Talanta 185 (2018) 573–580

Contents lists available at ScienceDirect

Talanta

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

Polymer brushes-containing coordination polymer networks on monolith for rapid solid phase extraction of multi-class drug residues in meat samples

Nan Li[a,b], Yue Song[a,b], Jing Qiu[a,b,*], Yue-Chen Zhao[a,b], Yong-Zhong Qian[a,b]

[a] Institute of Quality Standards and Testing Technology for Agro-Products, Key Laboratory of Agro-Product Quality and Safety, Chinese Academy of Agricultural Sciences, Beijing 100081, China

[b] Key Laboratory of Agri-Food Quality and Safety, Ministry of Agriculture, Beijing 100081, China

ARTICLE INFO

Keywords:
Monolithic coordination hybrid in syringe filter
Solid phase extraction
Multi-class analysis of veterinary drugs

ABSTRACT

A new solid phase extraction sorbent, based on poly(methacrylic acid) brushes-containing coordination polymer networks on monolith, was in-situ synthesized in a commercial syringe filter via surface grafting. Extraction of twenty model analytes, including nine sulfonamides, eight steroid hormones, and three quinolones, could be efficiently achieved by the monolithic hybrid filter due to multi-interactions. Through simple filtering steps, fast extraction (60 s of adsorption and 60 s of desorption) could be achieved. Furthermore, the monolithic hybrid filter was used to analyze the model compounds in chicken meat samples in combination with ultra-performance liquid chromatography-tandem mass spectrometry. Compared with other adsorption sorbents in reported literatures, the proposed monolithic hybrid filter allowed for shorter purification time, simplified sample pretreatment procedure, and comparable LODs and LOQs of 0.1–3 μg kg^{-1} and 0.4–10 μg kg^{-1}, respectively. The recoveries for all analytes ranged from 83.9% to 103% with inter-day relative standard deviation lower than 10%. The results demonstrated that the developed analytical method was highly efficient and operationally convenient, and had a great potential for high throughput analysis of multi-residues.

1. Introduction

Nowadays, veterinary drugs have played an inevitable role in stockbreeding. Sulfonamides, steroid hormones, and quinolones are commonly used drugs for animal. The irrational use of these compounds may result in existence of residues in food products, which possibly brings a great potential harm to human health, such as allergy, chronic toxicity, and even carcinogenicity [1]. In order to ensure food safety, the maximum residue limits (MRLs) of these drugs in food have been set by many countries [2,3]. In the past decades, increasing number of analytical methods for multi-residues has been emerging. However, the multi-residue analysis covering steroid hormones and other veterinary drugs still remains a great challenge due to high hydrophobicity of steroid hormones. On one hand, bio-interferences with similar hydrophobicity in food matrix bring about difficulties in sample purification, resulting in high matrix effects; on the other hand, the diverse hydrophobicity among target compounds brings difficulty to achieve satisfactory recoveries for all analytes [4]. In addition, complex and tedious sample pretreatment procedures are usually involved in traditional multi-residue analysis, which are not suitable for handling food safety incidents. To achieve better food control, development of new sample pretreatment sorbents allowing for efficient multi-residue analysis is still attractive [5–10].

Porous coordination polymers, including metal-organic frameworks (MOFs), own large surface areas and multiple chemical interaction sites. Recently, porous coordination polymers have been introduced as promising sample pretreatment sorbents for multi-class solid phase extraction. Nevertheless, their performance in chromatographic applications is usually limited by the small packing particle sizes and unsuitable morphologies [11–13]. The effective approach to solve the problem is the growth of porous coordination polymers on the chromatographic substrates. Among the various substrates, monolithic matrix is characterized by the fast mass transfer [14,15]. In addition, monolith can be easily adapted to commercially available equipment, such as capillary, disk, and pipette tips [16–18]. However, to our best knowledge, the research on design and preparation of monolithic coordination hybrid for the multi-residue analysis in real samples has so far not been reported.

In this work, poly(methacrylic acid) (PMAA) brushes-containing Fe (III) *p*-phthalic acid coordination polymer networks on polymer monoliths were prepared in a commercial syringe filter. The resultant monolithic coordination hybrid contains a modulated number of

* Corresponding author at: Institute of Quality Standards and Testing Technology for Agro-Products, Chinese Academy of Agricultural Sciences, No. 12 Zhongguancun South Street, Beijing 100081, PR China.
E-mail address: qiujing@caas.cn (J. Qiu).

https://doi.org/10.1016/j.talanta.2018.03.077
Received 11 October 2017; Received in revised form 12 March 2018; Accepted 24 March 2018
Available online 03 April 2018
0039-9140/

hydrophobic sites, electrostatic interaction sites, and coordination sites, leading to high adsorption capacities for various analytical compounds. The procedure for solid phase extraction was carried out by filtering steps. The obtained extraction solution was directly subjected to instrumental analysis without additional filtration. Twenty drugs, including nine sulfonamides, eight steroid hormones, and three quinolones, were used as model analytes to evaluate the developed solid phase extraction method. Furthermore, the monolithic hybrid filters were applied in simultaneous analysis of the model analytes in chicken meat samples with ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS).

2. Experimental

2.1. Chemicals and reagents

2-Azobisisobutyronitrile (AIBN, 98%), glycidyl methacrylate (GMA, 98%), triethylene glycol dimethacrylate (TEGDMA, 98%), methacrylic acid (MAA, 98%), and *p*-phthalic acid (98%) were purchased from Acros (Waltham, MA, USA). Iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 99%) was obtained from Alfa Chemistry (USA). All the analytical standards of hormones, sulfonamides, and quinolones used in this study were provided by Dr Ehrenstorfer (Augs-burg, German) and stored at − 20 °C prior to use. The water was got from a Milli-Q system (Bedford, MA, USA). LC/MS-grade organic solvents were purchased from Fisher Scientific (Waltham, MA, USA). The formic acid (FA, 99%) and ammonium formate (99%) were acquired from Sigma-Aldrich (St. Louis, MO, USA). Dodecanol (99%) and other unmentioned chemical reagents were purchased from Beijing Chemical Plant (Beijing, China).

2.2. Apparatus and analytical conditions

The morphologies and pore structures of the monolith and the monolithic coordination hybrid were characterized using a Hitachi Model S-4800 scanning electron microscope (Hitachi High Technologies, Tokyo, Japan). The specific surface areas were measured by Brunauer − Emmett − Teller (BET) model exploiting an ASAP2010 Accelerated Surface Area & Porosimetry System (Micromeritics, USA). Fourier transform infrared (FT-IR) absorption spectra were acquired using a Tensor-27 FT-IR spectrophotometer (Bruker, German) with KBr as medium.

UPLC-MS/MS analysis was conducted on a Waters Acquity UPLC system (Waters, Milford, MA, USA) coupled with an AB Sciex Triple Quad 3500 LC/MS/MS system (AB Sciex, USA). An Agilent XDB-C18 column (100 × 2.1 mm i.d., 1.8 μm particle sizes, Agilent Technologies, USA) was used for chromatographic separation. Mobile phases A and B are 1.0 mM ammonium formate with 0.1% formic acid in water and acetonitrile (ACN), respectively. The elution solvent (mobile phases A and B) had a flow rate of 0.30 mL min^{-1} with following gradient program: initial-2.00 min, 5% B; 2.10–10.0 min, 5.0–95% B; 15.0–20.0 min, 95% B; 20.0–23.0 min, 95% B; 23.1–25.0 min, 5% B. The volume of sample injection was 3.0 μL. The operating parameters for MS were as follows: ion spray voltage, 5.5 kV; source temperature, 500 °C; curtain gas, 20 psi; atomizing gas (GS 1), 50 psi; dry gas (GS 2) 50 psi. The data were obtained in multiple reaction monitoring (MRM) mode. The declustering potential (DP) and collision energy (CE) for each ion pair was optimized and listed in Table 1.

2.3. Preparation of monolithic coordination hybrid in syringe filter

The poly(TGDMA-*co*-GMA) monolithic matrix was in-situ prepared in a syringe filter (13 mm i.d). The synthesis procedures were similar with previously reported literatures [19–21] and described briefly in Supplementary material.

The PMAA was grafted on the poly(TGDMA-*co*-GMA) monolithic matrix via free radical polymerization [22]: firstly, 0.20 M H_2SO_4 was flowed through the poly(TGDMA-*co*-GMA) monolith at 65 °C using injection pump at the flow rate of 3.0 mL h^{-1}, resulting in hydrolysis of epoxy group of GMA unit to hydroxyl groups. Then, MAA (3.0 mL, 35 mmol) and $K_2S_2O_8$ (10 mg, 37 μmol) were dissolved in 20 mL of water. The resultant polymerization solution was flowed through the monolith at the flow rate of 3.0 mL h^{-1} for 4 h at 65 °C. Finally, the obtained monolith was washed with 50 mL water to remove the unreacted residues.

Fe (III) *p*-phthalic acid coordination polymer networks were fabricated on poly(TGDMA-co-GMA) monolith containing PMAA brushes via

Table 1
Tandem mass spectrometry parameters for the analysis of sulfonamides, steroid hormones, and quinolones.

Analytes	RT[a] (min)	Precursor ion(*m/z*)	Product ions (*m/z*)	DP[b] (eV)	CE[c] (eV)
Sulfonamides (9)					
n-Sulfanilylacetamide (A-1)	3.21	215	108/92.1	58	28/28
Sulfamethizole (A-2)	6.04	271	156/92.1	20	22/37
Sulfapyridine (A-3)	4.77	250	155.9/92.1	70	22/37
Sulfafurazole (A-4)	8.02	268	156/113.1	80	18/20
Sulfamerazine free acid (A-5)	5.11	265	156/108	80	25/34
Sulfamethoxypyridazine (A-6)	6.17	281	156.1/92	79	22/38
p-aminobenzenesulfonamide (A-7)	7.0	173	156.1/64.9	58	27/40
Sulfadimethoxine (A-8)	7.55	311	156/108	80	25/34
Sulfaphenazolum (A-9)	9.15	315	158.1/92.1	96	37/52
Steroid hormones (8)					
Hydroxyprogesterone caproate (B-1)	18.95	429.5	271.1/313.1	75	28/17
Prednisone (B-2)	5.99	359.3	341.2/256.3	100	34/54
Prednisolone (B-3)	9.19	361.3	343.2/146.9	77	14.3/33
Betamethasone (B-4)	10.47	393.4	237.1/279.2	40	50/24
Levonorgestrel (B-5)	14.05	313	245.2/109.1	115	40/40
Cyproterone Acetate (B-6)	15.75	417.5	309/301.1	90	22/28
Chlormadinone acetate (B-7)	16.2	405.2	309/301.1	40	40/40
Nandrolone Phenylpropionate (B-8)	19.68	407.4	257.2/105	100	24/50
Quinolones (3)					
Enoxacin (C-1)	5.39	321	303.3/232.1	91	47/28
Lomefloxacin (C-2)	5.92	352	265.1/308.3	94	33/24
Pefloxacin (C-3)	5.66	334	316/290.1	100	26/34

[a] RT, retention time.
[b] DP, declustering potential.
[c] CE, Collision energy.