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Turning cork by-products into smart and green materials for solid-phase extraction - gas chromatography tandem mass spectrometry analysis of fungicides in water

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ABSTRACT

During stoppers production, large amounts of cork by-products (CBPs) are generated, being used as low-value material. This project aims to turn CBPs into smart, natural and sustainable materials (sorbent) for solid-phase extraction (SPE) of pesticides from water. The study describes the use of CBPs for the extraction of 17 fungicides (metalaxyl, cyprodinil, tolylfluanid, procymidone, folpet, fludioxonil, myclobutanil, kresoxim methyl, iprovalicarb, benalaxyl, trifloxystrobin, fenhexamid, tebuconazole, iprodione, pyraclostrobin, azoxystrobin and dimethomorph) followed by gas chromatography-tandem mass spectrometry (GC-MS/MS) analysis. The most critical parameters affecting SPE were optimized by experimental design methodology. Under the optimal conditions, the method was successfully validated in terms of linearity, repeatability, and intermediate precision. Fungicide recovery was assessed in different real water samples including river, fountain, rainwater and spring water at 3 concentration levels (0.1, 0.5 and 10 μg L^{-1}). Recoveries ranged between 70-118% with RSD values lower than 20%, and matrix effects were not observed. Finally, the method was applied to samples from irrigation, rain, and river water, all collected in vineyards areas, revealing the presence of 10 of the 17 fungicides, at concentration up to hundreds of μg L^{-1}. The use of CBPs seems to be a promising low-cost and ecofriendly alternative to be employed as sorbent in SPE techniques to extract fungicides from the aquatic environment.

1. Introduction

Due to the high concern about the crop production control, nowadays the use of pesticides is unavoidable to protect agricultural products. Among them, fungicides, that have been widely applied due to their advantages such as low-cost and long-time persistence, are indispensable for food security. However, the continuous application of these organic compounds induces their persistent entrance in different environment compartments, and residues can easily reach different aquatic ecosystems through the crop soils lixiviation, representing a risk for environmental and human health [1]. The presence of fungicide residues has been reported in a broad range of water matrices including river, lakes, groundwater and even drinking water at concentration up to hundreds of μg L^{-1} [1–3]. Although the European Commission controls the presence of pesticides (0.1 μg L^{-1} for individual pesticide and 0.5 μg L^{-1} for the sum of pesticides) in groundwater and water intended for human consumption [4,5], there is still no specific regulation for fungicides. Thus, the development of fast and reliable analytical methodologies to monitor the fungicide residues in the aquatic environment is necessary.

Solid-phase extraction (SPE) has been the most widely employed technique to extract fungicides from aqueous samples due to its extraction capacity, high enrichment factor, and simplicity in comparison with traditional liquid-liquid extraction (LLE) techniques [6,7]. Undoubtedly, the most critical element to obtain a

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