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Extraction and enrichment of natural pigments from solid samples using ionic liquids and chitosan nanoparticles

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ABSTRACT

A green and economical method for the extraction and preconcentration of natural pigments (curcumin, demethoxycurcumin and bisdemethoxycurcumin) was developed using ultrasound-assisted extraction combined with dispersive micro solid-phase extraction. In this work, Ionic liquids (ILs) were used for the pre-extraction of natural pigments. The pure chitosan nanoparticles (CS NPs) were then used as a sorbent for the microextraction mode. The method involves the use of ultrahigh-performance liquid chromatography coupled with quadrupole time-of-flight tandem mass spectrometry. Operating parameters influencing the performance of extraction steps such as type and concentration of ILs, concentration of CS NPs, type of elution solvent, agitation time and pH of sample-extracting solution were investigated. Under the optimum conditions, the proposed method exhibited a low detection limit in the range of 0.11–0.36 ng/mL at S/N = 3, and good linearities with coefficients of determination (R^2) higher than 0.9990. The recoveries of turmeric samples were ranging from 90.45% to 105.04% for the three studied curcuminoids with SD of 3.27–6.58. The experimental results indicated that the ILs and CS NPs were the promising materials for the extraction and enrichment of target curcuminoids from complex solid samples.

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1. Introduction

Natural products contain rich sources of non-synthetic biologically active compounds, which usually have distinctive pharmacological effects based on their clinical practices and reliable therapeutic efficacies [1,2]. They include chemical compounds or substances from plants, sea creatures, insects, microbes and fungi, as well as form the basis of important synthetic and semisynthetic compounds. Analysis of natural product extracts is an attractive research field, which has gained considerable interest in recent years [3]. Despite substantial developments in extraction techniques, it is still a challenging task to produce multiple pure targets from natural products, especially for solid samples [4]. Recent studies have revealed that several solid–liquid extraction techniques such as ultrasound-assisted extraction (UAE) [5,6], soxhlet extraction [7], soaking extraction [8], reflux-assisted extraction [9], and supercritical fluid extraction [10], are available for natural product extraction. However, these procedures are time-consuming, expensive, inefficient, and require large volumes of hazardous solvents without pre-concentration. Therefore, the investigation of green and efficient pre-concentration methods for natural products is of high interest, particularly for solid samples.

Chitosan (CS) is a linear cationic polysaccharide obtained from the deacetylation of chitin that is composed of *N*-acetyl-D-glucosamine and D-glucosamine monomers linked by β-(1,4) glycosidic bonds. It has been widely regarded as a particularly potential bio-polymeric-material of great scientific interest on account of its abundant nature resource, cheapness, biocompatibility, broad-spectrum antibacterial function, biodegradability, nontoxicity, strong adsorption properties and ease of chemical modification [11–13]. In recent years, CS-based nanoparticles (NPs) have shown great potential in biological, pharmaceutical and food application prospects. Among various methods of preparing CS NPs, the ionic gelation process has attracted considerable attention as a result of its non-toxic, convenient and controllable procedure,

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which is based on the electrostatic interaction between the positively charged amino groups of chitosan and the negatively charged groups of sodium tri-polyphosphate (TPP) [14]. To date, CS NPs were used for delivery of therapeutic proteins, peptides, pDNA, siRNA and small drug molecules [14–16]. However, to the best of our knowledge, the pure CS NPs used in sample extraction have not been reported in the literature.

In nature, pigments constitute a group of chemically heterogeneous and biosynthetically unrelated molecules that are present in nearly all taxonomic groups (from bacteria, plants to animals) and have a common feature: their electronic structure contains a chromophore that is responsible for the typical colors of these compounds. Currently, natural pigments derived from plants have been used as additives or supplements in the food industry, cosmetics, pharmaceuticals, livestock feed and other applications [17]. *Curcuma longa* L., commonly known as turmeric, is one of the well-studied natural pigment plants and is used as a spice (main ingredient of curry for its characteristic scent), a pigment dye of textiles, a food coloring agent and traditional medicine [18,19]. Curcuminoids, isolated from the rhizome of turmeric, are obtained as a yellowish pigment and consist of three principal polyphenolic analytes: curcumin, demethoxycurcumin and bisdemethoxycurcumin [20]. Curcuminoids have a wide range of biological and pharmacological activities, including anti-tumor, anti-inflammatory, anti-viral, anti-oxidative, anti-Alzheimer's, anti-hepatotoxic, anti-HIV and cardiovascular protection [18,21]. Recently, the main turmeric extraction methods used are conventional methods such as subcritical and pressurized liquids extraction [22–24], microwave-assisted extraction (MAE) [25], heat-refluxed extraction (HRE) [26], ultrasound assisted extraction (UAE) [27] and solid-phase extraction (SPE) [28]. However, these methods are disadvantageous because they require large amounts of organic solvents without preconcentration, involve time-consuming extraction and clean-up procedures, and are relatively expensive. Therefore, the development of an environmentally-friendly preconcentration extraction methods is critical for the analysis of these curcuminoids.

In this work, a new UAE and dispersive micro solid-phase extraction (DMSPE) technique has been developed for the determination of pigments in solid plant samples. Unlike conventional methods, this procedure performs extraction, pre-concentration and clean-up together in one step. After UAE, the extract was transferred into a jar and subjected to the DMSPE process. The DMSPE process included clean-up and preconcentration of the target compounds before entering into the corresponding micro volume phase. Finally, the supernatant of the organic phase was removed and injected into an ultrahigh-performance liquid chromatograph (UHPLC) system for analysis. The effects of various experimental parameters on the extraction efficiency of curcuminoids were considered and optimized. The developed method provides a new strategy in the simultaneous analysis of polar biologically active compounds in complex solid matrices.

2. Experimental

2.1. Materials and reagents

All materials were of analytical or reagent grade, or the highest purity available from several suppliers and were used as received. Methanol, ethanol and acetonitrile were purchased from Tedia Company Inc. (Fairfield, US). Glacial acetic acid was supplied by Sigma Aldrich Shanghai Trading Co., Ltd. (Shanghai, China). Acetone was obtained from Hangzhou Chemical Reagent Co., Ltd. (Hangzhou, China). Trichloromethane was provided by Tianjin Siyou Fine Chemical Co. Ltd. (Tianjin, China). Ultrapure water was obtained from the Hangzhou Wahaha Group Co., Ltd. (Hangzhou, China). The ionic liquids (ILs), including 1-ethyl-3-methylimidazolium L-(+)-lactate ([Emim][L-L]), 1-hexylpyridinium tetrafluoroborate ($[HPy]BF_4$), 1-dodecyl-3-methylimidazolium bromide ($[C_{12}mim]Br$), 1-dodecyl-3-methylimidazolium chloride ($[C_{12}mim]Cl$), 1-dodecyl-3-methylimidazolium nitrate ($[C_{12}mim]NO_3$), and 1-dodecyl-3-methylimidazolium hydrogen sulfate ($[C_{12}mim]HSO_3$) were purchased from Shanghai Cheng Jie Chemical Co., Ltd. (Shanghai, China). Medium-molecular-weight chitosan (deacetylation: 75–85%, viscosity: 200–800 cps) and sodium tripolyphosphate (TPP) were both purchased from ANPEL Laboratory Technologies (Shanghai) Inc. (Shanghai, China). Standards of curcumin, demethoxycurcumin and bisdemethoxycurcumin were collected from Shanghai Winherb Medical Technology Co., Ltd. (Shanghai, China).

2.2. Instrumentation

The sorbent morphologies were recorded using scanning electron microscopy (SEM) (Zeiss Supra55, Oberkochen, Germany). The transmission electron microscope (TEM) (Zeiss Supra55, Oberkochen, Germany) image was maintained at 100 kV.

The analysis of curcuminoids was carried by a 1290 series UHPLC (Agilent Technologies Inc., USA) equipped with ultraviolet detector (UV) and quaternary gradient pump. The chromatographic separation and evaluation of the analytes was achieved with an Agilent SB-C_{18} (1.8 μm, 50 mm × 4.6 mm i.d.) operating at 25 °C. Acetonitrile and 4% aqueous glacial acetic acid were used as mobile phases and the gradient program contained the following steps: 0–4 min, 46–46% acetonitrile; 4–5 min, 46–48% acetonitrile; 5–7 min, 48–48% acetonitrile; 7–8 min, 48–50% acetonitrile; 8–8.5 min, 50–70% acetonitrile; 8.5–9 min, 70–100% acetonitrile. The flow rate was set at 0.4 mL/min, the injection volume was 1 μL and the detection wavelength was at 430 nm. The Waters Synapt G2 quadrupole time-of-flight tandem mass spectrometry (Q-TOF/MS) (Waters Manchester, UK) equipped with an electrospray ionization (ESI) source was used to quantify the target compounds. MS data were recorded in the negative ionization mode by scanning an m/z range of 100–1000 using the following operating parameters: capillary voltage, −2.5 kV; drying gas temperature, 350 °C; drying gas flow, 5 μL/min; cone and collision gas, nitrogen and argon; cone and collision gas flows, 80 L/h and 800 L/h; and cone voltage, 30 V. The Masslynxtv 4.1 (Waters Corporation) software was employed to record and analyze the data obtained.

The anthraquinones in rhubarb were analyzed by UHPLC-UV using 0.1% formic acid (v/v) and methanol as eluents. The gradient eluent program was as follows: 0–1 min, 10–50% methanol; 1–2 min, 50–70% methanol; 2–3 min, 70–85% methanol; 3–5 min, 85–100% methanol; 5–8 min, 100–100% methanol. The column temperature was maintained at 30 °C. The flow rate was set at 0.4 mL/min, the injection volume was 1 μL and the detection wavelength was at 254 nm.

2.3. Synthesis of CS NPs

CS was prepared at a concentration of 2% in 0.1% acetic acid solution. A solution of TPP at the concentration of 1.0 mg/mL was prepared with ultrapure water. CS NPs were prepared by ionic gelation process [14,29]. Firstly, 100 mL of the TPP solution was gradually added dropwise under constant stirring to 100 mL of the 2% CS solution. Then, the mixture was stirred constantly at room temperature for 24 h, until it formed an opalescent suspension. Thirdly, the resulting reaction mixture was separated by centrifugation at 4000 rpm for a period of 30 min. The supernatant liquid

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