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# High-performance liquid chromatography coupled to ultraviolet diode array detection and electrospray ionization mass spectrometry for the analysis of intermediates produced in the initial steps of the photocatalytic degradation of sulfonated azo dyes

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ABSTRACT

High-performance liquid chromatography coupled to ultraviolet diode array detection and electrospray ionization mass spectrometry was applied to monitor the photocatalytic degradation mediated by $TiO_2$ of three sulfonated monoazo dyes (Orange I, Orange II, and Ethylorange) present in aqueous solution. Photobleaching, organic carbon, nitrogen and sulfur evolution were also followed during the process. Delayed carbon mineralization was observed with respect to both dyes disappearance and photobleaching, due to the formation of transient intermediate compounds which were in turn completely degraded. Among the intermediates produced during the initial degradation steps the formation of several hydroxylated derivatives, mostly coloured, was evidenced. The $MS^2$ spectra allowed one to formulate hypothesis about the OH attack positions; a peculiar reactivity of the azo moiety was shown by Orange I and Orange II.


## 1. Introduction

In textile industry more than 100,000 different dyes are commercially available and it is estimated that about 15% of the world dyes production is lost during the dyeing process [1,2].

Azo dyes represent more than 50% of the total dyes amount and if present in the effluents of textile industry they are not only undesirable because of their colour but also because they can undergo reduction producing carcinogenic aromatic amines [3,4]; for these reasons an efficient degradation process is needed for the treatment of either industrial wastes or polluted natural water streams. Azo dyes are recalcitrant to aerobic degradation in municipal sewerage systems [5] and the common water treatments (precipitation, flocculation, adsorption on active carbon) only displace the problem and require further sludge treatment or carbon regeneration [6]. An alternative is represented by the Advanced Oxidation Processes (AOP's), able to degrade organic compounds until their mineralization occurs; among them heterogeneous photocatalysis in the presence of $TiO_2$ suspensions has been shown to be convenient since it operates at ambient condition and it uses a cheap and safe catalyst, atmospheric oxygen and solar light (or simulated) [7,8]. Many papers have been published concerning the $TiO_2$ mediated degradation of azo dyes in aqueous solutions and recently an exhaustive review appeared about this topic [9–13]. Most of these papers deal with the process parameters optimization and give an overlook of the process efficiency by monitoring the DOC evolution. Only few of them investigate the nature of the intermediates formed during the degradation and even in these cases the discussion concerns the nature of compounds formed after the chromophore cleavage and the molecule rupture, with particular attention to establish whether the attack occurs directly on the azo-group or on the C atom bearing it. GC–MS and FTIR have been reported in the literature as suitable methods for the assessment of the identity of Orange II intermediates, either in solution (after extraction with organic solvent) or starting from the dye adsorbed on the semiconductor [14,15]; recently ESI-MS technique has been proposed for the monitoring of the degradation of azo dyes [16]. At our knowledge there is generally a lack of information about the nature of intermediates formed during the initial degradation steps, in particular those still retaining the chromophoric group [17]. In the present research the degradation of three commercial sulfonated azo dyes (Fig. 1) has been attempted,

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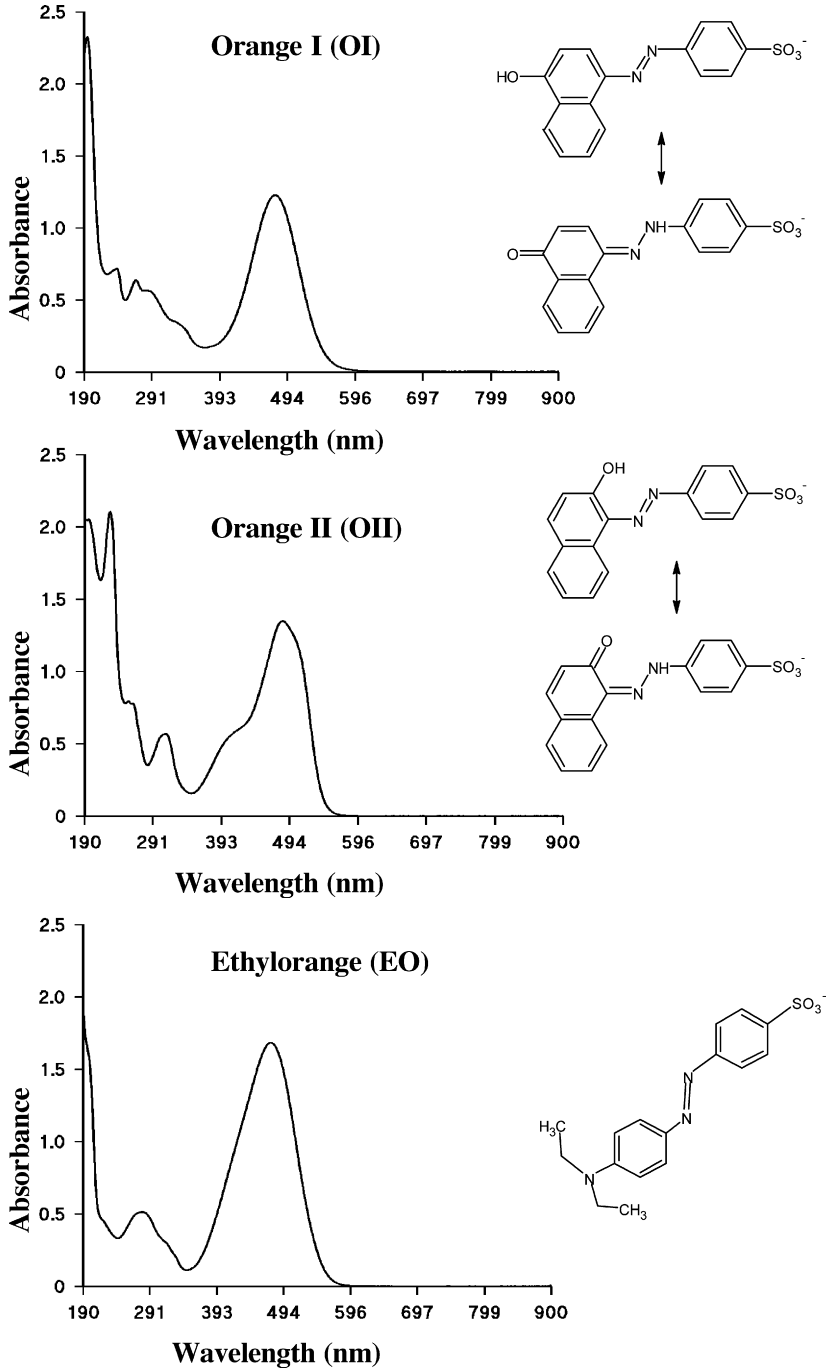


**Fig. 1.** Structure and UV–vis spectrum of the investigated dyes.

with particular attention devoted to the identification of the initial coloured and/or sulfonated intermediates. Beside their importance under the mechanicistic point of view, eventually formed coloured intermediates are also of environmental concern and sulfonated derivatives, being highly soluble in water and mobile in this environmental compartment, can extend the potential pollution risk. Among the chosen dyes, many authors have considered Orange II as an azo dye model and thus its $TiO_2$ mediated photodegradation was the object of studies concerning its degradability and other related topics [18–22].

Since sulfonated azo dyes have in general poor thermal stability and low volatility we considered the high-performance liquid chromatography coupled to ultraviolet diode array detection and electrospray ionization mass spectrometry (HPLC–DAD-ESI–MS) a suitable analytical approach for their determination together with their hydrophilic initial degradation products, without the needing of any derivatization and/or solvent extraction steps.

## 2. Experimental

### 2.1. Reagents and materials

The following sulfonated azo dyes were provided by Aldrich and were used without further purification: Orange I (OI, M.W.