

INHIBITION EFFECT OF BERBERINE ON THE CORROSION OF COPPER IN ACIDIC MEDIUM

Nurgul KARADAS^{a,b,*} and Ahmet AKBAŞ^{a,c}

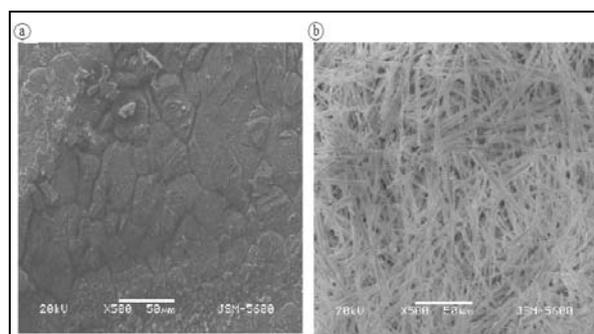
^a Department of Chemistry, Faculty of Science and Arts, Hitit University, Çorum, Turkey

^b Department of Analytical Chemistry, Faculty of Pharmacy, Ankara University, Ankara, Turkey

^c Department of Elementary Science Teaching, Faculty of Education, Mersin University, Mersin, Turkey

Received December 20, 2012

Inhibition of copper corrosion by berberine in 0.5 M HCl was investigated by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. The inhibition efficiency of berberine was studied for five concentrations in the range 5.0×10^{-5} – 5.0×10^{-3} M. Potentiodynamic polarization curves indicated that berberine act as mixed type inhibitor. The adsorption of the inhibitor was more suited with the Langmuir adsorption isotherm and kinetic parameters K_{ads} and ΔG_{ads} were determined at room temperature. The surface morphology of the copper after its exposure to 0.5 M HCl solution with and without 5.0×10^{-3} M berberine was examined by scanning electron microscopy (SEM). The results showed that berberine performed well inhibiting effect for the corrosion of the copper.



INTRODUCTION

Copper and its alloys are highly corrosion resistant in chloride medium. This is why these materials are widely employed in industrial applications such as heat exchangers and electronic devices. A good corrosion resistance of these materials is due to two reasons. Firstly, in acidic medium, the standard potential of Cu|Cu(I) is more positive than the hydrogen evolution potential. The spontaneous corrosion potential of copper will therefore locate in the immunity region in absence of dissolved oxygen. Secondary, in neutral medium, a uniform and an adherent film formed at the metal surface by corrosion products acts as a barrier layer against aggressive medium. To minimize the losses due to the corrosion many methods have been developed. Alloying and

incorporation of inhibitors have been extensively studied to reduce the corrosion of the copper and its alloys in water transport systems.¹⁻³

Organic sulphur, nitrogen and oxygen compounds have been used widely as inhibitors of the corrosion of various metals;⁴⁻¹³ the effect of such inhibitors can be described as altering the nature of the corrosion product, changing the type of adsorption on the surface and rearranging the corrosion current and potential. Up to now, berberine (5,6-dihydro-9,10-dimethoxybenzo[g]-1,3-benzodioxolo[5,6-a]quinolizinium) which is a quaternary ammonium salt from the proto berberine group of isoquinoline alkaloids, have been studied on inhibition of mild steel corrosion in H₂SO₄ solution.¹⁴ No report has been published on inhibition of copper from acidic medium by using this molecule.

* Corresponding author: nurgulk44@gmail.com

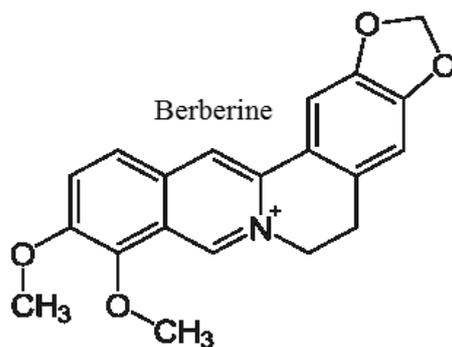


Fig. 1 – Schematic representation of berberine (5,6-dihydro-9,10-dimethoxybenzo[g]-1,3-benzodioxolo[5,6-a]quinolinium) molecule.

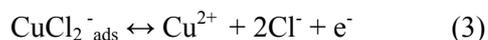
The aim of this study is to report on the inhibition effect of berberine on the corrosion behaviour of copper in 0.5 M HCl solution and clarify its inhibition mechanism.

RESULTS AND DISCUSSION

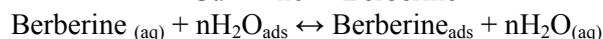
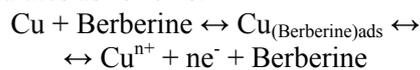
1. Potentiodynamic Polarization Technique

The potentiodynamic polarization curves of the copper in 0.5 M HCl solution with various concentrations of berberine were presented in Fig. 2. The kinetics and mechanism of the anodic dissolution of copper in chloride medium have been studied.^{15,16} The anodic copper dissolution is

controlled by both electrodisolution of copper and diffusion of soluble CuCl_2^- ads to the bulk solution:¹⁷



The inhibition mechanism of berberine can be presented by the $\text{Cu}_{(\text{Berberine})_{\text{ads}}}$ reaction intermediates as follows:



The cathodic corrosion reaction in an acidic chloride solution is:¹⁸

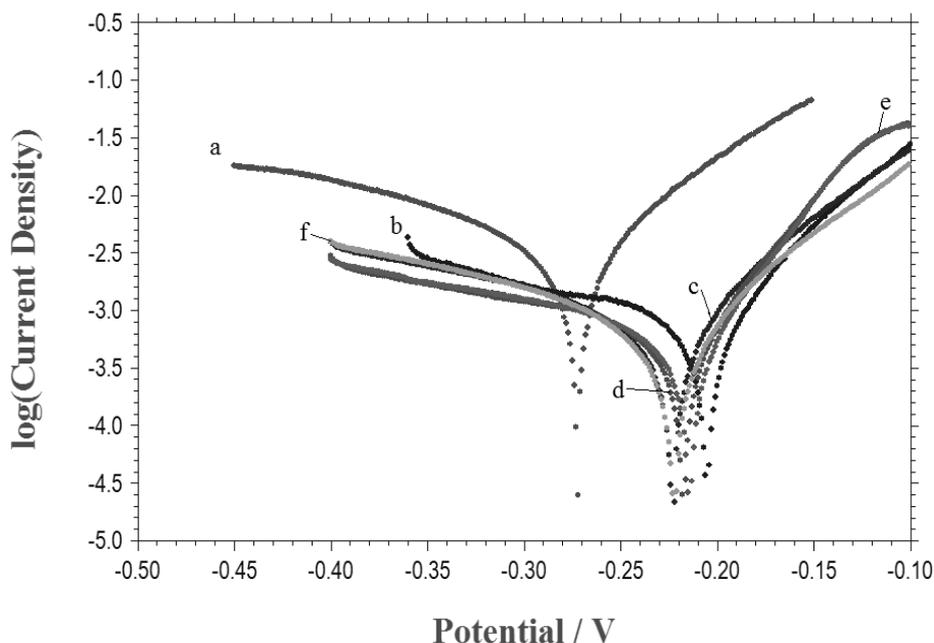
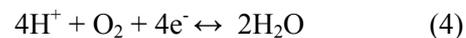


Fig. 2 – Polarization curves of copper corrosion in 0.5M HCl solution free (a) and containing 5.0×10^{-5} (b), 1.0×10^{-4} (c), 5.0×10^{-4} (d), 1.0×10^{-3} (e), 5.0×10^{-3} M (f) of berberine at 298 K.

Table 1

Electrochemical parameters obtained from polarization curves (Fig. 2) in 0.5 M HCl medium with and without berberine

C_{inh} (M)	E_{corr} vs. SCE (V)	I_{corr} ($\mu A.cm^{-2}$)	IE%	Φ
-	-0.272	278	-	-
5.0×10^{-5}	-0.223	59.2	78.7	0.787
1.0×10^{-4}	-0.217	56.7	79.6	0.796
5.0×10^{-4}	-0.214	54.5	80.4	0.804
1.0×10^{-3}	-0.222	48.8	82.4	0.824
5.0×10^{-3}	-0.245	25.6	90.8	0.908

It was observed that the addition of berberine affects both anodic and cathodic parts of the curves. Therefore, berberine acts as mixed-type inhibitor.

The related electrochemical parameters, corrosion potential (E_{corr}), corrosion current density (I_{corr}), surface coverage (θ) and inhibition efficiency (IE%) values were calculated from these curves and listed in Table 1. From this table, it is clear that the corrosion current densities decrease with increasing inhibitor concentration. The biggest effect was observed at 5.0×10^{-3} M, which is the optimum concentration of inhibitor required to achieve the efficiency. The inhibition efficiency, IE%, at different inhibitor concentrations was calculated from the polarization measurements using the Equation 5,¹⁹

$$\%IE = \left(\frac{I_0 - I_i}{I_0} \right) \times 100 \quad (5)$$

where, I_0 and I_i are the corrosion current densities for copper electrode in the uninhibited and inhibited solutions, respectively.

2. Electrochemical Impedance Spectroscopy (EIS)

Fig. 3 shows Nyquist plots of the impedance values of the copper in inhibitor-free and inhibitor containing 0.5 M HCl solutions. The obtained impedance loops were depressed semicircles with their centers below the real axis. These curves have been obtained after 30 min of immersion in the acidic media. The high frequency loop is attributed to the high frequency loop the charge transfer resistance and the double layer capacitance and the low frequency loop is attributed to convective and

diffusion mass transport of $CuCl_2^-$ from the surface.²⁰

According to Mansfeld *et al.*²¹ the impedance spectra shown in Fig. 3 may be analyzed with the electrical circuit in inset of Fig. 3. The fitting results are shown in Table 2. The corrosion resistance of each different concentration was determined by R_p . R_p is given by:

$$R_p = \lim_{\omega \rightarrow 0} \text{Re} \{Z_f\}_{E=E_{corr}} \quad (6)$$

where $\text{Re} \{Z_f\}$ represents the real part of the complex, Z_f faradaic impedance and ω corresponds to the angular velocity of the AC signal ($\omega = 2\pi f$, where f is frequency, Hz). R_p values were obtained by fitting the experimental Nyquist data to a simple semicircle and extrapolating to $Z_{im}=0$.

The polarization resistance increased with increasing inhibitor concentration. The polarization resistance R_p increases largely from 45.4 to 252 Ω and the electric double layer capacitor C_{dl} decreased from 114.7 to 8.517 $\mu F.cm^{-2}$ with the increase in berberine concentration. It shows decreasing of active surface of copper by the adsorption of the inhibitor molecule, in this way the corrosion process was prevented. Without berberine, copper exhibited a low polarization resistance due to the easy attack of the corrosive chloride ions on copper surfaces. The data analysis is estimated before the standard fitting procedure using software. The mechanisms of impedance behaviour of with and without copper electrode are represented by an equivalent circuit model in Fig. 3 (inset). R_s , R_p and C_{dl} are the solution resistance, polarization resistance and the double layer capacitance respectively.

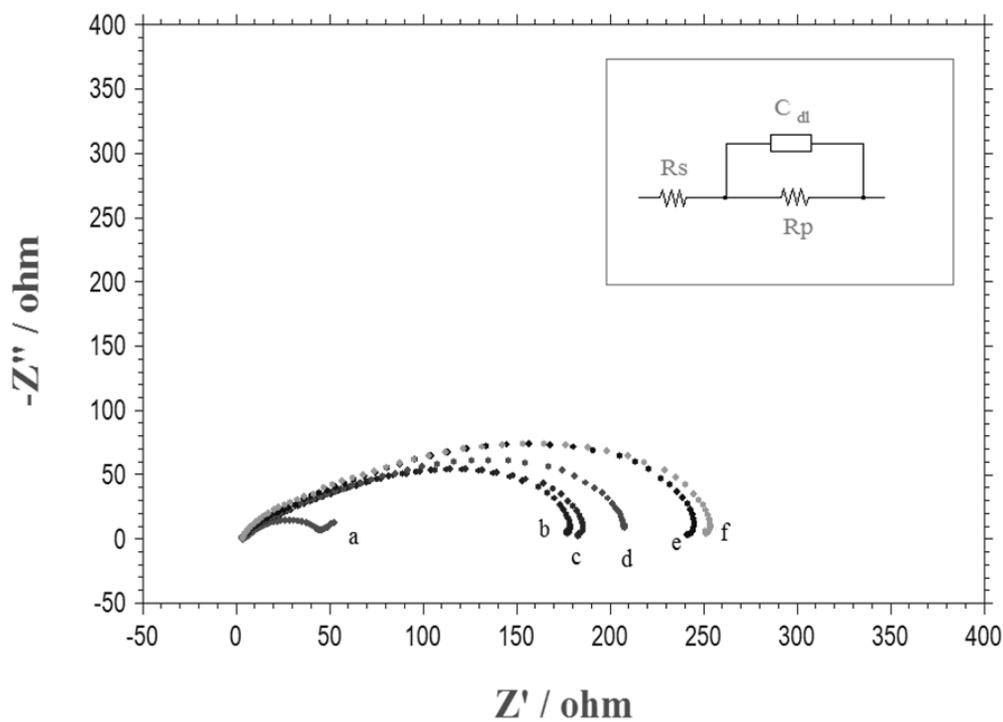


Fig. 3 – Impedance spectra plot of copper electrode without (a) and with 5.0×10^{-5} (b), 1.0×10^{-4} (c), 5.0×10^{-4} (d), 1.0×10^{-3} (e), 5.0×10^{-3} M (f) of berberine in 0.5 M HCl at 298 K, Equivalent circuit representing impedance behavior of copper with and without berberine (inset).

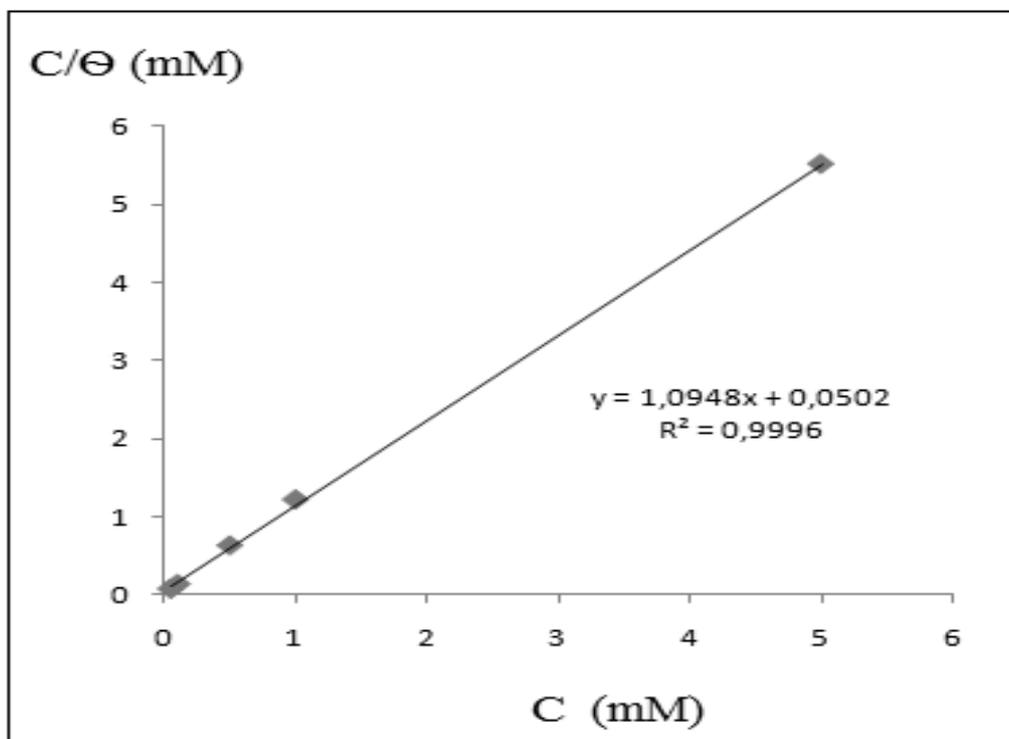


Fig. 4 – The Langmuir isotherm fitting of the obtained Tafel polarization data for the copper electrode after 1 h of its immersion in 0.5M HCl containing 5.0×10^{-5} , 1.0×10^{-4} , 5.0×10^{-4} , 1.0×10^{-3} , 5.0×10^{-3} M of berberine at 298 K.

Table 2

Impedance data (Fig. 3) of copper in 0.5 M HCl without and with addition of different concentrations of berberine

$C_{inh}(M)$	$R_s(\Omega)$	$R_p(\Omega)$	n	$C_{dl}(\mu F.cm^{-2})$	$IE(\%)$	Φ
-	2.424	45.4	0.79	114.7	-	-
5.0×10^{-5}	2.439	185	0.79	26.63	75.0	0.750
1.0×10^{-4}	2.462	190	0.82	14.52	76.1	0.761
5.0×10^{-4}	2.620	220	0.81	14.40	78.3	0.783
1.0×10^{-3}	2.764	249	0.80	11.03	81.3	0.813
5.0×10^{-3}	3.073	252	0.80	8.517	82.1	0.821

3. Adsorption phenomenon

To determine the mechanism of corrosion inhibition, the adsorption behaviour of the organic adsorbate on the metal surface must be known. The adsorption of organic compounds can be described by two main types of interactions: chemisorption and physical adsorption. These types of mechanism of inhibition of copper were proposed by literature. One was the formation of polymeric complexes with copper ions (Cu^+ , Cu^{2+}).²²⁻²⁴ The other was the chemical adsorption of berberine on copper surfaces.^{25,26} The useful corrosion kinetic parameters namely the corrosion potential (E_{corr}) and corrosion current density (I_{corr}), for inhibited solution and inhibitor free solution were obtained from the polarization curves summarized in Table 1. It is clear from Table 1 that the inhibition efficiency increases with increasing concentration of berberine. The inhibition efficiency of berberine on the copper surface was calculated from below equation:

$$\theta = 1 - I_{inh} / I_{corr} \quad (7)$$

where θ is the fractional surface coverage, I_{inh} and I_{corr} corrosion current densities for copper in the presence and absence of berberine compound in acidic media, respectively. Langmuir, Temkin, Bockris-Swinkels, Flory-Huggins and Frumkin adsorption isotherms were studied and checked to find the best suitable isotherm for adsorption of berberine molecule on the copper surface in the acid solution. At constant temperature, θ values which varied with the concentration of berberine conformed to the Langmuir adsorption isotherm, which is given by Eq. (8) was found more suitable with an average correlation coefficient of 0.9996 (Fig. 4).

$$C_{(inh)} / \theta = C + 1/K_{ads} \quad (8)$$

where $C_{(inh)}$ is inhibitor concentration, θ is the degree of the coverage on the metal surface and K_{ads} is the equilibrium constant for the adsorption-

desorption process. The value of equilibrium constant, K_{ads} calculated from the reciprocal of the intercept of isotherm line as $33.6 M^{-1}$. The high value of the adsorption equilibrium constant reflects the high adsorption ability of this inhibitor on copper surface. The free energy of the adsorption of inhibitor on copper surface can be evaluated with the following equation;

$$\Delta G_{ads} = -RT \ln (55.5K_{ads}) \quad (9)$$

where R is the gas constant and T is the absolute temperature. The constant value of 55.5 is the concentration of water in solution in mol/dm^3 . From Eq. (9), ΔG_{ads} was calculated as $-17.36 kJ.mol^{-1}$. The negative value of ΔG_{ads} indicates spontaneous adsorption of the berberine on the copper surface²⁷ and also the strong interaction between inhibitor molecules and the metal surface.²⁸ The value of ΔG_{ads} is less than $40 kJ mol^{-1}$ is commonly interpreted with the presence of physical adsorption by the formation of an adsorptive film with an electrostatic character.^{29,30}

In physisorption process, it can be assumed that acid anions such as Cl^- ions are specifically adsorbed on the copper surface, donating an excess negative charge to the metal surface. In this way, cationic inhibitor molecule was adsorbed by the nitrogen atom to the negatively charged copper surface. This is also mentioned by other researchers.^{31,32}

4. Surface Morphology Analyses

SEM photographs obtained from copper surface after specimens immersion in 0.5 M HCl solutions for 3 h in the absence and presence of $5.0 \times 10^{-3} M$ of berberine are shown in Fig. 5. It can be observed from Fig. 5(a) that the specimen surface was strongly damaged in the absence of the inhibitor. However, Fig. 5(b) shows an appreciable inhibiting ability to corrosion on copper surface, it is revealed that there is a good protective film adsorbed on specimens surface, which is responsible for the inhibition of corrosion.

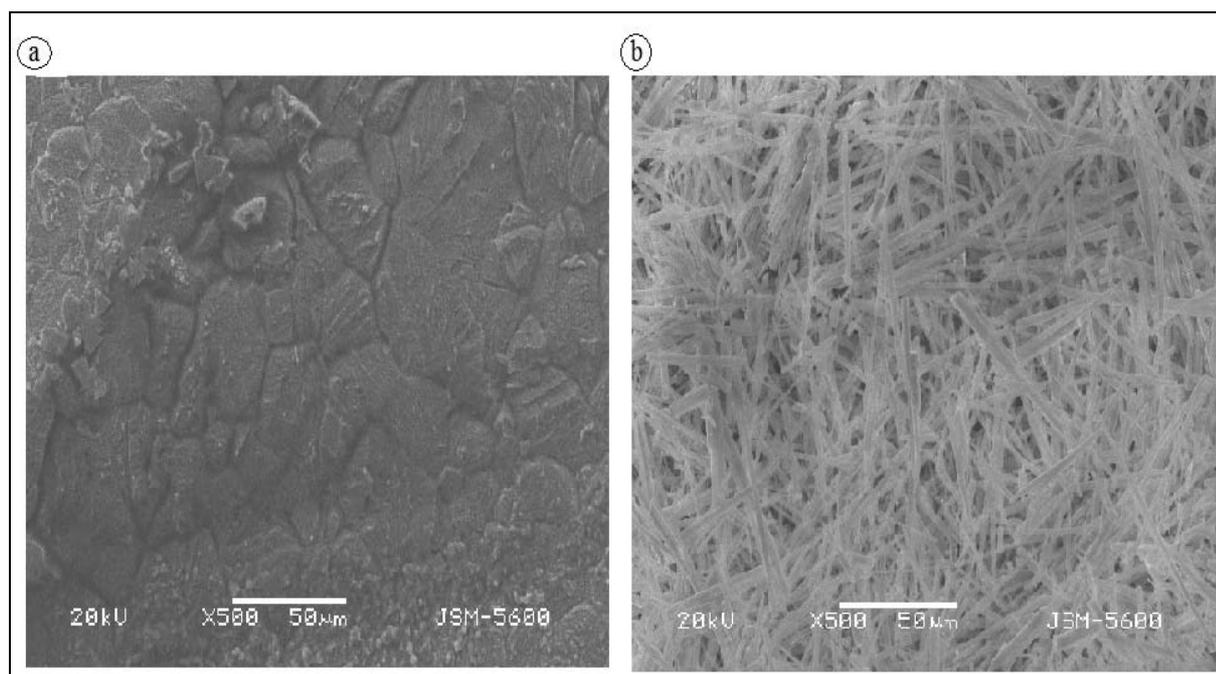


Fig. 5 – SEM micrographs of copper samples after immersion in 0.5M HCl in the absence (a) and presence of 5.0×10^{-3} M berberine (b).

EXPERIMENTAL

In all electrochemical experiments, an aqueous solution containing the inhibitor and 0.5 M hydrochloric acid was prepared by using doubly distilled water. Berberine chloride and analytical grade hydrochloride solution (Sigma-Aldrich) were used directly. Electrochemical measurements were carried out in a single compartment three-electrode cell with copper disc (1.0 cm^2) as working electrode, platinum foil as counter electrode and saturated calomel electrode (SCE) as reference electrode. In this study, copper metal has 99.9% purity. Pretreatment of copper working electrode included abrasion with SiC abrasive paper 800–1500 grades and $0.3 \mu\text{m}$ alumina slurry. The copper electrode ultrasonically cleaned with ethanol and deionized water respectively, and stored in a moisture free desiccator before use.³³

All electrochemical studies were carried out with CHI 660B electrochemical analyzer under computer control. The anticorrosive properties of Berberine chloride with and without copper electrodes were tested by polarizing from cathodic to anodic potentials with respect to open circuit potential at a scan rate of 1 mV/s in 0.5 M HCl solution. Electrochemical impedance measurements were carried out in the frequency range of 10^5 to 10^{-2} Hz with amplitude of 7 mV at the corrosion potential of electrode with and without inhibitor.

CONCLUSIONS

An effective inhibitor property has been obtained with berberine chloride compound. Although the most effective and efficient organic inhibitors that have π -bonds, the biological toxicity

of these products, are documented especially about their environmental harmful characteristics. From the standpoint of safety, the development of non-toxic and effective inhibitors is considered more important and desirable. Hence, in this study we investigated the corrosion property of copper at the presence of a good ecofriendly inhibitor berberine. The corrosion behaviour of copper without and with the berberine inhibitor under immersion in highly aggressive HCl solution was studied by Tafel test and EIS techniques. Berberine has been adsorbed on the copper surface blocking the active corrosion sites. The surface morphology of the copper after its exposure to 0.5M HCl solution with and without 5.0×10^{-3} M berberine was examined by scanning electron microscopy (SEM). The results show that compound exhibited effective protective behaviour in highly corrosive media containing acidic chloride anions and decreased the corrosion rate of copper. The inhibition is due to physical adsorption of the berberine on the copper surface and blocking its active sites. Berberine behaves as mixed-type inhibitor for copper in acidic medium. It decreases both of the anodic and cathodic reaction rates. Berberine easily adsorbed with its cationic form on the copper surface and formed protective complex with the Cu(I) ion, thereby copper surface prevented from corrosion in 0.5 M HCl.

REFERENCES

1. F. Mansfeld, "Corrosion Mechanisms", Marcel Dekker, New York, 1987, p. 119.
2. G. TrabANELLI, *Corrosion*, **1991**, *47*, 410-419.
3. A. Jardy, A. Legal Lasalle-Molin, M. Keddani and H. Takenouti, *Electrochim. Acta*, **1993**, *37*, 2195-2201.
4. M. H. Wahdan, A. A. Hermas and M. S. Morad, *Mater. Chem. Phys.*, **2002**, *76*, 111-118.
5. F. Bentiss, M. Traisnel and M. Lagrenee, *Corros. Sci.*, **2000**, *42*, 127-146.
6. X. Li, L. Tang, L. Li, G. Mu and G. Liu, *Corros. Sci.*, **2006**, *48*, 308-321.
7. M. Benabdellah, A. Aouniti, A. Dafali, B. Hammouti, M. Benkaddour, A. Yahyi and A. Ettouhami, *Appl. Surf. Sci.*, **2006**, *252*, 8341-8347.
8. K.C. Emregul and M. Hayvalı, *Mater. Chem. Phys.*, **2004**, *83*, 209-216.
9. M.A. Quraishi and F.A. Ansari, *J. Appl. Electrochem.*, **2006**, *36*, 309-314.
10. M.A. Quraishi, M.Z.A. Rafiquee, N. Saxena and S. Khan, *J. Corros. Sci. Eng.*, **2006**, *10*, 19-24.
11. S. Sayed, E.R. Abd, H. Hamdi, A. Hassan and A. Mohammed, *Mater. Chem. Phys.*, **2003**, *78*, 825-834.
12. F. Bentiss, M. Traisnel, N. Chaibi, B. Mernari, H. Vezin and M. Lagrenee, *Corr. Sci.*, **2002**, *44*, 2271-2289.
13. M. Lebrini, M. Lagrenee, H. Vezin, L. Gengembre and F. Bentiss, *Corros. Sci.*, **2005**, *47*, 485-505.
14. Y. Li and P. Zhao, *Appl. Surf. Sci.*, **2005**, *252*, 1245-1253.
15. D. Chadwick and T. Hashemi, *Corros. Sci.*, **1978**, *18*, 39-51.
16. D. Tromans and J.C. Silva, *J. Electrochem. Soc.*, **1996**, *143*, 458-465.
17. A.L. Bacarella and J.C. Griess, *J. Electrochem. Soc.*, **1973**, *120*, 459-465.
18. P.R. Roberge, Handbook of Corrosion Engineering, McGraw-Hill, New York, 2000.
19. S.S. Abd El-Rehim, H.H. Hassan and M.A. Amin, *Corros. Sci.*, **2004**, *46*, 5-25.
20. J.P. Diard, J. M. Le Canut, B. Le Garrec and C. Mantella, *Electrochim. Acta*, **1998**, *43*, 2469-2483.
21. D.J. Loren and F. Mansfeld, *Corrosion Sci.*, **1981**, *21*, 647-672.
22. S. L. F.A. da Costa, S. M. L. Agostinho and J.C. Rubim, *J. Electroanal. Chem.*, **1990**, *295*, 203-214.
23. V. Brusica, M. A. Frisch, B. N. Eldridge, F. P. Novak, F. B. Kauman, B. M. Rush and G. S. Frankel, *J. Electrochem. Soc.*, **1991**, *138*, 2253-2259.
24. M. M. Antonijevic and M. B. Petrovic, *Int. J. Electrochem. Sci.*, **2008**, *3*, 1-28.
25. M. M. Musiani and G. Mengoli, *J. Electroanal. Chem.*, **1987**, *217*, 187-202.
26. G. Lewis, *Corr. Sci.*, **1982**, *22*, 579-584.
27. L. Tang, X. Li, L. Li, G. Mu and G. Liu, *Mat. Chem. Phys.*, **2006**, *97*, 301-307.
28. S. Kertit and B. Hammouti, *Appl. Surf. Sci.*, **1996**, *93*, 59-66.
29. G. Moretti, F. Guidi and G. Grion, *Corros. Sci.*, **2004**, *46*, 387-403.
30. O.K. Abiola and N.C. Oforka, *Mater. Chem. Phys.*, **2004**, *83*, 315-322.
31. A. Popova, M. Christov, S. Raicheva and E. Sokolova, *Corrosion Sci.*, **2004**, *46*, 1333-1350.
32. G. Bereket, E. Hur and C. Ogretir, *Molecular Structure (Thochem)*, **2002**, *578*, 79-88.
33. D.K. Yadav, M.A. Quraishi and B. Maiti, *Corros. Sci.*, **2012**, *55*, 254-266.

