Development of magnetic solid-phase extraction coupled with dispersive liquid–liquid microextraction method for the simultaneous determination of biphenyl and biphenyl oxide in water samples

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A new and sensitive method, termed magnetic solid phase extraction combined with dispersive liquid–liquid microextraction (MSPE–DLLME), has been developed for the simultaneous determination of biphenyl and biphenyl oxide in water samples. Different parameters influencing the extraction efficiency, including the amount of sorbent, sorption time, type of elution solvent and its volume, type of extraction solvent and its volume, and elution time were optimized. The calibration curves were linear in the range of 0.5–100 μg/L for both of them. The limits of detection (LODs) were achieved, 0.03 μg/L for biphenyl and 0.07 μg/L for biphenyl oxide, respectively. Ultimately, the applicability of the method was successfully confirmed by the extraction and determination of biphenyl and biphenyl oxide in sea, river, tap, and water well.

Keywords: Magnetic solid-phase extraction, dispersive liquid–liquid microextraction, biphenyl, biphenyl oxide, gas chromatography

Introduction

Biphenyl is used as dry carrier for polyesters, feedstock, especially in the production of alkyl biphenyls, and a citrus fruit impregnated wrapping material to reduce spoilage. Biphenyl is also an intermediate for the production of a host of other organic compounds, such as emulsifier, optical brighteners, crop protection products, and plastics. Biphenyl oxide (BPO) is used in the production of emulsifiers, surfactant, and textile dye labeled as a chemical intermediate for the production of a host of other organic compounds, and plastics. Biphenyl is also used as a citrus fruit impregnated wrapping material to reduce spoilage and as a feedstock for the production of alkyl biphenyls. Biphenyl oxide is used as an intermediate for the production of a host of other organic compounds, such as emulsifiers, optical brighteners, crop protection products, and plastics.

Sample preparation prior to instrumental analysis is one of the most crucial steps in the overall analytical process. Generally, liquid–liquid extraction (LLE) and solid-phase extraction (SPE) are considered as the most commonly used techniques for the preconcentration of compounds from various samples [8]. SPE is a well-established method for the preconcentration and isolation of various analytes from different matrices. In SPE, selection of an appropriate sorbent is an important strategy in the elaboration of analytical procedure, and nano-sorbents have proved to be especially effective because of their high specific surface areas, highly active surface sites, and the absence of internal diffusion resistance in the separation process [9].

Magnetic nanoparticles (MNPs) have gained more attention in analytical field for trace analysis and speciation research owing to their susceptibility for bulk solution suspension, easy control, and fast magnetic separation under an external magnetic field [10, 11]. MNPs, such as Fe3O4, are good candidates for magnetic carrier technology considering the following main advantages: (1) MNPs can be produced in large quantity using a simple method, (2) it can be expected that their sorption capacity is high due to their large surface area, (3) they have strong magnetic properties and low toxicity [12, 13], and (4) these particles are superparamagnetic, which means metal-loaded sorbent can be easily separated from the treated water via an external magnetic field. However, the drawbacks of utilizing MNPs for sample preparation are their low selectivity toward target analytes, low stability in strong acidic aqueous media, and low dispersibility in various sample matrices. Therefore, the modification of MNPs with suitable coating has been proven to be one of the most efficient approaches. There has been an increasing interest in establishing new coating materials for MSPE [14, 15]. In magnetic solid phase extraction...
out on an Agilent GC-7890 system equipped with a split/splitless injector system and a flame ionization detector. Ultrapure helium gas (99.999%, Air Products, UK) was passed through a molecular sieve and oxygen trap (CRS, USA) and was used as a carrier gas with a flow rate of 2 mL/min. The injection port was held at 250 °C and operated in the splitless mode for 1 min, then split valve was opened, and a split ratio of 1:5 was applied. Separation was carried out on a DB5, 25 m × 0.32 mm i.d. and 0.25 μm film thickness from SGE (Victoria, Australia) capillary column. The oven temperature was kept at 100 °C for 2 min, and then increased to 250 °C at the rate of 10 °C/min, and was held for 3 min. The FID oven temperature was maintained at 270 °C. Hydrogen was generated by hydrogen generator (OGP-U-2200S, Shimadzu) for FID at a flow rate of 40 mL/min. The flow of air (99.999%, Air products) for FID was 400 mL/min.

The model 2010 D centurion scientific centrifuge (Westsussex, UK) was used for separation of sediment phase from sample solution.

Preparation of Magnetic Nanoparticles of Fe3O4. The chemical co-precipitation method was used in the preparation of the Fe3O4 nanoparticles (NPs) [26]. First, for preparing a stock solution, 10.4 g FeCl3·6H2O with 4.0 g FeCl2·4H2O and 1.7 mL HCl (12 mol/L) were mixed and dissolved in 50 mL deionized water in a beaker, which was then degassed using nitrogen gas for 20 min before use. Simultaneously, 500 mL of 1.5 mol/L NaOH solution was degassed (for 15 min) and heated to 80 °C in a reactor. The stock solution was then added dropwise using a dropping funnel for 30 min under nitrogen gas protection and with vigorous stirring (1000 rpm) using a glassware stirrer. During the whole process, the solution temperature was maintained at 80 °C, and nitrogen gas was used to prevent the intrusion of oxygen. After the reaction, the obtained Fe3O4 NPs precipitate was separated from the reaction medium using magnetic field and then washed four times with 500 mL of deionized water. Finally, the obtained NPs were resuspended in 500 mL of deionized water. The obtained NPs were stable under these conditions for up to about one month.

Preparation of the PPy/Fe3O4 Nanocomposites. The PPy–Fe3O4 nanocomposites were synthesized via in situ polymerization of Py monomer in the presence of FeCl3 as oxidant at an ambient temperature, where suspended Fe3O4 nanoparticles were encapsulated by the precipitating PPy moieties. In a typical polymerization technique, 0.2 g FeCl3 was added into 25 mL deionized water in a conical flask and ultrasonicated for 10 min for better dispersion of Fe3O4 into water. Three grams of FeCl3 oxidant was added into the deionized water containing Fe3O4 and was shaken for 10 min. To this mixture, 0.8 mL of polyacrylamide was syringed. Then, the reaction mixture was kept under constant shaking for 3 h at ambient temperature. Finally, to stop the reaction, acetone was added into the reaction mixture. The black powder obtained was filtered, washed with distilled water until the filtrate became colorless, and finally washed with acetone. Then, the composites were dried at 100 °C for 8 h.

MSPE–DLLME Procedure. 10 mL of the aqueous sample solution was transferred to a beaker and spiked at the given concentration of the target analytes. 25 mg of Fe3O4@PPy NPs was added to the solution and mechanically stirred for 10 min (Figure 1a). After extraction, the magnetic adsorbents were isolated from the solution with the magnet (Figure 1b). After decanting the supernatant solution, the adsorbed analytes were eluted with 800 μL acetonitrile under fierce vortex for 0.5 min (Figure 1c). Then, the eluent was separated from the NPs with the magnet (Figure 1d). In the next step, 20 μL of tetrachloroethylene was added to the eluting solution of MSPE (Figure 1e). The resulted solution was rapidly injected into 5 mL water with syringe. A cloudy solution resulting from the dispersion of fine droplets of tetrachloroethylene in the aqueous solution was formed in the test tube with a conical bottom
(Figure 1f). Then, the solution was centrifuged for 5 min at 2000 rpm (Figure 1g), and the dispersed fine particles of extraction phase settled at the bottom of the conical test tube (Figure 1h). After that, 2 μL of the settled phase was injected into GC–FID for analysis.

Results and Discussion

In this work, MSPE–DLLME–GC–FID was applied to the simultaneous determination of biphenyl and biphenyl oxide compounds from water samples. To achieve a high extraction recovery (ER) and preconcentration factor (PF), the MSPE and DLLME conditions were optimized. In order to obtain the best extraction performance, different parameters affecting the extraction process, such as sorbent amount, extraction time, elution solvent, volume of elution solvent, type of extraction solvent, volume of extraction solvent, type of disperser solvent, volume of disperser solvent, and desorption time, were studied and optimized. Optimization of the variables mentioned was performed using one-variable-at-a-time method.

Characterization of Fe₃O₄@PPy Nanoparticles. The shape, size, and morphology of the synthesized Fe₃O₄@PPy NPs were determined by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). In addition, the existence and amount of coated PPy were confirmed by Fourier transform infrared (FTIR) spectroscopy. The shape and size of the nanoparticles were observed by TEM (Figure 2a). The TEM images of Fe₃O₄@PPy particles show that an obvious coated

Figure 1. Schematic illustration for the MSPE-DLLME method. NPs was added to the solution and mechanically stirred (a), the magnetic adsorbents were isolated from the solution with the magnet (b), analytes adsorbed were eluted with acetonitrile (c), the eluent was separated from the NPs with the magnet (d), tetrachloroethylene was added to the eluting solvent of MSPE (e), a cloudy solution resulting from the dispersion of fine droplets of tetrachloroethylene in the aqueous solution (f), the solution was centrifuged (g), and the dispersed fine particles of extraction phase settled at the bottom of the conical test tube (h).

Figure 2. (a) TEM images of Fe₃O₄@PPy. SEM images of Fe₃O₄@PPy NPs: (b) 20,000× and (c) 40,000× magnification.
PPy is immobilized on the surface of Fe3O4 NPs. The coated PPy layer is clearly seen due to the different electron densities of magnetic nanoparticles core (with dark color) and PPy coating (with light color) in the TEM micrograph. The synthesized Fe3O4@PPy NPs showed a spherical shape with an average diameter of about 5–10 nm; however, the nanoparticles tended to aggregate to large particle. According to SEM images (Figure 2b and c), the Fe3O4@PPy NPs have a nearly spherical shape with a smooth and uniform surface morphology. Due to the agglomeration of the particles and less resolution of SEM as compared to TEM, the size of the particles in the SEM image is larger than that in the TEM image.

The coated PPy was characterized by FTIR in a range of 4000 and 400 cm$^{-1}$. The FTIR spectra for bare and PPy-coated Fe3O4 NPs were illustrated in Figure 3. The characteristic absorption peaks of Fe3O4 NPs, appeared in two spectra (a and b), correspond to the stretching vibrations of hydrogen-bonded surface water molecules and hydroxyl groups at 3400 cm$^{-1}$, and the Fe–O transverse vibration at 580 cm$^{-1}$ is observable. Coating of PPy onto Fe3O4 NPs was confirmed by the appearance of characteristic PPy bands in spectrum (b). The weak bands at 2800 and 2900 cm$^{-1}$ were assigned to the stretching vibrations of C–H bonds. The absorption peak at 1050 and 1314 cm$^{-1}$ were attributed to the bending vibration of C–H bond in the pyrrole ring and C–N stretching vibration. The absorption bands at 1549 and 1460 cm$^{-1}$ belong to C–C asymmetric and symmetric stretching vibrations of the pyrrole ring, respectively. These results indicate that PPy has been successfully coated on the surface of Fe3O4 NPs.

**Effect of Sorbent Amount.** Fewer amounts of nano-adsorbents, due to their greater aspect ratios, might lead to more satisfactory results than micro-adsorbents. To find the optimized adsorbents, due to their greater aspect ratios, might lead to more larger than that in the TEM image.

The volume of acetonitrile was also studied. As depicted in Figure 4e, the best results were obtained from 800 μL of acetonitrile. Since the desorption solvent in MSPE step plays the role of dispersive solvent in the DLLME process, further volume increase resulted in decreasing DLLME efficiency due to the raise in solubility of the analytes.

**Effect of Type of Extraction Solvent and its Volume.** The extraction solvent must be immiscible with water, higher density than water, compatible with the analysis instrument, and have high extraction capability for the analytes. According to these criteria, different organic solvents, such as chloroform, chlorobenzene, tetrachloroethylene, and carbon tetrachloride, were used. The obtained results (Figure 4d) revealed that tetrachloroethylene was the suitable extraction solvent in this method.

In order to study the effect of tetrachloroethylene volume on the extraction performance, different volumes of C2Cl4 in range of 10–40 μL were investigated. According to the results (Figure 4e), 20 μL of tetrachloroethylene was chosen as the optimum volume in further work.

**Desorption Time.** Desorption times were evaluated in the range of 0.5–10 min. The results showed that the time of 0.5 min is sufficient to quantitative desorption of the analytes.

**Sorption Capacity.** In order to investigate the sorption capacity of the magnetic sorbent, 10 mL of aqueous solution containing 1 mg of biphenyl and biphenyl oxide was used. To evaluate the maximum sorption capacity of each analyte, the difference between the concentration of the solution before and after extraction under the optimal condition was calculated. The sorption capacity of nanosorbent, for three parallel experiments, was found to be 21 and 30 mg/g for biphenyl and biphenyl oxide, respectively.

**Quantitative Aspects.** As summarized in Table 1, the calibration curve was obtained under the optimized MSPE–DLLME–GC–FID conditions. The analytes exhibited good linearity in the range 0.5–100 μg/L with proper correlation coefficients $r^2 = 0.999$ for both of the analytes. The limits of detection (LODs), based on signal-to-noise ratio (S/N) of 3, were

![Figure 3. FTIR spectra of (a) Fe3O4 and (b) Fe3O4@PPy](image-url)
0.03 and 0.07 μg/L for biphenyl and biphenyl oxide, respectively. The precision of the method was evaluated by carrying out five independent measurements of the studied compounds at 10.0 μg/L. The result showed that the relative standard deviations (RSDs) were 5.1 and 7.2% for biphenyl and biphenyl oxide, respectively.

Table 2 compares the proposed method with the other extraction methods for the determination of the target analytes in the water samples. The quantitative results of the proposed method are better than those of single drop microextraction (SDME) [1], solid-phase extraction (SPE) [36], and liquid-liquid extraction [37] methods. The comparison of extraction time of the proposed method with that of single drop microextraction [1] and liquid–liquid extraction [37] for the extraction of the target analytes indicates that this novel method has a very short equilibrium time as compared to the mentioned methods, and the extraction time needed for the proposed method is a few seconds. The quantitative results of the proposed method are comparable with the dispersive liquid–liquid microextraction (DLLME) [35]. However, the proposed method has potential for the determination of the target analytes in complex matrices such as waste water because of the MSPE clean-up before DLLME method. Also, it can be used in a large volume of sample, in contrast to the DLLME method. Finally, the proposed method has great potential for determining the selected analytes at the trace levels in water samples.

Table 2. Comparison of the proposed method with other extraction methods for the determination of biphenyl and biphenyl oxide compounds

| Methods           | RSD (%) | Dynamic linear range (μg/L) | Limit of detection (μg/L) | Extraction time (min) | Ref.   |
|-------------------|---------|-----------------------------|---------------------------|-----------------------|--------|
| DLLME–GC–FID      | 5.5–8.3 | 0.125–100                   | 0.015                     | A few seconds         | [35]   |
| SDME–GC–FID       | <5      | 5–500                       | 1.1–1.8                   | 30                    | [1]    |
| SPE–GC            | 2.1–5.9 | 50–1500                     | 0.01                      | 3                     | [36]   |
| LLE–GC            | <4      | 1000–1000000                | -                         | 25                    | [37]   |
| MSPE–DLLME–GC–FID | 5.1–6.7 | 0.5–100                     | 0.03–0.07                 | 10                    | This work |
Analysis of Real Samples. The proposed MSPE–DLLME technique was applied for the determination of biphenyl and biphenyl oxide compounds in the river water sample to elucidate the applicability and reliability of this method. The water sample was spiked with biphenyl and biphenyl oxide standard solution (10.0 µg/L concentration level) to assess the matrix effects. The obtained relative recovery was 91% for biphenyl and 95% for biphenyl oxide. The results show that matrix has negligible effect on MSPE–DLLME of biphenyl and biphenyl oxide. Figure 5 shows the GC–FID chromatograms of river water prior to (A) and after (B) spiking with biphenyl and biphenyl oxide at 10.0 µg/L level.

Conclusion

In the present study, combination of polypyrrole-coated Fe₃O₄-based MSPE and DLLME was successfully applied as an efficient sample pretreatment method for the trace determination of biphenyl and biphenyl oxide in different water samples. The analytical methodology offers numerous advantages such as ease of operation, high pre-concentration factor, low consumption of organic solvent, and feasibility for large volume samples. Furthermore, the proposed method is promising for the trace analysis of biphenyl and biphenyl oxide in natural water samples.

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