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Development of magnetic dispersive solid phase extraction using toner powder as an efficient and economic sorbent in combination with dispersive liquid–liquid microextraction for extraction of some widely used pesticides in fruit juices

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ABSTRACT

In this study, for the first time, a magnetic dispersive solid phase extraction method using an easy–accessible, cheap, and efficient magnetic sorbent (toner powder) combined with dispersive liquid–liquid microextraction has been developed for the extraction and preconcentration of some widely used pesticides (diazinon, ametryn, chlorpyrifos, penconazole, oxadiazon, diniconazole, and fenazaquin) from fruit juices prior to their determination by gas chromatography–flame ionization detection. In this method, the magnetic sorbent is mixed with an appropriate dispersive solvent (methanol–water, 80:20, *v/v*) and then injected into an aqueous sample containing the analytes. By this action the analytes are rapidly adsorbed on the sorbent by binding to its carbon. The sorbent particles are isolated from the aqueous solution in the presence of an external magnetic field. Then an appropriate organic solvent (acetone) is used to desorb the analytes from the sorbent. Finally, the obtained supernatant is mixed with an extraction solvent and injected into deionized water in order to achieve high enrichment factors and sensitivity. Several significant factors affecting the performance of the introduced method were investigated and optimized. Under the optimum experimental conditions, the extraction recoveries of the proposed method for the selected analytes ranged from 49–75%. The relative standard deviations were ≤7% for intra- (n = 6) and inter-day (n = 4) precisions at a concentration of 10 μg L^{-1} of each analyte. The limits of detection were in the range of 0.15–0.36 μg L^{-1}. Finally, the applicability of the proposed method was evaluated by analysis of the selected analytes in some fruit juices.

1. Introduction

Pesticides are chemical compounds that their consumption in agriculture is increased day by day in order to protect the agricultural products in counter to molds, fungi, insects, and any other agents that can affect crops quality and yield [1]. Although the use of pesticides has many merits, but overuse of them can constitute a great menace to the environment and human's health. Hence, it is indispensable to develop simple and sensitive analytical methods which are capable of detecting their trace residue concentrations in food and environmental samples. To date, the methods used for the analysis of pesticides are mostly based on the chromatographic techniques such as high–performance liquid chromatography [2,3] and gas chromatography (GC) [4,5]. In order to achieve the reliable results performing a sample preparation step before using the chromatographic techniques is essential. A perfect sample preparation method should be able to extract the analytes from sample matrix and transfer them into a suitable phase for injection into instrumental system [6]. Up to now, various sample preparation methods such as liquid–liquid extraction [7], solid phase extraction (SPE) [8], homogeneous liquid–liquid extraction [9], solid phase microextraction [10], single drop microextraction [11], dispersive liquid–liquid microextraction (DLLME) [12] and etc. have been used for isolation and preconcentration of pesticides from different matrices, and bioactive compounds [13] using also deep eutectic solvents and ionic liquids [14]. Among the above–mentioned methods, SPE is one of the mostly used for matrix simplification and enrichment because of its matured technology, facility of the operation, and the good adaptability towards the multiple sample matrices [15,16]. Nevertheless, SPE has also suffers some problems

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like obstruction of cartridges, and necessity of pretreatment of sorbents before extraction procedure [17–19]. In order to overcome these problems, several other methods based on the traditional SPE methodology, such as dispersive solid phase extraction (DSPE) [20,21] and magnetic dispersive solid phase extraction (MDSPE) [22,23] have been developed. In these cases, the sorbent is directly dispersed into the sample solution instead of its packing into a cartridge. Dispersing the sorbent into the sample solution can increase the contact interface between the sorbent and the analytes significantly, and it can improve the mass transfer of the analytes and extraction efficiency [24,25].

DSPE was introduced by Anastassiades et al. in 2003 [26]. In DSPE, an SPE sorbent is mixed with an appropriate organic solvent (disperser solvent) and dispersed into a sample solution containing the target analytes. After extraction, the sorbent containing the retained analytes is settled by centrifugation. Finally, the analytes are desorbed with an appropriate solvent. The sorbents such as primary secondary amine, C_{18} (octadecylsilane), and graphitized carbon black are mostly used in this method [27–29]. In spite of the simplicity and low cost of DSPE, this method needs centrifugation that is time–consuming and can increase the extraction time. MDSPE is a new version of DSPE in which a magnetic sorbent is used instead of the conventional non–magnetic sorbents. The main advantage of this sorbent is that, it can be collected and separated from the aqueous phase using an external magnetic field, which eliminates the centrifugation step and makes the sample pretreatment procedure more convenient, time–saving, and economic. In MDSPE, the type of magnetic sorbent plays a critical role for the effective extraction of the analytes. The commonly used materials for MDSPE include silica (Fe_3O_4@SiO_2) [30], surfactants [31], molecular imprinted polymers (Fe_3O_4@MIPs) [32], and carbon nanotubes (Fe_3O_4@CNTs) [33]. The main disadvantage of these magnetic sorbents is that, their synthesis and pretreatment processes are very time–consuming, tedious, and may involve toxic reagents. Therefore, searching a new magnetic sorbent that is simple, eco–friendly, cost effective, and has a high selectivity towards the selected analytes is highly desirable.

In this study, for the first time, a magnetic sorbent (toner powder) which is easy–accessible, and does not need any synthesis or pretreatment, was used as an efficient sorbent in the MDSPE combined with DLLME for the extraction and preconcentration of the trace concentrations of some pesticides from fruit juices prior to their determination by gas chromatography–flame ionization detection (GC–FID). MDSPE–DLLME does not only allow the analytes to be preconcentrated, but also the other compounds present in the sample matrix to be removed. However, MDSPE–DLLME is a bit more expensive and time–consuming than alone DLLME. In the first step of this method, small amount of the sorbent is mixed with the disperser and dispersed into the aqueous solution containing the analytes. Then, the sorbent is collected with the help of an external magnetic field. In the second step, for more enrichment of the analytes an appropriate organic solvent is used to elute the analytes from the sorbent for the following DLLME procedure. Simplicity in the operation, low cost, high enrichment factors (EFs), and rapidity due to use the sorbent which does not need any synthesis, pretreatment or conditioning step, are the main advantages of the proposed method.

2. Experimental

2.1. Chemicals and solutions

Seven pesticides used in this study including diazinon, oxadiazon, fenazaquin, chlorpyrifos, ametryn, penconazole, and diniconazole were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Acetone, acetonitrile (ACN), chloroform, *iso*–propanol, and methanol were obtained from Merck (Darmstadt, Germany). Sodium chloride, hydrochloric acid (37%), and sodium hydroxide were also supplied from Merck. 1,2–Dibromoethane (1,2–DBE), 1,1,1–trichloroethane (1,1,1–TCE), and 1,1,2–trichloroethane (1,1,2–TCE) were from Janssen (Beerse, Belgium). Two toner powder (HP 1010 universal, and Brother universal) produced by Beijing Jing Shu wei Ye Technology Company (Beijing, China) were purchased from local vendors (Tabriz, Iran). Also, another toner powder produced by Wuxi Jiateng Magnetic Powder Co. (Jiangsu, China) for Samsung ML1670 was purchased from local vendors. A cube (5 cm × 2 cm × 2 cm) NdFeB magnet was purchased from ENES Magnesy Pawel Zientek (Warszawa, Poland). Deionized water (Ghazi Company, Tabriz, Iran) was used in the preparation of aqueous solutions. A stock solution of the selected pesticides was prepared in methanol with a concentration of 1000 mg L^{-1} (each pesticide). Working standard solutions were prepared daily by diluting the stock solution with deionized water.

2.2. Samples

Packed fruit juice samples including sour cherry, grape, peach, mango, and orange juices (different brands) were purchased from local stores (Tabriz, Iran). All juices were centrifuged at 5000 rpm for 5 min before use. The obtained supernatants were diluted at a ratio of 1:2 with deionized water and then exposed to the proposed procedure.

2.3. Instrumentation

Analysis of the selected pesticides was carried out on a Shimadzu 2014 gas chromatograph (Kyoto, Japan) equipped with a split/splitless injector operated at 300 °C in splitless/split mode (sampling time, 1 min and split ratio of 1:10) and an FID. Helium (99.999%, Gulf Cryo, United Arab Emirates) was used as carrier gas at a linear velocity of 30 cm s^{-1} and make up gas at a constant flow rate of 30 mL min^{-1}. The analytes were separated on an SPB® –1 capillary column (100% dimethyl siloxane, 30 m × 0.25 mm i.d., and film thickness of 0.25 μm) (Supelco, Bellefonte, USA). The column oven temperature was initially held at 70 °C for 1 min, then programmed at a rate of 20 °C min^{-1} to 300 °C, and held for 5 min. The FID temperature was maintained at 300 °C. For FID, hydrogen gas was generated with a hydrogen generator (OPGU–1500S, Shimadzu, Japan) at a flow rate of 30 mL min^{-1}. The flow rate of air was 300 mL min^{-1}. Gas chromatography–mass spectrometry (GC–MS) analysis was performed by an Agilent 7890A–5975C gas chromatograph–mass spectrometer (Agilent Technologies, CA, USA) equipped with a split/splitless injector operated at 300 °C. The MS operational conditions were: electron impact ionization at 70 eV; ionization source temperature, 250 °C; transfer line temperature, 260 °C; mass range, *m/z* 55–400; acquisition rate, 20 Hz; and detector voltage, −1700 V. Library searching was performed using the commercial NIST library. The separation was performed on an HP–5 MS capillary column (60 m × 0.25 mm i.d., and film thickness of 0.25 μm). The carrier gas was helium at a flow rate of 1.0 mL min^{-1}. The column oven temperature programming was the same as used in the GC–FID analysis mentioned above. The pH measurements were performed with a Metrohm pH meter model 654 (Herisau, Switzerland) equipped with a glass electrode. The Hettich centrifuge, model D–7200 (Kirchlengern, Germany) was used for accelerating the phase separation. An ultrasonic water bath model LBS1–6 (59 KHz, 250V) from Falc (Treviglio, Italy) was used.