Cu in AS + 50 ppm NaCl	-183	60	81	76767	35.50 x10^{-7}

It is well known that, with lower CR, LPR value decreases and I_{corr} increases (Fig. 2). When R_p decreases, electron transfer from the metal surface to the medium is easy. So, current flow is stronger, and I_{corr} increases [11-15].

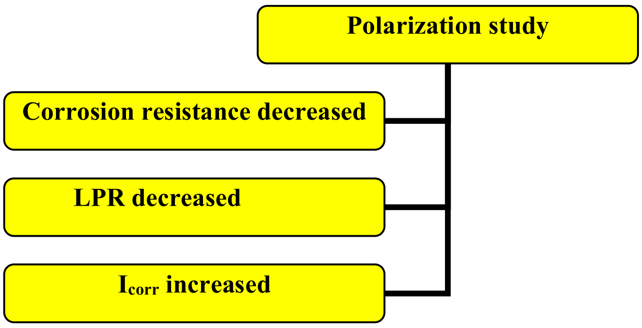

Figure 2: Correlation among corrosion parameters of PDP study.

Cu in a AS system

When Cu was immersed in a AS system, (Fig. 1) E_{corr} was -0.180 mV vs SCE. LPR value was 460267 Ohm/cm^2 and I_{corr} was 2.322 x 10^{-7}A/cm^2.

Cu in AS + 100 ppm NaCl system

When Cu i was immersed in a AS solution + NaCl system (Fig. 1), E_{corr} was -183 mV vs SCE. LPR value was 76767 Ohm/cm^2 and I_{corr} was 35.50 x 10^{-7}A/cm^2. LPR value decreased and I_{corr} increased. This indicates that, with excess of Cl ions in AS, CR of Cu decreased.

Implication

People wearing ornaments or watches made of Cu must be careful about NaCl level in their sweat.

Analysis of AC impedance spectra

AC impedance spectra and its parameters are shown in Figs. 3-10 and Table 2.

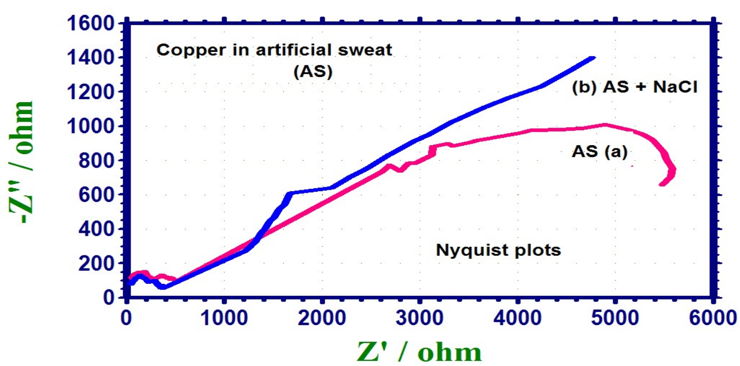

Figure 3: AC impedance spectra of Cu in **(a)** AS and **(b)** AS + NaCl.

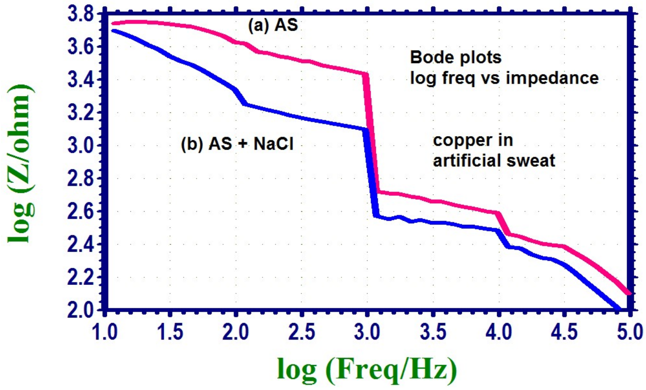

Figure 4: AC impedance spectra of (Bode plots- log freq *vs.* impedance) Cu in **(a)** AS and **(b)** AS + NaCl.

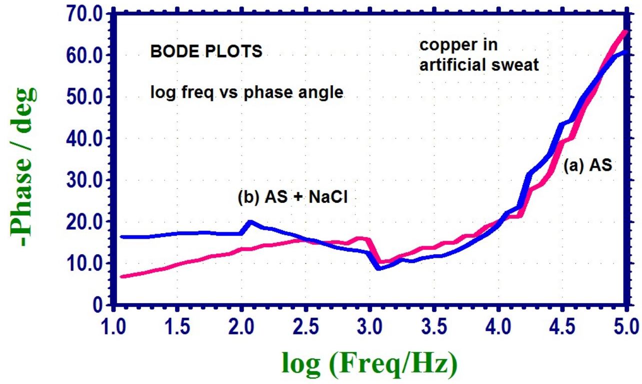

Figure 5: AC impedance spectra of (Bode plots- log freq vs phase angle) Cu in **(a)** AS and **(b)** AS + NaCl.

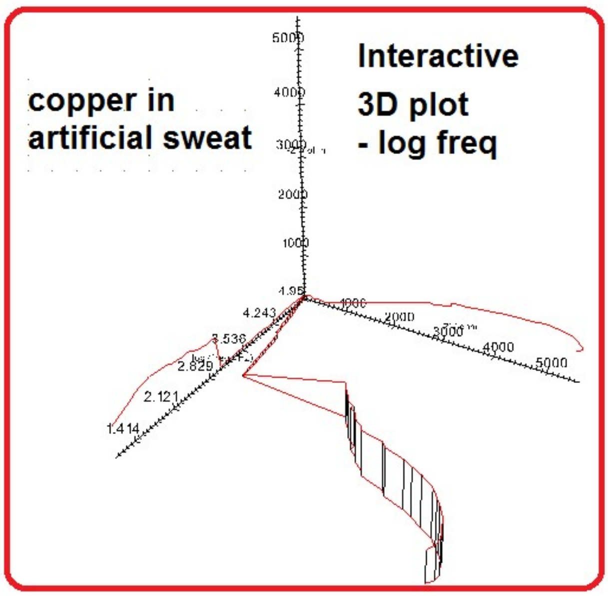

Figure 6: Interactive 3D plot- log freq of Cu in AS.

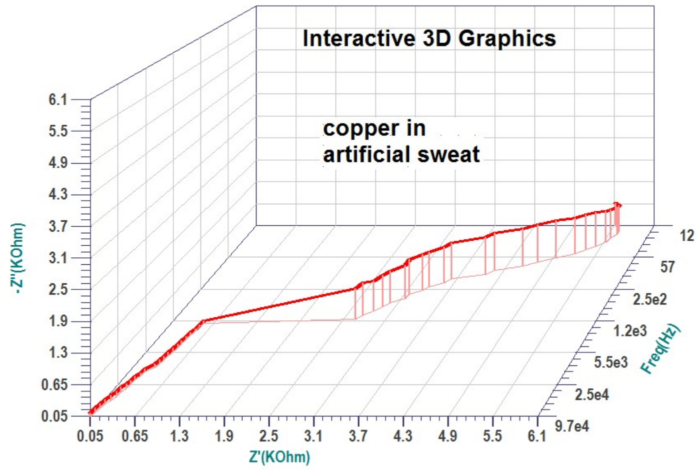

Figure 7: Interactive 3D Graphics of Cu in AS.

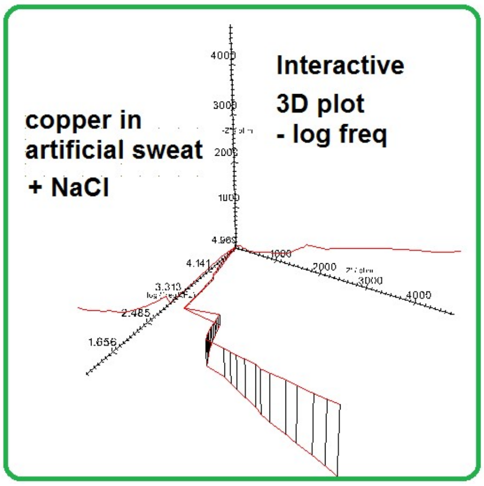

Figure 8: Interactive 3D plot- log freq of Cu in AS + NaCl.

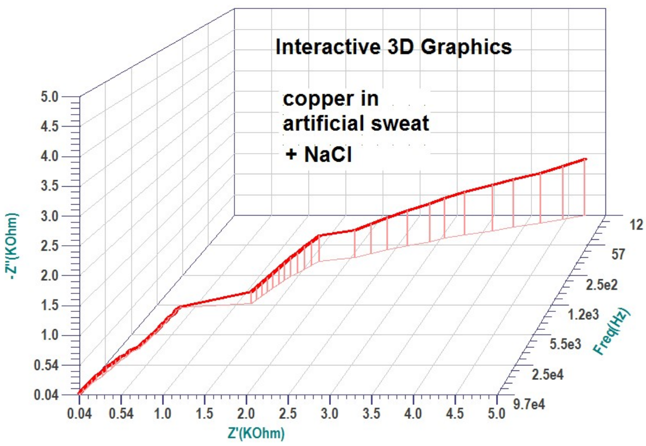

Figure 9: Interactive 3D graphics of Cu in AS + NaCl.

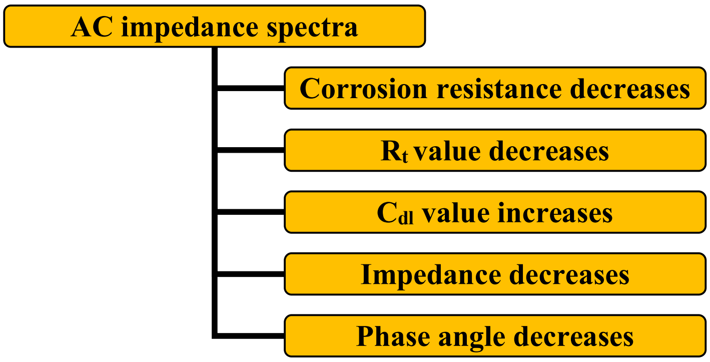

Figure 10: Correlation among corrosion parameters of AC impedance spectra.

Table 2: Corrosion parameters obtained from AC impedance spectra for Cu immersed in seawater without and with inhibitor systems.

System	R_{ct} (Ohm/cm^2)	Impedance log (Z/ohm)	Phase angle	C_{dl} (F/cm^2)
Cu in AS	5610	3.744	66.13	9.091×10^{-10}
Cu in AS + 50 ppm NaCl	4792	3.694	60.79	10.64×10^{-10}

Conclusion

CR of Cu in AS without and with 100 ppm NaCl was investigated by PDP and AC impedance spectra (EIS) electrochemical methods. The study revealed that, with excess of Cl ions in AS, CR of Cu decreased. C_{dl} decreased [16-20], which implies that people wearing ornaments or watches made of Cu must be careful about NaCl in their sweat.

Acknowledgement

The authors are thankful to the management for their help and support.

Authors' contributions

N. Anitha, **I. S. Vinnarasi**, **P. S. Kala**, **A. L. Jewelcy**, **T. A. Anucia, B. Gomathi**: conceptualization and validation; review and editing. **S. Rajendran**: writing; correspondence. All authors have read and agreed to the published version of the manuscript.

Abbreviations

AC: alternating current
AS: artificial sweat
C_{dl}: double layer capacitance
Cl: chlorine
CR: corrosion resistance
Cu: copper
E_{corr}: corrosion potential
EIS: electrochemical impedance spectra

Glu: glucose
I_{corr}: corrosion current
ISO: International Organization for Standardization
LPR: linear polarization resistance
NaCl: sodium chloride
NaOH: sodium hydroxide
NH_4Cl: ammonium chloride
OCP: open circuit potential
Ppm: parts per million
R_{ct}: charge transfer resistance
R_p: polarization resistance
SCE: saturated calomel electrode
SR: scan rate
SS: stainless steel

Symbols
β_a: anodic Tafel slope
β_c: cathodic Tafel slope

References

1. Luo Y, Wang X, Zhao J et al. Study on the Microstructure and Properties of Pt-Co-Mn Alloy. Mat Rep. 2023;37(10):21060215-5. https://doi.org/10.11896/cldb.21060215
2. Liu C, Sun J, Wu G. Effect of Superhydrophobic Surface on Corrosion Resistance of Magnesium-Neodymium Alloy in Artificial Hand Sweat. Metals. 2023;3(2):219. https://doi.org/10.3390/met13020219
3. Gowrani T, Anitha N, Dhanalakshmi M et al. Electrochemical studies on the corrosion resistance of Gold 18K and Thermo active alloy in artificial sweat in presence of sodium chloride. Zast Mater Mater Prot. 2023;64(1):38-47. https://doi.org/10.5937/zasmat2301038G
4. Anitha N, Prathipa V, Velkannan V et al. Corrosion resistance of SS 18/8 alloy and Gold 22 K alloy in artificial sweat in the presence of D-Glucose. Mater Prot. 2022;63(4):418-429. https://doi.org/10.5937/zasmat2204418A
5. Umamathi T, Parimalam R, Prathipa V et al. Influence of urea and glucose on corrosion resistance of Gold 21K alloy in the presence of artificial sweat. Mater Prot. 2022;63(3):341-352. https://doi.org/10.5937/zasmat2203341U
6. Yu B, Zhou X, Wu G et al. Corrosion assessment of passivation film generated on solder surface in artificial sweat solution. Mater Today Commun. 2022;33:104828. https://doi.org/10.1016/j.mtcomm.2022.104828
7. Jiang Y, Zhang W-J, Mi X-J et al. Antibacterial property, corrosion and discoloration resistance of pure copper containing Zn or Ni. Rare Met. 2022;41(12):4041-4046. https://doi.org/10.1007/s12598-022-02098-8
8. Magnano GC, Marussi G, Adami G et al. Assessment of dermal absorption of beryllium and copper contained in temple tips of eyeglasses. Toxicol Lett. 2022;361:64-71. https://doi.org/10.1016/j.toxlet.2022.04.001

9. Yu X, Sheng X, Zhou T et al. Corrosion behaviour of Cu-Zn-Ni-Sn imitation-gold copper alloy in artificial seawater and perspiration. Zhong Yous Jins Xueb/Chin J Nonferr Met. 2021;31(5):1143-1155.
10. Hanoz D, Settimi AG, Pezzato L et al. Effect of Precipitation Hardening on Corrosion Resistance of Cu-4.5 wt.%Ti. J Mat Eng Perform. 2021;30(2):1306-1317. https://doi.org/10.1007/s11665-020-05353-0
11. Rathod RL, Rajappa MR, Sajjan SK et al. Experimental and Theoretical Investigations of *Cordia Obliqua* Leaves Extract as an Environmentally Benign Inhibitor for Mild Steel Corrosion in a 1 M HCl Solution. Port Electrochim Acta. 2024;42(4):233-254. https://doi.org/10.4152/pea.2024420401
12. Khanna R, Kalia V, Kumar R et al. Synergistic experimental and computational approaches for evaluating pyrazole Schiff bases as corrosion inhibitor for mild steel in acidic medium. J Mol Struct. 2023;1297:136845. https://doi.org/10.1016/j.molstruc.2023.136845
13. Kamaruzzaman WMIWM, Shaifudin MS, Nasir NAM et al. Experimental, DFT and molecular dynamic simulation of *Andrographis paniculata* as corrosion inhibitor for mild steel in artificial seawater. Mat Chem Phys. 2024;312:128642. https://doi.org/10.1016/j.matchemphys.2023.128
14. Yıldız R, Arslanhan S, Döner A,et al. Corrosion behavior of mild steel in 1 M HCl with *Cyclotrichium niveum* as a green inhibitor. Mater Chem Phys. 2023;312:128654. https://doi.org/0.1016/j.matchemphys.2023.128654
15. Bedair MA, Abuelela AM, Melhi S et al. Highly effective inhibition of steel corrosion in 1.0 M HCl solution using a novel non-ionic surfactant with coumarin moiety: Practical and computational studies. Mater Chem Phys. 2024;312:128644. https://doi.org/10.1016/j.matchemphys.2023.128644
16. Shaaban MS, Shalabi K, Fouda A et al. New imidazolium-based ionic liquids for mitigating carbon steel corrosion in acidic condition. Zeitschr Physikal Chem. 2023;237(3)211-241. https://doi.org/10.1515/zpch-2022-0155
17. Nilavan A, Jewelcy Arockiaraj L, Thomas Antony AA et al. Corrosion resistance of mild steel immersed in simulated concrete pore solution in the presence of sodium potassium tartrate. Mater Prot. 2023;64(2):170-176. https://doi.org/10.5937/zasmat2302170N
18. Anita N, Joany RM, Dorothy R et al. Linear polarization resistance (LPR) technique for corrosion measurements. Electrochem Analytic Techn Sustain Corros Monit: Adv Chall Opportun. 2023:59-80. https://doi.org/10.1016/B978-0-443-15783-7.00005-0
19. Kumar RSS, Kumar RSS, Ramalingam S et al. Inhibition of corrosion of L 80 alloy in sodium hydroxide solution (pH=12) by succinic acid. Mater Prot. 2023;64(1):78-85. https://doi.org/10.5937/zasmat2301078K
20. Sheit HMK, Mubarak MS, Benitta G. Anti-Corrosive Efficiency of Mild Steel in Sodium Chloride Solution Using 5-Acetyl-3-Phenyl-2, 6-Dipyridin-2-Yltetra-Hydropyrimidin-4(1H)-1 Compound as an Inhibitor. J Bio- Tribo-Corros. 2022;8(4):103. https://doi.org/10.1007/s40735-022-00703-y