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Use of micellar liquid chromatography for rapid monitoring of fungicides post harvest applied to citrus wastewater

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ABSTRACT

A method based on micellar liquid chromatography has been developed to simultaneously monitor four pesticides largely post-harvest applied to citrus: thiabendazole, pyrimethanil, o-phenylphenol and imazalil. Water samples were filtered and directly injected without other treatment, thus avoiding extraction steps. The composition of the mobile phase was optimized using a chemometrical approach to achieve and excellent resolution to 0.07 mol/L SDS/5%, *V/V* 1-pentanol buffered at pH 3. Mobile phase run through a C18 column at 1 mL/min at room temperature. The detection was performing by UV–Visible absorbance using a wavelength program: 0–10 min, 305 nm (for thiabendazole); 10–12; 265 nm (for pyrimethanil) and 12–18, 220 nm (o-phenylphenol and imazalil). The developed method was validated following the guidelines of the US Environmental Protection Agency in terms of: quantitation range, (0.5–4 to 15 μg/mL), linearity ($r^2 > 0.9995$), sensitivity (LOD, 0.18–1.4 μg/mL), precision (<9.2%), trueness (93.9%–103.7%), and ruggedness (<9.9%). It was found that the fungicides remain up to eight days in surface water at outdoor conditions. The method was used to screen the presence of the analytes in several waste water samples, and was proved to be useful in routine analysis.

Introduction

The production of citrus and the related fruit processing industry have as strong importance in the Castellón area (Spain). In fact, the exportation of fruits has an important weight in its economy (Montoliu-Vidal, 2010). One of the problems of fruit trading is the spoilage of citrus during storage and transportation, caused by microorganism, fungi and insects. This reduces the economic yielding of the agricultural activity. To prevent this fruit decay, pesticides are post-harvest added to fruits (Burden and Wills, 1989). Thiabendazole (TBZ), pyrimethanyl (PYR), o-phenylphenol (OPP), and imazalil (IMZ) are pesticides widely post-harvest applied by citrus traders and fruit-processing industry to protect crops during storage and transportation, because of their broad spectrum and strong fungicide activity (US EPA 2015; Smilanick, 2011). TBZ and PYR are also pre-harvest used to protect the tree and citrus during growing against mold and fungi. They are applied to the soil or sprayed over crop fields (Smilanick, 2011; Picón-Zamora et al., 2000).

Because of their intensive use and persistence, pesticides represent an important source of contamination of environmental water, especially those near areas with strong fruit-related activity. These pesticides are highly toxic and potentially carcinogenic, and then represent a serious threat to the local flora and fauna (US EPA, 2015). The population is

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also exposed to these hazardous compounds by dermal contact, accidental ingestion, or inhalation of polluted water. Moreover, the main danger is the ingestion of animals of vegetables, which have been in contact with polluted water, due to because their high bioaccumulation in edible tissues of living organisms (Langenbach, 2013). For these reasons, the European Water Framework Directive recommends the implementation of actions to avoid these compounds arrive to underground and surface water (European Commission, 2008).

These pesticides are present in wastewater from agricultural field, drained by rain water (Langenbach, 2013), and in sewage water from fruit-processing plants. To avoid the pollution of environmental water by pesticides, sewerage and waste water are purified in wastewater treatment plants (WWTP) before discharging to the river streams. In order to evaluate the quality of waste and sewerage water, several local governments have implemented programs to periodically perform pesticide screening in water samples from their area. Moreover, the fruit processing industry has been requested to monitor these hazardous compounds in their own wastewater before throwing it, in order to reduce the environmental impact of their activity. The effectiveness of the WWTP treatment must also be evaluated by analyzing the influent and effluent flow (European Commission, 2008). Indeed, they must dispose of a reliable, easy-to-use and sensitive analytical method to simultaneously quantify thiabendazole, *o*-phenyl-phenol, pyrimethanyl and imazalil in water.

The preferred analytical methods to perform multiresidue pesticide analyses in wastewater are gas chromatography and liquid chromatography, coupled to mass spectrometry (Liang et al., 2014). However, this instrumentation is costly and requires expensive maintenance; thus, the analyses are sold at higher prices. In the current context of economic crisis, industries and government institutions are forced to reduce their budgets, and increasingly demand less expensive methods. Liquid chromatography can be coupled to affordable and reasonably selective detector, as UV–Visible, to detect TBZ (Cacho et al., 2009; Santaladchaiyakit and Srijaranai, 2012), PYR (Gao et al., 2012; Baggiani et al., 2007), OPP (Yu et al., 2001; Liu et al., 2014) and IMZ (Gao et al., 2012; Tian et al., 2012) in water and aqueous samples. However, the resolution of a pesticide mixture is normally performed using gradient-programmed mobile phases, complicating the screening of a large amount of samples (Cacho et al., 2009; Santaladchaiyakit and Srijaranai, 2012; Yu et al., 2001). Nevertheless, wastewater samples may contain sludge particles and oily compounds dispersed in water, which must be removed before analysis (Beltrán-Martinavarro et al., 2013). Thus, tedious and time-consuming clean-up steps must be introduced, as a liquid–liquid (Santaladchaiyakit and Srijaranai, 2012; Gao et al., 2012; Yu et al., 2001) or solid/liquid (Cacho et al., 2009; Baggiani et al., 2007; Liu et al., 2014; Tian et al., 2012) extraction. These steps require specific chemicals and materials, and increase the possibility of loss of analyte by low yielding or operator error.

Liquid chromatography using hybrid micellar mobile phases, containing sodium dodecyl sulfate (SDS) as surfactant and short-chain alcohol (to improve the elution power and the efficiency) as additive, is an interesting alternative to analyze contaminants in wastewater. The lipophylic environment inside the micelle allows the solubilization of hydrophobic compounds. Therefore, after a simple filtration, the water sample can be directly injected in the chromatographic system, thus expediting the experimental procedure (Romero-Cano et al., 2015). The retention mechanism is different from hydroorganic reverse phase-high performance liquid chromatography (RP-HPLC), because the monomer surfactant modifies the nature of the stationary phase, and the analyte also can interact with the core of the micelles. Hence, compounds with dissimilar hydrophobicity can be resolved in the same run under isocratic conditions. The behavior of the analytes in micellar liquid chromatography (MLC) is highly steady and reproducible. The retention parameters can be accurately predicted at different SDS/alcohol concentration by means of a statistical treatment from the results obtained by testing only few mobile phases. Moreover, SDS solutions are more stable, less toxic, non-flammable, biodegradable, and uses less amount of organic solvent (up to 12.5%, V/V), in comparison to hydroorganic mobile phases used in HPLC (Peris-Vicente et al., 2014). MLC has been already used to detect carbamate pesticides in water (Gil-Agustí et al., 2002; Capella-Peiró et al., 2004; Chin-Chen et al., 2012).

The aim of the work is to develop an analytical procedure based on micellar liquid chromatography for the screening of TBZ, PYR, OPP and IMZ in water. The method must be simple, rapid, inexpensive, reliable and environmental friendly. The sample preparation must be simplified to facilitate the study of a large amount of samples, in order to apply it to routine analysis. The analytical procedure would be in-house validated by the Validation and Peer Review of U.S. Environmental Protection Agency (EPA) Chemical Methods of Analysis guideline in terms of selectivity, quantitation range, linearity, sensitivity, precision, trueness and ruggedness (The FEM Method Validation Team, 2005). The analytical method would be applied to evaluate the stability of the fungicides in outdoor conditions, and to detect the concentration of pesticides in sewage and WWTP treated water streams.

1. Materials and methods

1.1. Reagents and solutions

The pesticides thiabendazole, pyrimethanil, *o*-phenyl-phenol and imazalil (purity >99.9%) were purchased from Dr. Ehrerstorfer (Augsburg, Germany). The characteristics are described in Table 1 (Agriculture and Environment Research Unit, 2014). SDS (purity >99%) was supplied by Merck (Germany). Methanol, 1-butanol and 1-pentanol (HPLC grade) were from Scharlab (Spain). Sodium dihydrogen phosphate monohydrate, hydrochloric acid, sodium hydroxide and 1-propanol were ordered from Panreac (Spain). Ultrapure water was in-situ generated using a Simplicity UV ultrapure water generator device (Millipore S.A.S., France). This ultrapure water was used to prepare all the aqueous solution throughout the whole work.

1.2. Solutions and mobile phase preparation

Stock solutions containing 100 μg/mL of each pesticide were prepared by weighting the appropriate amount of solid standard and solving in methanol, and stored at −4°C. Standard solutions were prepared by successive dilutions of