



Effective inhibition of the early copper ion burst release by purine adsorption in simulated uterine fluids



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ABSTRACT

Burst release of ions from copper-based intrauterine devices (IUD) occurs during the first day after the insertion in uterus and may induce side effects in the users. In the present work, we investigate the mechanism of the inhibitory action of ex-situ pretreatment of copper samples with purine (10^{-2} – 10^{-4} M PU) in simulated uterine fluids (SUF) with and without urea (UR). Quartz crystal microbalance measurements showed that the PU inhibition effect depends on the concentration and adsorption time increasing in presence of chloride. In particular, PU pretreatment (10^{-2} M– 10^{-3} M) leads to an inhibition of copper ions release over 24 h immersion time in SUF, without and with UR. UR may act for a few hours as a weak corrosion inhibitor leading to temporary control of corrosion, but the protection decreases quickly due to formation of soluble Cu-UR complexes, being the total amount of released copper higher when UR is present.

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1. Introduction

Copper-based intrauterine device (IUD) is the most common form of reversible contraception [1]. IUD is effective for concentrations as low as 2 µg/day. However, it was reported that higher corrosion rates of these devices were obtained during the first one-three days (burst release) after immersion in simulated uterine fluid (SUF). Since the overexposure to copper ions may induce side effects in the users [2,3], it is necessary to reduce the initial burst release effect by an ex-situ treatment with an inhibitor.

There are several interesting and detailed reports about the use of biocompatible inhibitors of metallic corrosion such as purine, adenine [4–8], some non-toxic polypyrrole and imidazole derivatives [9,10], and some amino acids [11,12], including cysteine

[13,14]. In the latter case, the molecule contains the amino group besides the -SH group, which has a high affinity for copper, leading to the formation of a Cu (I)-cys film on the electrode surface resulting in better corrosion protection.

The effect of purine on copper corrosion was investigated profusely in different media as chloride [15], nitrate [8] and neutral and acidic sulfate media [6,7] as well as in alkaline sulfate solutions [5]. The results show that the inhibition efficiency increases as the purine concentration increases and PU is adsorbed on copper surface according to the Langmuir adsorption isotherm irrespective of the medium used. This research had as priority to produce “green” or environmentally “friendly” inhibitors for industrial purposes. The results obtained cannot be extrapolated for medical applications since the corrosion protection is maintained with an inhibitor-containing solution and in the absence of other biological components that may interfere with the inhibitory action.

In recent years has been investigated [16,17] the effectiveness of biocompatible organic inhibitors to reduce the initial burst release effect of copper ions in simulated uterine fluid for biomedical applications. Among these inhibitors, purine (PU), tiourea (TU),

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pterin (PT) and 6-mercaptopurine (6-MP) were assayed and adequate inhibitory action was found with the exception of TU. Inhibitory efficiency values higher than 98% for pretreatments with 10^{-3} M PU were obtained. However, the mechanism that governs copper dissolution in SUF and its inhibition by the action of PU has not been elucidated and is probably complex since components of SUF such as chlorides, urea, carbonates and phosphates may interfere with the corrosion process on PU-treated copper surface.

The aim of this work is to investigate the mechanism by which copper ions release is inhibited in PU-treated copper immersed in SUF. With this purpose, quartz crystal microbalance (QCM), a fundamental tool able to sense PU adsorption and the mass change of copper during the immersion in SUF, was used. Measurements of electrochemical parameters such as polarization resistance (R_p), open circuit potential (OCP), reduction charges (Q) and XPS analysis were also employed to investigate in detail the effect of treatments with different PU concentrations on copper immersed in SUF.

2. Materials and Methods

2.1. Reagents and solutions

Synthetic uterine fluid (SUF), originally formulated by Zhang [18], has been widely used to test UID wires. SUF composition is as follows [19–21]: NaHCO_3 (0.25 g L^{-1}), $\text{NaH}_2\text{PO}_4 \cdot 2 \text{ H}_2\text{O}$ (0.072 g L^{-1}), CaCl_2 (0.167 g L^{-1}), KCl (0.224 g L^{-1}), NaCl (4.97 g L^{-1}) and glucose (0.5 g L^{-1}). SUF+UR has the same composition, but it also contains urea (0.48 g L^{-1}). They were prepared with analytical grade chemicals and ultrapure water by means of a Millipore Milli-Q system ($18.2 \text{ M}\Omega^{-1}$). Assays with SUF and SUF+ urea (UR) were made. All measurements were made at $37.0 \pm 0.1^\circ\text{C}$, $\text{pH} = 6.0$.

PU (98% from Sigma Aldrich) was dissolved at concentrations in the range of 10^{-4} – 10^{-2} M in 4.97 g L^{-1} NaCl solutions ($\text{pH} = 6.8$). PU treatments were performed in solutions at $25^\circ\text{C} \pm 0.1^\circ\text{C}$.

2.2. Voltamperometric tests

Voltamperometric tests were performed using a potentiostat Autolab PGSTAT 30 EcoChemie with GPES 4.9 software.

The electrochemical cell with a three-electrode setup was used [22]. A platinum wire (99.99% purity) served as the auxiliary electrode. All the potentials were quoted with respect to Ag/AgCl reference electrode. Copper electrodes (99.99% electrolytic metal copper; Merck, area of 2.25 cm^2) were employed as working electrodes. They were polished with emery paper grade 1200 and rinsed with ultrapure water and dried with N_2 .

Polarization curves were carried out with copper samples at $v = 1 \text{ mVs}^{-1}$ from the open circuit potential (OCP) in the cathodic direction up to -1.4 V in SUF ($T = 37^\circ\text{C}$ and $\text{pH} = 6.0$). I/E curves were recorded after immersion in ultrapure water, NaCl solution (4.97 g L^{-1}), SUF or SUF+UR at 37°C , for 24 h.

Copper samples were treated by immersion in a PU (10^{-4} M, 10^{-3} M or 10^{-2} M) NaCl solution (4.97 g L^{-1}) for 1 h and 3 h at 25°C ; samples without treatment were used as controls. OCP measurements were made during these treatments. Thereafter, cathodic polarization curves were performed in SUF ($T = 37^\circ\text{C}$ and $\text{pH} = 6.0$) to determine whether corrosion occurred during the adsorption time of inhibitor. R_p values were calculated from the slope of polarization curves ($\Delta E/\Delta I$) obtained in SUF at 37°C for a potential range around $\text{OCP} \pm 20 \text{ mV}$ before and after PU treatment.

Additionally, cathodic polarization curves were performed after 24 h immersion in SUF and SUF+UR of copper samples, without and with PU pretreatment, to determine the inhibitory effect of the PU treatment after 24 h after immersion in SUF.

2.3. Quartz crystal microbalance (QCM)

QCM measurements were performed with a QCM200, Stanford Research Systems (SRS) quartz crystal microbalance. Commercial QCM Cu-crystals (Cu-QCM) of 25 mm diameter and 300 nm thicknesses (Maxtek Inc., Santa Fe Springs, CA) were used as the test specimens. The Cu-crystals were cleaned by rinsing with ultrapure water and drying with nitrogen. The Crystal Holder was connected to the QCM25Crystal Oscillator. The QCM probe was stabilized in air obtaining a frequency value close to 5 MHz. Subsequently, it was immersed in the working solution to measure the change of frequency (related to mass change) corresponding to:

- The copper corrosion during the immersion in pure water, NaCl solutions or SUF (without and with urea) for 24 h ($T = 37^\circ\text{C}$, $\text{pH} = 6.0$).
- PU adsorption on Cu during 1 h or 3 h periods at different concentrations (10^{-2} , 10^{-3} and 10^{-4} M in 4.97 g L^{-1} NaCl solutions ($T = 25^\circ\text{C}$, $\text{pH} = 6.8$).
- PU adsorption on Cu during 1 h or 3 h periods at different concentrations followed by 24 h of Cu immersion in SUF or SUF+UR ($T = 37^\circ\text{C}$ $\text{pH} = 6.0$).

2.4. X-ray photoelectronic spectroscopy (XPS)

The XPS measurements were performed in an ultra-high vacuum (UHV) chamber with a base pressure of 1×10^{-10} mbar. The angle between the hemispherical analyzer (Specs-PHOI-BOS100) and the plane of the surface was kept at 60° and the X-ray radiation was the Mg K α line (1253.6 eV). The survey spectra were recorded with pass energy of 40 eV and an energy step of 0.25 eV. Narrow scans of C1s and Cu2p core levels and X-ray excited Cu LVV, were recorded using pass energy of 15 eV with an energy step of 0.1 eV. The binding energy (BE) scale was calibrated with respect to the C1s at 285 eV. The analysis of the XPS results was carried out with the Casa XPS software, using Gaussian with 30% Lorentzian for the fitting procedure. Before the XPS data were analyzed, the contribution of Mg K α satellite lines was subtracted. XPS measurements were performed with the aim of studying the composition and chemical state of the copper surface:

- Without any treatment.
- After immersion in SUF for 24 h ($T = 37^\circ\text{C}$, $\text{pH} = 6.0$).
- After immersion in SUF+UR for 24 h ($T = 37^\circ\text{C}$, $\text{pH} = 6.0$).
- After immersion for 1 and 3 h in 4.97 g L^{-1} NaCl solutions containing different PU concentrations (10^{-2} M, 10^{-3} M and 10^{-4} M; $T = 25^\circ\text{C}$, $\text{pH} = 6.8$).

3. Results

3.1. Burst release of copper ions from copper surface

3.1.1. QCM and voltamperometric measurements

In order to follow the change of copper mass after immersion in SUF, it is interesting to make firstly a comparative study in water and NaCl solution [Fig. 1(A, B)]. QCM measurements were performed over a period of 24 h in these media. The change of mass over a period of 24 hours immersion in each medium was calculated using Sauerbrey equation [23].

Fig. 1A shows the variation of the oscillation frequency of a Cu-QCM crystal with immersion time in ultrapure water ($T = 37^\circ\text{C}$, $\text{pH} = 6$). The typical decrease of frequency ($\Delta F = -776 \text{ Hz}$) associated with the immersion of a Cu-QCM crystal

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