



Liquid chromatographic–mass spectrometric monitoring of photodegradation of diphenylamine using experimental design methodology



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ABSTRACT

Diphenylamine (DPA) photodegradation was studied by applying the optimal response surface design methodology to the chromatographic data from pollutant solutions exposed to stressing irradiation. The procedure consisted of data analysis of aliquots collected at different reaction times and injected to a high-performance liquid chromatography coupled to diode array detection–mass spectrometry (HPLC–DAD–MS). The variables considered for the process optimization were irradiation power, irradiation time and pH of solution, for a solution with DPA concentration of 100 mg L⁻¹. This methodology allowed assessing and identifying the effects of different factors studied and their interactions in the process response. An appropriate quadratic model was developed in order to plot the response surface and contour curves and to perform the process optimization. The results obtained revealed that DPA photodegradation is strongly dependent on the solution pH and irradiation power. Under the optimal conditions (i.e., pH of 10, irradiation power of 2 × 15 W lamp and irradiation time of 150 min), it was possible to achieve an almost complete photodegradation of DPA. The process was found to follow a pseudo-first-order kinetic model. Mass spectrometric analysis allowed the identification of carbazole (CB) as the major photodegradation product. A possible pathway for the photodegradation of DPA was suggested. The optimized methodology was applied to preparation and separation of CB, as an important mediator in fine chemistry and pharmacy, from DPA by thin layer chromatography.

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1. Introduction

Photochemical reactions continue to receive an increasing interest, as they determine not only the chemistry of the atmosphere but also the environmental chemical changes [1–3]. Studies on photooxidation are extensive but those are rare with natural sunlight because of fluctuation of sunlight intensity even under clear sky [1].

Diphenylamine (DPA) is widely used as stabilizer for nitrocellulose-containing explosives and propellants, as antioxidant for various polymers and elastomers and as condensate for the insulation of rubber [4,5]. DPA is also used to prevent postharvest deterioration of apple and pear [6,7]. In addition,

DPA is a parent compound of many derivatives, which are used for the production of dyes, pharmaceuticals and photography chemicals [4]. However, DPA may lead to dermatitis (formation of vesicular and exudative eczemas) in workers exposed to DPA containing products. It has also been documented that DPA possesses some damaging effects on liver, spleen and kidney in experimental animals such as dogs, rats and mice [8,9], and is hazardous to some organisms in aquatic environment [10]. In the European Union, DPA has been listed as a prior pollutant [4].

Commonly, the photolytic degradation processes are carried out with an environmental sample (effluent) via absorption of UV light by a chemical species (direct photolysis), or are mediated by a natural photo-sensitizers such as nitrate ion (indirect photolysis) [11–14].

The efficiency of direct photolysis of compounds depends on several variables including temperature, irradiation power, irradiation time and pH [15]. In order to achieve high

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performances, these experimental conditions must be optimized. Until now, most published studies are based only on a single-factor-at-a-time approach, considering the effect of each variable independently and keeping all other conditions constant. However, this methodology does not take into account the interactions between parameters and, consequently, their effect on the process response. With the purpose of overcoming this disadvantage, the application of experimental design becomes essential. This statistical approach allows a multivariate analysis, using a minimum number of experiments [16–20].

To the best of our knowledge, there is no previous report on the application of experimental design to the process optimization for direct photodegradation of DPA, and also no detailed mechanistic photochemical works have already been conducted on this compound. Obtaining such information and providing the necessary methodology for monitoring and interpretation of complex photodegradation processes was the main goal of the present work. Complementary information about the identity of the photodegradation products was obtained by application of MS data with easily interpretable features. The double DAD and MS detection were used to propose the possible structure of the main detected photoproducts, a major one being identified as carbazole (CB).

2. Experimental

2.1. Chemicals and standards

Analytical-reagent grade or better chemicals as well as Milli-Q water were used in the experiments. DPA, biphenyl (BP) and HPLC grade acetonitrile (for extraction and sample preparation) were purchased from Sigma–Aldrich. DPA was purified by simple preparative chromatography on a silica gel column (3:1 *n*-hexane/acetonitrile as a mobile phase) and followed by thin layer chromatography (TLC) monitoring. Solutions of Britton–Robinson buffers were prepared in 0.04 M concentration. The pH of all solutions was adjusted with 1.0 M of NaOH or HCl, whenever required. The stock solutions were prepared by dissolving 10.0 mg of DPA and 2.25 mg of BP (as internal standard) in 100 mL of 60:40 (v/v) buffer aqueous solution and acetonitrile and stored in a refrigerator.

2.2. Apparatus and experimental setup

2.2.1. Photodegradation setup

DPA photodegradation experiments were carried out in a home-made cylindrical Pyrex reactor (2.5 cm i.d. and 38 cm in length, 50 mL) with a double-walled cooling-water jacket to keep the constant temperature of solutions throughout the experiments. A home-made dark woody cabinet equipped with light sources and a cooling fan as a heat controller device to emit and dissipate the generated heat was used. One high-pressure 7 W and two high-pressure 15 W mercury lamps (G15-T8, Philips, Holland) emitted predominantly at 254 nm were used as light sources. In all experiments, the reactor was fixed in a distance of 15 cm under the light sources.

2.2.2. Chromatographic setup

Chromatographic equipment consisted of two Waters 510 pumps (Waters, Milford, MA, USA) with a quaternary pump and a sample injector with a 10 μ L loop (Rheodyne, Cotati, CA, USA). The liquid chromatograph used was coupled to a Waters G1315B diode array detector (DAD), and a mass spectrometer (MS) detection system in tandem. Evaluation and quantification were made on a Millennium chromatography data system (Waters).

The analytes were separated on a 250 mm \times 4.6 mm i.d., 5 μ m C18 reversed phase Spherisorb column (Waters), with a sample injection volume of 10 μ L at a column temperature of 20 °C. A binary isocratic mobile phase (50:50, v/v acetonitrile/deionized water) was used at a flow rate of 1.00 mL min⁻¹.

The DAD detection system in the UV–vis region was operated at spectral resolution of 1.2 nm in the spectral range from 200 to 500 nm via collecting one spectrum per second, and the effluent was monitored at 254 nm. The peak identification was based on the retention time and the UV spectrum (obtained from DAD) against a standard. Routine sample calculation was made by comparison of the peak area with that of the BP standard.

MS detection was carried out on a bench top triple quadrupole mass spectrometer Quattro LC from Micromass (Manchester, UK) with an ESI spray chamber interface at the following conditions: nitrogen (99.999% purity) drying gas flow, 5 L min⁻¹ as desolvation gas; nebulizer pressure, 414 kPa; drying gas and vaporizer temperatures, 350 and 425 °C, respectively; coronal discharge, 4 μ A; fragmentor and capillary potentials, 130 and 4000 V, respectively. The MS detector was adjusted to monitor positive ions in scan mode (100–800 amu) with scan duration of 1 s/scan and an inter scan time of 0.1 s or in selective ion monitoring (SIM) mode when compounds were identified and increased sensitivity was required.

2.3. Photodegradation experiments

A stock solution of DPA (100 mg L⁻¹) in 60:40 (v/v) buffer aqueous solution and acetonitrile was properly diluted to obtain two other samples (34.0 and 67.0 mg L⁻¹) at desired pH values of 4.0, 7.0 and 10.0 by addition of HCl or NaOH. Then, reaction mixtures were filtered through a 0.2 μ m membrane. The samples were placed in the photoreactor and irradiated by different high-pressure mercury vapor lamps at room temperature. In each experiment, during the photodegradation process, the reaction was stopped at different time intervals by turning off the UV lamp and locating the reaction cell in an ice water container. To measure the residual DPA concentration after a certain reaction period, aliquots of 100 μ L of the reaction mixture was collected and mixed with an equal amount of a 22.5 mg L⁻¹ of biphenyl (BP), as an internal standard solution, in a sample tube and was completely blended. Then, 10 μ L of the mixture was injected into the HPLC column. The internal standard was used to eliminate the possible injection errors in liquid chromatography and also to correct the peak shift. Utterly, a total number of 24 samples for primary photodegradation studies were subjected to LC–MS analysis.

Each experiment was conducted in triplicate and all data reported in the text and in figures are reported as the average value.

2.4. Experimental design and process optimization

The statistical experiment design and response surface methodology (RSM) are widely used methods to determine the effects of multiple variables on the objective functions to be optimized [16–21].

In the present study, a second-order polynomial function (Eq. (1)) was used to model $C_{DPA}/C_{0,DPA}$ (dependent or *y*-variable) as a function of experimental variables including treatment time, pH and irradiation power ($n=3$), where $C_{0,DPA}$ and C_{DPA} are chromatographic peak areas of DPA relative to that of BP before and after exposing sample solution to UV light, respectively. The second-order model includes all terms in the first-order terms, all quadratic terms and the cross product terms, as:

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