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Employment of a novel magnetically multifunctional purifying material for determination of toxic highly chlorinated polychlorinated biphenyls at trace levels in soil samples

Jiabin Zhang, Muyun Pan, Ning Gan*, Yuting Cao*, Dazhen Wu

Faculty of Materials Science and Chemical Engineering, Ningbo University, 315211, China

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ABSTRACT

In this study, we developed a magnetically multifunctional purifying material for efficient removal of matrix interferences, especially certain organochlorine pesticide (DDT, DDE, and DDD), during the determination of toxic highly chlorinated polychlorinated biphenyls (PCBs) at trace levels in soil samples. The multifunctional adsorbent (CMCD-NH_2-MNPs) was prepared by grafting carboxymethyl-β-cyclodextrin on the surface of amino-functionalized magnetite (Fe_3O_4) nanoparticles. CMCD-NH_2-MNPs has stronger host–guest complexation with DDT, DDE, and DDD, but the same adsorbent shows weaker adsorption ability toward highly chlorinated PCBs (from tetra- to octa-chlorinated PCBs) owing to their steric hindrance effect. Based on this principle, a simple and rapid gas chromatography–mass spectrometry (GC–MS) method was developed for six indicator PCBs (PCB28, PCB52, PCB101, PCB138, PCB153, and PCB180) in soil. Comparative studies were conducted to determine the clean-up efficiency of the following three techniques: (i) Oasis-HLB, (ii) multi-layer silica column, and (iii) dSPE employing CMCD-NH_2-MNPs. The results indicate that CMCD-NH_2-MNPs as the purification material can easily and effectively remove DDT, DDE, and DDD in soil samples within a short duration of time. The recoveries for highly chlorinated PCBs were in the range of 85.4–102.2%, with RSDs varying between1.0 and 6.5%. The proposed method was verified as one of the most effective clean-up procedures for the analysis of highly chlorinated PCBs in real soil samples

1. Introduction

In recent years, polychlorinated biphenyls (PCBs) have caused significant environmental damage: this has been a grave matter of concern for both scientists and general public [1,2]. PCBs are industrial chemicals that do not degrade into the environment, thereby causing persistent damage to both man and environment. According to several research studies, a constant exposure to PCBs can trigger several life-threatening ailments, such as cancer and disorders of the reproductive and endocrine system [3,4] Compared to highly chlorinated PCBs, lowly chlorinated PCBs can be easily degraded in the soil under natural conditions. This indicates that highly chlorinated PCBs are more stable and non-degradable so that highly chlorinated PCBs cause greater detrimental effects on human health than lowly chlorinated PCBs [5]. Therefore, most countries have legal directives and monitoring programs to control the PCB residues, especially highly chlorinated PCBs. In accordance with the statutory directives of environmental protection in most countries, the PCB residues of industrial and manufacturing units should not exceed maximum residue levels (MRLs) [6]. Therefore, scientists are striving hard to develop a rapid and accurate analytical method for determining trace residues of highly chlorinated PCBs in environmental samples.

The analysis of PCBs in soil samples usually involves three critical processes: (i) extraction of analytes from the matrix; (ii) the subsequent clean-up procedure of extracts; and (iii) the final chromatographic analysis [7]. While performing trace analysis of PCBs in complex soil samples, the matrix effect is a major issue as it adversely affects the quantification of PCBs [7,8]. Matrix effects have been a major source of error while performing GC–MS analysis: the matrix components that co-elute with the analyte seem to be the primary cause of ionization matrix effects [9,10]. In case of soil samples, organochlorine pesticides (OCPs) are a major source of matrix effects. In this case, the structure and polarity of PCBs closely resemble certain organochlorine pesticides, such as DDT, DDE, and

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* Corresponding authors. Tel.: +86 574 87608347; fax: +86 574 87608347.
E-mail addresses: ganning@nbu.edu.cn, lanhangzhen@163.com (N. Gan), caoyuting@nbu.edu.cn (Y. Cao).

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DDD [11–15]. Before determining PCBs in soil samples, sample purification and clean-up procedures were conducted in order to minimize the matrix effect of OCPs [14–16]. While performing a classic clean-up procedure, a solid-phase extraction (SPE) was conducted using multi-layer silica column (activated silica, basic silica, acidic silica, $AgNO_3$ silica, and anhydrous sodium sulphate) and Florisil® (activated magnesium silicate) columns [17–19]. SPE is not only a time-consuming technique but it also involves the use of excessive amounts of hazardous solvents [9,20]. Over the last few decades, scientists have performed SPE using novel materials such as aminopropyl-modified silica and Oasis-HLB. These innovative materials have not only reduced processing time but also minimized solvent usage [21,22]. In recent times, based on the SPE technique, scientists have developed several improvised and advanced clean-up methods, including dispersive solid-phase extraction (dSPE), matrix solid phase dispersion (MSPD), and solid phase microextraction (SPME) [23,24]. These newly developed clean-up methods are quick, easy, cheap, effective, rugged, and safe [25,26]. To conduct the aforementioned clean-up procedures, we need to select an appropriate adsorbent as it plays an important role in achieving appreciable recovery and clean-up efficiency. In recent times, many new adsorbents, such as Octadecyl-bonded silica (C18), aminopropyl modified silica, and Oasis-HLB have been synthesized and used in sample clean-up procedures for the analysis of seafoods, soils, and meats [27,28]. These adsorbents can remove several interfering co-extractives and minimize the matrix effect that is commonly encountered when samples are analyzed using gas chromatography (GC) [29]. However, these adsorbents are not quite efficient in removing organochlorine pesticides from samples.

β-Cyclodextrin (β-CD) is a natural molecule that is derived from starch: this molecule contains 7 glucose units. β-CD has hydrophobic interior cavity and hydrophilic peripheral face so that can forms inclusion complexes with chlorobenzene [30–32]. In recent times, it has been found that some OCPs, such as DDT, DDE, and DDD can easily fit into the hydrophobic cavity of β-CD but highly chlorinated PCBs cannot do the same owing to steric hindrance [33]. DDT, DDE, and DDD are hydrophobic compounds containing a symmetrical chlorobenzene ring: the size of this ring is $0.2\,nm^3$ [34]. In contrast, the size of β-CD's cavity varies between 0.262 and $0.346\,nm^3$ in volume [33,35]. Therefore, DDT, DDE, and DDD molecules have a characteristic segment of chlorobenzene ring that fits into the cavity of β-CD. The molecular volume of PCBs varies between 0.376 and $0.584\,nm^3$ $molecule^{-1}$. The size of tetra- to octa-chlorinated PCBs exceeds $0.446\,nm^3$ $molecule^{-1}$[33]. Therefore, these compounds are too large to fit into the cavity of β-CD. In soil, PCBs degradation is primarily dependent on important factors, such as the number and position of chlorine atoms on the biphenyl ring. Highly chlorinated PCBs are more resistant to degradation than the lowly chlorinated PCBs [5,36,37]. Therefore, in order to avoid the interference of OCPs in the matrix, β-CD was chosen as the clean-up material for determining highly chlorinated PCBs. Because β-CD is soluble in the medium, it cannot be separated from the matrix after clean-up procedures. Hence, in this experiment, we synthesized a novel clean-up adsorbent ($CMCD-NH_2-MNPs$) by using amino-functionalized magnetite (Fe_3O_4) nanoparticles (NPs) as the carrier to immobilize carboxymethyl-β-CD. In this manner, we can easily achieve magnetic phase-separation and simplify the clean-up procedure. Using these high-performance materials for purification and enrichment processes, target PCBs could be detected with higher selectivity and sensitivity. Moreover, the amino groups on the surface of Fe_3O_4 eliminated other matrix interferences, such as organic acid and some polar compounds [29,38]. In this experiment, we expected that the multifunctional purifying material possessed superior clean-up ability to remove DDT, DDE, and DDD and other matrix interferences. The scheme was shown in Fig. 1.

In this work, a new dSPE procedure using a magnetically multifunctional composite ($CMCD-NH_2-MNPs$) as purification material combined with gas chromatography–mass spectrometry (GC–MS) method, has been developed for detection of trace highly chlorinated PCBs in soil with greater sensitivity and selectivity. The $CMCD-NH_2-MNPs$ effectively remove matrix interference in soil, especially DDT, DDE, and DDD. The purification material coupled with dSPE–GC–MS was successfully used to analyze highly chlorinated PCBs in real soil samples. Satisfactory results were obtained using this analytical procedure.

2. Experimental

2.1. Reagents and materials

Six indicator PCBs including 2,4,4′-trichlorobiphenyl (PCB28), 2,2′,5,5′-tetrachlorobiphenyl (PCB52), 2,2′,4,5,5′-pentachlorobiphenyl (PCB101), 2,2′,3,4,4′,5-hexachlorobiphenyl (PCB138), 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB153), 2,2′,3,4,4′,5,5′-heptachlorobiphenyl (PCB180), p,p′-DDD, p,p′-DDE, p,p′-DDT and α-BHC were obtained from Accu Standard (New Haven, CT, USA), *n*-hexane, ethylene glycol, ethyl acetate, methyl alcohol, isopropyl alcohol, dichloromethane (DCM), acetonitrile, acetone, ferric chloride ($FeCl_3{\cdot}6H_2O$), anhydrous sodium acetate, 1,6-hexanediamine basic silica, $AgNO_3$, anhydrous sodium sulphate N-hydroxysuccinimide (NHS) and N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC) were purchased from Beijing Chemicals Corporation (Beijing, China). The syringe filters were purchased from Xingya (Shanghai). Oasis HLB 3cc (60 mg) extraction Cartridges were purchased from Waters (USA). All other chemicals were used as received without further purification. The water in this work was deionized water. The structural formulas of six PCBs and four OCPs were shown in Fig. 1S.

2.2. Equipment

The transmission electron microscopic (TEM) image was obtained with a H600 transmission electron microscope (Hitachi, Japan). Scanning electron micrographs (SEM) were obtained with a S3400N scanning electron microscope (Hitachi, Japan). Infrared spectra were recorded with a Nicolet 6700 FT-IR spectrophotometer (Nicolet, USA). The thermal stability of the particles was measured using a thermo-gravimetric analyzer (Seiko TG/DTA 6300, Japan). The magnetic properties were analyzed through a vibrating sample magnetometer (VSM, PPMS-9), which was purchased from Quantum Design, Ltd., USA. Gas chromatography–mass spectrometry (GC-2010, GC–MS-QP-2010E) was purchased from SHIMADZU (Japan).

2.3. Synthesis of $CMCD-NH_2-MNPs$

The amino-functionalized magnetic nanoparticles ($Fe_3O_4–NH_2$) were synthesized as described in previous work [39]. The carboxymethyl-β-cyclodextrin modified $Fe_3O_4–NH_2$ nanospheres ($CMCD-NH_2-MNPs$) were prepared using this stepwise process. First, 1 g of carboxymethyl-β-cyclodextrin was activated using 0.5 g of N-hydroxy succinimide and 0.5 g of N-(3-dimethylaminopropyl)-N′-ethyl carbodiimide hydrochloride in phosphate buffer solution (100 mL, pH 7.4) [40]. After conducting this reaction for 8 h at room temperature, the amino-functionalized magnetite nanoparticles ($Fe_3O_4–NH_2$) were added and stirred for another 6 h to obtain the resulting $CMCD-NH_2-MNPs$ (Fig. 1) (step2).