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Metal-organic framework-derived three-dimensional porous Cu@graphitic octahedron carbon cages as highly efficient enrichment material for simultaneous determination of four fluoroquinolones

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ABSTRACT

A unique 3D porous Cu@graphitic octahedron carbon cages were constructed by rapid room-temperature synthesis of a Cu-based metal–organic framework (MOF) with further pyrolysis in N_2, which exhibited good enrichment ability for four fluoroquinolones (FQs) due to their superior chemical affinities to the target analytes. Applied Cu@graphitic octahedron carbon cages as adsorbent, a dispersive solid phase extraction (DSPE) method combined with HPLC was developed for detecting four FQs in real samples. Various parameters affecting residues FQs extraction efficiency were inquired in more detail. Under optimal conditions, the extraction recoveries of four FQs in chicken muscle, fish tissue, seawater and river water samples were in the range of 81.3∼104.3% and the RSDs (n = 5) were less than 5.2%. This method was successfully used to the determination of FQs in real samples.

1. Introduction

Nowadays, fluoroquinolones (FQs) for the treatment of infections are used on livestock farming, human medicine, and aquaculture [1,2]. Furthermore, FQs are also used as additives in ice to prevent rot of harvested seafood in fish markets. Currently, the extensive use of FQs to livestock farming and aquaculture has been of food security concerns. It is believed that high concentrations of FQs applied will retain in the meat, poultry and fish, and will then be assimilated in by people on consumption. Thus, it is important for us to check the FQs residues in foods of animal origin and environmental water samples. In recent years, a variety of analytical techniques such as Enzyme-linked immunosorbent assays [3], LC–MS/MS [4], electrochemical aptasensor [5], CE-FLD [6], UPLC-MS/MS [7] and HPLC [8,9] have been put forward to determine FQs, of which HPLC instrument is widely used to detect these compounds due to low cost and great robustness.

Considering that the trace concentrations of FQs exist in the samples, suitable technique is needed to separate and preconcentrate the analytes before determination. In recent years, a series of sample pretreatment methods were reported for separation and enrichment of FQs residues, such as liquid-liquid extraction [10], immunoaffinity chromatography [11], dispersive solid phase extraction (DSPE) [9], stir bar sorptive extraction (SBSE) [8] and solid phase extraction (SPE) [12–15]. Among them, DSPE is a popular pretreatment techniques due to its low solvent cost, less time consuming and simple operation process [16]. However, for DSPE, it is a great challenge to develop a novel adsorbing material with large specific surface area, excellent adsorption capacity and high enrichment properties.

Currently, carbon-based nanomaterials, for instance, activated carbon, carbon nanofibers [17], carbon nanotubes [18], grapheme [15,19] and 3D-graphene [20], have been widely explored as adsorbents. In particular, graphene and 3D-graphene are on the top notch owing to the specific structure and proprety. In addition, they are especially suited for sorption of aromatic compounds by Van der Waals force and π–π interaction [21]. However, the actual surface area of graphene is much lower than the theoretical values owing to the strong stacking of graphene sheets and the preparation of graphene is complex, time-consuming and risky. Therefore, there is an urgent need to develop a simple methodology to synthesize adsorbent materials with high adsorption capacity.

Porous coordination networks, also known as metal–organic frameworks (MOFs) with large specific surface area, ultrahigh porosity, and chemical tunability, have attracted broad research interests. In recent years, MOF have been testified as versatile

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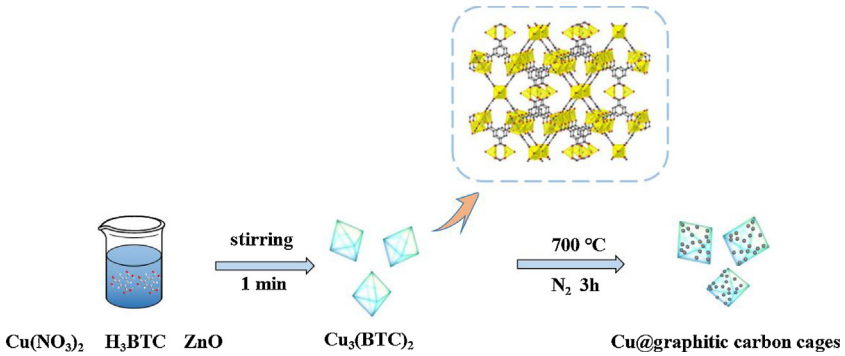

Fig. 1. The scheme of the Cu@graphitic carbon cages synthesis process.

templates and precursors for the synthesis of multifarious porous carbon materials, which have been adopted for widespread applications in many fields, including gas storage [22], separation [23,24], electrochemistry [25], energy storage [26], and catalysis [27–29]. So MOF derived porous carbon materials will possess a good potential application prospect in solid-phase extraction system, owing to their swoonsome diverse structures, satisfactory nanoscale porosities, uniform structured cavities and high surface area. However, the report about the carbon materials derived from MOF as adsorbents to determinate the FQs is very rare [30,31]. Therefore, there is more research work to be done in this field.

Herein, the main objective of this study was to synthesize an adsorbent with high adsorption capacity like porous carbon cages, where the porous structure enables the targets to access the adsorption sites without mass transfer limitations, meanwhile a quite thin graphitic carbon layers overlap on metal-organic cage will be conducive for adsorption of FQs. Firstly, Cu-based MOF was synthetized as the precursor, and then the porous Cu@graphitic carbon cages was obtained as enrichment material by further carbonization treatment under N_2 at 700°. A new strategy for the isolation of four FQs from food samples was developed by using 3D Cu@graphitic octahedron carbon cages followed by determination with HPLC.

2. Experimental

2.1. Reagents

1,3,5-benzenetricarboxylic acid (H_3BTC), ZnO, $Cu(NO_3)_2{\cdot}3H_2O$, Enrofloxacin (ENR), ciprofloxacin (CIP), norfloxacin (NOR), lomefloxacin (LOM), acetonitrile (HPLC-grade) and methanol (HPLC-grade) were obtained from Sinopharm Chemical Reagent Co.,Ltd (Shenyang, China). Deionised water was obtained from a MilliQ water purification system.

A stock standard solution of 1.0 g L^{-1} for each FQs were prepared in methanol (contain appropriate HCl). Their mixed standard solution containing 2 ppm of each FQs was obtained by diluting stock solution with deionized water.

2.2. Preparation of enrichment material

2.2.1. Synthesis of Cu-based MOF

$Cu_3(BTC)_2$ was rapidly synthesized according to the previous report [32]. Briefly, 0.293 g ZnO was dispersed in 24 mL of mixture solution (deionized water : DMF = 1:2 v/v) sonication for 10 min to form the nanoslurry. 1.740 g of $Cu(NO_3)_2{\cdot}3H_2O$ and 0.840 g of H_3BTC completely dissolved in 24 mL of mixture solution (deionized water : ethanol = 1:2 v/v) and then was poured into the above solution under continuous stirring. After 1 min of reaction, the blue products were collected and washed repeatedly with deionized water and ethanol. Then, the blue $Cu_3(BTC)_2$ product was dried at 70 °C in an overnight.

2.2.2. Synthesis of Cu@graphitic carbon cages

The above obtained $Cu_3(BTC)_2$ precursor was calcined to obtain Cu@graphitic octahedron carbon cages at 700 °C in N_2 atmosphere for 3 h with a ramping rate of 5 °C min^{-1}, and the schematic illustration of the fabrication of MOF-derived 3D porous Cu@graphitic octahedron carbon cages was presented in Fig. 1.

2.3. Characterization of the Cu@graphitic carbon cages

All as-prepared samples were characterized by scanning electron microscopy (SEM, Hitachi SU8000, Japan), transmission electron microscopy (TEM, JEOL JEM-2100, Japan), X-ray powder diffraction instrument (XRD, Bruker D8 diffractometer, Germany), X-ray photoelectron spectroscopy (XPS, Thermo electron Corporation ESCALAB 250 Xi, USA), Fourier transform infrared spectroscopy (FT-IR, Nicolet FT-IR 5700, USA), automated gas sorption analyzer (BET, Quantachrome ASIQ-C, USA) and Laser Confocal MicroRaman Spectroscope (Raman, HORIBA, LabRAM XploRA, France).

2.4. Sample treatment

Chicken muscle and fish tissue obtained at the local supermarket (Shengyang, China) were preserved at −6 ° before analysis. Firstly, 1.0 g samples were homogenized using mangler and put into 25 mL conical flask. Then the FQs with a series of concentration levels were spiked seriously, this mixture was treated with ultrasound for 5 min to make the analytes disperse thoroughly into matrix. After that, 10 mL of methanol was added to the mixture and sonicated for 10 min to extract FQs. Finally, in order to convenience for the DSPE procedure, the sample solution was filtrated using a membrane filter (0.22 μm) to dislodge suspended substance.

Seawater sample and River water sample were stored below 4 °C after filtered using a membrane filter (0.22 μm).

2.5. DSPE procedure

The DSPE procedure was illustrated in Fig. 2. In the extraction procedure, 36.0 mg Cu@graphitic carbon cages was added into 10 mL of standard solution sample (the concentration of each FQs were 2 ppm). The mixture was vibrated for 30 min at 200 rpm, the Cu@graphitic carbon cages were separated from the solution by centrifuging for 3 min at 8000 rpm. Then 8.0 mL EtOH/NaOH (1 mol L^{-1}) (7/1, v/v) was used as eluent to isolate the analyte from the Cu@graphitic carbon cages. Under a soft N_2 stream, the eluent was evaporated to dryness. At last the residue was redissolved with 200 μL methanol (contain appropriate HCl) and filtered through a 0.22 μm PTFE filter membrane for HPLC analysis.

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