Using nanometer TiO$_2$ modified with cetyl trimethyl ammonium bromide for separation and preconcentration of Parathion in water sample

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ABSTRACT

In this work, nanometer TiO$_2$ modified by cetyl trimethyl ammonium bromide (CTAB) was used as adsorbent for solid-phase extraction (SPE) of Parathion in environmental water samples. Adsorbed Parathion was then desorbed with different eluents and determined by gas chromatography (GC)/flame ionization detection. Greater selectivity, resolution, and sensitivity have been seen by GC compared with other methods. Parameters that might influence the extraction efficiency, such as the eluent type and its volume, adsorbent amount, sample volume, sample pH and sample flow rate, were optimized. Under the optimized extraction conditions with toluene as the eluent, the experimental results showed the excellent linearity of Parathion ($R^2 > 0.99$) over the range of 0.01–0.8 µg/mL, and the relative standard deviation was 6.3% ($n = 5$). The detection limit of the proposed method could reach 0.024 ng/mL based on the ratio of chromatographic signal to base line noise (S/N = 3). Recovery of 93% was achieved with spiked water samples. The method was successfully applied to the analysis of surface water samples.

Key words | CTAB, gas chromatography, nanometer TiO$_2$, Parathion, SPE

INTRODUCTION

During the last years, organophosphorus (OPP) pesticides have been widely used in agriculture due to the fact that they are inexpensive, effective in controlling pests of most crops and less persistent than other pesticides (Samadi et al. 2012; Soisungnoen et al. 2012; Zhao et al. 2014). Parathion is one of the OPP compounds. These pesticides are released to the environment, especially in surface and ground waters. Since they are acetylcholinesterase inhibitors, they are considered toxic to humans and their residues must be removed to satisfy the actual environmental regulations (Pedrosa et al. 2008; Soisungnoen et al. 2012; Zhao et al. 2014). Determination of these pesticides in environmental water requires a sensitive and accurate method. A large number of methods have been used for detection of different pesticides. For instrumental analysis, gas chromatography with flame ionization detection (GC/FID) (Pinheiro & Andrade 2009), electron-capture detection (ECD) (Dias et al. 2015), nitrogen-phosphorus detection (An & Shin 2011; Farajzadeh et al. 2014), flame photometric detection (Zhao et al. 2014), and mass spectrometric detection (Momplaisir et al. 2010; Ahmadi et al. 2015), and high performance liquid chromatography (HPLC) with UV detection (Li et al. 2013) and fluorescence detection (Azab et al. 2015) have been reported frequently. Prior to determination of the residues in samples, extraction and purification are required due to the matrices’ complexity and low concentration of analytes in sample (Li et al. 2010; Samadi et al. 2012). The solid-phase extraction (SPE), liquid-phase microextraction (LPME), solid-phase microextraction and dispersive liquid–liquid microextraction have been developed for analyte preconcentration. Among these pretreatment methods, SPE has become a well-established preconcentration technique in environmental analytical applications in recent years. SPE is an inexpensive, simple,
rapid method with high recovery and low consumption of organic solvents (Latorre et al. 2013; Khoeini Sharifabadi et al. 2014; Zhou & Fang 2015). Recently, nanostructured materials, especially metallic, silica, electrospun polymer nanofibers and carbon nanotubes, have been used as SPE adsorbent (Augusto et al. 2013; Pyrzynska 2013). For improving the solid adsorbents’ capability, their modification with cationic and anionic surfactants has been studied during the last few years (Xiong et al. 2008; Arnnok & Burakham 2014). However, there was no literature about the application of nano titanium dioxide modified with cetyl trimethyl ammonium bromide (CTAB) as SPE adsorbent for the enrichment of Parathion from environmental water samples. CTAB is a cationic surfactant that has been widely used as a surface group modifier for SPE adsorbents (Parham et al. 2012; Karimi et al. 2013). The adsorbent surface becomes hydrophobic by modification with CTAB, which increases the adsorption of organic compounds (Emmanuel & Odigie 2014). In this study, a very convenient, sensitive and economical method for simultaneous separation and preconcentration of Parathion was developed using a microcolumn packed with rutile nanometer TiO₂ modified with CTAB, and subsequent determination was done by GC/FID. Factors that may influence the enrichment of the target Parathion, such as kind and volume of eluent, sample flow rate, sample pH, sample volume and adsorbent amount, were optimized. Furthermore, the efficiency of the TiO₂ nanoparticles as adsorbent for the enrichment of selected Parathion at trace levels in surface waters was investigated.

MATERIALS AND METHODS

Reagents and solutions

Rutile nanometer TiO₂ (the diameter is 5–10 nm) was purchased from Merck. An aqueous solution of 0.02 mol/L CTAB was made by dissolving 0.72 g analytical reagent CTAB (Aldrich) in 50 mL water. Stock solutions (1.00 mg/mL) of Parathion (Figure 1) were prepared from analytical pure reagent (Merck). Toluene, methanol, ethanol, acetonitrile and dichloromethane were obtained from Merck. Standard solutions were prepared by serially diluting the stock solutions. HCl (Merck) and NaOH (Merck) solutions with the concentration of 0.1 to 2 mol/L were used to adjust the pH. Double-distilled deionized water was used throughout the experiment.

Water samples

Tap water and surface water samples were selected for validating the proposed method. Tap water sample was collected from Phase Separation & FIA Lab, Department of Chemistry, after it was allowed to flow for 10 min at a very high rate. However, dam water samples were obtained from SattarKhan and Khodafarin reservoirs. All the collected water samples were filtered through a Millipore membrane with pore size of 0.25 μm immediately after sampling and were stored in glass bottles at 25 °C. To avoid Parathion adsorption in the glass of bottles, samples were immediately extracted.

Modification of nano TiO₂ with CTAB

Rutile nanometer TiO₂ (10 g) was dispersed in 100 mL aqueous solution of 3 mol/L NaOH and placed into a teflon-lined autoclave with 80% filling factor. Then the autoclave was heated at 200 °C for 1 h to prepare the hydrolyzed nanoparticles sample. A white precipitate was isolated upon filtration and washed repeatedly with 500 mL of hot ultra-pure water until the supernatant pH value attained 9. In the second step, the aqueous solution containing the precipitate was neutralized using 0.1 mol/L HCl solution until the pH value of 7 was reached. The precipitate was then subsequently
washed with 250 mL double-distilled water to remove NaCl formed in excess. The obtained wet solids were dried in an oven at 120 °C for 1 h. Finally, nanoparticles were calcined at 700 °C under air for 20 min, then the obtained solids were dispersed in 10 mL aqueous solution of 0.02 mol/L CTAB and 90 mL double-distilled water for 30 min to prepare TiO₂ modified with CTAB. Finally, the obtained wet solids were dried in an oven at 120 °C for 20 min.

SPE procedure

A cartridge packed with 0.6 g nanometer TiO₂ modified with CTAB was prepared in a 3 mL polypropylene syringe and the ends of the polypropylene column were plugged with glass wool to retain the sorbent in the column. The packed cartridge was placed in a vacuum elution apparatus. The outlet tip of the cartridge was connected to a vacuum pump (Model DOA-P504-BN), and the inlet end of the cartridge was connected to a polytetrafluoroethylene suction tube whose other end was inserted into the sample solution. This solid phase was first conditioned with 10 mL of methanol and 10 mL of deionized water, then a known volume of sample Parathion was applied to the column. After that, the retained Parathion was eluted with an optimum volume of toluene. The amount of Parathion was determined by GC/FID and the recovery was obtained using the following equation:

\[ R (\%) = \frac{C_0 - C}{C_0} \times 100 \]

where \( R \) is recovery of Parathion, \( C_0 \) is the initial concentration and \( C \) is the equilibrium concentration of pesticide.

Instrumentation

Transmission electron microscopy (TEM) images were taken at an accelerating voltage of 200 kV on a JEOL 2010 (Japan) instrument. The analysis was performed on a gas chromatograph (GC-2014, Shimadzu, Japan) equipped with a FID and a splitless/split injector for separation and determination of the selected analytes. Helium (99.999%, Gulf Cryo, United Arab Emirates) was used as the carrier gas at a constant linear velocity of 30 cm s⁻¹. The injection port was held at 300 °C and used in the splitless/split mode with a sampling time of 1 min. Separation was carried out on an OPTIMA delta-3 capillary column (30 m × 0.25 mm i.d., and film thickness of 0.25 μm) (Macherey-Nagel, Germany). The oven temperature was programmed as follows: initial temperature 50 °C (held for 1 min), from 50 to 250 °C at a rate of 25 °C min⁻¹, from 250 °C to 300 °C at a rate of 30 °C min⁻¹, and held at 300 °C for 2 min. The FID temperature was maintained at 300 °C. Hydrogen gas was generated with a hydrogen generator (OPGU-1500S, Shimadzu, Japan) for FID at a flow rate of 30 mL min⁻¹. The flow rate of air for FID was 300 mL min⁻¹. The pH of the solutions was adjusted with electrical pH meter (Model CG 842, Camlab Ltd). A D100B peristaltic pump (Shanghai Qingpu Huxi Instrument Factory, China) was used in the separation and preconcentration process.

RESULTS AND DISCUSSION

Sorbent characterization

Figure 2 shows the TEM images of TiO₂ before and after modification with CTAB. Comparing Figure 2(a) and 2(b) shows that CTAB was successfully coated onto the TiO₂ nanoparticles, and the image shows porous and uniform size distribution of adsorbent.

Effect of sample pH

The effect of pH was investigated over the range of pH 1–12 and the results are shown in Figure 3. It was found that very low and high pH of solutions had a negative effect on the extractions. The reason is that the surface of TiO₂ is positively charged at pH values less than its isoelectric point, which is about 5.0, so the adsorption of CTAB (a cationic surfactant) molecules decreases. In alkaline pH (pH > pHzpc), due to the -OH on the surface, TiO₂ is negatively charged, so CTAB molecules are able to interact with the surface of the adsorbent. Since Parathion is a polar compound, at higher pH values (pH > 9) competition of OH ions with Parathion leads to less adsorption of sample (Liang et al. 2001; Karimi et al. 2013). When the
pH of solutions varies in the range of pH 4–9, the extraction increases. Therefore, pH = 9 was selected as the optimum pH of solutions.

**Effect of elution solvent**

To elute the Parathion from the cartridge, five types of eluents including toluene, methanol, ethanol, acetonitrile, and dichloromethane were examined. Elution of Parathion from the cartridge column was performed with 10 mL of the selected organic solvent. The recovery of Parathion is related to the solvent polarity and π–π interaction between adsorbent (solid phase) and solvent (liquid phase). The results show that toluene, with a low polarity, gave much high elution efficiency than other organic solvents. The influence of elution solvent on Parathion recovery is shown in Figure 4.
The volume of the eluent has a great effect on the elution efficiency. Eluent volumes in the range of 5–20 mL were tested. It suggested that to get the best recovery, Parathion needs a volume of eluent more than 5 mL. Thus, to achieve complete elution of the Parathion, 10 mL toluene was utilized in the experiments. Figure 5 shows the effect of eluent volumes on Parathion recovery.

**Effect of sample volume**

Different volumes (25–175 mL) of surface water were spiked with 0.1 μg/L of Parathion and preconcentrated by nanometer TiO₂ modified by CTAB packed cartridge column. The recovery decreased slightly with the increase of sample volume from 100 to 175 mL. Based on these results, the sample volume of 100 mL was selected in the subsequent analysis. Figure 6 shows the effect of sample volume on Parathion recovery.

**Effect of amount of cartridge packing**

The effect of the adsorbent amount on the recovery of Parathion was investigated. Eight different amounts were tested (0.1–0.8 g) for the preconcentration of Parathion in water. Obtained results (Figure 7) showed insignificant differences in recoveries among the different amounts of cartridge packing. Therefore, adsorbent amount of 0.6 g was recommended for the extraction of Parathion.

**Effect of sample flow rate**

Since the flow rate of the sample is an important factor for the recovery of parathion, its effect was examined under the optimum conditions over the range of 1–5 mL/min. As shown in Figure 8, optimal flow rate was 1 mL/min, which was selected for further use in this work.

**Application to environmental water samples**

To evaluate the feasibility of TiO₂ modified with CTAB in the application of environmental sample analysis, all
Figure 5 | Effect of eluent volume on Parathion recovery. Spiked sample concentration: 0.1 μg/mL; sample flow rate: 1 mL/min; sample pH: 9; sample volume: 100 mL and elution solvent: toluene.

Figure 6 | Effect of sample volume on Parathion recovery. Spiked sample concentration: 0.1 μg/mL; eluent volume: 10 mL; sample flow rate: 1 mL/min; sample pH: 9 and elution solvent: toluene.
Figure 7 | Effect of nanometer TiO$_2$ modified by CTAB amount on the Parathion recovery. Spiked sample concentration: 0.1 μg/mL; eluent volume: 10 mL; sample flow rate: 1 mL/min; sample pH: 9; sample volume: 100 mL and elution solvent: toluene.

Figure 8 | Effect of the sample flow rates on Parathion recovery. Spiked sample concentration: 0.1 μg/mL; eluent volume: 10 mL; sample pH: 9 and sample volume: 100 mL.
retained SPE conditions were assessed on real spiked water samples (tap and dam water). First, blanks of all samples were run, then 100 mL of spiked waters with Parathion level of 0.05 and 0.1 μg/mL were passed through the SPE cartridge. The analytical results of the proposed method are given in Table 1 and the chromatograms of the blank and spiked surface water are exhibited in Figure 9. Using this method, little matrix effect was found for the SPE of Parathion.

**Method characterization**

For the precision of this method, the experiment was carried out for five replicate samples spiked at 0.1 μg/mL, using the optimum conditions described above. The recovery of Parathion was 93.2% and the relative standard deviation was 6.3%. Under the conditions selected above, calibration graphs were linear in the range of 0.01–0.8 μg/mL. Calibration equations, correlation coefficient
as well as the detection limit (S/N = 3) of Parathion are illustrated in Table 2. Nanometer TiO₂ modified with CTAB, as SPE adsorbent, provided reproducible and reliable analytical results and showed a good linear correlation ($R^2 > 0.99$).

**CONCLUSION**

In this study, CTAB was used as a modifier on TiO₂ nanoparticles which enhanced the adsorption efficiency of the SPE method. The effects of sample pH, elution solvent and adsorbent amount on the recovery of Parathion were investigated. The method was efficient in the extraction of Parathion from spiked water samples, and under the optimized conditions, the method showed appropriate sensitivity (limit of detection = 0.024 ng/mL), good linearity and accuracy.

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**REFERENCES**


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**Table 2** Calibration equation, correlation coefficient and the detection limit of Parathion

<table>
<thead>
<tr>
<th>Linear range (ng/mL)</th>
<th>Calibration equation</th>
<th>$R^2$</th>
<th>Detection limit (ng/mL)</th>
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<tbody>
<tr>
<td>0.01–0.8</td>
<td>$y = 0.2802X – 0.0073$</td>
<td>0.9985</td>
<td>0.024</td>
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</tbody>
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