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Kinetic study and modelling of the UV photo-degradation of thiabendazole

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ABSTRACT

A consequence of the massive use of pesticides in fruit harvesting is that many fruit juices contain pesticide traces that can be hazardous to the health of consumers. The wastewater generated in the fruit process after cleaning the fruit also contains pesticides in concentrations that cannot be dumped into the environment so these substances have to be previously eliminated. As thermal and the biological treatments do not degrade most pesticides used, an alternative treatment has to be applied to eliminate these toxic compounds both in fruit juices and wastewater. In the present work, a photochemical treatment with UV radiation was applied to eliminate thiabendazole from aqueous solutions at different pH and temperatures, using a medium-pressure mercury lamp that emitted in the range of wavelengths between 255 and 750 nm. The absorbed radiation was calculated as a function of the concentration of thiabendazole. A reaction mechanism was proposed, so combining it with the mathematical relation found between the absorbed radiation and thiabendazole concentration suggests a pseudo-first-order kinetic model that, for the range of concentrations studied, can be simplified to a zero-order kinetic model, both of which fit the experimental data obtained well.

1. Introduction

Thiabendazole (2-(4-Thiazolyl)-1 H-benzimidazole) (TBZ) is a broad-spectrum systemic fungicide used for controlling some plagues, e.g. mold, rot, blight and stain in all kinds of crops, especially fruit and vegetables, both pre and post-harvesting (Farrow, Hoodless, Sargent, & Sidwell, 1977; Mestres, Tourte, & Campo, 1972; Norman, Fouse, & Craft, 1972; Papadopoulou-Mourkidou, 1991).

Although TBZ does not have a high risk of toxicity for human and animals (Zbozinek, 1984), its accumulation in the environment causes increasing resistance in some microorganisms (Roca-Jalil, Baschini, Rodríguez-Castellón, Infantes-Molina, & Sapag, 2014).

Many fruits are treated with TBZ solutions both in the orchards and prior to refrigerated storage to prevent further fungi growth. As a consequence, when the fruit is processed to produce juices and their derivatives, the pieces of fruit are impregnated with TBZ. The persistence of TBZ being high, this product can pollute the final juice. In fact, 21 different pesticides were found in 655 orange juice samples from different places in United States, the most frequent being benomyl, carbendazim, imazalil and thiabendazole (EFSA, 2011). In the case of fruit juices with pulp, the pesticide content was found to be significantly higher due to the addition of pulp previously obtained by concentrating the pulp fraction of the juice (Bedendo, Jardim, & Carasek, 2012). This presence can be minimized by increasing the intensity of the washing stage of the fruit.

However, washing fruit prior to be processed leads to the presence of pesticides in the wastewater stream generated in food processes. TBZ was the most frequently detected pesticide and at the highest concentration in this kind of wastewater (Sánchez-Pérez, Carra, Sirtori, Agüera, & Esteban, 2014). Due to its toxicity, environmental persistence and bioaccumulation, pesticides are an important source of pollution in water (EPA, 2002 & 2015; Montforts, 2006).

As TBZ can be found in fruit juices and wastewater from food processes, a treatment able to degrade TBZ needs to be found. In order to eliminate TBZ from aqueous solution, many natural adsorbents have been used (Roca-Jalil et al., 2014). Natural clay minerals have showed optimal adsorption capabilities due to their surface area and their cation-exchange capacity (Crini, 2006). Conventional biological treatments have been shown to be unable to remove TBZ (Bolong, Ismail, Salim, & Matsuura, 2009). The combination of a membrane bioreactor with an advanced oxidation process consisting of either the Fenton reaction or the Solar-Photo-Fenton reaction has also been studied (Sánchez-Pérez et al., 2014). In this case, TBZ showed resistance to the biological treatment but was totally eliminated when Fenton and solar photo-Fenton were applied as a tertiary treatment. As Fenton treatments suppose the addition of hydrogen peroxide and iron, they cannot be used to degrade TBZ when it is in either fruit juice or its derivatives, because it would affect its sensory and nutritional characteristics.

UV radiation has been shown to be effective at degrading other toxic pollutants in fruit juices and aqueous solutions (Ibarz et al., 2014 and

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2015) without significant changes in their physicochemical properties (Aguilar, Ibarz, Garvín, & Ibarz, 2016; Falguera, Pagán, & Ibarz, 2011). Thus, this work aims the study of the degradation of TBZ by UV radiation, in order to know if the photo-degradation takes place and obtain the reaction kinetics. Taking into account the pH values of most fruit juices (Falguera et al., 2012; Koutchma, 2009), the pH range studied was set between 3 and 5.

2. Material and methods

2.1. Irradiation model

When a solution is irradiated with an electromagnetic radiation, part of the power emitted by the lamp reaches the surface of the solution and only a part of this can be absorbed. Only a fraction of the absorbed radiation can cause any reaction. This fraction being the quantum yield of the total absorbed radiation, as the ratio between the number of molecules reacted over the number of photons absorbed. In fact, if the emission and absorption spectra did not match for any wavelength, the incident radiation on the surface of the solution would not be absorbed at all. Even in the case when some radiation were absorbed, no reaction would take place if the quantum yield of the specific reaction were nil. Thus, the incident radiation is not related to the reaction and therefore, in order to be able to estimate the quantum yield of the reaction, the absorbed radiation must be considered instead of the incident one.

Considering the Lambert–Beer's law, the *e*-base absorbance, a plane photo-reactor with a cylindrical lamp (Fig. 1) and a linear spherical emission model, Ibarz et al. (2014) and Garvín, Ibarz, and Ibarz (2015) obtained the following equations (each parameter is shown in Figs. 1-2 and/or defined below in the nomenclature section):

a.- The incident spectral radiant power reaching a specific point inside the solution:

$$P(x,y,z)=\sum_{\lambda}\int_{y_L=y_0}^{y_L=y_0+L}\frac{P_{emit,\lambda}/L}{4\pi D^2}\exp\left(-\mu_\lambda\frac{z}{\sin\beta}\right)dy_L \qquad (1)$$

b.- The incident spectral radiant power for a specific depth (z) of the reactor is obtained by integrating Eq. (1) for all the x and y values for the specific z value:

$$P(z)=\sum_{\lambda}\frac{P_{emit,\lambda}/L}{4\pi}\int_{x=0}^{x=A}\int_{y=0}^{y=B}\int_{y_L=y_0}^{y_L=y_0+L}\frac{e^{-\mu_\lambda\frac{z}{\sin\beta}}}{D^2}dy_L dy dx \qquad (2)$$

The values of $P(z)$ for $z = 0$ and $z = C$ are the incident radiation power on the surface ($P(0)$) and at the bottom of the reactor ($P(C)$), respectively.

c.- Spectral radiant power absorbed

c1.- In the case of diluted solutions, when the values of μ_λ are low ($\mu_\lambda = \varepsilon_\lambda \cdot C$), the spectral radiant power absorbed per volume unit can be calculated using the following simplified equation:

$$P_{abs}=\frac{1}{V}\sum_{\lambda}\int_{x=0}^{x=A}\int_{y=0}^{y=B}\int_{z=0}^{z=C}\int_{y_L=y_0}^{y_L=y_0+L}\frac{P_{emit,\lambda}/L}{4\pi D^2}\exp\left(-\mu_\lambda\frac{z}{\sin\beta}\right)\mu_\lambda\frac{dz}{\sin\beta}dy_L dx dy dz \qquad (3)$$

c2.- For any concentration, particularly for high concentration values, when the values of μ_λ are high, the spectral radiant power absorbed per volume unit has to be evaluated without any simplification. According to Garvín et al. (2015), in order to facilitate the solution, it is useful to divide the reactor into a number of layers n (Fig. 2):

$$P_{abs}=\frac{1}{V}\sum_{\lambda}\sum_{i(z)=1}^{i(z)=n}\int_{x=0}^{x=A}\int_{y=0}^{y=B}\int_{y_L=y_0}^{y_L=y_0+L}\frac{P_{emit,\lambda}/L}{4\pi D^2}dy_L\left[e^{-\mu_\lambda D_{i-1}}-e^{-\mu_\lambda(D-D_0)}\right]dx dy \qquad (4)$$

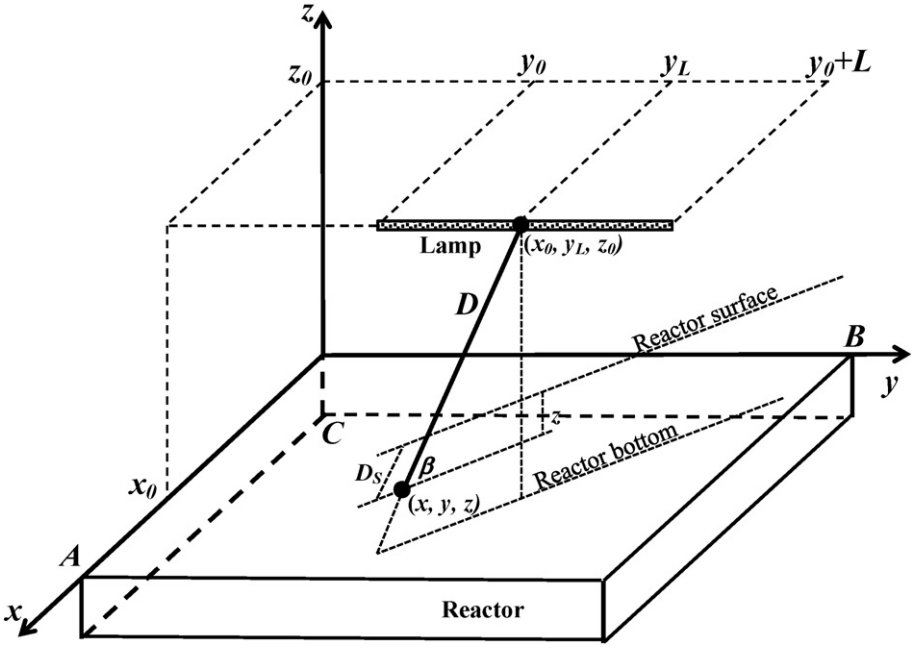

Fig. 1. Plane photoreactor scheme.