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Optochemical fiber sensor for Toluidine Blue detection in high turbidity media

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ABSTRACT

We report the analytical performance of an optochemical fiber optic sensor for the detection of dyes in aqueous media with high turbidity. Specifically, the analytical performance of this sensor was evaluated for the quantitative detection of Toluidine Blue (TB) in aqueous solution and also in turbid suspensions of TiO_2 anatase nanoparticles. The detection limit attained was 5×10^{-7} M with a linear sensitivity of 7×10^4 M^{-1} across a linear range from 5×10^{-7} to 5×10^{-6} M. We used the optochemical sensor for two main purposes: (1) in situ characterization of the adsorption isotherm of Toluidine Blue on TiO_2 nanoparticles; (2) in situ characterization of the photodegradation of Toluidine Blue mediated by UV irradiation of TiO_2 nanoparticles. The main aim of this report is to establish the construction and performance of a simple, cheap and small optochemical sensor with clear applications in the field of dye-polluted environmental monitoring.

1. Introduction

Wastewaters containing dyes can be highly toxic considering that 20% of the total industrial dyes are lost during dying processes and are released as effluents [1,2]. The detection and quantification of colorants is of great interest; with this purpose evanescent field fiber-optic absorption sensors are extensively applied in continuous monitoring of concentrations of reactants in chemical processes [3–9]. The optical fibers are highly sensitive to extern perturbation which makes them excellent candidates for the construction of optical sensors [10–12]. The evanescence wave spectroscopy applied to these sensors becomes then a really versatile, sensible, simple and low-cost experimental system. Khijwania et al. have reported a relative humidity sensor using an optic fiber coated with a $CoCl_2$ doped thin polymer film with fast response, full reversibility and large dynamic range [13]; Miled et al. have presented an optic pH sensor based on a dye activated mesostructured silica coated optical fiber, achieving excellent reversibility [14].

Elimination of a pollutant from a contaminated site is an important phase of the process known as remediation. The removal of colored pollutants can be done by physical techniques like adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents, ion exchange on synthetic adsorbent resins [15–19]. Nevertheless, as these strategies do not destroy the pollutants, different alternatives like chlorination and ozone treatment were evaluated, but the results have shown slow degradation rates and high operation costs [18,20–23].

Heterogeneous photocatalysis has attracted increasing attention in order to eliminate undesirable organic pollutants in aqueous phase [1,24,25]. When a semiconductor metal oxide absorbs a photon of energy equal to or greater than its band gap width, an electron may be promoted from the valence band to the conduction band resulting in an electron–hole pair that can move through the semiconductor and reach the catalyst surface participating in redox reactions with adsorbed species [24,25]. $TiO_{2(s)}$ has been proved to be an excellent catalyst in the photocatalytic degradation of organic pollutants, because is an effective, photostable, reusable, inexpensive, and non-toxic material [24–30].

There are few reports of techniques allowing the continuous and in situ monitoring of the concentration of dyes in turbid aqueous solutions for photodegradation tests [1,24,25]. This kind of characterizations are normally performed by exposing a solution of dyes containing nanosized TiO_2 to UV light, then centrifuging or filtrating the samples in order to measure the dye's concentration through spectrophotometry after sample concentration conditioning [1,24,25]. These drawbacks can be overcome by an optochemical sensor based on a fiber optic able to quantify the dye concentration without any sample pretreatment and continuously in real time. As far as we know, optical fiber sensor reports

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are mostly made of glass optical fibers. Plastic optical fibers are barely found in recent reports for dye detection. In addition there are also few reports for dye detection in high turbidity media based on plastic optical fiber.

In this paper, a plastic optical fiber sensor based on the interaction of the evanescent wave with Toluidine Blue adsorbed on the decladded and unfunctionalized fiber is presented. As a new analytical approach, we have used the optochemical sensor for two main purposes: (1) in situ characterization of the adsorption isotherm of Toluidine Blue on TiO_2 nanoparticles; (2) in situ characterization of the photodegradation of Toluidine Blue mediated by UV irradiation of TiO_2 nanoparticles.

2. Materials and methods

Toluidine Blue (TB) was obtained from ALDRICH. Mono- and dibasic potassium phosphate (Cicarelli) for buffer solutions were used as received. PH value was adjusted with hydrochloric acid or potassium hydroxide. Titanium (IV) oxides, anatase (25 nm particle size) and rutile nanopowders (100 nm particle size) were obtained from ALDRICH. Ultrapure water (18 MΩ cm) was obtained using a Milli-Q water purification system (Millipore).

To fabricate the sensor, plastic optical fibers were used. This kind of fiber is commercially available as standardized optical fiber connection systems (Toslink). The fiber is composed by a 920 μm OD polymethylmetacrilate (PMMA) core, a fluorinated polymer clad with a thickness of 20 μm and a black polyethylene jacket. The core and clad refraction indexes are 1.49 and 1.46, respectively.

A 10 cm piece of plastic fiber was cut and the black jacket was completely removed, the middle region of the fiber was carefully decladded to partially expose the core. The entire piece was bent slowly until it became U-shape with the decladded zone in the curved area, and immobilized on a polyamide plug by introducing the extremes in two positioned holes performed for this purpose. A white LED acts as light source at one end of the fiber while the output signal is directed to an optical fiber (Ocean Optics Inc.) coupled to a HR2000 Ocean Optics Spectrometer (Ocean Optics Inc.) connected to a laptop. A quartz beaker compatible in size with the fabricated polyamide plug was used to put the sensor in contact with 10 mM pH: 7.0 phosphate buffer solution. Several aliquots of 2.5×10^{-3} M TB standard solution were added to the buffer medium and the optical fiber attenuation was registered (computed as an absorbance change). The measured signal is produced by the interaction between adsorbed Toluidine Blue on the fiber surface and the evanescent wave in the interface fiber/solution. All the experimental work has been done with magnetic stirring at room temperature.

Adsorption of Toluidine Blue on Titanium IV oxide was used to evaluate the sensor performance in a high turbidity medium. A known quantity of TiO_2 was dispersed in a small volume of phosphate buffer or Toluidine Blue solutions taken from the experimental system using a Pasteur pipette and then the dispersion was returned immediately to the system. A Shimatzu P600 UV–visible spectrophotometer was used to contrast the obtained results.

Photodegradation of Toluidine Blue adsorbed on TiO_2 with different crystal phases was tested using the same optochemical sensor. For this purpose, TB adsorbed on TiO_2 was irradiated with a 300 W Osram Ultra Vitalux mercury tungsten blended UV reflector.

The sensor was cleaned and reused after every experiment. The cleaning process consists of a washing step with buffer solution during 20–30 min under convection, and then the fiber is gently cleaned with a wet tissue paper. The fiber was always stored into 10 mM pH 7.0 phosphate buffer solution.

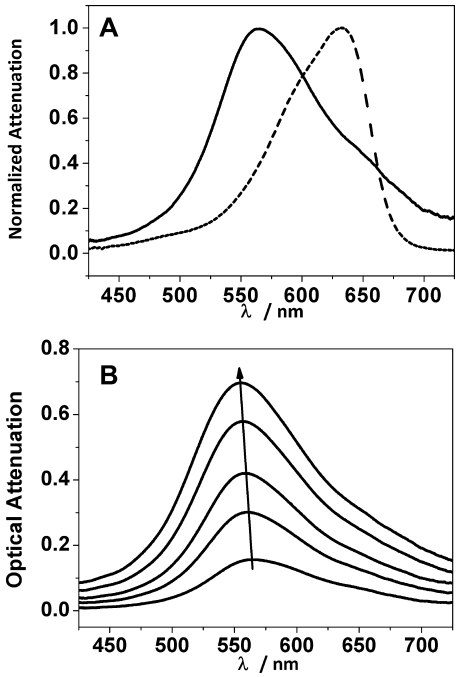

Fig. 1. (A) Normalized TB spectra obtained from optical attenuation of the fiber probe immersed in a TB solution (solid line) and visible spectrum of TB solution taken with a spectrophotometer (dash line). (B) Optical attenuation of fiber probe for increasing TB concentration: 2.5, 5.0, 19.0, 30.0 and 90.0 μM.

3. Results and discussion

3.1. Analytical performance

Fig. 1A shows the visible absorption spectra for two molecular states of Toluidine Blue (TB) adsorbed on the optical fiber (solid line) and TB in solution (dash line), respectively. The spectral change, the shifting of the maximum wavelength locus from 632 to 565 nm, evidences that the analytical response of the optical fiber is produced by the interaction between the evanescent wave and TB adsorbed on the fiber probe resulting in a hypsochromic shift of the spectrum. Ionic strength, pH value and temperature were carefully controlled, monitored and kept constant during the experiments. Spectral changes observed cannot be explained in terms of acid–base equilibrium, neither changes given by coupled reactions; in fact, the change must be given by the immobilization of the dye molecules on the fiber surface where the environment has different electrical properties.

Fig. 1 B shows the sensor performance detecting different TB concentration levels (2.5, 5.0, 19.0, 30.0 and 90.0 μM). All these spectra were obtained in a single step experiment successively adding known volumes of TB standard solution. Clearly, the increase of the optical signal is given by the detection of the added dye, evidenced by a spectral profile characteristic of TB adsorbed on the fiber (Fig. 1A, solid line). Changes of the spectral baseline or in different wavelength regions were not observed. Fig. 2A shows the continuous change of the optical fiber signal, at the wavelength of maxima (565 nm), with sequential additions of TB solution. The signal was registered as a function of time reaching an absorbance steady value after ten minutes for each standard addition. This experiment was performed by addition of 5 μL aliquots of a 2.5×10^{-3} M TB standard solution to a stirred 10 mM pH 7.0 phosphate buffer solution. These values, for each TB concentration, are shown in Fig. 2B. This profile, an isotherm-like shape, is also a clear indication that the adsorbed TB is being tested by the evanescent wave of the optical fiber. Considering the adsorption of TB on