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RESEARCH ARTICLE

Preparation of coal-derived magnetic carbon material for magnetic solid-phase extraction of fungicides from water samples

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ABSTRACT

A magnetic solid-phase extraction method has been developed for the extraction and analysis of some fungicides in environmental water samples. Azoxystrobin, chlorothalonil, cyprodinil and trifloxystrobin were the target fungicides selected. First, a carbon material was obtained from the raw coal sample collected from Zonguldak region by ash removal process and then a magnetic C/Fe_3O_4 composite was produced from the carbon material using a single-step thermal method. The magnetic C/Fe_3O_4 composite was characterized by N_2 adsorption-desorption, X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy. This composite was then used as an adsorbent for the magnetic solid-phase extraction of fungicides from water samples followed by high-performance liquid chromatographic analysis. Experimental parameters affecting the extraction efficiency such as adsorbent amount, type and volume of desorption solvent, adsorption and desorption time, ionic strength, and pH were optimized. Under the optimized conditions, the extraction efficiency for azoxystrobin, chlorothalonil, cyprodinil and trifloxystrobin was found to be 71%, 44%, 41% and 70%, respectively. The method detection limits for fungicides were found to be in the range of 0.4-1.1 µg L^{-1}. The relative standard deviations were found to be lower than 6.6% and 6.9% for intra-day and inter-day precisions, respectively. The extraction of related fungicides from water samples collected from Zonguldak region was carried out efficiently. The recoveries obtained from spiked water samples were in the range of 71–106%.

Keywords: Fungicides, liquid chromatography, magnetic solid-phase extraction, water samples

1. INTRODUCTION

Today, despite significant advances in instrument technology, a sample preparation step is still needed prior to instrumental analysis for target analytes particularly in environmental, food, and biological samples, which are described as complex matrices [1]. In this sense, the sample preparation is an important step for extracting and concentrating the analytes from various matrices as well as making the analytes more compatible for the instrumental system [2]. For years, the most commonly used sample preparation methods for aqueous samples have been liquid-liquid extraction (LLE) and solid-phase extraction (SPE). The disadvantages of the LLE method include excessive use of solvent, formation of emulsions during extraction, and most importantly, production of large quantities of environmental pollutants. The SPE method, on the other hand, spends a lower amount of solvents and gives higher extraction efficiency compared to LLE. However, traditional SPE is also time-consuming as it involves different steps such as column conditioning, sample loading, column washing and elution [3]. Over the past few years, several miniaturized and simplified versions of SPE have been developed in order to make SPE faster and more environmentally friendly.

Magnetic solid-phase extraction (MSPE) is a promising method based on the use of magnetic adsorbents for separation and enrichment of organic and inorganic analytes from large volumes of aqueous samples. In MSPE, the magnetic adsorbent is placed in a sample solution containing analytes. The target analytes are adsorbed on to the surface of the magnetic adsorbent with the aid of mechanical stirring or ultrasonication. The magnetic adsorbent containing the analytes is separated from the sample solution by an external

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magnetic field applied to the outside surface of the extraction vessel. Next, the analytes are eluted from the magnetic adsorbent with a suitable solvent and then analyzed [1]. The MSPE is a rapid and simple extraction method in which some steps needed in traditional SPE methods such as filling the adsorbent into a column, centrifugation or filtration are eliminated [4]. In MSPE, the separation of adsorbent from aqueous solution and also from desorption solvent is performed with a very practical approach. This process is easy and effortless thanks to a magnet held outside the extraction vessel. Although the mechanism of magnetic separation has been known for many years, the first analytical application was carried out by Šafaříková and Šafařík in 1999. In this study, some selected organic dyes were extracted from high volume samples (100-800 mL) using copper phthalocyanine modified silanized magnetite and magnetic charcoal as adsorbents, with an enrichment of up to 460-fold [5]. In the years following this study, a great deal of research has been carried out on the development of new magnetic adsorbents for the extraction/preconcentration of wide variety of analytes.

As a class of pesticides, fungicides are used to control mold and fungal diseases, especially for vegetables and fruits. Under good farming practices, fungicides need to be applied regularly to vegetables and fruits during the growing season, regardless of whether a fungal infection is present [6]. As a result, significant amounts of fungicides are used in places where vegetables and fruits are grown, resulting in fungicide contamination of nutrients, water, and environmental resources in the food chain. It is known that these chemicals can have significant negative effects on human health. In the European Union, the allowable amount of fungicides in drinking water is set to 0.1 μg L^{-1} for any single residue and 0.5 μg L^{-1} for total residues [7]. Therefore, determination of fungicide residues in environmental waters is of great importance for human health and environmental safety. In this sense, the development of reliable, precise and rapid analytical methods for the determination of fungicides at trace levels in environmental waters is a significant matter.

In this study, a MSPE method has been developed for the extraction and analysis of some fungicides in water samples. First, a carbon material was obtained from the raw coal sample collected from Zonguldak region by ash removal process and then a magnetic C/Fe_3O_4 composite was produced from the carbon material using a single-step thermal method. The feasibility of the C/Fe_3O_4 composite as a green and effective adsorbent in the MSPE of some selected fungicides was investigated.

2. MATERIALS AND METHODS

2.1. Chemicals and solutions

Standard fungicides (azoxystrobin, chlorothalonil, cyprodinil and trifloxystrobin) were obtained from Sigma-Aldrich. Acetonitrile (≥99.9%), acetone (≥99%) , methanol (≥99.7%) and NaCl were purchased from Sigma-Aldrich, whereas NaOH, HCl, HF, $NaH_2PO_4.2H_2O$, and $Fe(NO_3)_3.9H_2O$ were obtained from Merck. Water was used in experiments after purification with Zeener Power I Scholar-UV (18.2 MΩ) system.

Stock standard solutions were prepared with acetonitrile, containing fungicides at a concentration of 100 μg mL^{-1}. The working solutions at different concentrations were prepared by diluting stock solution with acetonitrile. These solutions were used in different stages of the experimental studies. All standard solutions were kept in the refrigerator at 4 °C. The tap water sample was taken from our laboratory and other water samples were collected from different streams located in Zonguldak city, Turkey. Water samples were placed in capped glass containers and stored in the refrigerator at 4 °C until processed. The raw coal sample used in the preparation of magnetic composite material was obtained from Kilimli district of Zonguldak province.

2.2. Instrumentation and chromatographic conditions

A Thermo Finnigan high-performance liquid chromatography with UV detector (HPLC-UV) was used in the chromatographic analysis of fungicides. The components of the HPLC-UV system were P1000 pump, UV1000 detector, S3000 automatic injection unit, SCM1000 degasser and SN4000 control system. ChromQuest 4.0 software was used to process the data. Chromatographic separation of fungicides was performed using C_{12} Max-RP (250×4.6 mm i.d., 4.0 μm) column. Acetonitrile and water were used as the mobile phase. The optimal separation for fungicides was obtained by isocratic elution. The mobile phase was prepared as a mixture containing 65% acetonitrile and 35% water and this solvent mixture was passed through the HPLC system for 30 min. The flow rate of the mobile phase was 1 mL min^{-1}, the UV wavelength was 250 nm, and the sample injection volume was 20 μL.

A Protech Lab KF-6 electric furnace was used for preparing magnetic composite material, a Kern ABJ 220-4m precision scale was used for weighing samples and chemicals, and a Protech ultrasonic bath was used for sample preparation. The N_2 adsorption-desorption measurement was carried out using a Quantachrome Autosorb 1C apparatus. A Fourier-transform infrared (FT-IR) spectrometer (Perkin Elmer), an X-ray diffraction (XRD) device (Pananalytical Empyrean), and a scanning electron microscope (SEM) (FEI Quanta 450 FEG) were used to characterize the magnetic composite material.

2.3. Preparation of magnetic composite material

After grinding the raw coal sample in the grinding machine, the grain size was kept at 100-300 μm using a sieve, and then the sample was dried in an oven at 110 °C for 24 h. The coal sample was treated for 4 h under a condenser at 70 °C with 20% (v/v) HCl to remove its inorganic content. After the acid treatment, the coal sample was washed with hot water to remove chloride ions. In order to minimize the ash content in the coal sample, the same treatment mentioned above was repeated with 20% HF (v/v). After washing with hot water again, the sample was dried for 24 h at 110

°C and taken to a desiccator [8]. The ash and volatile matter content of raw coal and ash-removed coal samples were determined in accordance with ASTM D 3174 and ASTM D 3175 standards. The fixed carbon percentage was calculated by subtracting the sum of volatile matter and ash percentages from 100. Fixed carbon, volatile matter, and ash percentages were 63.1%, 31.3%, and 5.6% in the raw coal sample, whereas in the ash-removed coal sample were 67.4%, 32.0%, and 0.6%, respectively.

The magnetic C/Fe_3O_4 composite was produced from the ash-removed coal sample using a single-step thermal method based on the procedures described in the literature [9, 10]. Firstly, 3 g of ash-removed coal sample, 6 g $Fe(NO_3)_3.9H_2O$, and 10 mL ethanol were stirred in a crucible at 45 °C with a magnetic stirrer for 2 h. Then the mixture was re-stirred at 60 ^oC for 1 h. After the stirring process, the ethanol in the mixture was removed in the oven. The crucible containing the mixture was closed with a lid and placed in the electric oven, and the temperature was raised to 800 ^oC using a ramp of 20 ^oC min^{-1}. After waiting 10 min at this temperature, the furnace was cooled to room temperature. The mixture was washed with hot water and then dried to obtain the C/Fe_3O_4 composite.

2.4. Magnetic solid-phase extraction procedure

For MSPE, 8 mL of the standard solution or water sample was transferred to 20 mL glass baker and 0.4 g NaCl was dissolved in the solution. Subsequently, 20 mg of C/Fe_3O_4 composite was added to the solution and the extraction was performed under sonication for 15 min. Next, an external magnet was placed to outside surface of the glass beaker to separate the composite material. After removing the aqueous solution, 200 µL of acetonitrile was used for desorption of analytes by sonication for 4 min. After separated with magnet, the desorption solution was transferred a vial for HPLC-UV analysis. Fig 1 shows a schematic of the C/Fe_3O_4-MSPE procedure.

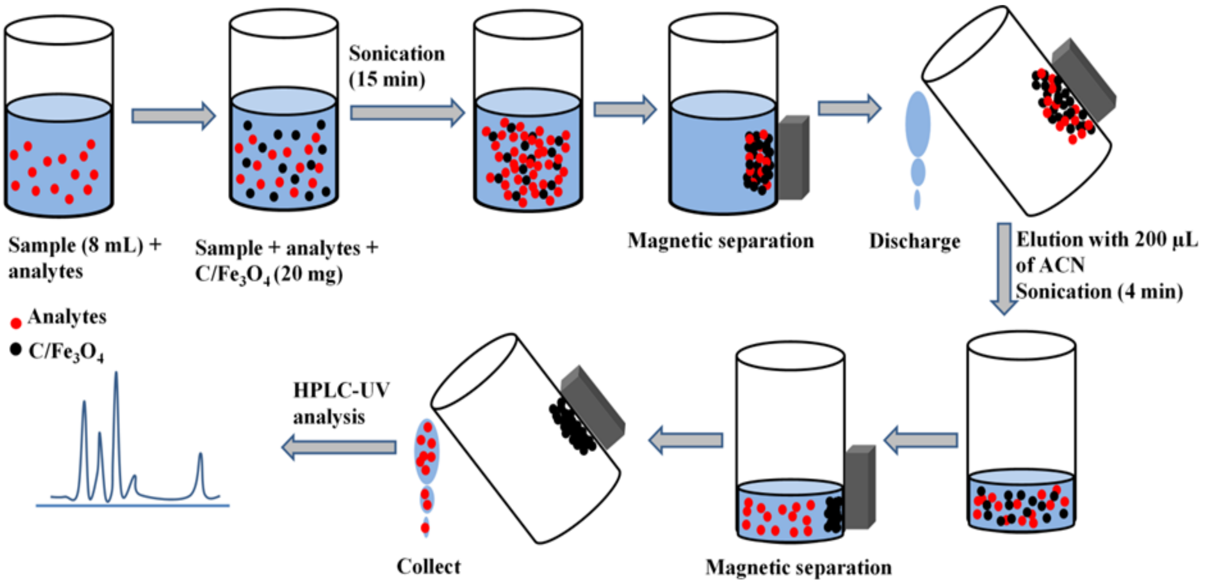

Fig 1. Schematic diagram of the C/Fe_3O_4-MSPE procedure.

3. RESULTS AND DISCUSSION

3.1. Characterization of the C/Fe_3O_4 composite

The surface properties of the C/Fe_3O_4 composite were investigated by adsorption-desorption experiments with N_2 gas at 77 K. The N_2 isotherm of the C/Fe_3O_4 composite fits the type I and II isotherms according to IUPAC classification (Figure 2a), which is usually associated with both microporous and mesoporous structures [11]. Additionally, the isotherm presents a type H4 hysteresis in the 0.99-0.4 relative pressure (P/P_0) range indicating narrow slit-like pores [12]. The BET (Brunauer-Emmett-Teller) surface area of the C/Fe_3O_4 composite was found to be 75.7 m^2 g^{-1}. The total pore volume and average pore width for C/Fe_3O_4 composite were 0.057 cm^3 g^{-1} and 1.475 nm, respectively.

Figure 2b shows the XRD spectrum of the C/Fe_3O_4 composite. The diffraction peaks of 2θ = 30.3^o, 35.5^o, 43^o, 53.5^o, 57^o, and 62^o correspond to the crystal planes of 220, 311, 400, 422, 511, and 440, respectively. These results indicate that the cubic Fe_3O_4 particles are present within the composite structure. Additionally, the dimensions of the Fe_3O_4 particles were determined using the Debye–Scherrer equation [13]. The average particle size calculated based on the diffraction peaks of 2θ = 30.3^o and 35.5^o was found to be approximately 42 nm.

The surface morphology and elemental composition of the C/Fe_3O_4 composite were determined by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX). The resulting SEM image and EDX spectrum for the C/Fe_3O_4 composite can be seen in Figure 2c. The SEM image shows that the outer surfaces of the C/Fe_3O_4 composite have irregularly dispersed slits and pores of different sizes. It also shows that Fe_3O_4 nanoparticles accumulate in the outer and inner surface pores of the composite. The EDX spectrum reveals that the C/Fe_3O_4 composite is composed of carbon, oxygen, and iron elements and that there are no additional impurities in the material.

Figure 2d shows the FT-IR spectrum of the C/Fe_3O_4 composite. The broad peak observed at 3448 cm^{-1} is due to O-H stretching vibrations, indicating the presence of hydroxyl groups on the surface. The peaks observed at 2923 and 2853 cm^{-1} are due to asymmetric and symmetric C-H stretching vibrations, respectively. The peak observed at 1635 cm^{-1} is due to aromatic C=C stretching vibrations and the peak observed at 1384 cm^{-1} is due to aliphatic C-H bending vibrations [14,15]. The peak observed at 560 cm^{-1} in the FT-IR spectrum is due to Fe-O-Fe stretching vibrations, proving that Fe_3O_4 nanoparticles are present in the composition of the material [16]. The results reveal that both hydrophilic (O-H) and hydrophobic groups (C=C) are present on the surface of C/Fe_3O_4 composite [17].

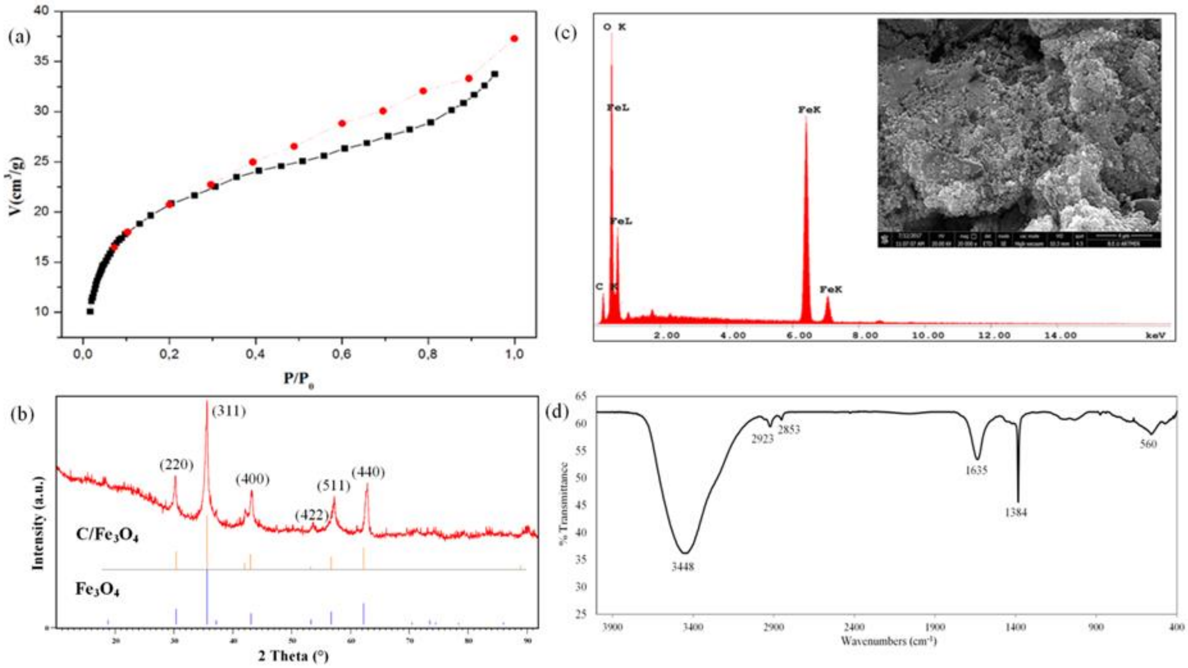

Fig 2. *a) N_2 adsorption-desorption isotherm, b) XRD spectrum, c) SEM image with EDX spectrum, and d) FTIR spectrum of C/Fe_3O_4 composite.*

3.2. Optimization of MSPE parameters

Some parameters such as the amount of adsorbent (C/Fe_3O_4), type and volume of desorption solvent, ionic strength, pH, adsorption and desorption time were optimized to determine the optimal MSPE conditions. Spiked water samples containing each fungicide at a fixed concentration of 12.5 µg L^{-1} were used in the optimization experiments. Enrichment factor (EF) and extraction recovery (ER) were calculated for each fungicide and ERs were considered in selecting the optimum conditions. Equation 1 and 2 were used to calculate EF and ER, respectively.

$$EF = \frac{C_a}{C_b} \tag{1}$$

$$ER = \frac{(C_a\, x\, V_a)}{(C_b\, x\, V_b)}\, x\, 100 = EF_x\, \frac{(V_a)}{(V_b)}\, x\, 100 \tag{2}$$

C_a and C_b are the concentration of analytes expressed in µg L^{-1} in the organic phase and in the sample solution, respectively. V_a and V_b are the volumes of the organic phase and sample solution, respectively.

The ideal amount of C/Fe_3O_4 was evaluated by increasing the dosage of C/Fe_3O_4 from 10 to 60 mg, while the other experimental parameters were kept constant. Acetonitrile was used as a desorption solvent with a fixed volume of 300 µL. The adsorption and desorption times were fixed at 5 and 2 min, respectively. Figure 3a shows the ERs obtained for fungicides by changing the amount of C/Fe_3O_4. The highest ERs for fungicides were achieved when 20 mg adsorbent was used, and a slight decrease in the extraction efficiency occurred over 20 mg. Therefore, 20 mg was selected as the optimal amount of C/Fe_3O_4 composite.

Acetonitrile, methanol, acetone and ethanol were tested to select the most appropriate desorption solvent. The other parameters including the amount of C/Fe_3O_4, the volume of desorption solvent, adsorption time and desorption time were fixed at 20 mg, 300 µL, 5 min and 2 min, respectively. Figure 3b shows the ERs obtained for the fungicides using different desorption solvents. The highest ERs were achieved when acetonitrile and acetone were used as desorption solvents. However, acetonitrile was chosen as desorption solvent since it was more compatible with the mobile phase used in the chromatographic analysis.

Selecting the optimal desorption solvent volume is an important step in MSPE methods. The use of high volumes of desorption solvent decreases the sensitivity of the method due to the dilution effect. As the volume of desorption solvent is reduced, the extraction efficiency for the analytes decreases due to the lower rate of solvent-adsorbent interaction. The effect of desorption solvent volume on the extraction efficiency was investigated in the range of 100-500 µL. Figure 3c shows the ERs obtained for fungicides with varying volumes of desorption solvent. By increasing desorption solvent volume from 100 µl to 200 µl, the extraction efficiency for some fungicides increased. No significant change occurred over 200 µl. For this reason, 200 µL was chosen as the most appropriate desorption solvent volume.

In order to investigate the effect of ionic strength on the extraction of fungicides, NaCl was added to the sample solution at various concentrations (0-8%, w/v) and the MSPE method was applied with keeping the other parameters constant. Figure 3d shows the ERs obtained for fungicides with varying salt concentrations. The ERs increased slightly with increasing salt concentration up to 5%, and remained nearly unchanged with further increase. Increased salt concentration decreases the solubility of analytes in aqueous solution, thus making it easier for the analytes to transfer from the sample solution to the adsorbent [18]. Therefore, the subsequent experiments were carried out in the presence of 5% NaCl.

Another important parameter affecting the extraction efficiency of analytes is the pH of the water samples. This is because the analytes are present in different forms under different pH conditions. Generally, pH value of the samples is kept lower than the p*K*a values of analytes in order to keep the analytes in their molecular state. In this way, the solubility of analytes in water decreases, while their interaction with the adsorbent surface increases [19]. The pH value of the aqueous solutions containing fungicides varied from 3 to 11 and the MSPE method was applied to these solutions. Figure 3e shows the ERs obtained for the fungicides at different pH values. The pH did not show any significant influence on the extraction efficiency of analytes in the range from 3 to 7, but when the pH value was above 7, there was a decrease in the ERs. The pH values of the water samples analyzed in this study were generally lower than 7. Hence, initial pH adjustment was not required.

To determine the optimal adsorption time, several experiments with varying sonication times from 3 to 30 min were carried out. According to the results (Figure 3f), the highest ERs were achieved with sonication for 15 min. Longer sonication periods did not produce a significant improvement in the extraction efficiency. Since the adsorption of fungicides reached equilibrium within 15 min, this time was selected as the most appropriate adsorption time. In addition, the optimal desorption time was also tested with varying sonication times in the range of 2–10 min. The best ERs for the fungicides were obtained under sonication for 4 min. The higher sonication times did not improve extraction efficiency. Thus, 4 min was selected as optimal desorption time.

Under the optimal MSPE conditions, the average extraction efficiencies (n=3) for azoxystrobin, chlorothalonil, cyprodinil and trifloxystrobin were found to be 71%, 44%, 41% and 70%, and the average enrichment factors (n=3) were 28, 18, 16, and 27, respectively.

3.3. Analytical performance

The analytical performance of the C/Fe_3O_4-MSPE method was assessed under optimized experimental conditions. The linearity, limit of detection (LOD), limit of quantification (LOQ), and intra-day and inter-day precisions of the method were assessed. Table 1 shows the analytical performance parameters of the C/Fe_3O_4-MSPE method for the determination of fungicides in water samples. Good linearity was obtained for all analytes in the concentration range of 1-50 µg L^{-1} with the coefficients of determination (r^2) higher than 0.9969. LODs and LOQs were calculated by considering the signal to noise ratio (S/N) as 3 and 10, respectively. LODs and LOQs were found to be in the range of 0.4–1.1 µg L^{-1} and 1.3–3.5 µg L^{-1}, respectively. The intra-day and inter-day precisions of the method were calculated as relative standard deviation (RSD), based on the repeated analysis of standard solutions (5 µg L^{-1}) in the same day (intra-day, n = 5) and in the consecutive days (inter-day, n = 5). The intra-day and inter-day precisions for the fungicides varied between 5.3-6.6% and 3.6-6.9%, respectively.

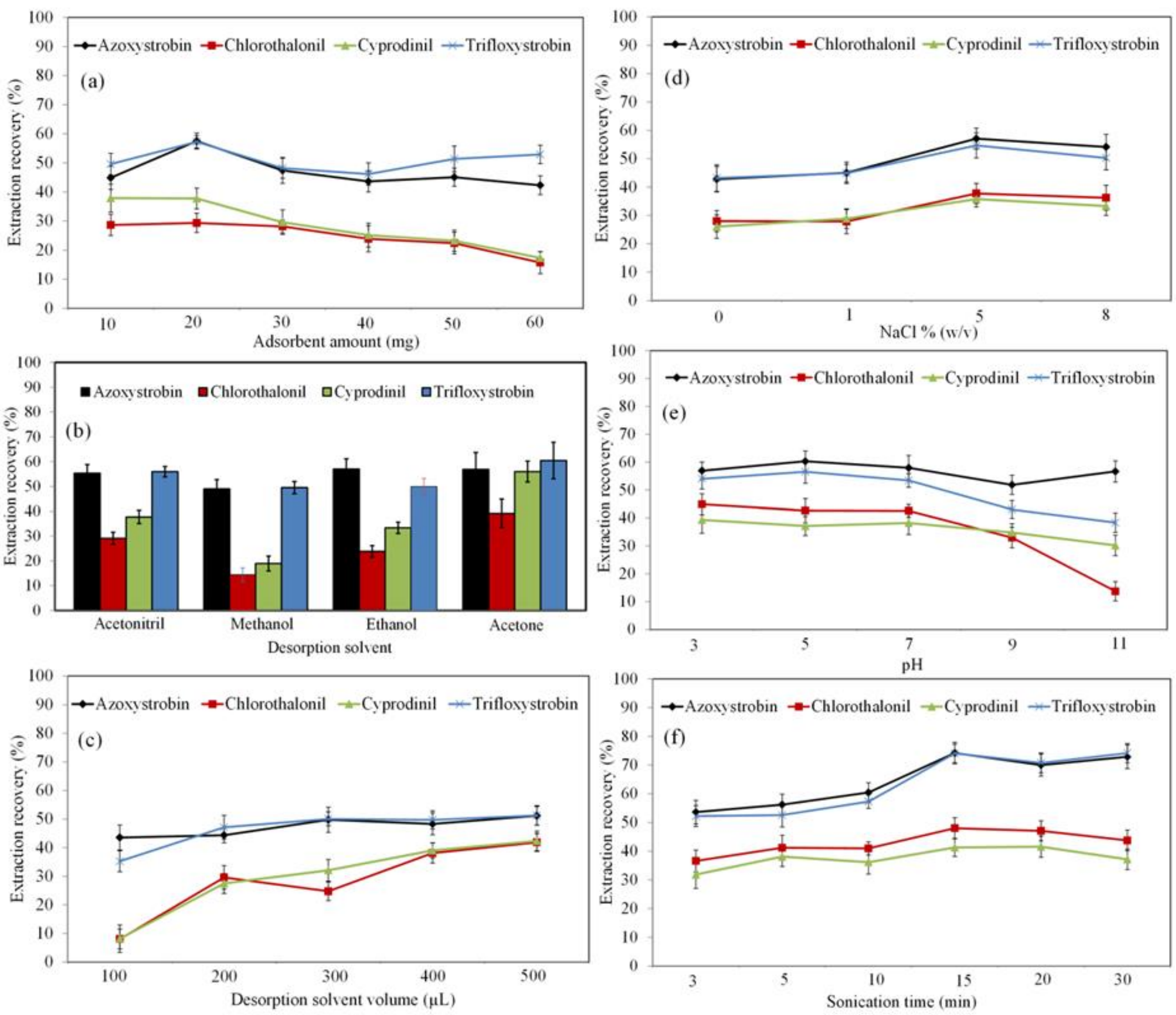

Fig 3. Effect of a) adsorbent amount, (b) desorption solvent type, c) desorption solvent volume, d) ionic strength e) pH, and f) adsorption time on the extraction of fungicides using C/Fe_3O_4-MSPE method.

Table 1. Analytical performance of the C/Fe_3O_4-MSPE method for the determination of fungicides in water samples.

Analytes	Linear range (μg L^{-1})	r^2	LOD (μg L^{-1})	LOQ (μg L^{-1})	RSD^a (%)	RSD^b (%)	EF^c	ER^d (%)
Azoxystrobin	1-50	0.9976	0.4	1.3	5.3	3.6	28	71
Chlorothalonil	1-50	0.9979	0.6	2.0	6.6	6.9	18	44
Cyprodinil	1-50	0.9987	1.1	3.5	6.3	6.8	16	41
Trifoxystrobin	1-50	0.9969	0.8	2.8	6.3	5.9	27	70

[a] Intra-day relative standard deviation (5 μg L^{-1}, n = 5)
[b] Inter-day relative standard deviation (5 μg L^{-1}, n = 5)
[c] Mean enrichment factor (12.5 μg L^{-1}, n = 3)
[d] Mean extraction recovery (12.5 μg L^{-1}, n = 3)

3.4. Real samples analysis

The applicability of the C/Fe_3O_4-MSPE method to different water samples was investigated. Tap water and stream water samples were analyzed both before and after spiking with standard fungicides at concentrations of 2.5 μg/L and 12.5 μg/L. No fungicides were detected in any of the non-spiked samples. The recovery values for fungicides were calculated using analysis results of the spiked samples, which was based on the ratio between the concentrations found after extraction and initially spiked. The recoveries were in the range of 71–106% with RSDs between 2.5 and 8.6%. Fig. 4 shows the HPLC chromatograms obtained from extraction and subsequent analysis of the stream water sample before and after spiking with standard fungicides.

The C/Fe_3O_4-MSPE method developed for the extraction of fungicides in water samples was compared with the sample preparation methods available in the literature. Sample volume, extraction solvent type and volume, extraction time, and some analytical performance parameters were selected for the comparison. Table 2 shows the comparison details between methods.

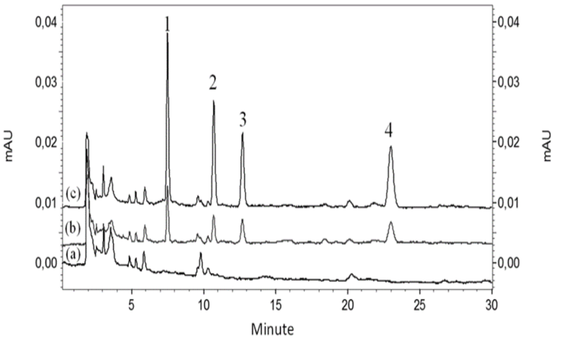

Fig 4. HPLC-UV chromatograms obtained after C/Fe$_3$O$_4$-MSPE of stream water sample (a) before and after spiking with fungicides at (b) 2.5 μg L^{-1} and (c) 12.5 μg L^{-1}. Peaks, 1:Azoxystrobin, 2:Chlorothalonil, 3:Cyprodinil, 4:Trifloxystrobi

The C/Fe$_3$O$_4$-MSPE method has advantages over existing methods in terms of the type and volume of the extraction solvent used. Some of the methods use expensive solvents such as 1-dodecanol [20], [C$_8$MIM][PF$_6$] [21] and [HMIM]NTf2 [22,23], whereas the C/Fe$_3$O$_4$-MSPE uses only little volume of acetonitrile, which has much lower cost. The solvent volume of 200 μL used in the C/Fe$_3$O$_4$-MSPE method is lower than the solvent volumes used in some other methods [22,24]. Additionally, the extraction time of the C/Fe$_3$O$_4$-MSPE method (15 min) is shorter than the extraction time of some existing methods [20,25]. Those mentioned above make the newly developed C/Fe$_3$O$_4$-MSPE method more economical and rapid. Moreover, the C/Fe$_3$O$_4$-MSPE method uses a practical process to separate the magnetic adsorbent from both aqueous solution and desorption solvent, and therefore, as in some existing methods, the adsorbent must be filled into a column [24] or an additional centrifugation step to separate the extraction solvent [21,23] is not needed. In terms of accuracy, precision and sensitivity, the C/Fe$_3$O$_4$-MSPE method gives similar recovery, RSD and LOD values with all other methods.

Table 2. Comparison of C/Fe$_3$O$_4$-MSPE with other methods for the determination of fungicides in aqueous samples

Method	Analytes	Sample Volume (mL)	Extraction solvent and its volume	Extraction time (min)	Recovery (%)	RSD (%)	LOD (μg L^{-1})	Ref.
DS-SFO - HPLC-DAD	Chlorothalonil Cyprodinil Trifoxystrobin	3	1-dodecanol (20 μL)	90	93-110	>7.0	0.2-1.1	[20]
IL-USAEME-HPLC-VWD	Azoxystrobin	5	[C$_8$MIM][PF$_6$] (40 μL)	15	106-115	>5.4	2.2	[21]
FPSE-HPLC-DAD	Azoxystrobin Chlorothalonil Cyprodinil Trifoxystrobin	8	[HIMIM]NTf2 Acetonitrile (500 μL)	2	78-101	>7.3	0.09-0.23	[22]
AALLME-HPLC-UV	Azoxystrobin Cyprodinil	5	[HMIM]NTf2 (45 μL)	~ 1	75-115	>6.2	0.4-1.8	[23]
SPE-HPLC-UV	Azoxystrobin Chlorothalonil	12.5	Acetonitrile (~1 mL)	-	75-95	>7.3	0.05	[24]
SPME-GC-MS/MS	Azoxystrobin Chlorothalonil Cyprodinil Trifoxystrobin	19	Thermal desorption	60	88-115	>20.7	2.3-72.3	[25]
C/Fe$_3$O$_4$-MSPE-HPLC-UV	Azoxystrobin Chlorothalonil Cyprodinil Trifoxystrobin	8	Acetonitrile (200 μL)	15	71-106	> 6.9	0.4-1.1	This method

DS-SFO: Directly suspended-solidified floating organic droplet microextraction, IL-USAEME: Ionic liquid-based ultrasound-assisted emulsification microextraction, FPSE: Fabric phase sorptive extraction, AALLME: Air-assisted liquid–liquid microextraction, SPE: Solid-phase extraction, SPME: Solid-phase microextraction, C/Fe$_3$O$_4$-MSPE: Magnetic solid-phase extraction with C/Fe$_3$O$_4$ composite, HPLC: High-performance liquid chromatography, DAD: Diode array detector, VWD: Variable wavelength detector, UV: Ultraviolet detector, GC: Gas chromatography, MS/MS: Tandem mass spectrometry, [C$_8$MIM][PF$_6$]: 1-octoyl-3-methylimidazolium hexafluorophosphate, [HMIM]NTf2: 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonimide).

4. CONCLUSIONS

A coal-derived magnetic C/Fe$_3$O$_4$ composite was successfully prepared and used as a MSPE adsorbent for the extraction of fungicides from water samples prior to HPLC-UV analysis. The C/Fe$_3$O$_4$-MSPE method was rapid, and the adsorbent was practically separated from the water samples. The method displayed low detection limits, good precisions and satisfied spiked recoveries for trace fungicides in water samples. In conclusion, this technique expands the application of liquid-liquid microextraction techniques and is expected to be extended to other analytes as well as other types of samples.

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REFERENCES

[1] M. Wierucka and M. Biziuk, “Application of magnetic nanoparticles for magnetic solid-phase extraction in preparing biological, environmental and food samples,” *TrAC Trends in Analytical Chemistry*, Vol. 59, pp. 59, 50–58, 2014.

[2] Y. Chen, Z. Guo, X. Wang and C. Qiu, “Sample preparation,” *Journal of Chromatography* A, Vol. 1184, pp. 191–219, 2008.

[3] S.M. Wille and W.E. Lambert, “Recent developments in extraction procedures relevant to analytical toxicology,” *Analytical and Bioanalytical Chemistry*, Vol. 388, pp. 1381–1391, 2007.

[4] J. Płotka-Wasylka, N. Szczepańska, M. de La Guardia and J. Namieśnik, “Miniaturized solid-phase extraction techniques,” *TrAC Trends in Analytical Chemistry,* Vol. 73, pp. 19–38, 2015.

[5] M. Šafaříková and I. Šafařík, “Magnetic solid-phase extraction,” *Journal of Magnetism and Magnetic Material*, Vol. 194, pp. 108–112, 1999.

[6] A.M. Wightwick, A.D. Bui, P. Zhang, G. Rose, M. Allinson, J.H. Myers, S.M. Reichman, N.W. Menzies, V. Pettigrove and G. Allinson, “Environmental fate of fungicides in surface waters of a horticultural-production catchment in southeastern Australia,” *Archives of Environmental Contamination and Toxicology*, Vol. 62, pp. 380–390, 2012.

[7] M. Yang, X. Xi, X. Wu, R. Lu, W. Zhou, S. Zhang and H. Gao, “Vortex-assisted magnetic β-cyclodextrin/attapulgite-linked ionic liquid dispersive liquid–liquid microextraction coupled with high-performance liquid chromatography for the fast determination of four fungicides in water samples,” *Journal of Chromatography A*, Vol. 1381, pp. 37–47, 2015.

[8] P. Davini, “SO2 adsorption by activated carbons with various burnoffs obtained from a bituminous coal,” *Carbon*, Vol. 39, pp. 1387–1393, 2001.

[9] N. Yang, S. Zhu, D. Zhang and S. Xu, “Synthesis and properties of magnetic Fe3O4-activated carbon nanocomposite particles for dye removal,” *Materials Letters*, Vol. 62, pp. 645–647, 2008.

[10] B. Qiu, H. Gu, X. Yan, J. Guo, Y. Wang, D. Sun, Q. Wang, M. Khan, X. Zhang and B.L. Weeks, “Cellulose derived magnetic mesoporous carbon nanocomposites with enhanced hexavalent chromium removal,” *Journal of Materials Chemistry A*, Vol. 2, pp. 17454–17462, 2014.

[11] K.Y. Foo and B.H. Hameed, “Microwave assisted preparation of activated carbon from pomelo skin for the removal of anionic and cationic dyes,” *Chemical Engineering Journal*, Vol. 173, pp. 385–390, 2011.

[12] J. Serafin, U. Narkiewicz, A.W. Morawski, R.J. Wróbel and B. Michalkiewicz, “Highly microporous activated carbons from biomass for CO2 capture and effective micropores at different conditions,” *Journal of CO2 Utilization*, Vol. 18, pp. 73–79, 2017.

[13] A.A. Asgharinezhad, S. Karami, H. Ebrahimzadeh, N. Shekari and N. Jalilian, “Polypyrrole/magnetic nanoparticles composite as an efficient sorbent for dispersive micro-solid-phase extraction of antidepressant drugs from biological fluids,” *International Journal of Pharmaceutics*, Vol. 494, pp. 102–112, 2015.

[14] J. Zhang, Z. Zhong, D. Shen, J. Zhao, H. Zhang, M. Yang and W. Li, “Preparation of bamboo-based activated carbon and its application in direct carbon fuel cells,” *Energy and Fuels*, Vol. 25, pp. 2187–2193, 2011.

[15] Y.-J. Zhang, Z.-J. Xing, Z.-K. Duan, M. Li and Y. Wang, “Effects of steam activation on the pore structure and surface chemistry of activated carbon derived from bamboo waste,” *Applied Surface Science*, Vol. 315, pp. 279–286, 2014.

[16] X. Yu, Y. Sun, C.-Z. Jiang, Y. Gao, Y.-P. Wang, H.-Q. Zhang and D.-Q. Song, “Magnetic solid-phase extraction and ultrafast liquid chromatographic detection of Sudan dyes in red wines, juices, and mature vinegars,” *Journal of Separation Science*, Vol. 35, pp. 3403–3411, 2012.

[17] L. Bai, B. Mei, Q.-Z. Guo, Z.-G. Shi and Y.-Q. Feng, “Magnetic solid-phase extraction of hydrophobic analytes in environmental samples by a surface hydrophilic carbon-ferromagnetic nanocomposite,” *Journal of Chromatography A*, Vol. 1217, pp. 7331–7336, 2010.

[18] S. Zhang, Z. Jiao and W. Yao, “A simple solvothermal process for fabrication of a metal-organic framework with an iron oxide enclosure for the determination of organophosphorus pesticides in biological samples,” *Journal of Chromatography A*, Vol. 1371, pp. 74–81, 2014.

[19] Q. Zhou, M. Lei, Y. Wu, X. Zhou, H. Wang, Y. Sun, X. Sheng and Y. Tong, “Magnetic solid phase extraction of bisphenol A, phenol and hydroquinone from water samples by magnetic and thermo dual-responsive core-shell nanomaterial,” *Chemosphere*, Vol. 238, pp. 124621, 2020.

[20] S. Li, X. Yang, L. Hu, X. Cui, S. Zhang, R. Lu, W. Zhou and H. Gao, “Directly suspended-solidified floating organic droplets for the determination of fungicides in water and honey samples,” *Analytical Methods*, Vol. 6, pp. 7510–7517, 2014.

[21] P. Liang, F. Wang and Q. Wan, “Ionic liquid-based ultrasound-assisted emulsification microextraction coupled with high performance liquid chromatography for the determination of four fungicides in environmental water samples,” *Talanta*, Vol. 105, pp. 57–62, 2013.

[22] M. Yang, Y. Gu, X. Wu, X. Xi, X. Yang, W. Zhou, H. Zeng, S. Zhang, R. Lu and H. Gao, “Rapid analysis of fungicides in tea infusions using ionic liquid immobilized fabric phase sorptive extraction with the assistance of surfactant fungicides analysis using IL-FPSE assisted with surfactant,” *Food Chemistry*, Vol. 239, pp. 797–805, 2018.

[23] X. You, X. Chen, F. Liu, F. Hou and Y. Li, “Ionic liquid-based air-assisted liquid–liquid microextraction followed by high performance liquid chromatography for the determination of

five fungicides in juice samples," *Food Chemistry*, Vol. 239, pp. 354–359, 2018.

[24] M. Catalá-Icardo, C. Gómez-Benito, E.F. Simó-Alfonso and J.M. Herrero-Martínez, "Determination of azoxystrobin and chlorothalonil using a methacrylate-based polymer modified with gold nanoparticles as solid-phase extraction sorbent," *Analytical and Bioanalytical Chemistry*, Vol. 409, pp. 243–250, 2017.

[25] J. Martins, C. Esteves, T. Simões, M. Correia and C. Delerue-Matos, "Determination of 24 pesticide residues in fortified wines by solid-phase microextraction and gas chromatography–tandem mass spectrometry," *Journal of Agricultural and Food Chemistry*, Vol. 59, pp. 6847–6855, 2011.