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Covalent triazine-based framework for micro solid-phase extraction of parabens

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ABSTRACT

Herein, nano-sized covalent triazine-based framework grafted magnetic particles were synthesized by a facile Friedel-Crafts reaction between cyanuric chloride as node and biphenyl as linker. The formation of the material has been confirmed by Fourier transform infrared spectroscopy, X-ray diffraction, field emission-scanning electron microscopy, thermogravimetric analysis, and N₂ adsorption-desorption measurement. With respect to the material structure, the large number of aromatic rings in the molecular framework provided a bed for extracting aromatic ring-containing compounds through π - π stacking interactions. The applicability of the prepared material as a new sorbent for micro solid-phase extraction of parabens was investigated. The effect of key experimental parameters affecting the extraction efficiency of the analytes including sorbent amount, sample pH, extraction time and desorption conditions were investigated. High-performance liquid chromatography with UV detection was used for determining the enriched analytes. The method was successfully applied for determining parabens in human urine, breast milk, personal care products, and shower wastewater. After optimization, the linearity range of 0.1–500 $\mu\text{g L}^{-1}$ and detection limit of 0.02 $\mu\text{g L}^{-1}$ were obtained for all the selected parabens. The relative standard deviations and recoveries for the real sample analysis were in the range of 2.3–5.0% and 86–102%, respectively.

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1. Introduction

As an important group of antimicrobial preservatives, parabens have been widely utilized in cosmetics and pharmaceutical products as well as in packaged foods and beverages. The antimicrobial activity of these compounds increases with increasing the length of the alkyl chain. Methylparaben (MP), ethylparaben (EP), propylparaben (PP) and butylparaben (BP) are the most common parabens found in the mentioned matrixes. Due to their broad range of antimicrobial activity, being odorless and tasteless, low cost, and worldwide regulatory acceptance, parabens have widespread applications. Human is exposed to these compounds by oral intake or absorption through the skin. In addition, their introduction to the environment has caused drastic concerns about the physical health of individuals exposed to them. Nevertheless, some investigations have disclosed that parabens can cause endocrine-disrupting effects and lead to some diseases such as miscarriage and infertility.

Recently, a possible relationship between parabens and breast cancer has been proposed after discovering these compounds in some human breast tumors [1]. Because of the concerns about human health, the European Union and USA legislation allowed the use of single parabens up to the maximum concentration of 0.4% (w/w) and parabens mixture up to 0.8% (w/w) in consumer products.

Considering the low concentration level of parabens in biological and environmental samples and the complexity of sample matrix, developing a precise and sensitive detection method is extremely needed. Up to date, various analytical methodologies have been applied for determining parabens in human biological fluids, environmental samples, and cosmetics [2–6]. Regarding the superiority of microextraction techniques over traditional sample preparation methods such as solid-phase extraction and liquid-liquid extraction from environmental, economic, simplicity and efficiency points of view, most of the developed methods for the determination of parabens utilize microextraction techniques. Generally, sorbent-based sample preparation techniques in which very low amounts of a usually reusable sorbent is utilized for extraction, compared to solvent-based techniques, consume less amounts of solvents and reagents. Up to date, a number of sorbent-based

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microextraction techniques such as solid-phase microextraction [2], stir bar sorptive extraction and bar adsorptive microextraction [3,4], and micro solid-phase extraction (MSPE) [5,6] have been applied for analyzing parabens in human biological fluids, cosmetic products, and water samples. Today, MSPE is becoming more famous due to its operational simplicity, good reproducibility, and the wide range of applications as well as worldwide acceptance. MSPE could be used in several versions such as dispersive MSPE, porous membrane protected MSPE and pipette tip-based MSPE. Among them, the dispersive mode of MSPE which utilizes a magnetic sorbent for analyte extraction is preferred due to its simplicity in sorbent collection. With the great advances in nanotechnology, developing efficient nano-sized sorbents has recently attracted a great deal of attention especially in MSPE. Among the developed nanosized materials, magnetic nanoparticles as a sorbent or a part of a sorbent have received special attention due to their fast and efficient extraction, high surface area, modifiable surface, biocompatibility, reusability, and simple isolation from the sample matrix [7]. From the analytical point of view, recent developments in MSPE have focused on improving method selectivity and sensitivity by introducing new sorbents.

Covalent organic frameworks (COFs), first developed by Yaghi's group in 2005 [8], have been regarded as promising materials in various branches of science. They are composed of light elements (B, C, N, O, Si) and connected by strong covalent bonds. In comparison with metal-organic frameworks (MOFs), which are widely applied as sorbent for extraction purposes, COFs have more significant chemical stability in different solvents and moisture. This is mainly because COFs are fabricated by covalent bonds, compared to coordination bonds in MOFs [9,10]. Other fantastic properties of COFs such as high thermal stability, high specific surface area, structural regularity, and adjustable structure, have attracted an increasing level of research interest in recent years especially in gas storage and catalysis [9]. Due to the unique properties of COFs, they are considered as promising materials to be used as sorbent in extraction techniques. At present, there are only a few reports concerning utilizing COFs in sample preparation methods [11–17].

COF materials are classified into three main categories: (1) covalent triazine-based COFs (CTFs), (2) boron-containing COFs, and (3) imine-based COFs [9]. Among COFs, porous CTF materials have lower crystallinity. However, they require low-cost starting materials for synthesis, facile synthesis conditions, and excellent thermal and chemical stability. CTFs are typically made by three main routes: (1) Friedel-Crafts (AlCl_3) reaction, (2) strong Brønsted acid conditions ($\text{CF}_3\text{SO}_3\text{H}$), and (3) ionothermal (ZnCl_2) conditions [10]. Of the aforementioned synthesis strategies, AlCl_3 -catalyzed Friedel-Crafts reaction offers meaningful advantages like easy facile synthesis condition, reagent availability, low reaction temperature, easy handling, and high yield [10]. The resulting sheets of CTFs can form tubular channels with diameters ranging from 1.2 nm to several nanometers, and a hexagonal lattice with an eclipsed AAA structure. Moreover, their pore diameter, specific surface area, structure, and functionality can easily be tailored by careful selection of the starting constitutional monomers [9,18]. As expected, due to the presence of a large number of aromatic rings in the structure of CTFs, there is a great potential for adsorption of a wide range of compounds. Due to the lack of analytical information about the efficiency of CTFs as a sorbent in sample preparation techniques, studying their analytical characteristics seems to be necessary.

Herein, we utilized a facile Friedel-Crafts alkylation reaction between cyanuric chloride and aromatic building blocks (biphenyl) to prepare CTF to serve as a new class of sorbents in MSPE. Following this strategy, nano-sized CTF was successfully grafted on the surface of Fe_3O_4 particles and used to extract selected parabens from human urine, breast milk, personal care products, and shower wastewater. The extracted analytes were analyzed

by high-performance liquid chromatography. As far as we know, no study on utilizing nano-sized magnetic CTF in MSPE has been reported.

2. Experimental

2.1. Chemicals and standards

All chemicals and reagents were at least 99% in purity. Ferric chloride hexahydrate, 25% (w/w) ammonia solution, 37% (w/w) hydrochloric acid, sodium hydroxide, tetraethoxysilane (TEOS), ethylene glycol, biphenyl, cyanuric chloride, anhydrous aluminum chloride, dimethylformamide, acetone, dichloromethane (DCM) and HPLC grade methanol and acetonitrile were obtained from Merck (Darmstadt, Germany). Methylparaben (MP), ethylparaben (EP), propylparaben (PP), butylparaben (BP), sodium metasilicate (Na_2SiO_3), and anhydrous sodium acetate were obtained from Sigma-Aldrich (Buchs, Switzerland). Phenyltrimethoxysilane (PTMS) was obtained from Fluka (Buchs, Switzerland). Anhydrous ethanol was purchased from Bidestan Co. (Ghazvin, Iran). Pure water was prepared by OES water purification system (Oklahoma, USA). The stock standard solution of each analyte (1000 mg L^{-1}) was prepared in acetonitrile and stored at 4°C in a refrigerator. A stock standard solution of the mixed analytes was prepared in acetonitrile at the concentration level of 25 mg L^{-1} for each analyte. Working standard solutions were prepared daily in pure water just before use.

2.2. Apparatus and chromatographic conditions

A RIGOL L-3000 high-performance liquid chromatography system equipped with a UV-vis detector (Beijing, China) and a 7125i injection valve with a $20\text{-}\mu\text{L}$ sample loop (Rheodyne, USA) was employed for the analysis of samples. The FT-IR spectra were recorded using a Jasco FTIR-350 (Tokyo, Japan) between 4000 and 400 cm^{-1} . The XRD data were acquired using a Philips X'pert MPD diffractometer (Eindhoven, Netherland) with the characteristic wavelength of 1.540 \AA generated from a Cu anode supplied with 45 kV and 100 mA . Diffractograms were collected between 2θ of $8\text{--}80^\circ$ at a scanning rate of $0.05^\circ \text{ min}^{-1}$. Field emission-scanning electron microscopy was performed on a MIRA3 TESCAN-XMU FE-SEM system (Razi Metallurgy Research Center, Tehran, Iran). Thermogravimetric analysis (TGA) was carried out on an STA503 (Bahr GmbH, Hüllhorst, Germany) instrument at a heating rate of $20^\circ\text{C min}^{-1}$ under argon atmosphere. N_2 adsorption-desorption measurement was performed on a porosimetry analyzer (Belsorp-mini II, BEL Japan) at 77 K . Separation of the analytes was performed using a Hector-M C18 column (150 mm , 3 mm i.d. , $3 \mu\text{m}$, RStech Co, Daejeon, Korea) connected to a C18 guard column (10 mm , 4 mm i.d. , $5 \mu\text{m}$, Merck Co, Darmstadt, Germany). Mobile phase consisted of methanol as solvent A and pure water as solvent B with a gradient elution program as follows: $0\text{--}2 \text{ min}$ 40% solvent A, and $2\text{--}10 \text{ min}$ 100% solvent A. Detection was performed at 254 nm for all the analytes. The flow rate of the mobile phase was set to 0.4 mL min^{-1} . All separations were performed at room temperature.

2.3. Synthesis procedures

2.3.1. Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2$

Monodispersed magnetic Fe_3O_4 spherical particles were synthesized by means of a modified solvothermal reaction [19]. Typically, 10.73 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 17.23 g of anhydrous sodium acetate were dissolved in 320 mL of ethylene glycol under vigorous stirring at room temperature to form a homogenous yellow solution. The mixture was ultrasonicated at 60°C for 5.0 min and

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