Fe$_3$O$_4$/CNT Magnetic Nanocomposites as Adsorbents to Remove Organophosphorus Pesticides from Environmental Water

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Abstract

In this study, a method for extraction and preconcentration of trace amounts of organophosphorus pesticides (OPPs) in environmental water using magnetic solid phase extraction (magnetic-SPE) followed by high performance liquid chromatography (HPLC) with UV detection was developed. The magnetic carbon nanotube adsorbents (Fe$_3$O$_4$/CNT) were synthesized by grafting carbon nanotubes to magnetic Fe3O4 particles by a facile hydrothermal method. The synthesized Fe$_3$O$_4$/CNT nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and vibrating sample magnetometer (VSM). These nanoparticles were used for extraction and preconcentration of OPPs (fenitrothion, profonofus, and ethion) in environmental water samples at low concentration. The influence of four variables including adsorption time, weight of sorbent, salt addition, and pH in the extraction process were predicted and optimized by Response Surface Method (RSM). Under optimized conditions, it showed good linearity between 0.5-10, 0.5-10, 0.5-30 ng ml^{-1} with determination coefficients (R^2) of 0.993, .0995, and 0.994 for extraction of ethion, profonofus, and fenitrothion, respectively. Limit of detection (LOD) for extraction of ethion, profonofus, and fenitrothion were also evaluated under optimized conditions as 0.124, 0.097, and 0.108, respectively. The analysis also showed good reproducibility with the RSD values 4.4, 2.7, and 4.5 at the 10 ng ml^{-1} level (n = 5) for ethion, profonofus, and fenitrothion, respectively.

Keywords: *Fe$_3$O$_4$/CNT nanoparticles, Solid phase extraction, Organophosphorus pesticides, Response surface method.*

1. INRODUCTION

Endocrine disrupting chemicals (EDCs) in the environment, such as bisphenols, dioxins, pesticides, phthalates, alkyl phenolic compounds, furans and synthetic steroids, can disturb the synthesis, secretion, transport and metabolic processes of natural hormones by mimicking or antagonizing the biological effects of natural hormones [1]. Pesticides are toxic and widely used in the agriculture and household in many countries to prevent and destroy any pests including animals, unwanted plant and microorganism, during the growth process of plants.

Organophosphorus pesticides (OPPs) compounds have been utilized as therapeutic agents, agricultural chemicals, plasticizers, lubricants, flame retardants, fuel additives, and, most notoriously, as chemical warfare agents [2-3]. The acute toxicity of most of these compounds is initiated by inhibition of the acetylcholinesterase in the central and peripheral nervous systems, resulting in respiratory, myocardial and neuromuscular transmission impairment [4]. The residues of OPPs in agriculture can be contaminated into canal water by watering or rising of rain and polluted to the consumer as well as the aquatic organism [5]. So to ensure

that environmental water is safe for consumer's health or any current use, the maximum residue limit (MRL) should be controlled. To determine the residues of organophosphorus compounds from polluted aqueous systems, several techniques have been developed, including solid-phase extraction (SPE) [6-8], solid phase microextraction (SPME) [9-13], hollow fiber membrane (HFM) combined with protected liquid-phase microextraction (LPME) [14], dispersive liquid–liquid microextraction (DLLME) [15-18] and other techniques based on DLLME principles, such as homogeneous liquid–liquid microextraction (HLLME) [19]. Nevertheless, much effort is being performed by many researchers to find a fast and efficient method for preconcentration and determination of trace amount of OPPs in water samples.

Recently, several reports have been focused on the use of Fe_3O_4 nanoparticles for the extraction of pesticides and drugs from aqueous samples [20-23]. For instance, Fe_3O_4-SiO_2-C18 paramagnetic nanoparticles have been synthesized and used as sorbent for the extraction of Zineb from agricultural aqueous samples [23]. Maddah et al. [24] used carbon-coated Fe_3O_4 nanoparticles for the preconcentration and extraction of organophosphorus pesticides in environmental water samples. In another study, the capability of polyaniline-coated Fe_3O_4 nanoparticles for magnetic-SPE of three parabens has been investigated by Tahmasebi et al. [25].

Recently, the adsorption method using carbon nanotubes (CNTs) as adsorbents has been extensively studied for using in the purification of drinking water sources and wastewater effluents; because the organic pollutants can be effectively removed through the strong bonding between organic molecules and CNTs [26-27]. It has been reported that CNTs showed excellent adsorption behavior to remove recalcitrant contaminants such as dioxi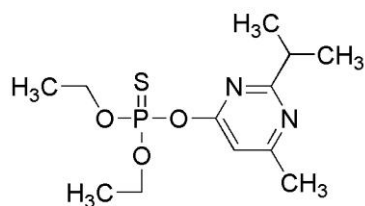n [28], ciprofloxacin [29], polycyclic aromatic hydrocarbons (PAHs) [30], chlorobenzene and chlorophenol [31], trichloromethane [32] and atrazine [33]. However, it is difficult to separate CNTs from aqueous suspensions due to their small size. The traditional methods such as high-speed centrifugation and time-consuming filtration are not effective ways to recover CNTs from an aqueous phase. Compared with traditional separation methods, the magnetic separation method is considered as a rapid and effective technique to separate nanoparticles from aqueous solutions. Thus, it could be anticipated that CNTs incorporated with magnetic Fe_3O_4 particles possess both the excellent adsorption capacities and magnetic features [34]. In continuation of our previous work [35] on extraction and preconcentration of trace amounts of pesticides from environmental water by modification of magnetite nanoparticle surface, in this study Fe_3O_4/CNTs magnetic nanoparticles have been synthesized by coating the Fe_3O_4 with CNTs. The coated nanoparticles were applied as magnetic-solid phase extraction (magnetic-SPE) adsorbent for extraction of fenitrothion, profonofus, and ethion which are the most-widely used for pest control in environmental water samples at low concentration. Then the extracted compounds were analyzed by HPLC in combination with UV detection.
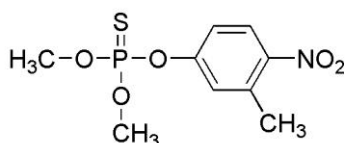
2. MATERIALS AND METHODS
2.1. Materials

All the chemicals and reagents were in analytical grade and used without further purification. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), single wall carbon nanotube 99%, ammonia solution (25 wt%), methanol, ethanol and acetonitrile (HPLC grade) were purchased from Merck (Darmstadt, Germany). Double distilled water was used throughout the experiments. Fenitrothion, ethion and porofenofus (Scheme 1) were purchased from Merck Co. (Germany).
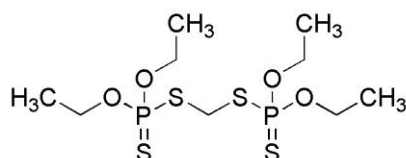
The concentration of pesticides ranging from 0.015 to 30 ng ml^{-1} in water was prepared as standards for calibration curve.

Profonofus

Fenitrothion

Ethion

Scheme 1. *Structure of fenitrothion, profonofus, and ethion.*

2.2. Measurements

The concentration of fenitrothion, ethion and porofenofus was determined by high performance liquid chromatography (HPLC) containing an EA4300F SMART LINE pump, RHEODYNE 7725i sample injector, and an S-2600 ultraviolet (UV) detector (knauer, Germany). Chromatographic separations were performed using the analytical HPLC C18 column (250 mm × 4.6 mm, 10μm) perfectsill Target ODS-3. The mobile phase was 80:20 (v/v) acetonitrile/water at a constant flow rate of 1.00 mL min^{-1}. A detection wavelength of 247, 220, and 220 nm was used for analyzing porofenofus, fenitrothion and ethion, respectively. A Heidolph motorstirrer (Schwabach, Germany) was applied for stirring of the solutions with a glassware stirrer. The magnetic properties of the prepared nanoparticles (NPs) were investigated with a vibrating sample magnetometry (VSM) system (LDJ9600, Troy, USA) at room temperature. Magnetic separation was performed by a strong magnet with 1.4 T magnetic fields (10 cm × 5 cm × 4 cm). An infrared spectrum was obtained using a Fourier Transform-Infrared (FTIR) Spectrometer (FTIR, Perkin Elmer, spectrum 100) in a KBr matrix to identify the functional groups and chemical bonding of the coated materials. X-ray powder diffraction measurements were performed using X-ray Diffractometer (XRD, Xport-PW 3040/60 Philips). Transmission electron microscopy (TEM) was performed on GHK-em 10 at 100kv Zeiss. The pH of solutions was measured with a Metrohm 781 pH/Ion meter (Herisau, Switzerland) supplied with a combined electrode.

2.3. Synthesis of Fe$_3$O$_4$ Magnetic Nanoparticles (MNPs)

Fe$_3$O$_4$ nanoparticles were synthesized according to previous published method [36]. An iron salt solution was vigorously stirred (700 rpm) by mixing 49.6 g iron (III) (FeCl$_3$.6H$_2$O) and 18.3 g iron (II) (FeCl$_2$.4H$_2$O) in 470 ml deoxygenated distilled water under N2 gas. Then, 30 ml of ammonia solution (25 wt%) was slowly added to the ferric salt solution under magnetic stirring for 1 h at 60 °C. A black precipitate was formed and separated from solution by a magnet and washed with the deoxygenated distilled water four times, followed with the deoxygenated anhydrous ethanol once, then vacuum-dried at 50 °C overnight, and thus the naked Fe$_3$O$_4$ nanoparticles were obtained.

2.4. Synthesis of MNPs Coated by Carbon Nanotubes (Fe$_3$O$_4$/CNTs)

The synthesis of MNPs coated by carbon nanotubes (Fe$_3$O$_4$/CNTs) were performed by hydrothermal method. In order to achieve this matter, the synthesized Fe$_3$O$_4$ magnetic nanoparticles (0.4 g) were added to a solution of carbon nanotube (0.5 M)

and the resulting mixture was stirred for 1 h. Then, the resulting mixture was heated for 4 h at 180 °C. Finally the synthesized Fe_3O_4/CNTs was separated by a magnet and washed with the deoxygenated distilled water, followed with the deoxygenated anhydrous ethanol and vacuum-dried at 50 °C overnight.

2.5. Analytical Procedure

The prepared solutions of fenitrothion (2 ng ml^{-1}), ethion (5 ng ml^{-1}) and porofenofus (10 ng ml^{-1}) in water were used as the test sample for magnetic SPE procedure. The Fe_3O_4/CNTs magnetic nanoparticles (0.4 g) as adsorbent were dispersed in 20 ml standard solutions in a beaker to form a suspension with the aid of ultrasonication. The mixtures were vibrated for 3 min to make sure the magnetic nanoparticles contacted with the analytes. Then, the adsorbent (Fe_3O_4/CNTs magnetic nanoparticles) which is associated with the analytes is separated from solution under the external magnetic field and washed with 30 ml water three times. Finally, the analytes (fenitrothion, ethion, and porofenofus) were moved from solid phase to organic phase when the solid phase was ultrasonically washed by acetonitrile for 4 min. The solution containing fenitrothion, ethion, and porofenofus was transferred to a glass tube under a magnetic field to be ready for analysis.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Magnetic Nanoparticles (MNPs)

The XRD pattern of Fe_3O_4 magnetic nanoparticles (MNPs) are shown in Figure 1. The crystalline diffraction peaks at 2θ = 30.2°, 35.6°, 43.3°, 53.3°, 57.1°, and 62.6° were identified as the (220), (311), (400), (511) and (440) planes of the spinel phase of Fe_3O_4 (JCPDS No. 65-3107), respectively [37]. The presence of similar diffraction peaks in XRD spectra of the Fe_3O_4 magnetic nanoparticles coated by carbon nanotubes (CNTs) (Fe_3O_4/CNT)

indicates that the coating of MNPs with carbon nanotubes does not cause a phase change in the spinel phase of synthesized Fe_3O_4 nanoparticles.
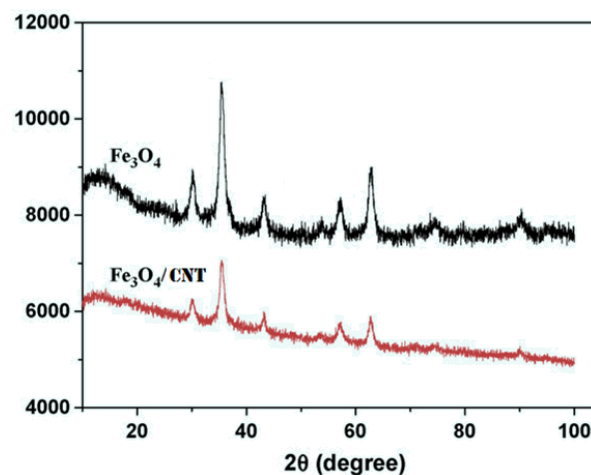

Figure 1. *XRD spectra of Fe_3O_4 and Fe_3O_4/CNT nanoparticles.*

The size and shape of synthesized nanoparticles of Fe_3O_4 and Fe_3O_4/CNT were considered by transmission electron microscopy (TEM). As can be seen from Figure 2, most of Fe_3O_4 nanoparticles are in quasi-spherical in the shape with an average diameter of approximately 10-20 nm. After coating the Fe_3O_4 nanoparticles by CNTs, the size of Fe_3O_4/CNT nanoparticles increases up to 30-40 nm and the nanoparticles stay in quasi-spherical shape.

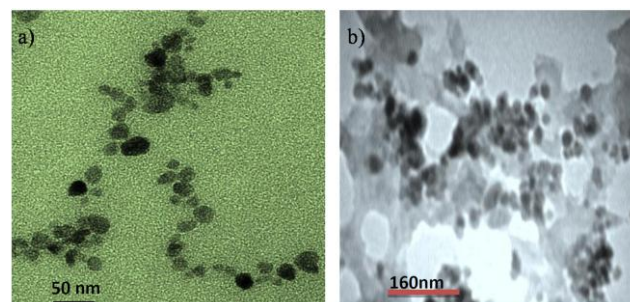***Figure 2.*** *TEM images of a) Fe_3O_4 b) Fe_3O_4/CNT.*

The Fe_3O_4 and Fe_3O_4/CNT nanoparticles were further analyzed by FTIR spectroscopy throughout the range of 500-4000 cm^{-1} (Figure 3). It is observed that the FTIR spectra of the Fe_3O_4 and

Fe₃O₄/CNT nanoparticles contain bands at 576 cm^{-1} assigned to the Fe–O–Fe stretching and bending modes [38-42], indicating the presence of Fe₃O₄ in the Fe₃O₄/CNT. The bands at 796 cm^{-1} and 1618 cm^{-1} were the characteristic graphite structure peak, which was assigned to the C=C groups of the CNTs [34]. In addition, it was noted that the bands at 1020 cm^{-1}, 1378 cm^{-1}, 1700 cm^{-1}, 2923 cm^{-1} and 3432 cm^{-1} were assigned to the stretching and bending modes of C–O, C=C, C=O, –CH₂ and –OH in the functional groups of the CNTs. The abundant functional groups in the Fe₃O₄/CNTs were beneficial for the adsorption of pollutants [41].
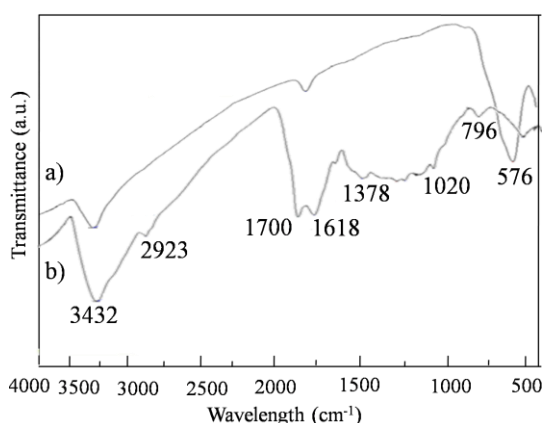

Figure 3. *FT-IR spectra of a) Fe₃O₄ and b) Fe₃O₄/CNT nanoparticles.*

The magnetic property of Fe₃O₄ and Fe₃O₄/CNT nanoparticles was characterized by using the vibrating sample magnetometer (VSM) at room temperature. Figure 3 shows the magnetic hysteresis loops of Fe₃O₄ and Fe₃O₄/CNT nanoparticles in an applied field of -20 000 to 20 000 Oe at room temperature. The hysteresis loops of both the magnetic particles exhibited superparamagnetic behavior and had little hysteresis, remanence and coercivity. The saturation magnetization of the Fe₃O₄ and Fe₃O₄/CNT is about 44 emu g^{-1} (Figure 3), relatively lower than the unsupported Fe₃O₄ (60 emu g^{-1}), which is due to the non-magnetic properties of carbon nanotube in the Fe₃O₄/CNT nanoparticles. This saturation magnetization of Fe₃O₄/CNT nanoparticles

shows that catalyst could be easily separated by applying an external magnet that minimizes the loss of Fe₃O₄/CNT nanoparticles during the separation stage.
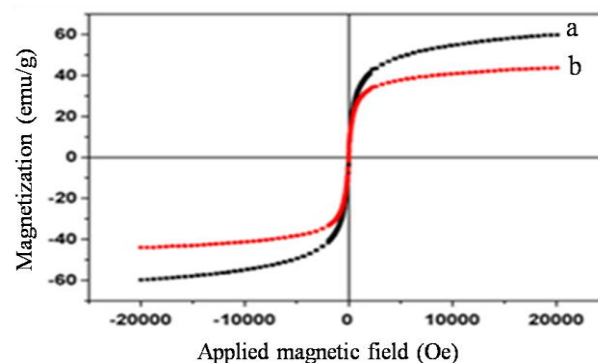

Figure 4. *Magnetization curves of a) Fe₃O₄ and b) Fe₃O₄/CNT nanoparticles.*

3.2. Analysis of Variance and Optimization

In order to optimize the extraction procedure, 19 tests with various conditions were designed by considering separately four main parameters, including adsorption time, weight of sorbent, salt addition, and the effects of pH by using response surface method. These conditions were summarized in Table 1.

The comparison between the predicted values of response in model and experimental values for fenitrothion, porofenofus, and ethion was obtained and revealed that the predicted values are in good agreement with the experimental values.

3.3. Effect of Significant Parameters
Effect of pH

An adjustment of the pH may improve the extraction yield for the compounds that can be protonated. In most cases, the pH is adjusted in order to obtain the analyte in its neutral associated form to enhance extraction yield, because only this form is extracted in the absorption phase. In this study, the pH value varied from 4 to 12 to evaluate the effect of the pH on the extraction. The results showed the pH can affect the absorption of fenitrothion, porofenofus, and ethion compounds. The

absorption of these compounds decreases with the increase of pH from 4 to 12. The absorption of porofenofus and ethion decreases with a more slope than that of fenitrothion when the pH values increases from 4 to 12. Therefore, the highest absorption values for these compounds can be expected to be in low pH values.

Table 1. Experimental design and results of the extraction process.

Number of experiments	pH	Adsorption time (min)	Weight of sorbent (mg)	Salt addition (mg)	Fenitrothion (%)	Porofenofus (%)	Ethion (%)
1	12	30	60	0	66.14	39.93	65.12
2	12	30	20	0	40.14	18.12	41.58
3	12	0	60	400	54.76	31.66	60.3
4	4	30	20	400	66.75	42.5	64.56
5	12	0	20	400	44.73	24.05	44.54
6	4	0	60	0	69.82	50.53	78.23
7	4	30	60	400	78.02	68.72	87.4
8	4	0	20	0	33.93	17.58	36.39
9	5.6	15	40	200	31.85	17.54	54.19
10	10.4	15	40	200	70.02	36.92	61.47
11	8	6	40	200	59.51	31.91	69.37
12	8	24	40	200	65.95	43	83.02
13	8	15	28	200	53.43	27.78	96.08
14	8	15	52	200	86.29	51.07	90.62
15	8	15	40	80	55.89	27.4	55.47
16	8	15	40	320	60.73	32.65	71.77
17	8	15	40	200	62.67	37.5	88.15
18	8	15	40	200	68.27	38.62	88.6
19	8	15	40	200	50.53	31.32	76.15

Absorption time

The effect of absorption time was also studied in the range of 0-40 min. It is found that the absorption time can also affect the absorption of fenitrothion, porofenofus, and ethion compounds. The absorption of these compounds increases with the increase of time from 0 to 40 min. The absorption of fenitrothion and porofenofus increases with a more slope than that of ethion when the time increases up to 40 min.

Weight of sorbent

The effect of the weight of Fe_3O_4/CNT nanoparticle as sorbent was studied in the range of 20–60 mg. It is observed that the weight of sorbent affect the absorption of fenitrothion, porofenofus, and ethion compounds. The absorption of fenitrothion and porofenofus increases with the increase of the weight of sorbent, although the absorption of ethion increases up to 45 mg and then decreases up to 60 mg.

Salt addition

In the extraction procedure the effect of salt addition can be employed to modify the matrix by adding salt, such as NaCl, to increase the ionic strength of the water so as to decrease the solubility of the analytes and release more analytes into the organic phase. The amount of NaCl salt was varied from 0 to 40 mg. The result showed that the absorption of fenitrothion, porofenofus, and ethion increases with the increase of salt values from 0 to 40 mg. The absorption of fenitrothion and porofenofus increases with a more slope than that of ethion when the amount of salt increases

up to 40 mg. This indicates that the amount of salt added to the solution should have a small effect on the absorption of ethion. Three-dimensional (3D) response surface for ethion yields as a function of salt, sorbent, adsorption time, and pH, as well as their interactions are shown in Figure 5. The combined effect of salt and sorbent in optimal values of pH (4.4) and adsorption time (30 min) are represented in Figure 5a. Increasing the ethion yields was observed with increasing the salt. Moreover, increasing the weight of sorbent causes an increase followed by a decrease in ethion yields. It was found that ethion yield increased by increasing the weight of sorbent to 47 mg and then it decreased with increasing weight of sorbent. Furthermore, maximum ethion yield occurred at absorption time of 30 min and pH=4, as shown in Figure 5b and Figure 5c, respectively. It is obvious that increasing the pH causes a mild decrease in ethion yield. The same behavior was also observed for fenitrothion and porofenofus.
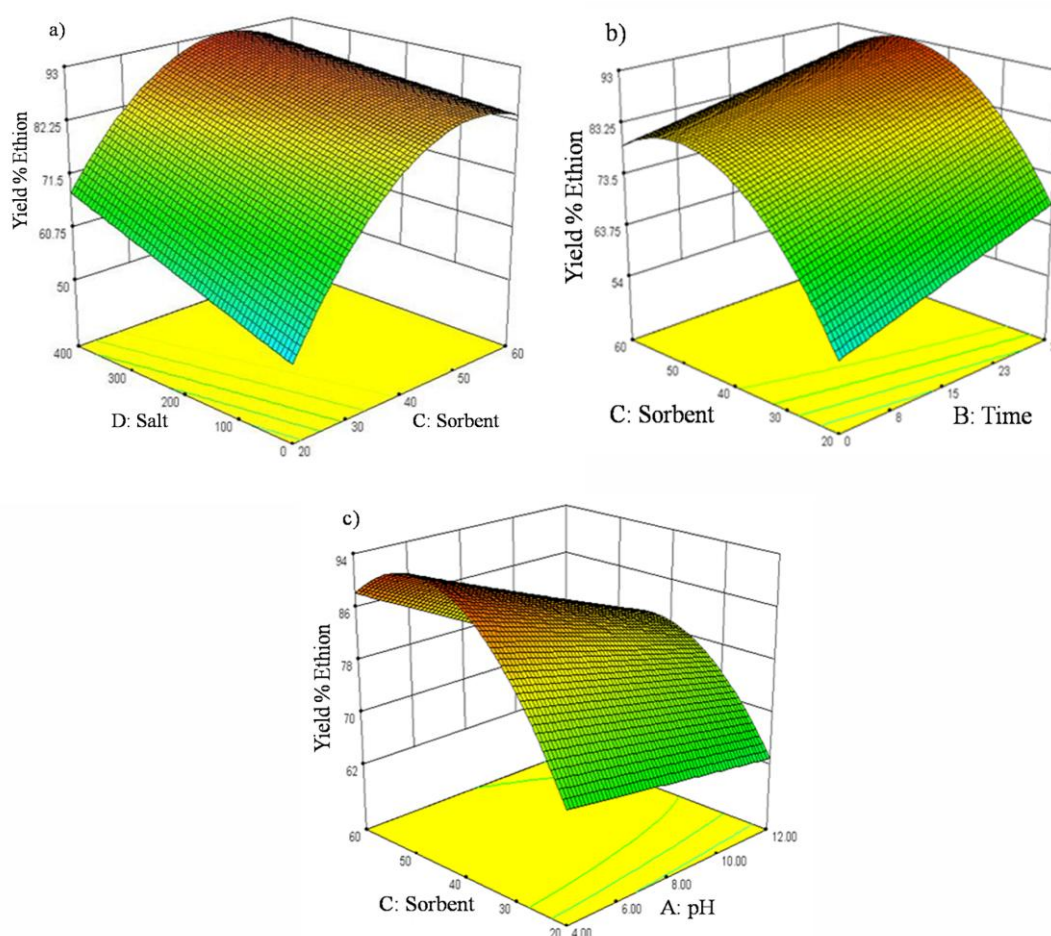

Figure 5. Response surface for ethion yield showing the effect of a) salt and sorbent in optimal values of pH (4.4) and adsorption time (30 min); b) sorbent and time in optimal values of salt (400 mg) and pH (4.4); c) sorbent and pH in optimal values of salt (400 mg) and time (30 min).

3.4. Quantitative Analysis

In order to investigate the applicability of the proposed method for determination of fenitrothion, porofenofus, and ethion in water sample, several factors including recovery, limit of detection (LOD), limit of quantification (LOQ) and repeatability

were evaluated under optimized conditions [42,43].

Table 2. *Analytical performance of magnetic-SPE procedure optimized for determination of fenitrothion, porofenofus, and ethion in water samples.*

Analyte	Linear dynamic range (ng ml^{-1})	R^2	LOD (S/N=3) (ng ml^{-1})	LOQ (S/N=10) (ng ml^{-1})	RSD (%) (n=5) (10 ng ml^{-1})	Enrichment factors (EF)
Fenitrothion	205	4.5	0.361	0.108	0.994	0.5 - 15
Porofenofus	181	2.7	0.323	0.097	0.995	0.5 - 10
Ethion	174	4.4	0.413	0.124	0.993	0.5 - 10

As seen from Table 2, determination coefficients of the calibration curves (Figure 6) for fenitrothion, porofenofus, and ethion were 0.994, 0.995, and 0.993, respectively. The repeatability of the proposed magnetic-SPE-HPLC method was evaluated by analyzing five replicates at 10 ng ml^{-1}. The method showed a good precision with relative standard deviation (RSD) 4.5, 2.7, and 4.4%, respectively. Detection limits, based on a signal-to-noise ratio of 3, were 0.108, 0.097, and 0.124 ng ml^{-1}, respectively. Finally, the preconcentration values of 205, 181, and 174 were found for fenitrothion, porofenofus, and ethion, respectively.

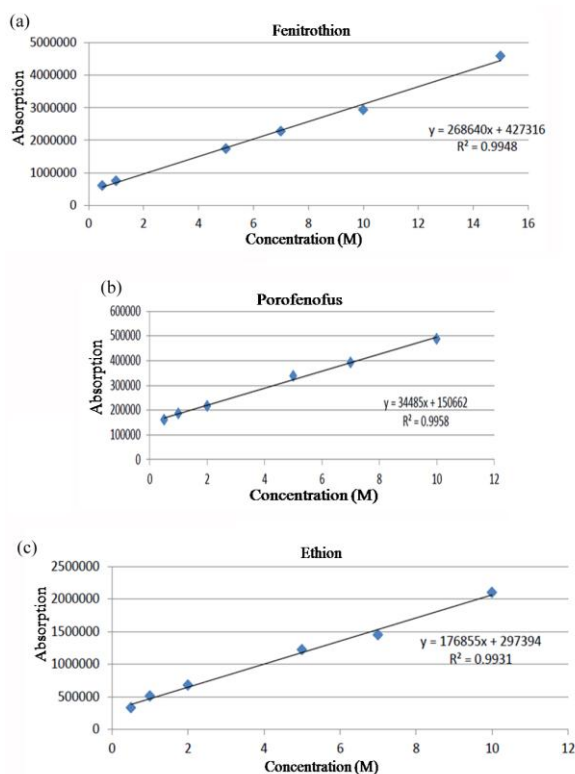*Figure 6. Calibration curve in optimal conditions for fenitrothion, porofenofus, and ethion compounds.*

3.5. Real Water Analysis

To evaluate the applicability of the proposed method and matrix effect, extraction and analysis were performed on ground water samples. The HPLC chromatograms resulted after magnetic-SPE of a ground water sample are shown in Figure 7. The relative recoveries (RR) along with RSD% (n = 5) were obtained to be 92%, 60% and 81% for fenitrothion, porofenofus, and ethion, respectively.
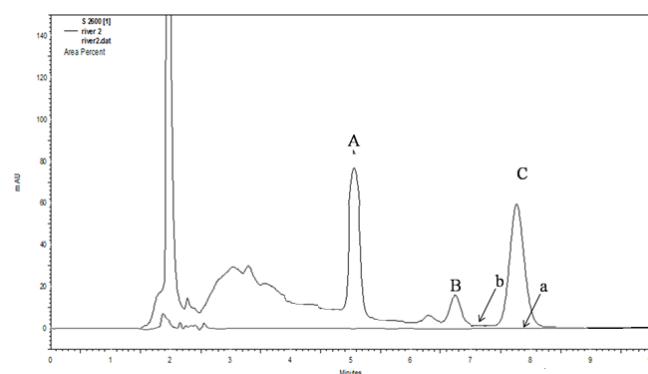

Figure 7. HPLC chromatograms obtained after magnetic-SPE of ground water sample (a) unspiked and (b) spiked at concentration level of 1 ng ml^{-1} of A: fenitrothion, B: porofenofus, and C: ethion under optimized conditions.

As seen from Table 3, the results predicted by RSM are very close to the results obtained from extraction process. This indicates the ability of RSM in the prediction of extraction conditions and also the ability of Fe_3O_4/CNT for extraction and

preconcentration of trace amounts of OPPs in environmental water.

Table 3. Comparison between responses obtained from extraction process and predicted results by RSM.

Factor	pH	Adsorption time	Weight of sorbent	Salt addition	Fenitrothion	Porofenofus	Ethion
RSM result	3.9	30	60	400	83	64	96
Experimental result	4.4	30	60	400	81	62	95

4. CONCLUSION

In this study, magnetic solid phase extraction followed by high performance liquid chromatography has been developed for the determination of organophosphorous pesticides (fenitrothion, profonofus, and ethion) in environmental water. Fe_3O_4/CNT nanoparticles as sorbent can be easily synthesized. They were easily separated via an external magnetic field during extraction process. OPPs in the low concentration range efficiently concentrated from environmental water by Fe_3O_4/CNT nanoparticles. The effects of adsorption time, weight of sorbent, salt addition, and pH as main parameters in the extraction process were investigated by using RSM and compared with the experimental results. Under optimized conditions, the proposed method showed good reproducibility, enrichment factor, linearity range and limits of detection for extraction of OPPs in environmental water.

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