



A hydrazone covalent organic polymer based micro-solid phase extraction for online analysis of trace Sudan dyes in food samples



Chengjiang Zhang^{a,b}, Gongke Li^{a,*}, Zhuomin Zhang^{a,*}

^a School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China

^b School of Pharmacy, Zunyi Medical College, Zunyi 563003, China

ARTICLE INFO

Article history:

Received 9 August 2015

Received in revised form

10 September 2015

Accepted 17 September 2015

Available online 21 September 2015

Keywords:

Hydrazone covalent organic polymer

μ -SPE

Online analysis

Sudan dyes

Food

ABSTRACT

Covalent organic polymers (COPs) connected by covalent bonds are a new class of porous network materials with large surface area and potential superiority in sample pretreatment. In this study, a new hydrazone linked covalent organic polymer (HL-COP) adsorbent was well-designed and synthesized based on a simple Schiff-base reaction. The condensation of 1,4-phthalaldehyde and 1,3,5-benzenetricarbohydrazide as organic building blocks led to the synthesis of HL-COP with uniform particle size and good adsorption performance. This HL-COP adsorbent with high hydrophobic property and rich stacking π electrons contained abundant phenyl rings and imine ($-C=N$) groups throughout the entire molecular framework. The adsorption mechanism was explored and discussed based on π - π affinity, hydrophobic effect, hydrogen bonding and electron-donor-acceptor (EDA) interaction, which contributed to its strong recognition affinity to target compounds. Enrichment factors were 305–757 for six Sudan dyes by HL-COP micro-solid phase extraction (μ -SPE), indicating its remarkable preconcentration ability. Furthermore, the adsorption amounts by HL-COP μ -SPE were 1.0–11.0 folds as those by three commonly used commercial adsorbents. Then, HL-COP was applied as adsorbent of online μ -SPE coupled with high performance liquid chromatography (HPLC) for enrichment and analysis of trace Sudan dyes in food samples with detection limit of 0.03–0.15 μ g/L. The method was successfully applied for online analysis of chilli powder and sausage samples. Sudan II and Sudan III in one positive chilli powder sample were actually found and determined with concentrations of 8.3 and 6.8 μ g/kg, respectively. The recoveries of chilli powder and sausage samples were in range of 75.8–108.2% and 73.8–112.6% with relative standard deviations of 1.2–8.5% and 1.9–9.4% ($n=5$), respectively. The proposed method was accurate, reliable and convenient for the online simultaneous analysis of trace Sudan dyes in food samples.

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1. Introduction

Covalent organic polymers (COPs), composed of light elements and connected by stronger covalent bonds (B–O, C–C, C–H, C–N, etc.), are a new class of porous network materials [1,2]. Recently, COPs have aroused sustainable attention due to their fascinating property of light framework density, large specific surface area, high porosity and tunable porous size as well as high hydrothermal stability. To date, several crystalline and amorphous COPs have been synthesized including covalent organic frameworks (COFs) [3,4], covalent triazine-based frameworks (CTFs) [5], microporous organic polymers (MOPs) [6], porous aromatic frameworks (PAFs)

[7], porous polymer networks (PPNs) [8] and polymeric organic frameworks (POFs) [9], etc. COPs have demonstrated great application potential for gas storage [10,11], separation [12,13] and sensing [14–16]. However, there are still few reports focusing on employing COPs as enrichment media in sample preparation. Currently, CTFs with good physicochemical stability have been used for adsorption of aromatic compounds [17], 4,4'-(propane-2,2-diyl) diphenol [18], rhodamine B [19] and surfactants from aqueous solution [20], and magnetic CTF composite (CTF/Fe₂O₃) has been also used to remove organic dye of methyl orange in aqueous solutions [21]. MOPs based on Schiff base network (SNW-1) were used as an enrichment coating for sampling volatile fatty acids from tea and tobacco shred samples [22]. Therefore, COPs would possess the possibility to be promising adsorbent and great application potential in sample pretreatment.

COPs can be designed and created by linking organic building blocks to form covalent bonds based on various reversible and

* Corresponding authors.

E-mail addresses: cesgkl@mail.sysu.edu.cn (G. Li), zzm@mail.sysu.edu.cn (Z. Zhang).

irreversible condensation reactions in reticular chemistry. It is difficult to synthesize crystalline COPs based on dynamic covalent controlled reversible reactions, since the preparation process usually requires harsh reaction conditions with high synthesis cost to form covalent bonds. On the contrary, amorphous COPs can be easily synthesized and constructed based on kinetic covalent controlled irreversibly reactions via facile synthetic protocols. Thus, amorphous COPs materials could be interesting alternatives to produce practical enrichment media. Various chemical reactions have been utilized to construct COPs. Schiff-base chemistry has been one of the most frequently used approaches for preparation of COPs, since Schiff-base condensation reactions do not require expensive catalysts and are usually high yielding [23].

Recently, some COPs based on imine linkages have been synthesized by Schiff-base reaction [11,16,24–27]. However, there are few hydrazone formations used for the synthesis of COPs [28–31], although hydrazones have much better hydrothermal stability than imines [32]. Moreover, the morphology control and functionalization of Schiff-base COPs with potentially excellent analytical performance still remains a great challenge, which arouses our interest in constructing a new COP by condensation reactions. To achieve this objective, an easy-controlled Schiff-based reaction for synthesis of a new hydrazone-linked COP (denoted as HL-COP) using 1,4-phthalaldehyde and 1,3,5-benzenetricarbohydrazide as organic monomers was attempted to be developed in our study. This HL-COP with throughout network, highly hydrophobic property and rich stacking π electrons is expected to contain abundant phenyl rings and $\text{C}=\text{N}$ groups throughout the entire molecular framework. Thus, this HL-COP would easily form strong π - π stacking interaction and hydrophobic effect as well as hydrogen-bond interaction with target compounds containing hydroxyl groups ($-\text{OH}$) by forming intermolecular bonds $\text{O}-\text{H}\cdots\text{N}=\text{C}$ [33,34]. Therefore, in the field of separation science HL-COP is expected to be an excellent selective enrichment medium for target compounds containing hydroxyl groups involving Sudan dyes.

Sudan dyes are a family of lipophilic azo dyes that are widely used in many industrial and scientific fields. Due to their color fastness, low cost and wide availability, Sudan dyes have been often illegally used as food colorants, although they are classified as category 3 carcinogen by the International Agency for Research on Cancer (IARC). Therefore, Sudan dyes in food are considered unsafe for human health at any levels and are strictly banned as food additives in the European Union (EU) and some other countries [35]. Several methods were described for analysis of Sudan dyes in food-stuffs, and the most extensively used method is HPLC coupled with different detectors such as ultraviolet-visible (UV-vis) [36,37] and mass spectrometry [38,39] etc. Due to the complicated food sample matrix as well as trace concentrations of Sudan dye residues in real samples, it is very crucial to simultaneously isolate and enrich Sudan dyes by efficient sample preparation methods before instrumental analysis. Various offline sample preparation methods such as cloud point extraction [36], solid-phase extraction (SPE) [40], liquid-liquid extraction and liquid-phase microextraction [41,42] for preconcentration and cleanup have been developed for isolation and enrichment of Sudan dyes which usually require long operation time and much labor with relatively poor reproducibility. Compared to offline methods, online methods may effectively reduce sample loss, shorten the time consumption with less labor and enhance the analytical precision and accuracy [43], which would greatly enhance the analytical efficiency and accuracy when facing a large number of food samples during food security analysis. However, there are still few reports [37,44,45] focusing on development of online sample preparation methods based on highly selective COPs as enrichment media for analysis of Sudan dyes. Since HL-COP possessed homogenous, porous and dense sheet-shape morphology, HL-COP based enrichment medium is expected to provide

high permeability and extraction selectivity and capacity for online analysis of trace Sudan dyes in food.

In this study, a well-defined and porous HL-COP enrichment medium with disk-shape morphology was well designed and synthesized based on a Schiff base reaction under optimal synthetic conditions. Then, a HL-COP based online μ -SPE technique with high permeability and extraction selectivity to Sudan dyes was developed in a stainless steel microcolumn for the simultaneous determination of six trace Sudan dyes in food samples including Sudan I, Sudan II, Sudan III, Sudan IV, Sudan Red G and Sudan Red 7B. The adsorption mechanism of HL-COP enrichment medium for Sudan dyes was tried to be discussed based on π - π stacking interaction, hydrophobic effect, hydrogen bonding interaction and EDA interaction. Finally, this HL-COP/ μ -SPE was practically applied for online analysis of trace Sudan dyes in real chilli powder and sausage samples coupled with HPLC-UV detection.

2. Experimental

2.1. Chemicals and materials

Trimesoyl chloride, anhydrous dioxane, mesitylene, 1,4-phthalaldehyde, hydrazine hydrate and the standard compounds including polycyclic aromatic hydrocarbons (PAHs) (naphthalene (NAP), acenaphthene (ANE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), pyrene (PYR)), 1-naphthylamine, 1-chloronaphthalene, 1-nitronaphthalene, 2-methylnaphthalene, 2-naphthol, 8-hydroxyquinoline and Sudan dyes (Sudan I, Sudan II, Sudan III, Sudan IV, Sudan Red G and Sudan Red 7B) were purchased from Aladdin (Shanghai, China). Acetonitrile and methanol were of HPLC grade and purchased from Dikma (Beijing, China). HPLC-grade formic acid and ethanol were obtained from Kemiou Chemical Reagent Co., Ltd (Tianjin, China). C18 silica gel sorbent with particle size of 15–40 μm was obtained from Elite Analytical Instruments Co., Ltd. (Dalian, China). Multiwall carbon nanotubes (MWCNTs, 99.95%, length $\leq 30 \mu\text{m}$) were purchased from Shenzhen Nanometer Gang Co., Ltd. (Shenzhen, China). Graphene (G) was acquired from Ningbo Morsh Tech. Co., Ltd. (Ningbo, China). All solvents and solutions for HPLC analysis were filtered through a Millipore filter (pore size, 0.45 μm). Other reagents were of analytical grade. Stock standard solutions of PAHs, naphthalene substituents and Sudan dyes (200.0 mg/L) were prepared by dissolving pure reference standards in acetonitrile. Working solutions were prepared by gradually diluting corresponding stock standard solutions with acetonitrile. These solutions were all stored at 4 °C in dark before used. Purified water was obtained from Millipore water purification system.

2.2. Instruments

Glass ampoules charged with reactive reagents and flash frozen with liquid N_2 evacuated using a Schlenk line were obtained from Synthware Glass Instrument CO., Ltd (Beijing, China). A 200 W entire intelligent ultrasonicator (KQ 5200, Kunshan, China) was used to extract chilli powder and sausage samples. HS-4 magnetic stirrer (IKA RET, Germany) was employed for stirring solutions during synthesis. HL-COP morphology was characterized by a JSM-6330F (JEOL, Tokyo, Japan) scanning electron microscopy (SEM). The X-ray diffraction (XRD) was performed on a D8 Advance X-ray diffractometer with $\text{Cu K}\alpha$ incident radiation. The thermal stability of HL-COP was evaluated by a thermogravimetric analyzer (TGA) (Net ch-209, Bavaria, Germany). Surface area measurement was performed on an ASAP-2020M gas adsorption instrument (Micromeritics, Atlanta, USA). NICOLET AVATAR 330 Fourier transform infrared spectrometer (FT-IR) was used to record IR spectra of this HL-COP. Elemental microanalysis was performed on a Germany

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