



## Photocatalytic degradation of carbofuran in TiO<sub>2</sub> aqueous solution: Kinetics using design of experiments and mechanism by HPLC/MS/MS

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### Abstract

The photocatalytic degradation kinetics of carbofuran was optimized by central composite design based on response surface methodology for the first time. Three variables, TiO<sub>2</sub> concentration, initial pH value and the concentration of carbofuran, were selected to determine the dependence of degradation efficiencies on independent variables. Response surface methodology modeling results indicated that the degradation efficiency of carbofuran was highly affected by the initial pH value and the concentration of carbofuran. Then nine degradation intermediates were detected by HPLC/MS/MS. The Frontier Electron Densities of carbofuran were calculated to predict the active sites on carbofuran attacked by hydroxyl radicals and photoholes. Point charges were used to elucidate the chemisorption pattern on TiO<sub>2</sub> catalysts during the photocatalytic process. By combining the experimental results and calculation data, the photocatalytic degradation pathways of carbofuran were proposed, including the addition of hydroxyl radicals and the cleavage of the carbamate side chain.

**Key words:** carbofuran; photocatalytic degradation; central composite design; kinetics; mechanism

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### Introduction

The presence of pesticide residues in the aqueous environment has raised increasing concerns in recent years due to their recalcitrance, toxicity, mutagenicity, carcinogenicity and tumorigenicity (Lu et al., 2010c; Muhammetoglu et al., 2010; Chelinho et al., 2012). Carbofuran is a broad-spectrum carbamate pesticide and nematicide which has been used against various foliar pests observed in fruit, vegetable and forest crops (Kazemi et al., 2009; Gammon et al., 2012). In addition, it is highly toxic and recognized as an inhibitor of acetylcholinesterase, an enzyme vital to the functioning of the central nervous system, and has been proved to be a potential endocrine disruptor (Hela et al., 2005; Barry et al., 2011). Several recent studies have demonstrated that carbofuran was found in waters and wastewater in many countries, such as Germany (Olson et al., 2000), The United States (Hix et al., 2001; Fleischli et al., 2004), Australia (Yang et al., 2010; Ashauer et al., 2011), China (Lin and Chen, 2006; Wu et al., 2011) and

so on. Its presence in environmental water, even at trace levels, may adversely affect aquatic ecosystems and human health. Therefore, its environmental fate, transfer, effect, and potential risks during water treatment are of concern.

Heterogeneous catalysis, one class of advanced oxidation processes (AOPs), can be used to achieve complete oxidation of organic and inorganic species (Yang et al., 2010a, 2010b; Wu et al., 2012). Several studies have reported the degradation of carbofuran using heterogeneous catalysis technology. For example, Kuo et al. (2006) and Tennakone et al. (1997) investigated the photocatalytic degradation of carbofuran using immobilized TiO<sub>2</sub>. Kuo et al., (2006) and Mahalakshmi et al. (2007) evaluated the effect of some classical parameters in a batch reactor by using a medium-pressure mercury vapor lamp and a 254 nm UV lamp, respectively. Lopez-Alvarez et al. (2011) studied the effect of different parameters on the degradation, toxicity and byproducts of carbofuran during a photocatalytic process by solar radiation. Although the possibility of degradation of carbofuran was confirmed from the above-mentioned studies, these studies are still not sufficient to fully elucidate the degradation kinetics

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and mechanism. Furthermore, photocatalytic kinetics optimization of carbofuran has usually been investigated by the single-variable-at-a-time (SVAT, the most common practice holding all other variables constant) method in previous studies (Kuo et al., 2006; Mahalakshmi et al., 2007). Nevertheless, the SVAT approach possesses many drawbacks, such as being time-consuming, inability to account for interactions between different variables and inefficiency in predicting the true optimum conditions (An et al., 2011). An alternative method, central composite design (CCD) based on response surface methodology (RSM) can overcome all the above shortcomings (Sakkas et al., 2010; Lu et al., 2011a). This is because the RSM can explore the relationships between several variables and one or more response variables. The main idea of RSM is to use a sequence of designed experiments to obtain an optimal response.

Therefore, in order to propose a more accurate model for the photocatalytic kinetics of carbofuran, CCD based on RSM was employed to assess the individual and interactive effects of several classic parameters on the photocatalytic efficiency of carbofuran degradation. Additionally, photocatalytic degradation pathways of carbofuran were also tentatively proposed based on the intermediates identified by HPLC/MS/MS as well as the theoretical calculation data of frontier electron densities (FEDs) and point charges (PC).

## 1 Materials and methods

### 1.1 Chemicals and reagents

Carbofuran was provided by the Hunan Research Institute of Chemical Industry ( $\geq 99\%$  purity). HPLC grade water was obtained from a Millipore Milli-Q System (Water, Millipore), which was treated by constant illumination with a Xe arc lamp at 172 nm to keep total organic carbon concentration below 13  $\mu\text{g/L}$ . Acetonitrile and methanol (HPLC grade) were purchased from Sigma.

### 1.2 Irradiation procedures

The adsorption and photocatalytic degradation of carbofuran were carried out in a Pyrex reactor (150 mL) with a double-walled cooling-water jacket to keep the temperature of solutions constant throughout all experiments. The light source was a high-pressure mercury lamp (GGZ-125, Shanghai Yaming Lighting, China,  $E_{\text{max}} = 365$  nm) with a power consumption of 125 W and light intensity of 0.47  $\text{mW/cm}^2$ , housed in one side of the photocatalytic reactor to provide the irradiation. The distance between light source and photocatalytic reactor was 15.5 cm. Prior to illumination, a suspension of 150 mL carbofuran (100  $\mu\text{mol/L}$ ) with different concentrations of the photocatalyst (Degussa P25) was stirred in the dark for 30 min to achieve adsorption-desorption equilibrium. Then, the UV light was turned on for the photocatalytic degradation experiments.

Samples of the reaction solution (3 mL) were obtained at regular intervals, filtered through 0.22  $\mu\text{m}$  Millipore filters and analyzed by HPLC and HPLC/MS/MS. All experiments were carried out at room temperature.

### 1.3 Analytical procedures

The photocatalytic degradation kinetics of carbofuran was investigated using a Cometro 6000 series HPLC under the following conditions: Kromasil C18 column, 150  $\times$  4.6 mm i.d., performed at 25°C. The mobile phase was composed of 20% H<sub>2</sub>O and 80% CH<sub>3</sub>OH that was filtered with a Water Associates (Milford; MA, USA) 0.45  $\mu\text{m}$  filter. The detection wavelength was 280 nm. The flow rate of the mobile phase was set at 1 mL/min.

Degradation intermediates were analyzed using a HPLC/MS/MS, a Shimadzu high performance liquid chromatography (HPLC) system with a Kromasil C18 column (150  $\times$  4.6 mm i.d), SIL-HT autosampler, LC-10 AT vacuum pump and API 3000 mass analyzer. HPLC separations were performed at 0.5 mL/min and 50% H<sub>2</sub>O and 50% CH<sub>3</sub>OH within 30 min. An electrospray interface (ESI) was used for the MS and MS-MS measurements in positive ionization mode and full scan acquisition between  $m/z$  50–300. The collision energy varied according to the requirements of the different measurements, and the other parameters were set as follows: the ESI was 5.5 keV, the source block and desolvation temperature were 130 and 400°C, respectively, the desolvation and nebulizer gas (N<sub>2</sub>) flow rates were set to 6 L/min and argon was used as a collision gas at 250,000 Pa.

### 1.4 Experimental design and data analysis

The stoichiometric approach was performed using a CCD in the form of RSM. Analysis of the experimental data was supported by Design-Expert software (trial version 8, Stat-Ease, Inc., MN, USA) (Sakkas et al., 2010; Abdullah et al., 2012). Three variables, TiO<sub>2</sub> concentration, initial pH value and initial concentration of carbofuran, were investigated in the multivariable experimental design. The multivariable experimental design was performed according to CCD based on RSM and the photocatalytic degradation efficiency of carbofuran was selected as the response. The three chosen variables were converted to dimensionless ones ( $x_1$ ,  $x_2$ ,  $x_3$ ), with the coded values at levels:  $-\alpha$ ,  $-1$ ,  $0$ ,  $+1$ ,  $+\alpha$ . The determined values of the variables are presented in **Table S1**. It can be seen that the five levels for controlling factor were 0.66, 1.00, 1.50, 2.00, and 2.34 g/L for the factor  $x_1$ , namely TiO<sub>2</sub> concentration; 66.36, 80.00, 100.00, 120.00 and 133.64  $\mu\text{mol/L}$  for the factor  $x_2$ , namely initial concentration of carbofuran; 1.64, 3.00, 5.00, 7.00 and 8.36 for the factor  $x_3$ , namely initial pH value. Therefore, 17 experiments were performed in the present study with three replications at the center point. The complete experimental design matrix and the responses are shown in **Table 1**.

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