



Contents lists available at ScienceDirect

# Journal of Chromatography A

journal homepage: [www.elsevier.com/locate/chroma](http://www.elsevier.com/locate/chroma)



## Facile synthesis of magnetic covalent organic framework nanobeads and application to magnetic solid-phase extraction of trace estrogens from human urine

Lei Chen<sup>a</sup>, Mingyue Zhang<sup>a</sup>, Fengfu Fu<sup>a</sup>, Jingguang Li<sup>b</sup>, Zian Lin<sup>a,\*</sup>

<sup>a</sup> Ministry of Education Key Laboratory of Analytical Science for Food Safety and Biology, Fujian Provincial Key Laboratory of Analysis and Detection Technology for Food Safety, College of Chemistry, Fuzhou University, Fuzhou, Fujian 350116, China

<sup>b</sup> China National Center for Food Safety Risk Assessment, Beijing 100022, China

### ARTICLE INFO

#### Article history:

Received 20 May 2018

Received in revised form 22 June 2018

Accepted 27 June 2018

Available online xxx

#### Keywords:

Magnetic covalent organic framework

Magnetic solid-phase extraction

Estrogens

Urine analysis

HPLC–MS

### ABSTRACT

A rapid and facile approach was developed for the synthesis of core-shell structured magnetic covalent organic framework nanobeads by using the monodisperse Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) as magnetic core, and 1,3,5-triformylbenzene (Tb) and benzidine (Bd) as two building blocks (denoted as Fe<sub>3</sub>O<sub>4</sub>@TbBd), which were explored as an adsorbent for magnetic solid-phase extraction (MSPE) of estrogens from human urine sample. The core-shell structured Fe<sub>3</sub>O<sub>4</sub>@TbBd nanobeads showed some attractive features involving high specific surface area (202.18 m<sup>2</sup>/g), uniform pore size distribution (2.8 nm), high magnetic responsivity (41.4 emu/g), as well as excellent thermal and chemical stability, which made it an ideal adsorbent for selective isolation and enrichment of estrogens. Some parameters influencing extraction efficiency, including adsorbent dosage, extraction time, pH, ion strength, desorption solvent and desorption time were investigated systematically. Combined with HPLC–MS, a simple, fast, and sensitive method was developed for the enrichment and sensitive determination of seven estrogens, which showed good linearity ( $r > 0.9978$ ) in the range of 0.005–10 μg/L, low limits of detection (0.2–7.7 ng/L, S/N = 3), low limits of quantification (0.6–25.6 ng/L, S/N = 10), high enrichment factors (75–197 fold), and good precision with relative standard deviations (RSD) lower than 4.8% for intra-day and 6.7% for inter-day. The proposed method was successfully applied to the analysis of trace estrogens in urine sample of pregnant woman with good recoveries (80.6–111.6%), demonstrating the promising potential of the Fe<sub>3</sub>O<sub>4</sub>@TbBd nanobeads as adsorbent in sample pretreatment.

© 2018 Elsevier B.V. All rights reserved.

### 1. Introduction

Estrogens are a type of prescription drugs for oral contraceptives and hormone therapy, which are mainly involved in growth, reproduction and sexual behaviors [1]. In recent years, the widespread use of estrogens has attracted considerable attention due to the potential risks to environment and human health. Numerous studies have revealed that estrone (E1), estradiol (E2), ethinyloestradiol (EE2) and diethylstilbestrol (DES) possess the potency to induce the abnormal production of vitellogenin (VTG) and disrupt sexual development in fishes even at ng/L levels [2–4]. Furthermore, the United States Environmental Protection Agency (US EPA) has particularly classified natural estrogens (e.g. E1, E2 and estriol (E3)) and synthetic estrogens (e.g. EE2) as contaminants of emerging con-

cern [5]. Therefore, development of a simple, selective and sensitive method to determine estrogens in complex sample is very important to environmental exposure and human health assessments.

Due to the ultralow concentrations of estrogens in biological samples and the complex matrix effect, pretreatment and enrichment processes are indispensable prior to HPLC–MS analysis. As an important branch of solid phase extraction (SPE), magnetic solid phase extraction (MSPE) has recently gained increasing attention [6–11]. In the typical MSPE procedure, magnetic sorbents are directly placed in the sample solution to absorb target analytes, and then isolated through magnetic separation instead of filtration or centrifugation, which can dramatically simplify the pretreatment procedure. Moreover, the MSPE technique also showed advantages of high recovery, high enrichment factor, short extraction time and low consumption of organic solvents [12]. Up to date, several magnetic composites have been successfully applied to the extraction of estrogens, including magnetic octadecylsilane [13], magnetic multi-walled carbon nanotubes [14], magnetic

\* Corresponding author.

E-mail address: [zianlin@fzu.edu.cn](mailto:zianlin@fzu.edu.cn) (Z. Lin).

molecularly imprinted polymers [15], magnetic nanobeads with carbon shell ( $\text{Fe}_3\text{O}_4@\text{C}$ ) [16], magnetic poly(dopamine) [17], cetyltrimethyl ammonium bromide (CTAB)-coated  $\text{Fe}_3\text{O}_4$ @caprylic acid [18] and so on.

Covalent organic frameworks (COFs) are an emerging class of crystalline porous materials, which are built through the connection of building blocks based on covalent bonds. COFs possess lots of fascinating features, including low density, tunable pore size, regular porosity, large specific surface area, high chemical stability and thermal stability. Moreover, COFs generally exhibit hydrophobic behavior due to the large delocalized  $\pi$ -electron system which can form strong  $\pi$ - $\pi$  stacking interactions with the aromatic ring-related compounds [19,20]. In the past few years, COFs have gained increasing concern in the field of separation science [21,22], such as stationary phases [23–28] and solid-phase microextraction [29–31], owing to the superior intrinsic properties as mentioned above. Against such a backdrop, the incorporation of the merits of COFs and magnetic materials to construct a novel type of magnetic nanocomposites is highly desirable. However, the existing strategies for the synthesis of magnetic COFs usually requires harsh reaction conditions and lengthy reaction time [32,33]. Therefore, to develop a simple approach for the synthesis of magnetic COFs is of great importance. More recently, an encouraging breakthrough in rapid room-temperature synthesis of core-shell structured magnetic COFs was achieved by our group [20,34], which have been successfully applied to capture peptides with simultaneous exclusion of proteins from complex biological samples. Despite some success has been made, the applications of magnetic COFs in the field of sample pretreatment are still scarce [35]. Further development is very necessary to address the merits and explore new applications of this type of magnetic composites.

Herein, we reported a rapid and facile approach for the synthesis of core-shell structured magnetic covalent organic framework ( $\text{Fe}_3\text{O}_4@\text{TbBd}$ ) nanobeads by using the monodisperse  $\text{Fe}_3\text{O}_4$  nanoparticles (NPs) as magnetic core and 1,3,5-triformylbenzene (Tb) and benzidine (Bd) as two building blocks to form the COF shells in the presence of dimethyl sulfoxide (DMSO). The as-prepared  $\text{Fe}_3\text{O}_4@\text{TbBd}$  nanobeads were characterized by several techniques. The adsorption performance of the  $\text{Fe}_3\text{O}_4@\text{TbBd}$  nanobeads was evaluated and the MSPE parameters for seven estrogens (Fig. S1, Supplementary information) were investigated in detail. In addition, taking the advantages of  $\text{Fe}_3\text{O}_4@\text{TbBd}$  nanobeads

as a magnetic adsorbent, a fast, simple, and sensitive method based on HPLC–MS with MSPE pretreatment was proposed and further applied to the analysis of trace estrogens in human urine samples. To the best of our knowledge, this is the first example on magnetic COFs applied as MSPE for estrogens.

## 2. Experimental

### 2.1. Chemicals and reagents

All the chemical reagents were of analytical grade or better. Ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), sodium citrate dehydrate ( $\text{Na}_3\text{Cit} \cdot 2\text{H}_2\text{O}$ ), ethylene glycol (EG) and Tb were purchased from J&K Chemical Ltd (Shanghai, China). Bd, acetonitrile (ACN), methanol (MeOH), E1, E2, E3, DES, EE2, hexestrol (HES), and dienestrol (DIS) were supplied by Aladdin Chemistry Co. Ltd (Shanghai, China). Deuterium isotope (E2-d4), served as an internal standard for the quantification evaluation, was obtained from Cambridge Isotope Laboratories Inc. (Andover, MA, USA). Deionized water ( $18.2\text{ M}\Omega\text{ cm}^{-1}$ ) was obtained from a Milli-Q water purification system (Millipore, Milford, USA).

The stock standard solutions of estrogens were individually prepared at the concentration of  $1000\text{ }\mu\text{g/mL}$  in MeOH and stored at  $4^\circ$ . The working standard solutions were obtained daily by appropriately diluting with deionized water. Pregnant and non-pregnant urine samples were collected from Fujian Provincial Official Hospital (Fuzhou, China) and were further diluted 20-fold with deionized water, followed by storage at  $4^\circ$  prior to use.

### 2.2. Apparatus

Scanning electron microscopy (SEM) images were recorded by a FEI Emission Scanning Electron Microscope (SU8020, Hitachi, Japan). Transmission electron microscopy (TEM) images were obtained with a Hitachi HT7700 (Japan). Fourier-transform infrared spectroscopy (FT-IR) was taken on Nicolet 6700 spectrometer (Thermo Fisher, USA). The crystal structure was determined by X'Pert-Pro MPD (Philips, Holland). The nitrogen adsorption and desorption isotherms were measured by using an ASAP 2020 (Micromeritics, USA). Thermogravimetric analysis (TGA) was performed on a Shimadzu thermogravimetric analyzer (Model DTG-60). The magnetization curves were calculated by a super-

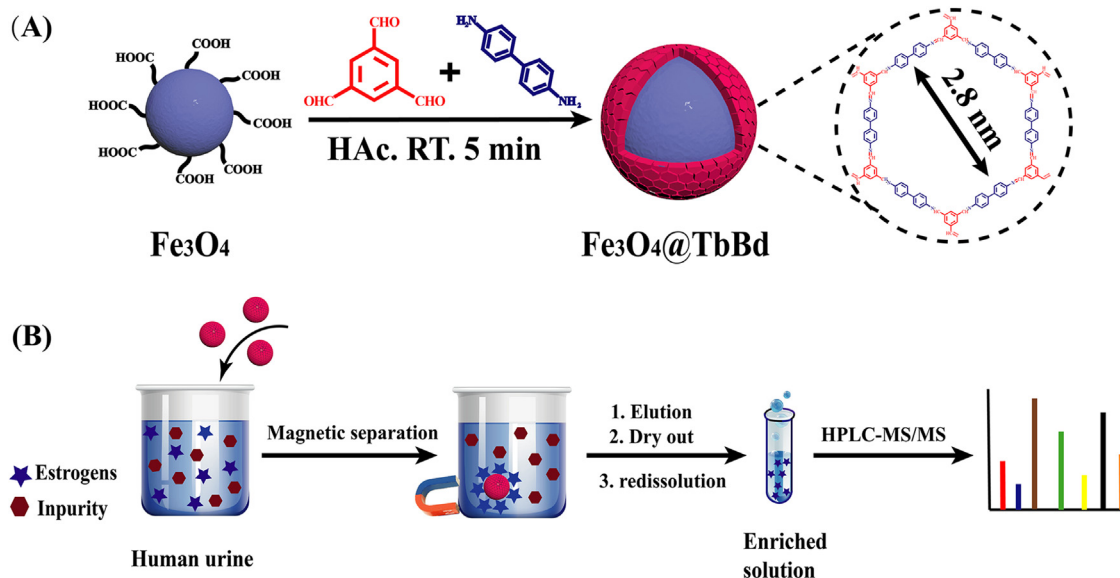


Fig. 1. (A) Preparation of the  $\text{Fe}_3\text{O}_4@\text{TbBd}$  nanobeads and (B) the MSPE process for estrogens in urine sample.

Download English Version:

<https://daneshyari.com/en/article/7607463>

Download Persian Version:

<https://daneshyari.com/article/7607463>

[Daneshyari.com](https://daneshyari.com)