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Spectroelectrochemical monitoring of contaminants during the electrochemical filtration process using free-standing carbon nanotube filters

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ABSTRACT

Real-time process monitoring is still relatively scarce but is fundamental to provide *in-situ* information about different chemical and electrochemical processes. Particularly, electrochemical filtration has received growing attention in recent years due to the wide range of applications in which it can be successfully employed. Electrochemical removal is considered as an attractive methodology for the treatment of wastewater due to its efficiency in the removal of a huge number of contaminants. In this work, the development of a new device based on the use of UV–vis bare optical fibers in long optical pathway configuration allows us to monitor continuously the electrochemical degradation process during the filtration of different compounds. Spectroelectrochemistry additionally supplies quantitative information allowing us to calculate the efficiency of the electrochemical filtration process. The material selected to fabricate the electrochemical filter was single-walled carbon nanotubes that display not only high physical and chemical stability, but also high electrical conductivity. Therefore, the combination of electrochemical degradation methods, free-standing single-walled carbon nanotube filters and operando spectroelectrochemical techniques makes this outstanding device very interesting in the study of different molecules. As proof of concept, three different systems have been studied to validate the cell and demonstrate the good performance of the spectroelectrochemical device: *o*-tolidine (reference system), indigo carmine (organic dye), and 4-nitrophenol (hazardous pollutant).

1. Introduction

Electrochemical detection and treatment of wastewater is an overwhelming subject that has received growing attention from the scientific community in a wide variety of fields, such as chemical, petrochemical, pharmaceutical, textile, tannery, food industry, agronomic, landfill leachate and urban wastewater [1–15]. Electrochemical filtration enables the removal of contaminants by adsorptive filtration, as well as electrochemical degradation of different molecules under a suitable applied potential. The versatility shown by these methods makes them very useful in the degradation of a wide range of contaminants. The development of new devices for *in-situ* real-time monitoring of electrochemical filtration processes allows to study and control the different kind of phenomena involved for a huge variety of systems [16–20]. *In-situ* spectroelectrochemical monitoring provides dynamic spectroscopic and electrochemical information at the same time that the redox reaction takes place. This is the main advantage respect to *ex-situ* methods that require taking one or more samples and analyzing it or them using external instruments. The implementation of real-time monitoring devices in agreement with the specific demands of the process provides direct information about all of these processes. These new devices will supply unique and outstanding possibilities very useful for good process control.

Although the interesting properties of carbon nanotube (CNT) filters are well-known [21–28], the simultaneous combination of this material with spectroelectrochemical techniques are notably absent in the literature for evaluation of filtration processes. Spectroelectrochemistry is a multiresponse technique that provides simultaneous electrochemical and spectroscopic information

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in a unique experiment. It shows the advantages of both techniques and offers very unique possibilities in the study of a huge variety of chemical systems [29–32]. Spectroelectrochemical measurements has allowed the monitoring of a wide range of systems, fundamental aspects as reaction mechanisms, or quantitative analysis [33–38].

The main objective of this work is the in-situ monitoring of the electrochemical treatment of different compounds using a new UV–vis absorption spectroelectrochemical filtration device, showing the capabilities and advantages of this novel setup in the study of the behavior of the designed electrochemical filter. We have analyzed three electrochemical systems to illustrate, in a general way, the good performance of this UV–vis absorption spectroelectrochemical filtration device. Firstly, *o*-tolidine (*o*-tol) has been chosen as reference system to validate the operation of the new spectroelectrochemical filtration setup. *o*-Tol is a well-known reference system for UV–vis absorption spectroelectrochemistry that exhibits a fast two electron transfer, and is widely used because it has a large molar absorption coefficient in water [39,40]. The second system studied was indigo carmine (IC), an organic dye employed in different fields not only as a dye in the pharmaceutical and food industry but also as redox indicator and mediator in biological systems [41,42]. Finally, the new spectroelectrochemical filtration device was employed to study the electrochemical reduction of 4-nitrophenol (4-NP). For the last decades, 4-nitrophenol has become one the most used compounds in the fabrication of drugs, pesticides, or leather [43–45]. However, 4-NP is a hazardous pollutant for humans, plants and animals, and in this way, it is important to eliminate this compound from the wastewater, atmosphere and ground because is one of the nitrophenols in the U. S. Environmental Protection Agency List of Priority Pollutants [46,47]. Furthermore, not only the use of 4-NP has increased in the industry during the last years, but also in other areas such as, for example, in agriculture, medical applications and domestic activities [48–50]. Although different methods can be followed to get rid of 4-NP of the industrial wastewater, our interest is focused on the electrochemical removal due to the simplicity to automatize this methodology, its high level of efficiency and its great compatibility with the environment [51,52]. The combination of electrochemical and UV–vis absorption spectroscopy techniques has allowed monitoring the degradation of 4-NP from an aqueous solution.

2. Materials and methods

2.1. Reagents and materials

Ammonium hexafluorophosphate (NH_4PF_6, Fluka), *o*-tolidine (*o*-tol, Sigma-Aldrich), acetic acid (HAc, VWR), perchloric acid ($HClO_4$, 60%, Panreac), indigo carmine (IC, Acros Organics), sulfuric acid (H_2SO_4, 95–97%, Merck), 4-nitrophenol (4-NP, Sigma-Aldrich) and sodium sulfate (Na_2SO_4, Merck) were of analytical grade. Aqueous solutions were freshly prepared, or stored at 4 °C, using ultrapure water (18.2 MΩ cm resistivity at 25 °C, Milli-Q Direct 8, Millipore).

Single-walled carbon nanotubes (SWCNTs, Sigma-Aldrich), 1,2-dichloroethane (DCE, 99.8% for HPLC, Acros Organics), acetone (VWR), nitrocellulose membrane (filter pore size 0.45 μm, Millipore), poly(ethylene terephthalate) (PET, 175 mm thick, HiFi Industrial Film), conductive silver paint (Electrolube) for ohmic contacts, and a high temp masking tape (Kapton) were used to fabricate the free-standing single-walled carbon nanotube (FS-SWCNT) filters.

2.2. Instrumentation

All electrochemical measurements were carried out at room temperature using a potentiostat/galvanostat AUTOLAB PGSTAT 302 N electrochemical system. A standard three-electrode cell was used in all experiments, consisting of a FS-SWCNT electrode as working electrode, a Pt wire as counter electrode and a homemade Ag/AgCl/KCl (3 M) as reference electrode.

UV–vis absorption spectroelectrochemistry measurements in parallel configuration (the light beam passes parallel and close to the electrode surface) [53] were performed using a QE65000 spectrometer (Ocean Optics). UV–vis spectrometer was properly synchronized with the potentiostat. The light beam, supplied by a light source (Halogen HL-2000, Avantes), was conducted to the spectroelectrochemical cell by a 100 μm bare optical fiber (Ocean Optics), and collected from the spectroelectrochemical cell to the spectrometer by a 100 μm bare optical fiber (Ocean Optics).

Raman spectra were obtained using a Confocal Raman Voyage (BWTEK). A 20 × objective was used, with an excitation line at 532 nm and a power of 5 mW. Raman spectra were collected by a CCD array, with a spectral resolution of 3.8 cm^{-1}.

Morphology was studied using a scanning electron microscope Field Emission JSM-7100F Analytical Microscopy.

Atomic-force microscopy (AFM) measurements were carried out using a Alpha300R - Alpha300A AFM WITec.

2.3. Fabrication of free-standing carbon nanotube filters

The methodology employed in the preparation of FS-SWCNT filters is based on previous works [37,54,55]. Briefly, it consists of seven consecutive steps: (1) Preparation of a homogeneous dispersion of SWCNTs in DCE (5 mg/L). Homogeneous dispersion is achieved using a CY-500 tip-sonicator (Optic ivymen System), applying a power of 250 W for 10 min and reducing the power to 100 W for another 5 min (2) Filtration of 3 mL of the SWCNT dispersion under vacuum using a nitrocellulose filter. (3) Transference of the SWCNT film to a poly(ethylene terephthalate) (PET) sheet with a hole of 2 mm diameter applying a gentle pressure around the edges of the nitrocellulose filter to improve adhesion of the SWCNT film to the PET. (4) Dissolution of the nitrocellulose filter by slow addition of acetone and rinsing of the SWCNT film with acetone for 15 min to ensure the complete removal of the filter. (5) Drying at room temperature of the SWCNT film. (6) An ohmic contact is made using a conductive silver paint that is dried in an oven at 75 °C for 30 min (7) Isolation of the ohmic contact with a high temperature masking tape.

2.4. Characterization of the free-standing SWCNT electrodes

Optimization of FS-SWCNT films was performed in a previous work [53]. The electrodes prepared by filtering 3 mL of the SWCNT dispersion display the best features for spectroelectrochemical purposes. Characterization of FS-SWCNT electrodes was performed by Raman spectroscopy. Fig. S1 shows the characteristic Raman spectrum of the SWCNTs, in which mainly four bands are observed: the radial breathing mode (150-250 cm^{-1}, RBM), the disorder induced mode (1250-1450 cm^{-1}, D), the tangential displacement mode (1550-1600 cm^{-1}, G) and the high frequency two phonon mode (2500-2800 cm^{-1}, G′) [47–52].

SEM image (Fig. S2) shows that FS-SWCNT film is completely uniform. As was establish in a previous work [53], the flexibility of this kind of films is an important property, FS-SWCNT electrodes remain intact even when the PET sheet is completely bent. Thickness of the 3 mL film was determined by AFM, obtaining a value of