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Magnetic titanium oxide nanoparticles for hemimicelle extraction and HPLC determination of organophosphorus pesticides in environmental water

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Abstract We report on a method for the extraction of organophosphorus pesticides (OPPs) from water samples using mixed hemimicelles and magnetic titanium dioxide nanoparticles (Fe_3O_4@TiO_2) modified by cetyltrimethylammonium. Fe_3O_4@TiO_2 nanoparticles were synthesized by a hydrothermal process and then characterized by scanning electron microscopy and Fourier transform IR spectrometry. The effects of the quantity of surfactant, extraction time, desorption solvent, pH value, extraction volume and reuse of the sorbent were optimized with respect to the extraction of OPPs including chlorpyrifos, dimethoate, and trichlorfon. The extraction method was applied to analyze OPPs in environmental water using HPLC along with UV detection. The method has a wide linear range (100–15,000 ng L^{-1}), good linearity (r>0.999), and low detection limits (26–30 ng L^{-1}). The enrichment factor is ~1,000. The recoveries (at spiked levels of 100, 1,000 and 10,000 ng L^{-1}) are in the range of 88.5–96.7 %, and the relative standard deviations range from 2.4 % to 8.7 %.

Keywords Organophosphorus pesticides · Magnetic titanium dioxide · Mixed hemimicelle · Environmental water

Introduction

Organophosphorous pesticides (OPPs) are widely used for agricultural activities due to their relatively low price and effective ability to control pests, weeds and diseases [1]. Many of these compounds display high toxicity and have been shown to result in high levels of acute neurotoxicity [2] and carcinogenicity [3]. The OPPs are a kind of abundant environmental and food chain pollutants and have attracted increasing global attention with respect to human, animal and insect health [2].

In recent years, the methods of extraction and determination of OPPs have been reported commonly. Determination of OPPs in water samples is usually performed by gas chromatography (GC) with mass spectrometry (MS) [4, 5], nitrogen phosphorus detection (NPD) [6], flame photometric detection (FPD) [7] and high-performance liquid chromatography (HPLC) followed by UV detector [8, 9], or mass spectrometry (MS) [10]. Before analysis, due to the complexity of the sample matrices, their incompatibility with the desired instrumental method and low concentrations of the analytes in water, a preliminary sample preconcentration and/or separation technique is required [7]. Solid-phase extraction (SPE) [4, 5, 10], solid-phase microextraction (SPME) [11], cloud point extraction (CPE) [8], single drop microextraction (SDME) [12], ultrasound-assisted emulsification microextraction (USAEME) [13], liquid phase microextraction (LLME) [14] and dispersive liquid – liquid microextraction (DLLME) [15, 16] have been used for preparation of water samples containing OPPs.

It is well known that, in traditional SPE mode (column passing) which was used in most papers, the recoveries of analytes may be decreased when the loading flow rate is too high due to the decrease of the interaction time between the analytes and the binding sites of sorbent. The low loading flow rate would increase the extraction time when analyzing a large volume of sample, especially an environmental one [17]. Moreover, magnetic solid-phase extraction (MSPE) technology can avoid such disadvantages successfully. A

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distinct advantage of this technology is that the separation process can be performed directly in crude samples [18].

Hemimicelles and admicelles have been recently used as sorbent materials for the SPE of organic compounds [19–21]. During adsorption of ionic surfactants on metal oxides surface, electrostatic interactions between ionic head groups and the surface result in neutralization of surface charge at low concentration of surfactants [22]. Currently magnetic hemimicelle was reported to separate phenolic compounds [23], mercury [24], anionic dye [25], malachite green and leuco-malachite green [26].

In this work, the aim of study was to develop a novel and rapid method for determination of OPPs in large volume water samples, including chlorpyrifos, dimethoate and trichlorfon which were widely used [27–29]. This method was based on magnetic titanium dioxide ($Fe_3O_4@TiO_2$) modified with cetyltrimethylammonium bromide (CTAB) extraction followed by HPLC analysis. Scanning electron microscopy (SEM), Fourier-transform infrared spectrometry (FTIR) and physical property measurement system (PPMS) were applied to the characterization of $Fe_3O_4@TiO_2$. The optimization pretreatment procedure for OPPs was conducted to obtain satisfactory recoveries of OPPs.

Experimental

Chemicals

The standards of chlorpyrifos, dimethoate and trichlorfon were purchased from Sigma-Aldrich (St. Louis, MO, USA, http://www.sigmaaldrich.com/united-states.html). Chromatographic grade acetonitrile was obtained from Fisher (Pittsburgh, PA, USA, http://www.fishersci.com.cn/cn/). Iron (II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), titanium tetrachloride ($TiCl_4$) was purchased from Aladdin (Shanghai, China, http://www.aladdin-reagent.com/). Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) was obtained from Yaohua (Tianjin, China, http://ccn.mofcom.gov.cn/199978). Ammonium hydroxide ($NH_3 \cdot H_2O$, 25 %), acetic acid (CH_3COOH), sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Guangfu (Tianjin, China, http://guangfuhuashi.cn.china.cn/). CTAB, methanol and ethanol were obtained from Kermel (Tianjin, China, http://www.chemreagent.com/). High purity water was obtained from a Milli-Q Water System (Millipore, Billerica, MA, USA, http://www.millipore.com/).

Three river water samples were collected from Harbin (China). All water samples which were stored at 4 °C. The spiked water samples were made by adding certain amounts of mixed stock solution of OPPs to the real water samples.

Standard solution preparation

Mixed stock solution of chlorpyrifos, dimethoate and trichlorfon (1 mg mL^{-1}) was prepared in methanol, which was stored in refrigerator at 4 °C. The working solutions were prepared daily by diluting the stock solution.

Apparatus

$Fe_3O_4@TiO_2$ was characterized by SEM (FEI Sirion, Phillips, Netherlands, http://www.philips.com.cn/), FTIR (Nicolet 360, Nicolet, Madison, WI, USA, http://www.artisan-scientific.com/69062.htm). The magnetic property of the prepared $Fe_3O_4@TiO_2$ was investigated with PPMS (Quantum Design Instrument, San Diego, CA, USA, http://www.qdusa.com/). Chromatographic analysis was performed on a LC-15C high performance liquid chromatograph (Shimadzu, Kyoto, Japan, http://www.shimadzu.com.cn/) with UV detector. A SZCL-4A digital display thermostat magnetic stirrer (Zhengzhou, China, http://zzyarong.testmart.cn/) was used in the extraction process. A KQ5200E ultrasonic apparatus (Kunshan Instrument, Kunshan, China, http://www.ks-csyq.com/) was used for assisting elution of OPPs from magnetic material.

Preparation of $Fe_3O_4@TiO_2$

The Fe_3O_4 magnetite was prepared firstly by a co-precipitation method, briefly, 0.01 mol $FeCl_2 \cdot 4H_2O$ and 0.02 mol $FeCl_3 \cdot 6H_2O$ were dissolved in water (100 mL). Then 10 mL ammonium hydroxide was added at 80 °C and the mixture was stirred for 1 h at 500 rpm under N_2 stream. After synthesis, the precipitation was separated by Nd-Fe-B permanent magnet and washed with purity water to pH 7.0.

$Fe_3O_4@TiO_2$ was synthesized with hydrothermal method. Magnetic Fe_3O_4 (1.0 g) was dispersed into about 50 mL water. One milliliter of $TiCl_4$ was added rapidly with stirring vigorously. The system was adjusted to about pH 9.0 with NaOH solution and stirred for 10 min to generate titanium dioxide precursor. Then the precursor was transferred into reaction still and annealed at 150 °C for 6 h. The precipitation was washed to pH 7.0 and then dried at 100 °C for 10 h.

Extraction experiment

The extraction experiment was conducted as follows. $Fe_3O_4@TiO_2$ (100 mg) and CTAB (100 mg) were added into a 500 mL water sample and then the solution was stirred for 20 min at ambient temperature. Afterwards the solid was separated by Nd-Fe-B permanent magnet and then the adsorbent was eluted by 3×1 mL acetonitrile-acetic acid solution (99.5: 0.5, v/v) assisted with sonication for 10 s. The eluate was combined and evaporated to near dryness under a nitrogen stream and was dissolved by chromatographic mobile phase, 85 % aqueous acetonitrile solution (0.5 mL). The eluate was filtered by filtration membranes of 0.22 μm. A 20 μL of this solution was injected into the HPLC system for analysis. Illustration of the whole procedure of the preparation of CTAB coated $Fe_3O_4@TiO_2$ and its application as SPE sorbent for enriching OPPs can be followed in Fig. 1.

Chromatographic conditions

The analysis of OPPs was performed by HPLC. A Zorbax SB-C18 column (150 mm×4.6 mm I.D., 5 μm) (Palo Alto, CA, USA, http://www.home.agilent.com/agilent/home.jspx?cc=CN&lc=chi) was used as an analytical column. The column temperature was kept at ambient temperature, and the injection volume was 20 μL. Chromatographic mobile phase was 85 % aqueous acetonitrile solution (acetonitrile: H_2O 85: 15, v/v). The detection wavelength was 210 nm, and the flow rate of mobile phase was 1.0 mL min^{-1}. The chromatogram of OPPs in spiked water sample was shown in Fig. 2.

Results and discussion

Characterization of $Fe_3O_4@TiO_2$

The SEM image of $Fe_3O_4@TiO_2$ was shown in Fig. 3a. It can be seen that they have nearly uniform distribution of particle size ranging several tens nanometer, which provides significantly large surface area.

In Fig. 3b the typical FTIR spectra of Fe_3O_4 (a) and $Fe_3O_4@TiO_2$ (b) were shown. As can be seen, the major peak at 589 cm^{-1} was corresponding to the characteristic absorption of Fe-O bond [30]. Moreover, the shoulder-like band at 641 cm^{-1} was attributed to the Ti–O stretching modes of the anatase TiO_2 [31], which also proved that titanium combined with magnetite successfully. The peaks at 1,636 cm^{-1} and 3,423 cm^{-1} were attributed to water absorbed [32].

The smooth curve of hysteresis loop of $Fe_3O_4@TiO_2$ at room temperature was shown in Fig. 3c. As can be seen, the saturation magnetization of the synthesized $Fe_3O_4@TiO_2$ was 28.6 emu g^{-1}. The synthesized $Fe_3O_4@TiO_2$ could be separated with additional magnetic field efficiently. As shown in Fig. 3c (inset), in the presence of an external magnetic field, the brown adsorbents were attracted to the wall of vial in a short time, in comparison with a brown homogeneous dispersion exists without an extrinsic magnetic field.

Optimization of the extraction conditions

The extraction conditions were optimized by analyzing recoveries of chlorpyrifos, dimethoate and trichlorfon in spiked water samples. The parameters affecting the performance of the extraction, for instance, the amount of surfactant, extraction time, desorption solvents, pH, extraction volume and reuse of the sorbent were investigated. When one parameter was changed, the other parameters were fixed at their optimal values. In all batch experiments, 100 mg of $Fe_3O_4@TiO_2$ was utilized in each water sample.

Effect of the amount of surfactant

The outer surface of hemimicelles is hydrophobic whereas that of admicelles is ionic, which provides different

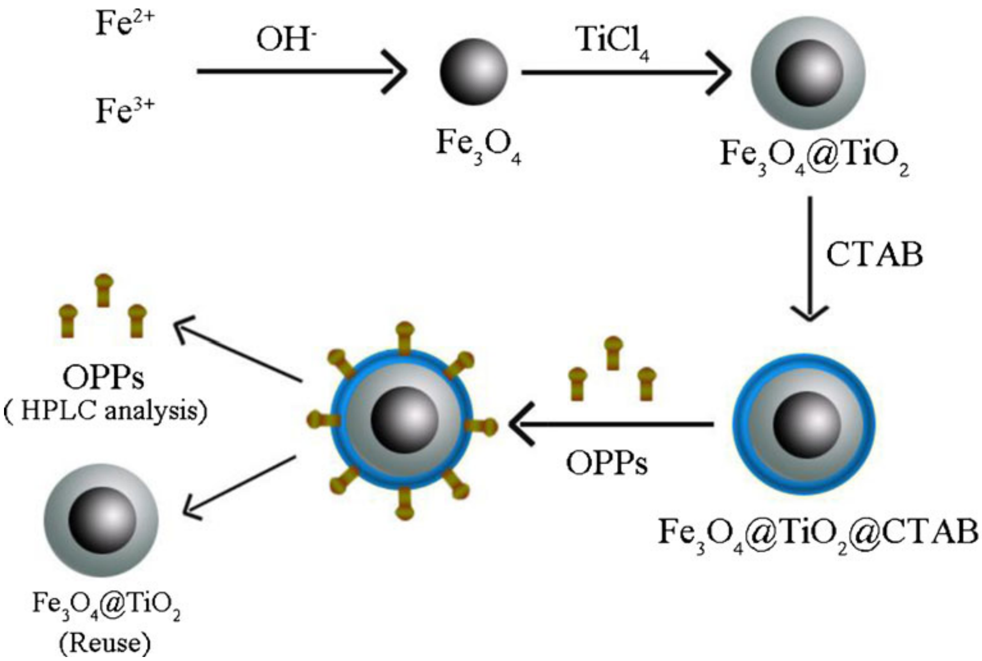

Fig. 1 Schematic illustration of the preparation of CTAB coated $Fe_3O_4@TiO_2$ and its application as SPE sorbent for enriching OPPs

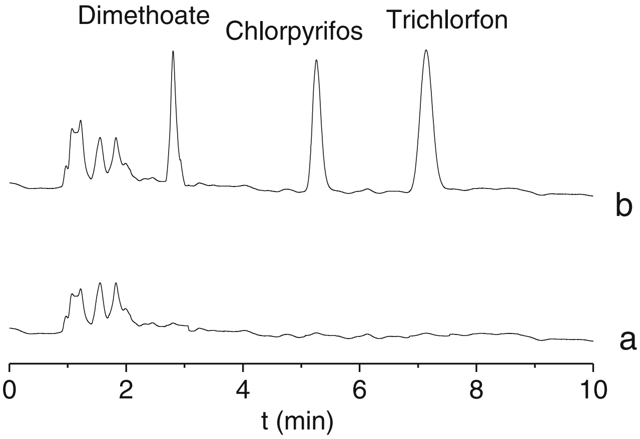

Fig. 2 The chromatogram of one of the water samples before (**a**) and after (**b**) spiking with OPPs

mechanisms for retention of organic compounds and are both suitable for the SPE method. In mixed micelles phase, both hemimicelles and admicelles are formed on the surface of mineral oxides and the adsorption is driven by both hydrophobic interaction and electrostatic attraction [23]. In the work, the ranges of 0 to 180 mg of CTAB for 100 mg of Fe_3O_4@TiO_2 were added into water samples (500 mL). In the absence of CTAB, the proportion of OPPs compounds adsorbed was lower with recoveries in the range of 28.2 %–46.1 %. As can be seen in Figure S1a, with the augmenting amount of surfactant, the recoveries of OPPs increased gradually, however, the adsorption decreased when the amount of CTAB was above 140 mg. When more surfactant was used, the mixed micelles on the surface of Fe_3O_4@TiO_2 reached saturation, and the concentration of micelles in aqueous solution increased which caused partition of analytes into aqueous phase [33]. Finally 100 mg of CTAB was selected for further experiments.

Effect of extraction time

In order to realize the most efficient extraction, the effect of extraction time on adsorption was investigated. The adsorption process of OPPs from water samples must equilibrate for enough time to obtain satisfactory recoveries. Figure S1b depicted that 20 min was sufficient for achieving complete adsorption with recoveries of three OPPs were above 93 %.

Desorption solvents

Desorption of analytes from the magnetic adsorbents was studied using different organic solvents including acetonitrile, methanol and ethanol. The better recoveries were obtained when acetonitrile was used. Desorption solution containing a small amount of acetic acid was also reported [17]. Thus acetonitrile -acetic acid (99.5: 0.5, v/v) and acetonitrile -acetic acid (99: 1, v/v) served as desorption solution. Figure S1c illustrated that 0.5 % acetonitrile-acetic acid solution has much stronger eluting power compared with other elution solvents. Quantitative recoveries of OPPs ranging from 91.4 % to 96.1 % were obtained with 3×1 mL acetonitrile-acetic acid solution (99.5: 0.5, v/v) assisted with sonication.

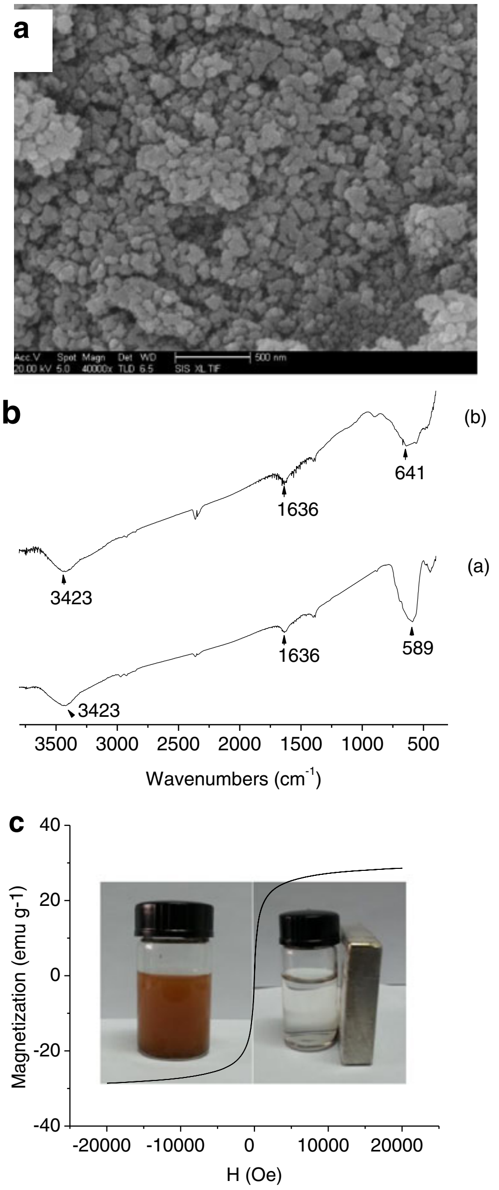

Fig. 3 The SEM images (**a**), IR spectrum (**b**) and hysteresis loop (**c**) of Fe_3O_4@TiO_2

pH conditions

pH is one of the prime factors influencing the adsorption behavior of a mixed hemimicelles system due to the different charge density of Fe_3O_4@TiO_2 surface at different pH conditions. When pH of the solution is above its point of zero charge (PZC), the surface of $Fe_3O_4@TiO_2$ is negatively charged, oppositely, its surface is positively charged. It was reported that the PZC of TiO_2 was about 5.8 [34]. That is to say, CTAB, a kind of cationic surfactant, can have a combination on the surface of TiO_2 in neutralization when pH of the solution was above 5.8. In this study, pH ranging from 3 to 8 was employed to examine the effect of pH on the adsorption. As shown in Figure S1d, CTAB coated $Fe_3O_4@TiO_2$ did not exhibit good adsorption for OPPs in pH below 6. The high recoveries of OPPs (93.1 %–96.5 %) were obtained at pH 7. Moreover the slightly decreased recoveries in the condition of pH 8 may be attributed to degradation of OPPs in alkaline medium [35].

Maximal extraction volume

The effect of solution volume on the enrichment of OPPs was examined by preconcentrating different volumes (300–800 mL) of aqueous solutions spiked with OPPs in the optimal conditions. Quantitative recoveries of OPPs (93.1–96.1 %) were obtained up to 500 mL. When the aqueous solution volume was 600 and 700 mL, the adsorption rate decreased to 88.3–92.8 % and 77.1–79.5 % respectively (Figure S1e). Thus, 500 mL was considered to be the maximal enrichment volume for water samples. By enriching 500 mL of aqueous solutions, drying 3 mL of desorption solution and redissolving the analytes in 0.5 mL of chromatographic mobile phase, concentration factor of 1,000 was achieved.

Reuse of the sorbent $Fe_3O_4@TiO_2$

The investigation of the ability of the sorbent to reuse to extract the analytes is of value since it will reduce the overall cost. After each extraction, the sorbent was easily recovered by the magnetic separation. Recycling experiments showed $Fe_3O_4@TiO_2$ was reusable under the investigated sorption conditions, preserving almost over 90 % of its initial sorption capacity after five cycles of reuse as shown in Figure S1f. Moreover, no memory effect was found when $Fe_3O_4@TiO_2$ was reused.

Adsorption kinetics

Adsorption kinetics which controls efficiency of the adsorption process was studied according to experiment results in "Effect of extraction time" section (Figure S1b). The adsorption amount of OPPs increased with increasing extraction time, and then remained constant. Two of the most widely used kinetic models, i.e. pseudo-first-order equation and pseudo-second-order equation were used to research the adsorption kinetic behavior of OPPs. The best-fit model was selected based on the linear regression correlation

Table 1 Comparison of the reported methods on the separation and determination of OPPs in water samples

Pretreatment method	Detection technique	Sample volume (mL)	Extraction Time	Concentrationfactor	Detection limit (ng L^{-1})	Recovery (%)	Precision (RSD, %)	Reference
Solid phase extraction	GC-MS	1000	250 min	1000	6.00×10^{-3}–8.50×10^{-1}	70.3–114.3	< 15.0	[4]
Solid phase extraction	GC-NPD	10	7.5 min	100	50–130	93.8–104.5	2.9–4.3	[6]
Cloud point extraction	HPLC-UV	10	15 min	20	30–28450	62.6–84.5	0.5–5.5	[8]
Dispersive liquid–liquid microextration	GC-FID	10	5 s	100	100	96.0–110.0	3.0–13.0	[15]
Dispersive liquid–liquid microextraction	HPLC-DAD	20	1 min	216–557	100–300	82.2–104.0	3.4–5.7	[16]
Magnetic titanium oxide nanoparticles for hemimicelle extraction	HPLC-UV	500	20 min	1000	26.8–30.2	88.5–96.7	2.4–8.7	This method

coefficient values (r). The pseudo-first-order and pseudo-second-order kinetic model [36, 37] were given as follows:

$$\log\left(Q_{eq}-Q_t\right) = \log\ Q_{eq}-\frac{k_1 t}{2.303} \tag{1}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 {Q^2}_{eq}}+\frac{t}{Q_{eq}} \tag{2}$$

where Q_t (μg g^{-1}) represents the amount adsorbed of OPPs at time t and Q_{eq} (μg g^{-1}) at equilibrium. k_1 (min^{-1}) and k_2 (g μg^{-1} min^{-1}) are the rate constant of pseudo-first order and pseudo-second-order which can be calculated from the plot of ln ($Q_{eq}-Q_t$) versus t and t/Q_t versus t, respectively. The analysis results including the regression equation and correlation coefficients (r) were:

Pseudo-first-order model:

$$\begin{array}{lll} \text{Chlorpyrifos}: & y = -0.1158x + 3.2567, & r = 0.967 \\ \text{Dimethoate}: & y = -0.1115x + 3.6542, & r = 0.974 \\ \text{Trichlorfon}: & y = -0.077x + 3.1543, & r = 0.948 \end{array}$$

Pseudo-second-order model:

$$\begin{array}{lll} \text{Chlorpyrifos}: & y = 0.018x + 0.0708, & r = 0.992 \\ \text{Dimethoate}: & y = 0.0164x + 0.1278, & r = 0.990 \\ \text{Trichlorfon}: & y = 0.0189x + 0.0605, & r = 0.998 \end{array}$$

Through the calculation of r, the adsorption data are well represented by pseudo-second-order kinetic model.

Analytical performance

The specificity of the method was checked by analyzing different blank water samples. No interfering peaks and false positive results were observed in the blank chromatograms, which indicated that the selectivity of the method is good.

The stability of analytes in standard solution was also checked. Stock solutions of the analyte standards (1 mg mL^{-1}) were found to be stable for 1 month at 4 °C in a refrigerator.

Quantitative parameters such as linear range, correlation coefficient, detection limit (LOD) and quantification limit (LOQ) were evaluated. The linearity was in a range of 100–15,000 ng L^{-1}. The correlation coefficient was between 0.9995 and 0.9997. LOD and LOQ in water samples was defined as the concentration providing three and ten times of signal-to-noise ration, respectively. The LODs obtained were 28.6, 30.2 and 26.1 ng L^{-1} for chlorpyrifos, dimethoate and trichlorfon, respectively. The LOQs obtained were 94.3, 100.5 and 92.1 ng L^{-1} for chlorpyrifos, dimethoate and trichlorfon, respectively. Furthermore, it should be point out that if MS detection was employed instead of UV detection in this study, the sensitivity of the developed method would be higher and the detection limit could reach lower.

Environmental water sample analysis

In this work, the method was applied to three environmental water samples obtained at random in different rivers in Harbin, China. No OPPs at detectable levels were found in these water samples. The recovery study was carried out by spiking environmental water samples with the OPPs at the level of 100, 1,000, and 10,000 ng L^{-1} (Table S1). The relative standard deviations (RSDs) obtained were ranging from 2.4 % to 8.7 %. In all three fortified levels, recoveries of OPPs are in the range of 88.5–96.7 %.

Important features of this method were compared with other reported methods [4, 6, 8, 15, 16] (Table 1). The detection limit, recovery, precision and concentration factor obtained in this work were comparable with other methods. This method can obtain a high concentration factor in short time, which was appropriate to analyzing large volume water samples. Moreover, magnetic adsorbents can facilitate separation process without the need of additional centrifugation or filtration procedures.

Conclusion

In this work, Fe_3O_4@TiO_2 was successfully synthesized and a new type of Fe_3O_4@TiO_2 mixed hemimicells solid phase extraction method was studied. This method was used for extraction and preconcerntration of OPPs from large volume water samples. The analytes were then determined by HPLC. Concentration factor of 1,000 was achieved in this method to extract 500 mL of water samples. The experiment was proved that the Fe_3O_4@TiO_2 can be reused at least five times without the obvious decrease of recovery of OPPs. Moreover, this method avoided the time consuming elution from a column or filtration potential in the separation, purification and concentration of analytes in large volume of environmental water samples.

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References

1. Barata C, Solayan A, Porte C (2004) Role of B-esterases in assessing toxicity of organophosphorus (chlorpyrifos, malathion) and carbamate (carbofuran) pesticides to *Daphnia magna*. Aquat Toxicol 66:125–139

2. Kamanyire R, Karalliedde L (2004) Organophosphate toxicity and occupational exposure occupational medicine. Occup Med 54:69–75
3. Alavanja MCR, Hoppin JA, Kamel F (2004) Health effects of chronic pesticide exposure: cancer and neurotoxicity. Annu Rev Public Health 25:155–197
4. Yan X, He H, Peng Y, Wang X, Gao Z, Yang S (2012) Determination of organophosphorus flame retardants in surface water by solid phase extraction coupled with gas chromatography–mass spectrometry. Chin J Anal Chem 40:1693–1697
5. Alves ACH, Gonçalves MMPB, Bernardo MMS, Mendes BS (2011) Determination of organophosphorous pesticides in the ppq range using a simple solid-phase extraction method combined with dispersive liquid–liquid microextraction. J Sep Sci 34:2475–2481
6. Ballesteros E, Parrado MJ (2004) Continuous solid-phase extraction and gas chromatographic determination of organophosphorus pesticides in natural and drinking waters. J Chromatogr A 1029:267–273
7. Samadi S, Sereshti H, Assadi Y (2012) Ultra-preconcentration and determination of thirteen organophosphorus pesticides in water samples using solid-phase extraction followed by dispersive liquid–liquid microextraction and gas chromatography with flame photometric detection. J Chromatogr A 1219:61–65
8. Sanz CP, Halko R, Ferrera ZS, Rodríguez JJS (2004) Micellar extraction of organophosphorus pesticides and their determination by liquid chromatography. Anal Chim Acta 524:265–270
9. He L, Luo X, Xie H, Wang C, Jiang X, Lu K (2009) Ionic liquid-based dispersive liquid–liquid microextraction followed high-performance liquid chromatography for the determination of organophosphorus pesticides in water sample. Anal Chim Acta 655:52–59
10. Deme P, Azmeera T, Kanjilal S, Jonnalagadda P, Upadhyayula VS (2012) LC-MS/MS determination of organophosphorus pesticide residues in coconut water. Food Anal Methods. doi:10.1007/s12161-012-9523-2
11. Bagheri H, Ayazi Z, Sistani H (2011) Chemically bonded carbon nanotubes on modified gold substrate as novel unbreakable solid phase microextraction fiber. Microchim Acta 174:295–301
12. Ahmadi F, Assadi Y, Hosseini SMRM, Rezaee M (2006) Determination of organophosphorus pesticides in water samples by single drop microextraction and gas chromatography-flame photometric detector. J Chromatogr A 1101:307–312
13. Wu C, Liu N, Wu Q, Wang C, Wang Z (2010) Application of ultrasound-assisted surfactant-enhanced emulsification microextraction for the determination of some organophosphorus pesticides in water samples. Anal Chim Acta 679:56–62
14. Khalili-Zanjani MR, Yamini Y, Yazdanfar N, Shariati S (2008) Extraction and determination of organophosphorus pesticides in water samples by a new liquid phase microextraction–gas chromatography–flame photometric detection. Anal Chim Acta 606:202–208
15. Hassan J, Sarkouhi M (2013) Miniaturized counter current liquid–liquid extraction for organophosphorus pesticides determination. Arab J Chem. doi:10.1016/j.arabjc.2013.02.003
16. Wu C, Liu H, Liu W, Wu Q, Wang C, Wang Z (2010) Determination of organophosphorus pesticides in environmental water samples by dispersive liquid –liquid microextraction with solidification of floating organic droplet followed by high-performance liquid chromatography. Anal Bioanal Chem 397:2543–2549
17. Chen L, Zhang X, Xu Y, Du X, Sun X, Sun L, Wang H, Zhao Q (2010) Determination of fluoroquinolone antibiotics in environmental water samples based on magnetic molecularly imprinted polymer extraction followed by liquid chromatography–tandem mass spectrometry. Anal Chim Acta 662:31–38
18. Karamani AA, Douvalis AP, Stalikas CD (2013) Zero-valent iron/iron oxide-oxyhydroxide/graphene as a magnetic sorbent for the enrichment of polychlorinated biphenyls, polyaromatic hydrocarbons and phthalates prior to gas chromatography–mass spectrometry. J Chromatogr A 1271:1–9
19. Merino F, Rubio S, Pérez-Bendito D (2004) Evaluation and optimization of an on-line admicelle-based extraction-liquid chromatography approach for the analysis of ionic organic compounds. Anal Chem 76:3878–3886
20. Merino F, Rubio S, Pérez-Bendito D (2003) Solid-phase extraction of amphiphiles based on mixed hemimicelle/admicelle formation: application to the concentration of benzalkonium surfactants in sewage and river water. Anal Chem 75:6799–6806
21. Cantero M, Rubio S, Pérez-Bendito D (2005) Determination of non-ionic polyethoxylated surfactants in wastewater and river water by mixed hemimicelle extraction and liquid chromatography–ion trap mass spectrometry. J Chromatogr A 1067:161–170
22. Parida SK, Dash S, Patel S, Mishra BK (2006) Adsorption of organic molecules on silica surface. Adv Colloid Interf 121:77–110
23. Zhao X, Shi Y, Wang T, Cai Y, Jiang G (2008) Preparation of silica-magnetite nanoparticle mixed hemimicelle sorbents for extraction of several typical phenolic compounds from environmental water samples. J Chromatogr A 1188:140–147
24. Faraji M, Yamini Y, Rezaee M (2010) Extraction of trace amounts of mercury with sodium dodecyle sulphate-coated magnetite nanoparticles and its determination by flow injection inductively coupled plasma-optical emission spectrometry. Talanta 81:831–836
25. Zargar B, Parham H, Hatamie A (2009) Fast removal and recovery of amaranth by modified iron oxide magnetic nanoparticles. Chemosphere 76:554–557
26. Afkhami A, Moosavi R, Madrakian T (2010) Fast removal and recovery of amaranth by modified iron oxide magnetic nanoparticles. Talanta 82:785–789
27. Mauriz E, Calle A, Lechuga LM, Quintana J, Montoya A, Manclús JJ (2006) Real-time detection of chlorpyrifos at part per trillion levels in ground, surface and drinking water samples by a portable surface plasmon resonance immunosensor. Anal Chim Acta 561:40–47
28. Karamfilov VK, Fileman TW, Evans KM, Mantoura RFC (1996) Determination of dimethoate and fenitrothion in estuarine samples by C-18 solid-phase extraction and high-resolution gas-chromatography with nitrogen-phosphorus detection. Anal Chim Acta 335:51–61
29. Zhu H, Liu W, Mao J, Yang M (2008) Cloud point extraction and determination of trace trichlorfon by high performance liquid chromatography with ultraviolet-detection based on its catalytic effect on benzidine oxidizing. Anal Chim Acta 614:58–62
30. Bianchi F, Chiesi V, Casoli F, Luches P, Nasi L, Careri M, Mangia A (2012) Magnetic solid-phase extraction based on diphenyl functionalization of Fe_3O_4 magnetic nanoparticles for the determination of polycyclic aromatic hydrocarbons in urine samples. J Chromatogr A 1231:8–15
31. Fan Y, Ma C, Li W, Yin Y (2012) Synthesis and properties of $Fe_3O_4/SiO_2/TiO_2$ nanocomposites by hydrothermal synthetic method. Mater Sci Semicond Process 15:582–585
32. Ojamäe L, Aulin C, Pedersen H, Käll P (2006) IR and quantum-chemical studies of carboxylic acid and glycine adsorption on rutile TiO_2 nanoparticles. J Colloid Interface Sci 296:71–78
33. López-Jiménez FJ, Rubio S, Pérez-Bendito D (2005) Determination of phthalate esters in sewage by hemimicelles-based solid-phase extraction and liquid chromatography–mass spectrometry. Anal Chim Acta 551:142–149
34. Kosmulski M (2002) The significance of the difference in the point of zero charge between rutile and anatase. Adv Colloid Interf 99:255–264
35. Heidari H, Razmi H (2012) Multi-response optimization of magnetic solid phase extraction based on carbon coated Fe_3O_4 nanoparticles using desirability function approach for the determination of the organophosphorus pesticides in aquatic samples. Talanta 99:13–21

36. Shen X, Shan X, Dong D, Hua X, Owens G (2009) Kinetics and thermodynamics of sorption of nitroaromatic compounds to as-grown and oxidized multiwalled carbon nanotubes. J Colloid Interface Sci 330:1–8

37. Pan J, Zou X, Wang X, Guan W, Yan Y, Han J (2010) Selective recognition of 2,4-dichlorophenol from aqueous solution by uniformly sized molecularly imprinted microspheres with β-cyclodextrin/attapulgite composites as support. Chem Eng J 162:910–918