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Silver release from polypyrrole matrix in well water

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ABSTRACT

Polypyrrole (PPy) films constituted by hollow rectangular microtubes were electrosynthesised from a salicylate (Sa) solution on 316L stainless steel (316L SS) electrodes. The covered electrodes were dipped in $AgNO_3$ solution achieving the immobilisation of silver species. After this, they were rotated at different speeds and silver transport from the PPy matrix to well water under open circuit potential (OCP) condition was studied. The results indicate that the diffusion process of silver from the polymeric matrix is accelerated when the electrode speed is increased. The disinfection process of well water contaminated with *Escherichia coli* was also analysed for the electrode covered with PPy/Ag films. A faster release of Ag species was obtained when a potential step was applied. The microtubular morphology of the polymer does not suffer any alteration during the experiments.

1. Introduction

Materials with antibacterial activity have been intensively investigated in the latest years. Different biomaterials with bactericidal species have been employed in fields such as medicine, dentistry and water treatment [1,2]. Recently, it was informed that 502,000 diarrhoea deaths were estimated to be caused by inadequate drinking water in 2012 [3]. According to this, it is essential to provide a safety environment, protect the human health and remove the pathogens from drinking water. Nowadays, in water treatments there is a challenge to find a disinfection system to avoid harmful by-products generated from using conventional chemical disinfectants [4]. The non-conventional antimicrobial compounds most frequently used in water disinfection are chitosan, carbon nanotubes and silver species [2]. Since ancient times, the silver species have been known to be effective against a broad range of microorganisms [5,6]. There are various mechanisms by which silver species affect the cell functionality. Some authors have shown that Ag^+ interact with thiol groups in proteins, resulting in inactivation of respiratory enzymes and leading to the production of reactive oxygen species (ROS) [7]. On the other hand it was also proposed that silver ions disrupt the deoxyribonucleic acid (DNA) replication and damage the cell membrane [8]. In recent years, silver species have been incorporated into different materials such as polymers [9] and silica composites [10] for water treatment applications. A material with antimicrobial activity employed in water disinfection not only requires antimicrobial capacity but also mechanical properties and flow resistance. Recently, some authors showed effective water filters constituted by silica [10] or alginate beds [11] containing Ag nanoparticles. Both filters exhibit a high disinfection performance in water contaminated with *Escherichia coli*.

On the other hand, the synthesis of polypyrrole-based micro- and nanostructures has become a topic of increasing interest due to their several applications [12,13]. One of the most interesting morphological features of these microstructures is a large surface area and the possibility to be useful as drug reservoirs. The active agents can be entrapped during the electropolymerisation in the polymeric matrix or they can be immobilised later [14,15].

Drug release can be carried out by simple immersion of the polymer-coated material. A faster rate of release can be obtained when an electrical stimulation such as a potential step is applied.

In a previous study it was demonstrated that the electrosynthesis of polypyrrole (PPy) in aqueous solutions of sodium salicylate (NaSa) leads to the formation of hollow rectangular-sectioned microtubes onto 316L stainless steel (316L SS) [16,17]. These microstructures were used to immobilise Ag and the modified electrode presented a very good performance towards inhibition of *Staphylococcus aureus* bacteria activity [18]. It was proposed that Ag immobilisation in the polypyrrole matrix occurs in two stages. Initially, when the electrode is immersed into the $AgNO_3$ solution, Ag^+ ions are concentrated in the film due to the high content of salicylate anions. Then, some of these cations can be reduced while non-oxidised segments within the polymer are oxidised. Therefore, both Ag^+ ions and metallic Ag are present in the PPy matrix.

It is of great importance to find a well water disinfection system which does not produce harmful by-products. In this way the Ag release from polymer surface forbid the by-product toxicity. There are several methods to modify the material surface with silver particles [19,20]

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and it is preferable to use a simple technique. The aim of this work was to evaluate the capacity of PPy/Ag films deposited onto 316L SS for the decontamination of well water. The effect of hydrodynamic conditions on the silver release from the PPy matrix was analysed. Lastly, the antimicrobial activity of covered PPy/Ag films against *E. coli* ATCC 25922 in contaminated well water was evaluated. *E. coli* is considered the best indicator of health risk from drinking and recreational water.

2. Experimental

The working electrode (WE) was a rod (3 mm in diameter) of 316L SS (wt.% is: 17.47 Cr, 10.32 Ni, 1.88 Mn, 1.90 Mo, 0.39 Si, 0.025 C and Fe balance) embedded in a Teflon holder. The exposed surface area of the WE is 0.07 cm^2. Before each experiment, the surface was abraded to a 1200 grit finish using SiC, then degreased with acetone and finally washed with triply distilled water. All the potentials were measured against Ag/AgCl (3 M KCl) reference electrode and a platinum sheet was used as a contraelectrode. The films were obtained potentiostatically at 0.80 V during 600 s from a solution containing 0.25 M pyrrole (Py) and 0.5 M NaSa. After PPy electrodeposition, the electrode was intensively washed with distilled water and dipped in a 0.05 M $AgNO_3$ solution during 8 h under open circuit potential (OCP) in dark conditions.

Electrochemical studies were carried out with a potentiostat/galvanostat Autolab/PGSTAT 128N. Morphological studies of films metalised with gold were performed by scanning electron microscopy (SEM) ISI DS 130 coupled with an energy dispersive X-ray (EDX) analyser model EDAX 9600. Silver release experiments were carried out in 30 mL of well water using a rotating disc electrode EDI 101 (Radiometer Analytical S.A.) with a CTV 101 rotation rate controller (Radiometer Analytical S.A.). The well water composition is presented in Table 1.

The antibacterial activity of the PPy/Ag films under hydrodynamic conditions was determined against a reference strain of *E. coli* ATCC 25922. For the experiments, a loop of frozen cells stored at −70 °C in a tripticase soy broth (TSB) (Biokar) supplemented with 20% v/v glycerol (Biopack) was grown in nutrient rich broth (Britania) for 24 h at 37 °C. Then, the cells were collected by centrifugation at 5000 rpm for 10 min, washed twice with distilled sterile water and diluted with sterile well water to give a working culture of approximately 10^5 CFU (colony forming units mL^{-1}) (N_o). Thirty millilitres of this cell suspension in well water was used for testing each hydrodynamic condition during 8 h at 20 °C. To determine the number of cells remaining in each treatment aliquots of 1 mL were taken every 2 h (N_t), serially diluted tenfold and the resulting dilutions plated onto plate count agar (PCA) (Britania) incubated at 37 °C for 24 h.

The bactericidal activity (BA) was calculated as follows:

$$BA\% = [(N_0 - N_t)/N_0] \times 100.$$

Released silver concentration in well water from PPy/Ag-coated 316L SS samples was determined using inductively coupled plasma atomic emission spectrometry (ICP-AES).

Table 1
Well water composition.

Element	Concentration ($mg\ L^{-1}$)
Na	356
Mg	28.5
Ca	95.8
S (sulphate)	86.5
P (phosphate)	0.151
Cl (chloride)	408.5
pH	7.7

3. Results and discussion

Electropolymerisation of Py onto 316L SS was performed in 0.50 M Sa and 0.25 M Py at 0.80 V during 600 s. In our previous work it was demonstrated that under this experimental condition the PPy film morphology is constituted by hollow rectangular-sectioned microtubes [16,17].

After the polymer synthesis, the covered electrode was dipped in a 0.05 M $AgNO_3$ solution during 8 h under OCP conditions. The measured potential was 0.46 V vs. Ag/AgCl during all the experiences which correspond to the potential of the Ag^+/Ag redox pair for a 0.05 M $AgNO_3$ solution [18]. Differences between concentrations of Ag determined by ICP-AES before and after immersion allowed that the estimated amount of silver species incorporated into the film was 2 mg.

SEM micrograph and EDX analysis of the electrode surface are presented in Fig. 1. The surfaces of the microtubes are covered randomly by rosette-like aggregates with a highly rough surface and the EDX analysis shows the Ag signal, which indicates the effective immobilisation of silver species.

The electrodes covered with PPy/Ag were rotated at different speeds during 8 h in the well water and the OCP was measured (Fig. 2). For comparative purposes the curve corresponding to the uncoated electrode is also presented (Fig. 2, curve e). The OCP vs. time curves

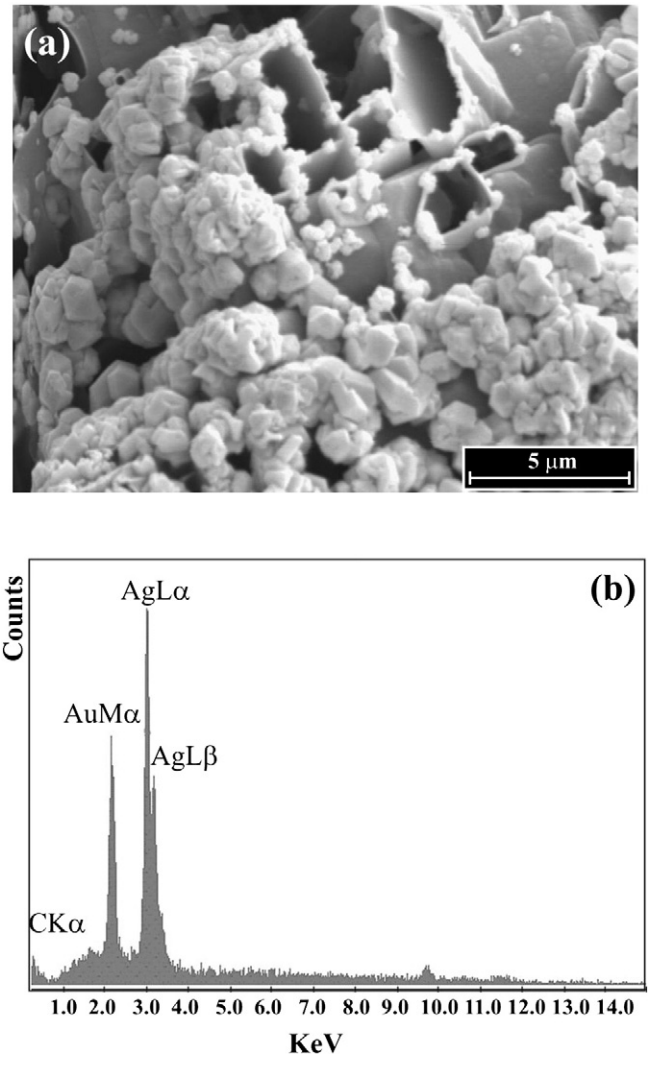

Fig. 1. (a) SEM image and (b) EDX analysis of PPy-coated steel electrode after immersion during 8 h in 0.05 M $AgNO_3$ under open circuit conditions. The film was formed potentiostically at 0.80 V vs. Ag/AgCl during 600 s in 0.5 M Sa solution containing 0.25 M Py.