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PHOTODECOMPOSITION OF CARBENDAZIM IN AQUEOUS SOLUTIONS

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Abstract—The kinetic of photodecomposition of carbendazim (methyl-2-benzimidazole carbamate) at different pHs (1, 5, 7, 8 and 11) and at two different concentrations of dissolved oxygen has been studied. According to the experimental results, the photodegradation process follows a first-order kinetic and the degradation rate of carbendazim increases with pH and dissolved oxygen concentration.

Key words—carbendazim, photodecomposition, kinetic

INTRODUCTION

The carbendazim [MBC (methyl-2-benzimidazole carbamate)] is a widely used systemic fungicide for controlling a broad range of fungi affecting fruits, nuts, vegetables, turf, and field crops. Additionally, the carbendazim and *n*-butylisocyanate (BIC) are degradation products of benomyl fungicide(methyl-1-(butylcarbamoyl)-2-benzimidazole carbamate) in water and in organic solvents (Arnold *et al*., 1957; Calmon and Sayag, 1974; Chiba and Cherniak, 1978).

As systemic fungicides, benomyl and carbendazim can be adsorbed through the roots, leaves, and green tissues of plants along with water (Ben-Aziz and Aharanson, 1974). These products, benomyl, carbendazim and BIC, are toxic for humans, animals and plants. This toxicity includes effects in the male mammalian reproductive system, embriotoxicity, teratogenesis (Axness and Fleeker, 1979; Hess *et al*., 1994; Somerville, 1986) and phytotoxicity (Shilling *et al*., 1994a,b).

Therefore, the quantitative determination is very important of carbendazim and benomyl in water, soil, wastewater, crops and foods. Recently, instrumental analytical methods as well as immunoassays for the quantitation of carbendazim and benomyl have been developed (Itak *et al*., 1993). Both carbendazim and benomyl are in widespread use and persist in the environment. In an aqueous medium, degradation may take place by the effect of ultraviolet radiation or by alkalinity and dissolved oxygen concentration of the medium. In a previously published paper (Ibarz *et al*., 1996), a study of the photodecomposition of benomyl in aqueous solution was presented showing the degradation of this fungicide. In this paper, the behavior of aqueous solutions of carbendazim at different pH values under ultraviolet radiation has been studied.

MATERIALS AND METHODS

The photochemical reactor (Ibarz and Pagán, 1986; Ibarz *et al*., 1996) used in the experiments was a rectangular box made of metacrylate, measuring 22.9 × 11.9 × 10 cm. The distance between the lamp and the solution surface was 22.3 cm and the volume, V, of the irradiated solutions was 4 l. The lamp used in the experiments was a mercury PHILIPS HPM-12 with 400 W of nominal power. The emission wavelength range for the lamp is 250–750 nm.

The carbendazim used in the experimentation was supplied by Du Pont Ibérica (>99%).The buffer solutions (pHs 1, 5, 7, 8 and 11) were prepared with bi-distilled water with additional degasification during 30 min in an ultrasonic bath. The reagents used in the preparation of the buffer solutions were of a quality for analysis and were supplied by Merck. The methanol used as co-solvent (Fluka) was of a quality for UV spectroscopy. Previously, it was degassed for 30 min in an ultrasonic bath.

The solutions were prepared by dissolving the carbendazim in methanol and diluting with the corresponding buffer solutions to 4 l. Initial concentrations of carbendazim were 5 mg/l.

The pH of the buffer solutions was tested with a Crison pH-meter at 20°C. In all cases, pH of buffer solution prepared were in ±0.1 interval. The dissolved oxygen concentration was determined with an oxygen-meter Oxy-91.

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Table 1. ϵ_λ values for carbendazim at different wavelength and pH

λ (nm)	ϵ_λ 10^{-5} (m^2/kmol)				
	pH = 1	pH = 5	pH = 7	pH = 8	pH = 11
255	3.47	4.34	4.39	4.47	4.98
265	7.73	5.08	4.94	4.79	4.14
275	12.16	10.02	10.02	10.03	8.88
285	6.40	10.39	11.56	11.65	11.72
295	–	3.13	5.10	5.69	5.89
305	–	–	–	–	0.40

The decay process was followed with HPLC, using a Waters 490 chromatograph. The column used was a Spherisorb C-18. The flow (isocratic) was 1.5 ml/min, with composition acetonitrile:buffer solution 60:40. The wavelength of detector was 286 nm. In all cases, the amounts of sample were 100 μl.

For determination of the molar extinction coefficient ϵ_λ at different pH values a spectrophotometer PHILIPS UV/VIS 8700 with a 1 cm quartz cell was used (Table 1). Figure 1 shows the absorbance spectra for MBC at different pH of aqueous medium. In the wavelength range of carbendazim absorption (250–310 nm), the photon flux entering the reactor was determined by uranyl–oxalate actinometry (Calvert and Pitts, 1967) to be $W_e = 5.3$ μeins/s.

RESULTS AND DISCUSSION

Figures 2 and 3 show the variation of the carbendazim concentration with the irradiation time at different pH levels and at two values of the concentration of dissolved oxygen (6 mg/l and 3 mg/l). The degradation was shown not to take place at very acidic conditions (pH = 1). In both cases, the degradation rate increases with the pH of the medium. At alkaline conditions, the degradation looks like a first-order reaction with respect to the carbendazim concentration. The maximum extensive rate achieved was 2 μmol/min at the initial time of the UV irradiation—at pH = 11 and 6 mg/l of oxygen. Additionally, no degradation was detected operating in the absence of ultraviolet radiation. Similar to other organic compounds at very low concentration (Ibarz *et al.*, 1996), a simple rate equation may be used to describe the ultraviolet photodegradation of carbendazim:

$$r_c = \Sigma \phi \epsilon_\lambda q_\lambda C_c \tag{1}$$

where ϵ_λ is the molar extinction coefficient to the wavelength λ (m^2/kmol), q_λ is the modulus of the radiation energy flux density vector to the wavelength λ (einstein/m^2 s), a function of the position (x, y, z) in the reaction chamber, C_c is the carbendazim concentration (kmol/m^3), ϕ is the quantum yield (mol decomposed/einstein absorbed), and r_c is the intensive degradation rate of carbendazim (kmol/(m^3 s)).

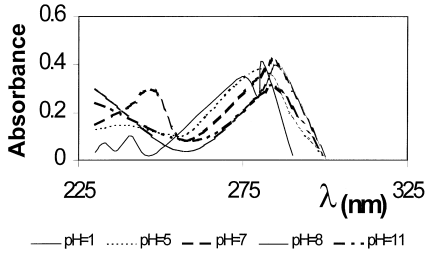


Fig. 1. UV Spectra for MBC at different pH.

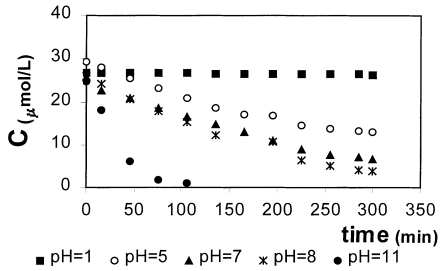


Fig. 2. Photodegradation of carbendazim for 6 mg/l of dissolved oxygen.

Taking into account the mass balance in the photochemical reactor and assuming perfect mixing in the reaction medium, it is possible to relate the carbendazim concentration with irradiation time (Esplugas and Vicente, 1991):

$$\frac{dC_c}{dt} = -\frac{1}{V}\int_V \sum_\lambda \phi \epsilon_\lambda q_\lambda C_c \, dV \tag{2}$$

where V is the reaction volume and the summation is extended to the wavelength range of carbendazim absorption (250–310 nm).

The amount of radiation energy absorbed by the compound is obtained from the expression:

$$W_{abs} = \int_V \sum_\lambda \epsilon_\lambda q_\lambda C_c \, dV \tag{3}$$

and because the carbendazim concentration does not remain constant during the experimentation and some of the photoproduct formed may absorb radiation, the value of W_{abs} varies with irradiation time. But, as q_λ varies with the composition of the system, the ratio W_{abs}/C_c may be assumed constant with time and equal to its value a zero time W^0_{abs}/C^0_c (Arántegui *et al.*, 1995). That means that the

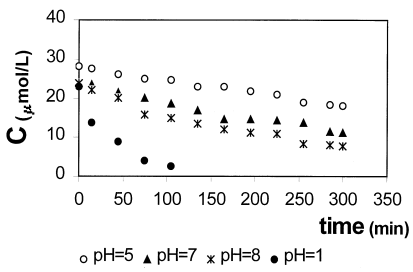


Fig. 3. Photodegradation of carbendazim for 3 mg/l of dissolved oxygen.

Table 2. Quantum yield at different pH

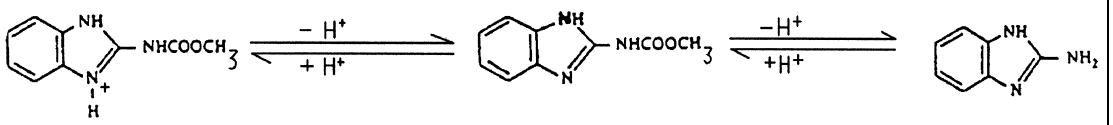
pH	$C_{O2}=3$ mg/l		$C_{O2}=6$ mg/l	
	ϕ (mmol/einstein)	Coefficient regression	ϕ (mmol/einstein)	Regression coefficient
5	0.56 ± 0.05	0.9898	1.1 ± 0.2	0.9888
7	0.76 ± 0.06	0.9946	1.3 ± 0.3	0.9959
8	0.90 ± 0.09	0.9917	1.6 ± 0.3	0.9881
11	4.0 ± 0.7	0.9943	6.3 ± 1.2	0.9951

photons absorbed by the carbendazim are proportional to its concentration. With this assumption, the differential equation (2) may be solved giving a logarithmic relation between the carbendazim concentration and the irradiation time:

$$\ln \frac{C_c}{C_c^0} = \frac{\phi W_{abs}}{C_c^0 V} t \qquad (4)$$

According to this simple equation, the experimental results were fitted to equation (4). Table 2 summarizes the regression coefficient obtained in the fitting, and the value of the quantum yield with a confidence interval of 95%.

Bearing in mind the experimental results, the degradative process follows a first-order kinetics. As for the influence of pH in the decay process, increasing pH promotes the degradative process, whereas at acidic pH, the decay process is negligible. It can be explained by the fact that at high acidity the protonation takes place in the benzimidazole ring, and the protonated product is more stable under UV radiation than the previous one (Fleeker *et al.*, 1977). Moreover, in alkaline media there is the loss of proton of the carbendazim and, consequently, the formation of 2-aminobenzimidazole takes place, this product being more sensitive toward UV radiation. In the following scheme it is possible to appreciate the pH influence.



In alkaline conditions, there will be more deprotonated species, which will be degraded by the ultraviolet radiation.

The increase of the oxygen concentration in the aqueous solution gives an increase in the degradation rate. As already found in the bibliography (Watkins, 1974), carbometoxyguanidine, diguanidine, and dimethyloxalate are photoproducts of the reaction of carbendazim with oxygen.

Instead of the experimental results showing degradation of the carbendazim in aqueous solution at alkaline conditions and with the presence of dissolved oxygen, the rate achieved is not very high. Carbendazim is a product difficult to degrade (quantum yield lower than 0.007 mol/einstein and small wavelength range spectra of absorption) and the use of more oxidative methods, as UV/ozone or UV/ hydrogen peroxide should be studied.

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