

Review

APPLICATION OF ENVIRONMENTALLY SAFE INHIBITORS FOR METAL CORROSION PROTECTION

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Abstract

Corrosion is the gradual destruction of metals caused by reactions with their environment. As metals are a large group of elements with numerous industrial uses in various settings, protecting their surfaces from aggressive ions is essential. Metal corrosion can lead to environmental pollution through the release of metal ions via dissolution, and leakage of chemicals stored in tanks or transported through pipes. Thus, metal corrosion poses threats in three main areas: economics, safety, and environmental protection. Corrosion should be reduced by applying appropriate methods, such as the use of suitable corrosion inhibitors. Recently, new corrosion inhibitors with minimal or zero negative environmental impact, known as eco-friendly or green inhibitors, have been researched and developed. Corrosion inhibitors adsorb onto metallic surfaces and protect them from deterioration. Pharmaceutical compounds, amino acids, purines, plant extracts, and similar substances have attracted special attention from researchers as environmentally safe inhibitors. These organic compounds contain heteroatoms, making them suitable as metal corrosion inhibitors in many aggressive environments, as confirmed by numerous studies. Over the last few decades, drugs have proven to be a good alternative to conventional corrosion inhibitors due to their non-toxicity and minimal environmental impact.

Keywords: corrosion inhibitors, environmentally safe, metals.

INTRODUCTION

Metals used in various branches of industry, construction, and as electrical conductors are subject to corrosion in their environments. The presence of ions such as chlorides and sulphates contributes to corrosion and leads to the deterioration of metal. Corrosion is recognised as a technical, economic, and environmental problem. To reduce the corrosion of metals and their alloys, corrosion inhibitors play a significant role. In order to protect the surface of metals from corrosion, overcome risky and hazardous corrosion effect, and thus reduce damage and losses due to dissolution, corrosion inhibitors have found significant application. Corrosion inhibitors can be organic [1,2] and inorganic compounds [3,4]. The most effective corrosion inhibitors are organic compounds [5,6]. The most representative compounds were from following groups: tetrazole compounds, triazole compounds, benzotriazole and benzotriazole derivatives [7–10]. Literature on this subject suggests that these

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compounds contain heteroatoms (S, N, O) and aromatic rings in their structures, and/or p bonds, which enable them to be adsorbed onto the metal surface. However, due to the numerous harmful effects of these compounds on the environment, their use is being questioned, and organic compounds that do not affect the environment with their action are gaining increasing importance. Thus, drugs [11,12], amino acids [13,14], plant extracts [15], purines [16] etc. have been particularly distinguished as effective, non-toxic, inexpensive corrosion inhibitors in various solutions.

DISCUSSION

Scientists have recently focused their research on the use of unused or expired drugs as environmentally safe corrosion inhibitors for metals and alloys. The drugs have shown good inhibitory properties in various environments, especially in acidic solutions.

Alsairi *et al.* [17] researched corrosion of Cu metal in 0.5M HCl and the inhibition of the expired drug Cefazolin. The study confirmed that Cefazolin is an effective inhibitor of copper corrosion, with the highest efficiency (87%) observed at the highest inhibitor concentration, namely 300 ppm of Cefazolin. It has been shown that temperature changes reduce the inhibition efficiency. Electrochemical measurements showed that the expired drug functioned as a mixed-type inhibitor. The adsorption of the drug on the copper surface followed Temkin's adsorption model. The estimated values of ΔG_{oads} range from -12.81 to -16.68 kJmol^{-1} , indicating that the drug is physically adsorbed on copper at the temperatures used. The formation of a protective antibiotic film on the electrode surface was confirmed using SEM techniques, and EDX studies confirmed the presence of drug molecules on the copper surface, which are observed as C, N and O peaks in the EDX pattern. Ceftazidime [18] also showed good inhibitory properties in an acidic chloride environment, i.e. in a 0.1 M HCl solution. The inhibition efficiency increased with increasing concentration and the highest inhibition value of 94.2% was achieved at a concentration of 300 ppm in a corrosive environment. As in the previous study, this antibiotic was shown to belong to the group of mixed inhibitors by the use of electrochemical methods.

In the absence of the antibiotic, copper metal dissociates and forms cuprous ions, which react with chloride ions in the solution to form CuCl. The latter does not provide sufficient protection for the copper metal, as it transforms into a soluble CuCl_2^- complex through reaction with chloride ions [19].



The formed CuCl_2^- is adsorbed on the copper surface and it can be dissolved according to the following equation [19]:



The formed CuCl_2^- might further oxidize to Cu^{2+} ions according to the reaction:



While the cathodic reaction proceeds as follows:



On the contrary, the presence of the Ceftazidime antibiotic within the solution, because the adsorption of the antibiotic molecules on the copper surface restricts the dissolution of copper and so, minimizing the corrosion rate. The adsorption of the antibiotic on the Cu surface belongs to Temkin's model and the estimated values of ΔG_{ads}^0 are around 20 kJmol^{-1} , referring that the adsorption of investigated inhibitor at copper is physisorption. The interaction of the expired antibiotic with the copper surface could be assigned to the existence of N, O atoms, and p-electrons in the structure of the expired antibiotic.

The antibiotics linezolid and piperacillin with expired shelf lives were tested as possible inhibitors of copper corrosion in a 1 M HNO_3 solution. It was also shown that increasing the concentration of the inhibitor in the solution increases corrosion inhibition and for the highest tested concentration of linezolid of 450 ppm was 91.73%, and for the piperacillin was 95.66%, while increasing the temperature decreases it. Potentiodynamic polarization confirmed that these drugs operate as mixed inhibitors [20]. The examined expired linezolid and piperacillin drugs inhibit the Cu from corroding in 1.0 M HNO_3 solution by adsorbing to its surface. The adsorption of both inhibitors follows the Langmuir isotherm. It is evident from the inhibitory efficiency and corrosion parameters obtained from different methodologies that the IE of the piperacillin drug is higher than that of the linezolid drug because piperacillin has a larger molar mass than linezolid. Therefore, the piperacillin drug will form a thicker adsorbed layer on the surface than linezolid, resulting in a higher IE. However, the molecular composition of the drugs under examination contains many heteroatoms, including O, N, and F in linezolid, and O, N, and S in piperacillin. These heteroatoms contribute to the adsorption process on the surface of copper through their lone pairs of electrons, which serve as chelating centres distributed along the molecule.

Tasić *et al.* [12] confirmed in their research the effective inhibitory properties of cephradine in preventing copper corrosion in a 0.9% NaCl solution. In the presence of cephradine, the corrosion current density decreased compared to the inhibitor-free solution. These changes in corrosion current density result from the adsorption of inhibitor molecules on the copper surface and the formation of a protective film which was approved by applying of the scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDS). The highest inhibition efficiency, 92.4%, was achieved at a concentration of $5 \cdot 10^{-3} \text{ M}$, based on data from potentiodynamic polarization measurements. the adsorption of cephradine on the copper surface obeys Langmuir adsorption isotherm. It is known that the ionisation of organic compounds depends on the pH value of the aqueous solution. In the pH range from 2.5 to 7.3, cephradine exists as a zwitterion. After the adsorption of chloride ions, the metal surface becomes negatively charged, which facilitates the adsorption of the zwitterion.

CONCLUSION

All presented researches confirm that the use of drugs as potential eco-friendly inhibitors demonstrates good inhibitory properties in aggressive environments, leading to reduced maintenance costs and environmental protection. The results of the studies confirm the

spontaneous adsorption of drug molecules on the electrode surface via the lone electron pairs of heteroatoms.

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