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Application of an electro-activated glassy carbon electrode (GCE) to the analytical monitoring and photochemical studying of acetaminophen

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The occurrence of emerging contaminants in surface waters, such as pharmaceuticals and personal-care products, is an environmental issue of high concern due to the toxic effects on ecosystems and humans (1). *Waste Water Treatment Plants* (WWTPs) are usually not able to remove these compounds from wastewater because they are water soluble and biorefractory. Therefore, emerging contaminants are often released in water bodies. As far as pharmaceuticals are concerned, antibiotics, analgesics and anticonvulsants are usually detected in surface waters (2). In these environments, xenobiotics can undergo both abiotic and biotic degradation. Among abiotic pathways, direct and indirect photochemical reactions can be key degradation processes. Direct photolysis occurs when the xenobiotic absorbs the solar light and undergoes subsequent chemical transformations. In contrast, indirect photolysis is triggered by *Photochemically Produced Reactive Intermediates* (PPRIs) that react with xenobiotics. The main PPRIs are HO[•], CO₃^{•-}, excited triplet states of Chromophoric Dissolved Organic Matter (³CDOM*) and ¹O₂. They are formed upon absorption of solar light by photosensitizing compounds, such as CDOM, nitrate and nitrite (3). Usually, photochemical reactions act as self-depuration processes in water bodies, but they can also induce formation of harmful photodegradation products. Luckily, the photochemical fate of xenobiotics (half-life times and photoproduction of intermediates) can be modeled, and thus foreseen, by knowing or measuring the relevant photoreactivity parameters (e.g., reactions rate constants and photoproducts formation yields) and by using suitable photochemical models (4). Therefore, the monitoring of xenobiotics concentration in both WWTPs influents/effluents and surface waters, and the understanding of the photochemical fate of these compounds, are important tools to assess the human impact on aquatic environments.

Acetaminophen (also known as paracetamol, hereafter APAP) is a widely used analgesic drug usually detected in surface waters (2) at concentrations up to 10 µg L⁻¹ (5). In this work, we have focused on the use of *Differential Pulse Voltammetry* (DPV), with a recently implemented electrochemically activated glassy carbon electrode (aGCE) (6), for the monitoring of APAP in the surface waters of the Po river basin, in the province of Turin (Piedmont, Italy). In order to confirm the reliability of the electrochemical response, we have compared DPV results with those obtained with *High Performance Liquid Chromatography* hyphenated with *High Resolution Mass Spectrometry* (HPLC-HRMS), commonly used to quantify pharmaceuticals. Furthermore, DPV with the aGCE was used to assess the photochemical degradation of APAP, and the relevant kinetic results were compared to those obtained in a previous work with a standard experimental methodology (7). The purpose is to make it possible to monitor the APAP photodegradation, and the formation of photoproducts, in real-time by developing an adequate electrochemical set-up.

References

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