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# Electrocatalytic Oxidation of Flumequine by Electrogenerated PPy-Ag Modified Electrode: Electrochemical and sensing properties.

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**Abstract:** An electrochemical sensor was designed and realized for flumequine (Flu) detection based on platinum (Pt) electrode coated with polypyrrole-silver (PPy-Ag) film. The formation PPy-Ag coating was assessed by cyclic voltammetry. Square-wave voltammetry was used for (Flu) monitoring. The incorporation rate of Ag particles was optimized. The Flumequine oxidation on both Pt and Ag-PPy was investigated. The limit of detection (LOD) of the designed senor was of order of 2.61 µg.$L^{-1}$ and the measured sensitivity (in the semi logarithmic representation) was equal to 19 µA.$M^{-1}$.

**Keywords:** Flumequine; Electrocatalytical oxidation; Detection, Polypyrrole.

## 1. Introduction

Antibiotics are used in aquaculture in order to control the infection outbreaks. They are natural, semisynthetic or synthetic compounds and their antibacterial effect lies on their ability to eliminate the bacteria or hinder their growth. Quinolones are often used in aquaculture. They can also be used in human disease treatment. Besides the use of antibiotics as bacterial infection treatment, sulfonamides, lactams and macrolides can be used as growth-promoting or infection-preventing agents. They are used in sub-therapeutic doses in animal feed or veterinary drugs [1]. The large use of antibiotics may cause severe problems to human health through the migration of antibiotics from aquaculture products to human organism, or in some cases, to the development of persistent microorganisms. Authorities in many countries have maintained strict regulations for antibiotics usage [2]. The development of rapid analytical methods for the daily control of the antibiotic residue in fish farming is needed. The antibiotic sensor devices are good candidates for this purpose that they can be used directly on-site.

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## 2. Results and Discussion

### 2.1. Preparation of the modified electrode.

Potential scans were carried out, in the positive direction, between -300 and 1200 mV at a scan rate of 50 $mV.s^{-1}$. The corresponding cyclic voltammograms are presented in Figure. 1(A). The observed increase in the anodic current density corresponds to pyrrole monomer oxidation and the further formation of its radical cation $Py^{\cdot+}$ according to the following equation:

$$Py \rightarrow Py^{\cdot+} + e^-$$

After this step, radicals are coupled to form dimer cations, followed by loss of protons leading to neutral dimers. Then, and for the propagation chain, where oxidized dimers couple with monomeric radical cations to build oligomers, which themselves couple with radical cations forming a conductive polymer doped with counter ions $ClO_4^-$.

The current loop in the negative scan is, for its part, associated to the nucleation and growth of the polymer [3].

Figure. 1(B) presents the cyclic voltammograms of PPy in the presence of different concentrations of $AgNO_3$. Beside of the oxidation peak of Py in the positive scan, an oxidation peak of Ag into $Ag^+$ appears at 0.4 V. in the negative scan, a reduction peak of $Ag^+$ into Ag appears at 0.45 V, which proves the formation of Ag particles inside the polypyrrole matrix.

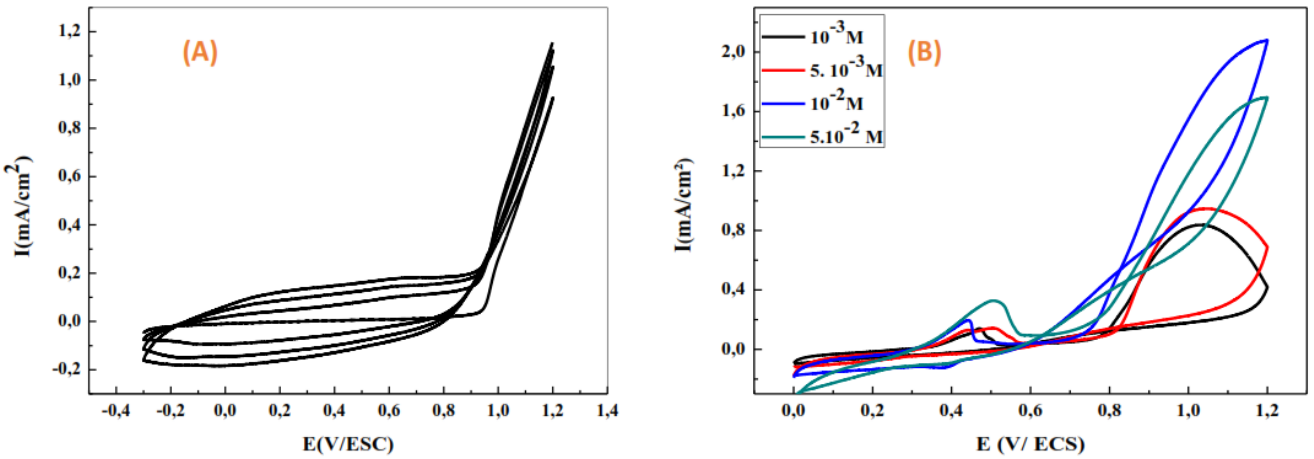


**Figure. 1.** Cylic voltammograms of (A) $10^{-2}$ M Py and (B) $10^{-2}$ Py in presence of different concentrations of $AgNO_3$ in 0.1 M $LiClO_4$ /ACN scan rate: 50 mV/s.

### 2.2. Electrocatalytic and sensing properties.

The first part of this study concerns the characterization of the electrochemical response of Flumequine on a platinum electrode. The square wave voltammograms presented in Figure. 2(A) shows a characteristic peak at 1.84 V relative to the oxidation of Flumequine. In order to lower this potential, we have incorporated Ag particles in the polymeric polypyrrole matrix. Results gathered in Figure 2(B) indicate that the optimum is reached for a concentration $5.10^{-2}$ M.

Flumequine sensing was investigated in a concentration range varying between $10^{-8}$ and $10^{-3}$ M. Results presented in Figure 2(C) indicate that the sensor's limit of detection (LOD) is of order of $10^{-8}$ M. The sensitivity (calculated from the semi-logarithmic calibration curve) was equal to 19 $\mu A.M^{-1}$.

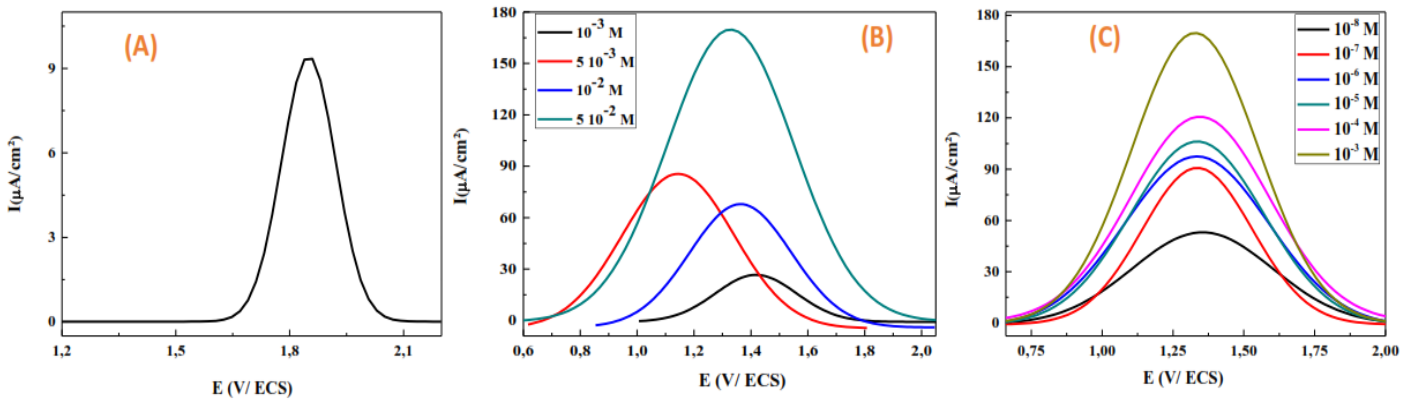


**Figure. 2.** Square wave voltammograms SWV of (A): Flumequine oxidation on a Pt electrode (B): Ag concentration effect on Flu oxidation on PPy-Ag electrode (C): Flu detection by PPy-Ag electrode. All measurements were done in 0.1 M $LiClO_4$ /ACN.

## 3. Materials and Methods

Lithium perchlorate, silver nitrate, Flumequine (Flu), acetonitrile (ACN) and pyrrole were purchased from Sigma Aldrich and used as received. Pyrrole (Py) was purified before its use by filtering through basic alumina column and stored in dark at 4°C.

Cyclic and square wave voltammetry measurements were carried out with a PGSTAT 402 using VoltaMaster 4 software. The SWV parameters are as follow: amplitude = 2 mV and frequency = 40 Hz. A three-electrode configuration was used: a platinum or PPy-Ag as working electrode, Pt wire as auxiliary electrode and saturated calomel electrode SCE as the reference electrode.

## 4. Conclusions

In the present work, a platinum electrode was functionalized with a one-step polypyrrole-silver film for flumequine detection in ACN medium. The formation of PPy-Ag film was assessed by cyclic voltammetry and square-wave voltammetry was used for (Flu) monitoring. The limit of detection (LOD) of the designed sensor was of order of 2.61 µg.$L^{-1}$, one of the lowest values ever reported in literature. The sensor's sensitivity (calculated from the calibration curve in the semi logarithmic representation) was equal to 19 µA.$M^{-1}$. These results pave the way for flumequine track in real media.

## Author Contributions

All the others have contributed to the present work.

## Conflicts of Interest

The authors declare no conflict of interest.

## References and Notes

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