

Electrochemical sensors for emerging contaminants: diclofenac preconcentration and detection on paper-based electrodes

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Highlights: A paper-based electrochemical sensor has been developed as a green tool for analysis of diclofenac. The electrochemical behaviour of diclofenac has been studied on carbon paper-based electrodes. A miniaturized device combining paper electrodes and reusable connections allows to perform decentralized analysis. The employment of a paper-based electrode allows simple on-site preconcentration of the analyte improving the sensitivity of the methodology.

Keywords: emerging contaminants, diclofenac, electroanalysis, paper-based electrodes, green technologies.

1. Introduction

Nowadays, the presence of emerging contaminants is a worldwide problem of increasing environmental concern. The term emerging contaminants (ECs) is referred to a heterogeneous group of substances, such as personal care products, pharmaceuticals and flame retardants, characterized by a widespread distribution due to their massive everyday use and persistence in the environment [1]. Additionally, current wastewater treatment plants are not specifically designed for eliminating these contaminants and, in consequence, these may reach environmental waters and so, potentially, drinking waters. Hence, it is mandatory to develop analytical devices for ECs determination not only sensitive enough for their application in environmental waters, but also miniaturized, simple, portable and mainly sustainable.

Diclofenac (Fig. 1A) is a non-steroidal anti-inflammatory drug widely prescribed as analgesic and in the treatment of rheumatic complaints and acute joint inflammation. Because of its broad consumption, diclofenac residues are detected in surface waters [2]. Thus, in this work, a paper-based analytical device, that combines a paper-based working electrode with pseudoreference and counter electrodes based on metallic wires, was developed for the electrochemical detection of diclofenac. The sustainability of the device is noticeable since electrochemical techniques are *green* in essence because [3]: i) they employ the electron as a cheap and clean reagent, ii) most of the reactions can be performed at room temperature, avoiding energy consumption and costs associated to temperature control, iii) they involve safe operations in low or null volatility reaction media reducing accidental solvent releases to atmosphere and iv) they are cost-effective since the required equipment and operations are usually simpler and cheaper than other techniques. Moreover, the employment of paper as substrate allows to reduce costs of fabrication and transportation since it is a widely available, light and flexible material, easy to transport and store [4]. Its porosity and high surface area, as well as its easy modification and printing, make it a versatile material, very suitable for combination with electrochemical techniques [5–8].

In addition, the small size of the developed device together with the availability of commercial portable potentiostats, make possible to perform decentralized analysis (out of laboratory). This is very interesting for environmental pollutants monitoring (especially in developing countries and remote locations) since the device allows completing the analysis on-site and taking decisions at real time.

2. Material and Methods

The main reagents and materials needed were: diclofenac disodium salt (DCF), N,N-dimethylformamide (DMF), carbon paste, Whatman™ paper grade 1, gold-plated connector headers and an edge connector. Working solutions

of diclofenac were prepared in purified water or in 0.1 M phosphate buffer solution pH 7.0 (PB). The carbon ink was prepared dispersing carbon paste in DMF (40%, w/w) by sonication (1 h).

The instrument employed was an Autolab potentiostat controlled by Nova 2.1.2 software. A wax printer ColorQube 8570 (XEROX) was used to wax-print the paper (Fig. 1B).

The electrochemical cell constructed combined a paper-based working electrode (WE) with pseudoreference and counter electrodes (RE and CE) based on metallic wires (provided by the gold-plated connector header) [7] (see Fig. 1C). The WE was constructed depositing a 2- μL drop of the carbon ink in a wax-defined paper area and leaving to dry at room temperature. To perform the measurements, a 10- μL drop of working solution was deposited on the topside of the electrochemical cell covering the three electrodes. The paper-based WE is single-use while the gold-plated connector header can be reused for several measurements after cleaning it with water in between.

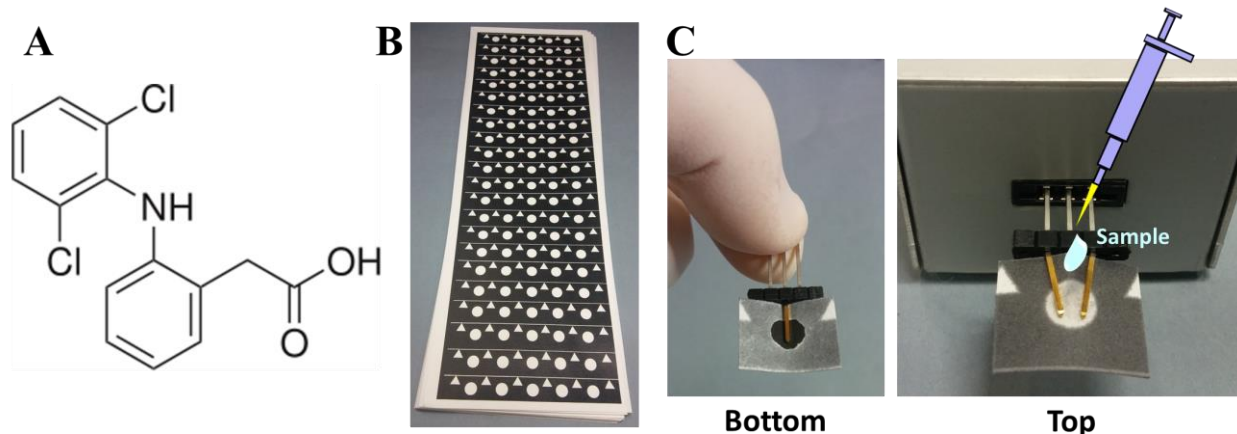


Figure 1. (A) Diclofenac structure. (B) Photograph of several sheets of paper after wax printing. (C) Photograph of the bottom (left) and top (right) sides of the paper-based electrochemical cell. In the right photograph, the paper-based platform is ready to use after being directly inserted in a commercial connector. The gold-plated header connector provides the RE and CE as well as the connection for the WE.

3. Results and Discussion

First, the electrochemical behaviour of DCF on carbon paper-based electrodes was studied performing cyclic voltammetry (CV). For a DCF concentration of 100 μM , an oxidation peak appeared at +0.48 V with a peak current intensity of 2.2 μA (Fig. 2A) and no reduction peak was present. Hence, the current intensity of this anodic peak was chosen as analytical signal. Differential pulse voltammetry (DPV) was also tested in order to increase the sensitivity. When DPV was performed (employing the same parameters as in a previous work [9]) in a 100 μM DCF solution, an oxidation peak with a peak current intensity of 3.5 μA was observed at +0.45 V (Fig. 2B). Therefore, employing DPV a better-defined and higher peak was obtained.

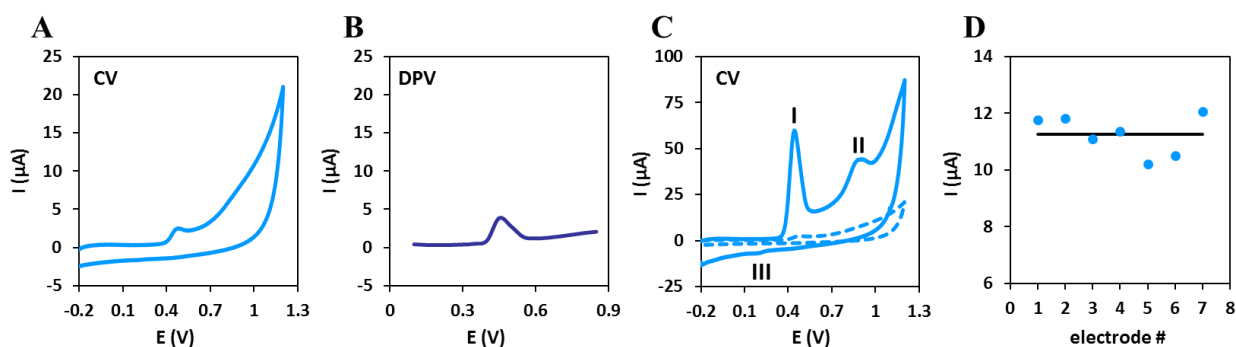


Figure 2. Cyclic (A) and differential pulse (B) voltammograms performed in 10 μL of 100 μM DCF in 0.1 M PB pH 7.0. (C) Comparison between cyclic voltammograms performed in 10 μL of a 100 μM DCF solution in 0.1 M PB pH 7.0 (dashed line) and in 10 μL of 0.1 M PB pH 7.0 after pre-concentration of 40 μL of 100 μM DCF in water (continuous line). (D) Comparison of peak current intensities of the first anodic peak obtained employing seven different paper-based WE when CVs are recorded in 10 μL of 0.1 M PB pH 7.0 after pre-concentration of 40 μL of 20 μM DCF in water (the black line indicates the mean value).

In order to increase the analytical signal even more, a different strategy was chosen. We took advantage of the porous nature of paper to pre-concentrate DCF in the paper-based WE. Then, a 40- μL drop of a 100 μM DCF

solution was deposited on the top side of the WE and was left to dry at room temperature. In a second step, CV was performed in 10 μL of 0.1 M PB pH 7.0 obtaining the CVs of Fig. 2C. Two anodic peaks, at +0.44 V (peak I) and +0.88 V (peak II) with current intensities of 58.8 and 28.0 μA respectively, and one cathodic peak (peak III) at +0.18 V with a current intensity of 2.0 μA were obtained. The presence of those peaks are in agreement with previous works [10]. The effect of preconcentration is clear in Fig. 2C, where voltammograms recorded with and without preconcentration are compared. The current intensity of the first anodic peak (peak I) is more than 24 times higher (58.8 vs. 2.2 μA). Therefore, the porous nature of the paper-based electrode allowed on-site preconcentration of DCF and, consequently, a notorious improvement of the sensitivity. Moreover, the paper-based device offers a good reproducibility as shown in Fig. 2D. Seven different paper-based WEs were tested (employing the same RE and CE) preconcentrating 40 μL of 20 μM DCF. A peak current intensity of $11.3 \pm 0.7 \mu\text{A}$ (RSD < 6.3%) was obtained.

Optimizing key parameters such as volume of the DCF solution deposited and temperature of drying, low limits of detection for DCF could be achieved. Moreover, this simple preconcentration methodology allows to perform the measurement in a different medium, optimum for the detection.

4. Conclusion

Electrochemical paper-based platforms are attractive tools for evaluation of water quality due to the combination of the great advantages of electrochemical techniques together with the friendly inherent characteristics of paper. Thus, small-size and portable devices can be developed for water analysis with good analytical characteristics achieved by simple on-site preconcentration without the need of extraction/preconcentration systems that increase not only the complexity of the determination, but also the cost and the waste generated.

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