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Magnetic solid-phase extraction based on $CoFe_2O_4$ magnetic nanoparticles for the determination of diazinon and fenitrothion in aqueous samples

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Extract target analytes can be isolated from the sample solution due to the magnetic nature. The effects of the experimental conditions on the extraction process were optimized. The limits of detection (LOD) with the selected pesticides varied from 0.5 to 0.9 μg/l. The calibration curves were linear over three orders of magnitude with R2 ≥0.99. The relative standard deviations of the analysis were 2.89 3.5%, and the relative recoveries from the aqueous samples were 87.5-91.3%.

Keywords: MSPE, organophosphorus pesticides, $CoFe_2O_4$ nanoparticles

INTRODUCTION

At present, organophosphorus compounds are one of the most generally used pesticides in agriculture. These pesticides act as cholinesterase inhibitors in insects and mammals, and bring about a non-reversible phosphorylation of esterases in the organisms' central nervous system [1,2].

The use of pesticides provides benefits for increasing agricultural production, but by accumulation through the food web they can become a risk or threat to both humans and animals. Because of their highly continuing properties and potential threat to human health, OC Ps have been interdicted to be produced and used inmost developed countries [3].

For the past three decades, pesticides have been the insecticides most commonly used by both professional pest supervise bodies and homeowners [4]. Nevertheless, the decision of the US Environmental Protection Agency (EPA) to phase out certain uses of the organophosphorus insecticides because of their potentially toxic effects to humans has led to their gradual substitutionby pyrethroid insecticides. Solid-phase extraction (SPE) is one of the most commonly used sample pretreatment techniques. To date, many new adsorbents, such as nanomaterials, ion imprinted materials, mesoporous materials, carbon nanotubes, and magnetic nanoparticles have been used in SPE and SPME [5-8]. Among these adsorbents, magnetic nanoparticles consisting of an iron oxide have attracted attention in the past few decades because of their unique physical and chemical properties. The purpose of this work was to assess the potential of Magnetic nanoparticles ($CoFe_2O_4$ nanoparticles) as sorbent material for extraction of trace diazinon and fenitrothion from environmental samples. Affecting factors the extraction efficiency of target analytes were investigated and optimized.

EXPERIMENTAL

Chemicals and materials

All of the reagents used were of analytical grade and all solutions were prepared in deionized water. Fenitrothion and diazinon were purchased from Riedel-de Haen (Seelze, Germany).The chemical structure and physical properties of diazinon and fenitrothion are shown in Fig. 1. HPLC-grade acetonitrile, ferric chloride ($FeCl_3.\cdot 6H_2O$), ferrous chloride ($FeCl_2\cdot 4H_2O$), and cobalt chloride hexahydrate ($CoCl_2,\cdot 6H_2O$), sodium hydroxide, methanol, acetone, ethanol, hydrochloric acidand NaCl were all purchased from Merck (Darmstadt, Germany).

Apparatus

The chromatographic analysis were performed using an Auto System XL GC (Perkin–Elmer, Norwalk, CT) equipped with an flame ionization detector and fitted with a DB-5 (5% biphenyl + 95% poly dimethylsiloxane) fused-silica capillary column (30m×0.25mm i.d. and 0.25μm film thickness) was applied for separation of the analytes.

Injector and detector temperature: 270◦C and 310◦C, respectively.

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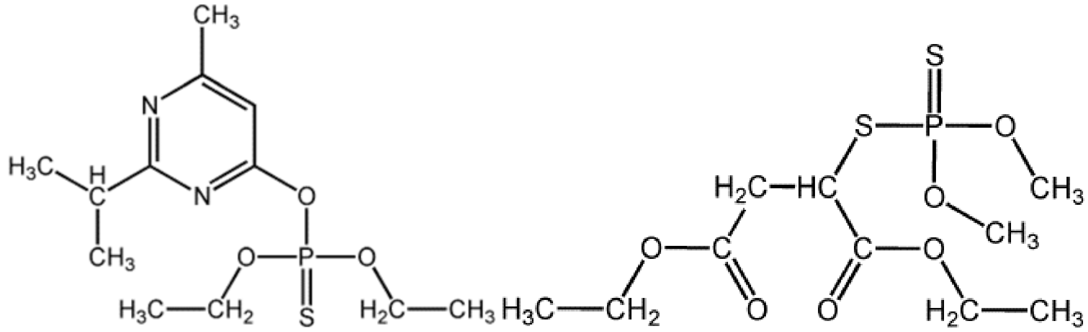

(a) (b)

Fig. 1. Chemical structure of (a) Diazinon (b) Fenitrothion.

The GC-ECD conditions were: oven temperature program: from 130 ◦C (1 min) to 210 ◦C at 10 ◦Cmin^{-1} (2 min), then to 290 ◦C at 15◦Cmin^{-1} (2 min). Helium (UP grade) was used as carrier gas at a flow rate of 1.5 mLmin^{-1}. Stirring of the solutions was carried out by a Heidolph MR3001 magnetic stirrer (Schwabach, Germany) and a 8mm×1.5mm magnetic stirring bar. The FT-IR instrument used for recording the infrared spectrum was Buck Scientific M-500 Fast-Scan IR Spectrometer (East Norwalk, CT 06855, USA). The microstructure of samples was investigated by scanning electron microscopy (SEM) (LEO, Model 1450VP, Germany). A Metrohm 780 pH-meter (Herisau,Switzerland) equipped with a combined glass electrode was used to determine pH values during the experiment.

Preparation $CoFe_2O_4$

$CoFe_2O_4$ nanoparticles were synthesized by co-precipitation method. Briefly, 27 g $FeCl_3 \cdot 6H_2O$ and 12 g $CoCl_2$, $6H_2O$ were dissolved in 100 mL distilled water with the aid of mechanical stirrer. 40 mL of 8 mol.L^{-1} NaOH solution was quickly dropped into the mixture under vigorous stirring at 85 °C. After the reaction, the black precipitation was obtained. Coating was carried out by adding aqueous solution
of 9 g sodium oleate in 30 mL water and stirring for 2 h. The suspensionwas slowly acidified with 1.5 M HCl until the pH = 5, and an oily black precipitate seem. The oily black precipitate was soluble in chloroform. In order to remove the larger particle, 30 mL of acetone was added to the chloroform, and the solution became cloudy. Laying for 90 min, the larger particle sedimentated to the bottom and the solution became transparent again. The clear solution was removed to another beaker and 250 mL of acetone was added to precipitate most of the particle, only the smaller particle existed still in the solution. The precipitate was dried in air and could be soluble in chloroform.

Analytical procedures

Thirty five miligrams of nanoparticles were firstly activated with methanol and distilled water, then dispersed into 700 µl of blank urine spiked with the proper amounts of target analytes. The mixture was then sonicated for 2 min: after 5 min of adsorption the nanoparticles were isolated by applying an external magnetic field and washed two times with 150 µl of methanol. One µl of this solution was then injected into the GC–FID system for analysis. Finally, the developed procedure was applied to the analysis of three aqueous samples.

Sample analysis

Agricultural wastewater samples were filtered through a filter paper before analysis.

RESULTS AND DISCUSSION

Experimental optimization for the MSPE In order to obtain high enrichment and extraction efficiency of the analytes using this extraction technique (MSPE), the main parameters were optimized.

Characterization of $CoFe_2O_4$ nanoparticles

The FT-IR spectra of $CoFe_2O_4$ nanoparticles were showed in Fig. 2 the peak around 1706 cm^{-1} disappears completely and a strong peak around 1559 cm^{-1} was shown in FT-IR spectrum of $CoFe_2O_4$ nanoparticle coated with oleic acid. This indicates that there is no free oleic acid in the CoFe2O4 nanoparticle sample and the complexation between the carboxylate and $CoFe_2O_4$ nanoparticles was formed [7]. The TEM image of the nanoparticles is shown in Fig. 3.

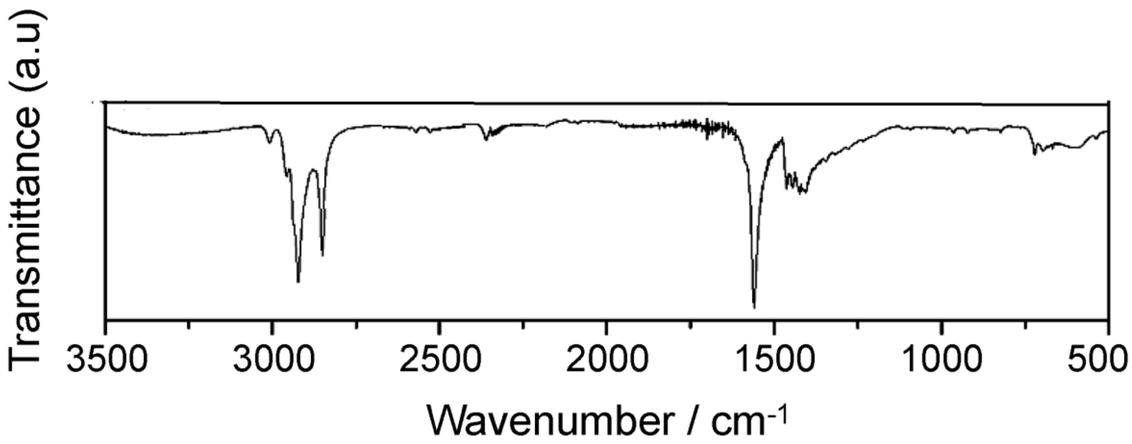

Fig. 2. FT-IR spectra $CoFe_2O_4$ nanoparticle coated with oleic acid.

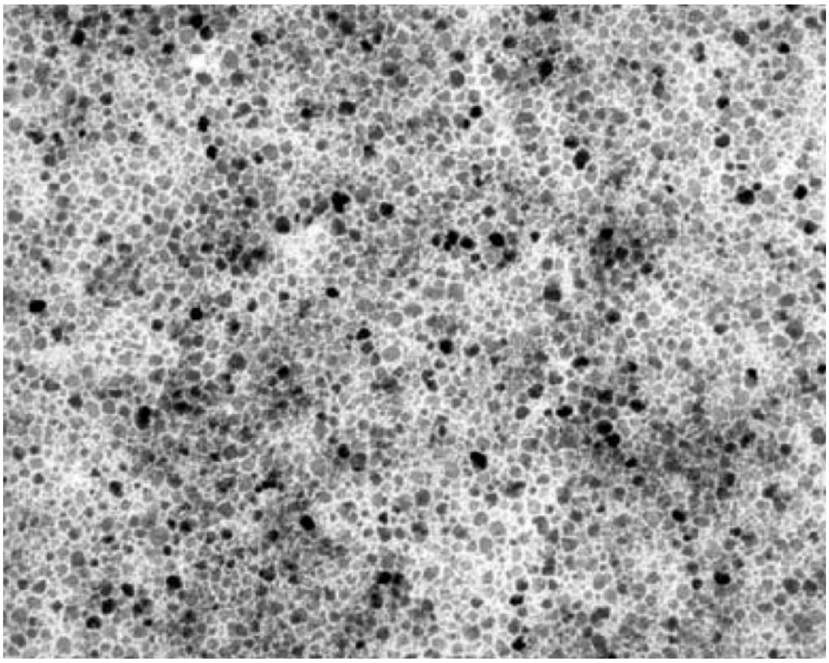

Figure 3. TEM image of $CoFe_2O_4$ nanoparticles.

Experimental optimization for the MSPE. Effect of the extraction time

Extraction was performed from 2 to 30 min to determine the Fig. 4 shows the peak area versus extraction time profiles for the analytes. It can be seen that equilibrium is attained after 10 min. However, the increase on the peak areas for these analytes after 10 min extraction can be considered as not significant, but the results shows that there is a degeneration on the method precision for longer extraction times. Therefore, the extraction time was fixed in 10 min.

The effect of the stirring rate

The extraction efficiency of the method is enhanced by stirring due to a increase in the mass transfer rate and also reduces the time required to reach thermodynamic equilibrium. The response of instrument was recorded for several stirring rates ranging from 50 to 400 rpm for an extraction time of 10 min of 10 mL aqueous samples with each target analyte concentration of 20 μg/mL. The results confirmed that agitation of the sample greatly enhances extraction. However, violent stirring (200 rpm) resulted in massive air bubbles and decreased the pre-concentration factors. Therefore, 200 rpm was selected for extraction at the subsequent experiments.

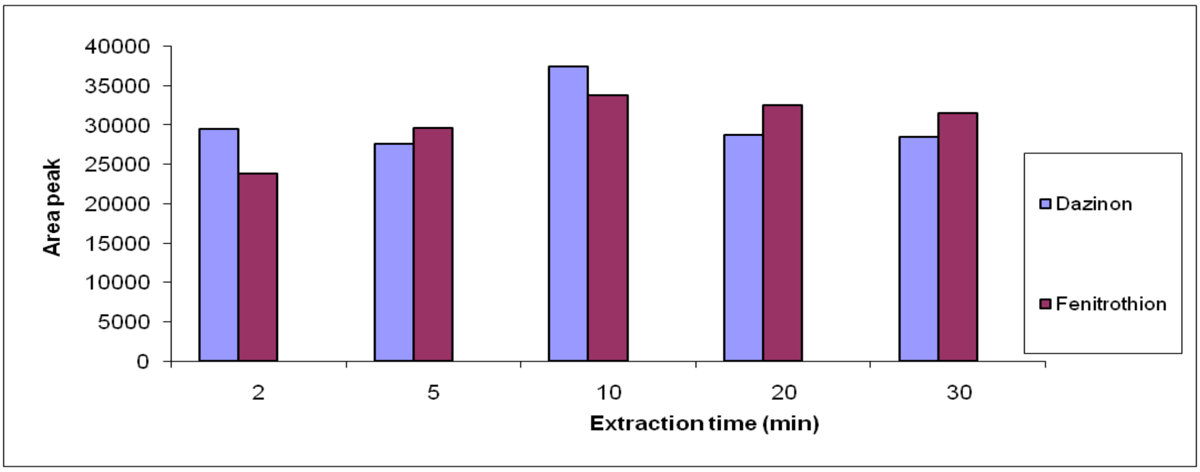

Fig. 4. The effect of extraction time on the extraction efficiency of diazinon and fenitrothin.

Effect of the donor phase volume

The enrichment of the analyte increases with rising the volume of sample solution [10, 20]. The pre-concentration factor in HF-SPME basically depends upon the phase's volume of the sample. As the volume of the sample increases, the pre-concentration factor also increases [11-18]. In the present work, the phase f donor and solutions was optimized by changing the volume of the donor phase between 2 and 25 mL while the amount of acceptor phase was kept constant at 20 mg. As can be seen in Fig. 5 the extraction results obtained for the target analytes were most favorable to suggest a phase ratio of 1987 (5 mL donor phase volume). Repeatability was decreased in the donor phase volumes more than 10 mL.

Effect of pH and addition of salt into water sample solution

The solution pH was measured at the beginning of each experiment.

Donor solution pH in range of 4–12 was tested, by adding the appropriate hydrocholoric acid or sodium hydroxide solution to the aqueous donor phase. The changes in solution pH throughout target analytes adsorption on MNPs sorbent were insignificant suggest that diazinon and fenitrothion were in the molecular forms during adsorption process and that ion-exchange does not play a part in target organophosphorus pesticides adsorption.

The results confirmed that the OPs extraction performance reached a better level at pH 6 (see Fig. 6).

The effect of adding NaCl to aqueous sample was studied in the range of 0–10% (w/v); however, adding NaCl decreased the response of organophosphorus pesticides OPs. This may be due to competitive interaction of Na (I) with active sites on the sorbent surface which is a decrease in sorption capacity of target analytes. In addition, the presence of salt caused a second effect; the physical properties of the aqueous-solid extraction film were changed [12]. So, further extractions were carried out without adding NaCl. The effect of desorption solvent volume and desorption time to reach the highest sensitivity, the desorption time was also appraised to ensure.

Experiments showed that for all the studied four OPs compounds, desorption was almost complete after 7 min. Repeatability decreased in the desorption time less than 7 min . On the other hand, above this time the amount of extracted analyte continue unchanged. Thus 7min was used as the optimal desorption time.

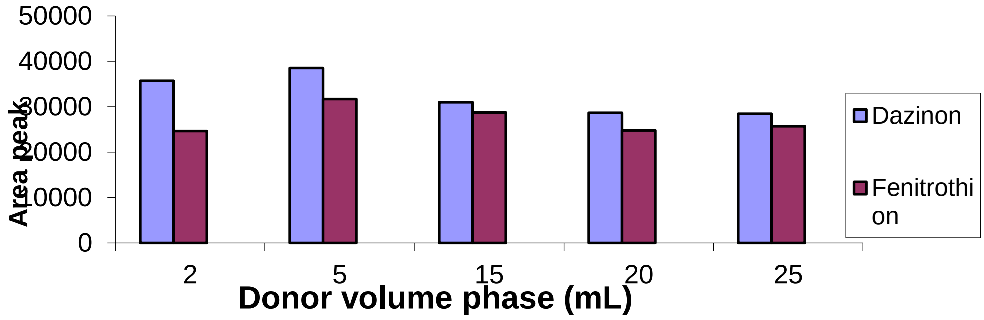

Fig. 5. The effect of aqueous feed volume on the extraction.

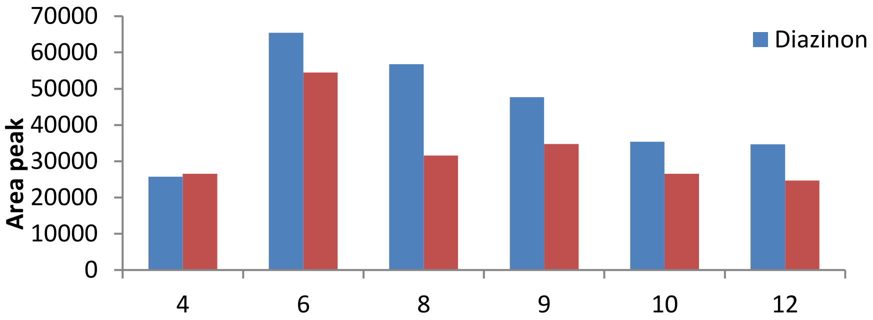

Fig. 6. The effect of pH of aqueous feed on the extraction efficiency.

Evaluation of the method performance. Figures of merit

Validation procedures were performed using spiked de-ionized water. The MSPE method was evaluated for linear range, limits of detection (LODs), correlation coefficients (R) and linear dynamic range (LDR) under the best conditions. Limits of detection were calculated in an experimental manner as the minimum concentration providing chromatographic area three times higher than background noise (S/N = 3).

Calibration curves in aqueous was plotted against the concentration levels of the OPs compounds. For each level, three replicate extractions were performed. The samples by the MSPE method were subsequently analyzed with the GC system, and calibration curves are plotted.

Table 1. Figures of merit of the proposed method in the determination of the organophosphorus compounds

Analyte	DLR (mg/L)	Regression equation	R^2	LOD (mg/L)	%RSD (n=5)
Diazinon	0.001-23	Y=4343.35+836C	0974	0.0009	2.89
Fenitrothion	0.0008-15	Y=12656.8+9787.6C	0.991	0.0005	3.5

Table 2. Comparison of some methods which were used for determination of pesticides compounds.

No	Date	Matrices	Extraction technique	LOD	R	RSD%	Reference
1	2004	Honey	SPME	0.08-20 mg kg^{-1}	0.996	3.6-7.6	[13]
2	2004	Herbal infusions	SPME	0.13-1.1 mg mL^{-1}	0.974	1.3-12.1	[14]
3	2004	Food	SPME	0.01-0.1 ng gr^{-1}	0.998	2.1-12.1	[15]
4	2007	Beverage	LPME	0.1-1.7 µg L^{-1}	0.95	6.1-11.5	[16]
5	2008	Water	SPME	0.17 -0.29 µg L^{-1}	0.998	2.-2.7	[17]
6	2008	Water	LPME	0.01-0.04 mg L^{-1}	0.999	—	[18]
7	2010	Water	SPME	0.1-1 pg mL^{-1}	0.996	2-10	[19]

Pesticides in aqueous samples

The results are tabulated in Table 1, for aqueous solution matrix. The method was compared with the other works (Table 2). The obtained results showed the linear range 1–23.000 ng/mL for diazinon and 0.8–15.000 ng/mL for fenitrothion with RSDs% about 2.89–3.5%. In comparison with the other conventional sample preparation methods, the developed method has the merits of considerable analysis speed, good separation efficiency, improved pre-concentration and notable precision.

Real samples

The developed MSPE method has also been evaluated for the determination of the analytes in the target OPs from aqueous samples. The analytical results of aqueous matrix are given in Table 3. It can be seen that the relative recovery for spiked samples was in the range of 90.7 –92.4%.

Table.3. Detected concentrations (ng/mL) of OPs compounds in wastewater and river water samples

		10µgL^{-1}spiked wastewater Found ± SDa	River water		10µgL^{-1} spiked Found ± SDa	
Analtye	Conc.[a]	RSD% [b]	RR%[c]	Conc.[a]	RSD % [b]	RR %
Diazinon	nd[d]	8.54 ± 0.11	91.3	nd[d]	12.4 ± 0.251	92.4
Fenitrothion	nd	12.9 ± 0.11	87.5	nd	7.9± 0.10	90.7

[a] Found concentration (ng/mL); [b] Relative standard deviation (n=5); [c] Relative recovery after spiked amount of analytes;. [d] Spiked amount of analytes.

CONCLUSION

In the present study, MSPE nanoparticles were fabricated. gas chromatography flame ionization detector was used to investigate the pre-concentration, extraction and determination of pesticides from aqueous samples. The method has excellent selective clean-up of pesticides in aqueous matrices as very complicated matrices. Good linearity and reasonable relative recovery were also achieved. The experimental operations involved in MSPE are very simple. Moreover, this procedure offers several advantages over traditional extraction techniques such as reduced extraction time, also this method is economical and easy to use. In our method, we introduced a reliable qualitative and quantitative technique for determination pesticides at low level of concentration in real samples.

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