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Research on thiamethoxam detection and ultraviolet degradation modeling based on fluorescence analysis

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ABSTRACT

The detection and degradation of thiamethoxam by fluorescence spectrometry were researched in this paper. Firstly, the fluorescence spectrum of thiamethoxam was measured and analyzed by LS55 fluorescence spectrometer, and there was a distinct fluorescence peak at 345nm under the excitation of 200 nm. The concentration prediction model was established by using the least square fitting method. Secondly, the fluorescence spectrum of mixed solution between thiamethoxam and apple juice was studied, the prediction model function of thiamethoxam concentration in apple juice was also established, and the correlation coefficient was more than 0.99 which represented a linear relationship between thiamethoxam concentration and fluorescence intensity at 345nm. At last, the thiamethoxam degradation experiment was carried out based on ultraviolet. The degradation model function was established between the time of ultraviolet irradiation and the fluorescence intensity of the characteristic peak, and the degradation rate corresponding to different degradation time was calculated. The results showed that the degradation rate increased with the prolonging of ultraviolet irradiation time. The degradation rate was 35.57% after ultraviolet irradiation for 10 min and it can reach 97.39% after 32 min. The results have a reference value for the detection and degradation of thiamethoxam residues by fluorescence spectrometry.

1. Introduction

Thiamethoxam is a second generation of nicotinic insecticides with the characteristics of high efficiency, low toxicity and broad spectrum [1,2]. It is used for foliar spray and soil irrigation because of its gastric toxicity, contact toxicity and internal sucking activity for insect pests. Thiamethoxam has good effect on the prickly sucking pests and has become a common agent for the control of insects such as aphids and planthoppers, usually used in rice, corn, potatoes, vegetables, fruit trees, cotton, snake hemp and lawns and other crops [3–5].

The use of thiamethoxam in agricultural production will cause potential danger to consumers. The research methods of thiamethoxam pesticide residues have been reported in some literatures. For example, Liu Bin used high performance liquid chromatography (HPLC) to determine the degradation dynamics and final residues of thiamethoxam in spinach [6]. Sun Juan used capillary electrophoresis with electric injection mode to determine thiamethoxam residues in vegetables [7]. Liu Yin used high performance liquid chromatography-mass spectrometry (HPLC-MS) to detect the residues of thiamethoxam pesticide in radix paeoniae alba [8].

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In addition, the degradation technology of pesticide residues is an important means to reduce pesticide residues and reduce pesticide toxicity. At present, the degradation technology of pesticide residues mainly includes physical, chemical and biological methods. The commonly used physical methods are ultrasonic and ionizing irradiation [9,10]. Chemical methods include photochemical degradation, chemical oxidation, photocatalysis and so on [11,12]. Microbial degradation mainly uses bacteria, fungi and actinomycetes to degrade pesticide residues [13,14]. The principle of UV irradiation degradation of pesticides is consistent with the photochemical method. It can produce chemical effects through 253.7 nm ultraviolet light medium wave, make the main components of the pesticides broken, destroy the combination of organic carbon and other elements which constitute pesticide, and decompose the refractory organic matter into small molecular substance [15–17].

In this paper, the fluorescence spectra of thiamethoxam was firstly analyzed by fluorescence spectroscopy, and then, the concentration prediction of thiamethoxam residues in apple juice was modeled and analyzed, at last, degradation experiments of thiamethoxam pesticide residues were performed based on ultraviolet light. The degradation effect was characterized by the intensity change of the thiamethoxam characteristic peaks, and the relationship between the degradation time and the degradation rate was obtained. The research results have some reference value for developing thiamethoxam pesticide detection method, selection of degradation technology and characterization of degradation effect.

2. Experiments

2.1. Materials

Thiamethoxam pesticide made by Liaoning Lingyun pesticide chemical company, apple juice and purified water were selected as experiment materials.

2.2. Experimental apparatus

The LS55 fluorometer (Perkin Elmer, USA) was used to record the fluorescence spectrum of the sample. The instrument used a pulse xenon lamp and a 1 cm quartz cuvette. The instrument sampling interval was set to 0.5 nm, the slit width was 10 nm, and the scanning wavelength ranged from 200 to 600 nm. In addition, the experiment of thiamethoxam degradation was carried out using the experimental platform for ultraviolet degradation pesticides designed in reference [18]. The main part of the degradation platform was a closed system, which mainly included ultraviolet light source module, module bracket and sample pool. The power timing control switch was set outside the closed system to control the exposure time of ultraviolet light source.

2.3. Procedures

Firstly, a certain amount of thiamethoxam pesticide was obtained by using electronic balance, and it was configured into standard liquid of different concentrations. The thiamethoxam pesticide of various concentrations were put into the cuvette, and the corresponding fluorescence spectra of thiamethoxam can be obtained by LS55, where the horizontal coordinates indicated the wavelength and the ordinate indicated the fluorescence intensity.

Then, the apple juice with concentration of 100% was diluted 30 times, and 3 ml diluted apple juice was added to the cuvette to measure its fluorescence spectrum. Added 0.1 ml, 0.3 ml, 0.5 ml, 0.7 ml, 0.9 ml thiamethoxam solution of certain concentration to the cuvette with a dropper, and shook well to fully fuse the thiamethoxam solution and apple juice. The fluorescence spectra of these five different concentrations of mixed solution between thiamethoxam and apple juice were measured by LS55, and the concentration prediction model of thiamethoxam residual in apple juice was further analyzed.

At last, 3 ml thiamethoxam solution of certain concentration was taken into the sample pool of ultraviolet degradation device. The fluorescence spectrum of the thiamethoxam solution was measured by LS55 after ultraviolet degradation for different time and the degradation process was analyzed and modeled.

3. Results and analysis

3.1. The fluorescence spectrum of thiamethoxam

The fluorescence spectrum of the thiamethoxam solution of different concentration was measured by LS55, the excitation wavelength was set to 200 nm. The fluorescence spectrum results were shown in Fig. 1(a) and the spectral range was 200–600 nm, the horizontal coordinate represented the wavelength, and the ordinate indicated the fluorescence intensity.

In Fig.1(a), thiamethoxam solution was corresponding to six different concentrations from curve 1 to curve 6. It was found that there was a strong fluorescence peak at 345 nm, and the peak value decreased with the decrease of the thiamethoxam concentration, which reduced from the maximum 564.29 to 54.49. Therefore, 345 nm can be used as the characteristic peak of the fluorescence spectrum of thiamethoxam.

In order to analyze the relationship between thiamethoxam concentration and fluorescence intensity, the least square linear regression analysis was carried out between the concentrations of the thiamethoxam solutions and the fluorescence intensity of the characteristic peaks. The specific results were shown in Fig. 1(b). The results showed that the thiamethoxam concentration and fluorescence intensity of fluorescence spectra at 345 nm had a good linear relationship, and the correlation coefficient was 0.9935.