

A Nanoparticle-Based Solid-Phase Extraction Procedure Followed by Spectrofluorimetry to Determine Carbaryl in Different Water Samples

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Nesse estudo, um novo método baseado em nanopartículas de magnetita Fe₃O₄ (MNPs) foi desenvolvido para a extração, preconcentração e determinação de traços de carbaril de amostras de água do meio ambiente. Fe₃O₄ MNPs foram sintetizadas e modificadas pelo surfactante dodecil sulfato de sódio (SDS) e aplicadas com sucesso na extração de carbaril e na sua determinação através de espectrofluorimetria. Fatores que afetam a adsolubilização do carbaril, como quantidade de SDS, pH, tempo de espera, solvente de desorção e volume máximo de extração foram otimizados. Sob as condições selecionadas, foi possível extrair carbaril quantitativamente. Recuperações (84,5-91,9%) e desvio padrão relativo (6,2%) aceitáveis foram alcançados ao analisar amostras de água adulterada. Um fator de concentração de 20 foi obtido na extração de 100 mL de amostras de água do meio ambiente. Os limites de detecção e quantificação encontrados foram 2,1 e 6,9 µg L⁻¹, respectivamente. O método proposto foi aplicado com sucesso na extração e determinação de carbaril em amostras de água do meio ambiente.

In this study, a new method based on Fe₃O₄ magnetite nanoparticles (MNPs) has been developed for the extraction, preconcentration and determination of trace amounts of carbaryl from environmental water samples. Fe₃O₄ MNPs were synthesized and modified by the surfactant sodium dodecyl sulfate (SDS), then successfully applied for the extraction of carbaryl and its determination by spectrofluorimetry. Main factors affecting the adsolubilization of carbaryl such as the amount of SDS, pH value, standing time, desorption solvent and maximal extraction volume were optimized. Under the selected conditions, carbaryl could be quantitatively extracted. Acceptable recoveries (84.5-91.9%) and relative standard deviations (6.2%) were achieved in analyzing spiked water samples. A concentration factor of 20 was achieved by the extraction of 100 mL of environmental water samples. The limit of detection and quantification were found to be 2.1 and 6.9 µg L⁻¹, respectively. The proposed method was successfully applied for the extraction and determination of carbaryl in environmental water samples.

Keywords: Fe₃O₄-MNPs, SPE, carbaryl, environmental water samples, spectrofluorimetry

Introduction

Recently, nanoparticles (NPs) have attracted substantial interest in the scientific community for the sample extraction. Compared with micrometer-sized particles used in the solid phase extraction (SPE), NPs offer a significantly higher surface area-to-volume ratio and a short diffusion route, resulting in a higher extraction capacity; rapid dynamics of extraction and higher extraction efficiencies.^{1,2} Also, NPs' surface functionality can be easily modified to

achieve the selective sample extraction or cell collection.^{1,2} In these NP-based extraction procedures, the NPs were collected after extraction either by centrifugation or by filtration, which would be difficult in some cases such as with large volume samples.¹

More recently, magnetite nanoparticles (MNPs) have received increasing attention. MNPs as adsorbents can be easily collected by using an external magnetic field placed outside of the extraction container.¹ Thus separation process can be performed directly in crude samples containing suspended solid material without additional centrifugation or filtration, which makes separation easier and faster.^{1,3}

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Because of their large surface area and unique physical and chemical properties, they have been widely applied in the analytical chemistry field. These MNPs (as bare or modified Fe_3O_4 adsorbents) can be used for the extraction and determination of trace amounts of organic^{1,4-16} and inorganic^{2,17-20} compounds from different samples.

The adsorption of ionic surfactants on MNPs can form hemimicelles and admicelles. Thus, new SPE methods based on hemimicelle assemblies have been proposed for the extraction and preconcentration of a variety of pollutants from complex environmental matrices.^{5-8,13-17} In these methods, the sorbents were produced by the adsorption of anionic^{6,8,13,17} or cationic^{5,15,16} surfactants on the surface of MNPs. By using hemimicelles in SPE, a new kind of adsorbents is obtained which has many advantages, such as high extraction yields, high breakthrough volumes, rapid separation and rapid elution of analytes. Furthermore, no clean-up steps are required additionally.^{5,7,15}

Determination of trace level pesticides in aquatic environment is very important due to their intense use in agriculture and to their persistence as well.¹ These compounds cause a variety of neurotoxic and endocrine disruptor effects. Thus, World Health Organization (WHO) and various national governmental institutions have established residue limits and published guidelines for quantification of pesticide residues in waters.^{21,22}

Carbaryl is a broad spectrum pesticide belonging to the *N*-methylcarbamate group and functioning as a reversible inhibitor of cholinesterase (ChE) activity. Carbaryl moderately binds to soil and has potential to leach to groundwater. It is not persistent in soil since it can be hydrolyzed, photo-degraded, oxidized and degraded by microbes. In alkaline or neutral water, hydrolysis is the major degradation route for carbaryl, with half-lives ranging from a few hours to a few days. It is also subject to microbial degradation in natural water. Photolysis plays a role in the degradation process, significantly reducing degradation half-life of carbaryl. The major degradation product is 1-naphthol. In general, carbaryl is slightly toxic to mammals, moderately to highly toxic to aquatic organisms and honeybees.²³

In Australia, the guideline for carbaryl in drinking water has recommended the health value (HV) to be 0.03 mg L^{-1} . The environmental quality standards in Japan are established the level for carbaryl as 0.05 mg L^{-1} in public water. Canadian drinking-water quality maximum acceptable concentration (MAC) value is 0.09 mg L^{-1} .¹

Analyses of carbamates by high performance liquid chromatography (HPLC) and by mass spectrometry (MS) coupled with HPLC and gas chromatography (GC) in environmental samples, either with direct or with derivatization methods, have been widely used.²⁴

However, GC based analysis of many carbamates is hindered by the thermal degradation of the analytes and precolumn derivation is required.^{25,26} On the other hand, the costs of HPLC and HPLC-MS methods are high. They usually use high volumes of toxic solvents and their separation procedure is time-consuming. Sometimes you have to develop an extremely complex gradient for the separation, specific preprocessing procedures for samples or sophisticated cleanup strategies.²⁷

Therefore, there is an increasing demand for developing sensitive, simple and reliable methods for determining pesticides in aquatic environments. Luminescence spectroscopy is considered as a sensitive and selective analytical technique. It offers remarkable analytical features for the determination of organic pollutants. However, its use (especially fluorescence) for analysis of organic pesticide residues has been limited by the fact that relatively few of these compounds are strongly luminescent.²⁸

In this work, Fe_3O_4 MNPs were synthesized and modified by the sodium dodecyl sulfate (SDS) surfactant. Then, a SPE procedure based on these modified NPs was developed for the extraction of carbaryl from environmental water samples and its determination by a simple, rapid and inexpensive spectrofluorimetric method. Predominant factors influencing the synthesis of SDS-coated Fe_3O_4 NPs as well as carbaryl extraction and determination were investigated and optimized.

Experimental

Apparatus

All fluorescence measurements were made using a Shimadzu RF-5301 PC spectrofluorophotometer (Kyoto, Japan) equipped with a 150 W Xenon lamp and 1.00 cm quartz cells. Instrument excitation and emission slits both were adjusted to 5 nm. A centrifuge from Hettich (EBA 20 model/Andreas Hettich GmbH & Co. KG, Tuttlingen, Germany) with 15 mL calibrated centrifuge tubes (Hirschmann, EM techcolor, Germany) was used to accelerate the phase separation process. The pH-meter model M120 (Halstead, Essex, England CO9 2DX) supplied with a glass combined electrode was used for the pH measurements. The mixtures were shaken using a Unimax 1010 Shaker-Inkubator (Heidolph, Germany).

Materials

Iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and SDS were purchased from E. Merck (Darmstadt, Germany). Carbaryl

was purchased from PolyScience Corporation (Chemical Division, Analytical Standards, Arlington Heights, Illinois 60004). All solvents and chemicals including acetone, acetonitrile, ethanol, methanol, chloroform, sodium chloride and HCl were obtained from E. Merck (Darmstadt, Germany).

A stock standard solution at a concentration of $500 \mu\text{g mL}^{-1}$ was prepared by dissolving appropriate amount of carbaryl in methanol and stored under dark conditions in refrigerator when not in use. This solution was stable for 1 month. Working standard solutions were obtained daily by appropriately diluting this stock solution with ultrapure water. The water used for sample preparation was deionized and purified using a Milli-Q system (Advantage A 10, Millipore, France).

Preparation and characterization of MNPs

Fe_3O_4 NPs were prepared by the co-precipitation method with some modifications.¹⁷ So, the mole ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ was approximately 1.7:1 instead of approximately 2:1 in the cited reference. Firstly, 4.6 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 2.0 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and 0.85 mL of HCl (12 mol L^{-1}) were dissolved in 25 mL of deionized water which was degassed with N_2 before use. The resulted clear yellowish green solution was added drop-wise into 250 mL of 1.5 mol L^{-1} NaOH solution (heated to 80°C), under vigorous stirring with N_2 passing continuously through the solution during the reaction. Upon addition, the solution turned black and was then stirred magnetically at 1000 rpm for 30 min. After the reaction, the obtained precipitate was separated from the reaction medium by magnetic field, washed with 200 mL of deionized water four times, and then re-suspended in 250 mL of deionized water. The average particle size of the obtained MNPs was observed by using a scanning electron microscope (SEM), model vega2 (Czech Republic).

Recommended procedure

For the batch adsorption experiments, a 100 mL sample solution containing 2-100 $\mu\text{g mL}^{-1}$ of carbaryl (or real water sample), 5 mL of NPs solution and 400 $\mu\text{g mL}^{-1}$ of SDS solution were put into a 250 mL beaker and the pH of the mixture was adjusted to the desired value with 0.1 mol L^{-1} HCl. Secondly, the mixture was shaken at 200 rpm and allowed to complete the extraction process for 5 min. Subsequently, a strong magnet was placed at the bottom of the beaker, and the SDS-coated Fe_3O_4 NPs was isolated from the solution. After about 5 min, the solution became limpid and supernatant solution was decanted. Finally, the preconcentrated target analyte was eluted from the isolated

particles with methanol ($2 \times 2.5 \text{ mL}$) to desorb the target analyte with the aid of stirring. The fluorescence intensity of final solution (i.e., 5 mL) was measured at $334 \pm 3 \text{ nm}$ with the excitation wavelength set at $279 \pm 3 \text{ nm}$.

Sample collection

All water samples were obtained from different districts of Azerbaijan-e-sharghi. Tap water samples were taken from our lab in Tabriz and a well water sample came from the Jolfa. River water samples were collected from Aras river (Jolfa). Bottled mineral water samples were obtained from local markets in Tabriz. All samples were collected randomly and filtered through $0.45 \mu\text{m}$ filter paper before use in order to remove suspended solids. The filtered water samples were stored at 4°C until analysis. Then, a 100 mL portion of clear samples was subjected to the extraction and spectrofluorimetric determination. The spiked water samples were made by adding certain amounts of carbaryl standard solution to the real water samples of fixed volume.

Results and Discussion

Synthesis of Fe_3O_4 MNPs

Co-precipitation is a facile and convenient way to synthesize Fe_3O_4 NPs from aqueous $\text{Fe}^{2+}/\text{Fe}^{3+}$ salt solutions by the addition of a base under inert atmosphere at room temperature or at elevated temperature. The size, shape and composition of MNPs depends on the type of salts used (e.g., chlorides, sulfates, nitrates), the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, the reaction temperature, the pH value and ionic strength of the media.¹³

In this work, different conditions were investigated for the NPs synthesis consisting of: using chloride or sulfate salts, changing the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio from 1:1 to 1:2.5, adjusting the sample pH with NH_4OH or NaOH and finally the addition of base to $\text{Fe}^{2+}/\text{Fe}^{3+}$ solution or reverse order. The results showed that using this procedure, the quality of MNPs is fully reproducible once the synthesis is performed using chloride salts, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio fixed at 1:1.7 and addition of $\text{Fe}^{2+}/\text{Fe}^{3+}$ mixture to NaOH solution (heated at 80°C). The SEM image (Figure 1) of the dispersed Fe_3O_4 NPs in water shows that the synthesized MNPs have rather high surface area and also the substructures with dimensions less than 42 nm could be observed.

Effect of pH

In the mixed hemimicelle based SPE, value of pH plays a critical role in the hemimicelles formation and the target

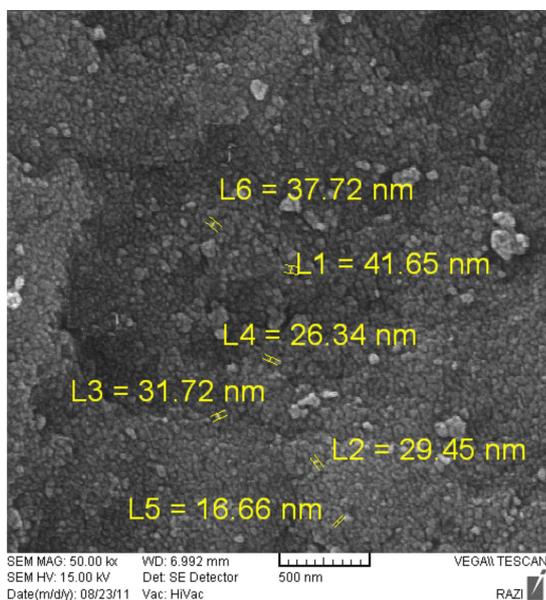


Figure 1. SEM image of the dispersed Fe_3O_4 NPs.

compound extraction. The surface charge density of Fe_3O_4 NPs is a main factor affecting the extraction of analyte and its amount varies strongly with the pH values.¹³ The effect of pH on the adsorption of carbaryl was investigated in the range between 1.5-9.5 by using 0.1 mol L^{-1} HCl or NaOH solution for pH adjustment (see Figure 2). The percent adsorption and thus analytical signal was increased by increasing pH and reached maximum at pH 3.0, then remained nearly constant up to pH 3.5 and decreased at higher pH values. Thus, a pH of 3.0 was chosen for all subsequent experiments and HCl solution used for the pH adjustment.

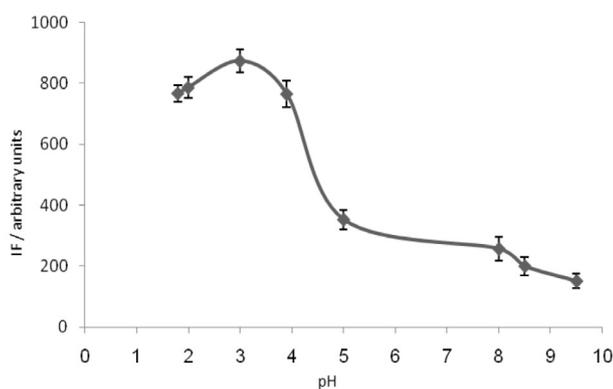


Figure 2. The effect of pH on the analytical signals.

The surface charge of bare Fe_3O_4 NPs is neutral at the pH ca. 6.5 ($\text{pH}_{\text{zpc}} = \text{pH}$ zero point charge).^{8,13,17} Therefore, it is concluded that the surface of these particles has a positive charge at acidic pHs. The positively charged surface of Fe_3O_4 NPs in acidic solutions was favorable for the adsorption of anionic surfactants and thus targeted analyte.

When pH was above the isoelectric point of the Fe_3O_4 NPs, the positive charge density on the surface of the Fe_3O_4 NPs is decreased, thus the adsorption of SDS molecules on NPs surfaces becomes less favorable^{8,11,13,17} and this could lead to a remarkable depression in the analytical signal. However, in quite acidic medium, the analytical signal was decreased probably due to dissolution of Fe_3O_4 NPs at pHs below 2 or protonation of SDS molecules, which could reduce the hemimicelles formation efficiency.¹³

The amounts of Fe_3O_4 NPs and sample volume

Compared to ordinary sorbents (micron-size particle sorbents), NP sorbents have higher surface areas. Therefore, satisfactory results can be achieved with fewer amounts of NP sorbents. The influence of MNPs content was studied by adding different amounts of Fe_3O_4 suspension, ranging from 1-6 mL. The results showed that an amount of 5 mL of suspension was the optimum value.

Effect of sample volume on the adsorption of carbaryl was studied so, the 50, 100, 150 and 200 mL solutions containing 100 $\mu\text{g L}^{-1}$ carbaryl were selected. Then adsorption and desorption processes were performed under the optimum conditions as described in experimental section. The results showed that the carbaryl present in the volumes up to 100 mL was completely and quantitatively adsorbed with NPs. The adsorption then remained constant at higher volumes. Therefore, for determination of trace quantities of carbaryl in samples, a sample volume of 100 mL was selected.

Effect of SDS amount

It was observed that MNPs can't adsorb carbaryl from aqueous solution at all, while their SDS modified form adsorbed carbaryl efficiently. The adsorption of surfactants on the surface of mineral oxides is a favorable process and based on the added surfactants, they can form various aggregates on the surface (i.e., hemimicelles, mixed hemimicelles and admicelles), below and above the critical micelles concentration (CMC).^{6,8,17} In this study, SDS was added to the solution at concentrations lower than its CMC (2.3 g L^{-1})²⁹ to modify the surface of Fe_3O_4 NPs. The effect of SDS amounts on the adsorption of carbaryl was considered in the ranges of 15-180 mg for the surfactant when 100 mL of water containing 100 $\mu\text{g L}^{-1}$ of carbaryl was used (see Figure 3). According to the results, with increase in the SDS amount, the adsorption amount of the carbaryl increased remarkably. The increase in adsorption can be explained by the gradual formation of SDS aggregates on the Fe_3O_4 NP surface and the carbaryl is adsorbed gradually. Maximum adsorption was

obtained when SDS amounts were between 50-90 mg. At higher amounts of SDS, the adsorption of carbaryl decreased gradually due to formation of SDS aggregates in the solution, which can compete with formation of SDS aggregates on the surface of Fe_3O_4 . Given these findings, 80 mg of SDS (final concentration of $400 \mu\text{g mL}^{-1}$) was selected for the next studies.

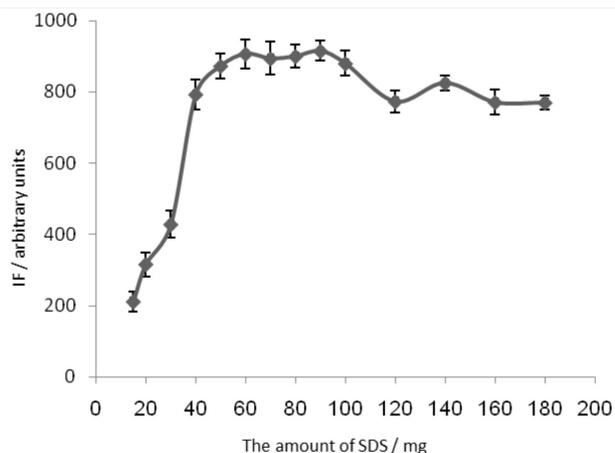


Figure 3. The effect of SDS amount on the analytical signals.

Extraction time

In the SPE process, the shaking time is one of the prime factors influencing the target analytes extraction. The extraction time profiles were studied by varying the mixing time of MNPs-sample suspension in the range of 1-10 min. Results reveals that a rapid extraction could occur in about 5 min. The high surface area of MNPs along with homogeneous distribution of the nano-sorbent throughout the sample could be the possible reasons for achieving such a fast extraction process. Thus, a short shaking time of 5 min was selected for adsorption in subsequent experiments.

Desorption condition

Organic solvents can rapidly and completely disrupt the mixed hemimicelles and therefore the analyte is removed from the surface of NPs. In this work, methanol, ethanol, acetone and acetonitrile were studied for desorption of analyte from the SDS-coated Fe_3O_4 NPs by gently shaking the solution. The maximum signal was observed when methanol was used. Therefore, desorption of analyte was carried out by using 2×2.5 mL of methanol. For achieving the more efficient desorption condition, desorption time was investigated in the range of 1-10 min. A duration time of 5 min appeared to be sufficient for complete desorption.

Analytical parameters

Under the optimum experimental conditions, calibration graphs were obtained by extraction of 100 mL of standard solutions and under the experimental conditions specified in the procedure. The calibration curve for the detection of carbaryl was linear over the concentration range of 2 to $100 \mu\text{g L}^{-1}$. The corresponding fitted equation was $\text{FI} = 7.23(\pm 0.51) C + 14.18(\pm 0.92)$ ($n = 9$) and the coefficient of correlation (r^2) was 0.9989. In this equation, the FI is the fluorescence intensity and C is the carbaryl concentration in $\mu\text{g L}^{-1}$. The relative standard deviation (RSD) obtained for the repetitive determinations of $50 \mu\text{g L}^{-1}$ of carbaryl was found to be 6.2% ($n = 6$). The limit of detection (LOD) and quantification (LOQ) by using the criterion $3S_b/m$ and $10S_b/m$, were found to be 2.1 and $6.9 \mu\text{g L}^{-1}$, respectively, where S_b is the standard deviation of the blank measurements and m is the calibration slope.

In order to highlight the advantageous features of the proposed method, its performance in the extraction of carbaryl was compared with other methods reported in the literature. The distinct features of these methods are summarized in Table 1. Compared with references^{21,30-34} which use GC-MS or HPLC for the determination of targeted analyte, the proposed method does not require high investment and maintenance costs of the instruments. Also, it is evident that the concentration factor (C_F) obtained with the SDS-coated Fe_3O_4 NPs is relatively high in comparison with some of these methods.^{31,34-36} More importantly, our LOD is comparable to or even better than some of these methods which use very sensitive detection techniques.^{31,33-37}

Mukdasai *et al.*³⁷ has used a two-step micro-extraction method for the extraction of carbaryl. This method is based on the derivatization reactions for both carbaryl and its SPE sorbent, which is a laborious and time-consuming method. This method uses a high concentration factor (i.e., 2730); however, our LOD is approximately ten times better than that reported in this work. The second method uses graphene (G) grafted silica-coated Fe_3O_4 nanocomposite for the extraction of carbaryl and its determination by HPLC.³⁸ Some reported features in this work are better than our method. But a simple, rapid and low-cost spectrofluorimetric method in combination with a different sorbent has been adopted in this work for the extraction and determination of carbaryl.

The validation and application of the method

The present method was validated by different water samples spiked with known amount of carbaryl. As shown

Table 1. Analytical characteristics of different methods used for extraction and determination of carbaryl

Extraction/determination method	Sample	Concentration range / ($\mu\text{g L}^{-1}$)	r^2	RSD / %	LOD / ($\mu\text{g L}^{-1}$)	Mean recovery / %	C_F	Ref.
DLLME/GC-MS/MS	water	0.08-40	0.9989	7.3-8.0	1.0-3.1 ($\times 10^{-3}$)	98.0-127.0	100	21
DLLME/HPLC(UV)	water	1-10 ($\times 10^3$)	0.9980	4.5	0.1	66.3-97.6	100	30
DLLME- MEC(DAD)	juice	4-200	0.9940	3.5-6.9	1.0	93.4-101.7	100	31
DLLME/HPLC(F)	water & FJ	0.1-1000	0.9999	2.7	12.3 ($\times 10^{-3}$)	96.3-114.2	87	32
DLLME/HPLC(DAD)	water	5-500	0.9994	5.1	1.3	82.0-93.0	112	33
CPE/HPLC(UV)	fruits	0.05-10 ($\times 10^3$)	0.9998	3.6	5.0	103.0-110.0	ca. 14	34
AC-CPE/S	water & V	100-7000	0.9990	2.3	50.0	91.0-103.0	ca. 2	35
AC-CPE/F	water	20-1000	> 0.9996	< 6.0	1.9	90.7-98.6	ca. 7	36
DLME & DSPE/S	water & FJ	10-100	–	8.5	8.0	97.3-108.0	2730	37
NP-SPE/HPLC(UV)	FJ	0.5-100 ng/g	0.9956-0.9984	2.4-5.8	0.08-0.2 ng/g	–	–	38
MHM-SPE/F	water	2-100	0.9989	6.2	2.1	84.5-91.9	20	This work

GC-MS = gas chromatography-mass spectrometry; HPLC = high performance liquid chromatography; MEC = micellar electrokinetic chromatography; DAD = diode array detector; AC-CPE = acid-induced cloud point extraction; S = spectrophotometry; F = spectrofluorimetry; C_F = concentration factor; FJ = fruit juice; V = vegetables.

in Table 2, the overall recoveries of carbaryl added to water samples were in the range of 75.2 to 87.0% which were acceptable except for the river water samples. The addition of a neutral salt such as NaCl, can increase these values (up to 84.5-91.9%) due to known salting out effect.

Figure 4 shows typical excitation and emission spectra for carbaryl in different samples. The coincidence of excitation and emission spectra in this figure along with acceptable recoveries indicated that no significant matrix effect occurred in the proposed method. In order to test the applicability of the proposed method, four different water samples were collected and analyzed under the optimum conditions. The results have been summarized in Table 2.

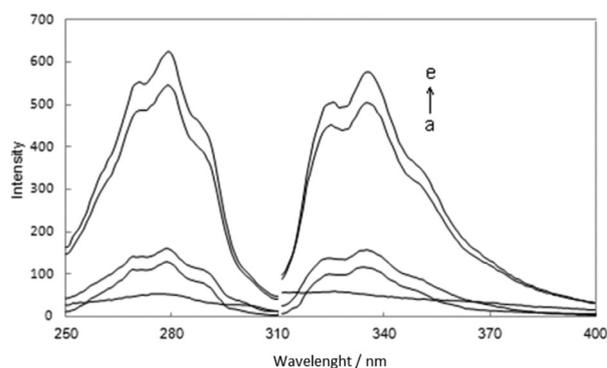


Figure 4. Excitation and emission spectra after NP based-SPE: (a) reagent's blank, (b) a blank spiked with the concentration in the range of LOQ, (c) river water sample, (d) river water spiked with carbaryl at $60 \mu\text{g L}^{-1}$ and (e) standard solution of carbaryl ($75 \mu\text{g L}^{-1}$).

Table 2. Results of recoveries of spiked water samples

Sample	Added / ($\mu\text{g L}^{-1}$)	Found \pm SD (n = 3) / ($\mu\text{g L}^{-1}$)	Recovery / %
Tap water	–	nd	–
	20.0	17.40 ± 1.12	87.0 (90.3) ^a
	40.0	34.10 ± 2.15	85.2 (89.5) ^a
Well water	–	5.33 ± 0.32	–
	20.0	21.50 ± 1.33	80.9 (85.6) ^a
	40.0	38.50 ± 2.64	82.9 (88.3) ^a
River water	–	8.87 ± 0.56	–
	20.0	23.90 ± 1.57	75.2 (84.5) ^a
	40.0	40.10 ± 2.60	78.1 (89.3) ^a
Bottled mineral water	–	nd	–
	20.0	17.00 ± 1.05	85.0 (91.9) ^a
	40.0	33.60 ± 2.22	84.0 (90.6) ^a

^aRecoveries in the presence of NaCl (5% m/v); nd = not detected.

By considering the guidelines for carbaryl in drinking water, the merit of analytical figures indicates that the present method is sensitive enough for the monitoring of carbaryl in different water samples. On the other hand, the carbaryl concentration in these samples was lower than specified levels.

Conclusions

In this work, SDS-coated Fe₃O₄ NPs combined with spectrofluorimetric detection was developed for the extraction and determination of carbaryl in different water samples. The proposed method offers a simple, safe, sensitive, and inexpensive method for extraction and determination of carbaryl. Method validation using spiked real samples demonstrated that the method is capable of detecting trace carbaryl with adequate trueness and precision. In addition, sensitivity of the method is enough for the determination of carbaryl in variety of environmental samples. The proposed methodology possessed several advantages like simplicity, proper preconcentration factor and low cost, especially if more sophisticated techniques such as HPLC or GC are not available.

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