Food Chemistry 241 (2018) 268–274

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

3D hierarchical magnetic hollow sphere-like $CuFe_2O_4$ combined with HPLC for the simultaneous determination of Sudan I–IV dyes in preserved bean curd

Xueyan Liu, Xinyu Qi, Lei Zhang*

College of Chemistry, Liaoning University, Shenyang 110036, China

A R T I C L E I N F O

Chemical compounds studied in this article::
Sudan I (PubChem CID: 5858445)
Sudan II (PubChem CID: 5809936)
Sudan III (PubChem CID: 5379348)
Sudan IV (PubChem CID: 5876571)

Keywords:
3D hierarchical magnetic hollow sphere-like $CuFe_2O_4$
Sudan dyes
Magnetic solid-phase extraction
Preserved bean curd

A B S T R A C T

Three-dimensional (3D) hierarchical magnetic hollow sphere-like $CuFe_2O_4$ (3D HMHS-$CuFe_2O_4$) were designed to sensitively detect four Sudan dyes combined with HPLC–DAD. The formation mechanism of 3D HMHS-$CuFe_2O_4$ is also discussed. Compared to the particle-like $CuFe_2O_4$ (PL-$CuFe_2O_4$), the as-obtained 3D HMHS-$CuFe_2O_4$ provided a higher extraction efficiency for the four Sudan dyes (I, II, III and IV) due to its hierarchical hollow structure with properly interconnected pores where the targets can easily diffuse into the reaction sites. Thus, a magnetic solid-phase extraction (MSPE)-HPLC method was established for the simultaneous measurement of the four Sudan dyes. Under optimized conditions, good linearity (5–4000 ng g^{-1}, $r^2 \geq 0.9991$), limits of detection (LODs, 0.56–0.60 ng g^{-1}), recoveries (91.1% – 99.3%) and precision (RSDs ≤ 4.9%) for the four Sudan dyes were obtained. The proposed MSPE-HPLC-DAD method is a convenient, effective, sensitive and time-saving method for the rapid isolation and determination of four Sudan dyes in preserved bean curd.

1. Introduction

Preserved bean curd, which contains abundant amino acids, proteins, vitamins B12, calcium, iron and zinc, has been used by more people with the understanding of its benefits increases. The red material on the surface of preserved red bean curd, known as “monascus”, has been shown to be effective in lowering cholesterol. Unfortunately, in order to improve the appearance, increase red-orange color and stimulate consumption, some red synthetic chemical colorants have been used by some merchants as additives in preserved red bean curd (Chang et al., 2011). Among them, Sudan dyes, food colorants, are attractive because of their bright and vivid red color, colorfastness as well as low cost. But, Sudan dyes (Sudan I – IV, Fig. S1 Supplementary materials) are classified as category 3 carcinogen by the International Agency for Research on Cancer (IARC), and not permitted to present in foodstuff for any purpose at any concentration level (Chang et al., 2011; Li, Luo, Luo, & Li, 2015; Yu, Liu, Li, Zhang, & Yu, 2015). Consequently, to monitor the abuse of Sudan dyes in preserved bean curd, it is urgently required to develop a simple, highly effective and practicable method for the analysis of the target Sudan dyes.

Until now, various methods, including electrophoresis (Mejia, Ding, Mora, & Garcia, 2007), plasmon resonance light scattering (Wu, Li, Huang, & Zhang, 2006), enzyme-linked immunosorbent assay (Chang et al., 2011; Oplatowska, Stevenson, Schulz, Hartig, & Elliott, 2011), and high performance liquid chromatography (HPLC) (Yan et al., 2012; Zhong et al., 2011), have been developed for the detection of Sudan dyes. Among them, HPLC associated with various detectors, such as ultraviolet (UV) (Fan et al., 2009), mass spectrometry (MS) (Murty, Sridhara Chary, Prabhakar, Prasada Raju, & Vairamani, 2009), and diode array detection (DAD) (Qi, Zeng, Wen, Liang, & Zhang, 2011), was extensively used. Although HPLC-MS is a very efficient, accurate and sensitive technique for identification and quantification of Sudan dyes, the instrument itself and its running cost are both expensive and not available in many laboratories. To the best of our knowledge, HPLC-UV or DAD for determination of Sudan dyes because of their low cost was mostly used. However, owing to poor sensitivity and specificity of HPLC–UV or DAD, the low levels of analytes as well as complexity of sample matrices, a simple and effective pretreatment procedure is crucial to simultaneously isolate and enrich analytes prior to chromatographic analysis.

Recently, several pretreatment approaches, such as liquid–solid extraction (Rebane, Leito, Yurchenko, & Herodes, 2010), liquid–liquid microextraction (Long et al., 2011; Petigara Harp, Miranda-Bermudez, & Barrows, 2013; Saad, Bari, Saleh, Ahmad, & Talib, 2005), ultrasonic-assisted extraction (Hongyuan, Jindong, Hui, Gengliang, & Kyung Ho, 2011), solid-phase extraction (SPE) (He et al.,

* Corresponding author.
E-mail address: zhanglei63@126.com (L. Zhang).

http://dx.doi.org/10.1016/j.foodchem.2017.08.113
Received 19 May 2017; Received in revised form 17 August 2017; Accepted 30 August 2017
Available online 01 September 2017
0308-8146/

2007; Zhong et al., 2011) and so on, have been developed. However, SPE is still regarded as one of the most popular methods to purify the analytes from food samples because of its ease of use, low solvent-cost as well as high enrichment performance.

Nowadays, based on the use of magnetic materials as new adsorbents to substitute for the routine nonmagnetic SPE materials, magnetic solid-phase extraction (MSPE) has got extensive attention in sample pretreatment (Chen et al., 2014; Mehdinia, Khodaee, & Jabbari, 2015). Compared with traditional SPE process, MSPE exhibits the excellent advantage of a facile phase separation using a magnet without the need for additional filtration or centrifugation separation, which simplifies the separation process and improves the rate of separation. Ferrite (Ding, Wang, Zhang, Li, & Liu, 2015; Sengupta, Rao, & Bahadur, 2017), as a conventional magnetic material, has attracted great attention owing to their outstanding adsorption properties and magnetic properties.

Usually, 3D hierarchical hollow materials often possess special physical/chemical properties compared with solid particles because of their large specific surface area and low density (Zhou et al., 2013). Considering the excellent properties of hollow architectures as well as magnetic ferrites, hierarchical hollow ferrites would be quite attractive for practical applications as a new type of MSPE materials. Therefore, to prepare a novel 3D hollow magnetic ferrite with features of large specific surface area, strong absorption for Sudan dyes, and excellent magnetic property is very meaningful and urgent. Conventional approach to fabricate hollow structures usually requires structural directing reagents or hard templates as sacrificial materials, which may increase the cost and complicate the process. Hence, it is highly desirable but challenging to design a method for the synthesis of 3D hierarchical hollow architectures with surfactant free, low cost, facile operation and large-scale production.

Herein, we prepared 3D hierarchical magnetic hollow sphere-like $CuFe_2O_4$ microspheres (3D HMHS-$CuFe_2O_4$) through a template free solvothermal approach. A possible formation mechanism for the hollow magnetite spheres was proposed. Then, the synthesized 3D HMHS-$CuFe_2O_4$ was used as a MSPE adsorbent for the first time to simultaneously extract and sensitively detect four Sudan dyes (I, II, III and IV) followed by HPLC-DAD, exhibiting higher extraction ability to the four Sudan dyes compared with solid $CuFe_2O_4$ nanoparticles. The influences of the MSPE factors (i.e., type and dosage of the sorbent, pH and ionic strength of the solution, extraction time, type and volume of the eluent, etc.) on the quantitative analysis of target analytes were investigated in detail. Ultimately, the optimized procedure was applied to the analysis of the four illegal Sudan dyes in preserved bean curd samples. Thus, a convenient, effective, low toxic, time saving and sensitive method for the analysis of Sudan dyes has been successfully established.

2. Experimental

2.1. Chemicals and reagents

Sudan dyes were gained from J & K scientific Co., Ltd. (Shanghai, China), and their corresponding structures were presented in Fig. S1 (Supplementary materials). The mixed standard stock solutions (50 μg mL^{-1} each) were obtained by dissolving Sudan dyes into ethanol (EtOH) and stored under dark condition at 4 °C. The mixed working solutions were prepared daily through appropriately diluting the mixed standard stock solution with EtOH/H_2O (1:9, v/v). Chromatographic grade acetonitrile (MeCN) and analytical grade sodium acetate, acetic acid, copper nitrate, ferric nitrate, EtOH, methanol (MeOH), acetone (Me_2CO), chloroform ($CHCl_3$) and ethyl acetate (EtOAc) were offered by Sinopharm Chemical Reagent Co., Ltd. (Shenyang, China), and used directly without further treatment. Pure water was obtained by a Millipore Milli-Q water instrument (USA).

2.2. Instruments

The detection of Sudan dyes were performed on a Agilent 1100 HPLC (USA) attached with an autosampler, a column oven, a Zorbax Extend XDB-C18 column (150 × 4.6 mm, 5 μm) and a diode array detector. The injection volume was 20 μL. The mobile phase was MeCN/H_2O (95:5, v/v) with 1.0 mL min^{-1} at 30 °C. The detection and reference wavelengths were 510 and 750 nm, respectively.

Scanning electron microscopy (SEM) analysis were performed on a Hitachi SU8000 instrument (Japan). The crystal phase and purity of samples were analyzed via a X-ray diffractometer (XRD, Bruker D8, Germany) with CuKα-radiation. The BET surface area was obtained from a 3020 surface area analyzer (Norcross, GA). The magnetic property of samples was estimated by a 7407 vibrating sample magnetometer (VSM, Lakeshore, USA).

2.3. Preparation of 3D HMHS-$CuFe_2O_4$

The 3D sphere-like hollow $CuFe_2O_4$ powders were prepared using a simple solvothermal method. Typically, 0.003 mol $Cu(NO_3)_2{\cdot}3H_2O$, 0.006 mol $Fe(NO_3)_3{\cdot}9H_2O$ and 0.3 g urea were dissolved in 60 mL absolute EtOH under vigorous magnetic stirring. After 30 min, the above solution was poured and sealed in a 100 mL autoclave at 180 °C for 12 h. The obtained product was collected by a magnet, washed for several times with deionized water and EtOH, and dried at 60 °C overnight. Finally, the obtain product was annealed at 500 °C in air for 3 h with a rate of 2 °C min^{-1} to obtain the 3D HMHS-$CuFe_2O_4$ powder. For comparison, solid $CuFe_2O_4$ was also prepared under the same conditions without urea.

2.4. Sample pretreatment

The preserved bean curd samples were selected for the valuation of 3D sphere-like hollow $CuFe_2O_4$, which were gained from the local supermarket. 1.0 g of preserved bean curd was homogenised in 5 mL of MeCN, and treated for 5.0 min by ultrasound. The obtained homogenates were centrifuged at 3000 rpm for 5.0 min, and the supernatants were collected. The extraction process was repeated once and the extracts were pooled together. For the spiking analysis, 1.0 g preserved bean curd was mixed with appropriate amounts of Sudan dyes mixed standard solution, prior to above extraction procedures. The resulting solution was evaporated to dryness under vacuum at 40 °C, and then redissolved with 10 mL EtOH/H_2O (1:9, v/v) for further MSPE procedure.

2.5. MSPE procedure

10 mg of the as-prepared 3D HMHS-$CuFe_2O_4$ was uniformly dispersed into 10.0 mL of Sudan working standard solution or sample solution, and the suspensions were shaken with a speed of 180 rpm at 25 °C. After shaking for 10 min, the 3D HMHS-$CuFe_2O_4$ was quickly isolated by an external magnet. The target analytes were eluted by ultrasonic from the 3D HMHS-$CuFe_2O_4$ with 3.0 mL of MeCN/EtOAc (3:2, v/v) for 3 min. Afterwards, the 3D HMHS-$CuFe_2O_4$ was separated magnetically from the eluents. Finally, the eluent was evaporated to dryness under vacuum at 40 °C, while the residue was reconstituted with 0.5 mL MeCN/H_2O (95:5, v/v) for subsequent analysis.

3. Results and discussion

3.1. Characterization of 3D HMHS-$CuFe_2O_4$

The phase composition of the as-synthesized 3D HMHS-$CuFe_2O_4$ was identified by XRD. As presented in Fig. S2a (Supplementary materials), the characteristic peaks at 2θ = 35.7°, 38.7°, 40.9°, 54.1°, 57.6°, and 62.5° can be ascribed to the (3 1 1), (3 2 0), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) crystal planes of $CuFe_2O_4$ (JCPDS 25-0283) (Zhao,