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UNIVERSITY OF SPLIT
FACULTY OF CHEMISTRY AND TECHNOLOGY

# WHITE WILLOW BARK EXTRACT AS A COPPER CORROSION INHIBITOR IN 0.5 M NaCl SOLUTION

# EKSTRAKT KORE BIJELE VRBE KAO INHIBITOR KOROZIJE BAKRA U 0,5 M NaCl OTOPINI

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Corrosion can be generally defined as the degradation of materials in a reaction between the material and its environment (1). Due to its corrosive effects, the corrosion of copper and its alloys has been widely studied in chloride media (2). Copper Cu-DHP is phosphoric oxygen-free copper that does not contain arsenic and is mainly used for making pipelines, in construction, and appliances (3).

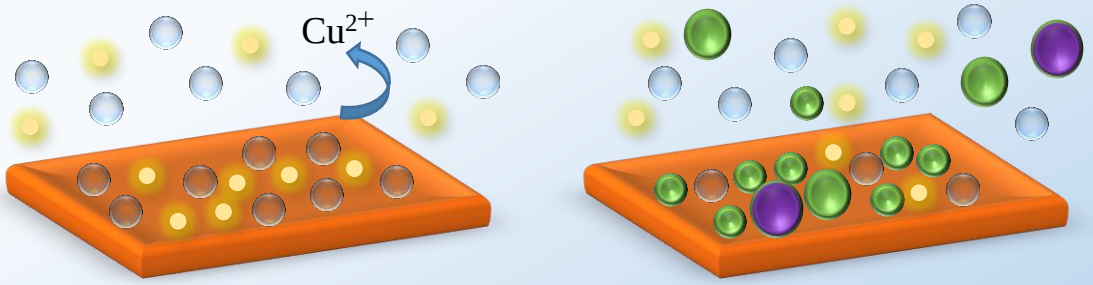
The study of white willow bark extract (WWBE) on the corrosion process of Cu-DHP in a 0.5 M NaCl solution was carried out using a non-destructive electrochemical method of electrochemical frequency modulation (EFM) and electrochemical impedance spectroscopy (EIS). The 0.5 M NaCl solutions without and with the addition of WWBE (0.1-0.5 g/L) were used as electrolytes. The 0.5 M NaCl solution with the addition of 0.5 g/L WWBE, without and with a copper plate was analysed by ultraviolet visible spectroscopy (UV-VIS). The white willow bark extract was prepared by evaporating the aqueous extract obtained by extracting dry white willow bark, with distilled water.

The EFM results show that WWBE acts as a cathodic copper corrosion inhibitor (4). The highest value for the inhibition efficiency was obtained in the 0.5 M NaCl solution with 0.5 g/L WWBE.

| $C_{inh}$ (g/L) | $j_{corr}$ (nA/cm$^2$) | $\beta_1$ (V/dec) | $\beta_2$ (V/dec) | CF-2 | CF-3 | CR (mpy) | $IE_{EFM}$ (%) |
|---|---|---|---|---|---|---|---|
| 0 | 20929 | 0.067 | 0.194 | 1.717 | 2.545 | 160.00 | - |
| 0.1 | 9271 | 0.096 | 0.155 | 1.923 | 3.834 | 70.79 | 55.70 |
| 0.3 | 7177 | 0.083 | 0.128 | 1.717 | 2.540 | 159.80 | 65.71 |
| 0.5 | 4294 | 0.075 | 0.090 | 1.710 | 3.103 | 32.79 | 79.48 |

| Method | $K_{ads}$ | $-\Delta G_{ads}^{\circ}$ (kJ/mol) |
|---|---|---|
| EFM | 11.65 | 15.87 |
| EIS | 9.57 | 15.39 |

$H_2O$ $Cl^-$ WWBE $Cu^{2+}$ + → organometallic complex

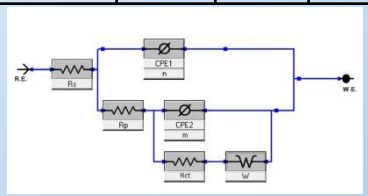


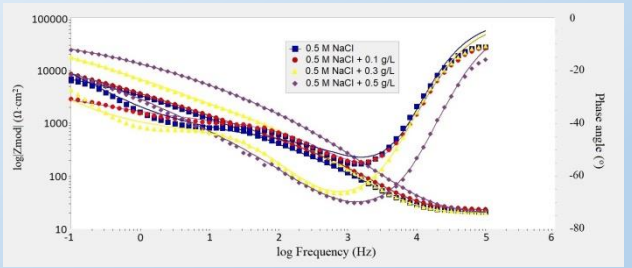

Copper corrosion

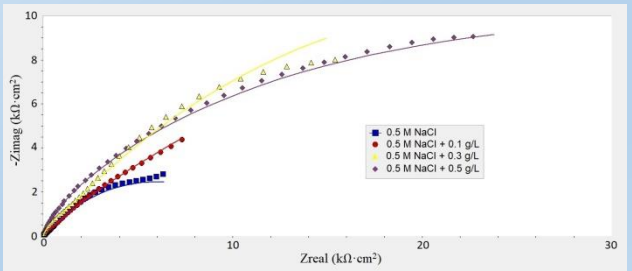
Copper corrosion inhibition

The Bode and Nyquist diagrams were created on the basis of the EIS results. The results were fitted using an electrochemical equivalent circuit. The Nyquist diagram shows imperfect semicircles due to frequency dispersion (5). A linear line corresponding to the Warburg coefficient was found (4). An increase in the phase angle in the Bode plot in the presence of WWBE indicates the formation of a protective inhibitor film. The calculated values show that the corrosion process is diffusion-controlled without and with the addition of WWBE. Both electrochemical methods show that WWBE is adsorbed on the copper surface in 0.5 M NaCl solution by physisorption according to the Langmuire adsorption isotherm (4). The Gibbs free energy values of adsorption are similar for EFM and EIS. The UV-VIS results show that immersion of copper in an electrolyte containing 0.5 g/L WWBE for 24 hours leads to a change in the absorbance maximum, indicating the presence of a copper-WWBE complex (6).

| Cinh (g/L) | 0 | 0.1 | 0.3 | 0.5 |
|---|---|---|---|---|
| Rs ($\Omega\cdot cm^2$) | 17.48 | 20.41 | 19.29 | 16.09 |
| Rp ($\Omega\cdot cm^2$) | 11200 | 21650 | 27900 | 39320 |
| Rct ($\Omega\cdot cm^2$) | 0.485 | 552.4 | 1354 | 6284 |
| CPE1 ($10^{-5}\cdot\Omega^{-1}\cdot cm^{-2}\cdot s^n$) | 87.7 | 102.7 | 43.98 | 32.490 |
| n | 0.490 | 0.483 | 0.582 | 0.481 |
| CPE2 ($10^{-5}\cdot\Omega^{-1}\cdot cm^{-2}\cdot s^m$) | 2.572 | 7.3 | 3.787 | 4.092 |
| m | 0.862 | 0.787 | 0.872 | 0.787 |
| W ($10^{-3}\cdot\Omega^{-1}\cdot cm^{-2}\cdot s^{1/2}$) | 2.407 | 598.4 | 204.1 | 2.124 |
| Goodness of Fit | 7.673 | 1.021 | 5.017 | 7.208 |
| IE (%) | | 49.55 | 61.71 | 75.44 |

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