

Rapid and Selective Determination of Trace Benzimidazole Fungicides in Fruit Juices by Magnetic Solid-Phase Extraction Coupled with High-Performance Liquid Chromatography-Fluorescence Detection

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Abstract In this paper, a new method was established for the determination of benzimidazole fungicides in fruit juices by magnetic solid-phase extraction coupled with high-performance liquid chromatography-fluorescence detection. The extraction adsorbent was synthesized to form a core-shell $\text{Fe}_3\text{O}_4@\text{SiO}_2$ structure surface functionalized with benzenesulfonic acid. The negative charges of the benzenesulfonic acid groups can promote strong electrostatic interaction with positively charged analytes to exhibit efficient and selective extractive ability. After the extraction, the magnetic adsorbent can be rapidly isolated from the matrix by an external magnet. Main factors influencing the extraction efficiency including amount of adsorbent, solution pH, extraction time, and volume of desorption solution were studied and optimized. Under the optimal conditions, recoveries of the spiked samples ranged from 83 to 96 % with the relative standard deviations lower than 10 %. The limits of detection were 0.55 and 0.14 μgkg^{-1} for carbendazim and thiabendazole, respectively. The proposed method was successfully applied for selective and efficient determination of benzimidazole fungicides in various juice samples.

Keywords Magnetic microspheres · Benzenesulfonic acid · Magnetic solid-phase extraction · Benzimidazole fungicides · High-performance liquid chromatography

Introduction

Benzimidazole fungicides are systemic pesticides and widely used for the pre- or postharvest protection of a variety of crops, fruits, and vegetables. In particular, carbendazim (MBC) and thiabendazole (TBZ) are the most extensively applied compounds to prevent fruits diseases. Very often, in industrial practice, these are used in washing or spraying to prevent postharvest decay on cleaned fruit and minimize fungal spore contamination. Residues left after benzimidazole fungicide treatments may penetrate plant tissues and appear in pulp and juice of fruits and vegetables, although their concentrations are in general lower than those observed in the whole fruit. However, most benzimidazole fungicides create some risk to human health and also were very persistent in water, soil, crops, and food (Lazartigues et al. 2011). Therefore, determining benzimidazole fungicide residues in fruit juices has a particular importance. To guarantee consumer safety and regulate international trade, maximum residue limits (MRLs) for a large number of pesticide residues in food have been established by both the European Union (EU) and the Codex Alimentarius Commission (CAC) of the Food and Agriculture Organization of the United Nations (Commission Regulation (EC) No 396/2005; Commission Regulation (EU) No 559/2011; Codex Alimentarius, Pesticide Residues in Food and Feed).

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A variety of methods have been developed for the determination of MBC and TBZ in food and water, such as fluorescence spectroscopy (Garrido Frenich et al. 2003), micellar electrokinetic chromatography (Rodriguez et al. 2001), immunoassay (Blazkova et al. 2010), and high-performance liquid chromatography (HPLC) with ultraviolet detection, fluorescence detection (FLD), or mass spectrometric detection (Muccio et al. 1999; Halko et al. 2004; Dreassi et al. 2010). HPLC methods are among the most common choice (Malik et al. 2010). Due to the low concentrate of the target compounds and the complex nature of the matrices, the trace level detection and identification with prior efficient sample preparation are of key important aspects in the analytical method. For this purpose, different preconcentration methods have been applied for the extraction of benzimidazole fungicides, including liquid–liquid extraction (Dreassi et al. 2010), solid-phase extraction (SPE) (Tharsis et al. 1997), solid-phase microextraction (Lopez Monzon et al. 2007; Ji et al. 2009), matrix solid-phase dispersion (Radisic et al. 2009), hollow-fiber liquid-phase microextraction (Barahona et al. 2010), dispersive liquid–liquid microextraction (Wu et al. 2009), ionic liquid-dispersive liquid–liquid microextraction (Asensio-Ramos et al. 2011), supramolecular solvent-based microextraction (Moral et al. 2009a; Moral et al. 2009b), and microwave-assisted extraction (Coscolla et al. 2009). Some of these methods are tedious, multistep, or time-consuming procedures. Then, developing more simple, rapid, and efficient methods for sample preparation is of high interest and demand. In recent years, magnetic solid-phase extraction (MSPE) has attracted much attention in bioseparation and chemical analyses (Horak et al. 2007; Aguilar-Arteaga et al. 2010; Chen et al. 2011). It usually utilizes iron oxide materials as sorbents, which endow some unique properties such as excellent superparamagnetic properties, large surface areas, surface modifiability, and great biocompatibility. As for sample treatment procedures, the magnetic particles can be easily isolated from sample matrix with the aid of an external magnetic field without additional filtration or centrifugation procedures, which makes sample collection and separation easier and faster. Additionally, MSPE is suitable for direct analysis of samples containing particles or microorganisms, which widely exist in environmental or biological matrices and may arouse blockage and lead to extraction failure on conventional SPE cartridges (Ding et al. 2010). All of these merits mentioned above render MSPE a promising technique for sample preparation.

In order to improve the selectivity of the extraction system, magnetic particles are usually subjected to a surface functionalization with proper recognition molecules, such as octadecyl (Ding et al. 2010; Sha et al. 2008), phenyl (Ibarra et al. 2011; Bianchi et al. 2012), and polymers (Chen et al. 2009; Meng et al. 2011). In this study, a novel benzenesulfonic acid-functionalized magnetic microspheres were prepared by coating submicron-sized magnetite particle with

silica layer and subsequently modified with 2-(4-chlorosulfonylphenyl)-ethyltrichlorosilane. The synthesized magnetic microspheres were used as adsorbent for selective extraction of benzimidazole fungicides in fruit juice samples. Final analysis was carried out by high-performance liquid chromatography coupled with fluorescence detection (HPLC-FLD). Various parameters affecting the extraction efficiency were studied and optimized. The accuracy and applicability of the proposed method were also evaluated.

Materials and Methods

Material and Chemicals

Ferric chloride, ethylene glycol, sodium acetate (NaAc), polyethylene glycol, toluene, N, and *N*-Dimethylformamide (DMF) were analytical grade and purchased from Kernel Chemical Reagent Co. Ltd. (Tianjin, China). Tetraethyl orthosilicate (TEOS) and 2-(4-chlorosulfonylphenyl)-ethyltrichlorosilane (50 % in toluene) were used as received from Gelest, Inc. (USA). LC-grade acetonitrile and methanol were obtained from Dikma Technologies Inc. (Beijing, China). Ultrapure water was dispensed from a PURIST Plus Ultrapure water system of Replile (Shanghai, China). All HPLC solvents were filtered by a 0.45- μm filter before used.

Carbendazim (MBC, methyl benzimidazol-2-yl-carbamate) and thiabendazole (TBZ, 2-thiazol-4-yl-benzimidazole) standards of purity higher than 99 % were acquired from Dikma Technologies Inc. (Beijing, China). Individual stock solutions of the fungicides at a concentration of 100 $\mu\text{g mL}^{-1}$ were prepared in methanol and stored in amber bottles at 4 °C. A series of working solutions were prepared daily from the stock solutions by dilution with methanol.

Fruit Juice Samples

Commercially available grape juice used for optimization and validation of the analytical method was previously tested and proven to be free from the pesticides considered. Grape, peach, orange, and pear juices used for the real sample analysis were purchased in a local supermarket of Tianjin (China) and analyzed for benzimidazole fungicide residues. All juice samples were preserved at 4 °C.

Preparation of Benzenesulfonic Acid-Modified $\text{Fe}_3\text{O}_4@SiO_2$ Microspheres

Firstly, magnetic Fe_3O_4 microspheres were prepared by a solvothermal reduction method according to Deng et al. (2005). Briefly, 1.35 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 40 mL of ethylene glycol to form a clear solution, followed by the addition of 3.6 g of NaAc and 1.0 g of polyethylene

glycol. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave. The autoclave was heated and maintained at 200 °C for 8 h then cooled to room temperature. The black products were recovered by a magnet and washed four times with 20 mL of ethanol and 20 mL of ultrapure water, respectively, then dried under vacuum at 60 °C for 6 h.

Subsequently, the silica-coated magnetic microspheres were prepared via a sol–gel polymerization approach (He et al. 2005). Of magnetic Fe₃O₄ microspheres, 1.0 g was dispersed in 120 mL of ethanol and 30 mL of ultrapure water, followed by the addition of 3.0 mL of ammonia hydroxide solution (25–28 %, w/w) and 0.5 mL of TEOS. The reaction was allowed to proceed under mechanical stirring for 12 h. The harvested particles were collected by a magnet, washed three times with 20 mL of ethanol and 20 mL of ultrapure water, respectively, and dried under vacuum at 60 °C for 6 h.

Finally, 1.0 g of the obtained Fe₃O₄@SiO₂ microspheres was dispersed in 90 mL of DMF and 60 mL of toluene under sonication to produce a homogeneous suspension. And then, 10 mL of 2-(4-chlorosulfonylphenyl)-ethyltrichlorosilane (50 % in toluene) was added. The resulted mixture was sonicated for 5 min and stirred for 24 h. The products were washed three times sequentially with 20 mL of toluene, 20 mL of ethanol, and 60 mL of ultrapure water with the help of an external magnet and then dried at 80 °C under vacuum overnight.

Apparatus

HPLC analyses were performed with a Shimadzu HPLC-20A system (Shimadzu, Kyoto, Japan) equipped with a RF-20Ax fluorescence detector, a CTO-20AC column oven, a SIL-20AC autosampler, and two LC-20AT pumps. The chromatographic separation was performed on a reversed-phase Spursil C₁₈ column (250×4.6 mm I.D., 5.0 μm particles) obtained from Dikma Technologies Inc. (Beijing, China). The mobile phase consisted of phosphate buffer–acetonitrile (75:25, v/v), and the flow rate was 1.0 mLmin⁻¹. Phosphate buffer was prepared as 1.42 g of sodium dihydrogen phosphate and 1.4 g of disodium hydrogen phosphate in a 1 L of water, which adjusted pH to 4.0. The excitation/emission wavelengths of fluorescence measurements were set as follows: 0 min at 280/310 nm and 9 min at 300/350 nm.

The shape and particle size of the microspheres were studied using a transmission electron microscope (TEM, Tecnai G2F20, FEI, USA) equipped with energy-dispersive X-ray spectroscopy (EDS, EDAX, USA) operated at a 200-kV accelerated voltage. Magnetic properties of the particles were studied using a vibrating sample magnetometer integrated in a physical property measurement system equipment (PPMS-9, Quantum Design, USA).

Magnetic Solid-Phase Extraction Procedure

Initially, 100 mg of benzenesulfonic acid-modified magnetic microspheres was firstly activated with 10 mL of methanol and 10 mL of deionized water and then dispersed into 10.0 mL of fruit juice sample with pH value adjusted to 3.0 by formic acid. The mixture was vibrated for 3 min to form a homogeneous dispersion solution. After that, magnetic microspheres were isolated rapidly from the solution under an external magnetic field. And the supernatant was decanted, while the solid phase was washed with 2 mL of distilled water and 2 mL of methanol in sequence. Finally, the analytes were eluted with 3 mL of methanol–ammonia (95:5, v/v) solution. The eluate was evaporated to dryness with a stream of nitrogen at 40 °C, and the residue was redissolved with 1.0 mL of phosphate buffer–acetonitrile (75:25, v/v). Twenty microliters of this solution was injected into HPLC system for analysis.

Method Validation

Validation of the method was performed with the final optimized parameters. The calibration curves were fabricated by plotting peak areas versus corresponding concentration of the analytes in the range of 2.0–200 μgkg⁻¹ for MBC and 0.5–50 μgkg⁻¹ for TBZ. The limit of detection (LOD) of the method was calculated by the analysis of the fruit juice samples with low concentration at a signal-to-noise ratio (*S/N*) of 3. And the limit of quantification (LOQ) was calculated on the basis of *S/N*=10.

Four kinds of pesticide-free fruit juices samples spiked with the standard at three different concentration levels (low, medium, and high) were prepared and processed according to the magnetic solid-phase extraction procedure. Mean recoveries of each benzimidazole fungicides were then calculated based on HPLC measurements with three replicated measurements. Precision was calculated in terms of the relative standard deviation of the recoveries obtained at different spiking levels.

Results and Discussion

Characterization of Prepared Magnetic Adsorbent

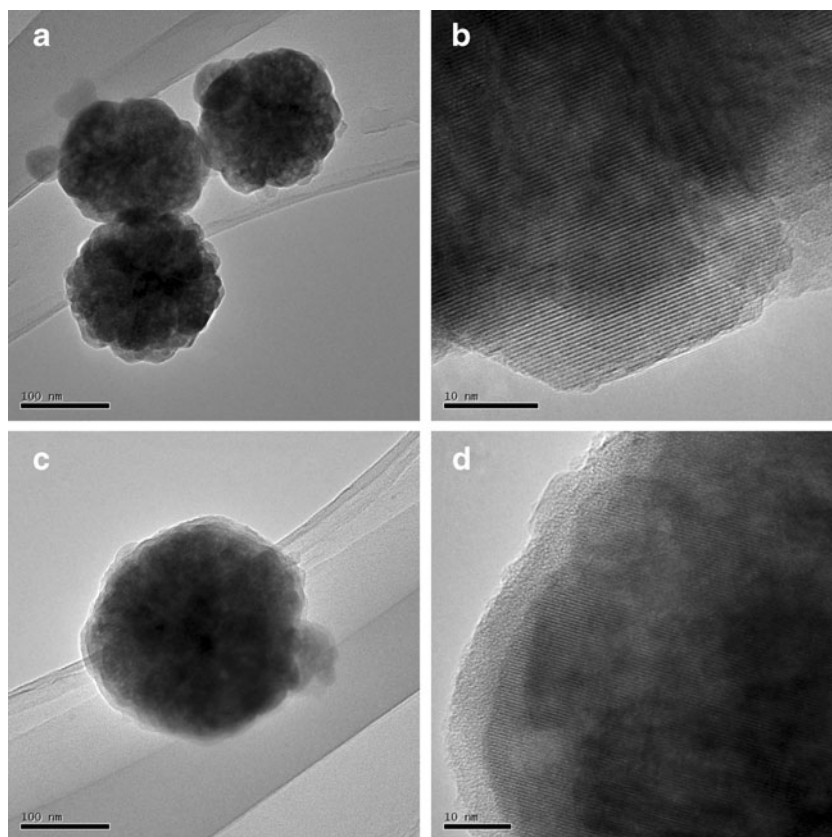
The magnetic microspheres prepared by the solvothermal reduction method are easily coated with amorphous silica by conventional sol–gel method. The silica shell could improve stability and antioxidative properties of magnetic particles and also protects them from leaching in an acidic environment (Sha et al. 2008). What is more, due to the existence of abundant silanol groups on the silica layer, silica-coated magnetic microspheres could be

easily activated to provide the surface with various tailorable functional groups. Subsequently, postsynthetic modification of the magnetic silica microspheres is contributed to control the surface properties. Benzenesulfonic acid groups can promote strong electrostatic interaction with cationic compounds including MBC and TBZ.

TEM image of the prepared magnetite microspheres is shown in Fig. 1. These magnetite microspheres were sphere like with an average diameter of approximately 180 nm. The silica shell thickness was estimated about 8 nm according to Fig. 1d. The silica shell thickness could vary with the different dosage of TEOS and reaction time. In addition, the content of sulfur element in functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres was 0.8 % determined by EDS analysis, which proved that benzenesulfonic acid was bonded to the surface of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres.

Both the magnetization curves of bare Fe_3O_4 microspheres and benzenesulfonic acid-modified $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres have little hysteresis, remanence, and coercivity, which indicates their typical superparamagnetic property. Although the deposition of silane layers leads to a decreased saturation magnetizations, the obtained benzenesulfonic acid-modified $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres have a high saturation magnetization of 47 emu g^{-1} . These imply that the particles could be easily dispersed in solution and rapidly separated from the matrix by using an external magnetic field.

Fig. 1 TEM images of (a, b) Fe_3O_4 microspheres and (c, d) benzenesulfonic acid-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres



Optimization of Extraction Conditions

In this study, to improve the extraction efficiency of the analytes, four important parameters including amount of adsorbent, solution pH, extraction time, and volume of desorption solution were optimized. Experiments were carried out with 10 mL grape fruit sample spiked with 5 ng mL^{-1} of MBC and 1 ng mL^{-1} of TBZ (pH was adjusted to 3.0 by formic acid), 100 mg of adsorbent, extraction time for 3 min, and $3 \times 1.0 \text{ mL}$ of methanol–ammonia (95:5, v/v) as desorption solvent. Parameters were kept constant except the tested one.

Effect of Amount of Adsorbent

To obtain satisfactory recovery of target compounds, different amounts of magnetic microspheres (25, 50, 75, 100, 150, and 200 mg) were investigated and the results are shown in Fig. 2a. The recovery increased as the amount of sorbent increased from 20 to 100 mg. When the amount of the magnet microspheres further increased over 100 mg, there was no distinct increase to extraction efficiency. Thus, 100 mg of adsorbent was selected as the optimal amount.

Effect of Solution pH

The pH of the sample solution would change the charge properties of the benzimidazole fungicides as well as the

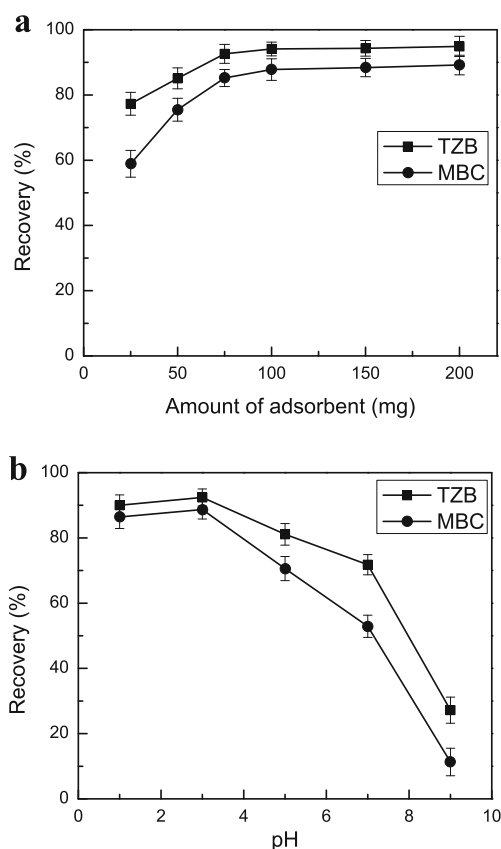


Fig. 2 Effect of **a** the amount of adsorbent and **b** solution pH on the recoveries of MBC and TBZ

functional groups on the adsorbent, thus influencing the interaction between the target analytes and the adsorbent. In this work, the effect of solution pH on the extraction of benzimidazole fungicides was investigated in the pH range of 1.0 to 9.0 (Fig. 2b). It is clear shown that the recoveries decreased rapidly with a pH greater than 3, which mainly attributed to the different ionization degrees related to their acidic dissociation constants (pK_a , 4.2 for MBC and 4.73 for TBZ). In the pH range investigated, the benzenesulfonic acid groups on the adsorbents were fully ionized and negatively charged, while the benzimidazole fungicides were only positively charged under lower pH conditions. Under pH higher than 7.0 conditions, the deprotonation of amino groups would decrease the electrostatic attraction between benzimidazole fungicides and the adsorbents, resulting in lowered recoveries. Therefore, pH 3 was selected as the optimal pH for subsequent experiments.

Effect of Extraction Time

Sufficient contact time is required for sorbent to achieve adsorption equilibrium. The effect of the extraction time was examined from 1 to 10 min. The results indicated that when the extraction time increased to 3 min, the recoveries of TBZ and MBC achieved maximum that were 93.6 and 88.3,

respectively. And the recoveries of TBZ and MBC slightly decreased to 92.0 and 86.9, respectively, when extraction time prolonged to 10 min. It may be interpreted as that the interaction between the analytes and benzenesulfonic acid-modified $Fe_3O_4@SiO_2$ microspheres was strong, and the distribution equilibrium was easy to be achieved in only 3 min, but the analytes could not be pulled down easily by the washing solvent with the further increase of time. Therefore, 3 min is considered to be the best extraction time in the following work. And the extraction procedure meets the requirement of rapid extraction. In addition, the time elapsed between extraction and elution of analytes had no obviously influence on recoveries.

Effect of Volume of Desorption Solution

The analytes are easily dissolved in organic solvent, and under alkaline condition, the electrostatic interaction between the analytes and the sorbent will be inhibited. Therefore, methanol–ammonia (95:5, v/v) was selected as desorption solution for its intersolubility with water. Different volumes of desorption solution (1.0 mL, 2×1.0 mL, 3×1.0 mL, 4×1.0 mL, and 5×1.0 mL) were investigated. The results have shown that 3.0 mL (1.0 mL each time and eluted three times) of methanol–ammonia (95:5, v/v) was enough for desorption of benzimidazole fungicides from the sorbent with reliable and reproducible analytical results. The recovery of analytes by desorption with 3 mL of methanol–ammonia (95:5, v/v) in a single step was also tested. The results have shown that the obtained recoveries were slightly lower than that desorption in three times, which may be contributed to the nonspecific physical adsorption. The results obtained were in agreement with those reported by other authors (Sha et al. 2008; Bianchi et al. 2012).

Regeneration of the Adsorbents

The benzenesulfonic acid-modified magnetic silica microspheres could be used as sorbent repeatedly after conveniently regenerated. To be specific, 1.0 g of used benzenesulfonic acid-modified magnetic silica microspheres was washed with 10 mL of methanol and 2 mL of sulfuric acid (2 mol L^{-1}), respectively, and then washed with a large volume of water until pH was neutral. In this study, it has been checked that the benzenesulfonic acid-modified magnetic silica microspheres could be reused at least five times.

Method Validation

Good linearity was observed in the range of 2.0–200 $\mu\text{g kg}^{-1}$ for MBC and 0.5–50 $\mu\text{g kg}^{-1}$ for TBZ. Meanwhile, the regression coefficients (R^2) were more than 0.999. LOD

and LOQ are considered as the analyte minimum concentrations that can be identified and quantified by the method. The LOD values for MBC and TBZ in the fruit juices were 0.55 and 0.14 μgkg^{-1} , respectively. And the LOQ values for MBC and TBZ were 1.8 and 0.5 μgkg^{-1} , respectively. To our knowledge, there were no regulations available for pesticide residues in fruit juices. MRLs of MBC and TBZ in food set by the CAC of the Food and Agriculture Organization of the United Nations range from 0.02 to 20 and 0.05 to 60 mgkg^{-1} , respectively (Codex Alimentarius, Pesticide Residues in Food and Feed). However, the calculated LODs and LOQs of this work were lower than the established MRLs for fruits. All the results indicated that the proposed method is suitable for quantification of MBC and TBZ in fruit juices.

The recovery studies were carried out by spiking pesticide-free fruit juice samples with MBC and TBZ standards at the levels of 2.5, 10, 50 μgkg^{-1} and 0.5, 2, 10 μgkg^{-1} , respectively. As seen from Table 1, the recoveries are satisfactory, ranging from 83 to 96 % with relative standard deviations less than 10 % according to the three-time determinations. Figure 3 shows representative chromatograms of extracts from real juice sample using the current MSPE method.

Comparison with Other Extraction Methods

Preliminary experiments were carried out in order to compare the results obtained from naked and benzenesulfonic acid-modified magnetic microspheres. The functionalization of the magnetic microspheres allowed to perform a suitable extraction of the investigated compounds. However, by

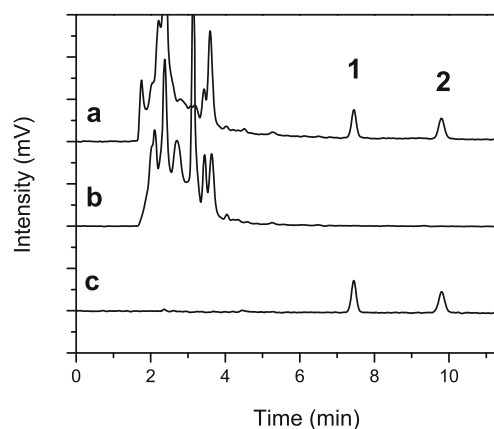


Fig. 3 Chromatograms of *a* juice sample spiked with 5 ngmL^{-1} of MBC and 1 ngmL^{-1} of TBZ, *b* blank juice sample, and *c* standard solution of MBC and TBZ. Peaks: 1, MBC; 2, TBZ

contrast, no obvious adsorption of benzimidazole fungicides was observed when the naked Fe_3O_4 beads were used. In comparison with other extraction techniques (Muccio et al. 1999; Moral et al. 2009a), the proposed MSPE method had used less amount of adsorbent to get high extraction ability and shortened extraction time to a great extent as well. The results revealed that the proposed method was an efficient approach for the analysis of benzimidazole fungicides in fruit juices.

Application of the Proposed Method to the Real Sample Analysis

To demonstrate the applicability of the proposed magnetic solid-phase extraction followed by HPLC-FLD determination

Table 1 Recovery studies of the developed method on fortified fruit juice samples with MBC and TBZ at three concentration levels ($n=3$)

Samples	Spiked (μgkg^{-1})		Detected ^a (μgkg^{-1})		Recovery \pm s ^b (%)	
	MBC	TBZ	MBC	TBZ	MBC	TBZ
Grape juice	0.00	0.00	ND	ND		
	2.5	0.5	2.15	0.45	86 \pm 7	90 \pm 5
	10	2	8.9	1.84	89 \pm 5	92 \pm 6
	50	10	44	9.4	88 \pm 2	94 \pm 2
Peach juice	0.00	0.00	ND	ND		
	2.5	0.5	2.08	0.43	83 \pm 9	86 \pm 8
	10	2	8.5	1.76	85 \pm 5	88 \pm 6
	50	10	43	9.0	86 \pm 3	90 \pm 4
Orange juice	0.00	0.00	ND	ND		
	2.5	0.5	2.18	0.45	87 \pm 7	90 \pm 6
	10	2	8.8	1.92	88 \pm 6	96 \pm 5
	50	10	45	9.5	90 \pm 4	95 \pm 2
Pear juice	0.00	0.00	ND	ND		
	2.5	0.5	2.1	0.45	84 \pm 7	90 \pm 4
	10	2	8.8	1.86	88 \pm 4	93 \pm 4
	50	10	43.5	9.1	87 \pm 5	91 \pm 3

ND not detected

^aMean of three determinations

^bStandard deviation for three determinations

method, a survey on MBC and TBZ in available fruit juices samples was performed. Twelve concentrated grape, peach, orange, and pear juice samples were taken from the local market and analyzed following the proposed method. The results showed that MBC was found in two orange juice samples, one peach sample, and one pear sample at the concentration of 7.9, 16.5, 5.3, and 3.3 μgkg^{-1} , respectively. And TBZ was found in one orange juice sample and one pear juice sample at the concentration of 1.5 and 4.7 μgkg^{-1} , respectively. Out of 12 analyzed fruit juice samples, 7 were found to be without detectable MBC and TBZ residues. It was previously reported that no benzimidazolic fungicides were detected in the non-fortified fruit and vegetable samples analyzed (Moral et al. 2009a). Other authors reported that postharvest fungicides MBC and TBZ were found in 80.0 and 63.4 % of 60 commercial citrus juices, respectively (Dreassi et al. 2010). Likewise, MBC and TBZ were found in almost 48 and 13 % of the 23 investigated juice samples, respectively (Gilbert-Lopez et al. 2007). However, detected pesticide residues were always below the MRLs in fruits set by the EU. The results show that pesticide concentration varies widely by site. The presence of pesticide residues may be associated with their use dosage in the sampling site and during the period of storage.

Conclusions

In this study, benzenesulfonic acid-modified magnetic silica microspheres were synthesized and used as adsorbent for the extraction of benzimidazole fungicides in fruit juices for the first time. Due to the strong ion exchange interaction between the functionalized magnetic silica microspheres and the benzimidazole fungicides, the adsorbent could selectively extract and enrich benzimidazole fungicides from fruit juices rapidly and efficiently. What is more, the high magnetic response property of the Fe_3O_4 core made the sorbent easy to collect under an external magnetic field without additional centrifugation or filtration. The proposed method was sensitive with LODs of 0.55 and 0.14 μgkg^{-1} for MBC and TBZ, respectively. The results show that the benzenesulfonic acid-modified magnetic silica microspheres can be used as a promising adsorbent for selective and effective extraction of trace cationic compounds such as MBC and TBZ in various solution samples.

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